Lecture #2 The spread of inorganic polymers in nature. The differences between the HMC and inorganic polymers.

Major classes of inorganic polymers

Borates

These compounds are salts of the oxyacids of boron (B), such as boric acid, H_3BO_3, metaboric acid, HBO_2, and tetraboric acid, $H_2B_4O_7$. Borates result either from the reaction of a base with a boron oxyacid or from the melting of boric acid or boron oxide, B_2O_3, with a molten metal oxide or hydroxide. Borate anion structures range from the simple trigonal planar BO_3^{3-} ion to rather complex structures containing chains and rings of three- and four-coordinated boron atoms. (See the article chemical bonding for a description of molecular shapes.) For example,calcium metaborate, CaB_2O_4, consists of infinite chains of $B_2O_4^{2-}$ units (see Figure 16A), while potassium borate, $K[B_5O_6(OH)_4]$ $2H_2O$ (commonly written as KB_5O_8 $4H_2O$), consists of two B_3O_3 rings linked through a common four-coordinated boron atom (see Figure 16B). The tetraborates, $B_4O_5(OH)_4^{2-}$, contain both three- and four-coordinated boron surrounded trigonally and tetrahedrally, respectively, by oxygen (O) atoms (see Figure 16C). Commercially, the most important borate is borax, or sodium tetraborate decahydrate, $Na_2B_4O_710H_2O$. Borax is found naturally in dry lake beds, such as Searles Lake in California. It can be used to soften water and to make washing compounds. Its usefulness arises from the insolubility of calcium and magnesium borates and the alkaline or basic nature of aqueous solutions of borax. Borax is also used in the manufacture of borosilicate glass and enamels and as a fire retardant.

Silicates

Silicates are salts containing anions of silicon (Si) and oxygen. There are many types of silicates, because the silicon-to-oxygen ratio can vary widely. In all silicates, however, silicon atoms are found at the centres of tetrahedrons with oxygen atoms at the corners. The silicon is always tetravalent (*i.e.,* has an oxidation state of +4). The variation in the silicon-to-oxygen ratio occurs because the silicon-oxygen tetrahedrons may exist as discrete, independent units or may share oxygen atoms at corners, edges, or--in rarer instances--faces, in several ways. Thus, the silicon-to-oxygen ratio varies according to the extent to which the oxygen atoms are shared by silicon atoms as the tetrahedrons are linked together. The linkage of these tetrahedrons provides a rather convenient way of classifying silicates. Seven different classifications are commonly recognized.

1. In some silicates, individual SiO_4^{4-} tetrahedrons exist as independent units. Silicates of magnesium (Mg_2SiO_4) and zirconium ($ZrSiO_4$) are examples. The tetrahedral structure of the SiO_4^{4-} is shown in Figure 17A.

2. Two SiO_4 tetrahedrons share one corner oxygen atom to form discrete $Si_2O_7^{6-}$ions (Figure 17B). Two compounds with this type of linkage are $Ca_2ZnSi_2O_7$ and $Zn_4(OH)_2Si_2O_7$ H_2O.

3. SiO_4 tetrahedrons may share corners and form closed rings. In $BaTiSi_3O_9$three SiO_4 tetrahedrons share corners, while in $Be_3Al_2Si_6O_{18}$ (beryl, the deep green variety of which is known as emerald) six tetrahedrons share corners to form a closed ring.

4. SiO_4 tetrahedrons in which each tetrahedron shares two oxygen atoms from two other tetrahedrons exist as chains in some silicates. An example of this type of silicate is $CaMg(SiO_3)_2$. From the formula it appears that SiO_3^{2-} ions exist, but these ions do not occur as independent entities. Parallel chains extend the full length of the crystal and are held together by the positively charged metal ions lying between them.

5. When SiO_4 tetrahedrons in single chains share oxygen atoms, double silicon-oxygen chains form (Figure 17E). Metal cations link the parallel chains together. Many of these silicates are fibrous in nature because the ionic bonds between the metal cations and the silicate anions are not as strong as the silicon-oxygen bonds within the chains. A class of fibrous silicate minerals that belongs to this group is collectively called asbestos. The best known and most abundant kind of asbestos is chrysotile, which has the formula $Mg_3(Si_2O_5)(OH)_4$. This compound exists as fibres more than 20 millimetres (0.8 inch) in length. It was used in the past in many fireproofing and insulation applications, but its use for these purposes has been discontinued because it appears that prolonged exposure to airborne asbestos fibres may cause cancer of the lungs.

6. When oxygen atoms are shared between double chains, silicon-oxygen sheets are formed. Metal ions form ionic bonds between the sheets. These ionic bonds are weaker than the silicon-oxygen bonds within the sheets, so silicates with this structure cleave into thin layers. An example of this class of silicates includestalc, $Mg_3Si_4O_{10}(OH)_2$.

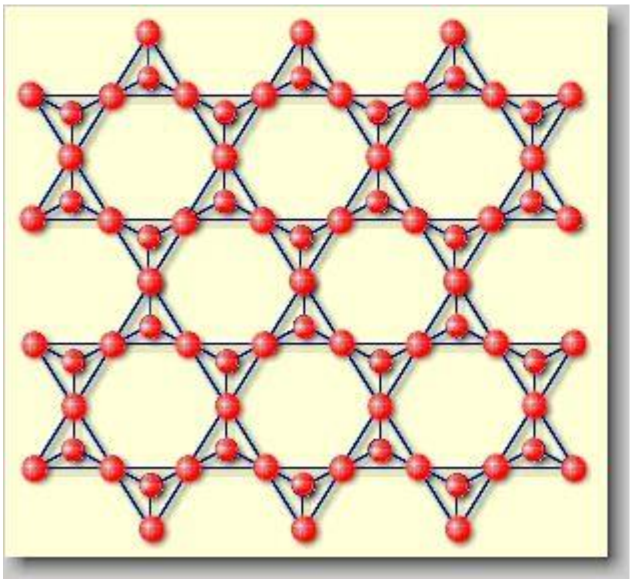

Fig. $Mg_3Si_4O_{10}(OH)_2$

7. A most interesting class of silicates consists of the zeolites. These compounds are three-dimensional silicon-oxygen networks with some of the tetravalent silicon ions replaced by trivalent aluminum (Al^{3+}) ions. The negative charge that results--because each Al^{3+} ion has one less positive charge than the Si^{4+} ion it replaces--is neutralized by a distribution of positive ions throughout the network. An example of a zeolite is $Na_2(Al_2Si_3O_{10})\ 2H_2O$.

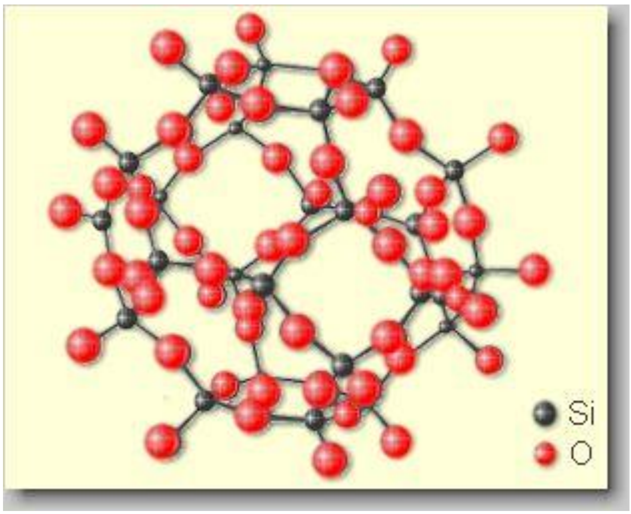

Fig. $Na_2(Al_2Si_3O_{10})\ 2H_2O$

Zeolites are characterized by the presence of tunnels and systems of interconnected cavities in their structures. Zeolites are used as molecular sieves to remove water and other small molecules from mixtures, and they can also be employed to separate molecules for which the molecular masses are the same or similar but the molecular structures are different. In addition, they are used as solid supports for highly dispersed catalysts and to promote specific size-dependent chemical reactions.

References:

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