

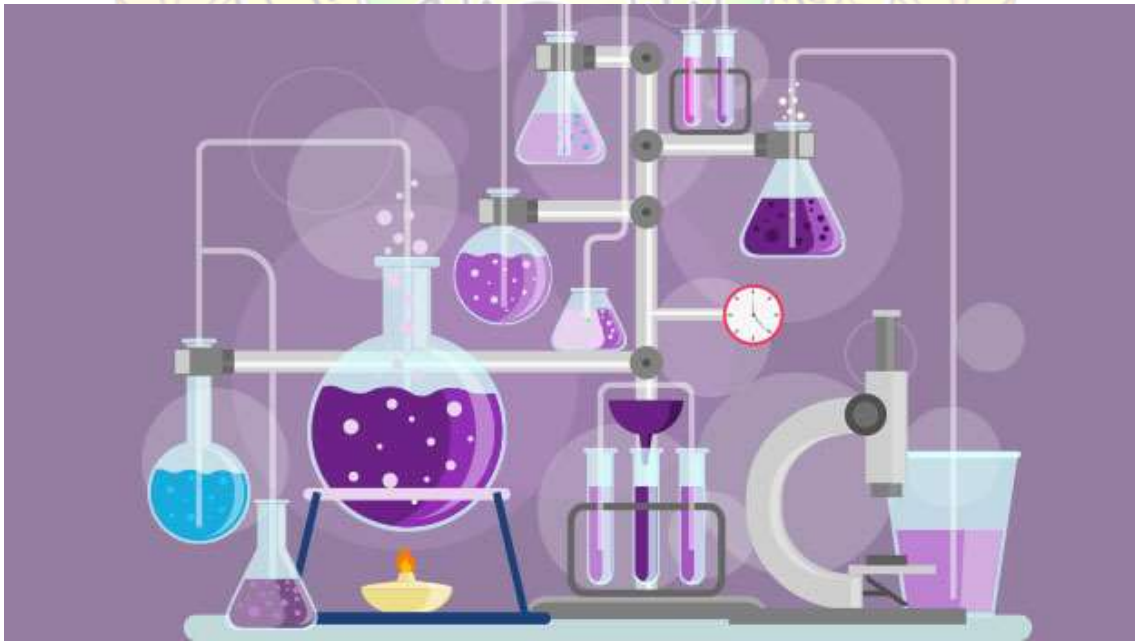
Mustansiriyah University  
College of Engineering  
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الجامعة المستنصرية  
كلية الهندسة  
قسم الهندسة المدنية

# CHEMISTRY

المرحلة الاولى – Freshman Level



2022 – 2023

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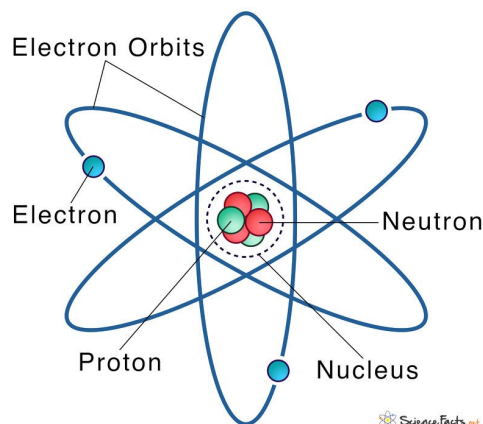
## ***Introduction and Basic Concepts Concerning the Elementary Principles of General Chemistry***

**Chemistry** is the scientific discipline involved with elements and compounds composed of atoms, molecules and ions: their composition, structure, properties, behavior and the changes they undergo during a reaction with other substances.

The word chemistry comes from alchemy, which referred to an earlier set of practices that encompassed elements of chemistry, metallurgy, philosophy, astrology, astronomy, mysticism and medicine. An alchemist was called a 'chemist' in popular speech, and later the suffix "-ry" was added to this to describe the art of the chemist as "chemistry".

The modern word *alchemy* in turn is derived from the Arabic word *al-kīmīā* (الكيمياء). In origin, the term is borrowed from the Greek *χημία* or *χημεία*. This may have Egyptian origins since *al-kīmīā* is derived from the Greek *χημία*, which is in turn derived from the word Kemet, which is the ancient name of Egypt in the Egyptian language. Alternately, *al-kīmīā* may derive from *χημεία*, meaning "cast together".

The atom is the basic unit of chemistry. It consists of a dense core called the atomic nucleus surrounded by a space occupied by an electron cloud. The nucleus is made up of positively charged protons and uncharged neutrons (together called nucleons), while the electron cloud consists of negatively charged electrons which orbit the nucleus. In a neutral atom, the negatively charged electrons balance out the positive charge of the protons. The nucleus is dense; the mass of a nucleon is approximately 1,836 times that of an electron, yet the radius of an atom is about 10,000 times that of its nucleus.



A chemical reaction is a transformation of some substances into one or more different substances. The basis of such a chemical transformation is the rearrangement of electrons in the chemical bonds between atoms. It can be symbolically depicted through a chemical equation, which usually involves atoms as subjects. The number of atoms on the left and the right in the equation for a chemical transformation is equal. (When the number of atoms on either side is unequal, the transformation is referred to as a nuclear reaction or

radioactive decay.) The type of chemical reactions a substance may undergo and the energy changes that may accompany it are constrained by certain basic rules, known as chemical laws.

In chemistry, matter is defined as anything that has rest mass and volume (it takes up space) and is made up of particles. The particles that make up matter have rest mass as well – not all particles have rest mass, such as the photon. Matter can be a pure chemical substance or a mixture of substances.

A chemical element is a pure substance which is composed of a single type of atom, characterized by its particular number of protons in the nuclei of its atoms, known as the atomic number and represented by the symbol  $Z$ . The mass number is the sum of the number of protons and neutrons in a nucleus. The standard presentation of the chemical elements is in the periodic table, which orders elements by atomic number. The periodic table is arranged in groups, or columns, and periods, or rows. The periodic table is useful in identifying periodic trends.

1																	18
1	2											13	14	15	16	17	2
H Hydrogen 1.008	He Helium 4.003											B Boron 10.81	C Carbon 12.011	N Nitrogen 14.007	O Oxygen 15.999	F Fluorine 18.998	Ne Neon 20.180
3	4											5	6	7	8	9	10
Li Lithium 6.941	Be Beryllium 9.012											Al Aluminum 26.982	Si Silicon 28.086	P Phosphorus 30.974	S Sulfur 32.06	Cl Chlorine 35.453	Ar Argon 39.948
11	12	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Na Sodium 22.990	Mg Magnesium 24.305											Al Aluminum 26.982	Si Silicon 28.086	P Phosphorus 30.974	S Sulfur 32.06	Cl Chlorine 35.453	Ar Argon 39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K Potassium 39.098	Ca Calcium 40.078	Sc Scandium 44.956	Ti Titanium 47.88	V Vanadium 50.942	Cr Chromium 51.996	Mn Manganese 54.938	Fe Iron 55.845	Co Cobalt 58.933	Ni Nickel 58.693	Cu Copper 63.546	Zn Zinc 65.38	Ga Gallium 69.723	Ge Germanium 72.63	As Arsenic 74.922	Se Selenium 78.96	Br Bromine 79.904	Kr Krypton 83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb Rubidium 85.468	Sr Strontium 87.62	Y Yttrium 88.906	Zr Zirconium 91.224	Nb Niobium 92.906	Mo Molybdenum 95.94	Tc Technetium 98.906	Ru Ruthenium 101.07	Rh Rhodium 102.905	Pd Palladium 106.42	Ag Silver 107.868	Cd Cadmium 112.411	In Indium 114.818	Sn Tin 118.710	Sb Antimony 121.757	Te Tellurium 127.6	I Iodine 126.905	Xe Xenon 131.29
55	56	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs Cesium 132.905	Ba Barium 137.327	Lu Lutetium 174.967	Hf Hafnium 178.49	Ta Tantalum 180.948	W Tungsten 183.84	Re Rhenium 186.207	Os Osmium 190.23	Ir Iridium 192.222	Pt Platinum 195.084	Au Gold 196.967	Hg Mercury 200.59	Tl Thallium 204.384	Pb Lead 207.2	Bi Bismuth 208.980	Po Polonium 209	At Astatine 210	Rn Radon 222
87	88	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr Francium 223	Ra Radium 226	Lr Lawrencium 262	Rf Rutherfordium 261	Db Dubnium 262	Sg Seaborgium 263	Bh Bohrium 264	Hs Hassium 265	Mt Meitnerium 266	Ds Darmstadtium 267	Rg Roentgenium 268	Cn Copernicium 269	Uut Ununtrium 270	Fl Flerovium 271	Uup Ununpentium 272	Lv Livermorium 273	Uus Ununseptium 274	Uuo Ununoctium 276
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106
La Lanthanum 138.905	Ce Cerium 140.12	Pr Praseodymium 140.908	Nd Neodymium 144.24	Pm Promethium 144.913	Sm Samarium 150.36	Eu Europium 151.964	Gd Gadolinium 157.25	Tb Terbium 158.925	Dy Dysprosium 162.50	Ho Holmium 164.930	Er Erbium 167.259	Tm Thulium 168.934	Yb Ytterbium 173.054	Lu Lutetium 174.967			
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106
Ac Actinium 227	Th Thorium 232.038	Pa Protactinium 231.036	U Uranium 238.029	Np Neptunium 237.048	Pu Plutonium 244.064	Am Americium 243.061	Cm Curium 247.070	Bk Berkelium 247.070	Cf Californium 251.080	Es Einsteinium 252	Fm Fermium 257.105	Md Mendelevium 258.10	No Nobelium 259				

Salts are a reaction between Cations and Anions to produce a crystalline lattice such as NaCl.

A *phase* is a set of states of a chemical system that have similar bulk structural properties, over a range of conditions, such as pressure or temperature.

## Acidity and basicity

Q: What are the differences between acids and base?

- 1- An acid is a substance that produces hydronium ions when it is dissolved in water, and a base is one that produces hydroxide ions when dissolved in water.
- 2- Acids are substances that donate a positive hydrogen ion to another substance in a chemical reaction; by extension, a base is the substance which receives that hydrogen ion.
- 3- An acid is a substance which is capable of accepting a pair of electrons from another substance during the process of bond formation, while a base is a substance which can provide a pair of electrons to form a new bond.

## Why Civil Engineers Study Chemistry?

Engineering requires applied science, and chemistry is the center of all science. The more chemistry an engineer understands, the more beneficial it is. In the future, global problems and issues will require an in-depth understanding of chemistry to have a global solution.

Chemistry is an important fundamental topic for civil engineers, for several reasons:-

- 1- In understanding the properties of building materials.
- 2- The natural environment (atmosphere and solutions) and the reaction of building materials with the environment (corrosion of metals, durability).
- 3- The field of civil engineering is ever expanding where technology grows and advances at a very fast pace. Newer constructional materials are introduced every year to cater to these needs.

### **Q: Does civil engineering involve chemistry? If so, how?**

Civil engineering involves chemistry in the following manner:

- 1- Chemistry is involved in water treatment, removal all pollutants to make it potable.
- 2- Chemistry is involved in sewage treatment, and rendering the solids harmless and the effluent suitable for agriculture or horticulture or simply car washing.
- 3- Chemistry is involved in the construction of marine structures and consider the salt content to prevent the steel from getting rusted, and corroded.
- 4- Chemistry is involved in the selection of suitable sources of water for human consumption and for livestock.

Cement is all chemistry, its manufacture, reaction with water and setting to form a solid used in almost all structures.

Most building materials that are used for erecting a new building are man-made or artificial:

- To produce cement limestone and clay are made to react at high temperatures. The individual elements Ca, Si, O, Al, Fe rearrange themselves to form reactive cement. When mixed with water this cement will harden to become hydrated or hardened cement.
- In the production of concrete grit or stone particles as well as water are added to cement. In order to make the properties of concrete, e.g. its flowability or hardening speed, meet the special requirements of a building project, concrete additives are used. These additives also use chemical processes to change first the fresh concrete and later on the solid concrete.
- Lime mortar or cement mortar - often used as tile adhesives, floor fillers or plaster in the construction of interiors and the making of facades - are also the result of chemical reactions.

- The most different types of engineering Plastics are used in the construction industry as well. Concrete components, floors, roofs and facades are sealed or soundproofed to protect them from damages.
- Wood cannot become a long-lasting building material unless wood preservatives are used to protect the building components against pest infestation. And also flame inhibitors that make wood and woodworking materials flame resistant cannot dispense with chemical substances.

The life cycles of all buildings are limited irrespective of the diligence and precautions that were applied during their erection. Manifold environmental influences act upon buildings and are likely to damage their structure. Hereby not only mechanical stress (e.g. a high traffic volume) plays an important role but also chemical deterioration mechanisms. Due to the chemical reaction of alkaline concrete and carbon dioxide from the air, for example, the building material carbonates, its ph-value decreases and steel that is embedded in the concrete may corrode. Penetrating moisture and salts can trigger various deterioration mechanisms such as the efflorescence of salts which has a considerable blast effect, the conversion of beta phases into weaker substances or the corrosion of structural steel. In addition to this, component damages often result from chemical reactions that modify the original material and thereby strongly affect the strength of a structure or its aesthetic value.

To enable useful counteracting the damaging mechanisms have to be recognized first. After this identification process, effective countermeasures can be developed. Corrosion prevention not only has to consider the mechanical stress buildings are exposed to but also the chemical impact on buildings and structures.

Damaged structures can often be rescued by restoration and renovation. For these purposes the building industry knows a range of products that is equally large as that available for the construction of new buildings.

An important aspect that goes beyond the purely functional aspect of construction chemistry is the interaction of construction chemical products with people, their health and the environment. A responsible use of the applied materials and additives means that the effects of these substances after the initial construction period are taken into consideration.

Building without chemistry is not feasible. The better we understand the chemical processes involved, the clearer we can target at influencing them and the better and the more durable the results will be. This is the reason why it makes sense for all architects and civil engineers to concern themselves with the chemistry of building materials.

*Chemistry of Gypsum & Lime***Gypsum****a) Natural plasters**

Gypsum is a soft sulfate mineral composed of calcium sulfate dihydrate, with the chemical formula  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Gypsum is used in a wide variety of applications such as:

- Gypsum board is primarily used as a finish for walls and ceilings, and is known in construction as dry wall, wall board, sheet rock or plaster board.
- Gypsum blocks are used like concrete blocks in building construction.
- Gypsum mortar is a mortar used in building construction.
- Plaster ingredients are used in surgical splints, casting moulds and modeling.

**PRODUCTION STEPS**

Excavating  $\Rightarrow$  Crushing (~25mmdiameter)  $\Rightarrow$  Grinding  $\Rightarrow$   
 Heating (calcining)  $\Rightarrow$  Cooling  $\Rightarrow$  Pulverizing  $\Rightarrow$  Marketing in  
 Bags.

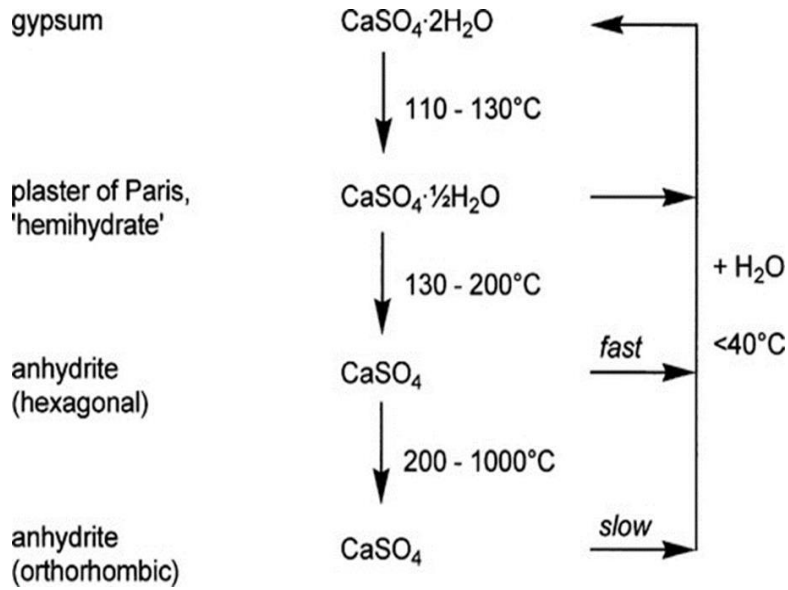
**CALCINATION**

Gypsum rock when heated to  $100-130^\circ\text{C}$  loses  $\frac{3}{4}$  of its water.  
 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2\text{O}$

So we get Plaster of Paris. This is low burning process named as INCOMPLETE CALCINATION.

When calcination is carried out at temperatures above  $130^\circ\text{C}$  all water is removed.  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$

So we get gypsum anhydrite. This is high-burning process named as COMPLETE CALCINATION.



### The life cycle of gypsum

Typically begins with the extraction and processing of raw materials, continues with the manufacture and use of the plaster board, and then reaches end-of-life (EoL) that involves either land filling, recycling or other forms of recovery.





**The setting process (40-60 minutes)**

When Calcium Sulphate hemihydrate is mixed with water, a chemical reaction takes place, and the hemihydrate is converted back to Calcium Sulphate dihydrate. This chemical reaction, which is exothermic, is written as follows:

**Initial Set:**

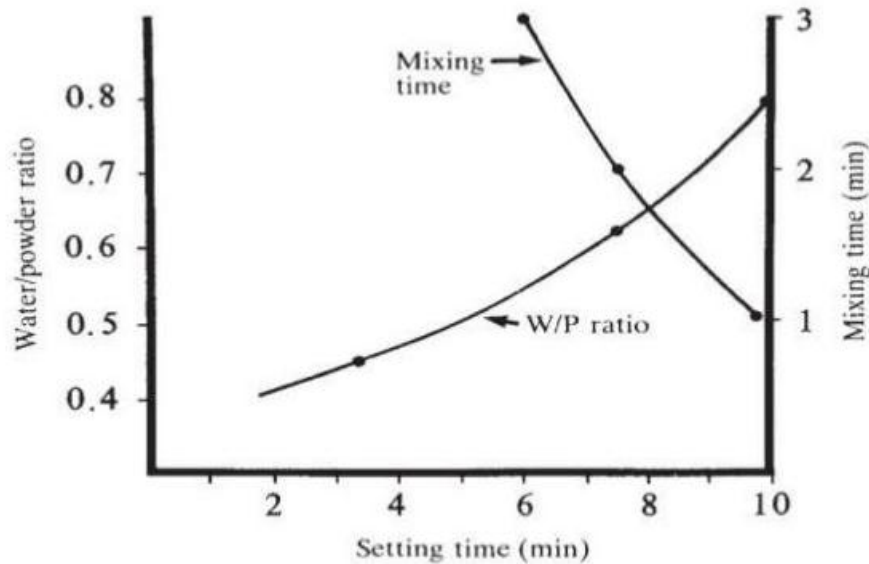
- 1-Time between start of mixing until material loses gloss
- 2-Solid enough to handle
- 3-Still moist and pliable

**Final Set:**

- 1-After all heat is driven away.
- 2- Cool, hard and dry.

**Relationship between Water & Powder Ratio**

- 1-Less water produce: Shortens setting time; dry and crumbly.
- 2-More water produce: Thin mixture; weaker product with air bubbles.
- 3-After mix starts: adding water to thin or powder to thicken lead to weakens final product.
- 4-Increasing water temperature: cause faster set with no affect on quality of final product.



The effect of water/powder ratio and mixing time on setting time for a typical dental plaster.

### b) Synthetic gypsums

Gypsum is also generated as a by-product of various industrial processes. For instance, at desulphurisation of flue gases with limestone, REA gypsum is formed (fine texture, Calcium-sulphate-dehydrate).

*REA gypsum: It is a method of producing gypsum industrially through industrial products of other products. It was invented in Germany in 1983 and spread to Europe.*

*The only difference between natural & REA gypsum being that this process takes place in fast motion within a few hours, whereas nature needed millions of years to form the layers of gypsum.*

## Lime

Lime is an important building material used in building construction from ancient time.

Lime is a calcium-containing inorganic mineral composed primarily of oxides, and hydroxide (usually calcium oxide CaO and/or calcium hydroxide Ca(OH)<sub>2</sub>).

The rocks and minerals from which these materials are derived, typically lime stone or chalk, are composed primarily of calcium carbonate CaCO<sub>3</sub>. They may be cut, crushed, or pulverized and chemically altered.

Pure limestone → CaCO<sub>3</sub>

Impurities → MgCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>

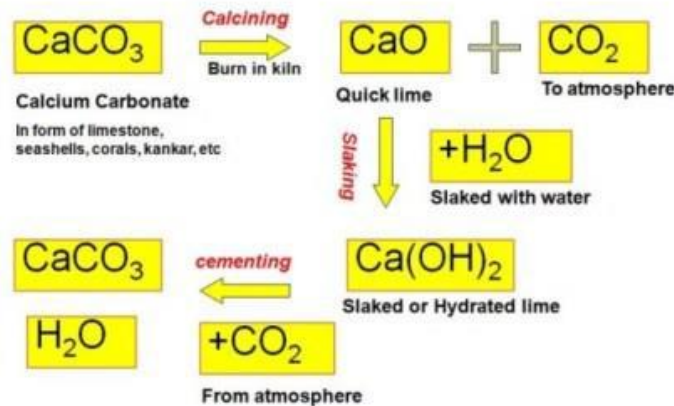


### PRODUCTION STEPS

1-Excavation of limestone → Crushing → Grinding.

2-Calcination → Quicklime

The process by which limestone (calcium carbonate) is converted to quick lime by heating, then to slaked lime by hydration, and naturally reverts to calcium carbonate by carbonation is called the lime cycle (as seen in the figure). The conditions and compounds present during each step of the lime cycle have a strong influence of the end product, thus the complex and varied physical nature of lime products.



3-Pulverize Quicklime

4-Mixed with water under pressure → Slaked Lime

5-Drying of Slaked Lime

6-Pulverizing

7-Marketing in bags.

## CLASSIFICATION OF QUICKLIME

### A-According to Particle Size

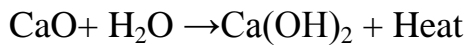
- 1- Lump Lime (10-30 cm lumps)
- 2- Pebble Lime (2-5 cm)
- 3- Granular Lime (1-2 cm)
- 4- Crushed Lime (~5-8 mm)
- 5- Ground Lime (passes #10 sieve, by grinding crushed lime)
- 6- Pulverized Lime (passes #100 sieve)

### B-According to Chemical Composition

- 1- High-Calcium Quicklimes (~90% of  $\text{CaO}$ )
- 2- Calcium Quicklime (75% of  $\text{CaO}$ )
- 3- Magnesian Quicklime (at least 20% of  $\text{MgO}$ )
- 4- Dolomitic Quicklime (at least 25% of  $\text{MgO}$ )

**C-According to Intended Use**

- 1- Mortar Lime
- 2- Plaster Lime

**SLAKING (HYDRATION) OF LIME**

CaO is mixed with water in a slaking box until a “putty” has been formed.

The putty is then covered with sand to protect it from the action of the air and left for seasoning.

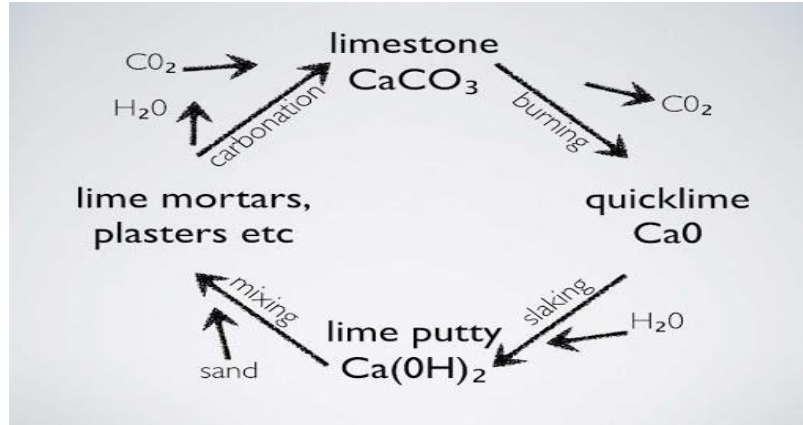
Time of seasoning → 1 week for mortar use

→ 6 weeks for plaster use

**PROPERTIES OF LIME MORTARS**

By adding sand to lime, lime mortar is obtained.

- 1-Adjusting plasticity
- 2-Gaining economy
- 3-Decreasing shrinkage effects.



## STRENGTH OF LIME MORTARS

Depends on:

- 1-Chemical composition of lime
- 2-Magnesian Limes versus Calcium Limes
- 3-Sand amount and properties
- 4-Adding sand decreases strength
- 5-Amount of water
- 6-Voids are formed after evaporation
- 7-Setting conditions
- 8-Lower humidity and higher  $\text{CO}_2$  higher strength.

## *Chemistry of Major Compounds of Cement*

Cements, in a general sense, are adhesive materials which are capable of bonding together fragments or particles of solid matter into a compact whole.

The term hydraulic cements referred to cements that harden by reaction with water and form a water-resistant product. Thus, Portland cement is a hydraulic cement capable of setting, hardening and remains stable under water.



### *Raw material for Portland Cement (P.C)*

(60%) Calcareous material such as Limestone, chalk, etc.  $\longrightarrow$  Calcium ( $\text{CaO} + \text{CO}_2$ )

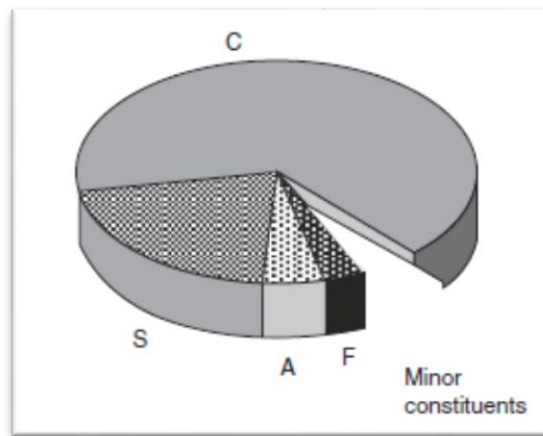
(30%) Argillaceous materials such as Clays and shales  $\longrightarrow$  Silica ( $\text{SiO}_2$ ) and Oxides  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ )

(4%) Gypsum  $\longrightarrow$   $\text{SO}_3$

Accordingly, Portland cement consists of mainly of lime ( $\text{CaO}$ ), silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ) and iron oxide ( $\text{Fe}_2\text{O}_3$ ) which, internationally referred to as C, S, A and F respectively. The combined content of the four oxides is approximately 90% of the cement weight and they are generally referred to as “major oxides”. The remaining 10% consists of magnesia ( $\text{MgO}$ ), alkali oxides ( $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ), titania ( $\text{TiO}_2$ ), phosphorous pentoxide ( $\text{P}_2\text{O}_5$ ) and gypsum. These are referred to as “minor constituents”.

Oxide	Common Name	Abbreviation	Approx. Amount (%)
CaO	Lime	C	60-67
SiO <sub>2</sub>	Silica	S	17-25
Al <sub>2</sub> O <sub>3</sub>	Alumina	A	3-8
Fe <sub>2</sub> O <sub>3</sub>	Iron-oxide	F	0.5-6
MgO	Magnesia	M	0.1-4
Na <sub>2</sub> O	Soda	N	0.2-1.3
K <sub>2</sub> O	Potassa	K	
SO <sub>3</sub>	Sulfuric Anhydride	Š	1-3

The amount of oxides in a P.C. depends on the proportion of the raw materials and how well the burning is done in the kiln.



## ***Manufacturing process***

### **a) Clinker production**

Burning of raw flour (clay + limestone grist), in a rotary kiln:

*Drying* takes place with face-flowing exhaust gases coming from the opposite direction.

*Preheating*: around 450-550°C, clay minerals lose their water of crystallization, at temperatures ranging between 600-800°C, the MgCO<sub>3</sub> becomes is de-carbonated (→ MgO)



*Calcination:*  $>900^{\circ}\text{C}$   $\text{CaCO}_3$  becomes de-carbonated ( $\rightarrow \text{CaO}$ ), around  $1200^{\circ}\text{C}$  silicate producing reactions kick in.

*Shrinkage:* up to  $1450^{\circ}\text{C}$ . Within the frame of exothermic process of clinker minerals are formed.

*Cooling, resting:* Through this, free  $\text{CaO}$  reacts with water in the air, and with Carbon-dioxide (subsequent transformation would cause swelling)

## b) Cement production

The cooled down clinker is grinded up with the gypsum stone and – in case of heterogeneous cement production – grinded or added to hydraulic complements.

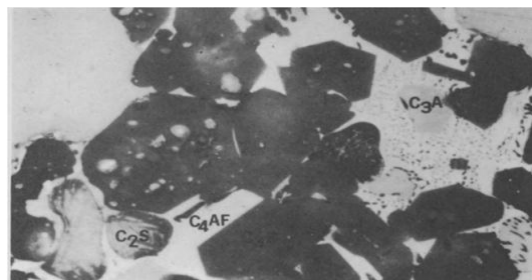
It is of utmost importance that the clinker is cooled adequately, because

- Hot grinding damages the crushing plants,
- Reactive semi-hydrate can be formed from gypsum-stone, which when used in cement, hardens rather quick with water (pseudo bonding)

## COMPOUND COMPOSITION OF P.C.

Oxides interact with each other in the kiln to form more complex products (compounds) in Clinker form. Basically, the major compounds of P.C. can be listed as:

Name	Chemical Formula	Abbreviations
Tri Calcium Silicate	$3\text{CaO}.\text{SiO}_2$	$\text{C}_3\text{S}$
Di Calcium Silicate	$2\text{CaO}.\text{SiO}_2$	$\text{C}_2\text{S}$
Tri Calcium Aluminate	$3\text{CaO}.\text{Al}_2\text{O}_3$	$\text{C}_3\text{A}$
Tetra Calcium Alumino Ferrite	$4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$	$\text{C}_4\text{AF}$



### ***Types of clinkers minerals and their characterization***

Silicate chemistry abbreviations: C = CaO, S = SiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub>, F = Fe<sub>2</sub>O<sub>3</sub>, H = H<sub>2</sub>O, furthermore Cs = CaSO<sub>4</sub>, and CH = Ca (OH)<sub>2</sub>

The 3CaO SiO<sub>2</sub>, alite, tricalcium-silicate (abbr.: C<sub>3</sub>S), is the main clinker mineral having large initial strength and high bonding temperature. The amount of it in cement: 37 to 60%

- The 2SiO<sub>2</sub>CaO, Belite, di-Calcium-silicate (abbr.: βC<sub>2</sub>S), is having slow initial hardening, small bonding temperature and favorable post hardening properties. Its amount in cement by percentage is: 15-37%

- 3CaOAl<sub>2</sub>O<sub>3</sub>, Felite, tricalcium-aluminate (abbr.: C<sub>3</sub>A), the fastest bonder, the most heat developer clinker mineral showcasing poor Sulphate resistance (to retard processes gypsum is added). Amount in cement: 7-15%

- Al<sub>2</sub>O<sub>3</sub>Fe<sub>2</sub>O<sub>3</sub>4CaO Celite, tetracalcium-aluminate-ferrite (abbr.: C<sub>4</sub>AF), low strength, favorable Sulphate-resistance

### ***Chemistry of Minor Components of Cement***

Minor constituents it's the oxides less than 10% of cements weight which consists of magnesia (MgO), alkali oxides (Na<sub>2</sub>O and K<sub>2</sub>O), titania (TiO<sub>2</sub>), phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>) and gypsum. The term minor compounds refers to the quantity of these compounds, not to their importance as shown in the Table 1.1.

**Table 1.1** Minor Components of Cement (According to Iraqi standard No.5/2018)

Oxide	Common Name	Abbreviations	Approx. Amount (%)
MgO	Magnesia	M	≤ 5
Na <sub>2</sub> O	Soda	N	0.2- 1.3
K <sub>2</sub> O	Pottasa	K	
SO <sub>3</sub> when C <sub>3</sub> A < 3.5 when C <sub>3</sub> A > 3.5	Gypsum	S	≤ 2.5
Chloride			≤ 2.8
Loss in ignition		LOI	≤ 4.0
Insoluble Residue		IR	≤ 1.5

Table 1.2 indicates the typical UK levels of the most commonly encountered minor constituents and summarizes their impact on the cement manufacturing process. The inputs of alkali metal oxides (Na<sub>2</sub>O and K<sub>2</sub>O), SO<sub>3</sub> and chloride have to be closely controlled because they are volatilized in the kiln and can cause severe operational problems associated with their condensation and the formation of build-ups in the kiln 'back end' and preheater.

**Table 1.2** Influence of most commonly encountered minor constituents on manufacturing process

Minor constituent	Typical range of levels in UK clinkers	Influence on process
Na <sub>2</sub> O	0.07–0.22	Alkali sulfates are volatilized in the kiln and condense in lower-temperature regions resulting in build-ups and blockages
K <sub>2</sub> O	0.52–1.0	
SO <sub>3</sub>	0.5–1.5	
Fluorine	0.01–0.20	Greatly assists combination by virtue of mineralizing action
Chloride	0.005–0.05	Alkali chlorides are highly volatile and cause build-ups and blockages
MgO	0.8–2.5	Slight fluxing action
Trace metals	5–100ppm	Slight – but some (e.g. thallium) have to be minimized to limit emissions to the environment

The alkali metals  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  have a very strong affinity for  $\text{SO}_3$  and a liquid phase containing  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions is formed which is immiscible with the main clinker liquid (molten  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$ ). On cooling this crystallizes to yield alkali sulfates such as  $\text{K}_2\text{SO}_4$ , aphthitalite ( $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ ) and calcium langbeinite ( $\text{K}_2\text{SO}_4 \cdot 2\text{CaSO}_4$ ).

The crystallization products depend on the relative levels of the two alkali oxides and the level of  $\text{SO}_3$ . If there is insufficient  $\text{SO}_3$  to combine with the alkali metal oxides then these may enter into solid solution in the aluminate and silicate phases.  $\text{C}_2\text{S}$  can be stabilized at temperatures above  $1250^\circ\text{C}$  thus impeding the formation of  $\text{C}_3\text{S}$ . A similar stabilization of  $\text{C}_2\text{S}$ , requiring 'hard burning' to lower the free lime level to an acceptable level, can occur if there is a large excess of  $\text{SO}_3$  over alkalis.

A deficiency of  $\text{SO}_3$  in the clinker is associated with enhanced  $\text{C}_3\text{A}$  activity and difficulties in achieving satisfactory early age concrete rheology.

Fluorine occurs naturally in some limestone deposits, for example in the Pennines in England, and has a beneficial effect on clinker combination. It acts as both a flux and mineralizer, increasing the quantity of liquid formed at a given temperature and stabilizing  $\text{C}_3\text{S}$  below  $1250^\circ\text{C}$ . The level in the clinker, however, must be controlled below  $\sim 0.25\%$  in order to avoid a marked reduction in the early reactivity of cement.

Minor constituents also have to be controlled on account of their impact on cement properties and also concrete durability. Related to this, the levels of alkalis,  $\text{SO}_3$ , chloride and  $\text{MgO}$  are also limited by national cement standards or codes of practice.

Soundness of Cement refers to the ability of a hardened cement paste to retain its volume after setting without delayed destructive expansion. This destructive expansion is caused by excessive amounts of free lime ( $\text{CaO}$ ), ( $\text{SO}_3$ ) or magnesia ( $\text{MgO}$ ).

The hydrating speed of the over burnt  $\text{CaO}$  or  $\text{MgO}$  is slow,  $\text{CaO}$  or  $\text{MgO}$  begins to hydrate after cement hardening and causes the hardened cement to expand and crack.

When added too much, gypsum continues to react with calcium aluminate hydrate to form calcium sulfoaluminate hydrate, whose volume increase 1.5 times as big as gypsum and causes the hardened cement paste to crack. At this time, sulfoaluminate hydrate is called cement bacillus.

*False setting* is the rapid development of rigidity in freshly mixed Portland cement paste, mortar, or concrete occurs after few minutes of mixing cement with water without the

generation of much heat. It can be controlled by re-mixing without additional water or strength loss, Fig. 1-1. Causes of false setting are:

1. **Drying of gypsum:** when gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) gridding with hot clinker it loss 75% of its water and formed ( $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ ) and if temperature of clinker increase gypsum loss all water in its composition and formed  $\text{CaSO}_4$ . When water adds to cement  $\text{CaSO}_4$  react causes rapid setting.
2. **Bad storage:** alkalis in cement react with carbon dioxide forming Alkali carbonate which reacts with calcium hydroxide forming  $\text{CaCO}_3$  causing setting of cement paste.
3. **Activate effective  $\text{C}_3\text{A}$  exposed to humidity:** during bad storage water adhere on cement particles surface and during mixing these active surface combined rapidly with water within minutes.

*Flash setting* is a rapid development of rigidity in freshly mixed Portland – cement paste, mortar, or concrete. Further mixing can't dispel this rigidity, and a large amount of heat is produced in the process. It happened Due to rapid reaction of aluminates – when insufficient sulfate present so to prevent, a small amount of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) gridding with the cement clinker retards the hydration reaction of tricalcium aluminate so that the calcium silicates can set firstly Fig. 1-1.

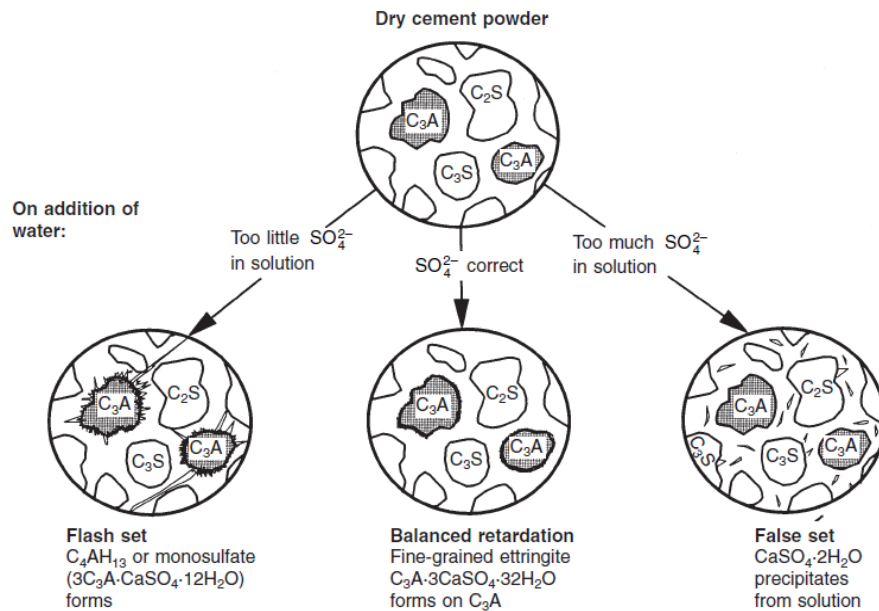


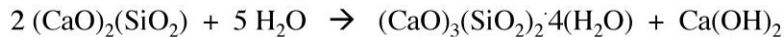
Figure 1-1 False and Flash Set of Cement

## *Chemistry of Hydration of Cement*

The addition of water to dry cement powder results in a thin cement slurry that can be easily manipulated and cast into different shapes. In time, the slurry sets and develops strength through a series of hydration reactions. Hydration of cement is not linear through time, it proceeds very slowly at first, allowing the thin mixture to be properly placed before hardening. The chemical reactions that cause the delay in hardening are not completely understood; however, they are critical to developing a rational methodology for the control of cement setting.

### **Tri- and di-calcium silicates**

The tri- and di-calcium silicates ( $C_3S$  and  $C_2S$ , respectively) comprise over 80% by weight of most cement. It is known that  $C_3S$  is the most important phase in cement for strength development during the first month, while  $C_2S$  reacts much more slowly, and contributes to the long-term strength of the cement. Both the silicate phases react with water as shown below to form calcium hydroxide and a rigid calcium-silicate hydrate gel, C–S–H.



The detailed structure of C–S–H is similar to a mineral called “TOBERMORITE”. As a result it is named as “TOBERMORITE GEL” is not completely known, however it is generally agreed upon that it consists of condensed silicate tetrahedra sharing oxygen atoms with a central, calcium hydroxide-like  $CaO_2$  layer. Calcium hydroxide consists of hexagonal layers of octahedrally coordinated calcium atoms and tetrahedrally coordinated oxygen atoms as shown in Fig. 1.

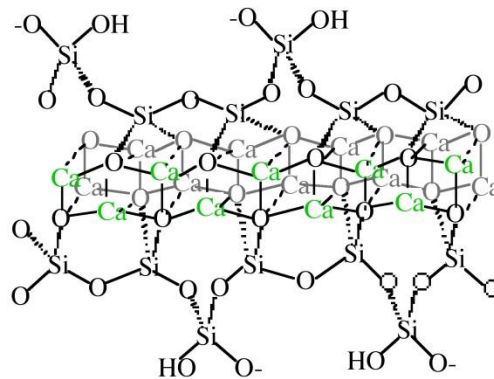
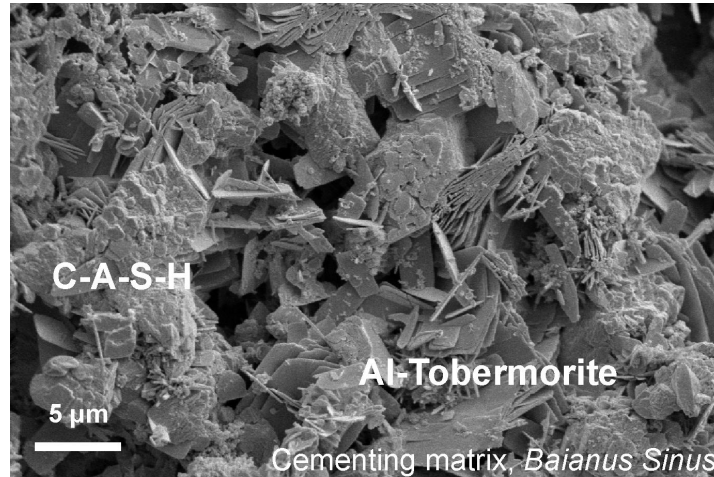


Figure 1. Schematic representation of Tobermorite.

Although the precise mechanism of  $C_3S$  hydration is unclear, the kinetics of hydration is well known. The hydration of the calcium silicates proceeds via four distinct phases as shown in Fig. 2. The first 15-20 minutes, termed the pre-induction period (Fig.2a), is marked by rapid heat evolution. During this period calcium and hydroxyl ions are released into the solution. The next, and perhaps most important, phase is the induction period (Fig.2b), which is characterized by very slow reactivity. During this phase, calcium oxide continues to dissolve producing a pH near 12.5. The chemical reactions that cause the induction period are not precisely known; however, it is clear that some form of an activation barrier must be overcome before hydration can continue. It has been suggested that in pure  $C_3S$ , the induction period may be the length of time it takes for C-S-H to begin nucleation, which may be linked to the amount of time required for calcium ions to become supersaturated in solution. Alternatively, the induction period may be

caused by the development of a small amount of an impermeable calcium-silicon-hydrate (C–S–H) gel at the surface of the particles, which slows down the migration of water to the inorganic oxides. The initial Ca/Si ratio at the surface of the particles is near 3. As calcium ions dissolve out of this C–S–H gel, the Ca/Si ratio in the gel becomes 0.8-1.5. This change in Ca/Si ratio corresponds to a change in gel permeability, and may indicate an entirely new mechanism for C–S–H formation. As the initial C–S–H gel is transformed into the more permeable layer, hydration continues and the induction period gives way to the third phase of hydration, the acceleratory period (Fig.2c).

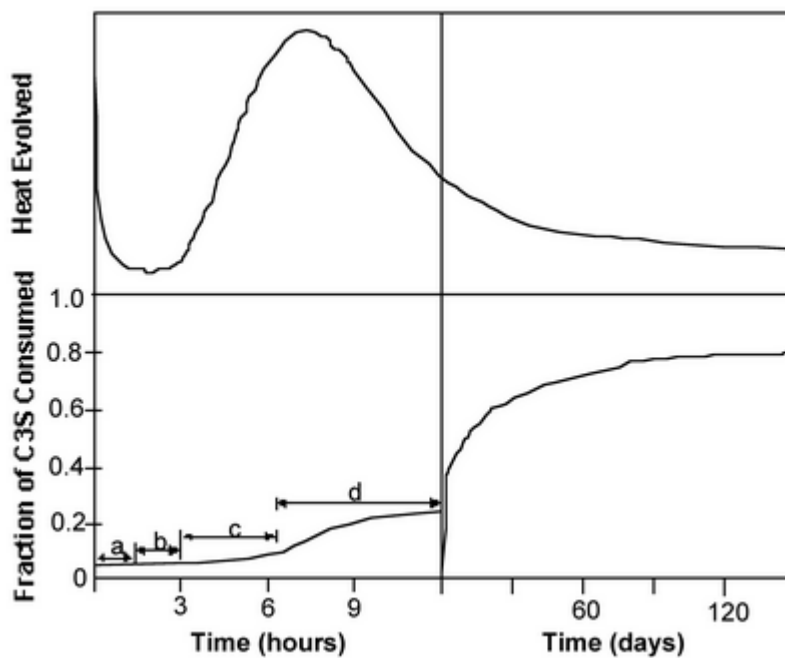


Figure 2. Hydration of  $C_3S$  over time: (a) the pre-induction period, (b) the induction, (c) period the acceleratory period, and (d) the deceleratory period.

After 3 hours of hydration, the rate of C–S–H formation increases with the amount of C–S–H formed. Solidification of the paste, called setting, occurs near the end of the third period. The fourth stage (Fig.2d) is the deceleratory period in which hydration slowly continues hardening the solid cement until the reaction is complete. The rate of hydration in this phase is determined either by the slow migration of water through C–S–H to the inner, unhydrated regions of the particles, or by the migration of  $H^+$  through the C–S–H



to the anhydrous CaO and SiO<sub>2</sub>, and the migration of Ca<sup>2+</sup> and Si<sup>4+</sup> to the OH<sup>-</sup> ions left in solution.

### Calcium aluminate and ferrite

In spite of the fact that the aluminate and ferrite phases comprise less than 20% of the bulk of cement, their reactions are very important in cement and dramatically affect the hydration of the calcium silicate phases, see below. Relative to C<sub>3</sub>S, the hydration of C<sub>3</sub>A is very fast. In the absence of any additives, C<sub>3</sub>A reacts with water to form two intermediate hexagonal phases, C<sub>2</sub>AH<sub>8</sub> and C<sub>4</sub>AH<sub>13</sub>. The structure of C<sub>2</sub>AH<sub>8</sub> is not precisely known, but C<sub>4</sub>AH<sub>13</sub> has a layered structure based on the calcium hydroxide structure, in which one out of every three Ca<sup>2+</sup> is replaced by either an Al<sup>3+</sup> or Fe<sup>3+</sup> with an OH<sup>-</sup> anion in the interlayer space to balance the charge. All of the aluminum in C<sub>4</sub>AH<sub>13</sub> is octahedral. C<sub>2</sub>AH<sub>8</sub> and C<sub>4</sub>AH<sub>13</sub> are meta-stable phases that spontaneously transform into the fully hydrated, thermodynamically stable cubic phase, C<sub>3</sub>AH<sub>6</sub>. In C<sub>3</sub>A, aluminum coordination is tetrahedral. The structure consists of rings of aluminum tetrahedra linked through bridging oxygen atoms, which slightly distorts the aluminum environment. In C<sub>3</sub>AH<sub>6</sub>, aluminum exists as highly symmetrical, octahedral Al(OH)<sub>6</sub> units.



If the very rapid and exothermic hydration of C<sub>3</sub>A is allowed to proceed unhindered in cement, then the setting occurs too quickly and the cement does not develop strength. Therefore, gypsum [calcium sulfate dihydrate, CaSO<sub>4</sub>·2(H<sub>2</sub>O)] is added to slow down the C<sub>3</sub>A hydration. In the presence of gypsum, tricalcium aluminate forms ettringite, [Ca<sub>3</sub>Al(OH)<sub>6</sub>·12(H<sub>2</sub>O)]<sub>2</sub>·(SO<sub>4</sub>)<sub>3</sub>·2(H<sub>2</sub>O), which can also be written as C<sub>3</sub>A·3(CaSO<sub>4</sub>)·32(H<sub>2</sub>O). Ettringite grows as columns of calcium, aluminum and oxygen surrounded by water and sulfate ions, as shown in Fig. 3a.

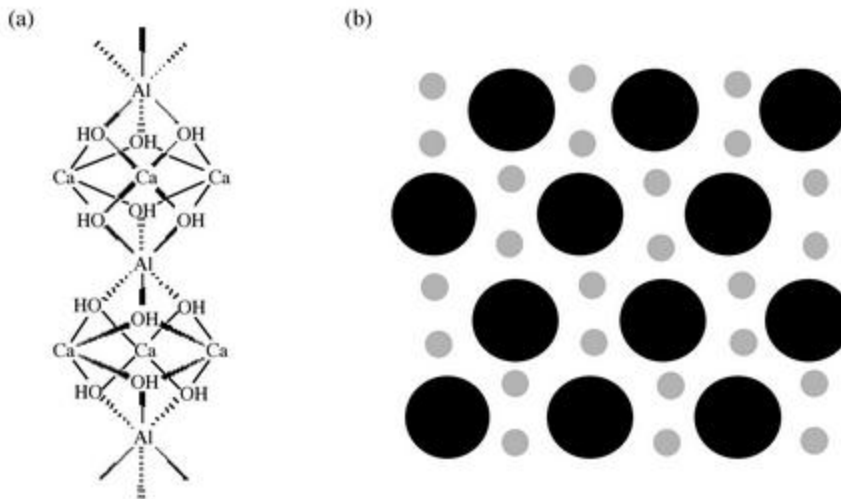


Figure 3. (a) Ettringite columns consisting of octahedral aluminum, tetrahedral oxygen, and 8-coordinate calcium. The coordination sphere of each calcium is filled by water and sulfate ions. (b) The packing of the columns represented by large circles, the smaller circles represent channels containing with water and sulfate ions.

Tetracalcium aluminoferrite ( $C_4AF$ ) reacts much like  $C_3A$ , i.e., forming ettringite in the presence of gypsum. However, hydration the ferrite phase is much slower than hydration of  $C_3A$ , and water is observed to bead up on the surface of  $C_4AF$  particles. This may be due to the fact that iron is not as free to migrate in the pastes as aluminum, which may cause the formation of a less permeable iron rich layer at the surface of the  $C_4AF$  particles and isolated regions of iron hydroxide. In cement, if there is insufficient gypsum to convert all of the  $C_4AF$  to ettringite, then an iron-rich gel forms at the surface of the silicate particles which is proposed to slow down their hydration.

### **Portland cement**

The hydration of cement is obviously far more complex than the sum of the hydration reactions of the individual minerals. The typical depiction of a cement grain involves larger silicate particles surrounded by the much smaller  $C_3A$  and  $C_4AF$  particles. The setting (hydration) of cement can be broken down into several distinct periods. The more reactive aluminate and ferrite phases react first, and these reactions dramatically affect the hydration of the silicate phase.

In the first few minutes of hydration (Fig.4b), the aluminum and iron phases react with gypsum to form an amorphous gel at the surface of the cement grains and short rods of ettringite grow. After this initial period of reactivity, cement hydration slows down and the induction period begins. After about 3 hours of hydration, the induction period ends and the acceleratory period begins. During the period from 3 to 24 hours, about 30% of cement reacts to form calcium hydroxide and C–S–H. The development of C–S–H in this period occurs in 2 phases. After 10 hours hydration (Fig.4c), C<sub>3</sub>S has produced “outer C–S–H,” which grows out from the ettringite rods rather than directly out from the surface of the C<sub>3</sub>S particles. Therefore, in the initial phase of the reaction, the silicate ions must migrate through the aluminum and iron rich phase to form the C–S–H. In the latter part of the acceleratory period, after 18 hours of hydration, C<sub>3</sub>A continues to react with gypsum, forming longer ettringite rods (Fig.4d). This network of ettringite and C–S–H appears to form a “hydrating shell” about 1 μm from the surface of anhydrous C<sub>3</sub>S. A small amount of “inner C–S–H” forms inside this shell. After 1–3 days of hydration, reactions slow down and the deceleratory period begins (Fig.4e). C<sub>3</sub>A reacts with ettringite to form some monosulfate. “Inner C–S–H” continues to grow near the C<sub>3</sub>S surface, narrowing the 1 μm gap between the “hydrating shell” and anhydrous C<sub>3</sub>S. The rate of hydration is likely to depend on the diffusion rate of water or ions to the anhydrous surface. After 2 weeks hydration (Fig.4f), the gap between the “hydrating shell” and the grain is completely filled with C–S–H. The original, “outer C–S–H” becomes more fibrous.

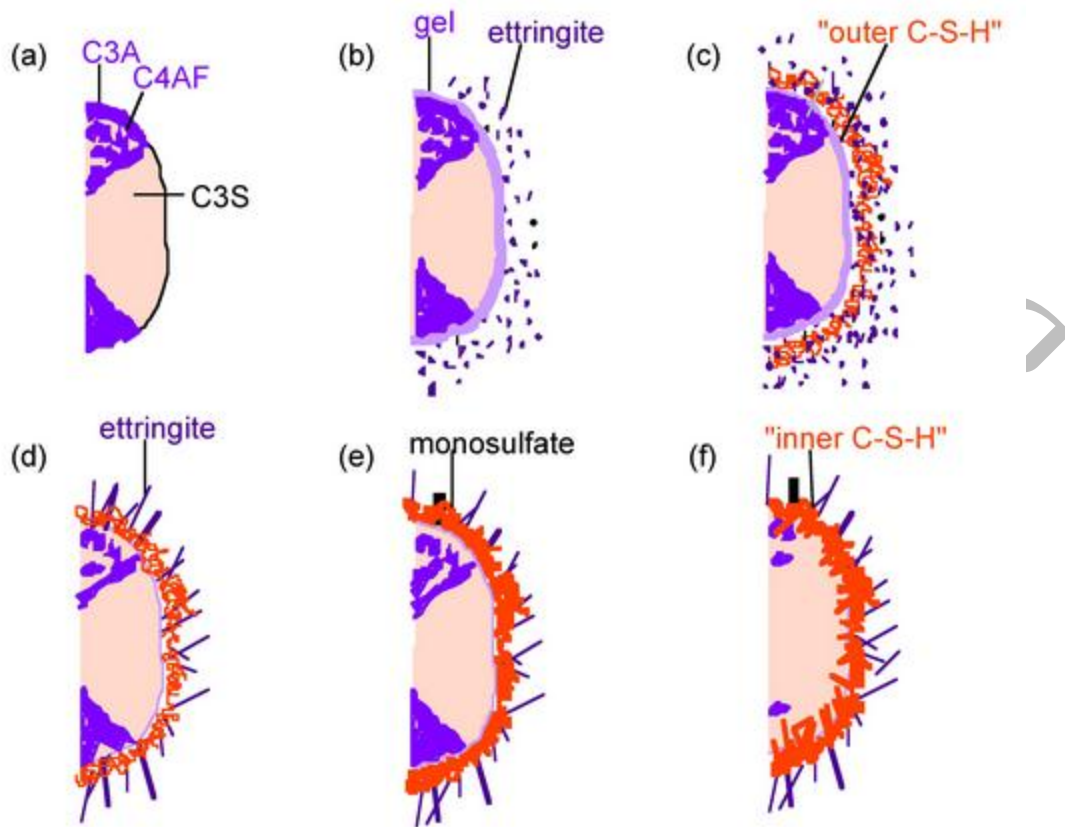


Figure 4. Schematic representation of anhydrous cement (a) and the effect of hydration after (b) 10 minutes, (c) 10 hours, (d) 18 hours, (e) 1–3 days, and (f) 2 weeks.

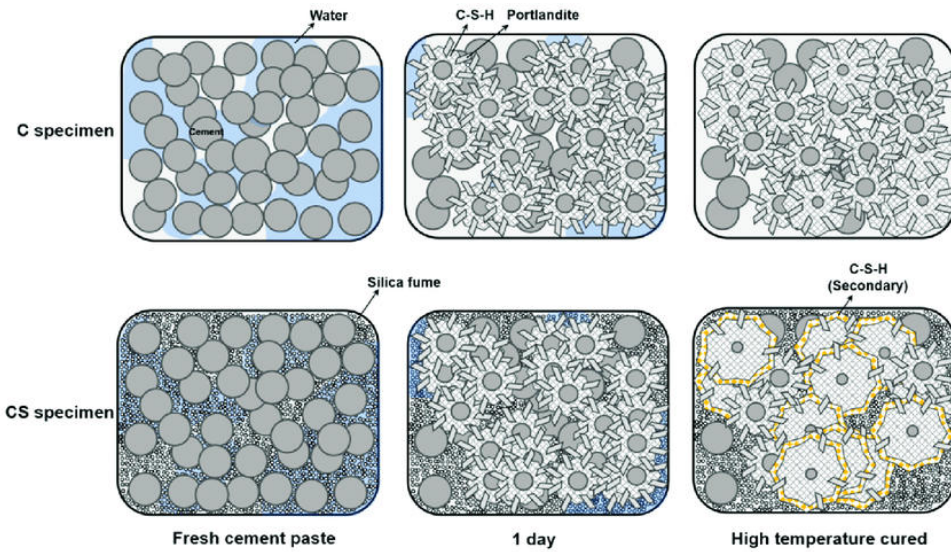
Compounds	Strength	Heat of Hydration
$C_3S$	Starts within 1-4 weeks then decrease	High (120) cal/gm
$C_2S$	Starts after 4 weeks and increase	Very Low (62) cal/gm
$C_3A$	Starts 1-3 days then decrease	Very High (207) cal/gm
$C_4AF$	Same as $C_3A$	Low (100) cal/gm

**At any stage of hydration, the hardened cement paste consists of:**

1. Hydration products (calcium silicates hydrate, tricalcium aluminates hydrate and calcium ferrite), known as gel.
2.  $Ca(OH)_2$  produced from the hydration of the silicates.
3. Some minor components.

4. Un-hydrated cement.
5. Voids (pores).

Structure of hydrate paste

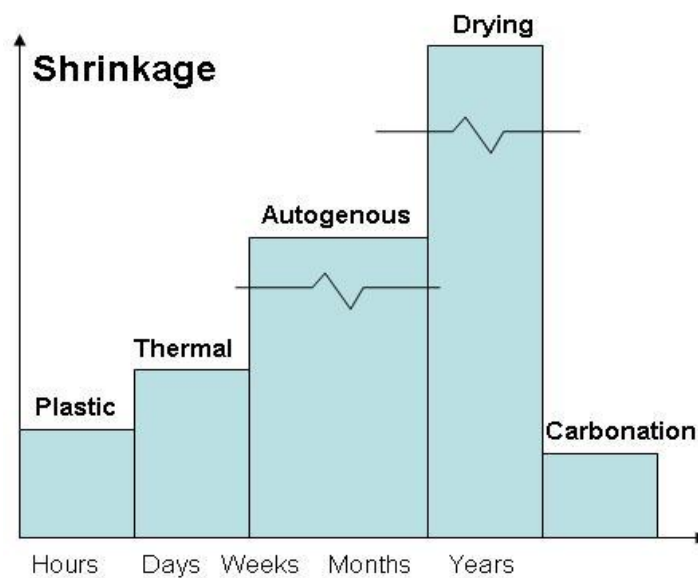


## *Chemistry of Shrinkage of Cement*

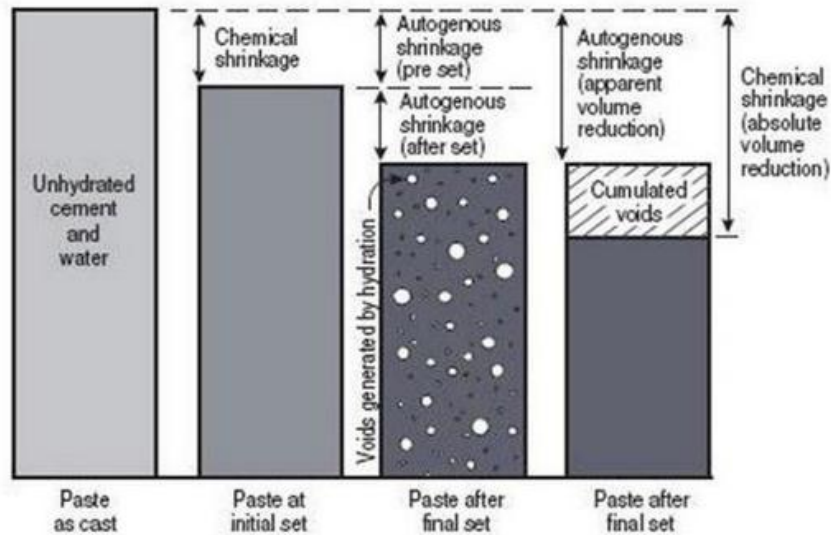
Shrinkage is the broad term given to the reduction of volume of concrete as shown in Fig.1. A number of types of shrinkage can occur in concrete, namely, plastic shrinkage, chemical shrinkage, autogenous shrinkage, drying shrinkage, and carbonation shrinkage. The relative magnitudes of the different types of shrinkage are presented in Fig.2. While, Fig. 3 illustrated the chemical and autogenous shrinkage of cement paste



**Figure 1. Concrete Shrinkage**



**Figure 2. Relative magnitudes of different types of shrinkage**



**Figure 3. Autogenous and Chemical Shrinkage of Cement**

When a restraint to the volumetric contraction is present, cracking occurs in the concrete. There are various sources of restraint in concrete structures: (a) Restraint due to aggregate, (b) Restraint due to reinforcing bars, (c) Restraint by a base or a pavement, (d) Restraint due to differential shrinkage within a concrete member, (e) Restraint due to differential shrinkage between concrete members.

Although shrinkage cracks are not a structural concern, they can affect the long-term durability by providing easy access to water and aggressive species into the interior of concrete.

### **Plastic shrinkage**

This type of shrinkage, is associated with drying when concrete is in a plastic state. Plastic shrinkage cracking is controlled by both capillary pressure and the effect of sand particles. The advantageous effects of sand particles in reducing plastic shrinkage cracks are due to their ability to: (1) arrest cracking, and (2) generate relatively large water-filled channels, gaps, or pores, at and near the cement paste – sand interfaces. These channels tend to get

filled up when fine mineral admixtures are used. Most drying in the early periods occurs through water-filled channels.

Plastic shrinkage can be controlled by:

- Reducing the rate of evaporation of water (by decreasing the temperature of the concrete, placing the concrete rapidly, curing as soon as possible). Evaporation rates should not exceed  $1 \text{ kg/m}^2/\text{hour}$ .
- Reduction of the cement content (by optimizing the paste volume, using complementary materials).
- Utilization of shrinkage-reducing admixtures
- Use of non-metallic fibers

Cracking can also develop over obstructions to uniform settlement, e.g. over reinforcing bars, or large aggregates particles. This is called plastic settlement cracking. In order to avoid this type of cracking, it is absolutely essential to provide adequate top cover (should be at least 5 mm more than the maximum aggregate size). Additionally, the viscosity of the concrete should be controlled.

### **Chemical shrinkage**

The overall volume of products formed in cement hydration is smaller than the volume of the reactants. Thus, there is a shrinkage associated with this chemical reaction, which is thus called chemical shrinkage, as shown in Fig. 3. The remainder of the volume goes towards the porosity of the cement paste.

### **Autogenous shrinkage**

This is the shrinkage associated with the withdrawal of water from the capillary and gel pores for the hydration of the unhydrated cement. This phenomenon is also called self-desiccation. Typical values of  $40 \times 10^{-6}$  at 1 month and  $100 \times 10^{-6}$  at 5 years have been reported by researchers. The factors that affect autogenous shrinkage are fineness of cement, degree and quality of mineral admixtures, and the  $C_3A$  content of cement. The shrinkage is severe at low  $w/c$ , where a great degree of unhydrated cement is present. A value of  $700 \times 10^{-6}$  was reported



for a w/c of 0.17. For normal concrete, the strains are much smaller than drying shrinkage strains.

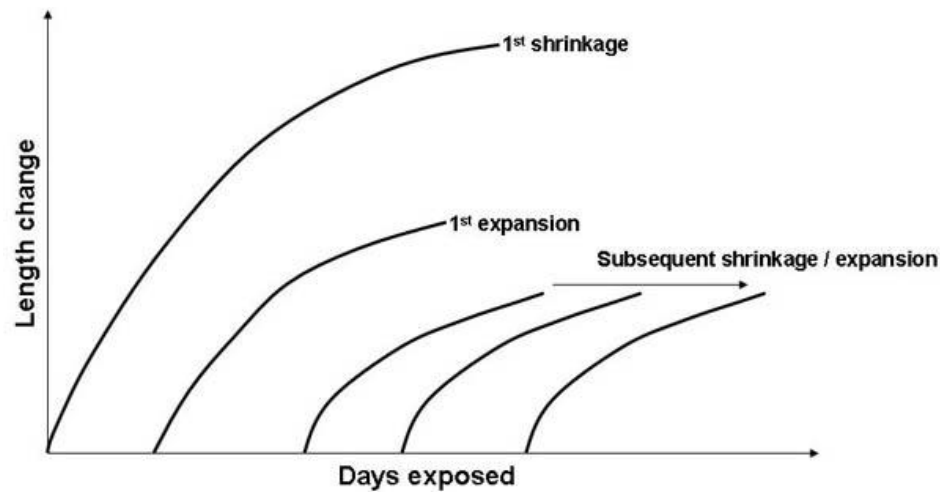
### **Drying shrinkage**

This is the shrinkage associated with the removal of water from concrete by drying. Only the cement paste in concrete is susceptible to drying shrinkage. Numerous factors affect drying shrinkage, such as – ambient conditions, w/c, specimen size, amount of aggregate, and degree of hydration.

### ***Drying and wetting cycles***

Concrete seldom undergoes continuous drying. Usually the processes of drying and wetting occur alternately. The shrinkage behaviour of concrete can be studied by subjecting it to drying and wetting cycles. Upon wetting, the cement gel absorbs water and swells. Water molecules act against the cohesive forces and tend to force the gel particles apart. Swelling might be an adverse factor for concrete in seawater, because of the prevalent high pressure. However, swelling is overall beneficial, since the resistance to swelling caused by restraints such as aggregates and reinforcing bars causes a compression in the paste. This pre-compression is able to compensate for the tensile stresses that get generated by shrinkage.

The first shrinkage is greater than any subsequent expansion or shrinkage. This is because the arrangement of gel particles and groups of gel particles is changed during the first shrinkage. At a given aggregate content, the extent of the first shrinkage increases with the w/c, since the average initial spacing of gel particles also depends on the w/c. For subsequent shrinkages, the volume changes are independent of w/c because after once having been dried, the spacing between adjacent gel particles will be more a function of humidity and the corresponding degree of drying rather than of the original spacing. Fig. 4 depicts the volume change associated with drying and wetting cycles. In the long term, the degree of swelling and shrinkage gradually become equal.



**Figure 4. Effect of drying and wetting cycles**

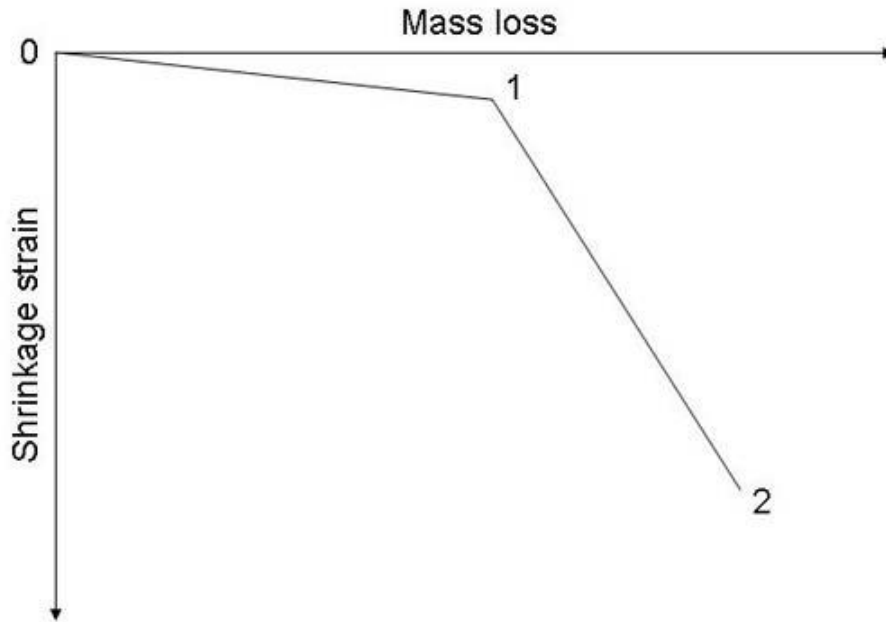
### ***Mechanism of drying shrinkage***

The change in volume of the paste and concrete is not equal to the volume of the water removed. This suggests that some other causes are also at play during the process of shrinkage. Some leading causes that drive the mechanism, as postulated by researchers, are:

- Nature of C-S-H gel or colloids: Typically, C-S-H has a very high surface area (200000 – 300000 m<sup>2</sup>/kg) and a layered structure. Removal of water could therefore result in a collapse of this structure.
- Physical structure of paste: The paste is composed to many gel pores and capillary pores, which provide interconnected network channels.
- The nature of water associated with the hydrated cement paste – capillary, adsorbed, interlayer, or bound.

A study of the mechanism of drying shrinkage can be conducted by simultaneously measuring the mass and length of concrete specimens. The loss in mass is an indicator of the volume of water lost, and the change in length can indicate the reduction in volume of the specimen. A typical behavior of concrete is shown in Fig. 5. The stage 0-1 corresponds to the loss of water from capillary pores. These pores store the maximum amount of water within the paste. However, due to their relatively large sizes, the strains associated with the removal of water

are not high. On the other hand, stage 1-2 corresponds to the removal of water from gel pores. This type of water is mainly adsorbed or interlayer water. While the amount of water removed is not high, the shrinkage strain associated with this removal is substantial, suggesting that a collapse of the structure has indeed taken place.



**Figure 5. Typical behavior of concrete during shrinkage**

### *Factors affecting drying shrinkage*

- w/c
- Age and degree of hydration of concrete
- Curing and drying conditions (ambient temperature and RH)
- Cement composition and fineness
- Specimen size
- Amount and quality of aggregate

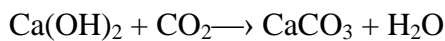
Aggregates provide a restraint to the shrinkage of the paste. Thus, an increase in the proportion of aggregates causes a reduction in shrinkage. The shrinkage of paste and concrete is related in the following manner.

$$S_c = S_p (1 - V_a)^k,$$

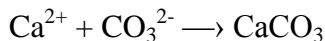
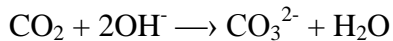
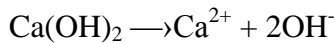
where  $S_c$  = shrinkage of concrete,  $S_p$  = shrinkage of paste,  
 $V_a$  = volume fraction of aggregate, and  $k$  is a factor that depends on the modulus of elasticity of the aggregate (typical values between 1.2 and 1.7).

### Carbonation Shrinkage

This type of shrinkage is not associated with the loss of water or any other loss of material from concrete. In fact, carbonation, or the attack of concrete by atmospheric  $\text{CO}_2$ , actually causes an increase in the mass. The reaction of carbonation can be written as follows:



The  $\text{CaCO}_3$  that forms resembles calcite or aragonite. Although it seems as if this reaction leads to the production of water, moisture is actually necessary for this reaction to take place. In stages, the same reaction may be written as:



The reaction described above actually leads to an increase in the solid volume, by as much as 3.29%. The exact mechanism by which shrinkage occurs is not well established. One of the hypotheses states that  $\text{Ca(OH)}_2$  in the paste is under a compressive stress due to the existence of menisci in the pores. These crystals act as supports and prevent collapse of the C-S-H gel particles. But when carbonation occurs, CH dissolves, and causes a collapse of C-S-H, leading to shrinkage.

Carbonation increases the level of drying shrinkage, at RH levels around 50%. At high RH levels ( $> 80\%$ ), the absorption of  $\text{CO}_2$  does not easily occur through the saturated pores. At very low RH levels ( $\sim 30\%$ ), dissolution of CH does not occur, and as a consequence, carbonation cannot take place.

Carbonation increases strength and reduces permeability of concrete. However, the alkalinity of concrete is reduced, rendering the concrete susceptible to corrosion.

## Alkali- Silica Reaction (ASR)

The alkali-silica reaction (ASR), more commonly known as "concrete cancer", is a swelling reaction that occurs over time in concrete between the highly alkaline cement paste and the reactive non-crystalline (amorphous) silica found in many common aggregates, given sufficient moisture. In most concrete, aggregates are more or less chemically inert. However, some aggregates react with the alkali hydroxides in concrete, causing expansion and cracking over a period of many years; this alkali- silica reaction as shown in Fig.1.

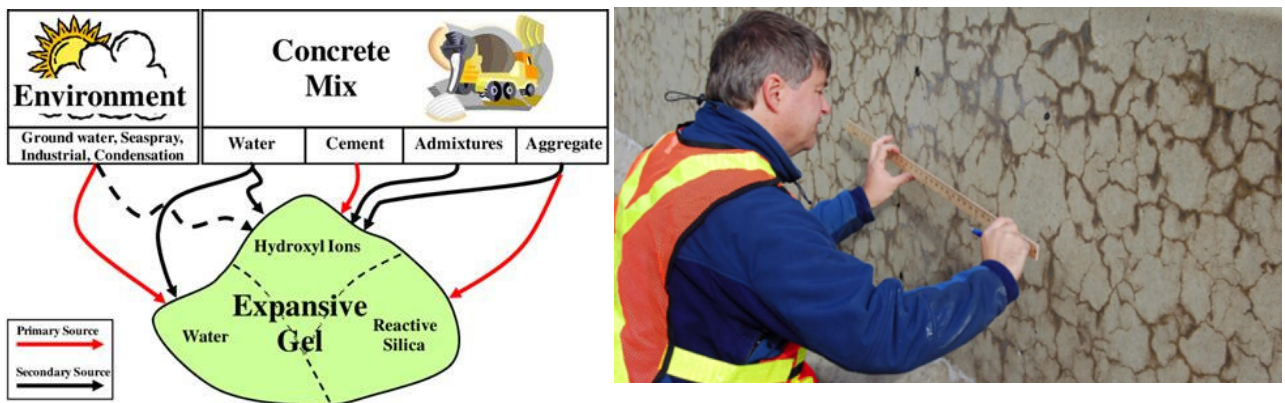


Figure 1. Alkali- Silica Reaction (Concrete Cancer)

### Mechanism of Reaction

Alkali-silica reaction is one of the most recognized deleterious phenomena in concrete. Various types of silica present in aggregates react with the hydroxyl ions present in the pore solution in concrete. The silica, now in solution, reacts with the sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) alkalis to form a volumetrically unstable alkali silica gel. Water absorbed by the gel can be water not used in the hydration reaction of the cement, free water from rain, snowmelt, rivers, water condensed from air moisture.

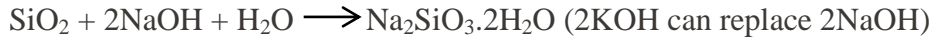
The reaction is followed by expansion / swelling of the aggregate particles due to the formation of alkali-silicate gel that absorbs water and tends to increase in volume. Since the gel is confined by

the cement paste, it builds up pressure causing expansion, due to which multidirectional cracking (map cracking) appears on surface of concrete

### **Adverse effect of ASR**

In general, the reaction can be viewed as a two-step process:

Step 1: Silica+alkali  $\longrightarrow$  alkali-silica gel (sodium silicate)



Step 2: Gel reaction product + water  $\longrightarrow$  expansion since the gel is restrained by the surrounding mortar; an internal pressure is generated by the swelling. Once that pressure is larger than the tensile strength of the concrete, cracks occur leading to additional water migration or absorption and additional gel swelling.

### **Mechanism of concrete deterioration**

The mechanism of ASR causing the deterioration of concrete can thus be described in four steps as follows:

1. The very basic solution (NaOH / KOH) attacks the siliceous aggregates (silicic acid dissolution at high pH), converting the poorly crystallized or amorphous silica to a soluble but very viscous alkali silicate gel (N-S-H, K-S-H).
2. The consumption of NaOH / KOH by the dissolution reaction of amorphous silica decreases the pH of the pore water of the hardened cement paste. This allows the dissolution of  $\text{Ca}(\text{OH})_2$  (portandite) and increases the concentration of  $\text{Ca}^{2+}$  ions into the cement pore water. Calcium ions then react with the soluble sodium silicate gel to convert it into solid calcium silicate hydrates (C-S-H). The C-S-H forms a continuous poorly permeable coating at the external surface of the aggregate.
3. The penetrated alkaline solution (NaOH / KOH) converts the remaining siliceous minerals into bulky soluble alkali silicate gel. The resulting expansive pressure increases in the core of the aggregate.
4. The accumulated pressure cracks the aggregate and the surrounding cement paste when the pressure exceeds the tolerance of the aggregate.

## Structural effects of ASR

The cracking caused by ASR can have several negative impacts on concrete, including:

1. Expansion: The swelling nature of ASR gel increases the chance of expansion in concrete elements.
2. Compressive strength: The effect of ASR on compressive strength can be minor for low expansion levels, to relatively higher degrees at larger expansion.
3. Tensile strength / Flexural capacity: Researches show that ASR cracking can significantly reduce the tensile strength of concrete; therefore reducing the flexural capacity of beams. Some research on bridge structures indicate about 85% loss of capacity as a result of ASR.
4. Modulus of elasticity/UPV: The effect of ASR on elastic properties of concrete and ultrasound pulse velocity (UPV) is very similar to tensile capacity. The modulus of elasticity is shown to be more sensitive to ASR than pulse velocity.
5. Fatigue: ASR reduces the load bearing capacity and the fatigue life of concrete.
6. Shear strength: ASR enhances the shear capacity of reinforced concrete with and without shear reinforcement.

## Mitigation

ASR can be mitigated in new concrete by several complementary approaches:

1. Limit the alkali metal content of the cement. Many standards impose limits on the "Equivalent  $\text{Na}_2\text{O}$ " content of cement.
2. Limit the reactive silica content of the aggregate. Certain volcanic rocks are particularly susceptible to ASR because they contain volcanic glass (obsidian) and should not be used as aggregate. The use of calcium carbonate aggregates is sometimes envisaged as an ultimate solution to avoid any problem. However, while it may be considered as a necessary condition, it is not a sufficient one. In principle, limestone ( $\text{CaCO}_3$ ) is not expected to contain a high level of silica, but it actually depends on its purity.
3. Add very fine siliceous materials to neutralize the excessive alkalinity of cement with silicic acid by deliberately provoking a controlled pozzolanic reaction at the early stage

of the cement setting. Convenient pozzolanic materials to add to the mix may be, e.g., pozzolan, silica fume, fly ash, or metakaolin. These react preferentially with the cement alkalis without formation of an expansive pressure, because siliceous minerals in fine particles convert to alkali silicate and then to calcium silicate without formation of semipermeable reaction rims.

4. Another method to reduce the ASR is to limit the external alkalis that come in contact with the system.
5. By limiting the contact of underground or meteoritic water infiltrations with the concrete structure (water tight membrane, roofing, sufficient water drainage ...).

### **Curative treatment**

There are no curative treatments in general for ASR affected structures. Repair in damaged sections is possible, but the reaction will continue. In some cases, when a sufficient drying of thin components (walls, slabs) of a structure is possible, and is followed by the installation of a watertight membrane, the evolution of the reaction can be slow down, and sometimes stopped, because the lack of water to continue to fuel the reaction. Indeed, water plays a triple role in the alkali-silica reaction: solvent for the reaction taking place, transport medium for the dissolved species reacting, and finally also reagent consumed by the reaction itself.

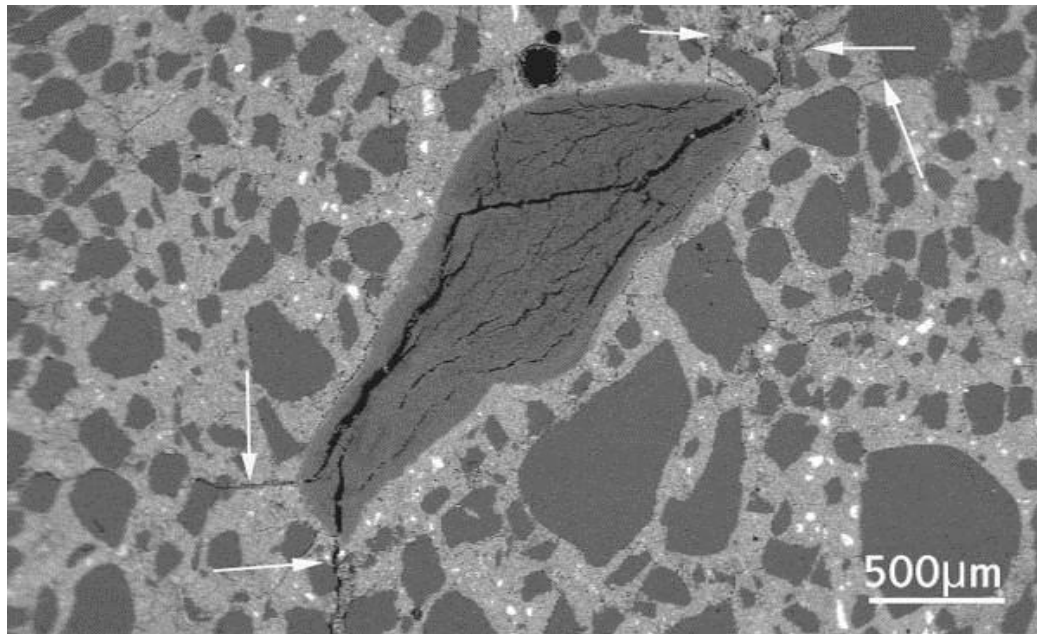
### **Identification of alkali-silica reaction**

Gel may be present in cracks and within aggregate particles. The best technique for the identification of ASR is the examination of concrete in thin section, using a petrographic microscope. Alternatively, polished sections of concrete can be examined by scanning electron microscopy (SEM); this has the advantage that the gel can be analyzed using X-ray microanalysis in order to confirm the identification beyond any doubt as shown in Fig.2.

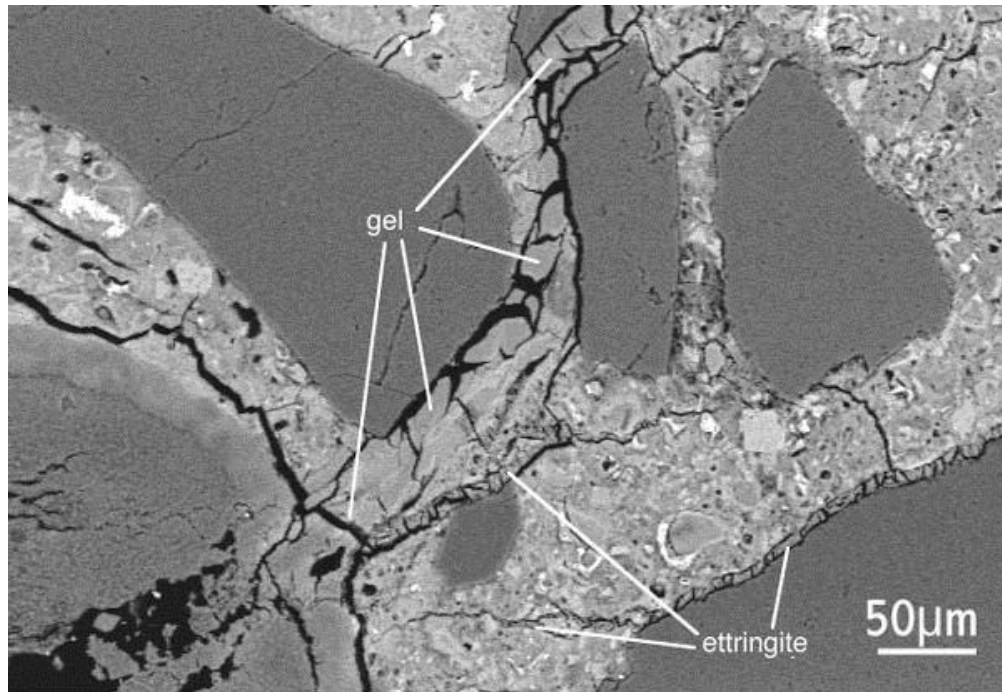




*Figure 2 Concrete thin-section, viewed with a petrographic microscope, showing a chert aggregate particle (at the right of the image) from which alkali-silica gel has extruded into adjacent cracks.*



*Figure 3 Polished section of concrete, scanning electron microscope image: chert aggregate particle with internal cracks due to ASR extending from the aggregate into the nearby concrete (arrowed).*



*Figure 4 Detail of chert particle in previous image, showing alkali-silica gel extruded into cracks within the concrete. Ettringite is also present within some cracks.*

**The conditions required for ASR to occur are:**

- A sufficiently high alkali content of the cement (or alkali from other sources)
- A reactive aggregate, such as chert
- Water - ASR will not occur if there is no available water in the concrete, since alkali-silica gel formation requires water.

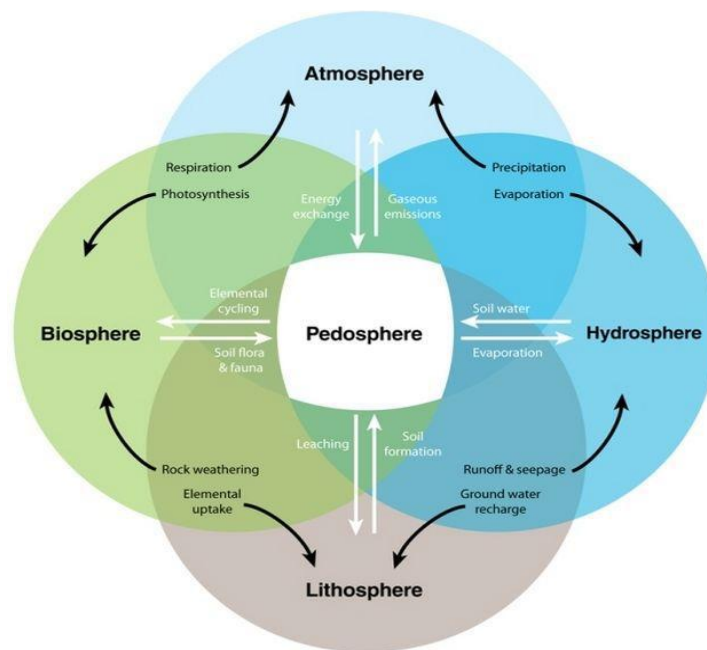
## Chemistry of Soil

Soil is a mixture of organic matter, minerals Inorganics, gases, liquids, and organisms that together support life.

Earth's body of soil, called the pedosphere, has four important functions:

1. As a medium for plant growth
2. As a means of water storage, supply and purification
3. As a modifier of Earth's atmosphere
4. As a habitat for organisms

All of these functions, in their turn, modify the soil.



### Parent Material of the Soil

The mineral material from which a soil forms is called parent material. Rock, whether its origin is igneous, sedimentary, or metamorphic, is the source of all soil mineral materials and the origin of all plant nutrients with the exceptions of nitrogen, hydrogen and carbon. As the parent material is

chemically and physically weathered, transported, deposited and precipitated, it is transformed into a soil.

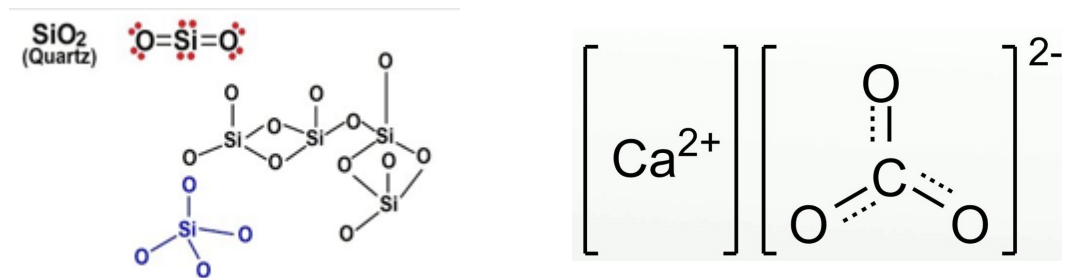
Typical soil parent mineral materials are:

Quartz:  $\text{SiO}_2$

Calcite:  $\text{CaCO}_3$

Feldspar:  $\text{KAlSi}_3\text{O}_8$

Mica (biotite):  $\text{K}(\text{Mg,Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$



Soil particles can be classified by their chemical composition (mineralogy) as well as their size. The particle size distribution of a soil (its texture) determines many of the properties of that soil, in particular hydraulic conductivity and water potential, but the mineralogy of those particles can strongly modify those properties. The mineralogy of the finest soil particles (clay) is especially important.

## Gravel, sand and silt

Gravel, sand and silt are the larger soil particles, and their mineralogy is often inherited from the parent material of the soil, but may include products of weathering (such as concretions of calcium carbonate or iron oxide), or residues of plant and animal life (such as silica phytoliths). Quartz is the most common mineral in the sand or silt fraction as it is resistant to chemical weathering, except under hot climate; other common minerals are feldspars,

mica sand ferromagnesian minerals such as pyroxenes, amphiboles and olivines, which are dissolved or transformed in clay under the combined influence of physico-chemical and biological processes.

## Physical properties

The physical properties of the soil, which affect the properties of the soil which in turn affect the uses of the soil such as crop production, are: (texture, structure, bulk density, porosity, consistency, and color).

**Soil texture** is determined by the relative proportion of the three kinds of soil mineral particles, called soil separates: sand, silt, and clay. At the next larger scale, **soil structures** called peds or more commonly soil aggregates are created from the soil separates when iron oxides, carbonates, clay, silica and humus, coat particles and cause them to adhere into larger, relatively stable secondary structures.

**Soil bulk density**, when determined at standardized moisture conditions, is an estimate of soil compaction.

**Soil porosity** consists of the void part of the soil volume and is occupied by gases or water. **Soil consistency** is the ability of soil materials to stick together.

### *Influence of Soil Texture Separates on Some Properties of Soils*

Property/behavior	Sand	Silt	Clay
Water-holding capacity	Low	Medium to high	High
Aeration	Good	Medium	Poor
Drainage rate	High	Slow to medium	Very slow
Soil organic matter level	Low	Medium to high	High to medium
Decomposition of organic matter	Rapid	Medium	Slow
Warm-up in spring	Rapid	Moderate	Slow
Compactability	Low	Medium	High
Susceptibility to wind erosion	Moderate (High if fine sand)	High	Low
Susceptibility to water erosion	Low (unless fine sand)	High	Low if aggregated, otherwise high
Shrink/Swell Potential	Very Low	Low	Moderate to very high
Sealing of ponds, dams, and landfills	Poor	Poor	Good
Suitability for tillage after rain	Good	Medium	Poor
Pollutant leaching potential	High	Medium	Low (unless cracked)
Ability to store plant nutrients	Poor	Medium to High	High
Resistance to pH change	Low	Medium	High

## **Chemistry of the Soil**

The chemistry of a soil determines its ability to supply available plant nutrients and affects its physical properties and the health of its living population. In addition, a soil's chemistry also determines its corrosivity (stability) and ability to absorb pollutants and to filter water. It is the surface chemistry of mineral and organic colloids that determines soil's chemical properties. A colloid is a small, insoluble particle ranging in size from 1 nanometer to 1micrometer, thus small enough to remain suspended by Brownian motion in a fluid medium without settling. Most soils contain organic colloidal particles called humus as well as the inorganic colloidal particles of clays.

The very high specific surface area of colloids and their net electrical charges give soil its ability to hold and release ions. Negatively charged sites on colloids attract and release cations in what is referred to as cation exchange. Cation-exchange capacity (CEC) is the amount of exchangeable cations per unit weight of dry soil. Similarly, positively charged sites on colloids can attract and release anions in the soil giving the soil an ion exchange capacity (AEC).