Silicon

Contents :

1 – Introduction :

Silicon (Latin: *silicium*) is the most common metalloid or chemical element that has the symbol **Si** and atomic number 14.The atomic mass is 28.0855. A tetra valent metalloid, silicon is less reactive than its chemical analog carbon. As the eighth most common element in the universe by mass, silicon very rarely occurs as the pure free element in nature, but is more widely distributed in dusts, planetoids and planets as various forms of silicon dioxide (silica) or silicates. On Earth, silicon is the second most abundant element (after oxygen) in the crust , making up 25.7 % of the crust by mass.

Silicon has many industrial uses. Elemental silicon is the principal component of most semiconductor devices, most importantly integrated circuits or *microchips*. Silicon is widely used in semiconductors because it remains a semiconductor at higher temperatures than the semiconductor germanium and because its native oxide is easily grown in a furnace and forms a better semi conductor / dielectric interface than any other material.

In the form of silica and silicates, silicon forms useful glasses, cements, and ceramics. It is also a constituent of silicones, a class-name for various synthetic plastic substances made of silicon, oxygen, carbon and hydrogen, often confused with silicon itself.

Silicon is an essential element in biology, although only tiny traces of it appear to be required by animals · It is much more important to the metabolism of plants, particularly many grasses, and silicic acid (a type of silica) forms the basis of the striking array of protective shells of the microscopic diatoms.

Name , symbol , number	Silicon , Si , 14
Element category	metalloids
Group, period, block	14, 3, p
Appearance	Crystalline , reflective Bluish - tinged
Standard atomic weight	28 $g \cdot mol^{-1}$
Electron configuration	[Ne] $3s^2$ $3p^2$
Electrons per shell	2 , 8 , 4

Phase	solid
Density (near r.t.)	2.3290 g·cm^{-3}
Liquid density at m.p.	2.57 g·cm^{-3}
Melting point	1420 °C
Boiling point	3265 °C
Heat of fusion	50.21 kJ·mol^{-1}
Heat of vaporization	359 kJ·mol^{-1}
Specific heat capacity	(25 °C) 19.789 J·mol^{-1}·K^{-1}
Crystal structure	Diamond cubic
Oxidation states	4, 3 [1], 2 [2], 1 [3] (amphoteric oxide)
Electro negativity	1.90 (Pauling scale)
Ionization energies (more)	1st: 786.5 kJ·mol^{-1}
	2nd: 1577.1 kJ·mol^{-1}
	3rd: 3231.6 kJ·mol^{-1}
Thermal expansion	(25 °C) 2.6 µm·m^{-1}·K^{-1}
Speed of sound (thin rod)	(20 °C) 8433 m/s
Mohs hardness	7
Band gap energy at 300 K	1.12 eV

2 - Notable characteristics :

The outer electron orbitals (half filled sub shell holding up to eight electrons) have the same structure as in carbon and the two elements are sometimes similar chemically. Even though it is a relatively inert element, silicon still reacts with halogens and dilute alkalis, but most acids (except for some hyper-reactive combinations of nitric acid and hydrofluoric acid) do not affect it. Having four bonding electrons however gives it, like carbon, many opportunities to combine with other elements or compounds under the right circumstances.

Both silicon and carbon are semiconductors, readily either donating or sharing their four outer electrons allowing many different forms of chemical bonding. Pure silicon has a negative temperature coefficient of resistance, since the number of free charge carriers increases with temperature. The electrical resistance of single crystal silicon significantly changes under the application of mechanical stress due to the piezo resistive effect.

In its crystalline form, pure silicon has a gray color and a metallic luster. It is similar to glass in that it is rather strong, very brittle, and prone to chipping.

2 – 1 - Properties

Some of the most useful properties of silicone include :

1. Thermal stability (constancy of properties over a wide operating range of −100 to 250 °C) .
2. Though not a hydrophobe , the ability to repel water and form watertight seals.
3. Excellent resistance to oxygen, ozone and UV light (sunlight). This has led to widespread use in the construction industry (e.g. coatings, fire protection, glazing seals), and automotive industry (external gaskets, external trim).
4. Good electrical insulation. Because silicone can be formulated to be electrically insulative or conductive, it is suitable for a wide range of electrical applications.
5. Non - stick.
6. Low chemical reactivity.
7. Low toxicity, but does not support microbiological growth.
8. High gas permeability: at room temperature (25 °C) the permeability of silicone rubber for gases like oxygen is approximately 400 times that of butyl rubber, making silicone useful for medical applications (though precluding it from applications where gas-tight seals are necessary).

3 – History :

Silicon was first identified by Antoine Lavoisier in 1787 as a component of the Latin *silex* , or *silicis* (meaning what were more generally termed "the flints" or "Hard Rocks" during the Early Modern era where nowadays as we would say "silica" or "silicates"), and was later mistaken by Humphry Davy in 1800 for a compound. In 1811 Gay-Lussac and Thénard prepared impure amorphous silicon through the heating of potassium with silicon tetra fluoride . It was first isolated as an element by Berzelius in 1823. In 1824, Berzelius prepared amorphous silicon using approximately the same method as Gay- Lussac. Berzelius also purified the product by repeatedly washing it.

4 . Technical details :

More precisely called polymerized siloxanes or poly siloxanes , silicones are mixed inorganic - organic polymers with the chemical formula $[R_2 SiO]_n$, where R is an organic group such as methyl , ethyl, or phenyl. These materials consist of an inorganic silicon - oxygen backbone (- Si - O - Si - O - Si - O -) with organic side groups attached to the silicon atoms, which are four - coordinate.

In some cases organic side groups can be used to link two or more of these – Si - O – back bones together. By varying the – Si – O - chain lengths, side groups, and cross linking , silicones can be synthesized with a wide variety of properties and compositions. They can vary in consistency from liquid to gel to rubber to hard plastic. The most common siloxane is linear poly di methyl siloxane (PDMS) , a silicone oil. The second largest group of silicone materials is based on silicone resins, which are formed by branched and cage-like oligo siloxanes .

4 . 1 . Synthesis :

Silicones are synthesized from chloro silanes , tetra ethoxy silane, and related compounds. In the case of PDMS, the starting material is di methyl di chloro silane , which reacts with water as follows:

$$n\,\mathrm{Si\,(CH_3)_2\,Cl_2} + n\,\mathrm{H_2O} \rightarrow [\,\mathrm{Si\,(CH_3)_2\,O}\,]_n + 2n\,\mathrm{H\,Cl}$$

During polymerization, this reaction evolves hazardous hydrogen chloride gas. For medical uses, a process was developed where the chlorine atoms in the silane precursor were replaced with acetate groups, so that the reaction product of the final curing process is nontoxic acetic acid (vinegar) . As a side effect, the curing process is also much slower in this case. This is the chemistry used in many consumer applications, such as silicone caulk and adhesives.

Silane precursors with more acid - forming groups and fewer methyl groups, such as methyl tri chloro silane, can be used to introduce branches or cross - links in the polymer chain. Ideally, each molecule of such a compound becomes a branch point. This can be used to produce hard silicone resins. Similarly, precursors with three methyl groups can be used to limit molecular weight, since each such molecule has only one reactive site and so forms the end of a siloxane chain.

Modern silicone resins are made with tetra ethoxy silane , which reacts in a more mild and controllable manner than chloro – silanes .

4 . 2 . Chemical terminology :

Silicone is often mistakenly referred to as "silicon." Although silicones contain silicon atoms, they are not made up exclusively of silicon, and have completely different physical characteristics from elemental silicon.

F. S. Kipping coined the word "silicone" in 1901 to describe poly di phenyl siloxane by analogy of its *formula,* Ph_2SiO, with the formula of the ketone benzo phenone , Ph_2CO (Ph stands for phenyl , C_6H_5). Kipping was well aware that poly di phenyl siloxane is polymeric whereas benzo phenone is monomeric and noted that Ph_2SiO and Ph_2CO had very different chemistry .

A true *silicone group* with a double bond between oxygen and silicon does not commonly exist in nature; chemists find that the silicon atom much prefers a single bond with each of two oxygen atoms, rather than a double bond to a single atom. Polysiloxanes are still more commonly known as "silicones".

Molecules containing silicon - oxygen double bonds do exist and are called silanones . Several silanones have been studied in argon matrices and in the gas phase, but they are highly reactive .

Despite their reactivity, silanones are important as intermediates in gas - phase processes such as chemical vapor deposition in microelectronics production, in the formation of ceramics by combustion , and in astro chemistry .

5 – Occurrence :

Measured by mass, silicon makes up 25.7 % of the Earth's crust and is the second most abundant element in the Earth's crust, after oxygen. Pure silicon crystals are only occasionally found in nature; they can be found as inclusions with gold and in volcanic exhalations. Silicon is usually found in the form of silicon dioxide (also known as silica), and silicate.

Silica occurs in minerals consisting of (practically) pure silicon dioxide in different crystalline forms. Sand, amethyst, agate, quartz, rock crystal, chalcedony, flint, jasper, and opal are some of the forms in which silicon dioxide appears. (They are known as "lithogenic", as opposed to "biogenic", silicas) ,

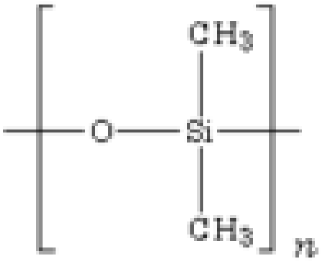
Silicon also occurs as silicates (various minerals containing silicon, oxygen and one or another metal), for example feldspar. These minerals occur in clay, sand and various types of rock such as granite and sandstone. Asbestos, feldspar, clay, hornblende, and mica are a few of the many silicate minerals.

Silicon is a principal component of aerolites, which are a class of meteoroids, and also is a component of tektites, which are a natural form of glass.

6 – Isotopes :

Silicon has numerous known isotopes, with mass numbers ranging from 22 to 44. ^{28}Si (the most abundant isotope, at 92.23 %) , ^{29}Si (4.67 %) , and ^{30}Si (3.1 %) are stable; ^{32}Si is a radioactive isotope produced by argon decay. Its half-life has been determined to be approximately 170 years (0.21 MeV) , and it decays by beta - emission to ^{32}P (which has a 14.28 day half-life) and then to ^{32}S.

7 - Compounds :



PDMS – a silicone compound

Silicon forms binary compounds called silicides with many metallic elements whose properties range from reactive compounds e.g. magnesium silicide , Mg_2Si through to high melting refractory compounds such as molybdenum di silicide , $MoSi_2$. Silicon carbide, Si C , (carborundum) is a hard, high melting solid and is the well known abrasive.

Silane, SiH_4, is a pyrophoric gas with a similar tetra hedral structure to methane, CH_4. Additionally there is a range of catenated silicon hydrides that form a homologous series of compounds, Si_nH_{2n+2} where n = 2-8 (analogous to the alkanes) . These are all readily hydrolyzed and are thermally unstable, particularly the heavier members.

Disilenes contain a silicon-silicon double bond (analogous to the alkenes) and are generally highly reactive requiring large substituent groups to stabilize them.

Tetra halides , SiX_4, are formed with all of the halogens. Silicon tetra chloride for example readily reacts with water unlike its carbon analogue, carbon tetrachloride . Silicon di halides are formed by the high temperature reaction of tetra halides and silicon, with a structure analogous to a carbene they are reactive compounds . Silicon di fluoride condenses to form a polymeric compound, $(SiF_2)_n$.

Silicon dioxide, is a high melting solid with a number of different crystal forms the most familiar of which is the mineral quartz . In quartz each silicon atom is surrounded by four oxygen atoms that bridge to other silicon atoms to form a three dimensional lattice . Silica is soluble in water at high temperatures forming *mono silicic acid* ($Si(OH)_4$) and this property is used in the manufacture of quartz crystals used in electronics .

Under the right conditions mono silicic acid readily polymerizes to form more complex silicic acids, ranging from the simplest condensate, *di silicic acid* ($H_6Si_2O_7$)to linear, ribbon, layer and lattice structures which form the basis of the many different silicate minerals Silicates are also important constituents of concretes . With oxides of other elements the high temperature reaction of silicon dioxide can give a wide range of glasses with various properties. Examples include soda lime glass, boro silicate glass and lead crystal glass.

Silicon sulfide, SiS_2 is a polymeric solid (unlike its carbon analogue the gas CS_2.

Silicon forms a nitride, Si_3N_4 which is a ceramic. Silatranes a group of tri cyclic compounds containing five coordinate silicon may have physiological properties.

Many transition metal complexes containing a metal-silicon bond are now known, which include complexes containing, SiH_nX_{3-n} ligands , SiX_3 ligands, $Si(OR)_3$ ligands .

Silicones are large group of polymeric compounds with an (Si - O – Si) backbone an example is the silicone oil, PDMS, poly di methyl siloxane) . These polymers can be cross linked to produce resins and elestomers .

Many organo silicon compounds are known which contain a silicon - carbon single bond. Many of these are based on a central tetrahedral silicon atom and some are optically active when central chirality exists. In 1981 a silene with a silicon - carbon double bond and a di silene with a silicon-silicon double bond were isolated . A compound with silicon-silicon triple bond was first isolated in 2004, although as the compound is non-linear, the bonding is dissimilar to that in alkynes.

Long chain polymers containing a silicon backbone are known for example poly di methyl silylene ($SiMe_2$) $_n$. Poly carbo silane , $[(SiMe_2)_2CH_2]_n$ with a backbone containing a repeating -Si-Si-C unit is a precursor in the production of silicon carbide fibers .

8 - Applications :

As the second most abundant element in the earth's crust, silicon is vital to the construction industry as a principal constituent of natural stone, glass, concrete and cement. Silicon's greatest impact on the modern world's economy and lifestyle has resulted from silicon wafers used as substrates in the manufacture of discrete electronic devices such as power transistors, and in the development of integrated circuits such as computer chips.

8 – 1 – Alloys :

The largest application of pure silicon (metallurgical grade silicon), representing about 55 % of the world consumption, is in the manufacture of aluminium - silicon alloys to produce cast parts, mainly for the automotive industry. Silicon is an important constituent of electrical steel, modifying its resistivity and ferromagnetic properties. Silicon is added to molten cast iron as ferro silicon or silico calcium alloys to improve its performance in casting thin sections, and to prevent the formation of cementite at the surface.

8 – 2 – In electronic applications :

Pure silicon is used to produce ultra - pure silicon wafers used in the semi conductor industry, in electronics and in photo voltaic applications. Ultra-pure silicon can be doped with other elements to adjust its electrical response by controlling the number and charge (positive or negative) of current carriers. Such control is necessary for transistors, solar cells, integrated circuits, micro processors , semi conductor detectors and other semiconductor devices which are used in electronics and other high-tech applications. In Photonics, silicon can be used as a continuous wave Raman laser medium to produce coherent light, though it is ineffective as a light source. Hydrogenated amorphous silicon is used in the production of low-cost, large-area electronics in applications such as LCDs, and of large-area, low-cost thin-film solar cells.

8 – 3 – Silicones :

The second largest application of silicon (about 40 % of world consumption) is as a raw material in the production of silicones, compounds containing silicon-oxygen and silicon-carbon bonds that have the capability to act as bonding intermediates between glass and organic compounds, and to form polymers with useful properties such as impermeability to water, flexibility and resistance to chemical attack. Silicones are used in water proofing treatments, molding compounds and mold-release agents, mechanical seals, high temperature greases and waxes, caulking compounds and even in applications as diverse as breast implants, explosives and pyrotechnics.

- Construction : Silicon dioxide or silica in the form of sand and clay is an important ingredient of concrete and brick and is also used to produce Portland cement.
- Pottery / Enamel is a refractory material used in high-temperature material production and its silicates are used in making enamels and pottery.
- Glass : Silica from sand is a principal component of glass. Glass can be made into a great variety of shapes and with many different physical properties. Silica is used as a base material to make window glass, containers, insulators, and many other useful objects.
- Abrasives : Silicon carbide is one of the most important abrasives.
- Silly Putty was originally made by adding boric acid to silicone oil. Now name - brand Silly Putty also contains significant amounts of elemental silicon. (Silicon binds to the silicone and allows the material to bounce 20 % higher)

9 . Uses

9 . 1 . Cook ware :

- As a low taint, non - toxic material, silicone can be used where contact with food is required. Silicone is becoming an important product in the cook ware industry, particularly bake ware and kitchen utensils.
- It is used as an insulator in heat resistant potholders and similar, however it is more conductive of heat than the less dense fiber - based ones. Silicone oven mitts are able to withstand temperatures up to 357 °C , and allow reaching into boiling water .
- Molds for chocolate, ice, cookies, muffins, etc.
- Some novel designs are steamer, egg boiler, vegetables cooker, cooking lids, pot handle, kitchen mats, etc.

9 . 2 . De foaming

Silicones are used as active compound in defoamers due the the low water solubility and good spreading properties.

9 . 3 . Dry Cleaning :

Liquid silicone can be used as a dry cleaning solvent. Touted as an " environmentally friendly " alternative to the traditional per chloro ethylene (or perc) solvent, the deca methyl penta cyclo siloxane (D5) process has been patented by the company Green Earth Cleaning.

The solvent degrades into silica and trace amounts of water and CO_2 , and waste produced from the D5 dry cleaning process is nontoxic and non hazardous. This significantly reduces the environmental impact of a typically high - polluting industry.

Additionally, liquid silicone is chemically inert, meaning it does not react with fabrics or dyes during the cleaning process. This reduces the amount of fading and shrinking that most dry -cleaned garments experience.

9 . 4 . Electronics

Electronic components are some times encased in silicone to increase stability against mechanical and electrical shock, radiation and vibration. This is often called " potting " .

Silicones are used where durability and high performance are demanded of components under hard conditions, such as in space (satellite technology) . They are selected over poly urethane or epoxy encapsulation when a wide operating temperature range is required (− 65 to 315 °C) . Silicones also have the advantage of little exothermic heat rise during cure, low toxicity, good electrical properties and high purity.

The use of silicones in electronics is not without problems, however. Silicones are relatively expensive and can be attacked by solvents . Silicone easily migrates as either a liquid or vapor onto other components.

Silicone contamination of electrical switch contacts can lead to failures by causing an increase in contact resistance, often late in the life of the contact, well after any testing is completed . Use of silicone - based spray products in electronic devices during maintenance or repairs can cause later failures.

9 . 5 . Fire Stops :

Silicone foams have been used in North American buildings in an attempt to fire stop openings within fire – resistance - rated wall and floor assemblies to prevent the spread of flames and smoke from one room to another.

Silicone foam fire stops have been the subject of controversy and press attention due to smoke development from pyrolysis of combustible components within the foam, hydrogen gas escape, shrinkage and cracking. These problems have been exposed by whistleblower Gerald W . Brown and have led to a large number of reportable events among licensees (operators of nuclear power plants) of the Nuclear Regulatory Commission (NRC) .

When properly installed, silicone-foam firestops can be fabricated for building code compliance. Advantages include flexibility and high dielectric strength. Disadvantages include combustibility (hard to extinguish) and significant smoke development. Silicone can also be found in air craft technology.

9 . 6 . Lubricants :

Silicone greases are used for many purposes, such as bicycle chains. A dry - set lubricant is delivered with a solvent carrier to penetrate the chain. The solvent evaporates, leaving a clear film that lubricates but does not attract dirt and grit as much as a traditional " wet " lubricant . Silicone personal lubricants are also available, for use in medical procedures or sexual activity.

9 . 7 . Medicine :

Silicone, particularly the gel form, is used in bandages and dressings, in breast implants and a variety of other medical uses.

Poly di methyl siloxane (PDMS) has been used as the hydrophobic block of amphiphilic synthetic block copolymers used to form the physical membrane of poly mersomes .

9 . 7 . Mold Making :

Two - part silicone systems are used to create rubber molds which can be used for production casting of resins , foams, rubber and low - temp alloys.

A mold made of silicone generally requires little or no mold release or surface preparation as most materials do not adhere to mold making silicone.

For experimental uses, ordinary one - part silicone can also be used, either to make molds, or to mold into shapes. Common vegetable cooking oils and petroleum jelly can be used on mating surfaces as a mold release agent .

9 . 9 . Personal Care :

Silicones are ingredients in many hair conditioner, shampoo, and hair gel products. Some silicones, notably the amine functionalized amodimethicones , are excellent conditioners. They improve comb ability , feel, and softness, and also lessen frizz. Another silicone family, the phenyl tri methicones , are used in reflection - enhancing and color - correcting hair products, where they increase shine and glossiness (and possibly effect subtle color changes) . Phenyl tri methicones , unlike the conditioning amo di methicones , have refractive indices (typically 1.46) close to that of human hair (1.54) It should be noted that achieving both high-shine and excellent conditioning in one hair care product is much more difficult than simply adding two different silicones to the formulation, because amo di methicone and phenyl tri methicone interact with and dilute each other. This is one reason why modern hair care products, and cosmetics generally, are among the most highly engineered consumer products.

Silicones are also used in some shaving products ' and personal lubricants. Menstrual cups are often made of silicone for its durability and reusability. Silicone is also material of choice for soft sex toys, due to its durability, clean ability and lack of phthalates, chemicals suspected of having carcinogenic and mutagenic effects on the skin and mucous membranes . One review of the health risks of phthalates advocated moving away from medical devices containing phthalates because of their toxicity .

Specific grades of silicone rubber are used widely in the production of baby bottle teats due to their cleanliness, aesthetic appearance, and low extractable content.

9 . 10 . Plumbing and building construction :

The strength and reliability of silicone rubber is widely acknow ledged in the construction industry .

One - part silicone sealants and caulks are in common use to seal gaps, joints and crevices in buildings. One - part silicones cure by absorbing atmospheric moisture, which helps in the professional installation.

In plumbing, silicone grease is typically applied to O - rings in faucets and valves. Whilst the film is extant it prevents lime from sticking to the brass work.

9 . 11 . Toys :

Silicone balls have become a juggler's favorite due to the high bounce back , and are used as a response system in many low response yo-yos . Silicone has the potential of replacing plastic in creating many forms of toys.

10 – Production :

Silicon is commercially prepared by the reaction of high-purity silica with wood, charcoal, and coal, in an electric arc furnace using carbon electrodes. At temperatures over 1,900 °C. the carbon reduces the silica to silicon according to the chemical equation

$$SiO_2 + C \rightarrow Si + CO_2.$$
$$SiO_2 + 2C \rightarrow Si + 2CO.$$

Liquid silicon collects in the bottom of the furnace, and is then drained and cooled. The silicon produced via this process is called *metallurgical grade silicon* and is at least 98% pure. Using this method, silicon carbide, Si C , can form. However, provided the amount of SiO_2 is kept high, silicon carbide may be eliminated, as explained by this equation:

$$2\ Si\ C + Si\ O_2 \rightarrow 3\ Si + 2\ CO.$$

It has been reported in recent years that, by molten salt electrolysis, pure silicon can be directly extracted from solid silica and this new electrolysis method, known as the FFC Cambridge Process, has the potential to produce directly the solar grade silicon without any CO_2 emission at much lower energy consumption .

11 - Purification :

The use of silicon in semi conductor devices demands a much greater purity than afforded by metallurgical grade silicon. Historically, a number of methods have been used to produce high-purity silicon.

11 – 1 - Physical methods :

Early silicon purification techniques were based on the fact that if silicon is melted and re-solidified, the last parts of the mass to solidify contain most of the impurities. The earliest method of silicon purification, first described in 1919 and used on a limited basis to make radar components during World War II, involved crushing metallurgical grade silicon and then partially dissolving the silicon powder in an acid. When crushed, the silicon cracked so that the weaker impurity-rich regions were on the outside of the resulting grains of silicon. As a result, the impurity-rich silicon was the first to be dissolved when treated with acid, leaving behind a more pure product.

In zone melting, also called zone refining, the first silicon purification method to be widely used industrially, rods of metallurgical grade silicon are heated to melt at one end. Then, the heater is slowly moved down the length of the rod, keeping a small length of the rod molten as the silicon cools and re-solidifies behind it. Since most impurities tend to remain in the molten region rather than re-solidify, when the process is complete, most of the impurities in the rod will have been moved into the end that was the last to be melted. This end is then cut off and discarded, and the process repeated if a still higher purity is desired.

11 – 2 - Chemical methods

Today, silicon is purified by converting it to a silicon compound that can be more easily purified by distillation than in its original state, and then converting that silicon compound back into pure silicon . Tri chloro silane is the silicon compound most commonly used as the intermediate , although silicon tetra chloride and silane are also used. When these gases are blown over silicon at high temperature, they decompose to high-purity silicon.

At one time, DuPont produced ultra - pure silicon by reacting silicon tetra chloride with high - purity zinc vapors at 950 °C, producing silicon according to the chemical equation

$$\mathrm{Si\ Cl_4 + 2\ Zn \rightarrow Si + 2\ Zn\ Cl_2.}$$

How ever, this technique was plagued with practical problems (such as the zinc chloride by product solidifying and clogging lines) and was eventually abandoned in favor of the Siemens process.

In the **Siemens process**, high-purity silicon rods are exposed to tri chloro silane at 1150 °C. The tri chloro silane gas decomposes and deposits additional silicon onto the rods, enlarging them according to chemical reactions like

$$\mathrm{2\ HSi\ Cl_3 \rightarrow Si + 2\ H\ Cl + Si\ Cl_4.}$$

Silicon produced from this and similar processes is called *polycrystalline silicon*. Polycrystalline silicon typically has impurity levels of less than 10^{-9}.

In 2006 REC announced construction of a plant based on fluidized bed technology using silane .

$$\mathrm{3Si\ Cl_4 + Si + 2H_2 \rightarrow 4HSi\ Cl_3}$$
$$\mathrm{4HSi\ Cl_3 \rightarrow 3Si\ Cl_4 + SiH_4}$$
$$\mathrm{SiH_4 \rightarrow Si + 2H_2}$$

12 - Crystallization :

Silicon, like carbon and other group IV elements form face-centered diamond cubic crystal structure. Silicon, in particular, forms a face - centered cubic structure with a lattice spacing of 5.430710 Å (0.5430710 nm).

The majority of silicon crystals grown for device production are produced by the Czochralski process, (CZ-Si) since it is the cheapest method available and it is capable of producing large size crystals. However, silicon single-crystals grown by the Czochralski method contain impurities since the crucible which contains the melt dissolves. For certain electronic devices, particularly those required for high power applications, silicon grown by the Czochralski method is not pure enough. For these applications, float-zone silicon (FZ-Si) can be used instead. It is worth mentioning though, in contrast with CZ-Si method in which the seed is dipped into the silicon melt and the growing crystal is pulled upward, the thin seed crystal in the FZ-Si method sustains the growing crystal as well as the polysilicon rod from the bottom. As a result, it is difficult to grow large size crystals using the float-zone method. Today, all the dislocation-free silicon crystals used in semiconductor industry with diameter 300mm or larger are grown by the Czochralski method with purity level significantly improved.

13 - In popular culture :

Because silicon is an important element in semi conductors and high-tech devices, the high-tech region of Silicon Valley, California is named after this element. Other geographic locations with connections to the industry have since characterized themselves as siliconia as well.

It also appears as one of the resources and Name of the Scilicons in "Submarine Titans".

Silicon dioxide

Contents

1 . Introduction :

The chemical compound **silicon dioxide**, also known as **silica** (from the Latin *silex*) , is an oxide of silicon with a chemical formula of **$Si\ O_2$** and has been known for its hardness since antiquity.[1] Silica is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms. It is a principal component of most types of glass and substances such as concrete. Silica is the most abundant mineral in the Earth's crust.

Other Names	Silica . quartz
Molecular Formula	$Si\ O_2$
Molar Mass	60 g/mol
Appearance	white powder
Density	2.634 g / cm^3
Melting Point	1650 (±75) ° C
Boiling Point	2230 °C
Solubility in Water	0.012 g / 100 mL
Flash Point	Non - Flammable

2 . **Structure and properties**

SiO_2 has a number of distinct crystalline forms in addition to amorphous forms. With the exception of stishovite and fibrous silica, all of the crystalline forms involve tetrahedral SiO_4 units linked together by shared vertices in different arrangements. Silicon-oxygen bond lengths vary between the different crystal forms, for example in α - quartz the bond length is 161 pm, whereas in α – tri dymite it is in the range 154 - 171 pm . The Si - O - Si angle also varies between a low value of 140° in α-tri dymite , up to 180° in β- tri dymite . In α - quartz the Si - O - Si angle is 144 ° .

Fibrous sulfur has a structure similar to that of SiS_2 with chains of edge - sharing SiO_4 tetra hydra . Stishovite , the highest pressure form, in contrast has a rutile like structure where silicon is 6 coordinate. The density of stishovite is 4.287 g / cm^3, which compares to α-quartz , the densest of the low pressure forms, which has a density of 2.648 g / cm^3 . The difference in density can be ascribed to the increase in coordination as the six shortest Si - O bond lengths in stishovite (four Si - O bond lengths of 176 pm and two others of 181 pm) are greater than the Si - O bond length (161 pm) in α - quartz . The change in the coordination increases the ionicity of the Si – O bond .

Note that the only stable form under normal conditions is α-quartz and this is the form in which crystalline silicon dioxide is usually encountered. In nature impurities in crystalline α-quartz can give rise to colours ˙

Faujasite - silica is another form of crystalline silica. It is obtained by de alumination of a low-sodium, ultra - stable Y zeolite with a combined acid and thermal treatment. The resulting product contains over 99 % silica, has high crystallinity and high surface area (over 800 m^2 / gr). Faujasite - silica has very high thermal and acid stability (it maintains high crystallinity even after boiling in concentrated hydrochloric acid) .

Crystalline Forms of Si O_2

Form	Crystal Class	Structural features	Notes
α-quartz	rhombohedral (tri gonal)	Helical chains making individual single crystals optically active	A - quartz converts to β - quartz at 573 ° C
B - quartz	hexagonal	closely related to α -quartz (with an Si-O - Si angle of 155 °) and optically active	B - quartz converts to β – tri dymite at 870°C
α – tri dymite	orthorhombic	Meta stable form under normal pressure	
β-tri dymite	hexagonal	closely related to α-tri dymite	B – tri dymite converts to β - cristobalite 1470° C
α - cristobalite	tetragonal	Meta stable form under normal pressure	
B - cristobalite	cubic	closely related to α-cristobalite	melts at 1705 ° C
keatite	tetra gonal	Si_5O_{10} , Si_4O_{14} , Si_8O_{16} rings	synthesized from amorphous silica and alkali at high pressure
coesite	mono clinic	Si_4O_8 and Si_8O_{16} rings	high pressure form (higher than keatite)
stishovite	tetra gonal	rutile like with 6 - fold coordinated Si	high pressure form (higher than coesite) and the densest of the poly morphs
melanophlogite	cubic	Si_5O_{10} , Si_6O_{12} rings	mineral always found with hydro carbons in interstitial spaces-a clathrasil
fibrous	ortho rhombic	like SiS_2	

		consisting of edge sharing chains	
faujasite	cubic	sodalite cages connected by hexagonal prisms ; 12-membered ring pore opening; faujasite structure .	

Molten silica exhibits several peculiar phySi Cal characteristics that are similar to the ones observed in liquid water: negative temperature expansion, density maximum and a heat capacity minimum .

3 . Molecular forms of silicon dioxide

When molecular silicon monoxide , Si O , is condensed in an argon matrix cooled with helium along with oxygen atoms generated by microwave discharge, molecular Si O_2 is produced which has a linear structure . The Si - O bond length is 148.3 pm which compares with the length of 161 pm in α-quartz. The bond energy is estimated at 621.7 kJ / mol .

Dimeric silicon dioxide, (Si O_2) $_2$ has been prepared by reacting O_2 with matrix isolated dimeric silicon monoxide, (Si_2 O_2) . In dimeric silicon dioxide there are two oxygen atoms bridging between the silicon atoms with an Si - O - Si angle of 94° and bond length of 164.6 pm and the terminal Si - O bond length is 150.2 pm .

4 . Chemistry

Silicon dioxide is formed when silicon is exposed to oxygen (or air). A very thin layer (approximately 1 nm or 10 Å) of so-called 'native oxide' is formed on the surface when silicon is exposed to air under ambient conditions. Higher temperatures and alternative environments are used to grow well-controlled layers of silicon dioxide on silicon, for example at temperatures of 600 - 1200 °C so - called " dry " or " wet " oxidation using O_2 or H_2O respectively . The thickness of the layer of silicon replaced by the dioxide is 44 % of the thickness of the silicon dioxide layer produced . Alternative methods used to deposit a layer of $Si\ O_2$ include :

- Low temperature oxidation (LTO) of silane

$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$ (at 400 - 450 °C)

- Decomposition of tetra ethyl ortho silicate (TEOS) at 680 – 730 ° C

$Si\ (\ O\ C_2H_5\ )_4 \rightarrow SiO_2 + H_2O + 2C_2H_4$

- Plasma enhanced chemical vapour deposition using TEOS at approximately 400 ° C

$Si\ (\ O\ C_2H_5\ )_4 + 12\ O_2 \rightarrow Si\ O_2 + 10\ H_2O + 8\ CO_2$

- Polymerization of tetra ethyl ortho silicate (TEOS) at less than 100°C using amino acid as catalyst .

Pyrogenic silica (some times called fumed silica or silica fume) which is a very fine particulate form of silicon dioxide, is prepared by burning $Si\ Cl_4$ in an oxygen rich hydrocarbon flame to produce a " smoke " of SiO_2 :

$Si\ Cl_4 + 2H_2 + O_2 \rightarrow Si\ O_2 + 4H\ Cl$

Amorphous silica, silica gel, is produced by the acidification of solutions of sodium silicate to produce a gelatinous precipitate that is then washed and then dehydrated to produce colorless microporous silica .

Quartz exhibits a maximum solubility in water at around 340°C. This property is used to grow single crystals of quartz in a hydrothermal process where natural quartz is dissolved in superheated water in a pressure vessel which is cooler at the top. Crystals of 0.5 – 1 kg can be grown over a period of 1 – 2 months . These crystals are a source of very pure quartz for use in electronic applications . Fluorine reacts with silicon dioxide to form SiF_4 and O_2 whereas the other halogen gases (Cl_2 , Br_2 , I_2) react much less readily .

Silicon dioxide is attacked by hydrofluoric acid (HF) to produce " hexa fluoro silicic acid " :

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

HF is used to remove or pattern silicon dioxide in the semiconductor industry.

Silicon dioxide dissolves in hot concentrated alkali or fused hydroxide (e.g) :

$$SiO_2 + Na\ OH \rightarrow Na_2\,SiO_3 + H_2O$$

Silicon dioxide reacts with baSi C metal oxides (e.g. sodium oxide , potassium oxide , lead (II) oxide, zinc oxide or mixtures of oxides forming silicates and glasses as the Si - O - Si bonds in silica are broken successively) . As an example the reaction of sodium oxide and Si O_2 can produce sodium ortho silicate , sodium silicate and glasses, depending on the proportions of reactants :

$$2Na_2O + SiO_2 \rightarrow Na_4SiO_4$$
$$Na_2O + SiO_2 \rightarrow Na_2SiO_3$$
$$(0.25 - 0.8)Na_2O + SiO_2 \rightarrow \text{glasses}$$

Examples of such glasses have commercial significance e.g. soda lime glass, boro silicate glass , lead glass. In these glasses silica is termed the network former or lattice former . With silicon at high temperatures gaseous Si O is produced :

$$SiO_2 + Si \rightarrow 2SiO\ (\text{gas})$$

5 . Manufactured forms

Silica is manufactured in several forms including:

- Glass (a colorless , high - purity form is called *fused silica*)
- Synthetic amorphous silica , silica gel
- Fumed silica (also known as pyrogenic silica , colloidal silica , or under the genericized trade mark, AEROSIL)

- Precipitated silica is produced by precipitation from a water glass solution by acidification.
- Silica aero gel .

6 . Applications

Silica is used in the production of various products.

- Inexpensive soda-lime glass is the most common and typically found in drinking glasses, bottles, and windows.
- A raw material for many white ware ceramics such as earthenware, stoneware and porcelain.
- A raw material for the production of Portland cement.
- A food additive, primarily as a flow agent in powdered foods, or to absorb water .
- It is the primary component of diatomaceous earth which has many uses ranging from filtration to insect control.
- An oxide layer grown on silicon is hugely beneficial in microelectronics. It is a superior electric insulator, with high chemical stability. In electrical applications, it can protect the silicon, store charge, block current, and even act as a controlled pathway to allow small currents to flow through a device. The traditional method of manufacture such an oxide layer has been to heat the silicon in a high-temperature furnaces within an oxygen ambient (thermal oxidation) .
- Raw material for aero gel in the Stardust spacecraft
- Used in the extraction of DNA and RNA due to its ability to bind to the nucleic acids under the presence of chaotropes.
- As hydrophobic silica it is used as a de foamer component.
- As hydrated silica in toothpaste (abrasive to remove plaque.)
- As a high - temperature thermal protection fabric.
- In cosmetics for its light-diffusing properties and its absorbency.

- Liquid silicon dioxide (colloidal silica) is used as a wine and juice fining agent.
- As a glidant in pharmaceutical products silicon dioxide aids powder flow when tablets are formed.
- In the production of tires
- Thermal enhancement compound used in thermal grouts for the ground source heat pump industry .

7 . Health effects

Inhaling finely divided crystalline silica dust in very small quantities (OSHA allows 0.1 mg / m^3) over time can lead to silicosis, bronchitis or (much more rarely) cancer, as the dust becomes lodged in the lungs and continuously irritates them, reducing lung capacities (silica does not dissolve over time) . This effect can be an occupational hazard for people working with sandblasting equipment, products that contain powdered crystalline silica and so on. Children, asthmatics of any age, allergy sufferers and the elderly (all of whom have reduced lung capacity) can be affected in much shorter periods of time. Amorphous silica, such as fumed silica is not associated with development of silicosis . Laws restricting silica exposure with respect to the silicosis hazard specify that the silica is both crystalline and dust - forming.

In respects other than inhalation, pure silicon dioxide is inert and harmless. Because some silicas take on water, extended exposure may cause local drying of the skin or other tissue. Pure silicon dioxide produces no fumes and is insoluble *in vivo.* It is indigestible, with zero nutritional value and zero toxicity. When silica is ingested orally, it passes unchanged through the gastrointestinal (GI) tract, exiting in the feces, leaving no trace behind. Small pieces of silicon dioxide are equally harmless, as long as they are not large enough to mechanically obstruct the GI tract, or jagged enough to lacerate its lining . A study which followed subjects for 15 years found that higher levels of silica in water appeared to decrease the risk of dementia. The study found that for every 10 milligram - per - day intake of silica in drinking water , the risk of dementia dropped by 11 % .

Quartz

Quartz crystal cluster from Tibet

Contents :

1 – Introduction :

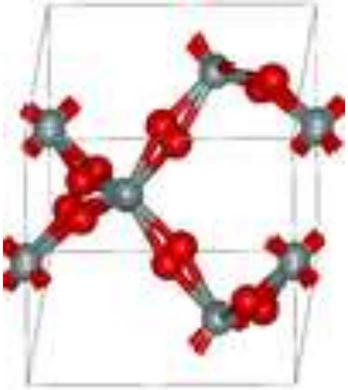
Quartz is the second-most-abundant mineral in the Earth's continental crust, after feldspar. It is made up of a continuous framework of SiO_4 silicon – oxygen tetra hedra , with each oxygen being shared between two tetra hedra , giving an overall formula SiO_2. There are many different varieties of quartz, several of which are semi-precious gemstones. Especially in Europe and the Middle East, varieties of quartz have been since antiquity the most commonly used minerals in the making of jewelry and hard stone carvings.

Category	Silicate mineral
Chemical formula	Silica (silicon dioxide , SiO_2)
Color	From colorless to black , through various colors
Crystal habit	6 -sided prism ending in 6 -sided pyramid (typical) , drusy , fine - grained to micro crystalline, massive
Crystal system	α - quartz : trigonal trapezohedral class 3 2 ; β - quartz : hexagonal 622
Mohs scale hardness	7 – lower in impure varieties (defining mineral)
Luster	Vitreous – waxy to dull when massive
Streak	White
Diaphaneity	Transparent to nearly opaque
Specific gravity	2.65; variable 2.59–2.63 in impure varieties
Optical properties	Uniaxial (+)
Refractive index	n_ω = 1.543–1.545 , n_ε = 1.552–1.554
Melting point	1670 °C (β tridymite) 1713 °C (β cristobalite)
Other characteristics	Piezoelectric, may be triboluminescent, chiral (hence optically active if not racemic)

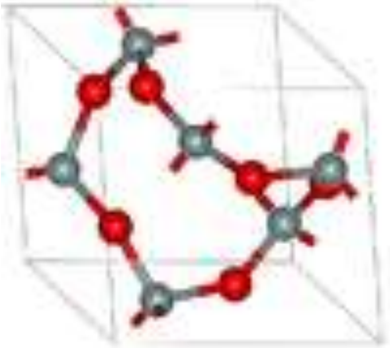
2 - Crystal habit and structure :

Quartz belongs to the trigonal crystal system. The ideal crystal shape is a six-sided prism terminating with six-sided pyramids at each end. In nature quartz crystals are often twinned, distorted, or so intergrown with adjacent crystals of quartz or other minerals as to only show part of this shape, or to lack obvious crystal faces altogether and appear massive. Well-formed crystals typically form in a 'bed' that has unconstrained growth into a void, but because the crystals must be attached at the other end to a matrix, only one termination pyramid is present. A quartz geode is such a situation where the void is approximately spherical in shape, lined with a bed of crystals pointing inward.

2 – 1 - α - quartz and β - quartz :



β-quartz



Crystal structure of α-quartz

α-quartz crystallizes in the trigonal crystal system, space group $P3_121$ or $P3_221$. β-quartz belongs to the hexagonal system, space group $P6_221$ or $P6_421$. These space groups are truly chiral (they each belong to the 11 enantiomorphous pairs). Both α-quartz and β-quartz are examples of chiral crystal structures composed of achiral building blocks (SiO_4 tetra hedra in the present case). The transformation between α- and β-quartz only involves a comparatively minor rotation of the tetra hedra with respect to one another, without change in the way they are linked, this process is called the quartz inversion.

3 - Occurrence :

Quartz is an essential constituent of granite and other felSi C igneous rocks . It is very common in sedimentary rocks such as sandstone and shale and is also present in variable amounts as an accessory mineral in most carbonate rocks. It is also a common constituent of schist, gneiss, quartzite and other metamorphic rocks.

Because of its resistance to weathering it is very common in stream sediments and in residual soils. Quartz, therefore, occupies the lowest potential to weather in the Goldich dissolution series.

Quartz occurs in hydro thermal veins as gangue along with ore minerals. Large crystals of quartz are found in pegmatites . Well-formed crystals may reach several meters in length and weigh as much as 1,400 pounds (640 kg) . Naturally occurring quartz crystals of extremely high purity, necessary for the crucibles and other equipment used for growing silicon wafers in the semiconductor industry, are expensive and rare. A major mining location for high purity quartz is the Spruce Pine Gem Mine in Spruce Pine, North Carolina, United States .

3 – 1 - Related silica minerals :

Tridymite and cristobalite are high-temperature polymorphs of SiO_2 that occur in high-silica volcanic rocks. Coesite is a denser polymorph of quartz found in some meteorite impact sites and in metamorphic rocks formed at pressures greater than those typical of the Earth's crust. Stishovite and Seifertite are yet denser and higher-pressure polymorphs of quartz found in some meteorite impact sites. Lechatelierite is an amorphous silica glass SiO_2 which is formed by lightning strikes in quartz sand.

3 – 2 - Synthetic quartz :

Most quartz used in microelectronics is produced synthetically. Large, flawless and un twinned crystals are produced in an autoclave via the hydrothermal process. The process involves treating crushed natural quartz with hot aqueous solution of a base such as sodium hydroxide. The hydroxide serves as a "mineralizer", i.e. it helps dissolve the "nutrient" quartz. High temperatures are required, often around 675 °C. The dissolved quartz then recrystallizes at a seed crystal at slightly lower temperatures. Approximately 200 tons of quartz were produced in the US in 2005; large synthesis facilities exist throughout the world. Synthetic quartz is often evaluated on the basis of its Q factor, a measure of its piezoelectric response and an indicator of the purity of the crystal.

A synthetic silicon dioxide crystal grown by the hydro thermal method, about 19 cm long and weighing about 127 grams

4 - Uses :

Quartz is the source of many silicon compounds such as silicones (e.g. high performance polymers), silicon (e.g. micro electronics), and many other compounds of commercial importance. Quartz in the form of sand is reduced by carbothermic reaction as a first step in these energy-intensive processes.

Owing to its high thermal and chemical stability and abundance, quartz is widely used many large-scale applications related to abrasives, foundry materials, ceramics, and cements.

4 – 1 - Piezoelectricity :

Quartz crystals have piezoelectric properties: they develop an electric potential upon the application of mechanical stress. An early use of this property of quartz crystals was in phonograph pickups. A common piezoelectric uses of quartz today is as a crystal oscillator. The quartz clock is a familiar device using the mineral. The resonant frequency of a quartz crystal oscillator is changed by mechanically loading it, and this principle is used for very accurate measurements of very small mass changes in the quartz crystal microbalance and in thin-film thickness monitors . Quartz's piezoelectric properties were discovered by Jacques and Pierre Curie in 1880. The quartz oscillator or resonator was first developed by Walter Guyton Cady in 1921.[10] George Washington Pierce designed and patented quartz crystal oscillators in 1923. Warren Marrison created the first quartz oscillator clock based on the work of Cady and Pierce in 1927 .

4 – 2 - Gemstone and lapidary varieties :

The most important distinction between types of quartz is that of *macro crystalline* (individual crystals visible to the unaided eye) and the microcrystalline or cryptocrystalline varieties (aggregates of crystals visible only under high magnification).

4 – 2 - 1 - Coarsely crystalline varieties :

Pure quartz, traditionally called *rock crystal* (sometimes called *clear quartz*), is colorless and transparent or translucent. Common colored varieties include citrine, rose quartz, amethyst, smoky quartz and milky quartz.

4 – 2 - 1 – 1 – Citrine :

Citrine

Citrine is a variety of quartz whose color ranges from a pale yellow to brown. Natural citrines are rare; most commercial citrines are heat-treated amethyst. Citrine contains traces of Fe^{3+} and is rarely found naturally. The name is derived from Latin citrina which means "yellow".

4 – 2 - 1 – 2 – Rose quartz :

An elephant carved in rose quartz, 4 inches (10 cm) long

Rose quartz is a type of quartz which exhibits a pale pink to rose red hue. The color is usually considered as due to trace amounts of titanium, iron, or manganese, in the massive material. Some rose quartz contains microscopic rutile needles which produces an asterism in transmitted light. Recent X-ray diffraction studies suggest that the color is due to thin microscopic fibers of possibly dumortierite within the massive quartz.

In crystal form (rarely found) it is called *pink quartz* and its color is thought to be caused by trace amounts of phosphate or aluminium. The color in crystals is apparently photosensitive and subject to fading. The first crystals were found in a pegmatite found near Rumford, Maine, USA, but most crystals on the market come from Minas Gerais , Brazil.

4 – 2 - 1 – 3 – Amethyst :

Amethyst is a form of quartz that ranges from a bright to dark or dull purple color.

4 – 2 - 1 – 4 – Smoky quartz :

Smoky quartz is a gray, translucent version of quartz. It ranges in clarity from almost complete transparency to a brownish-gray crystal that is almost opaque.

4 – 2 - 1 – 5 – Milky quartz :

Milky quartz sample

Milky quartz may be the most common variety of crystalline quartz and can be found almost anywhere. The white color may be caused by minute fluid inclusions of gas, liquid, or both, trapped during the crystal formation. The cloudiness caused by the inclusions effectively bars its use in most optical and quality gemstone applications.

4 – 2 - 2 – Micro crystalline varieties :

The cryptocrystalline varieties are either translucent or mostly opaque, while the transparent varieties tend to be macro crystalline . Chalcedony is a cryptocrystalline form of silica consisting of fine intergrowths of both quartz, and its monoclinic polymorph moganite . Other opaque gemstone varieties of quartz, or mixed rocks including quartz, often including contrasting bands or patterns of color, are agate, onyx, carnelian, and jasper.

4 – 2 - 3 – Varieties (according to micro structure) :

Although many of the varietal names historically arose from the color of the mineral, current scientific naming schemes refer primarily to the microstructure of the mineral. Color is a secondary identifier for the cryptocrystalline minerals, although it is a primary identifier for the macro crystalline varieties. This does not always hold true.

Macro crystalline varieties

Rock crystal	Clear, colorless
Amethyst	Purple, transparent
Citrine	Yellow to reddish orange to brown, greenish yellow
Prasiolite	Mint green, transparent
Rose quartz	Pink, translucent
Rutilated quartz	Contains acicular (needles) inclusions of rutile
Milk quartz	White, translucent to opaque
Smoky quartz	Brown to gray, opaque

Micro crystalline varieties

Chalcedony	Cryptocrystalline quartz and moganite mixture. The term is generally only used for white or lightly colored material. Otherwise more specific names

	are used.
Agate	Multi-colored, banded chalcedony, semi-translucent to translucent
Onyx	Agate where the bands are straight, parallel and consistent in size.
Jasper	Opaque cryptocrystalline quartz, typically red to brown
Aventurine	Translucent chalcedony with small inclusions (usually mica) that shimmer.
Tiger's Eye	Fibrous gold to red-brown colored quartz, exhibiting chatoyancy.
Carnelian	Reddish orange chalcedony, translucent

4 – 2 - 4 – Synthetic and artificial treatments :

Not all varieties of quartz are naturally occurring. Prasiolite , an olive colored material, is produced by heat treatment; natural prasiolite has also been observed in Lower Silesia in Poland. Although citrine occurs naturally, the majority is the result of heat-treated amethyst. Carnelian is widely heat-treated to deepen its color.

5 – History :

The word "quartz" is derived from the German word "quarz" and its Middle High German ancestor "twarc", which probably originated in Slavic (cf. Czech tvrdý ("hard"), Polish twardy ("hard")) *Quarz* (help·info) , which is of Slavic origin (Czech miners called it *křemen*). Other sources attribute the word's origin to the Saxon word *Querkluftertz*, meaning *cross - vein ore*.

Quartz is the most common material identified as the mystical substance maban in Australian Aboriginal mythology. It is found regularly in passage tomb cemeteries in Europe in a burial context, such as New grange or Carrow more in the Republic of Ireland. The Irish word for quartz is *grian cloch* , which means 'stone of the sun'. Quartz was also used in Prehistoric Ireland, as well as many other countries, for stone tools; both vein quartz and rock crystal were knapped as part of the lithic technology of the prehistoric peoples.[21]

Roman naturalist Pliny the Elder believed quartz to be water ice, permanently frozen after great lengths of time. (The word "crystal" comes from the Greek word *κρύσταλλος*, "ice".) He supported this idea by saying that quartz is found near glaciers in the Alps, but not on volcanic mountains, and that large quartz crystals were fashioned into spheres to cool the hands. He also knew of the ability of quartz to split light into a spectrum. This idea persisted until at least the 17th century.

In the 17th century, Nicolas Steno's study of quartz paved the way for modern crystallography. He discovered that no matter how distorted a quartz crystal, the long prism faces always made a perfect 60° angle.

Charles B. Sawyer invented the commercial quartz crystal manufacturing process in Cleveland, Ohio, United States. This initiated the transition from mined and cut quartz for electrical appliances to manufactured quartz.

Silicon carbide

Contents :

1 – Introduction :

Silicon carbide (**Si C**) , also known as **carborundum** , is a compound of silicon and carbon with chemical formula Si C. It occurs in nature as the extremely rare mineral moissanite . Silicon carbide powder has been mass-produced since 1893 for use as an abrasive. Grains of silicon carbide can be bonded together by sintering to form very hard ceramics which are widely used in applications requiring high endurance, such as car brakes, car clutches and ceramic plates in bulletproof vests. Electronic applications of silicon carbide as light emitting diodes (LEDs) and detectors in early radios were first demonstrated around 1907, and nowadays Si C is widely used in high-temperature/high-voltage semiconductor electronics. Large single crystals of silicon carbide can be grown by the Lely method; they can be cut into gems known as synthetic moissanite . Silicon carbide with high surface area can be produced from SiO_2 contained in plant material.

Preferred IUPAC name : Silicon carbide

Systematic name : Methanidylidynesilylium

Other names : Carborundum , Moissanite

Molecular formula	C Si
Molar mass	40 g mol^{-1}
Appearance	Colorless crystals
Density	3.21 g/cm^3 (all poly types)
Melting point	2730 °C, (decomposes)
Electron mobility	~900 $cm^2 / (V \cdot s)$ (all poly types)
Refractive index (n_D)	2.55 (infra red ; all poly types)

2 - Discovery and early production :

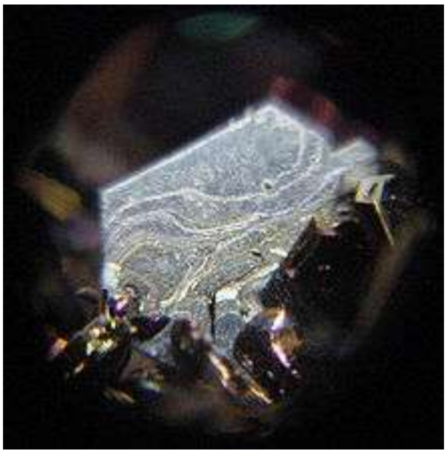
Non-systematic, less-recognized, and often unverified syntheses of silicon carbide were reported early, including: J. J. Berzelius's reduction of potassium fluorosilicate by potassium (1810); Charles Mansuète Despretz's (1792-1863) passing an electric current through a carbon rod embedded in sand (1849); Robert Sydney Marsden's

(1856 - 1919) dissolution of silica in molten silver in a graphite crucible (1881); Albert Colson's heating of silicon under a stream of ethylene (1882); and Paul Schuetzenberger's heating of a mixture of silicon and silica in a graphite crucible (1881). Nevertheless, wide-scale production is credited to Edward Goodrich Acheson in 1890. Acheson was attempting to prepare artificial diamond when he heated a mixture of clay (aluminum silicate) and powdered coke (carbon) in an iron bowl. He called the blue crystals that formed *Carborundum* believing it to be a new compound of carbon and aluminum, similar to corundum. In 1893, Henri Moissan discovered the very rare naturally-occurring Si C mineral while examining rock samples found in Arizona in the Canyon Diablo meteorite. The mineral was named moissanite in his honor. Moissan also synthesized Si C by several routes, including: the dissolution of carbon in molten silicon; melting a mixture of calcium carbide and silica; and by reducing silica with carbon in an electric furnace. How ever, Moissan ascribed the original discovery of Si C to Acheson in 1903.

Acheson patented the method for making silicon carbide powder on February 28, 1893. Acheson also developed the electric batch furnace by which Si C is still made today and formed The Carborundum Company to manufacture bulk Si C , initially for use as an abrasive. In 1900 the company settled with the Electric Smelting and Aluminum Company when a judge's decision gave "priority broadly" to its founders "for reducing ores and other substances by the incandescent method". It is said that Acheson was trying to dissolve carbon in molten corundum (alumina) and discovered the presence of hard, blue-black crystals which he believed to be a compound of carbon and corundum: hence carborundum. Or, he named the material "carborundum" by analogy to corundum, which is another very hard substance (9 on the Mohs scale) .

Historically, the first use of Si C was as an abrasive. This was followed by electronic applications. In the beginning of the 20th century, silicon carbide was used as a detector in the first radios, and in 1907 Henry Joseph Round produced the first LED by applying a voltage to a Si C crystal and observing yellow, green and orange emission at the cathode. Those experiments were later repeated by O. V. Losev in the Soviet Union in 1923.

3 - Natural occurrence :



Moissanite single crystal (≈1 mm in size)

Naturally occurring moissanite is found only in minute quantities in certain types of meteorite and in corundum deposits and kimberlite. Virtually all the silicon carbide sold in the world, including moissanite jewels, is synthetic. Natural moissanite was first found in 1893 as a small component of the Canyon Diablo meteorite in Arizona by Dr. Ferdinand Henri Moissan, after whom the material was named in 1905. Moissan's discovery of naturally occurring Si C was initially disputed because his sample may have been contaminated by silicon carbide saw blades that were already on the market at that time.

While rare on Earth, silicon carbide is remarkably common in space. It is a common form of stardust found around carbon-rich stars, and examples of this stardust have been found in pristine condition in primitive (unaltered) meteorites. The silicon carbide found in space and in meteorites is almost exclusively the beta-polymorph. Analysis of Si C grains found in the Murchison carbonaceous chondrite meteorite has revealed anomalous isotopic ratios of carbon and silicon, indicating an origin from outside the solar system; 99 % of these Si C grains originate around carbon - rich asymptotic giant branch stars. Si C is commonly found around these stars as deduced from their infrared spectra.

4 - Production

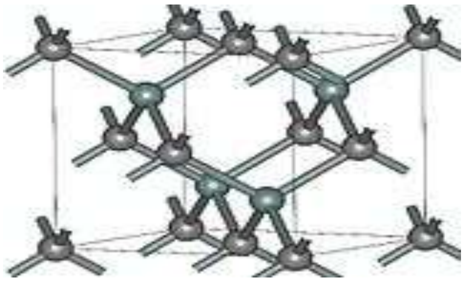
Due to the rarity of natural moissanite, silicon carbide is typically man-made. Most often it is used as an abrasive, and more recently as a semiconductor and diamond simulant of gem quality. The simplest manufacturing process is to combine silica sand and carbon in an Acheson graphite electric resistance furnace at a high temperature, between 1600 and 2500 °C. Fine SiO_2 particles in plant material (e.g. rice husks) can be converted to Si C by heating in the excess carbon from the organic material. The silica fume, which is a byproduct of producing silicon metal and ferrosilicon alloys, also can be converted to Si C by heating with graphite at 1500 °C.

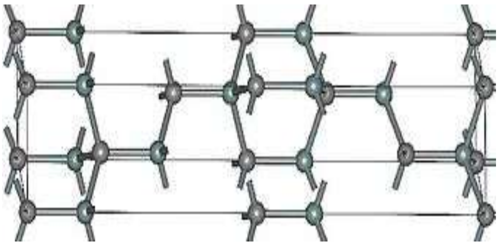
 *Synthetic Si C Lely crystals*	 *Synthetic Si C crystals ~3 mm in diameter*

The material formed in the Acheson furnace varies in purity, according to its distance from the graphite resistor heat source. Colorless, pale yellow and green crystals have the highest purity and are found closest to the resistor. The color changes to blue and black at greater distance from the resistor, and these darker crystals are less pure. Nitrogen and aluminium are common impurities, and they affect the electrical conductivity of Si C .

Pure silicon carbide can be made by the so-called Lely process, in which Si C powder is sublimated in argon atmosphere at 2500 °C and redeposited into flake-like single crystals, sized up to 2×2 cm^2, at a slightly colder substrate. This process yields high-quality single crystals, mostly of 6H-Si C phase (because of high growth temperature). A modified Lely process involving induction heating in graphite crucibles yields even larger single crystals of 4 inches (10 cm) in diameter, having a section 81 times larger compared to the conventional Lely process . Cubic Si C is usually grown by the more expensive process of chemical vapor deposition (CVD).[16][19] Pure silicon carbide can also be prepared by the thermal decomposition of a polymer, poly (methyl silyne) , under an inert atmosphere at low temperatures. Relative to the CVD process, the pyrolysis method is advantageous because the polymer can be formed into various shapes prior to thermalization into the ceramic .

5 - Structure and properties :


(β) 3 C- Si C


(α) 6 H - Si C

Silicon carbide exists in about 250 crystalline forms . The polymorphism of Si C is characterized by a large family of similar crystalline structures called poly types. They are variations of the same chemical compound that are identical in two dimensions and differ in the third. Thus, they can be viewed as layers stacked in a certain sequence.

Alpha silicon carbide (α - Si C) is the most commonly encountered polymorph; it is formed at temperatures greater than 1700 °C and has a hexagonal crystal structure (similar to Wurtzite). The beta modification (β - Si C) , with a zinc blende crystal structure (similar to diamond), is formed at temperatures below 1700 °C. Until recently, the beta form has had relatively few commercial uses, although there is now increasing interest in its use as a support for heterogeneous catalysts, owing to its higher surface area compared to the alpha form.

Pure Si C is colorless. The brown to black color of industrial product results from iron impurities. The rainbow - like luster of the crystals is caused by a passivation layer of silicon dioxide that forms on the surface.

The high sublimation temperature of Si C (approximately 2700 °C) makes it useful for bearings and furnace parts. Silicon carbide does not melt at any known pressure. It is also highly inert chemically. There is currently much interest in its use as a semiconductor material in electronics, where its high thermal conductivity, high electric field breakdown strength and high maximum current density make it more promising than silicon for high-powered devices. Si C also has a very low coefficient of thermal expansion (4.0×10^{-6} / K) and experiences no phase transitions that would cause discontinuities in thermal expansion.

5 – 1 - Electrical conductivity :

Silicon carbide is a semi conductor , which can be doped n-type by nitrogen or phosphorus and p-type by aluminium, boron, gallium or beryllium.[2] Metallic conductivity has been achieved by heavy doping with boron, aluminium or nitrogen. Superconductivity has been detected in 3C-Si C:Al, 3C-Si C:B and 6H-Si C:B at the same temperature of 1.5 K.[26][28] A crucial difference is however observed for the magnetic field behavior between aluminium and boron doping: Si C:Al is type-II, same as Si:B. On the contrary, Si C : B is type-I. In attempt to explain this difference, it was noted that Si sites are more important than carbon sites for superconductivity in Si C. Whereas boron substitutes carbon in Si C, Al substitutes Si sites. There fore, Al and B " see " different environment that might explain different properties of Si C:Al and Si C:B.

6 - Uses :

6 – 1 - Abrasive and cutting tools :

Cutting disks made of Si C

In the arts, silicon carbide is a popular abrasive in modern lapidary due to the durability and low cost of the material. In manufacturing, it is used for its hardness in abrasive machining processes such as grinding, honing, water-jet cutting and sandblasting. Particles of silicon carbide are laminated to paper to create sandpapers and the grip tape on skateboards.

In 1982 an exceptionally strong composite of aluminium oxide and silicon carbide whiskers was discovered. Development of this laboratory-produced composite to a commercial product took only three years. In 1985, the first commercial cutting tools made from this alumina and silicon carbide whisker-reinforced composite were introduced by the Advanced Composite Materials Corporation (ACMC) and Greenleaf Corporation.

6 – 2 - Structural material :

Silicon carbide is used for inner plates of ballistic vests

In the 1980s and 1990s, silicon carbide was studied in several research programs for high-temperature gas turbines in Europe, Japan and the United States. The components were intended to replace nickel super alloy turbine blades or nozzle vanes. How ever, none of these projects resulted in a production quantity, mainly because of its low impact resistance and its low fracture toughness.

Like other hard ceramics (namely alumina and boron carbide), silicon carbide is used in composite armor (e.g., Chobham armor), and in ceramic plates in bulletproof vests. Dragon Skin, which is produced by Pinnacle Armor, uses disks of silicon carbide.[33]

6 – 3 - Automobile parts :

The Porsche Carrera GT's carbon-ceramic (silicon carbide) disc brake

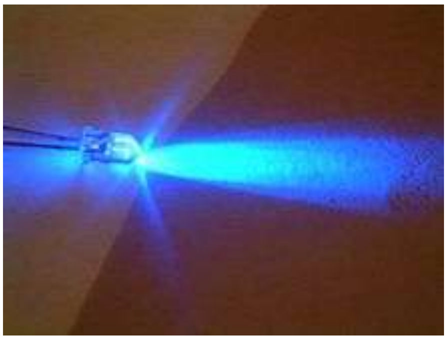
Silicon-infiltrated carbon-carbon composite is used for high performance "ceramic" brake discs as it is able to withstand extreme temperatures. The silicon reacts with the graphite in the carbon-carbon composite to become carbon fiber reinforced silicon carbide (C/Si C). These discs are used on some road going sports cars, including the Porsche Carrera GT, the Bugatti Veyron, the Chevrolet Corvette ZR1, Bentleys, Ferraris, Lamborghinis, and some specific high performance Audis. Silicon carbide is also used in a sintered form for diesel particulate filters.

6 – 4 - Electric systems :

The earliest electrical application of Si C was in lightning arresters in electric power systems. These devices must exhibit high resistance until the voltage across them reaches a certain threshold V_T, at which point their resistance must drop to a lower level and maintain this level until the applied voltage drops below V_T.

It was recognized early on that Si C had such a voltage-dependent resistance, and so columns of Si C pellets were connected between high-voltage power lines and the earth. When a lightning strike to the line raises the line voltage sufficiently, the Si C column will conduct, allowing strike current to pass harmlessly to the earth instead of along the power line. Such Si C columns proved to conduct significantly at normal power-line operating voltages and thus had to be placed in series with a spark gap. This spark gap is ionized and rendered conductive when lightning raises the voltage of the power line conductor, thus effectively connecting the Si C column between the power conductor and the earth. Spark gaps used in lightning arresters are unreliable, either failing to strike an arc when needed or failing to turn off afterwards, in the latter case due to material failure or contamination by dust or salt. Usage of Si C columns was originally intended to eliminate the need for the spark gap in a lightning arrester. Gapped Si C lightning arresters were used as lightning-protection tool and sold under GE and Westinghouse brand names, among others. The gapped Si C arrester has been largely displaced by no-gap varistors that use columns of zinc oxide pellets.

6 – 5 - Electronic circuit elements :



Ultra violet LED

Silicon carbide is used for ultrafast , high-voltage Schottky diodes, MOSFETs and high temperature thyristors for high-power switching. A major problem for Si C commercialization has been the elimination of defects edge dislocations, screw dislocations (both hollow and closed core), triangular defects and basal plane dislocations . As a result, devices made of Si C crystals initially displayed poor reverse blocking performance though researchers have been tentatively finding solutions to improving the breakdown performance. Apart from crystal quality, problems with the interface of Si C with silicon dioxide have hampered the development of Si C - based power MOSFETs and insulated-gate bipolar transistors.

The history of Si C LEDs is quite remarkable: the first LED action was demonstrated in 1907 using Si C and the first commercial LEDs were again based on Si C. Yellow LEDs made from 3C-Si C were manufactured in the Soviet Union in the 1970s, and blue ones (6H-Si C) worldwide in the 1980s. The production was soon stopped because gallium nitride showed 10 – 100 times brighter emission. This difference in efficiency is due to the unfavorable indirect band gap of Si C whereas GaN has a direct band gap which favors light emission. However, Si C is still one of the important LED components – it is a popular substrate for growing GaN devices, and it also serves as a heat spreader in high-power LEDs.

6 – 6 - Astronomy :

The low thermal expansion coefficient, high hardness, rigidity and thermal conductivity make silicon carbide a desirable mirror material for astronomical telescopes. The growth technology (chemical vapor deposition) has been scaled up to produce disks of polycrystalline silicon carbide up to 3.5 meters in diameter, and several telescopes (like the Herschel Space Telescope) are already equipped with Si C optics.

6 – 7 - Thin filament pyrometry :

Image of the test flame and glowing Si C fibers.
The flame is about 7 cm tall.

Silicon carbide fibers are used to measure gas temperatures in an optical technique called thin filament pyrometry. It involves the placement of a thin filament in a hot gas stream. Radiative emissions from the filament can be correlated with filament temperature. Filaments are Si C fibers with a diameter of 15 micrometers, that is about 5 times thinner than human hair. Because the fibers are so thin, they do little to disturb the flame and their temperature remains close to that of the local gas. Temperatures of about 800 – 2500 K can be measured.

6 – 8 - Heating elements :

References to silicon carbide heating elements exist from the early 20th century when they were produced by Acheson's Carborundum Co. in the U.S. and EKL in Berlin. Silicon carbide offered increased operating temperatures compared with metallic heaters. Silicon carbide elements are used today in the melting of non-ferrous metals and glasses, heat treatment of metals, float glass production, production of ceramics and electronics components, igniters in pilot lights for gas heaters, etc.

6 – 9 - Nuclear fuel particles :

Silicon carbide is an important material in TRISO - coated fuel particles, the type of nuclear fuel found in high temperature gas cooled reactors (such as the Pebble Bed Reactor). A layer of silicon carbide gives coated fuel particles structural support and is the main diffusion barrier to the release of fission products.

6 – 10 - Jewelry :

A moissanite ring

As a gemstone used in jewelry, silicon carbide is called "synthetic moissanite" or just "moissanite" after the mineral name.

Moissanite is similar to diamond in several important respects: it is transparent and hard (9 - 9.5) on the Mohs scale (compared to 10 for diamond), with a refractive index between 2.65 and 2.69 (compared to 2.42 for diamond) . Moissanite is somewhat harder than common cubic zirconia. Unlike diamond, moissanite can be strongly birefringent . This quality is desirable in some optical applications, but not in gemstones. For this reason, moissanite jewels are cut along the optic axis of the crystal to minimize birefringent effects. It is lighter (density 3.21 g/cm^3 vs. 3.53 g/cm^3), and much more resistant to heat than diamond. This results in a stone of higher luster, sharper facets and good resilience. Loose moissanite stones may be placed directly into wax ring moulds for lost-wax casting; unlike diamond, which burns at 800 °C, moissanite remains undamaged by temperatures up to 1800 °C. Moissanite has become popular as a diamond substitute, and may be misidentified as diamond, since its thermal conductivity is much closer to that of diamond than any other diamond substitute. Many thermal diamond testing devices cannot distinguish moissanite from diamond, but the gem is distinct in its birefringence and a very slight green or yellow fluorescence under ultraviolet light. Some moissanite stones also have curved string-like inclusions, which diamonds never have.

6 – 11 - Steel production :

Piece of silicon carbide used in steel making

Silicon carbide dissolved in a ba Si C oxygen furnace used for making steel acts as a fuel. It is cleaner than coal, allowing a reduction in scrap output. It can also be used to raise tap temperatures and adjust the carbon content. Silicon carbide is cheaper than of a combination of ferrosilicon and carbon, produces cleaner steel due to low level of trace elements, has a low gas content, and does not lower the temperature of steel.

6 – 12 - Catalyst support :

The natural resistance to oxidation exhibited by silicon carbide, as well as the discovery of new ways to synthesize the cubic β-Si C form, with its larger surface area, has led to significant interest in its use as a heterogeneous catalyst support. This form has already been employed as a catalyst support for the oxidation of hydrocarbons, such as n-butane, to maleic anhydride.

6 – 13 - Carborundum print making :

Silicon carbide is used in carborundum printmaking – a collagraph print making technique. Carborundum grit is applied in a paste to the surface of an aluminium plate. When the paste is dry, ink is applied and trapped in its granular surface, then wiped from the bare areas of the plate. The ink plate is then printed onto paper in a rolling-bed press used for intaglio printmaking. The result is a print of painted marks embossed into the paper.

6 – 14 - Graphene production :

Silicon carbide is used to produce graphene by graphitization at high temperatures. This is considered as one of the promising methods to synthesize graphene at large scale for practical applications.

Silicate

Contents :

1 . Introduction :

A **silicate** is a compound containing an anion in which one or more central silicon atoms are surrounded by electro negative ligands. This definition is broad enough to include species such as hexa fluoro silicate (" fluoro silicate") , $[SiF_6]^{2-}$, but the silicate species that are encountered most often consist of silicon with oxygen as the ligand . Silicate anions, with a negative net electrical charge, must have that charge balanced by other cations to make an electrically neutral compound.

Silica, or silicon dioxide, SiO_2, is sometimes considered a silicate, although it is the special case with no negative charge and no need for counter - ions. Silica is found in nature as the mineral quartz , and its polymorphs.

In the vast majority of silicates, including silicate minerals, the Si atom shows tetrahedral coordination by 4 oxygens. In different minerals the tetra hydra show different degrees of polymerization: they occur singly, joined together in pairs, in larger finite clusters including rings, in chains, double chains, sheets, and three - dimensional frame works. The minerals are classified into groups based on these anion structures; a list is given below.

Silicon may adopt octa hydral coordination by 6 oxygens at very high pressure, as in the dense stishovite polymorph of silica that is found in the lower mantle of the Earth, and which is also formed by shock during meteorite impacts. Lack of space around the oxygen atoms makes this coordination for Si very rare at normal pressure, but it is known in the hexa hydroxy silicate anion, $[Si (OH)_6]^{2-}$, as found in the mineral thaumasite .

2 . Silicate rock

In geology and astronomy, the term **silicate** is used to denote types of rock that consist predominantly of silicate minerals. Such rocks include a wide range of igneous, metamorphic and sedimentary types. Most of the Earth's mantle and crust are made up of silicate rocks. The same is true of the Moon and the other rocky planets .

On Earth, a wide variety of silicate minerals occur in an even wider range of combinations as a result of the processes that form and re - work the crust. These processes include partial melting, crystallization, fractionation, metamorphism, weathering and diagenesis . Living things also contribute to the silicate cycle near the Earth's surface. A type of plankton known as diatoms construct their exoskeletons, known as tests, from silica. The tests of dead diatoms are a major constituent of deep ocean sediment

Silicates have been observed in space, around evolved stars and planetary nebulae such as NGC 6302. They are found in both amorphous form and crystalline form, though the range of types that have been found is far smaller than those found on Earth.

3 . Mineralogy of Silicate

Mineralogically, silicate minerals are divided according to structure of their silicate anion into the following groups :

- Neso silicates (lone tetra hedron) - $[SiO_4]^{4-}$, eg olivine.
- Soro silicates (double tetra hedra) - $[Si_2O_7]^{6-}$, eg epidote, melilite group.
- Cyclo silicates (rings) - $[Si_nO_{3n}]^{2n-}$, eg tourmaline group.
- Ino silicates (single chain) - $[Si_nO_{3n}]^{2n-}$, eg pyroxene group.
- Ino silicates (double chain) - $[Si_{4n}O_{11n}]^{6n-}$, eg amphibole group.
- Phyllo silicates (sheets) - $[Si_{2n}O_{5n}]^{2n-}$, eg micas and clays.
- Tecto silicates (3D frame work) - $[Al_xSi_yO_{2(x+y)}]^{x-}$, eg quartz, feldspars, zeolites.

Note that tecto silicates can only have additional cations if some of the silicon is replaced by a lower - charge cation such as aluminium, to give a negative charge over all. This substitution can also take place in other types of silicate.

Some rare minerals have more than one type of anion coexisting in their crystal structures, or complex - shaped anions that are intermediate between the simple types above.

Silicate minerals

Contents

1 . Introduction :

The **silicate minerals** make up the largest and most important class of rock - forming minerals, comprising approximately 90 percent of the crust of the Earth. They are classified based on the structure of their silicate group. Silicate minerals all contain silicon and oxygen.

2 . Neso silicates or iso silicates

Neso silicates, or ortho silicates, have isolated $[\mathrm{Si\,O_4}]^{4-}$ tetra hedra that are connected only by interstitial cations.

- Phenacite group
  - Phenacite - $Be_2 SiO_4$
  - Willemite - $Zn_2 SiO_4$
- Olivine group
  - Forsterite - $Mg_2 SiO_4$
  - Fayalite - $Fe_2 SiO_4$
- Garnet group
  - Pyrope - $Mg_3Al_2 (SiO_4)_3$
  - Almandine - $Fe_3Al_2 (SiO_4)_3$
  - Spessartine - $Mn_3Al_2 (SiO_4)_3$
  - Grossular - $Ca_3Al_2 (SiO_4)_3$
  - Andradite - $Ca_3Fe_2 (SiO_4)_3$

    - Uvarovite - $Ca_3Cr_2 (SiO_4)_3$
    - Hydrogrossular - $Ca_3Al_2Si_2O_8 (SiO_4)_{1-m} (OH)_{4m}$
- Zircon group
    - Zircon – $Zr SiO_4$
    - Thorite - $(Th, U)_2 SiO_4$

- Al_2SiO_5 group
    - Andalusite - $Al_2 SiO_5$
    - Kyanite - $Al_2 SiO_5$
    - Sillimanite - $Al_2 SiO_5$
    - Dumortierite - $Al_{6.5-7} BO_3 (SiO_4)_3 (O,OH)_3$
    - Topaz - $Al_2SiO_4 (F, OH)_2$
    - Staurolite - $Fe_2Al_9 (SiO_4)_4 (O,OH)_2$
- Humite group - $(Mg, Fe)_7 (Si O_4)_3 (F, OH)_2$
    - Norbergite - $Mg_3 (SiO_4) (F \ OH)_2$
    - Chondrodite - $Mg_5 (SiO_4) (F, OH)_2$
    - Humite - $Mg_7 (SiO_4) (F, OH)_2$
    - Clinohumite - $Mg_9 (SiO_4) (F, OH)_2$
- Datolite – $CaB SiO_4 (OH)$
- Titanite – $CaTi SiO_5$
- Chloritoid - $(Fe, Mg, Mn)_2 Al_4 Si_2O_{10} (OH)_4$

3 . Soro silicates

Soro silicates have isolated double tetra hedra groups with $(Si_2O_7)^{6-}$ or a ratio of 2 : 7 .

- Hemimorphite (calamine) - $Zn_4 (Si_2O_7) (OH)_2 \cdot H_2O$
- Lawsonite - $CaAl_2 (Si_2O_7) (OH)_2 \cdot H_2O$
- Ilvaite - $CaFe^{2+}{}_2Fe^{3+} O (Si_2O_7) (OH)$
- Epidote group (has both $(SiO_4)^{4-}$ and $(Si_2O_7)^{6-}$ groups)
    - Epidote - $Ca_2 (Al,Fe)_3O (SiO_4) (Si_2O_7) (OH)$
    - Zoisite - $Ca_2Al_3O (SiO_4) (Si_2O_7) (OH)$
    - Clinozoisite - $Ca_2Al_3O (SiO_4) (Si_2O_7) (OH)$
    - Tanzanite - $Ca_2Al_3O (SiO_4) (Si_2O_7) (OH)$
    - Allanite – $Ca (Ce,La,Y,Ca)Al_2 (Fe^{2+},Fe^{3+}) O (SiO_4)(Si_2O_7)(OH)$

- Vesuvianite (idocrase) - $Ca_{10} (Mg, Fe)_2 Al_4 (SiO_4)_5 (Si_2O_7)_2 (OH)_4$

4 . Cyclo Silicates

Cyclo Silicates, or ring silicates, have linked tetrahedra with $(Si_xO_{3x})^{2x-}$ or a ratio of 1 : 3 . These exists as 3- member $(Si_3O_9)^{6-}$, 4 - member $(Si_4O_{12})^{8-}$ and 6 - member $(Si_6O_{18})^{12-}$ rings.

- 3 - member ring
  - Benitoite – $BaTi (Si_3O_9)$
- 4 - member ring
  - Axinite - $(Ca,Fe,Mn)_3 Al_2 (BO_3) (Si_4O_{12}) (OH)$
- 6 - member ring
  - Beryl / Emerald - $Be_3Al_2 (Si_6O_{18})$
  - Cordierite - $(Mg, Fe)_2 Al_3 (Si_5AlO_{18})$
  - Tourmaline - $(Na,Ca) (Al,Li,Mg)_3(Al,Fe,Mn)_6(Si_6O_{18})(BO_3)_3(OH)_4$

5 . Ino Silicates

Ino silicates, or chain silicates, have inter locking chains of silicate tetra hedra with either SiO_3 , 1 : 3 ratio, for single chains or Si_4O_{11} , 4 : 11 ratio, for double chains.

5 . 1 . Single chain ino silicates

- Pyroxene group
  - Enstatite – ortho ferro silite series
    - Enstatite – $Mg SiO_3$
    - Ferrosilite – $Fe SiO_3$
  - Pigeonite - $Ca_{0.25} (Mg, Fe)_{1.75} Si_2O_6$
  - Diopside – heden bergite series
    - Diopside – $Ca Mg Si_2O_6$
    - Hedenbergite – $Ca Fe Si_2O_6$
    - Augite - $(Ca,Na) (Mg, Fe, Al) (Si, Al)_2 O_6$
  - Sodium pyroxene series
    - Jadeite – $Na Al Si_2O_6$
    - Aegirine (Acmite) – $Na Fe^{3+} Si_2 O_6$

  - Spodumene – Li Al Si_2 O_6
- Pyroxenoid group
  - Wollastonite – Ca SiO_3
  - Rhodonite – Mn SiO_3
  - Pectolite – Na Ca_2 (Si_3O_8) (OH)

5 .2 . Double chain ino silicates

- Amphibole group
  - Anthophyllite - (Mg , Fe$)_7$ Si_8 O_{22} (OH $)_2$
  - Cumingtonite series
    - Cummingtonite - Fe_2 Mg_5 Si_8 O_{22} (OH $)_2$
    - Grunerite - Fe_7 Si_8 O_{22} (OH $)_2$
  - Tremolite series
    - Tremolite - Ca_2 Mg_5 Si_8 O_{22} (OH $)_2$
    - Actinolite - Ca_2 (Mg , Fe $)_5$ Si_8 O_{22} (OH $)_2$
  - Hornblende - (Ca , Na $)_{2-3}$ (Mg , Fe , Al $)_5$ Si_6 (Al , Si $)_2$ O_{22} (OH $)_2$
  - Sodium amphibole group
    - Glaucophane - Na_2 Mg_3 Al_2 Si_8 O_{22} (OH)
    - Riebeckite (asbestos) - Na_2 Fe^{2+}_3 Fe^{3+}_2 Si_8 O_{22} (OH $)_2$
    - Arfvedsonite - Na_3 (Fe , Mg $)_4$ Fe Si_8 O_{22}(OH$)_2$

6 . Phyllo Silicates

Phyllo Silicates (from Greek φύλλον *phyllon*, leaf) , or sheet silicates, form parallel sheets of silicate tetrahedra with Si_2O_5 or a 2 : 5 ratio .

- Serpentine group
  - Antigorite - Mg_3 Si_2 O_5 (OH$)_4$
  - Chrysotile - Mg_3 Si_2 O_5 (OH$)_4$
  - Lizardite - Mg_3 Si_2 O_5 (OH$)_4$
- Clay mineral group
  - Kaolinite - Al_2 Si_2 O_5 (OH$)_4$
  - Illite –
  - (K,H_3O) (Al, Mg , Fe$)_2$ (Si , Al$)_4$ O_{10} [(OH$)_2$, (H_2O)]
  - Smectite -

  - Montmorillonite –
  - $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot n\,H_2O$
  - Vermiculite - $(MgFe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$
  - Talc - $Mg_3Si_4O_{10}(OH)_2$
  - Palygorskite - $(Mg,Al)_2Si_4O_{10}(OH) \cdot 4(H_2O)$
  - Pyrophyllite - $Al_2Si_4O_{10}(OH)_2$
- Mica group
  - Biotite – $K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$
  - Muscovite – $KAl_2(AlSi_3O_{10})(OH)_2$
  - Phlogopite – $KMg_3Si_4O_{10}(OH)_2$
  - Lepidolite – $K(Li,Al)_{2-3}(AlSi_3O_{10})(OH)_2$
  - Margarite – $CaAl_2(Al_2Si_2O_{10})(OH)_2$
  - Glauconite - $(K,Na)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$
- Chlorite group
  - Chlorite –
  - $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \bullet (Mg,Fe)_3(OH)_6$

7 . Tecto Silicates

Tecto silicates, or " frame work silicates ", have a three-dimensional frame work of silicate tetra hedra with SiO_2 or a 1:2 ratio. This group comprises nearly 75% of the crust of the Earth. Tecto silicates, with the exception of the quartz group, are alumino silicates.

- Quartz group
  - Quartz - SiO_2
  - Tridymite - SiO_2
  - Cristobalite - SiO_2
- Feldspar group
  - Alkali - feldspars
    - Potassium - feldspars
      - Microcline – $KAlSi_3O_8$
      - Orthoclase – $KAlSi_3O_8$
      - Sanidine – $KAlSi_3O_8$
    - Anorthoclase - $(Na,K)AlSi_3O_8$
    - Albite – $NaAlSi_3O_8$
  - Plagioclase feldspars

- Albite – $Na\,Al\,Si_3\,O_8$
- Oligoclase - $(Na,Ca)\,(Si,Al)_4\,O_8$ (Na : Ca 4 : 1)
- Andesine - $(Na,Ca)\,(Si,Al)_4\,O_8$ (Na : Ca 3 : 2)
- Labradorite - $(Na,Ca)(Si,Al)_4O_8$ (Na : Ca 2 : 3)
- Bytownite - $(Na,Ca)\,(Si,Al)_4O_8$ (Na : Ca 1 : 4)
- Anorthite – $Ca\,Al_2\,Si_2O_8$
- Feldspathoid group
    - Nosean - $Na_8\,Al_6\,Si_6\,O_{24}\,(SO_4)$
    - Cancrinite - $Na_6\,Ca_2\,(CO_3\,,\,Al_6\,Si_6\,O_{24})\,.2H_2O$
    - Leucite – $K\,Al\,Si_2\,O_6$
    - Nepheline - $(Na\,,\,K)Al\,Si\,O_4$
    - Sodalite - $Na_8\,(Al\,Si\,O_4)_6\,Cl_2$
        - Hauyne - $(Na,Ca)_{4-8}\,Al_6\,Si_6\,(O,S)24\,(SO_4,Cl)_{1-2}$
    - Lazurite - $(Na\,,\,Ca)_8\,(AlSiO_4)_6\,(SO_4\,,\,S\,,\,Cl)_2$
- Petalite – $Li\,Al\,Si_4\,O_{10}$
- Scapolite group
    - Marialite - $Na_4\,(Al\,Si_3\,O_8)_3\,(Cl_2\,,\,CO_3\,,\,SO_4)$
    - Meionite - $Ca_4\,(Al_2\,Si_2\,O_8)_3\,(Cl_2\,,\,CO_3\,,\,SO_4)$
- Analcime – $Na\,Al\,Si_2\,O_6 \bullet H_2O$
- Zeolite group
    - Natrolite - $Na_2\,Al_2\,Si_3\,O_{10} \bullet 2H_2O$
    - Chabazite – $Ca\,Al_2\,Si_4\,O_{12} \bullet 6H_2O$
    - Heulandite – $Ca\,Al_2\,Si_7\,O_{18} \bullet 6H_2O$
    - Stilbite – $Na\,Ca_2\,Al_5\,Si_{13}\,O_{36} \bullet 17H_2O$

Silicic acid

Other names :

Mono silicic acid
Ortho silicic acid

Molecular formula	$H_4\ O_4\ Si$
Molar mass	$96\ g\ mol^{-1}$
Acidity (pK_a)	9.84, 13.2

- Introduction :

Silicic acid is a general name for a family of chemical compounds of the element silicon, hydrogen, and oxygen, with the general formula $[SiO_x\ (OH)_{4-2x}\ ]_n$. Some simple silicic acids have been identified in very dilute aqueous solution, such as *meta silicic acid* (H_2SiO_3), *ortho silicic acid* (H_4SiO_4, $pK_{a1}=9.84$, $pK_{a2}=13.2$ at 25°C), *di silicic acid* ($H_2Si_2O_5$), and *pyro silicic acid* ($H_6Si_2O_7$); however in the solid state these probably condense to form polymeric silicic acids of complex structure.

Silicic acids may be formed by acidification of silicate salts (such as sodium silicate) in aqueous solution. When heated they lose water to form silica gel, an active form of silicon dioxide.

In the oceans, silicon exists primarily as ortho silicic acid (H_4SiO_4), and its biogeochemical cycle is regulated by the group of algae known as the diatoms . These algae polymerize the silicic acid to so - called biogenic silica, used to construct their cell walls (called frustules).

Continuing research of the correlation of aluminium and Alzheimer's disease has in the last few years included the use of silicic acid in beverages , due to its abilities to both reduce aluminium uptake in the digestive system as well as cause renal excretion of aluminium.

Ortho silicic acid is the form predominantly absorbed by humans and is found in numerous tissues including bone, tendons, aorta, liver and kidney. Compelling data suggest that silica is essential for health although no RDI has been established. However, deficiency induces deformities in skull and peripheral bones, poorly formed joints, reduced contents of cartilage, collagen, and disruption of mineral balance in the femur and vertebrae . Study has shown that physiological concentration of ortho silicic acid stimulates collagen type 1 synthesis and osteoblastic differentiation in human osteoblast - like cells in vitro.

Choline - stabilized ortho silicic acid is a bio available nutritional supplement. It has been shown to prevent the loss of hair tensile strength , have positive effect on skin surface and skin mechanical properties, and on brittleness of hair and nails , abate brittle nail syndrome , partially prevent femoral bone loss in the aged ovariectomized rat model , increase collagen concentration in calves , and have potential beneficial effect on bone collagen formation in osteopenic females .

Calcium silicate

Calcium silicate passive fire protection board being clad around steel structure in order to achieve a fire - resistance rating.

Contents

1 – Introduction :

Calcium silicate (often referred to by its shortened trade name **Cal - Sil** or **Calsil**) is the chemical compound $Ca_2 Si O_4$, also known as calcium ortho silicate and some times formulated $2CaO.SiO_2$. It is one of group of compounds obtained by reacting calcium oxide and silica in various ratios e.g. $3CaO.SiO_2$, Ca_3SiO_5 ; $2CaO.SiO_2$, Ca_2SiO_4; $3CaO.2SiO_2$, $Ca_3Si_2O_7$ and $CaO.SiO_2$, $CaSiO_3$. Calcium ortho silicate is a white powder with a low bulk density and high phySi Cal water absorption. It is used as an anti - caking agent and an antacid . A white free - flowing powder derived from limestone and diatomaceous earth, calcium silicate has no known adverse effects to health . It is used in roads, insulation, bricks, roof tiles, table salt[2] and occurs in cements, where it is known as belite (or in cement chemist notation C_2S).

IUPAC name : Calcium silicate

Systematic name : Dicalcium silicate

Other names :
Belite , Calcium ortho silicate , Gram mite , Micro – cell , Silene , Silicic acid calcium salt

Molecular formula	$Ca_2 O_4 Si$
Molar mass	172 g mol^{-1}
Appearance	White crystals
Melting point	1540 °C, 1813 K, 2804 °F
Flash point	Not applicable

2 - High temperature insulation :

Calcium silicate is commonly used as a safe alternative to asbestos for high temperature insulation materials. Industrial grade piping and equipment insulation is often fabricated from calcium silicate. Its fabrication is a routine part of the curriculum for insulation apprentices. Calcium silicate competes in these realms against rock wool as well as proprietary insulation solids, such as perlite mixture and vermiculite bonded with sodium silicate. Although it is popularly considered an asbestos substitute, early uses of calcium silicate for insulation still made use of asbestos fibers.

3 - Passive fire protection :

One of the most successful materials in fire proofing in Europe is calcium silicate. Where North Americans use spray fire proofing plasters, Europeans are more likely to use cladding made of calcium silicate. Calcium silicate is easily damaged by water. Therefore, silicone treated sheets are available to fabricators to mitigate potential harm from high humidity or general presence of water. Fabricators and installers of calcium silicate in passive fire protection often also install fire stops .

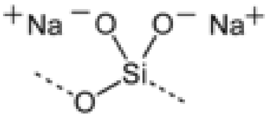
4 - Acid mine drainage remediation :

Calcium silicate is also a constituent of the slag that is produced when molten iron is made from iron ore and calcium carbonate in a blast furnace. When this material is processed into a highly refined, repurposed calcium silicate aggregate, it is used in the remediation of acid mine drainage (AMD) on active and passive mine sites.[3] Calcium silicate neutralizes active acidity in AMD systems by removing free hydrogen ions from the bulk solution, thereby increasing pH. As its silicate anion captures H^+ ions (raising the pH), it forms mono silicic acid (H_4SiO_4), a neutral solute. Mono silicic acid remains in the bulk solution to play other important roles in correcting the adverse effects of acidic conditions. As opposed to limestone (a popular remediation material) , calcium silicate effectively precipitates heavy metals and does not armor over, prolonging its effectiveness in AMD systems .

5 - As a product of sealants :

When sodium silicate is applied as a sealant to cured concrete or the shells of fresh eggs, it chemically reacts with calcium hydroxide or carbonate to form calcium silicate hydrate, sealing pores with a relatively impermeable material.

Sodium silicate



Contents

1 – Introduction :

Sodium silicate is the common name for a compound sodium meta silicate, Na_2SiO_3, also known as **water glass** or **liquid glass**. It is available in aqueous solution and in solid form and is used in cements, passive fire protection , refractories , textile and lumber processing, and automobiles . Sodium carbonate and silicon dioxide react when molten to form sodium silicate and carbon dioxide :

$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$

Anhydrous sodium silicate contains a chain polymeric anion composed of corner shared {SiO_4} tetrahedral, and not a discrete SiO_3^{2-} ion . In addition to the anhydrous form, there are hydrates with the formula $Na_2SiO_3 \cdot nH_2O$ (where n = 5, 6, 8, 9) which contain the discrete, approximately tetrahedral anion $SiO_2(OH)_2^{2-}$ with water of hydration. For example, the commercially available sodium silicate penta hydrate $Na_2SiO_3 \cdot 5H_2O$ is formulated as $Na_2SiO_2(OH)_2 \cdot 4H_2O$ and the nona hydrate $Na_2SiO_3 \cdot 9H_2O$ is formulated as $Na_2SiO_2(OH)_2 \cdot 8H_2O$.

In industry, the different grades of sodium silicate are characterized by their SiO_2:Na_2O ratio, which can vary between 2 : 1 and 3.75 : 1 . Grades with this ratio below 2.85 : 1 are termed 'alkaline'. Those with a higher SiO_2 : Na_2O ratio are described as 'neutral'.

IUPAC name: Sodium meta silicate	
Other names : Liquid glass , Water glass	
Molecular formula	$Na_2\ O_3\ Si$
Molar mass	122 g mol^{-1}
Appearance	White, opaque crystals
Density	2.4 g cm^{-3}
Melting point	1088 °C
Refractive index (n_D)	1.52

2 - History :

Water Glass was defined in Von Wagner's *Manual of Chemical Technology* (1892 translation) as any of the soluble alkaline silicates, first observed by Van Helmont in 1640 as a fluid substance made by melting sand with excess alkali. Glauber made what he termed "fluid silica" in 1648 from potash and silica. Von Fuchs, in 1825, obtained what is now known as water glass by treating silicic acid with an alkali, the result being soluble in water, "but not affected by atmospheric changes". Von Wagner distinguished *soda*, *potash*, *double*(soda and potash), and *fixin* as types of water glass. The *fixing* type was "a mixture of silica well saturated with potash water glass and a sodium silicate" used to stabilize inorganic water color pigments on cement work for outdoor signs and murals.

3 - Properties :

Sodium silicate is a white powder that is readily soluble in water, producing an alkaline solution. It is one of a number of related compounds which include sodium ortho silicate, Na_4SiO_4, sodium pyro silicate, $Na_6Si_2O_7$, and others. All are glassy, colourless and dissolve in water.

Sodium silicate is stable in neutral and alkaline solutions. In acidic solutions, the silicate ion reacts with hydrogen ions to form silicic acid, which when heated and roasted forms silica gel, a hard, glassy substance.

4 - Uses

4 – 1 - Metal repair :

Sodium silicate is used, along with magnesium silicate, in muffler repair and fitting paste. When dissolved in water, both sodium silicate, and magnesium silicate form a thick paste that is easy to apply. When the exhaust system of an internal combustion engine heats up to its operating temperature, the heat drives out all of the excess water from the paste. The silicate compounds that are left over have glass-like properties, making a temporary, brittle repair.

4 – 2 - Automotive repair :

Sodium silicate can be used to seal leaks at the head gasket. A common use is when an aluminum alloy cylinder head engine is left sitting for extended periods or the coolant is not changed at proper intervals, electrolysis can "eat out" sections of the head causing the gasket to fail.

Rather than remove the cylinder head, "liquid glass" is poured into the radiator and allowed to circulate. The water glass is injected via the radiator water into the hotspot at the engine. This technique works because at 100 - 105 °C the sodium silicate loses water molecules to form a very powerful sealant that will not re-melt below 810 °C.

A sodium silicate repair of a leaking head gasket can hold for up to two years and even longer in some cases. The effect will be almost instant, and steam from the radiator water will stop coming out the exhaust within minutes of application. This repair only works with water - to - cylinder or water-to-air applications and where the sodium silicate reaches the "conversion" temperature of 100-105 °C.

4 – 3 – Home brewing :

Sodium silicate flocculent properties are also used to clarify wine and beer by precipitating colloidal particles. But as a clearing agent sodium silicate (water glass) is some times confused with isinglass (a form of gelatin prepared from collagen extracted from the dried swim bladders of sturgeon and other fishes). Eggs preserved in a bucket of water glass gel, and their shells, are some times also used (baked and crushed) to clear wine .

4 – 4 - Car engine disablement :

Sodium silicate solution is used to inexpensively, quickly, and permanently disable automobile engines. Running an engine with about 2 liters of a sodium silicate solution instead of motor oil causes the solution to precipitate, catastrophically damaging the engine's bearings and pistons within a few minutes . In the United States, this procedure was required by the Car Allowance Rebate System (CARS) program .

4 – 5 – Adhesive :

One common example of its use as a paper cement was for producing paper cartridges for black powder revolvers produced by Colt's Manufacturing Company during the period from 1851 until 1873, especially during the American Civil War. Sodium silicate was used to seal combustible nitrated paper together to form a conical paper cartridge to hold the black powder, as well as to cement the lead ball or conical bullet into the open end of the paper cartridge. Such sodium silicate cemented paper cartridges were inserted into the cylinders of revolvers, thereby speeding the reloading of cap and ball black powder revolvers. This use largely ended with the introduction of Colt revolvers employing brass-cased cartridges starting in 1873 .

When used as a paper cement, the tendency is for the sodium silicate joint eventually to crack within a few years, at which point it no longer holds the paper surfaces cemented together.

4 – 6 – Aquaculture :

Sodium silicate gel is also used as a substrate for algal growth in aquaculture hatcheries.

4 – 7 - Food preservation :

Sodium silicate was also used as an egg preservation agent in the early 20th century with large success. When fresh eggs are immersed in it, bacteria which cause the eggs to spoil are kept out and water is kept in. Eggs can be kept fresh using this method for up to nine months. When boiling eggs preserved this way, it is well advised to pin - prick the egg to allow steam to escape because the shell is no longer porous.

4 – 8 - Drilling fluids :

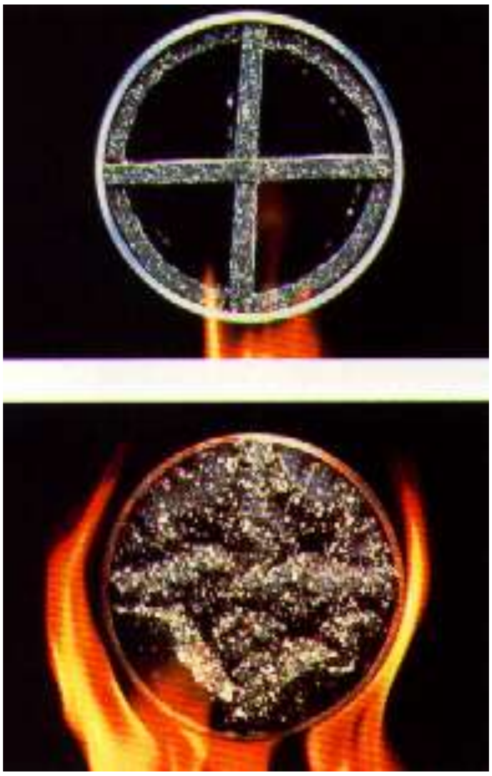
Sodium silicate is frequently used in drilling fluids to stabilize borehole wells and to avoid the collapse of bore walls.

It is particularly useful when drill holes pass through argillaceous formations containing swelling clay minerals such as smectite or montmorillonite .

4 – 9 - Concrete and general masonry treatment :

Concrete treated with a sodium silicate solution helps to significantly reduce porosity in most masonry products such as concrete , stucco , plasters . A chemical reaction occurs with the excess $Ca(OH)_2$ (portlandite) present in the concrete that permanently binds the silicates with the surface making them far more wearable and water repellent. It is generally advised to apply this treatment only after the initial cure has taken place (7 days or so depending on conditions). These coatings are known as silicate mineral paint.

4 – 10 - Passive fire protection (PFP) :



Expantrol proprietary sodium silicate suspended in an about 6.5 mm thick layer of red rubber, type 3M FS195, inserted into a metal pipe, then heated, to demonstrate hard char in tumescence , strong enough to shut a melting plastic pipe.

Palusol based in tumescent plastic pipe device used for commercial fire stopping.

Sodium silicates are inherently in tumescent . They come in prill (solid beads) form, as well as the liquid, water glass. The solid sheet form (Palusol) must be water proofed to ensure long - term passive fire protection.

Standard, solid, bead form sodium silicates have been used as aggregate within silicone rubber to manufacture plastic pipe fire stop devices. The silicone rubber was insufficient waterproofing to preserve the intumescing function and the products had to be recalled, which is problematic for firestops that are concealed behind dry wall in buildings.

Pastes for caulking purposes are similarly unstable. This too has resulted in recalls and even litigation. Only 3M's "Expantrol" version, which has an external heat treatment that helps to seal the outer surface, as part of its process standard, has achieved sufficient longevity to qualify for DIBt approvals in the US for use in fire stopping

Not unlike other in tumescents , sodium silicate, both in bead form and in liquid form are inherently endothermic, due to liquid water in the water glass and hydrates in the prill form. The absence in the US of mandatory aging tests, whereby PFP systems are made to undergo system performance tests *after* the aging and humidity exposures, are at the root of the continued availability, in North America, of PFP products that can become inoperable within weeks of installation. Indiscriminate use of sodium silicates without proper water proofing measures are contributors to the problems and risk. When sodium silicates are adequately protected, they function extremely well and reliably for long periods. Evidence of this can be seen in the many DIBt approvals for plastic pipe fire stop devices using Palusol , which use waterproofed sodium silicate sheets.

4 – 11 - Safe construction :

A mixture of sodium silicate and sawdust has been used in between the double skin of certain safes. This not only makes them more fire resistant, but also makes cutting them open with an oxy acetylene torch extremely difficult due to the smoke emitted.

4 – 12 - Refractory use :

Water glass is a useful binder of solids, such as vermiculite and perlite. When blended with the aforementioned light weight aggregates, water glass can be used to make hard, high - temperature insulation boards used for refractories , passive fire protection and high temperature insulations, such as moulded pipe insulation applications. When mixed with finely divided mineral powders, such as vermiculite dust (which is common scrap from the exfoliation process), one can produce high temperature adhesives. The in tumescence disappears in the presence of finely divided mineral dust, whereby the water glass becomes a mere matrix. Water glass is inexpensive and abundantly available, which makes its use popular in many refractory applications.

4 – 13 - Water treatment :

Water glass is used as coagulant / flocculent agent in waste water treatment plants. Water glass binds to colloidal molecules, creating larger aggregates that sink to the bottom of the water column. The microscopic negatively charged particles suspended in water interact with sodium silicate. Their electrical double layer collapses due to the increase of ionic strength caused by the addition of sodium silicate (doubly negatively charged anion accompanied by two sodium cations) and they subsequently aggregate. This process is called coagulation / flocculation .

4 – 14 - Detergent auxiliaries :

It also can be used in detergent auxiliaries like complex sodium di silicate and modified sodium di silicate .

4 – 15 - Magic crystals :

Water glass was used in the Magic rocks toys invented in 1940. When water glass was combined with a selection of different metals in solution, the water glass would cause the metals to precipitate. Each metal would precipitate separately causing a different color stalagmite.

An early mention of crystals of metallic salts forming a "chemical garden" in sodium silicate is found in the 1946 Modern Mechanix magazine . This results in very colorful gardens — much more than shown in the illustrations.

In Europe the ingredients for such chemical gardens were available already around the early 1930s.

4 – 16 - Dye auxiliary :

Sodium silicate solution is used as a fixative for hand dyeing with reactive dyes that require a high pH in order to react with the textile fiber. After the dye is applied to a cellulose - based fabric, such as cotton or rayon, or onto silk, it is allowed to dry, after which the sodium silicate is painted on to the dyed fabric, covered with plastic to retain moisture, and left to react for an hour at room temperature .

4 – 17 - Sealing of leaking water containing structures :

Sodium silicate with additives was injected into the ground in order to harden it and thereby to prevent further leakage of highly radioactive water from the Fukushima Daiichi nuclear power plant in Japan in April, 2011 . The residual heat carried by the water used for cooling the damaged reactors accelerated the setting of the injected mixture.

Talc (magnesium silicate)

A block of talc.

Contents

1 – Introduction :

Talc (derived from the Persian *tālk* (تالک), Arabic *talk* (تلك)) is a mineral composed of hydrated magnesium silicate with the chemical formula $H_2Mg_3(SiO_3)_4$ or $Mg_3Si_4O_{10}(OH)_2$. In loose form, it is the widely-used substance known as talcum powder. It occurs as foliated to fibrous masses, its crystals being so rare as to be almost unknown. It has a perfect basal cleavage, and the folia are non-elastic, although slightly flexible. It is the softest known mineral and listed as *1* on the Mohs hardness scale. It can be easily scratched by a fingernail. It is also sectile (can be cut with a knife). It has a specific gravity of 2.5–2.8, a clear or dusty luster, and is translucent to opaque. Talc is not soluble in water, but it is slightly soluble in dilute mineral acids. Its colour ranges from white to grey or green and it has a distinctly greasy feel. Its streak is white . Soap stone is a meta morphic rock composed predominantly of talc.

Category	Silicate mineral
Chemical formula	$Mg_3\ Si_4\ O_{10}\ (\ OH\ )_2$
Crystal symmetry	Either monoclinic 2 m or triclinic 1
Unit cell	a = 5.291 Å, b = 9.173 Å, c = 5.290 Å; α = 98.68°, β = 119.90°, γ = 90.09°; Z = 2 or a = 5.287 Å, b = 9.158 Å, c = 18.95 Å, β = 99.3°; Z = 4
Color	Light to dark green, brown, white
Crystal habit	Foliated to fibrous masses, rare as platey to pyramidal crystals
Crystal system	monoclinic or triclinic
Mohs scale hardness	1 (defining mineral)
Luster	Wax like or pearly
Streak	White to very pearly green
Diaphaneity	Translucent
Specific gravity	2.58 to 2.83
Optical properties	Biaxial (-)
Refractive index	n_α = 1.538 – 1.550 n_β = 1.589 – 1.594 n_γ = 1.589 – 1.600

Birefringence	$\delta = 0.051$
Pleochroism	Weak in dark varieties
Ultra violet fluorescence	Short UV = orange yellow, long UV = yellow

2 - Formation :

Talc is a metamorphic mineral resulting from the metamorphism of magnesian minerals such as serpentine, pyroxene, amphibole, olivine, in the presence of carbon dioxide and water. This is known as *talc carbonation* or *steatization* and produces a suite of rocks known as talc carbonates.

Talc is primarily formed via hydration and carbonation of serpentine, via the following reaction ;

serpentine + *carbon dioxide* → *talc* + *magnesite* + *water*

$$2\,Mg_3\,Si_2\,O_5\,(OH)_4 + 3CO_2 \rightarrow Mg_3\,Si_4\,O_{10}\,(OH)_2 + 3\,Mg\,CO_3 + 3\,H_2O$$

Talc can also be formed via a reaction between dolomite and silica, which is typical of skarnification of dolomites via silica-flooding in contact metamorphic aureoles ;

dolomite + *silica* + *water* → *talc* + *calcite* + *carbon dioxide*

$$3\,Ca\,Mg\,(CO_3)_2 + 4\,SiO_2 + H_2O \rightarrow Mg_3\,Si_4\,O_{10}\,(OH)_2 + 3\,Ca\,CO_3 + 3\,CO_2$$

Talc can also be formed from magnesian chlorite and quartz in blue schist and eclogite metamorphism via the following metamorphic reaction :

chlorite + *quartz* → *kyanite* + *talc* + *water*

In this reaction, the ratio of talc and kyanite is dependent on aluminium content with more aluminous rocks favoring production of kyanite. This is typically associated with high - pressure, low-temperature minerals such as phengite , garnet, glaucophane within the lower blue schist facies . Such rocks are typically white, friable, and fibrous, and are known as *white schist*.

Talc is a tri-octahedral layered mineral; its structure is similar to that of pyro phyllite , but with magnesium in the octahedral sites of the composite layers.

3 – Occurrence :

Talc output in 2005

Talc is a common metamorphic mineral in metamorphic belts which contain ultra mafic rocks , such as soapstone (a high-talc rock), and within white schist and blue schist metamorphic terranes. Prime examples of white schists include the Franciscan Metamorphic Belt of the western United States, the western European Alps especially in Italy, certain areas of the Musgrave Block, and some collisional orogens such as the Himalayas which stretches along Pakistan, India, Nepal and Bhutan.

Talc carbonate ultra mafics are typical of many areas of the Archaean cratons, notably the komatiite belts of the Yilgarn Craton in Western Australia. Talc - carbonate ultra mafics are also known from the Lachlan Fold Belt, eastern Australia, from Brazil, the Guiana Shield, and from the ophiolite belts of Turkey , Oman and the Middle East.

Notable economic talc occurrences include the Mount Seabrook talc mine, Western Australia, formed upon a polydeformed, layered ultra mafic intrusion. The France-based Luzenac Group is the world's largest supplier of mined talc; its largest talc mine at Trimouns near Luzenac in southern France produces 400,000 tones of talc per year, representing 8% of world production.

4 - Uses :

Talc is used in many industries such as paper making, plastic, paint and coatings, rubber, food, electric cable, pharmaceuticals, cosmetics, ceramics, etc. A coarse grayish-green high-talc rock is soap stone or steatite and has been used for stoves, sinks, electrical switchboards, crayons, soap, etc. It is often used for surfaces of lab counter tops and electrical switchboards because of its resistance to heat, electricity and acids. Talc finds use as a cosmetic (talcum powder), as a lubricant, and as a filler in paper manufacture. Talc is used in baby powder, an astringent powder used for preventing rashes on the area covered by a diaper . It is also often used in basketball to keep a player's hands dry. Most tailor's chalk is talc, as is the chalk often used for welding or metal working.

Talc is also used as food additive or in pharmaceutical products as a glidant. In medicine talc is used as a pleurodesis agent to prevent recurrent pleural effusion or pneumothorax . In the European Union the additive number is E553b.

Talc is widely used in the ceramics industry in both bodies and glazes. In low-fire art ware bodies it imparts whiteness and increases thermal expansion to resist crazing. In stone wares , small percentages of talc are used to flux the body and therefore improve strength and vitrification . It is a source of Mg O flux in high temperature glazes (to control melting temperature). It is also employed as a matting agent in earthenware glazes and can be used to produce magnesia mattes at high temperatures.

ISO standard for quality (ISO 3262) :

Type	**Talc content min. wt%**	**Loss on ignition at 1000 °C, wt %**	**Solubility in HCl , max. wt %**
A	95	4 – 6.5	5
B	90	4 – 9	10
C	70	4 – 18	30
D	50	4 – 27	30

Patents are pending on the use of magnesium silicate as a cement substitute. Its production requirements are less energy-intensive than ordinary Portland cement at around 650 °C, while it absorbs far more carbon dioxide as it hardens. This results in a negative carbon footprint overall, as the cement substitute removes 0.6 tones of CO_2 per tone used. This contrasts with a carbon footprint of 0.4 tone per tone of conventional cement.

Talc is sometimes used as an adulterant to illegal heroin, to expand volume and weight and thereby increase its street value. With intravenous use, it may lead to talcosis , a granulomatous inflammation in the lungs.

5 - Safety

Talc powder is a house hold item , sold globally for use in personal hygiene and cosmetics and used by many millions every year. Some suspicions have been raised about the possibility its use promotes certain types of diseases, mainly cancers of the ovaries and lungs. This is not widely recognised as an established link .

The studies reference, by subject: pulmonary issues, lung cancer, skin cancer and ovarian cancer. One of these, published in 1993, was a US National Toxicology Program report, which found that cosmetic grade talc containing no asbestos-like fibres was correlated with tumour formation in rats (animal testing) forced to inhale talc for 6 hours a day, five days a week over at least 113 weeks. A 1971 paper found particles of talc embedded in 75% of the ovarian tumors studied.

The US Food and Drug Administration (FDA) considers talc (magnesium silicate) to be generally recognized as safe (GRAS) for use as an anti-caking agent in table salt in concentrations smaller than 2% .

Asbestos

 *Asbestos*	 *Asbestos*
 *Blue asbestos (crocidolite) from Wittenoom, Western Australia. The ruler is 1 cm.*	 *Fibrous asbestos on muscovite*
 *Asbestos fibers*	 *Chrysotile asbestos*

Contents :

1 – Introduction :

Asbestos (from Greek ἄσβεστος, "unquenchable" or "inextinguishable") is a set of six naturally occurring silicate minerals exploited commercially for their desirable phySi Cal properties . They all have in common their, eponymous, asbestiform habit, long, (1:20) thin fibrous crystals. The inhalation of asbestos fibers can cause serious illnesses, including malignant lung cancer, mesothelioma (a formerly rare cancer strongly associated with exposure to amphibole asbestos) , and asbestosis (a type of pneumoconiosis). Long exposure to high concentrations of asbestos fibers is more likely to cause health problems. The European Union has banned all use of asbestos and extraction, manufacture and processing of asbestos products .

Asbestos became increasingly popular among manufacturers and builders in the late 19th century because of its sound absorption, average tensile strength, and its resistance to fire, heat, electrical and chemical damage. It was used in such applications as electrical insulation for hotplate wiring and in building insulation. When asbestos is used for its resistance to fire or heat, the fibers are often mixed with cement (resulting in fiber cement) or woven into fabric or mats. Commercial asbestos mining began in the Eastern Townships of Quebec, Canada and the world's largest asbestos mine is located in the town of Asbestos, Quebec.

2 - Types and associated fibers :

Six minerals are defined by the United States Environmental Protection Agency as "asbestos" including those belonging to the serpentine class chrysotile and those belonging to the amphibole class amosite, crocidolite , tremolite , anthophyllite and actinolite. There is an important distinction to be made between serpentine and amphibole asbestos due to differences in their chemical composition and their degree of potency as a health hazard when inhaled. However asbestos and all commercial forms of asbestos (including chrysotile asbestos) are known to be human carcinogens based on sufficient evidence of carcinogenicity in humans.

2 – 1 - Serpentine :

2 – 1 - 1 – White :

Chrysotile, CAS No. 12001-29-5, is obtained from serpentinite rocks which are common throughout the world. Its idealized chemical formula is $Mg_3 (Si_2O_5) (OH)_4$. Chrysotile fibers are curly as opposed to fibers from amosite , crocidolite , tremolite, actinolite, and anthophyllite which are needlelike . Chrysotile, along with other types of asbestos, has been banned in dozens of countries and is only allowed in the United States and Europe in very limited circumstances. Chrysotile has been used more than any other type and accounts for about 95 % of the asbestos found in buildings in America.[8] Applications where chrysotile might be used include the use of joint compound. It is more flexible than amphibole types of asbestos; it can be spun and woven into fabric. The most common use is within corrugated asbestos cement roof sheets typically used for outbuildings, warehouses and garages. It is also found as flat sheets used for ceilings and sometimes for walls and floors. Numerous other items have been made containing chrysotile including brake linings, cloth behind fuses (for fire protection), pipe insulation, floor tiles, and rope seals for boilers .

2 – 2 - Amphibole :

2 – 2 - 1 – Brown :

Amosite , CAS No. 12172-73-5, is a trade name for the amphiboles belonging to the cummingtonite - grunerite solid solution series, commonly from Africa, named as an acronym from Asbestos Mines of South Africa. One formula given for amosite is $Fe_7Si_8O_{22}(OH)_2$. It is found most frequently as a fire retardant in thermal insulation products and ceiling tiles.

2 – 2 - 2 – Blue

Crocidolite, CAS No. 12001-28-4 is an amphibole found primarily in southern Africa, but also in Australia. It is the fibrous form of the amphibole riebeckite. One formula given for crocidolite is $Na_2 Fe^{2+}{}_3Fe^{3+}{}_2Si_8O_{22}(OH)_2$.

Crocidolite commonly occurs as soft friable fibers. Asbestiform amphibole may also occur as soft friable fibers but some varieties such as amosite are commonly straighter. All forms of asbestos are fibrillar in that they are composed of fibers with breadths less than 1 micrometer that occur in bundles and have very great widths. Asbestos with particularly fine fibers is also referred to as "amianthus". Amphiboles such as tremolite have a crystal structure containing strongly bonded ribbonlike silicate anion polymers that extend the width of the crystal. Serpentine (chrysotile) has a sheetlike silicate anion which is bowed and which rolls up like a carpet to form the fiber.

2 – 2 - 3 – Other materials :

Other regulated asbestos minerals, such as tremolite asbestos, CAS No. 77536-68-6, $Ca_2Mg_5Si_8O_{22}(OH)_2$; actinolite asbestos, CAS No. 77536-66-4, $Ca_2(Mg, Fe)_5(Si_8O_{22})(OH)_2$; and anthophyllite asbestos, CAS No. 77536-67-5, $(Mg, Fe)_7Si_8O_{22}(OH)_2$; are less commonly used industrially but can still be found in a variety of construction materials and insulation materials and have been reported in the past to occur in a few consumer products.

Other natural and not currently regulated asbestiform minerals, such as richterite, $Na\ (CaNa)(Mg, Fe^{++})_5(Si_8O_{22})(OH)_2$, and winchite, $(CaNa)Mg_4(Al, Fe^{3+})(Si_8O_{22})(OH)_2$, may be found as a contaminant in products such as the vermiculite containing zonolite insulation manufactured by W.R. Grace and Company. These minerals are thought to be no less harmful than tremolite, amosite, or crocidolite, but since they are not regulated, they are referred to as "asbestiform" rather than asbestos although may still be related to diseases and hazardous :) .

3 - Producing nations :

In 2006, 2.3 million tones of asbestos were mined world wide , in 11 or 12 countries. Russia was the largest producer with about

40.2% world share followed by China (19.9 %) , Kazakhstan (13.0 %) , Canada (10.3 %) , and Brazil (9.9 %).

Asbestos output in 2005

4 - Uses :

4 – 1 - Historical usage :

Asbestos use in human culture dates back at least 4,500 years, when evidence shows that inhabitants of the Lake Juojärvi region in East Finland strengthened earthenware pots and cooking utensils with the asbestos mineral anthophyllite . Asbestos was named by the ancient Greeks. One of the first careful descriptions of the material is attributed to Theophrastus in his text *On Stones*, around 300 BC, although the naming of minerals was not very consistent at that time (the more consistent name of this material in both modern and ancient Greek is *amiantos* (undefiled, pure) whence the names of it in other languages like French *amiante*; the modern Greek word ἀσβεστος or ασβέστης stands consistently and solely for lime, not for the material known as asbestos in English). The term asbestos is traceable to Roman naturalist Pliny the Elder's manuscript *Natural History*, and his use of the term *asbestinon* , meaning "unquenchable". While Pliny is popularly attributed with recognizing the detrimental effects of asbestos on slaves,[12] examination of primary sources shows that this is not so. Charlemagne, the first Holy Roman Emperor (800-814), is said to have had a tablecloth made of asbestos.

According to Tabari, one of the curious items belonging to Khosrow II Parviz, the great Sassanian king (r. 531-579), was a napkin that he cleaned by simply throwing it into fire. This is believed to be made of asbestos. (This is also mentioned in The New Encyclopedia Britannica, vol. 6, 2003, page 843). Wealthy Persians, who bought asbestos imported over the Hindu Kush, amazed guests by cleaning the cloth by simply exposing it to fire. According to Biruni in his book of *Gems*, any cloths made of asbestos (Persian: آذرشست, *āzarshost*) were called (Persian: شستکه) *shostakeh*. Some of the Persians believed the fiber was fur from an animal (named *samandar*, Persian: سمندر) that lived in fire and died when exposed to water, hence the old mistaken myth that the salamander tolerated fire.

While traveling to Siberia, Marco Polo described being offered garments that could not burn. He was told that the wool was from the salamander, but did not accept this explanation. At last he was told that these garments were made from a mineral from the mountains, which contained threads just like wool .

Some archeologists believe that ancients made shrouds of asbestos, wherein they burned the bodies of their kings, in order to preserve only their ashes, and prevent their being mixed with those of wood or other combustible materials commonly used in funeral pyres.[19] Others assert that the ancients used asbestos to make perpetual wicks for sepulchral or other lamps . In more recent centuries, asbestos was indeed used for this purpose. Although asbestos causes skin to itch upon contact, ancient literature indicates that it was prescribed for diseases of the skin, and particularly for the itch. It is possible that they used the term *asbestos* for soap stone, because the two terms have often been confused throughout history.

4 – 2 - Recent usage :

The U.S. asbestos industry began in 1858 when fibrous anthophyllite was mined for use as asbestos insulation by the Johns Company, a predecessor to the current Johns Manville at a quarry at Ward's Hill on Staten Island, New York. Asbestos became more widespread during the industrial revolution; in 1866 it was used as insulation in the U.S. and Canada. Development of the first commercial asbestos mine began in 1874 in the Appalachian foothills of Quebec . By the mid 20th century uses included fire retardant coatings, concrete, bricks, pipes and fireplace cement, heat, fire, and acid resistant gaskets, pipe insulation, ceiling insulation, fireproof drywall, flooring, roofing, lawn furniture, and drywall joint compound.

Approximately 100,000 people in the United States have died, or will die, from asbestos exposure related to ship building. In the Hampton Roads area, a shipbuilding center, mesothelioma occurrence is seven times the national rate . Thousands of tons of asbestos were used in World War II ships to wrap the pipes, line the boilers, and cover engine and turbine parts. There were approximately 4.3 million shipyard workers in the United States during WWII; for every thousand workers about fourteen died of mesothelioma and an unknown number died from asbestosis.

Asbestos fibers were once used in automobile brake pads, shoes, and clutch discs. Since the mid-1990s, a majority of brake pads, new or replacement, have been manufactured instead with linings made of ceramic, carbon, metallic and aramid fiber (Twaron or Kevlar—the same material used in bulletproof vests) .

Kent's filtered cigarette used crocidolite asbestos in its "Micronite" filter from 1952 to 1956 .

The first documented death related to asbestos was in 1906. In the early 1900s researchers began to notice a large number of early deaths and lung problems in asbestos mining towns. The first diagnosis of asbestosis was made in the UK in 1924. By the 1930s, the UK regulated ventilation and made asbestosis an excusable work related disease, about ten years sooner than the U.S . The term mesothelioma was first used in medical literature in 1931; its association with asbestos was first noted sometime in the 1940s.

The United States government and asbestos industry have been criticized for not acting quickly enough to inform the public of dangers, and to reduce public exposure. In the late 1970s court documents proved that asbestos industry officials knew of asbestos dangers since the 1930s and had concealed them from the public. A similar situation had arisen in the 1920s with the careless handling of radium and the ensuing scandal of the Radium Girls.

Artificial Christmas snow, known as flocking, was previously made with asbestos.

In Japan, particularly after World War II, asbestos was used in the manufacture of ammonium sulfate for purposes of rice production, sprayed upon the ceilings, iron skeletons, and walls of railroad cars and buildings (during the 1960s), and used for energy efficiency reasons as well. Production of asbestos in Japan peaked in 1974 and went through ups and downs until about 1990, when production began to drop severely.

In Australia, asbestos was widely used in construction and other industries between 1945 and 1980. From the 1970s there was increasing concern about the dangers of asbestos and its use was phased out. Mining ceased in 1983. The use of asbestos was phased out in 1989 and banned entirely in Dec 2003. The dangers of asbestos are now well known in Australia and there is help and support for sufferers from asbestosis or mesothelioma.

4 – 3 - Specific products :

4 – 3 – 1 - Serpentine group :

Serpentine minerals have a sheet or layered structure. Chrysotile is the only asbestos mineral in the serpentine group. In the United States, chrysotile has been the most commonly used type of asbestos. According to the U.S. EPA Asbestos Building Inspectors Manual, chrysotile accounts for approximately 95% of asbestos found in buildings in the United States. Chrysotile is often present in a wide variety of products and materials, including:

- drywall and joint compound
- plaster
- gas mask filters pre 1960's
- mud and texture coats
- vinyl floor tiles, sheeting, adhesives
- roofing tars, felts, siding, and shingles
- "transite" panels, siding, countertops, and pipes
- popcorn ceilings, also known as acoustic ceilings

- fireproofing
- caulk
- gaskets
- packing, a system for sealing a rotating shaft
- brake pads and shoes
- clutch plates
- stage curtains
- fire blankets
- interior fire doors
- fireproof clothing for firefighters
- thermal pipe insulation
- filters for removing fine particulates from chemicals, liquids, and wine
- dental cast linings
- HVAC flexible duct connectors
- drilling fluid additives

A household heat spreader for cooking on gas stoves, made of asbestos (probably 1950s; "Amiante pur" is French for "Pure Asbestos")

In the European Union and Australia it has recently been banned as a potential health hazard and is not used at all. Japan is moving in the same direction, but more slowly. Revelations that hundreds of workers had died in Japan over the previous few decades from diseases related to asbestos sparked a scandal in mid-2005. Tokyo had, in 1971, ordered companies handling asbestos to install ventilators and check health on a regular basis; however, the Japanese government did not ban crocidolite and amosite until 1995, and a full-fledged ban on asbestos was implemented in October 2004.

4 – 3 – 2 - Amphibole group :

Five types of asbestos are found in the amphibole group: amosite , crocidolite , anthophyllite, tremolite, and actinolite. Amosite, the second most likely type to be found in buildings, according to the U.S. EPA Asbestos Building Inspectors Guide, is the "brown" asbestos.

Amosite and crocidolite were formerly used in many products until the early 1980s. The use of all types of asbestos in the amphibole group was banned in much of the Western world by the mid-1980s, and by Japan in 1995. These products were mainly

- Low density insulation board and ceiling tiles;
- Asbestos-cement sheets and pipes for construction, casing for water and electrical/telecommunication services;
- Thermal and chemical insulation (*e.g., fire rated doors, limpet spray, lagging and gaskets).*

5 - Health problems :

Left-sided mesothelioma: chest CT

Amosite and crocidolite are the most hazardous of the asbestos minerals because of their long persistence in the lungs of exposed people. Tremolite often contaminates chrysotile asbestos, thus creating an additional hazard. Chrysotile asbestos, like all other forms of asbestos, has produced tumors in animals. Mesotheliomas have been observed in people who were occupationally exposed to chrysotile, family members of the occupationally exposed, and residents who lived close to asbestos factories and mines.[31] According to the NCI, "A history of asbestos exposure at work is reported in about 70 percent to 80 percent of all cases. However, mesothelioma has been reported in some individuals without any known exposure to asbestos " . The most common diseases associated with chronic exposure to asbestos include: asbestosis and pleural abnormalities (mesothelioma, lung cancer).

Asbestos exposure becomes a health concern when high concentrations of asbestos fibers are inhaled over a long time period. People who become ill from inhaling asbestos are often those who are exposed on a day - to - day basis in a job where they worked directly with the material. As a person's exposure to fibers increases, because of being exposed to higher concentrations of fibers and/or by being exposed for a longer time, then that person's risk of disease also increases. Disease is very unlikely to result from a single, high-level exposure, or from a short period of exposure to lower levels.

5 – 1 - Mechanisms which might be triggering cancer development :

Stanton and Layard concluded in 1977 –78 that asbestos toxicity is *not* initiated by *chemical* effects , that is any trigger - effects of asbestos must presumably be *phySi Cal*, such as (A) *mechanical* damage or (B) unwanted *signal channels* (a plausible property for slender transparent fibres) which might disrupt normal cell activity— especially mitosis.

(A) Mechanical Damage. There is experimental evidence that very slim fibers (< 60 nm , < 0.06 μm in breadth) do tangle destructively with chromosomes (being of comparable size) . Clearly that is likely to cause the sort of mitosis disruption expected in cancer.

(B) Unwanted Signal channels. This has recently been explored theoretically, but not yet experimentally. The theory argues that this effect would only be feasible for asbestos fibers >120 nm in breadth, which suggests that we should be on the look-out for a possible mixture of different mechanisms for the different fiber-diameter-ranges .

One popular idea of the causal chain is (1) Asbestos fiber → → (3) inflammation → (4) other pathology. While that may be true, it does not explain "**(2)**, the actual trigger":

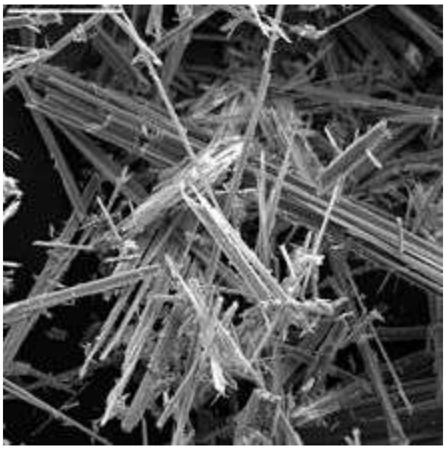
> "What is the *phySi Cal* property of asbestos which *initiates* any such inflammation?" (After all, inflammation is usually seen as caused by *chemical*-based processes: immunological &/or bacterial). So inflammation (&/or oxidation etc.) may well be part of the causal chain, *but not the crucial first step*.

5 – 2 - Other asbestos - related diseases :

- **Asbestosis** : Progressive fibrosis of the lungs of varying severity, progressing to bilateral fibrosis, honeycombing of the lungs on radiological view with symptoms including rales and wheezing.
- **Asbestos warts** : caused when the sharp fibers lodge in the skin and are overgrown causing benign callus-like growths.
- **Pleural plaques**: discrete fibrous or partially calcified thickened area which can be seen on X-rays of individuals exposed to asbestos. Although pleural plaques are themselves asymptomatic, in some patients this develops into pleural thickening.
- **Diffuse pleural thickening**: similar to above and can sometimes be associated with asbestosis. Usually no symptoms shown but if exposure is extensive, it can cause lung impairment.

5 – 3 - Asbestos as a contaminant :

Most respirable asbestos fibers are invisible to the unaided human eye because their size is about 3–20 µm wide and can be as slim as 0.01 µm. Human hair ranges in size from 17 to 181 µm in breadth . Fibers ultimately form because when these minerals originally cooled and crystallized, they formed by the poly meric molecules lining up parallel with each other and forming oriented crystal lattices. These crystals thus have three cleavage planes, and in this case, there are two cleavage planes which are much weaker than the third. When sufficient force is applied, they tend to break along their weakest directions, resulting in a linear fragmentation pattern and hence a fibrous form. This fracture process can keep occurring and one larger asbestos fiber can ultimately become the source of hundreds of much thinner and smaller fibers.



Asbestos fibers (SEM micrograph)

As asbestos fibers get smaller and lighter, they more easily become airborne and human respiratory exposures can result. Fibers will eventually settle but may be re-suspended by air currents or other movement.

Friability of a product containing asbestos means that it is so soft and weak in structure that it can be broken with simple finger crushing pressure. Friable materials are of the most initial concern because of their ease of damage. The forces or conditions of usage that come into intimate contact with most non-friable materials containing asbestos are substantially higher than finger pressure.

5 – 4 - Environmental asbestos :

Asbestos can be found naturally in the air outdoors and in some drinkable water, including water from natural sources. Studies have shown that members of the general (non-occupationally exposed) population have tens of thousands to hundreds of thousands of asbestos fibers in each gram of dry lung tissue, which translates into millions of fibers and tens of thousands of asbestos bodies in every person's lungs.

Asbestos from natural geologic deposits is known as "naturally occurring asbestos" (NOA). Health risks associated with exposure to NOA are not yet fully understood, and current US federal regulations do not address exposure from NOA. Many populated areas are in proximity to shallow, natural deposits which occur in 50 of 58 California counties and in 19 other U.S. states. In one study, data was collected from 3,000 mesothelioma patients in California and 890 men with prostate cancer, a malignancy not known to be related to asbestos. The study found a correlation between the incidence of mesotheliomas and the distance a patient lived from known deposits of rock likely to include asbestos; the correlation was not present when the incidence of prostate cancer was compared with the same distances. According to the study, risk of mesothelioma declined by 6 % for every 10 km that an individual had lived away from a likely asbestos source.

Portions of El Dorado County, California are known to contain natural amphibole asbestos formations at the surface.[42][43] The USGS studied amphiboles in rock and soil in the area in response to an EPA sampling study and subsequent criticism of the EPA study. The EPA study was refuted by its own peer reviewers and never completed or published. The study found that many amphibole particles in the area meet the counting rule criteria used by the EPA for chemical and morphological limits, but do not meet morphological requirements for commercial-grade-asbestos. The executive summary pointed out that even particles that do not meet requirements for commercial-grade-asbestos may be a health threat and suggested a collaborative research effort to assess health risks associated with "Naturally Occurring Asbestos."

However, the main criticism pointed at EPA was that their testing was conducted in small isolated areas of El Dorado where there were no amphibole asbestos deposits, thus the language regarding amphibole, non fibrous "particles". Actual surface amphibole deposits in residential areas were ignored for testing purposes. Thus no final findings were published by ATSDR since the criticism was correct and the effort of combined EPA/ATSDR teams were wasted time and money.

Great deals of Fairfax County, Virginia were also found to be underlain with tremolite. The county monitored air quality at construction sites, controlled soil taken from affected areas, and required freshly developed sites to lay 6 inches (150 mm) of clean, stable material over the ground.

For environmental samples, one must normally resort to electron microscopy for positive identification . Today, gravimetric and PCM / PLM techniques are employed. However, the latter techniques cannot readily identify the smallest, most hazardous, fibers, because they are limited to PM10 particulate size evaluation, which completely ignores ultrafine particles (UFPs).

6 - History of health concerns and regulation :

By the first century AD, Greeks and Romans are claimed to have observed that slaves involved in the weaving of asbestos cloth were afflicted with a Si Ckness of the lungs , although this is not confirmed by examination of primary sources .

Early concern in the modern era on the health effects of asbestos exposure can be found in several sources. Among the earliest were reports in Britain. The annual reports of the Chief Inspector of Factories reported as early as 1898 that asbestos had "easily demonstrated" health risks.

At about the same time, what was probably the first study of mortality among asbestos workers was reported in France. While the study describes the cause of death as chalicosis, a generalized pneumoconiosis , the circumstances of the employment of the fifty workers whose death prompted the study suggest that the root cause was asbestos or mixed asbestos-cotton dust exposure.

7 - Contamination of other products :

7 – 1 - Asbestos and vermiculite :

Vermiculite is a hydrated laminar magnesium-aluminum-iron silicate which resembles mica. It can be used for many industrial applications and has been used as a replacement for asbestos. Some ore bodies of vermiculite have been found to contain small amounts of asbestos . One vermiculite mine operated by W. R. Grace and Company in Libby, Montana exposed workers and community residents to danger by mining contaminated vermiculite. In 1999 the EPA began cleanup efforts and now the area is a Superfund cleanup area. The EPA has determined that harmful asbestos is released from the mine as well as through other activities that disturb soil in the area.

7 – 2 - Asbestos and Talc :

Talc is sometimes contaminated with asbestos . In 2000, tests in a certified asbestos - testing laboratory found the tremolite form of amphibole asbestos in three out of eight bigger brands of children's crayons (oil pastels) that are made partly from talc: Crayola, Prang, and RoseArt . In Crayola crayons, the tests found asbestos levels from 0.05 % in *Carnation Pink* to 2.86 % in *Orchid*; in Prang crayons, the range was from 0.3% in *Periwinkle* to 0.54 % in *Yellow*; in Rose Art crayons, it was from 0.03% in *Brown* to 1.20% in *Orange*. Overall, 32 different types of crayons from these brands contained more than trace amounts of asbestos, and eight others contained trace amounts. The Art and Creative Materials Institute, a trade association which tests the safety of crayons on behalf of the makers, initially insisted the test results must be incorrect, although they later said they do not test for asbestos. In May 2000 , Crayola said tests by a materials analyst, Richard Lee, whose testimony has been accepted in lawsuits over 250 times on behalf of the asbestos industry, showed two of its crayons were negative for asbestos . In June 2000, Binney & Smith, the maker of Crayola , and the other makers agreed to stop using talc in their products, and changed their product formulations in the United States . The mining company, R T Vanderbilt Co of Gouverneur, New York, which supplied the talc to the crayon makers, insists there is no asbestos in its talc "to the best of our knowledge and belief", but a news article claimed that the United States Mine Safety and Health Administration (MSHA) did find asbestos in four talc samples that it tested in 2000 . At the time, however, the Assistant Secretary for Mine Safety and Health informed the news reporter that his article was in error and that the reporter had misquoted him stating that “In fact, the abbreviation ND (non detect) in the laboratory report – indicates no asbestos fibers actually were found in the samples ”. Further supporting the claim of Vanderbilt that asbestos is not found in this industrial grade talc (composed of a very complex mineral mixture) is a decades old record of analytical work that does not find asbestos in this talc by mineral scientists in academia, government and contract laboratories. Human, animal and cell health studies conducted on Vanderbilt’s controversial talc also lend no support for the presence of asbestos in this talc. Several non fully peer-reviewed health reports concerning Vanderbilt talc do exist and suggest a "same as" asbestos risk, some of which were referenced in the previously cited news articles.

8 - Asbestos in construction :

8 – 1 - Asbestos construction in developed countries :

1929 newspaper advertisement from Perth, Western Australia, for asbestos sheeting for residential building construction.

The use of asbestos in new construction projects has been banned for health and safety reasons in many developed countries or regions, including the European Union, Australia, Hong Kong, Japan, and New Zealand. A notable exception is the United States, where asbestos continues to be used in construction such as cement asbestos pipes. The 5th Circuit

Court prevented the EPA from banning asbestos in 1991 because although EPA research showed it would cost between $450 and 800 million and save around 200 lives in a 13-year length, the EPA did not provide adequate evidence for the safety of alternative products. Until the mid-1980s, small amounts of white asbestos were used in the manufacture of Artex , a decorative stipple finish , how ever, some of the lesser-known suppliers of Artex were still adding white asbestos until 1999. Removing or disturbing Artex is not recommended, as it may contain white asbestos.

Prior to the ban, asbestos was widely used in the construction industry. Many older buildings built before the late 1990s contain asbestos. In the United States, there is a minimum standard for asbestos surveys as described by ASTM Standard E 2356-04. The U.S. Environmental Protection Agency includes some but not all asbestos-contaminated facilities on the Superfund National Priorities list (NPL). Renovation and demolition of asbestos contaminated buildings is subject to EPA NESHAP and OSHA Regulations. Asbestos is not a material covered under CERCLA's innocent purchaser defense. In the UK, the removal and disposal of asbestos and of substances containing it are covered by the Control of Asbestos Regulations 2006 .

In older buildings (e.g. those built prior to 1999 in the UK, before white asbestos was finally banned), asbestos may still be present in some areas e.g. old bath panels, concrete water tanks and many other places. Being aware of asbestos locations reduces the risk of disturbing asbestos.

Removal of asbestos building components can also remove the fire protection they provide, therefore fire protection substitutes are required for proper fire protection that the asbestos originally provided.

8 – 2 - Asbestos construction in developing countries :

Some developing countries, such as India and China, and also Russia, have continued widespread use of asbestos. The most common is corrugated asbestos-cement sheets or "A/C Sheets" for roofing and for side walls. Millions of homes, factories, schools or sheds and shelters continue to use asbestos. Cutting these sheets to size and drilling holes to receive 'J' bolts to help secure the sheets to roof framing is done on-site. There has been no significant change in production and use of A/C Sheets in developing countries following the widespread restrictions in developed nations.

8 – 3 - Asbestos and 9 / 11 :

More than 1,000 tons of asbestos are thought to have been released into the air during the destruction of the Twin Towers in New York on 9 / 11. Inhalation of a mixture of asbestos and other toxicants is thought to be linked to the unusually high death rate of emergency service workers from cancer since the disaster.[94] Many thousands more are now thought to be at risk of developing cancer due to this exposure with those who have died so far being only the 'tip of the iceberg'. Some commentators have criticised authorities for using asbestos in the Towers' construction (see 'Other criticism' below).

9 - Litigation :

Asbestos litigation is the longest, most expensive mass tort in U.S. history, involving more than 8,400 defendants and 730,000 claimants as of 2002 according to the RAND Corporation, and at least one defendant reported claim counts in excess of 800,000 in 2006.

Current trends indicate that the worldwide rate at which people are diagnosed with asbestos-related diseases will likely increase through the next decade. Analysts have estimated that the total costs of asbestos litigation in the USA alone is over $250 billion.

The federal legal system in the United States has dealt with numerous counts of asbestos related suits, which often included multiple plaintiffs with similar symptoms. In 1999 there were 200,000 related cases pending in the federal court system of the United States. Further, it is estimated that within the next 40 years, the number of cases may increase to 700,000. These numbers help explain how there are thousands of current pending cases.

Litigation of asbestos materials has been slow. Companies sometimes counter saying that health issues do not currently appear in their worker or workers, or sometimes are settled out of court. The Research and Development (RAND) think tank has appropriated certain legal information which is readily available for proclaimed victims of natural resource accidents. This information has helped many workers, regardless of health condition, earn compensation through companies. RAND, along with the Institute for Civil Justice (ICJ) have been proponents of the organization of past cases in order to determine one aspect of fair compensation for workers.

1999 saw the introduction of the Fairness in Asbestos Compensation Act. Ultimately many asbestos companies were forced to file for bankruptcy. While companies filed for bankruptcy, this limited payouts to those who were actually affected by the material. Christopher Edley said what the 1999 Act ultimately did was "limit punitive damages that seek retribution for the decisions of long-dead executives for conduct that took place decades ago (Professor Christopher Edley, Jr.)."

Litigation exists outside the United States in England, Scotland, Ireland, the Netherlands, France, Australia, and Japan among other nations. See the companion article for further information.

The volume of the asbestos liability has concerned manufacturers and insurers and reinsurers . The amounts and method of allocating compensation have been the source of many court cases, and government attempts at resolution of existing and future cases.

10 - Critics of safety regulations :

10 – 1 – Canada - EU dispute :

Natural Resources Canada states chrysotile, one of the fibres that make up asbestos, is not as dangerous as once thought. According to their fact sheet, "current knowledge and modern technology can successfully control the potential for health and environmental harm posed by chrysotile".

In May 1998, Canada requested consultations before the WTO and the European Commission concerning France's 1996 prohibition of the importation and sale of asbestos. Canada said that the French measures contravened provisions of the Agreements on Sanitary and Phytosanitary Measures and on Technical Barriers to Trade, and the GATT 1994. The EC claims that substitute materials have been developed in place of asbestos, which are safer to human health. It stressed that the French measures were not discriminatory, and were fully justified for public health reasons. The EC claimed that in the July consultations, it had tried to convince Canada that the measures were justified, and that just as Canada broke off consultations, it was in the process of submitting substantial scientific data in favour of the asbestos ban. The Canadian federal government has in response claimed that chrysotile is much less dangerous than other types of asbestos, and Canada does not export the other asbestos fiber . Chrysotile continues to be used in new construction across Canada, in ways that are very similar to those for which chrysotile is exported.[107] The Chrysotile Institute, an asbestos industry funded organization, said that the use of chrysotile does not pose an environmental problem and the inherent risks in its use are limited to the workplace. The Canadian government continues to draw both domestic and international criticism for its stance on chrysotile, most recently in international meetings on the Rotterdam Convention hearings regarding chrysotile.

The CFMEU pointed out that most exports go to developing countries. Canada has pressured countries, including Chile, and other UN member states to avoid chrysotile bans.

10 – 2 – Other criticism :

Asbestos regulation critics include the asbestos industry and Fox News "junk science" columnist Steven Milloy. Critics sometimes argue that increased government regulation does more harm than good and that replacements to asbestos are inferior. An example is the suggestion by Dixy Lee Ray and others that the shuttle Challenger disintegrated because the maker of O-ring putty was pressured by the EPA into ceasing production of asbestos-laden putty. However, the putty used in *Challenger*'s final flight *did* contain asbestos, and failures in the putty were not responsible for the failure of the O-ring that led to loss of the shuttle.

Asbestos was used in the first forty floors of the World Trade Center north tower causing an airborne contamination among lower Manhattan after the towers collapsed in the attacks on September 11th, 2001. Steven Milloy suggests that the World Trade Center towers could still be standing or at least would have stood longer had a 1971 ban not stopped the completion of the asbestos coating above the 64th floor.[115] This was not considered in the National Institute of Standards and Technology's report on the towers' collapse. All fireproofing materials, regardless of what they are made of, are required to obtain a fire-resistance rating prior to installation. All fiber-based lightweight commercial spray fireproofing materials are vulnerable to kinetic energy impacts that are outside of the fire testing upon which their ratings are based, including asbestos-based materials, and may have been removed in large areas by the impact of the planes .

11 - Substitutes for asbestos in construction :

Fiber glass insulation was invented in 1938 and is now the most commonly used type of insulation material. The safety of this material is also being called into question, as research shows that the composition of this material (asbestos and fiberglass are both silicate fibers) causes similar toxicity as asbestos.

In 1978, a highly texturized fiber glass fabric was invented by Bal Dixit, called Zetex. This fabric is lighter than asbestos, but offers the same bulk, thickness, hand, feel, and abrasion resistance as asbestos. The fiberglass was texturized to eliminate some of the problems that arise with fiberglass, such as poor abrasion resistance and poor seam strength .

In Europe stone- and glass wool are the main insulators in houses.

Many companies that produced asbestos-cement products that were reinforced with asbestos fibers have developed products incorporating organic fibers. One such product was known as Eternit and another "Everite" now use "Nutec" fibers which consist of organic fibers, Portland cement and silica. Cement-bonded wood fiber is another substitute. Stone fibers are used in gaskets and friction materials.

Another potential fiber is poly benzimidazole or PBI fiber. Poly benzimidazole fiber is a synthetic fiber with high melting point of 760 °C that also does not ignite. Because of its exceptional thermal and chemical stability, it is often used by fire departments and space agencies.

Asbestos alternatives for industrial use include sleeves, rope, tape, fabric, textiles and insulation batt materials made from fiberglass and silica.

12 - Recycling and disposal :

In most developed countries, asbestos is typically disposed of as hazardous waste in landfill sites.

Asbestos can also be recycled by transforming it into harmless silicate glass. A process of thermal decomposition at 1000–1250 °C produces a mixture of non-hazardous silicate phases, and at temperatures above 1250 °C it produces silicate glass. Microwave thermal treatment can be used in an industrial manufacturing process to transform asbestos and asbestos-containing waste into porcelain stoneware tiles, porous single-fired wall tiles, and ceramic bricks.

Silica gel

Contents :

1 – Introduction :

Silica gel is a granular, vitreous, highly porous form of silica made synthetically from sodium silicate . Despite its name, silica gel is a solid. It is a naturally occurring mineral that is purified and processed into either granular or beaded form. As a deSi Ccant, it has an average pore size of 24 angstroms and has a strong affinity for water molecules.

Silica gel is most commonly encountered in every day life as beads packed in a vapor - permeable plastic. In this form, it is used as a deSi Ccant to control local humidity in order to avoid spoilage or degradation of some goods. Because of poisonous do pants and their very high absorption of moisture, silica gel packets usually bear warnings for the user not to eat the contents. If consumed, the pure silica gel is unlikely to cause acute or chronic illness . Food - grade deSi Ccant should not include any poisons which would cause long-term harm to humans if consumed in the quantities normally included with the items of food.

2 - History :

The synthetic route for producing silica gel was patented by chemistry professor Walter A. Patrick at Johns Hopkins University, Baltimore, Maryland, USA in 1919. It was used in World War I for the absorption of vapors and gases in gas mask canisters, as part of his patent. The substance was in existence as early as the 1640s as a scientific curiosity.

In World War II, silica gel was indispensable in the war effort for keeping penicillin dry , protecting military equipment from moisture damage, as a fluid cracking catalyst for the production of high octane gasoline, and as a catalyst support for the manufacture of butadiene from ethanol, feed stock for the synthetic rubber program.

3 - Properties :

Silica gel's high surface area (around 800 m^2 / g) allows it to absorb water readily, making it useful as a deSi Ccant (drying agent) . Once saturated with water, the gel can be regenerated by heating it to 120 °C for two hours. Some types of silica gel will " pop " when exposed to enough water.

4 – Preparation :

A solution of sodium silicate is acidified to produce a gelatinous precipitate that is washed, then dehydrated to produce colorless silica gel , When a visible indication of the moisture content of the silica gel is required , ammonium tetra chloro cobalt (II) $(NH_4)_2 Co Cl_4$ or cobalt chloride $Co Cl_2$ is added . This will cause the gel to be blue when dry and pink when hydrated .

5 - Applications :

5 – 1 – Desiccant :

In many items, moisture encourages the growth of mold and spoilage. Condensation may also damage other items like electronics and may speed the decomposition of chemicals, such as those in vitamin pills. By adding packets of silica gel, these items can be preserved longer.

Silica gel may also be used to keep the relative humidity (RH) inside a high frequency radio or satellite transmission system waveguide as low as possible. Excessive moisture buildup within a wave guide can cause arcing inside the wave guide itself , damaging the power amplifier feeding it. Also, the beads of water that form and condense inside the waveguide change the characteristic impedance and frequency, degrading the signal. It is common for a small compressed air system (similar to a small home aquarium pump) to be employed to circulate the air inside the wave guide over a jar of silica gel.

Silica gel is also used to dry the air in industrial compressed air systems. Air from the compressor discharge flows through a bed of silica gel beads. The silica gel absorbs moisture from the air, preventing damage at the point of use of the compressed air due to condensation or moisture. The same system is used to dry the compressed air on railway locomotives, where condensation and ice in the brake air pipes can lead to brake failure.

Silica gel is some times used as a preservation tool to control relative humidity in museum and library exhibitions and storage.

Other applications include diagnostic test strips, inhalation devices, syringes, drug test kits, bacteria and hospital sanitation kits.

5 – 2 – Chemistry :

In chemistry, silica gel is used in chromatography as a stationary phase. In column chromatography the stationary phase is most often composed of silica gel particles of 40 - 63 µm . Different particle sizes are used for achieving a desired separation of certain molecular sizes. In this application, due to silica gel's polarity, non - polar components tend to elute before more polar ones, hence the name normal phase chromatography. How ever, when hydrophobic groups (such as C_{18} groups) are attached to the silica gel then polar components elute first and the method is referred to as reverse phase chromatography. Silica gel is also applied to aluminium, glass, or plastic sheets for thin layer chromatography.

The hydroxy (OH) groups on the surface of silica can be functionalized to afford specialty silica gels that exhibit unique stationary phase parameters. These so - called functionalized silica gels are also used in organic synthesis and purification as insoluble reagents and scavengers.

Chelating groups have also been covalently bound to silica gel. These materials have the ability to remove metal ions selectively from aqueous media. Chelating groups can be covalently bound to poly amines that have been grafted onto a silica gel surface producing a material of greater mechanical integrity. Silica gel is also combined with alkali metals to form a M - SG reducing agent.

Silica gel is not expected to biodegrade in either water or soil .

5 – 3 – Cat litter :

Silica gel is also used as cat litter , by itself or in combination with more traditional materials, such as clays including bentonite. It is trackless and virtually odorless. Silica in this form can be a cost effective way for retail consumers to easily purchase silica gel for application in such things as keeping tools rust free in damp environments, long term storage, and preservation of dried food for long term storage.

6 – Hazards :

Silica gel is non - toxic, non - flammable, and non - reactive and stable with ordinary usage. It will react with hydrogen fluoride, fluorine , oxygen di fluoride , chlorine tri fluoride , strong acids, strong bases, and oxidizers . Silica gel is irritating to the respiratory tract, may cause irritation of the digestive tract, and dust from the beads may cause irritation to the skin and eyes, so precautions should be taken . Some of the beads may be doped with a moisture indicator, such as cobalt (II) chloride , which is toxic and may be carcinogenic. Cobalt (II) chloride is deep blue when dry (anhydrous) and pink when moist (hydrated) .

Crystalline silica dust can cause silicosis but synthetic amorphous silica gel is non - friable, and so does not cause silicosis.

Silicone rubber

Contents

1 . Introduction :

Silicone rubber is a polymer that has a " back bone " of silicon - oxygen linkages, the same bond that is found in quartz, glass and sand. Normally, heat is required to vulcanize (set) the silicone rubber; this is normally carried out in a two stage process at the point of manufacture into the desired shape, and then in a prolonged post - cure process. It can also be injection molded.

2 . History

The first silicone elastomers were developed in the search for better insulating materials for electric motors and generators. Resin-impregnated glass fibers were the state - of – the - art materials at the time. The glass was very heat resistant, but the phenolic resins would not withstand the higher temperatures that were being encountered in new smaller electric motors. Chemists at Corning Glass and General Electric were investigating heat - resistant materials for use as resinous binders when they synthesized the first silicone polymers, demonstrated that they worked well and found a route to produce poly di methyl siloxane commercially.

Corning Glass formed a joint venture with Dow Chemical in 1943 to produce this new class of materials. As the unique properties of the new silicone products were studied in more detail, their potential for broader usage was envisioned, and GE opened its own plant to produce silicones in 1947. Wacker Chemie also started production of silicones in Europe in 1947.

3 . Properties

Silicone rubber offers good resistance to extreme temperatures, being able to operate normally from - 55° C to + 300° C. At the extreme temperatures, the tensile strength, elongation, tear strength and compression set can be far superior to conventional rubbers although still low relative to other materials. Organic rubber has a carbon to carbon backbone which can leave them susceptible to ozone, UV, heat and other ageing factors that silicone rubber can withstand well. This makes it one of the elastomers of choice in many extreme environments.

Compared to other organic rubbers, how ever, silicone rubber has a very low tensile strength. For this reason, care is needed in designing products to withstand even low imposed loads. Silicone rubber is a highly inert material and does not react with most chemicals. Due to its inertness, it is used in many medical applications and in medical implants. However, typical medical products like breast implants and catheters have failed because of poor design.

3 . 1 . Structure

Poly siloxanes differ from other polymers in that their backbones consist of Si-O-Si units unlike many other polymers that contain carbon backbones. One interesting characteristic is an extremely low glass transition temperature of about -127 ˚C . Poly siloxane is very flexible due to large bond angles and bond lengths when compared to those found in more baSi C polymers such as polyethylene. For example, a C - C back bone unit has a bond length of 1.54 Å and a bond angle of 112 ˚ , whereas the siloxane backbone unit Si-O has a bond length of 1.63 Å and a bond angle of 130 ˚ .

The siloxane back bone differs greatly from the baSi C poly ethylene back bone, yielding a much more flexible polymer . Because the bond lengths are longer, they can move further and change conformation easily, making for a flexible material. Another advantage of poly siloxanes is in their stability. Silicon is in the same group (IV) on the periodic table as carbon, but the properties of these elements are quite different. Silicon has the same oxidation state as carbon, but has the ability to use 3d orbitals for bonding by expanding its valence shell. Si-Si bonds have far less energy than C - C bonds and so are more stable, though in practice Si - Si - bonds are very hard to create.

4 . Special grades

There are also many special grades and forms of silicone rubber, including : Steam resistant, metal detectable, electrically conductive, chemical / oil /acid / gas resistant, low smoke emitting, and flame - retardant. A variety of fillers can be used in silicone rubber , although most are non-reinforcing and lower the tensile strength .

5 . Liquid Silicone

Liquid silicone rubber is a high purity platinum - cure silicone .

Medical device manufacturers favour liquid silicone because of its bio compatibility and excellent part quality. Moreover, the lack of human contact reduces risk of contamination, especially when manufactured in a clean room environment. However, failures of medical implants have occurred due to poor manufacture or poor design.

It is typically supplied in two parts with one of the parts containing the platinum catalyst. These are then automatically mixed with any colours and ingredients which may be required. The mixing produces a very homogeneous material that leads to products that are not only very consistent throughout the part, but also from part to part.

6 . Applications

Once milled and coloured , silicone rubber can be extruded into tubes, strips, solid cord or custom profiles according the size restrictions of the manufacturer. Cord can be joined to make "O" Rings and extruded profiles can be joined to make seals. Silicone rubber can be moulded into custom shapes and designs.

Becoming more and more common at the consumer level, silicone rubber products can be found in every room of a typical home. From automotive applications; to a large variety of cooking, baking, and food storage products; to apparel , undergarments, sportswear, and foot wear ; to electronics ; to home repair and hardware, and a host of unseen applications .

Non - dyed silicone rubber tape with an iron-oxide additive (making the tape a red - orange colour) is used extensively in aviation and aerospace wiring applications as a splice or wrapping tape due to its non - flammable nature. The iron-oxide additive adds high thermal conductivity but does not change the high electrical insulation property of the silicone rubber. This type of tape self - fuses or amalgamates without any added adhesive.

7 . Self - Healing

Recently, silicone rubber formed the matrix of the first autonomic self-healing elastomer . The micro capsule - based material was capable of recovering almost all of the original tear strength. Additionally, this material had improved fatigue properties as evaluated using a torsion-fatigue test .

Glass

	
Roman Cage Cup from the 4th century A.D.	*Moldavite, a natural glass formed by meteorite impact, from Besednice , Bohemia*

Contents

1 – Introduction :

Glass is an amorphous (non - crystalline) solid material. Glasses are typically brittle and optically transparent.

The most familiar type of glass, used for centuries in windows and drinking vessels, is soda-lime glass, made of about 75 % silica (SiO_2) plus Na_2O, Ca O , and several minor additives. Often, the term *glass* is used in a restricted sense to refer to this specific use.

In science, however, the term *glass* is usually defined in a much wider sense, including every solid that possesses a non-crystalline (i.e., amorphous) structure and that exhibits a glass transition when heated towards the liquid state. In this wider sense, glasses can be made of quite different classes of materials: metallic alloys, ionic melts, aqueous solutions, molecular liquids, and polymers. For many applications (bottles , eye wear) polymer glasses (acrylic glass, poly carbonate, poly ethylene tere phthalate) are a lighter alternative to traditional silica glasses.

Glass, as a substance, plays an essential role in science and industry. Its chemical, phySi Cal, and in particular optical properties make it suitable for applications such as flat glass, container glass, optics and opto electronics material, laboratory equipment, thermal insulator (glass wool), reinforcement materials (glass - reinforced plastic, glass fiber reinforced concrete), and glass art (art glass, studio glass) .

2 - Silicate glass :

Silica (the chemical compound SiO_2) is a common fundamental constituent of glass. In nature , verification of quartz occurs when lightning strikes sand, forming hollow, branching rootlike structures called fulgurite .

2 – 1 - History :

The history of creating glass can be traced back to 3500 BCE in Mesopotamia.[1] The term *glass* developed in the late Roman Empire. It was in the Roman glassmaking center at Trier, now in modern Germany, that the late - Latin term *glesum* originated, probably from a Germanic word for a transparent, lustrous substance .

2 – 2 - Glass ingredients :

Quartz sand (silica) is the main raw material
in commercial glass production

While fused quartz (primarily composed of SiO_2) is used for some special applications, it is not very common due to its high glass transition temperature of over 1200 °C . Normally, other substances are added to simplify processing. One is sodium carbonate (Na_2CO_3), which lowers the glass transition temperature. However, the soda makes the glass water soluble, which is usually undesirable, so lime (calcium oxide (Ca O), generally obtained from limestone), some magnesium oxide (Mg O) and aluminium oxide (Al_2O_3) are added to provide for a better chemical durability. The resulting glass contains about 70 to 74 % silica by weight and is called a soda - lime glass. Soda - lime glasses account for about 90% of manufactured glass.

Most common glass has other ingredients added to change its properties. Lead glass or flint glass is more 'brilliant' because the increased refractive index causes noticeably more specular reflection and increased optical dispersion. Adding barium also increases the refractive index. Thorium oxide gives glass a high refractive index and low dispersion and was formerly used in producing high-quality lenses, but due to its radioactivity has been replaced by lanthanum oxide in modern eye glasses . Iron can be incorporated into glass to absorb infrared energy, for example in heat absorbing filters for movie projectors, while cerium (IV) oxide can be used for glass that absorbs UV wavelengths.

Borosilicate glasses (e.g. Pyrex) have as main constituents silica and boron oxide. They have very low coefficients of thermal expansion (7740 Pyrex COE is 32.5×10^{-7}/°C as compared to 8.36×10^{-5}/°C for one type of soda-lime glass),[6] making them more dimensionally stable. The lower COE also makes them less subject to stress caused by thermal expansion, thus less vulnerable to cracking from thermal shock. They are commonly used for reagent bottles, optical components and household cookware.

Another common glass ingredient is "cullet" (recycled glass). The recycled glass saves on raw materials and energy; however, impurities in the cullet can lead to product and equipment failure.

Fining agents such as sodium sulfate, sodium chloride, or antimony oxide may be added to reduce the number of air bubbles in the glass mixture . Glass batch calculation is the method by which the correct raw material mixture is determined to achieve the desired glass composition.

2 – 3 - Contemporary glass production :

A modern green house in Wisley Garden, England ,
made from float glass

Following the glass batch preparation and mixing, the raw materials are transported to the furnace. Soda-lime glass for mass production is melted in gas fired units. Smaller scale furnaces for specialty glasses include electric meters , pot furnaces, and day tanks.

After melting, homogenization and refining (removal of bubbles), the glass is formed. Flat glass for windows and similar applications is formed by the float glass process, developed between 1953 and 1957 by Sir Alastair Pilkington and Kenneth Bickerstaff of the UK's Pilkington Brothers, who created a continuous ribbon of glass using a molten tin bath on which the molten glass flows unhindered under the influence of gravity. The top surface of the glass is subjected to nitrogen under pressure to obtain a polished finish.[7] Container glass for common bottles and jars is formed by blowing and pressing methods. Further glass forming techniques are summarized in the table Glass forming techniques.

Once the desired form is obtained, glass is usually annealed for the removal of stresses. Surface treatments, coatings or lamination may follow to improve the chemical durability (glass container coatings, glass container internal treatment), strength (toughened glass, bulletproof glass, windshields), or optical properties (insulated glazing, anti-reflective coating).

2 – 3 - 1 - Architecture

The use of glass in buildings is a transparent feature to allow light to enter into rooms and floors, illuminating enclosed spaces and framing an exterior view through a window. It is also a material for internal partitions and external cladding.

2 – 4 - Glass making in the laboratory :

New chemical glass compositions or new treatment techniques can be initially investigated in small - scale laboratory experiments. The raw materials for laboratory - scale glass melts are often different from those used in mass production because the cost factor has a low priority . In the laboratory mostly pure chemicals are used . Care must be taken that the raw materials have not reacted with moisture or other chemicals in the environment (such as alkali oxides and hydroxides, alkaline earth oxides and hydroxides, or boron oxide), or that the impurities are quantified (loss on ignition) . Evaporation losses during glass melting should be considered during the selection of the raw materials, e.g., sodium selenite may be preferred over easily evaporating SeO_2. Also, more readily reacting raw materials may be preferred over relatively inert ones, such as $Al(OH)_3$ over Al_2O_3. Usually, the melts are carried out in platinum crucibles to reduce contamination from the crucible material. Glass homogeneity is achieved by homogenizing the raw materials mixture (glass batch), by stirring the melt, and by crushing and re-melting the first melt. The obtained glass is usually annealed to prevent breakage during processing .

In order to make glass from materials with poor glass forming tendencies, novel techniques are used to increase cooling rate, or reduce crystal nucleation triggers. Examples of these techniques include aerodynamic levitation (cooling the melt whilst it floats on a gas stream), splat quenching (pressing the melt between two metal anvils) and roller quenching (pouring the melt through rollers).

See also: Optical lens design, Fabrication and testing of optical components

3 - Other glasses :

3 – 1 - Net work glasses :

A CD-RW (CD). Chalcogenide glasses form the basis of re -writable CD and DVD solid-state memory technology.

Some glasses that do not include silica as a major constituent may have phySi Co - chemical properties useful for their application in fiber optics and other specialized technical applications. These include fluoride glasses, alumino silicates , phosphate glasses, borate glasses, and chalcogenide glasses.

There are three classes of components for oxide glasses: network formers, intermediates, and modifiers. The network formers (silicon, boron, germanium) form a highly cross - linked network of chemical bonds. The intermediates (titanium, aluminium, zirconium, beryllium, magnesium, zinc) can act as both network formers and modifiers, according to the glass composition. The modifiers (calcium, lead, lithium, sodium, potassium) alter the network structure; they are usually present as ions, compensated by nearby non-bridging oxygen atoms, bound by one covalent bond to the glass network and holding one negative charge to compensate for the positive ion nearby. Some elements can play multiple roles; e.g. lead can act both as a network former (Pb^{4+} replacing Si^{4+}), or as a modifier.

The presence of non-bridging oxygens lowers the relative number of strong bonds in the material and disrupts the network, decreasing the viscosity of the melt and lowering the melting temperature.

The alkaline metal ions are small and mobile; their presence in glass allows a degree of electrical conductivity, especially in molten state or at high temperature. Their mobility however decreases the chemical resistance of the glass, allowing leaching by water and facilitating corrosion. Alkaline earth ions, with their two positive charges and requirement for two non-bridging oxygen ions to compensate for their charge, are much less mobile themselves and also hinder diffusion of other ions, especially the alkalis. The most common commercial glasses contain both alkali and alkaline earth ions (usually sodium and calcium), for easier processing and satisfying corrosion resistance . Corrosion resistance of glass can be achieved by de alkalization, removal of the alkali ions from the glass surface by reaction with e.g. sulfur or fluorine compounds. Presence of alkaline metal ions has also detrimental effect to the loss tangent of the glass, and to its electrical resistance; glasses for electronics (sealing, vacuum tubes, lamps...) have to take this in account.

Addition of lead (II) oxide lowers melting point, lowers viscosity of the melt, and increases refractive index. Lead oxide also facilitates solubility of other metal oxides and therefore is used in colored glasses. The viscosity decrease of lead glass melt is very significant (roughly 100 times in comparison with soda glasses); this allows easier removal of bubbles and working at lower temperatures, hence its frequent use as an additive in vitreous enamels and glass solders. The high ionic radius of the Pb^{2+} ion renders it highly immobile in the matrix and hinders the movement of other ions; lead glasses therefore have high electrical resistance, about two orders of magnitude higher than soda-lime glass ($10^{8.5}$ vs $10^{6.5}$ Ohm·cm, DC at 250 °C). For more details, see lead glass .

Addition of fluorine lowers the dielectric constant of glass. Fluorine is highly electro negative and attracts the electrons in the lattice, lowering the polarize ability of the material. Such silicon dioxide - fluoride is used in manufacture of integrated circuits as an insulator. High levels of fluorine doping lead to formation of volatile SiF_2O and such glass is then thermally unstable. Stable layers were achieved with dielectric constant down to about 3.5–3.7.[13]

3 – 2 - Amorphous metals :

In the past, small batches of amorphous metals with high surface area configurations (ribbons, wires, films, etc.) have been produced through the implementation of extremely rapid rates of cooling. This was initially termed "splat cooling" by doctoral student W. Klement at Caltech, who showed that cooling rates on the order of millions of degrees per second is sufficient to impede the formation of crystals, and the metallic atoms become "locked into" a glassy state. Amorphous metal wires have been produced by sputtering molten metal onto a spinning metal disk. More recently a number of alloys have been produced in layers with thickness exceeding 1 millimeter. These are known as bulk metallic glasses (BMG). Liquid metal

Technologies sell a number of zirconium-based BMGs. Batches of amorphous steel have also been produced that demonstrate mechanical properties far exceeding those found in conventional steel alloys.

In 2004, NIST researchers presented evidence that an iso tropic non-crystalline metallic phase (dubbed "q-glass") could be grown from the melt. This phase is the first phase, or "primary phase," to form in the Al-Fe-Si system during rapid cooling. Interestingly, experimental evidence indicates that this phase forms by a *first-order transition*. Transmission electron microscopy (TEM) images show that the q-glass nucleates from the melt as discrete particles, which grow spherically with a uniform growth rate in all directions. The diffraction pattern shows it to be an isotropic glassy phase. Yet there is a nucleation barrier, which implies an interfacial discontinuity (or internal surface) between the glass and the melt.[17]

3 – 3 - Electrolytes :

Electrolytes or molten salts are mixtures of different ions. In a mixture of three or more ionic species of dissimilar size and shape, crystallization can be so difficult that the liquid can easily be super cooled into a glass. The best studied example is $Ca_{0.4} K_{0.6} (NO_3)_{1.4}$.

3 – 4 - Aqueous solutions :

Some aqueous solutions can be super cooled into a glassy state, for instance Li Cl : R H_2O in the composition range $4 < R < 8$.

3 – 5 - Molecular liquids :

A *molecular liquid* is composed of molecules that do not form a covalent net work but interact only through weak van der Waals forces or through transient hydrogen bonds. Many molecular liquids can be super cooled into a glass; some are excellent glass formers that normally do not crystallize.

Under extremes of pressure and temperature solids may exhibit large structural and phySi Cal changes which can lead to poly amorphic phase transitions . In 2006 Italian scientists created an amorphous phase of carbon dioxide using extreme pressure. The substance was named amorphous carbonia (a n - n CO_2) and exhibits an atomic structure resembling that of silica n.

3 – 6 - Colloidal glasses :

Concentrated colloidal suspensions may exhibit a distinct glass transition as function of particle concentration or density.[20]

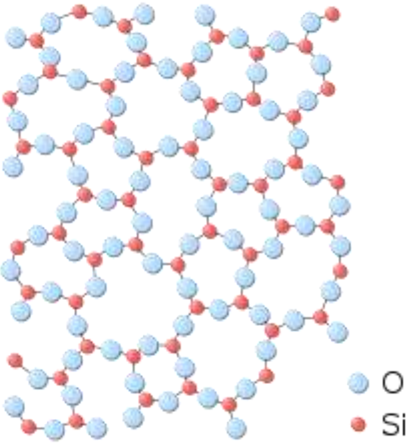
3 – 7 - Glass – ceramics :

A high strength glass - ceramic cook top
with negligible thermal expansion.

Glass-ceramic materials share many properties with both non-crystalline glass and crystalline ceramics. They are formed as a glass, and then partially crystallized by heat treatment. For example, the micro structure of white ware ceramics frequently contains both amorphous and crystalline phases. Crystalline grains are often embedded within a non-crystalline inter granular phase of grain boundaries. When applied to white ware ceramics, vitreous means the material has an extremely low permeability to liquids, often but not always water, when determined by a specified test regime.[21][22]

The term mainly refers to a mix of lithium and alumino silicates which yields an array of materials with interesting thermo mechanical properties. The most commercially important of these have the distinction of being impervious to thermal shock. Thus, glass-ceramics have become extremely useful for countertop cooking. The negative thermal expansion coefficient (TEC) of the crystalline ceramic phase can be balanced with the positive TEC of the glassy phase. At a certain point (~70 % crystalline) the glass-ceramic has a net TEC near zero. This type of glass-ceramic exhibits excellent mechanical properties and can sustain repeated and quick temperature changes up to 1000 °C .

4 – Structure :



The amorphous structure of glassy Silica (SiO_2) in two dimensions. No long range order is present, however there is local ordering with respect to the tetrahedral arrangement of Oxygen (O) atoms around the Silicon (Si) atoms.

As in other amorphous solids, the atomic structure of a glass lacks any long range translational periodicity. However, due to chemical bonding characteristics glasses do possess a high degree of short-range order with respect to local atomic poly hedra .

5 - Glass versus super cooled liquid :

In physics , the standard definition of a glass (or vitreous solid) is a solid formed by rapid melt quenching . How ever, the term glass is often used to describe any amorphous solid that exhibits a glass transition temperature T_g. If the cooling is sufficiently rapid (relative to the characteristic crystallization time) then crystallization is prevented and instead the disordered atomic configuration of the super cooled liquid is frozen into the solid state at T_g. Generally, the structure of a glass exists in a meta stable state with respect to its crystalline form, although in certain circumstances, for example in atactic polymers, there is no crystalline analogue of the amorphous phase.

Glass is an amorphous solid. It exhibits an atomic structure close to that observed in the super cooled liquid phase but displays all the mechanical properties of a solid . The notion that glass flows to an appreciable extent over extended periods of time is not supported by empirical research or theoretical analysis .

Some people consider glass to be a liquid due to its lack of a first-order phase transition where certain thermo dynamic variables such as volume, entropy and enthalpy are discontinuous through the glass transition range. How ever, the glass transition may be described as analogous to a second-order phase transition where the intensive thermodynamic variables such as the thermal expansivity and heat capacity are discontinuous . Despite this, the equilibrium theory of phase transformations does not entirely hold for glass, and hence the glass transition cannot be classed as one of the classical equilibrium phase transformations in solids .

Although the atomic structure of glass shares characteristics of the structure in a super cooled liquid , glass tends to behave as a solid below its glass transition temperature . A super cooled liquid behaves as a liquid, but it is below the freezing point of the material, and in some cases will crystallize almost instantly if a crystal is added as a core. The change in heat capacity at a glass transition and a melting transition of comparable materials are typically of the same order of magnitude, indicating that the change in active degrees of freedom is comparable as well. Both in a glass and in a crystal it is mostly only the vibrational degrees of freedom that remain active, whereas rotational and translational motion is arrested. This helps to explain why both crystalline and non - crystalline solids exhibit rigidity on most experimental time scales.

5 – 1 - Behavior of antique glass :

The observation that old windows are sometimes found to be thicker at the bottom than at the top is often offered as supporting evidence for the view that glass flows over a timescale of centuries. The assumption being that the glass was once uniform, but has flowed to its new shape, which is a property of liquid . However, this assumption is incorrect; once solidified, glass does not flow anymore. The reason for the observation is that in the past, when panes of glass were commonly made by glass blowers , the technique used was to spin molten glass so as to create a round, mostly flat and even plate (the crown glass process, described above). This plate was then cut to fit a window. The pieces were not, however, absolutely flat; the edges of the disk became thicker as the glass spun. When installed in a window frame, the glass would be placed thicker side down both for the sake of stability and to prevent water accumulating in the lead cames at the bottom of the window. Occasionally such glass has been found thinner side down or thicker on either side of the window's edge, the result of carelessness during installation .

Mass production of glass window panes in the early twentieth century caused a similar effect. In glass factories, molten glass was poured onto a large cooling table and allowed to spread. The resulting glass is thicker at the location of the pour, located at the center of the large sheet. These sheets were cut into smaller window panes with nonuniform thickness, typically with the location of the pour centred in one of the panes (known as "bull's-eyes") for decorative effect. Modern glass intended for windows is produced as float glass and is very uniform in thickness.

Several other points can be considered which contradict the "cathedral glass flow" theory:

- Writing in the American Journal of PhySi Cs, phySi Cist Edgar D. Zanotto states "...the predicted relaxation time for GeO_2 at room temperature is 10^{32} years. Hence, the relaxation period (characteristic flow time) of cathedral glasses would be even longer." (10^{32} years is many times longer than the estimated age of the Universe.)
- If medieval glass has flowed perceptibly, then ancient Roman and Egyptian objects should have flowed proportionately more — but this is not observed. Similarly, prehistoric obsidian blades should have lost their edge; this is not observed either (although obsidian may have a different viscosity from window glass) .

- If glass flows at a rate that allows changes to be seen with the naked eye after centuries, then the effect should be noticeable in antique telescopes. Any slight deformation in the antique telescopic lenses would lead to a dramatic decrease in optical performance, a phenomenon that is not observed .
- There are many examples of centuries-old glass shelving which has not bent, even though it is under much higher stress from gravitational loads than vertical window glass.

The above does not apply to materials that have a glass transition temperature close to room temperature, such as certain plastics used in daily life like poly styrene and poly propylene. Over time, they may well show visco elastic behavior , and this is a serious concern when applying these materials in construction.

6 - Physical properties :

6 – 1 - Optical properties :

Glass is in widespread use largely due to the production of glass compositions that are transparent to visible wavelengths of light. In contrast, poly crystalline materials do not in general transmit visible light . The individual crystallites may be transparent, but their facets (grain boundaries) reflect or scatter light resulting in diffuse reflection. Glass does not contain the internal subdivisions associated with grain boundaries in poly crystals and hence does not scatter light in the same manner as a polycrystalline material. The surface of a glass is often smooth since during glass formation the molecules of the supercooled liquid are not forced to dispose in rigid crystal geometries and can follow surface tension, which imposes a microscopically smooth surface. These properties, which give glass its clearness, can be retained even if glass is partially light-absorbing i.e. colored .

Glass has the ability to refract, reflect and transmit light following geometrical optics, without scattering it, and it is used in the manufacture of lenses and windows. Common glass has a refraction index around 1.5. According to Fresnel equations, the reflectivity of a sheet of glass is about 4 % per surface (at normal incidence), and its trans emissivity about 92 %. Glass also finds application in optoelectronics e.g. for light transmitting optical fibers .

6 – 2 - Color :

Common soda-lime float glass appears green in thick sections because of Fe^{2+} *impurities.*

Color in glass may be obtained by addition of electrically charged ions (or color centers) that are homogeneously distributed, and by precipitation of finely dispersed particles (such as in photo chromic glasses) . Ordinary soda - lime glass appears colorless to the naked eye when it is thin, although iron (II) oxide (Fe O) impurities of up to 0.1 wt % produce a green tint which can be viewed in thick pieces or with the aid of scientific instruments. Further Fe O and Cr_2O_3 additions may be used for the production of green bottles. Sulfur, together with carbon and iron salts, is used to form iron poly sulfides and produce amber glass ranging from yellowish to almost black . A glass melt can also acquire an amber color from a reducing combustion atmosphere. Manganese dioxide can be added in small amounts to remove the green tint given by iron (II) oxide.

7 - Glass art :

A vase being created at the Reijmyre glass works , Sweden

Paperweight with items inside the glass, Corning Museum of Glass

A glass sculpture by Dale Chihuly, "The Sun" at the "Gardens of Glass" exhibition in Kew Gardens, London. The piece is 13 feet (4 metres) high and made from 1000 separate glass objects.

Glass tiles mosaic (detail).

A display at Canberra Glassworks, Australia

From the 19th century, various types of fancy glass started to become significant branches of the decorative arts. Cameo glass was revived for the first time since the Romans, initially mostly used for pieces in a neo - clasSi Cal style. The Art Nouveau movement in particular made great use of glass, with René Lalique, Émile Gallé, and Daum of Nancy important names in the first French wave of the movement, producing colored vases and similar pieces, often in cameo glass, and also using lustre techniques. Louis Comfort Tiffany in America specialized in secular stained glass, mostly of plant subjects, both in panels and his famous lamps. From the 20th century, some glass artists began to class themselves as in effect sculptors working in glass, and as part of the fine arts.

Several of the most common techniques for producing glass art include: blowing, kiln – casting , fusing , slumping , pate – de – verre flame - working, hot-sculpting and cold-working. Cold work includes traditional stained glass work as well as other methods of shaping glass at room temperature. Glass can also be cut with a diamond saw, or copper wheels embedded with abrasives, and polished to give gleaming facets; the technique used in creating Water ford crystal. Art is sometimes etched into glass via the use of acid, caustic, or abrasive substances. Traditionally this was done after the glass was blown or cast. In the 1920s a new mould-etch process was invented, in which art was etched directly into the mould, so that each cast piece emerged from the mould with the image already on the surface of the glass. This reduced manufacturing costs and, combined with a wider use of colored glass, led to cheap glassware in the 1930s, which later became known as Depression glass . As the types of acids used in this process are extremely hazardous, abrasive methods have gained popularity.

Another technique is devitrification .

Objects made out of glass include not only traditional objects such as vessels (bowls, vases, bottles, and other containers), paper weights , marbles , beads, but an endless range of sculpture and installation art as well. Colored glass is often used, though sometimes the glass is painted, innumerable examples exist of the use of stained glass.

7 – 1 – Museums :

Apart from historical collections in general museums, modern works of art in glass can be seen in a variety of museums, including the Chrysler Museum, the Museum of Glass in Tacoma, the Metropolitan Museum of Art, the Toledo Museum of Art, and Corning Museum of Glass, in Corning, NY, which houses the world's largest collection of glass art and history, with more than 45,000 objects in its collection .

The Harvard Museum of Natural History has a collection of extremely detailed models of flowers made of painted glass. These were lamp worked by Leopold Blaschka and his son Rudolph, who never revealed the method he used to make them. The Blaschka Glass Flowers are still an inspiration to glassblowers today.

Glass recycling

Public glass waste collection point in a neighborhood area for separating colorless, green and amber glass

Contents

1 - Introduction :

Glass recycling is the process of turning waste glass into usable products. Glass waste should be separated by chemical composition, and then, depending on the end use and local processing capabilities, might also have to be separated into different colors. Many recyclers collect different colors of glass separately since glass retains its color after recycling. The most common types used for consumer containers are colorless glass, green glass, and brown/amber glass.

Glass makes up a large component of household and industrial waste due to its weight and density. The glass component in municipal waste is usually made up of bottles, broken glass ware, light bulbs and other items. Adding to this waste is the fact that many manual methods of creating glass objects have a defect rate of around forty percent. Glass recycling uses less energy than manufacturing glass from sand, lime and soda.

Every metric ton (1,000 kg) of waste glass recycled into new items saves 315 kilograms of carbon dioxide from being released into the atmosphere during the creation of new glass . Glass that is crushed and ready to be re melted is called **cullet.**

2 - Glass reuse :

Reuse of glass containers is prefer able to recycling according to the waste hierarchy. Refillable bottles are used extensively in many European countries, Canada and until relatively recently, in the United States. In Denmark 98 % of bottles are refillable and 98% of those are returned by consumers . A similarly high number is reported for beer bottles in Canada . These systems are typically supported by container deposit laws and other regulations. In some developing nations like India and Brazil, the cost of new bottles often forces manufacturers to collect and refill old glass bottles for selling carbonated and other drinks.

3 - Glass collection :

Vehicle emptying a glass bank in Europe

Glass collection points, known as **Bottle Banks** are very common near shopping centers , at civic amenity sites and in local neighborhoods in the United Kingdom. The first Bottle Bank was introduced by Stanley Race CBE, then president of the Glass Manufacturers’ Federation and Ron England in Barnsley on 6 June 1977 n;

Bottle Banks commonly stand beside collection points for other recyclable waste like paper, metals and plastics. Local, municipal waste collectors usually have one central point for all types of waste in which large glass containers are located. There are now over 50,000 bottle banks in the United Kingdom .

Most collection points have separate bins for clear, green and amber / brown glass. Glass re processors require separation by colour as the different colours of glass are usually chemically incompatible. Heat-resistant glass like Pyrex or borosilicate glass should **not** be disposed of in the glass container as even a single piece of such material will alter the viscosity of the fluid in the furnace at remelt.

3 – 1 - Secondary uses for recycled glass :

In the United Kingdom, the waste recycling industry cannot consume all of the recycled container glass that will become available over the coming years, mainly due to the colour imbalance between that which is manufactured and that which is consumed. The UK imports much more green glass in the form of wine bottles than it uses, leading to a surplus amount for recycling.

The resulting surplus of green glass from imported bottles may be exported to producing countries, or used locally in the growing diversity of secondary end uses for recycled glass.[7] Cory Environmental are presently shipping glass cullet from the UK to Portugal.

The use of the recycled glass as aggregate in concrete has become popular in modern times, with large scale research being carried out at Columbia University in New York. This greatly enhances the aesthetic appeal of the concrete. Recent research findings have shown that concrete made with recycled glass aggregates have shown better long term strength and better thermal insulation due to its better thermal properties of the glass aggregates.[9] Secondary markets for glass recycling may include:

- Glass in ceramic sanitary ware production
- Glass as a flux agent in brick manufacture

- Glass in Astroturf and related applications (e.g. top dressing, root zone) material or golf bunker sand
- Glass in recycled glass countertops
- Glass as water filtration media
- Glass as an abrasive
- Glass as an aggregate

Glass aggregate, a mix of colors crushed to a small size, is substituted for many construction and utility projects in place of pea gravel or crushed rock, often times saving municipalities like the City of Tumwater, Washington Public Works, thousands of dollars (depending on the size of the project). Glass aggregate is not sharp to handle. In many cases, the state Department of Transportation has specifications for use, size and percentage of quantity for use. Common applications are as pipe bedding--placed around sewer, storm water or drinking water pipes to transfer weight from the surface and protect the pipe. Another common use would be as fill to bring the level of a concrete floor even with a foundation.

Mixed waste streams may be collected from materials recovery facilities or mechanical biological treatment systems. Some facilities can sort out mixed waste streams into different colours using electro-optical sorting units.