Nature and Properties of Zeolites

Condensed from a report prepared by Peter Cooksey, B.E., a mineralogist and wastewater consultant employed in the zeolite field.

1. WHAT ARE ZEOLITES?

General

A satisfactory definition for zeolites can only be explained if you have an understanding of the words used in its description.

Before attempting a definition here are a few facts about the nature and properties of zeolites.

The Basic Nature of Zeolites

"Zeolites are:

. Substances which occur naturally as minerals, and may be found in rocks and soils of igneous origin, but which can also be synthesised quite easily from non-zeolite materials.

. *Crystalline*, but formation of crystals of significant size requires long periods under very specific conditions, so zeolites are usually micro-crystalline.

. *Alumino-silicates* so their structure is based on linked tetrahedra, in each of which a silicon or aluminium atom is surrounded by four uniformly arranged oxygen atoms.   ....

. *Hydrated*, so the structure incorporates water which results in the formation of *uniformly sized channels and cavities of near-molecular size*.

Important Properties of Zeolites

. *Bonding* in zeolites is *three-dimensional*, and results in a *rigid structure* which retains its shape and dimensions on dehydration (by heating to about 400° C) and rehydration.

. The channels and cavities in zeolites result in reduced density with respect to materials which have similar composition apart from hydration.

. The channels and cavities provide a large surface area per unit weight (or unit volume) of material, which greatly facilitates surface reactions.

. The *cations* which balance the framework charge are located in these channels and cavities, and hence *are available for exchange* with cations in the surrounding liquid.

. Such cation exchange does not damage the structure of the zeolite.

Differentiation from Other Materials

The wording which has been italicised in the above covers the major features and properties which are usually emphasised in definitions of zeolites.

Some of this wording is necessary to cover characteristics of zeolites themselves, while the remainder is necessary to distinguish them from other materials.

Some consideration of the materials from which they specifically require differentiation is also necessary.

Because zeolites may be either natural or synthetic, any definition must cover both possibilities, but because of the greater variation in natural materials differentiation from other minerals is probably hardest to define.

Small crystal size was a major hindrance to identification of natural zeolites until more recent developments in analytical techniques became available, and until the 1950's resulted in a belief that zeolites were relatively rare in nature.

Until that time the alumino-silicate nature of the deposits was generally recognised, as was their hydrated state, but the materials were frequently classified as clays.

Both clays and zeolites are hydrated alumino-silicates, but:

- **In clays, bonding is two-dimensional**.
  The minerals tend to form plates, with the water lying between the plates, so that dehydration and rehydration tends to result in contraction and expansion perpendicular to the plates.

- **In zeolites, bonding is three-dimensional**
  Bonding may be stronger in one or two directions than the third, so that zeolites may still be "platey" or "fibrous", but the attached water lies in the channels and cavities, so that dimensions do not tend to change with dehydration and rehydration.

The essential features distinguishing zeolites from other materials are therefore:

- Zeolites, together with clays, are distinguished from most other crystals by the fact that they are hydrated alumino-silicates. (Inclusion of the word crystalline may be considered superfluous, since most alumino-silicates are crystalline, but is probably necessary because alumino-silicate gels also exist.)

- Distinction between clays and zeolites is then made by inclusion of the three-dimensional nature of the zeolite framework.

- There is one further group of materials which may not be distinguished from zeolites on the basis of the above and these are substances known as clathralites. .... clathralites are also hydrated alumino-silicates with a three-dimensional structure, but these are distinguished from zeolites by the fact that their channels, while regularly arranged, are too small to facilitate the free exchange of cations.

Definition of Zeolites

.... Zeolites are **hydrated alumino-silicate compounds** having **rigid three-**

dimensional crystalline structures containing **regularly arranged, near-molecular size channels and cavities** which facilitate the **exchange of associated cations**.

Even this relatively complex definition is not completely satisfactory .... but it does cover most of the features currently considered significant.

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Distinction Between Individual Zeolites

Distinction between individual zeolites is no less complex than the distinction between zeolites and other materials.

About 45 different natural zeolites are recognised, and approximately 300 types have been synthesised. ....

Further Considerations

An understanding of zeolites:

a.   begins with the nature of silicates, and of characteristics arising from substitution of aluminium for silicon in some of the tetrahedra

b.   Is extended by consideration of the consequences of hydration during crystallisation

c.   Is consolidated by examination of the differences between individual zeolites and how these arise from differences in structure and silicon to aluminium ratios (Si:Al)

This task has been begun above, but will be pursued in more detail in the notes that follow.

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2.   ZEOLITES AS SILICATES AND ALUMINO-SILICATES

Silicates

Oxygen and silicon are both found in abundant quantities in the earth's crust, and oxygen reacts strongly with elements such as silicon that can give up electrons, so it is hardly surprising that a large number of naturally occurring minerals are silicates.

The primary building unit of a silicate consists of four oxygen atoms around a silicon atom, the oxygens being attracted to the silicon by electrostatic forces resulting from the exchange of electrons.

The oxygen atoms are drawn in towards the silicon to an extent which is limited by the electrons surrounding them............. .

The silicon atom is small enough to fit between the oxygens, even when the oxygens have been drawn into contact with each other.

The oxygen atoms, being identical to each other, can be visualised as forming a theoretical .... structure having four similar triangular faces (i.e. a tetrahedron) ....

Alumino-Silicates

Aluminium, like silicon and oxygen, is quite abundant in the earth's crust, and often substitutes for silicon at the centre of some tetrahedra, thus forming alumino-silicates in place of silicates.

This substitution can occur because aluminium is similar in size to silicon, and will occur to an extent determined by the relative availability of aluminium and silicon in the solution from which the material crystallises.

Replacement of some of the silicon by aluminium is significant because the charge imbalance so introduced is compensated for by cations attracted to, but not actually part of, the crystal structure.

These cations can be exchanged with others in adjacent solutions, the degree of exchange depending on material types and concentrations, and this gives alumino-silicates many interesting properties.

Uneven distribution of surface charge in alumino-silicates also results in the attraction of polar molecules, and this characteristic results in adsorption of numerous molecules onto the solid surface.

Zeolites, being porous, exhibit much greater surface areas per unit volume than other alumino-silicates, and therefore have higher cation exchange and polar molecule adsorption capacities than other alumino-silicates.

Retention of structural characteristics (i.e. channels and cavities) on dehydration allows zeolites also to exhibit strong adsorption of polar gases. This characteristic is enhanced in dehydrated zeolites over the hydrated condition due to removal of competition from highly polar water molecules.

Occurrence of Natural Zeolites

Historical Report

Zeolites were once thought to be quite rare, and to occur naturally only as crystals within cracks and cavities in igneous rocks. Individual crystals in such situations may be quite large, but zeolite quantities in any given area are insufficient to be of practical significance.

Zeolites are now known to occur in both igneous and metamorphic rocks, and to be common constituents of many sedimentary rocks of igneous origin. While the quantity of zeolites found in any particular location might be large, the crystals are very fine-grained, so that recognition may be difficult.

Apparent rarity was largely a result of inadequacy of analytical techniques for mineral identification ....

.........The first discovery of a natural zeolite was made in 1756 by a Swedish mineralogist, Baron Axel Fredrick Cronstedt, who found well-formed crystals in cavities in igneous rock at the Svappavari copper mine at Lappmark in Sweden. The specific mineral found by Cronstedt was stilbite.

Commercial Deposits

About 45 natural zeolites have now been discovered but .... only ten or eleven zeolite types have been found to satisfy ..... criteria. *(Clinoptilolite is among the zeolites generally considered to be an exploitable natural reserve.)*

As already stated, the porous structure typical of zeolites results from incorporation of water into the molecule during crystallisation, and this occurs only under suitable conditions of temperature and pressure.

Zeolite formation generally requires:

.   long periods of crystallisation

.   relatively high pH (ph > 9 suggested)

.   slightly elevated temperature and/or pressure

.... typical temperatures for formation of natural zeolites are of the order of 70°C to 350°C and deposits accumulate over geological time scales (sometimes over hundreds of thousands of years). There are also suggestions that under special circumstances (e.g. deposition of volcanic ash in shallow water) much shorter time scales may be required.

Usually the original igneous rock is first dissolved, and then recrystallised as zeolite as a result of changes in conditions from those originally causing solution (e.g. different pH, temperature, or concentrations of elements in solution).

The change in conditions may occur either because water moves through, or evaporates from, the system, or because continuing solution and precipitation gradually change the concentration of components in solution.

Many igneous rocks are impervious to water, so little material can dissolve from the limited surface area available. For significant zeolitisation of such rocks to occur the parent rock must first be broken down into smaller fragments (e.g by erosion).

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Zeolite Synthesis

Only a few natural zeolites (six) can be synthesised, probably because their formation requires long time scales. Many zeolites can be synthesised, however, which have no known natural counterparts, and the number of zeolite types so far synthesised is of the order of 300.

.... current zeolite synthesis involves crystallisation from a gel at temperatures ranging from room temperature to 200°C, and at normal pressures. The **gels are usually prepared from aqueous solutions of sodium aluminate, sodium silicate, and an alkali metal hydroxide** such as sodium or potassium hydroxide.

.... the synthesis product depends on the gel composition, the nature of the reagents, and the crystallisation conditions, ... the molecular processes involved remain largely empirical.

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Economic incentive for research into the synthesis of zeolites were provided by the belief *(incorrect)* that rarity of zeolites in nature would prevent development of applications which could benefit from their unique properties.

At about the time that suitable methods of synthesis were developed (in the mid-1950s) however, it was found that natural zeolites occurred much more widely in nature than was previously thought. Despite this, and the higher cost of synthetic zeolites, synthetic zeolites are still preferred in some applications because:

.   a number of synthetic zeolites do not have natural counterparts, and some of these synthetic zeolites have special properties

.   the uniformity of characteristics of synthetically produced zeolites over their natural counterparts justifies their higher cost.

In other applications natural zeolites are preferred because of their lower cost, and it has been found that the markets for natural and synthetic zeolites are generally compatible rather than competitive.

Moisture Content of Zeolites

The name zeolite derives from two Greek words, zein and lithos (meaning "boiling stones"), which results from the tendency of zeolites to froth and give off water when heated in the flame from a blow-pipe.

Zeolites in their natural state contain relatively high quantities of water (frequently 15-20% or more by weight), but this water is chemically bound to the zeolite framework, and hence the material normally appears quite dry.

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Typical ranges for water content have been specified by various authors (based on chemical content) ....

In general:

. % water by weight tends to increase with increasing Al:Si ratio (at least for low Al/Si)

. The H20:Al ratio tends to decrease as the Al:Si ratio increases

. The H20:02 ratio tends to increase with increasing Al:Si ratio (at least for low Al/Si)

. The void volume/%water ratio stays fairly constant, irrespective of the Al:Si ratio

Zeolites in their natural state have insufficient attraction for additional moisture to become damp, so that even when finely ground they will be found to flow freely in relatively humid environments.

Changes in their moisture content with the relative humidity of their surroundings are quite readily measured, however, and care must therefore be taken when relating zeolite properties to unit weight of the material.

When heated at moderate temperatures (only a few hundred degrees centigrade) the attached moisture is driven off without significantly affecting the structure of the material, and this leaves a substance with high attraction for water and other polar molecules.

Reference may often be seen in literature to the use of zeolites as desiccants (i.e. agents which keep surrounding materials or environments dry by preferential adsorption of moisture). This characteristic is strong, but is only utilisable after the zeolite has been dehydrated by heating.

Molecular sieving of gases (i.e. separation of molecules depending on whether or not they are small enough to penetrate the pores of the zeolite) is also possible once the material has been dehydrated, as in the hydrated state the water occupies the pores and cavities.

APPENDIX A ZEOLITES AS ALUMINO-SILICATES

1. GENERAL

Rocks and Minerals

The earth's crust is made up of materials of variable hardness and composition known as "rock".

Rock has no distinctive shape of its own, is not homogeneous, and does not have definite chemical composition, although various "types" of rock are identified by similarities in structure.

Rocks are subdivided on a broad scale in terms of their mode of formation into:

. igneous - where the rock has solidified from molten material (the molten material existing in abundance deep within the earth, and solidifying if allowed to approach, or extrude onto, the surface)

. sedimentary - where organic matter or mineral particles deposited at the earth's surface are cemented together to form solid material

. metamorphic - where the structure of igneous or sedimentary rocks has been modified by the effects of temperature and/or pressure due to burial or proximity to igneous material

The materials contained in rock may be of organic or inorganic origin, and are grouped into compounds known as "minerals".

Minerals, in geological terms, may be considered to be substances with definite chemical composition, or a definite range of chemical compositions, which results in regular internal molecular structure.

Because both oxygen and silicon are found in abundant quantities in the earth's crust, and because oxygen has high oxidising power, it is hardly surprising that a large number of naturally occurring minerals are silicates.

Many oxides, including silicates, take the form of crystals, so before considering silicates in detail it is appropriate to consider what crystals are, the nature of bonds between elements, and how these bonds result in the formation of crystals.

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Crystals and the Unit Cell Concept

Chambers "Everyday Dictionary" defines a crystal as:

"..... a body, generally solid, whose atoms are arranged in a definite pattern, expressed outwardly by geometrical form with plane faces .....".

Important aspects of this definition are that crystals have definite geometrical forms, and that these forms result from patterned arrangements of the atoms. One aspect that this definition does not highlight is that the pattern of atoms is repeated at regular intervals.

According to Rutley's "Elements of Mineralogy"

"Every crystal consists of certain atoms or groups of atoms arranged in a three-
dimensional pattern, which is repeated throughout the crystal. The smallest complete unit of pattern is called the **unit cell**, and the whole pattern is formed by stacking unit cells together."

A unit cell is an arrangement of atoms or ions that is *seen* to repeat itself within the crystal, and does not relate in any specific way to the bonds between atoms or ions.

In particular, atoms or ions at the boundaries of a unit cell may be bonded to other atoms (or ions) within <u>that</u> unit cell, or may be bonded to atoms (or ions) within an <u>adjacent</u> unit cell.

This lack of relationship to bonding can be rather confusing to anyone familiar with

the concepts of atoms linked together to form molecules, but the concept is similar to isolation of similar coloured squares from a cloth woven with regularly arranged coloured strands.

The individual squares in the cloth can be identified, but the strands continue on, and whether the square "starts" with (for example) blue, and goes through green, yellow and red before repeating, or starts with yellow and goes to green, is unimportant, the only significance being that a recognisable pattern is continually repeated.

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2. SILICATES

General
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The fundamental unit in the building of silicate minerals is the SiO_4^{4-} group in which a silicon ion is situated at the centre of a tetrahedron whose corners are occupied by four oxygen ions.

Classification of the silicates is based on the different ways in which the SiO_4 tetrahedra occur, but while there is good agreement on the groups involved, there is considerable variation in nomenclature.

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Neosilicates

Separate SiO_4-groups (Orthosilicates)

Here separate tetrahedra are stacked together in a regular manner throughout the crystal structure, and are linked together through cations which lie between them.

.... Olivine is an example of this type of mineral.

Sorosilicates

Structures with Si_2O_7-groups

In these minerals the SiO_4-tetrahedra occur in pairs and one oxygen, being shared between two silicons, is inert. The Si_2O_7 groups are then spaced throughout the crystal, being bound together by other cations (these divalent cations being needed to balance charges).

The mineral melilite, ... has a structure of this kind.

Cyclosilicates

Ring Structures, $n(SiO_3)$

If each SiO_4-tetrahedron shares two of its oxygens with neighbouring tetrahedra then rings may be formed, with the minerals containing silicon and oxygen in multiples of SiO_3.

Examples are given in Rutley's of a three tetrahedra ring (benitoite) and a six tetrahedra ring (beryl), and the comment is made that in beryl the rings are stacked together in columns with an empty "tunnel" running through the middle, and that gases have been passed through these "tunnels".

Inosilicates

Chain Structures, $n(Si_2O_6)$

As with ring structures, each SiO_4-tetrahedron (except those at the ends of the chain) shares two of its oxygens with neighbouring tetrahedra.

Conceptually a ring structure may be considered as a chain with its ends joined except, of course, that one oxygen must be lost in forming the ring in order to allow one more oxygen to be shared.

.... A feature of chain structure minerals is that the apexes of the tetrahedra all point in the same direction, and chains run parallel to each other bonded together by cations which lie between them.

An important group of minerals known as pyroxenes are ...... an example of chain structure silicates ....

Double Chain Structures, $n(Si_2O_{11})$

In these minerals two single chains occur side by side, with the apexes of all tetrahedra pointing one way and the chains being linked by sharing oxygen atoms at regular intervals.

Phyllosilicates

Sheet Structure, $n(Si_2O_{10})$

A sheet structure is formed when the SiO_4-tetrahedra are linked by three of their corners, and extend indefinitely in a **two-dimensional** network or "sheet" which has a silicon to oxygen ratio of 4:10.

Micas, chlorites and a number of other flaky minerals are silicates with sheet structure.

In the micas silicon is replaced by aluminium to the extent of about one atom in four, and the resultant charge is balanced by the addition of potassium ions which are located between one pair of sheets and the next. Because the bonding between the potassiums and the pairs of sheets is much weaker than the bonding holding the pair of sheets together cleavage takes place relatively easily parallel to the sheet structure.

In the mineral **talc** there is no replacement of Si by Al, and hence no K-ions between the pairs of sheets, but the bonding between pairs of sheets is then not ionic, being due to residual or stray electrical forces. This weak linkage is reflected in the characteristic softness of talc.

Tektosilicates

Framework Structures, n(SiO$_2$)

A three-dimensional framework is formed when each tetrahedron is linked by all four corners, so that every oxygen is shared between two tetrahedra. Minerals which have this structure include **quartz** (SiO$_2$) and other forms of silica.

When aluminium replaces some of the silicon other important minerals such as the felspars, felspathoids and **zeolites** are formed.

The Tektosilicates can be subdivided into the following groups:

.   SiO$_2$
.   felspars
.   scapolites
.   felspathoids
.   zeolites

Apart from the SiO$_2$ group *(quartz)* these are all alumino-silicates, but the **zeolites are the only group in which the minerals are hydrated**.

3.   ALUMINO-SILICATES

General

As indicated above, replacement of some silicon by aluminium is not unusual in silicates of the chain, sheet and framework types. The minerals then formed are termed alumino-silicates.

This substitution can occur because aluminium is similar in size to silicon, and will occur if both aluminium and silicon are available in the solution from which the material crystallises.

Lowenstein's Rule

The degree of substitution of aluminium for silicon in alumino-silicates will be largely dependent on the relative availability of the two elements in the solution from which the material crystallises.

Because aluminium is slightly larger than silicon, however, it cannot replace silicon in adjacent tetrahedra. This criterion is known as Lowenstein's Rule ....

Consequences of Aluminium Substitution

The properties of alumino-silicates, and of **zeolites in particular**, are often related to aluminium content, generally in terms of Si:Al ratios (which because of Loewenstein's Rule must be greater than 1, and for natural zeolites are found to range up to about 6).

The proportion of aluminium is significant because aluminium is a trivalent metal while silicon is tetravalent. Substitution of aluminium for silicon in a tetrahedron therefore leads to the **development of a negative charge** which is balanced by cations attracted onto, but not part of, the alumino-silicate.

In order to maintain electrical neutrality, the number of cations attracted is determined by the number of aluminium molecules in the alumino-silicate, and on the charge of the cations ....

The total positive charge due to the attached cations increases as the aluminium content of the material increases. ....

Obviously many cations within a solidified crystal may not be accessible for such exchange.

Differences Between Zeolites and Other Alumino-Silicates

The fundamental difference between zeolites and other alumino-silicates is that the rigid porous structure of zeolites makes the exchangeable cations, and surfaces in general, much more accessible than with other alumino-silicates.

Properties arising from cation exchange, adsorption, etc, are therefore much more pronounced with zeolites than with other alumino-silicates such as **clays**, felspars, etc., and this is significant with respect to catalysis in particular.

The porous nature of zeolites arises from incorporation of water of hydration into a three dimensional framework during crystallisation.

In most zeolites the water of hydration is held in such a way that it can be driven off by heating without changing the dimensions of the material, thus leaving open pores and channels of very uniform dimensions.

Clays also contain water of hydration, but because the structure of clays is two-dimensional incorporation of the water of hydration does not result in a rigid structure with pores and channels, so that clays generally shrink when the water of hydration is driven off.

While clays, felspars, scapolites, felspathoids and zeolites are all alumino-silicates, clays are sheet structures with formulae based on $n(Si_4O_{10})$, while zeolites, felspars, scapolites and felspathoids are framework structures with formulae based on $n(SiO_2)$.

Clays have lower specific surface areas than zeolites (i.e. lower surface area per unit volume) and generally expand and contract as water of hydration is added or removed.

Felspars, scapolites and felspathoids do not contain water of hydration, and hence have compact structures and relatively high density, while the water of hydration in zeolites results in a porous structure of lower density and with high specific surface area.

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Notes:

meq/100g means milli equivalents per 100 g. It is a measure of electron charge.

Polar molecule is one which is neutral overall, one end is negative, one end is positive. From memory it is a "straight" molecule. The positive charged end of the polar molecule is attracted to the negative charged surface of the zeolite.

Water is polar. H_2O is not a straight molecule, it is V shaped.

Zeolite is a cation exchange agent.

Zeolite especially attracts ammonium which is NH4+. Anything with a + means that it is positive charged. The cation exchange on the surface of the zeolite gives out a negative charge attracting positive charges.

The moisture content of Australian zeolite is approximately 25%.