CHAPTER 2

NATURAL ZEOLITES

2.1 Introduction

More than two centuries have passed since zeolite was discovered and named by Cronstedt in 1756. With hind sight, one wonders why it took so long for the scientific community to realise the potentialities of zeolites. Until the early part of this century, collection and mineralogical description of pretty, coarse crystals were the primary studies of zeolites. In their beauty and variety they were treated as the pride of mineralogists.

Researches on zeolites in alkaline saline lake deposits by Hay, Gude and Sheppard in USA opened our eyes to the zeolite formation at or near the earth's surface. From deep sea sediments zeolites were already reported by Murray and Renard in 1891. The deep sea drilling project (1968-1975) by Glomar Challenger curises shed more light on the deep sea zeolites. Our knowledge on zeolites and zeolitic rocks has expanded remarkably rapidly during the last two decades. In less than 30 years, the exploitation of basic ion-exchange,
adsorption, dehydration and catalytic properties has brought about their transformation from museum curiosities to full-fledged industrial mineral resources.

By definition, zeolites are crystalline hydrated aluminosilicates of alkali and alkaline earth cations, having infinite three dimensional structures. They are further characterised by their ability to lose and gain water reversibly, and to exchange constituent cations without any major change of structure.

The zeolites constitute one of the largest groups of minerals known; more than 40 distinct species have been recognised, and nearly 100 species having no natural counterparts have been synthesized in the laboratory. The potential applications of both natural and synthetic zeolites stem, of course, from their fundamental physical and chemical properties, which in turn are directly related to their chemical compositions and crystal structures.

This chapter includes an account of chemical composition, structure, geology, important commercial properties and utilization of natural zeolites, followed by a review of earlier work done on stilbite, heulandite and analcime, which have been
the crystals for investigation, in the present work.

2.2 Chemical composition

The composition of zeolites can be expressed by the empirical formula $M_{2n}^\frac{2}{n} \cdot 0_3 Al_{2}O_3 \cdot x SiO_2 \cdot y H_2O$, where $x \geq 2$ and $n$ is the valence of cation $M$. The maximum value of $x$, for naturally occurring zeolites, is 10. As will be seen later, this value approaches or equals infinity for some of the synthetic materials. Compositionally, zeolites can be visualised as being derived from silica ($SiO_2$). Consider a three dimensional crystalline framework of silica in which some of the Si atoms are replaced by three valent aluminium atoms. The substitution of the three valent Al for the four valent silicon generates an anionic site in the environs of the Al atoms. To preserve electroneutrality, a cation is required. This charge balance is reflected in the empirical formula given above. In compliance with the rule that tetra co-ordinate Al cannot share the same oxygen, it follows that $x$ in the empirical formula cannot be smaller than 2.

Although zeolites have generally been classified as aluminosilicates, the IUPAC nomenclature
rules for heteropolyions indicate that they should more properly be called silicoaluminates as the anionic charge in the zeolite framework is centred on the Al ion. Synthetic zeolites can be prepared containing small quantities of Al, approaching the composition of pure silica ($\text{SiO}_2$). It seems inevitable that erroneous custom will prevail over correctness, as unfortunates often happen, and the use of the term aluminosilicate will continue.

2.3 Crystal structure

It is convenient to describe and classify zeolite structures in terms of fundamental building units as listed in Table 2.1. These units include the primary building unit of $\text{TO}_4$ tetrahedra, so called secondary building units (SBU), which consist of both single rings of four, five, six, eight, ten and twelve tetrahedra, and double rings of four, six and eight tetrahedra, and larger symmetrical polyhedra described in terms of archimedean solids. Several of the secondary building units and the larger symmetrical polyhedra are shown in Fig. 2.1.

Detailed structural classifications of
<table>
<thead>
<tr>
<th>Table 2.1 Building Units in Zeolite Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary Building Unit - Tetrahedron (TO₄)</strong></td>
</tr>
<tr>
<td>Tetrahedron of four oxygen ions with a central ion (T) of Si⁴⁺ or Al³⁺</td>
</tr>
<tr>
<td><strong>Secondary Building Units (SBU)</strong></td>
</tr>
<tr>
<td>Rings: S-4, S-5, S-6, S-8, S-10, S-12</td>
</tr>
<tr>
<td>Double Rings: D-4, D-6, D-8</td>
</tr>
<tr>
<td><strong>Larger Symmetrical Polyhedra</strong></td>
</tr>
<tr>
<td>Truncated octahedron or sodalite unit</td>
</tr>
<tr>
<td>11-Hedron or cancrinite unit</td>
</tr>
<tr>
<td>14-Hedron or Gmelinite unit</td>
</tr>
</tbody>
</table>
natural and synthetic zeolites have been proposed by Smith, Fischer and Meier, and Breck. Although Meier was the first to propose a classification based on secondary building units contained in the structure, Breck's classification is based on a combination of framework topology as well as secondary building units. Breck's division of zeolites into seven groups based on these criteria is shown in Table 2.2.

2.4 Geology

Zeolites occur in rocks of many types and in a wide variety of geologic settings. It is a great monument that the concept of zeolite facies was established by Eskola in 1936 as the lowest grade of the metamorphic facies. The concept was greatly developed by Coombs, having further been visualised by Iijima and Utada, Hay, Sheppard, Gottardi and Obradovic and Sersale. Recently, an overview of geology of natural zeolites and zeolitic rocks in the world was reported by Iijima, at the 5th International conference on zeolites held at Italy.

Twentythree types of framework have been known in natural zeolites. Gottardi, emphases that the ratio $R = \frac{Si}{Si + Al + Fe}$ of a zeolite, which
<table>
<thead>
<tr>
<th>Group</th>
<th>SBU</th>
<th>Corresponding natural zeolites</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$S^4_R$ (Single 4-ring)</td>
<td>Analcime, phillipsite, gismondine, laumontite, paulingite, harmotome and Yugawarakite</td>
</tr>
<tr>
<td>2</td>
<td>$S^6_R$ (Single 6-ring)</td>
<td>Erionite, offretite, levynite</td>
</tr>
<tr>
<td>3</td>
<td>$D^4_R$</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>$D^6_R$</td>
<td>Faujasite, chabazite and gmelinite</td>
</tr>
<tr>
<td>5</td>
<td>$T^5_{10}$ Unit</td>
<td>Natrolite, scolecite, mesolite, thomsonite, gonnadrite, edingtonite</td>
</tr>
<tr>
<td>6</td>
<td>$T^8_{16}$ Unit</td>
<td>Mordenite, dachiardite, ferrierite, epistilbite, bikitaite</td>
</tr>
<tr>
<td>7</td>
<td>$T^10_{20}$ Unit</td>
<td>Heulandite, stilbite, brewsterite, clinoptilolite</td>
</tr>
</tbody>
</table>
represents the percentage of the tetrahedra occupied by Si, is an important chemical parameter with respect to the order disorder relation in zeolites. Zeolites are classified into "basic" with $0.50 \leq R < 0.625$, "intermediate" with $0.625 \leq R < 0.75$ and acidic with $R > 0.75$. These three classes seem to be closely related to the chemical composition of host rocks which include zeolites in them. Zeolites in undersaturated alkali rocks largely belong to "basic", whereas those in oversaturated acidic rocks are "intermediate" to "acidic". Zeolites often show a wide compositional variation even in the same species, in particular phillipsite, chabazite, clinoptilolite-heulandite, erionite, ferrierite, and analcime. The variation reflects various factors which act on the zeolite formation, such as P-T conditions, chemistry of original material, pore water and others.

Zeolites form at present or have formed in the past in various sediments or rocks under varying physical and chemical environments. Genetic classification of occurrence has been attempted by several workers, e.g. Hay, Iijima and Utada, Iijima, Sheppard, Gottardi and Obradovic, and Mumpton. Much work in field and laboratory has explicitly proved that
temperature is an important factor to control zeolite formation\(^{32-36}\). Another significant factor is the chemistry of pore-water in which zeolites precipitate.\(^{12,37,38}\)

As a result of the geothermal or chemical gradient, zeolites commonly occur in a vertically or laterally zonal arrangement which is usually mappable as zeolite zones. Therefore, temperature and nature of pore-water should be emphasized as the criteria to classify the genetic type of occurrence. In addition, zeolite species formed are influenced by the original material such as acidic or basic volcanic glass, clay etc. Nine genetic types are classified as shown in Table 2.\(^3\) More than two types frequently overlap one another to make a complex type. It is sometimes difficult to distinguish a specific type of occurrence from the shallow-burial diagenesis, percolating ground water, low temperature hydrothermal and contact metamorphism without regional mapping of zeolite zones.

Geological synthesis on natural zeolite formation has been discussed in detail by Iijima\(^{17}\). The types of occurrence of various zeolite species is tabulated as shown in Table 2.\(^4\) The temperature indicated is only approximate.
## Table 2.3 Genetic types of occurrence of zeolites

<table>
<thead>
<tr>
<th>A</th>
<th>Zeolite form at elevated temperature, the zones being primarily caused by geothermal gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Magmatic primary zeolites</td>
</tr>
<tr>
<td>2</td>
<td>Contact metamorphism</td>
</tr>
<tr>
<td>3</td>
<td>Hydrothermal</td>
</tr>
<tr>
<td>4</td>
<td>Burial diagenesis (or metamorphism)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B</th>
<th>Zeolites form at or near the surface condition, the zones being principally caused by chemical gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Percolating ground water</td>
</tr>
<tr>
<td>6</td>
<td>Weathering</td>
</tr>
<tr>
<td>7</td>
<td>Alkaline, saline lake deposits</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>Zeolites form at low temperature, any zones being not recognized</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Marine environment</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>D</th>
<th>Zeolites form in impact craters</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Impact crater</td>
</tr>
</tbody>
</table>
Table 2.4 Geological synthesis and occurrence of natural zeolites

<table>
<thead>
<tr>
<th>Type of occurrence</th>
<th>Temp.</th>
<th>Zeolite species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deep sea sediments</td>
<td>4 - 50°C</td>
<td>Ph, Cp, (An)</td>
</tr>
<tr>
<td>Earth's surface -</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Weathering, alkaline, saline lake percolating ground water (in basic tephra)</td>
<td></td>
<td>Ph, Cp, Ch, Er, Mo, Gl, Fa, Go, Na, An, (He)</td>
</tr>
<tr>
<td>Percolating water (in acidic tephra) shallow burial diagenesis low temperature hydrothermal</td>
<td>20 - 50°C</td>
<td>Ph, Cp, Ch, Er, Mo, Fe, An, Th, Me, Se, He, St etc. except La, Wa, Yu</td>
</tr>
<tr>
<td>Deep burial diagenesis Moderate - Temp. hydrothermal</td>
<td></td>
<td>La, An</td>
</tr>
<tr>
<td>Low grade meta-morphism. High Temp. hydrothermal</td>
<td></td>
<td>Wa, Yu, An</td>
</tr>
<tr>
<td>Magmatic primary</td>
<td></td>
<td>An</td>
</tr>
</tbody>
</table>

Ph = phillipsite, Cp = clinoptilolite, Ch = chabazite, Er = erionite, Mo = mordenite, Gl = gismondine, Fa = faujsite, Go = gonnardite, An = analcime, Na = natrolite, He = heulandite, Th = thomsonite, Me = mesolite, Se = scolecite, St = stilbite, La = laumontite, Wa = wairakite, Yu = yugawarakite.
2.5 Commercial properties of natural zeolites

All commercial applications of natural zeolites make use of one or more of several physical or chemical properties: such as (a) ion-exchange, (b) adsorption and related molecular sieve properties, (c) dehydration and rehydration and (d) siliceous composition. These properties, of course, are functions of the specific crystal structure of each individual zeolite species and of their framework and cationic compositions.

2.5.1 Adsorption properties

Crystalline zeolites are unique adsorbent materials. Under normal conditions, the large central cavities and the channels of zeolites are filled with water molecules forming hydration spheres around the exchangeable cations. If the water is removed, usually by heating, molecules having effective cross sectional diameters small enough to pass through the entry channels are readily adsorbed in the dehydrated channels and the cavities. Molecules too large to pass through the channels are excluded, giving rise to the well known "molecular sieving" property of most zeolites. As for example, consider the calcium-exchanged zeolite A which has a pore diameter of 4.5 Å. Normal hydrocarbons
such as pentane and octane having effective cross sectional
diameter of about 4.3 Å are easily taken up by this
zeolite. However, branch chain hydrocarbon, such as iso-
-pentane and iso-octane, with diameters of 5.0 Å or larger
are essentially not adsorbed. Thus, the separation of
mixtures of straight- and branch-chain hydrocarbons can
be accomplished by passing gaseous stream through columns
packed with dehydrated zeolites for their pore-size
distribution. A schematic illustration of the above
described process is shown in Fig. 2.2.

Because of the uniform size of the rings of
oxygen in the framework structures, zeolites have
relatively narrow pore-size distributions, in contrast to
the wide range of pre-size of other commercial adsorbents. Adsorption on crystalline zeolites is therefore
caracterized by Langmuir type isotherms such as that
shown in Fig. 2.3. The quantity adsorbed (x), relative
to the quantity of complete pore-filling (x_a), is
maximised at very low partial pressures of the adsorbate.
While the total amount of a gas adsorbed may not be as
great as for other types of adsorbents, crystalline
zeolites are excellent adsorbents for removing last trace
of a particular gas from a system. This property is
especially important in certain desiccation applications
where it is essential to lower the water content to less than 0.1 ppm.

The surface area available for adsorption ranges up to several hundred sq. m./gm, and some zeolites are capable of adsorbing up to about 30% of their dry weight. Most of the surface area is found within the zeolite structure and represents the inner surface of dehydrated channels and cavities.

In addition to their ability to separate gas molecules on the basis of size and shape, the unusual charge distribution within the dehydrated void volume due to the presence of cations, hydroxyl groups and field gradients generated by the substitution of aluminium for silicon in the framework, allows many species with permanent dipole moments to be adsorbed with a selectivity unlike that of any other adsorbent. Thus polar molecules such as H₂O, CO₂ and H₂S are adsorbed preferentially over non-polar molecules, and adsorption processes have been developed using natural zeolites to remove CO₂ and other contaminants from impure natural gas to give pure methane products. In addition, the small but finite quadrupole moment of N₂ allows it to be adsorbed selectively from air.
2.5.2 Cation-exchange properties

The cation-exchange properties of zeolite minerals were first observed more than a century ago and have recently been the subject of extensive reviews by Barrer and Sherry. The exchangeable cations of a zeolite are only loosely bonded to the tetrahedral framework and can be removed or exchanged easily by washing with a strong solution of another ion. As such, crystalline zeolites are some of the most effective ion-exchanges known to man, with capacities of up to three or four milliequivalents per gram. The ion-exchange capacity is basically a function of the degree of substitution of aluminium for silicon in the framework structure. In practice, however, the cation-exchange behaviour is dependent on a number of other factors as well, including (a) the nature of cation species (size, charge etc.), (b) temperature, (c) concentration of cation species in solution and (d) the structural characteristics of the particular zeolite under investigation.

In certain species cations may be trapped in structural positions that are relatively inaccessible, thereby reducing the effective exchange capacity.
of that species for that ion. Also, cation sieving may take place if the size of the cation in solution is too large to pass through the channels into the central cavities of the structure. Analcime for example will exchange almost completely its Na\(^+\) for Rb\(^+\) (ionic radius = 1.49 \(\text{Å}\)), but not at all for Cs\(^+\) (ionic radius = 1.65 \(\text{Å}\))\(^{43}\).

Unlike other non-crystalline ion-exchangers, the framework of a crystalline zeolite dictates its selectivity towards competing ions, and different structures offer different sites for the same cation. The hydration spheres of high field strength ions prevent their close approach to the seat of charge in the framework; therefore, in many zeolites ions with low field strength are more tightly held and selectively taken up from solutions than other ions.

The cation-exchange reaction can be expressed simply as

\[
A_Z + B_s = A_s + B_Z
\]

where \(A\) is the cation in the zeolite and \(B\) is the cation in the solution. Cation-exchange equilibria between a zeolite and a solution are usually depicted
by an ion-exchange isotherm which plots equivalent molal fraction of the exchanging cation in the zeolite phase \( (A_z) \) as a function of the equivalent molal fraction of the exchanging cation in the solution phase \( (A_g) \).

Five types of isotherms are illustrated in Fig. 2.4:
(a) selectivity for the entering cation over the entire range of zeolite composition; (b) the entering cations shows a selectivity reversal with increasing equivalent fraction in the zeolite; (c) selectivity for the leaving cation over the entire range of zeolite compositions; (d) exchange does not go to completion although the entering cation is initially preferred (the degree of exchange \( x_{\text{max}} < 1 \), where \( x \) is the ratio of equivalents of the entering cation to the gram equivalent of Al in the zeolite); (e) hysteresis effects may result from formation of two zeolite phases. The different kinds of selectivities and isotherm shapes shown in Fig. 2.4 reflect the diversity of zeolite frameworks and stability of cations in various sites within the structures.

2.5.3 Dehydration and dehydroxylation phenomena

Based on dehydration behaviour, zeolites may
be classified as (a) those which show no major structural changes during dehydration and which exhibit continuous weight loss curves as a function of temperature, and (b) those which undergo major structural changes during dehydration and which exhibit discontinuities in their weight loss curves. The latter group includes those zeolites whose structures collapse on heating to elevated temperatures. Natural zeolites such as chabazite, mordenite, analcime, clinoptilolite belong to the first group, whereas the zeolites of natrolite group and heulandite group belong to the second group. A summary of the dehydration behaviour of zeolite is listed by Breck. Structural hydroxyl groups can be introduced into zeolites by (a) cation hydrolysis or (b) de-ammoniation of NH₄⁺-exchanged zeolites (also referred to as decationization). The presence of hydroxyl groups in zeolites is especially important in their use as catalysts. The active sites for hydrocarbon conversions and other catalytic reactions are acidic protons associated with structural OH groups.

2.6 Utilization of natural zeolites

There have been a number of comprehensive
and excellent reviews of the uses of natural zeolites in the last about five years\textsuperscript{2,44-46}. A summary adopted from these references is given in Table 2.5. The major use of natural zeolites is in bulk mineral applications\textsuperscript{44} in Europe in the building and construction industry, where proximity to building location makes them cost effective; and in the far East as filler in the paper industry, largely because of the unavailability of alternative mineral resources. A modest market for zeolite minerals has developed as a molecular sieve adsorbent in acid-gas drying in the natural gas industry, in NH\textsubscript{4} removal in water treatment systems by ion-exchange, and in the production of oxygen and nitrogen via adsorptive air separation, especially in Japan\textsuperscript{47}.

Growth of bulk chemical and consumer applications for natural zeolites appears to be certain. In addition to those applications included in Table 2.5, Breck\textsuperscript{46} has proposed their use in agriculture, beverage carbonation and raw materials for ceramics.

The future trends in materials will no doubt see the re-evaluation of the host of known zeolites which never achieved commercial success. The commercialization of 'stored' or 'shelved' zeolites has largely
<table>
<thead>
<tr>
<th>Bulk applications</th>
<th>Molecular sieve applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filler in paper</td>
<td>Separation of $O_2$ and $N_2$ from air</td>
</tr>
<tr>
<td>Fozzolanic cements and concrete</td>
<td>Acid resistant adsorbents in drying and purification</td>
</tr>
<tr>
<td>Dimensions stone</td>
<td>Ion exchangers in pollution abatement processes</td>
</tr>
<tr>
<td>Light weight aggregate</td>
<td></td>
</tr>
<tr>
<td>Fertilizers and soil conditioners</td>
<td></td>
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<tr>
<td>Dietary supplement in animal nutrition</td>
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</table>
been hampered by the lack of their general availability and their apparent inability to compete performance-wise with the current commercial products. With the worldwide expansion of scientific zeolite centres with the capability of synthesizing non-commercial zeolites and determining their properties and potential applications, it is likely that several "old" zeolites will achieve commercial success.

2.7 Review of earlier work done on stilbite, heulandite and analcime

In the present work, mainly two varieties of natural zeolites viz. stilbite and heulandite are used to study their ion-exchange behaviour and consequential changes in their structure, framework vibrations, thermal stability and adsorption properties. These crystals were collected from the quarries of Pashan area near Poona. In addition, natural analcime crystals were used for the microtopographical studies. A brief summary of the earlier work done on these zeolite crystals is given in what follows.

2.7.1 Stilbite

Stilbite was the first zeolite to be
discovered by Cronstedt in 1756\(^1\,^4,^8\). Stilbite is commonly found as a vein mineral or locally as a replacement product in volcanogenic rocks in association with heulandite group minerals or laumontite. It has been described from New Zealand\(^1\,^4,^9\), Japan\(^2\,^3,^3\), California\(^5\,^0\), Iceland\(^5\,^1\), and India\(^5\,^2,\,^53\). Staples\(^5\,^4\) described the replacement and filling of fossil shells by stilbite and other zeolites as a result of hydrothermal solutions. Stilbite is usually a calcium-rich zeolite containing small amount of sodium. But Harada and Tomita\(^5\,^5\) have found a sodium rich variety in Japan.

The crystal structure of stilbite has been determined by Maynard Slaughter\(^5\,^6\) and later refined by Galli\(^5\,^7\). The hydrothermal transformation of stilbite to wairakite at about 300°C was studied by Harada and Tomita\(^5\,^5\). Barrer and Vaughan\(^5\,^8\) have studied the adsorption behaviour of stilbite. The alkali metal cation-exchange in natural stilbite has been investigated by Ames\(^5\,^9\). Dehydration studies on this zeolite have partially been carried out by several workers\(^5\,^8,\,^60-62\). Preparation and properties of hydrogen form of stilbite and heulandite have been studied by Jacobs and Uytterhoeven\(^6\,^2\).
2.7.2 Heulandite

The calcium zeolite, heulandite, is a widely occurring mineral which is potentially important as a geologic indicator. Heulandite is found in an environment which is saturated or oversaturated with respect to SiO\textsubscript{2}. It occurs as an alteration product of acid-igneous rocks or volcanic glass, a cavity filling in basaltic rocks and as an authigenic mineral in sedimentary rocks. The synthesis of heulandite by Koizumi and Roy\textsuperscript{64} in a limited temperature and pressure range (200 - 360°C at 15000 - 37000 psi) and the destruction of both the natural and artificial minerals at temperatures of 400°C and above indicate that heulandite could be used as a geologic thermometer.

The structure of heulandite has been determined and refined by Merkle and Slaughter\textsuperscript{65}. The dehydration behaviour was studied by several workers\textsuperscript{45,62,64,66-69}. Preparation and properties of hydrogen form of heulandite have been reported by Jacobs and Uytterhoeven\textsuperscript{62}. Adsorption behaviour of heulandite has been reported by Barrer et al\textsuperscript{58,70}.
2.7.3 Analcime

Analcime is a common zeolite in both igneous basalts and in sedimentary rocks. Although it is relatively complex, the crystal structure of analcime was one of the first to have been determined\(^7\). In hydrated analcime, the Na\(^+\) ions are in a distorted coordination octahedron with four framework oxygens and two H\(_2\)O molecules. The water content of analcime varies linearly with the silica content. As the silica content increases, the cation population decreases, and there is a concurrent increase in the number of water molecules. A neutron diffraction study of analcime has shown that the H\(_2\)O molecules are not hydrogen bonded\(^7\). 

Analcime is a structurally stable zeolite, and may be completely dehydrated. After dehydration, analcime adsorbs small polar molecules. Analcime is reportedly unchanged in structure at 700°C\(^6\),\(^7\).\(^8\).\(^9\). The Na\(^+\) ions in analcime can be exchanged by alkali metal cations (Li\(^+\), K\(^+\)), NH\(_4\)^+, Ag\(^+\) and divalent ions (Ca\(^{2+}\), Mg\(^{2+}\)) at high temperatures\(^7\). An ion-sieve effect was observed in the exchange of sodium for cesium, while extensive exchange was obtained with rubidium\(^9\).\(^3\).
Synthetic materials with chemical composition corresponding to that of analcime have been claimed by many investigators, and a summary of these reports has been given by Barrer. The first synthesis of an analcime-type zeolite substantiated by X-ray diffraction analysis was by Barrer and White. The analcime-type was commonly obtained in the form of icositetrahedra, but in the presence of NaF, it was obtained as cubes possessing hemihedral faces. Although large crystals of the mineral analcime have been found, synthetic analcime-type zeolite crystals have not exceeded 100 microns in diameter. The difficulty in growing larger crystals is in sustaining crystal growth after the initial formation of small crystals.
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Captions of the figures

Fig. 2.1 The secondary building units (SBU) in zeolite structures.

Fig. 2.2 Schematic illustration of the selective adsorption.

Fig. 2.3 Langmuir-type isotherm for adsorption on crystalline zeolites.

Fig. 2.4 Five types of ion-exchange isotherms.
Fig. 2.1

Fig. 2.2
**Fig. 2.3**

complete pore filling, \( x = x_s \)

**Fig. 2.4**