Hydration of Cement

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1. What & Why Cement?:

- Cementitious materials constituents of it contributes to 30-50% of everything we produce.
- But in contrast, they only make 5-10% of the carbon emissions.
- Most emissions of cement production basically comes from the Lime stone breakdown.
- The population has increased 3 folds and the production of cement has increase 34 times as compared to steel which has merely doubled
- 99.99% of the cement today is made from “Portland Cement Clinker”.
- Clinkers are marble sized modules which come out of a cement kiln (mixer) and this is the main constituent which forms the cement.

Image of a cement kiln (mixer)

Cement Clinkers (Marble sized Granular shaped)

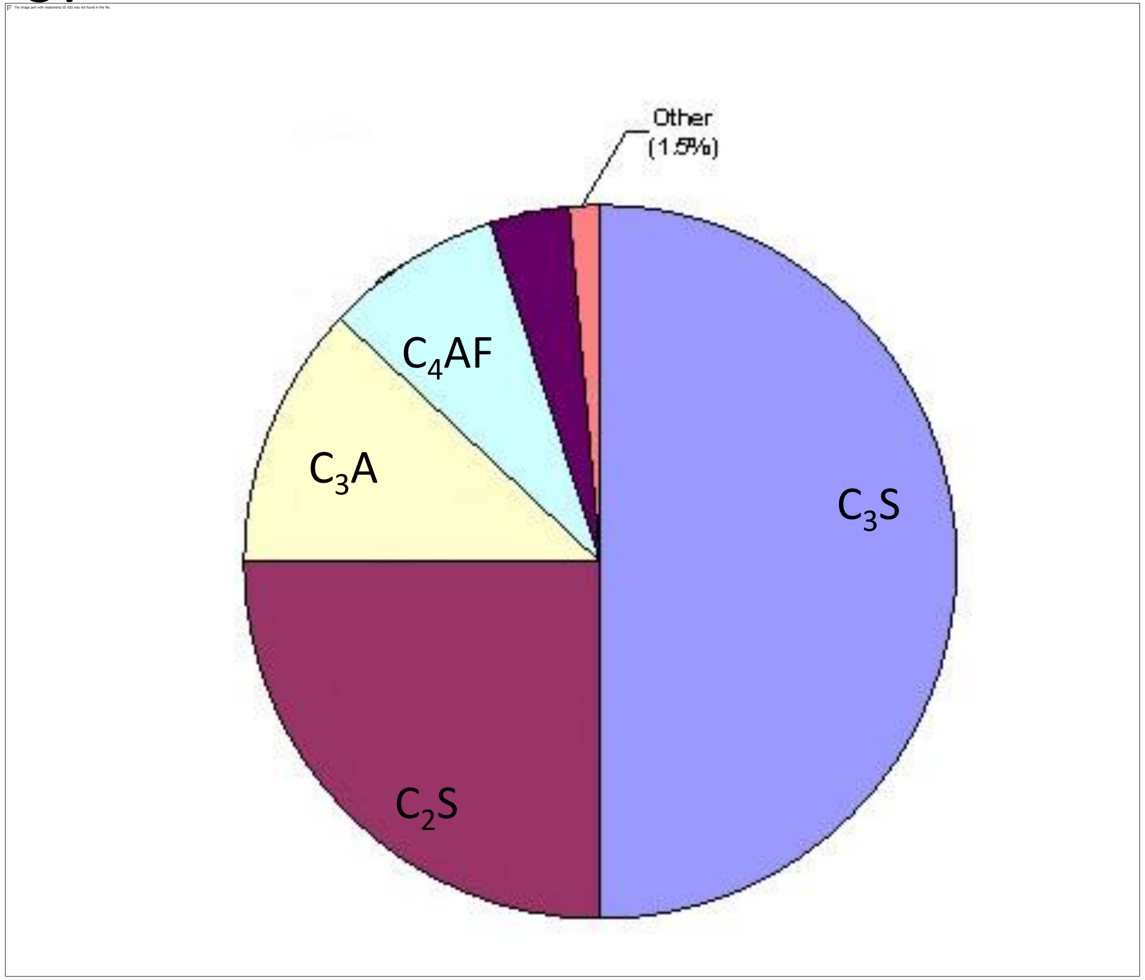
Composition of OP-Cement

- Cement(Portland) basically constitutes of –
  - Alite (C_3S)
  - Belite (C_2S)
  - Celite/Aluminates (C_3A)
  - Ferrites (C_4AF)
  - Hydrotalcite

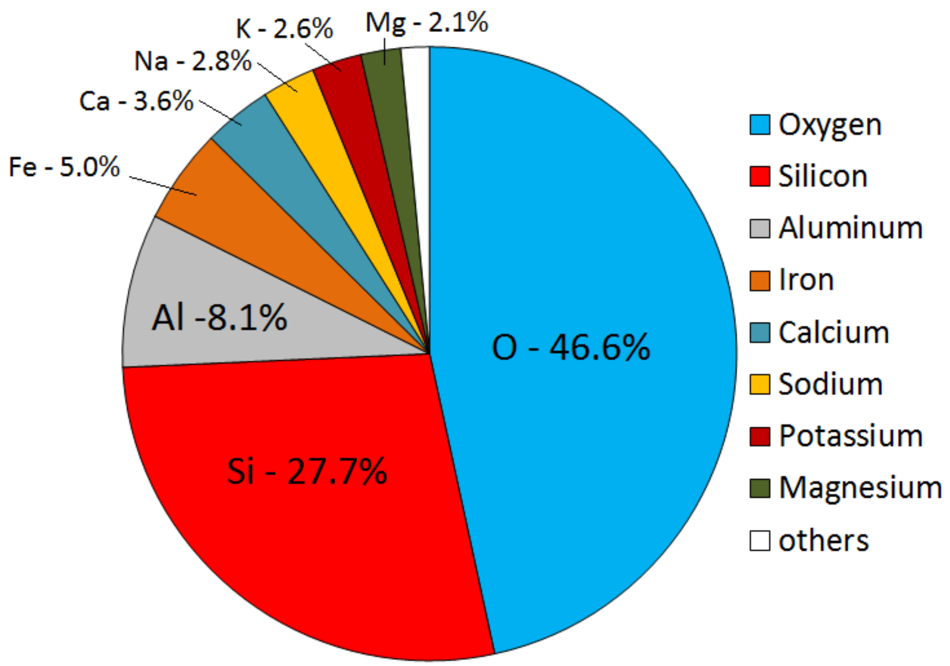
Clinkers

(Cement Chemistry Notations)

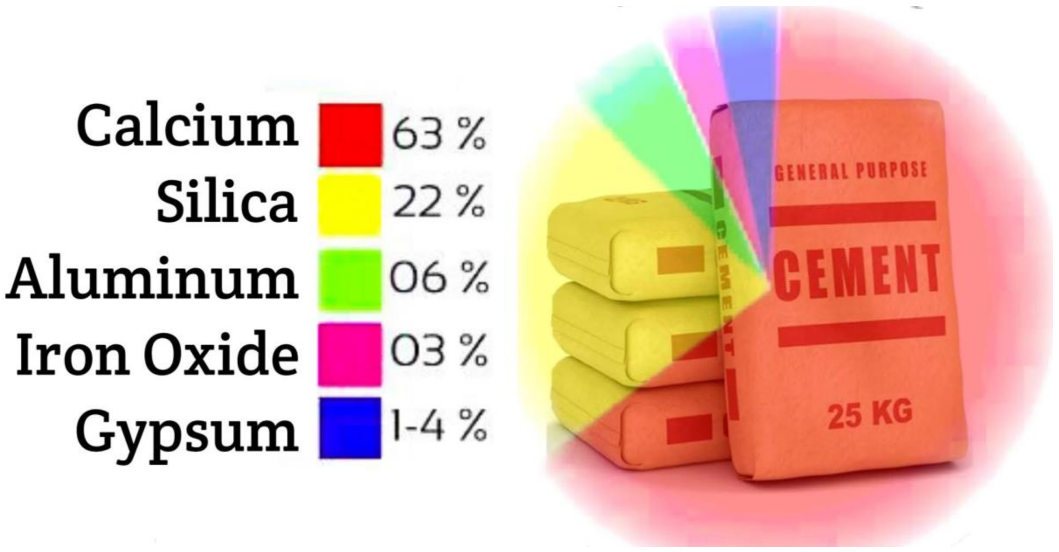
$C=CaO_2$	
$S=SiO_2$	$T=TiO_2$
$A=Al_2O_3$	$H=H_2O$
$F=Fe_2O_3$	and
$K=K_2O$	
$N=Na_2O$	$\bar{S}=SO_3$
$M=MgO$	$\bar{C}=CO_2$



- The resources from which the OPC is made up of, is the most of the elements which are abundant on the crust of the earth.
- These 8 elements constitutes 98% of the earth's crust

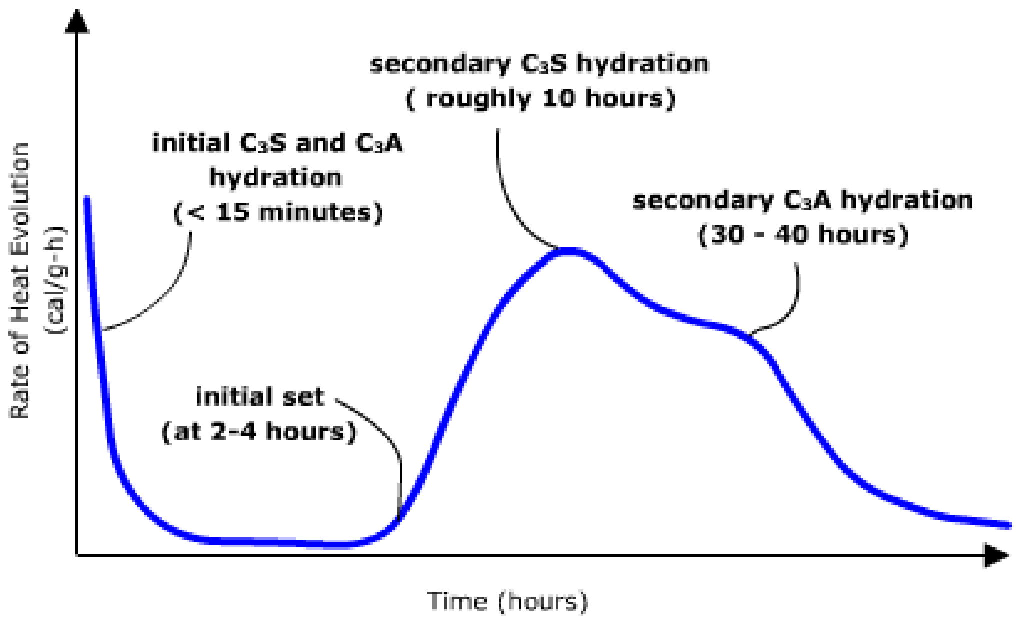


Composition of Earth's crust



Cement Composition

- Portland cement is robust.
- Initial huge spike of heat evolution.
- Hardens in matter of days.
- Open time of several hours thus easy to manipulate.
- Cements based on Portland clinker will be most important materials for foreseeable future.



- Widely available raw materials.
- Economy of scale means very low cost
- Easy to use even by unskilled workers.

Environmental Impact

- As said earlier, most emissions are contributed by the breakdown of limestone.
- The impact can be reduced by adding other materials which will replace/substitute the clinkers.
- These materials are called as “Supplementary Cementitious Materials” or as SCMs in short.

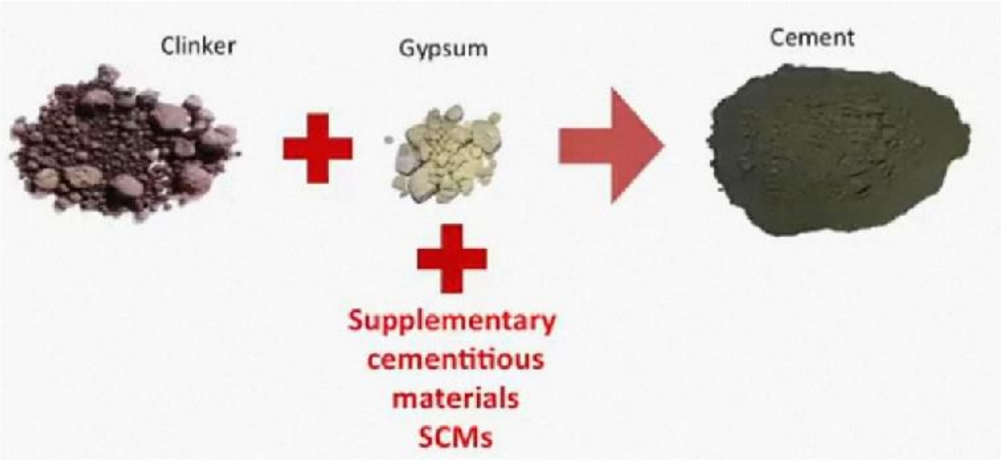


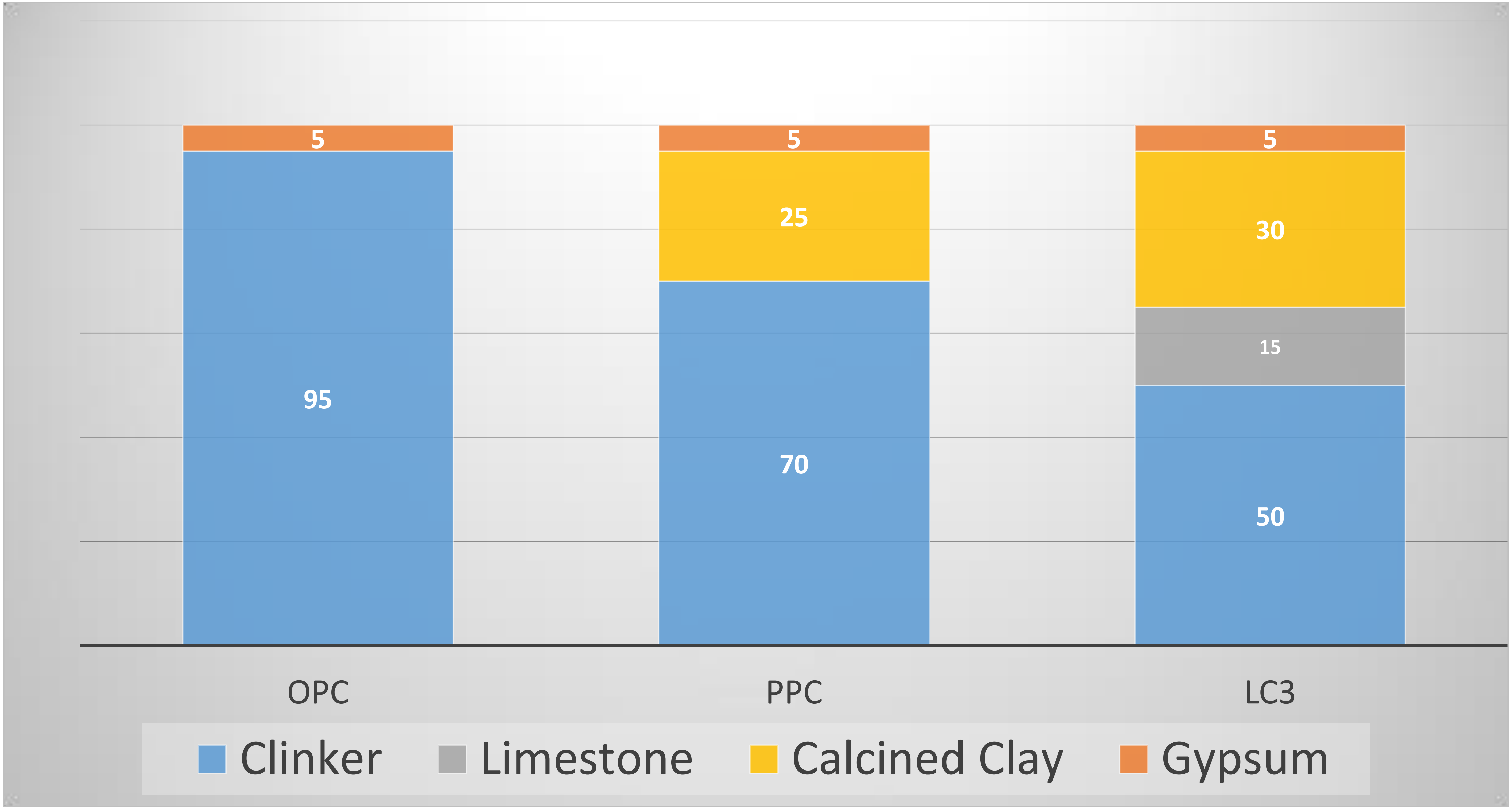
Fig - SCMs in cement making

- SCMs can substitute up to 20% clinkers in traditional OPCs.
- This substitution can significantly help in reducing the environmental impact of the cement production.
- SCMs examples are –
  - Limestone
  - Fly ash
  - Slag
  - Natural Pozzolan
  - Calcined Clay
- Use of a specific type of SCMs depends heavily on local availability.

• Different types of SCMs :-

- Limestone as a SCM beyond 10% is not beneficial as the property of the cement decreases after the limestone percentage is >10%.
- Thus a healthy substitute of limestone as SCM would be Calcined Clay which are more available.
- A cement where Limestone & Calcined Clay both are used as SCMs to increase the Clinker substitution in order to minimize the carbon emissions is what refered as “LC_3” or “Limestone Calcined Clay Cement”.

Composition of various SCM cements:-

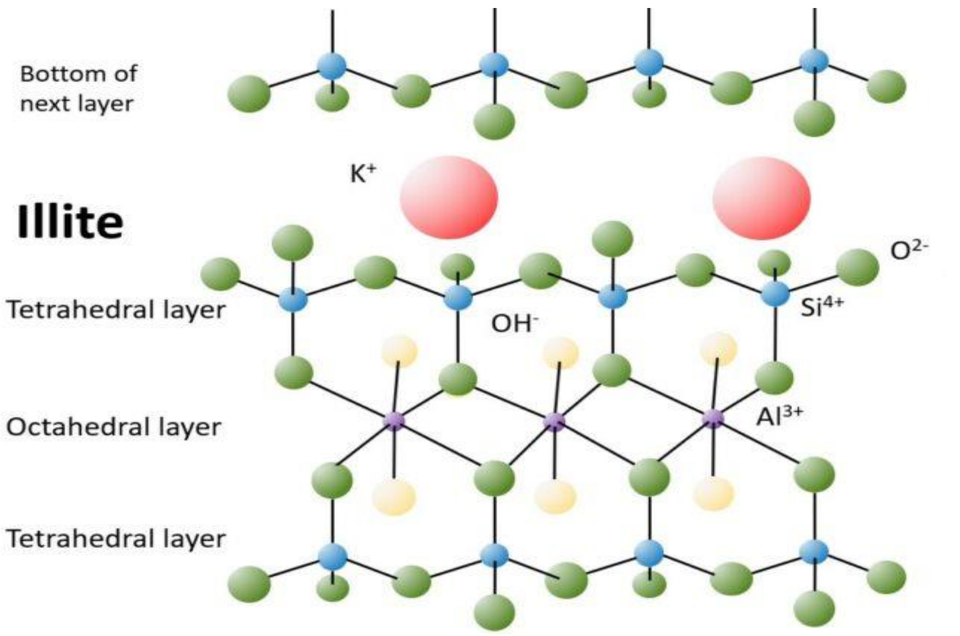


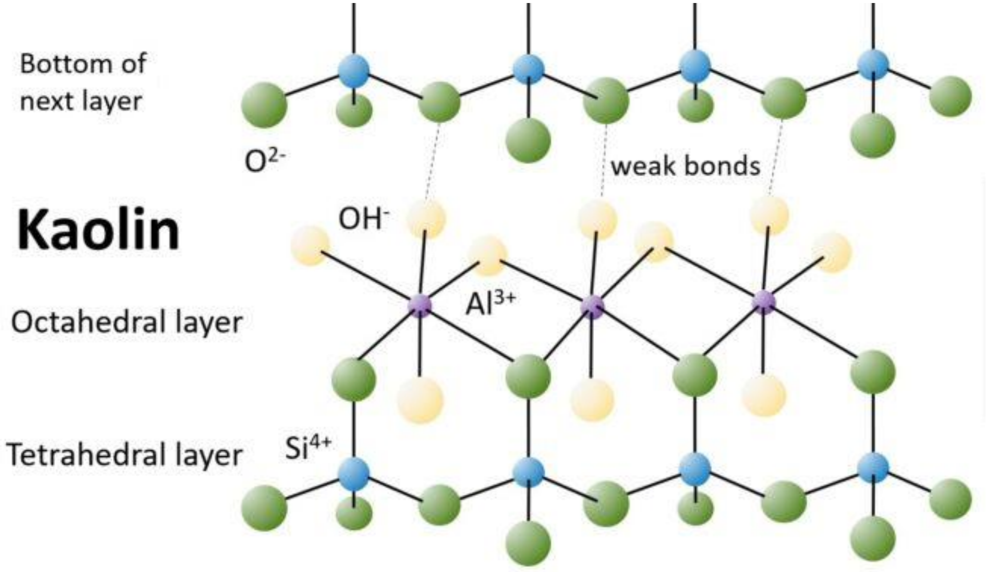
Clay as SCM :-

- Clay are basically layered type of structures.
- There are three types of clays minerals :
  - Illite (2:1) :-
    - Also called as Micas.

  - Montmorillonite (2:1) :-
    - Known as Sonetites.
    - The intermediate layer could be of Aluminate ions.
  - Kaolinte (1:1) :-
    - Most available form of clay.
- These clay minerals are then calcined.

(Heated at high temperatures)





- Calcination of clay:-
  - The clay is found to be most reactive at the temperature ~800 °C.
  - At 850 °C the effect of coarsening/sintering/rearrangement happens thus decreasing the reactivity thereafter.
- The combination of Calcined Clay + Limestone allows high level of klinker substitution.
- Kaolintic clay shows high pozzolanic acitivtiy after calcinations.
- Optimum range of calcination of clay is (750 °C ~ 850 °C).

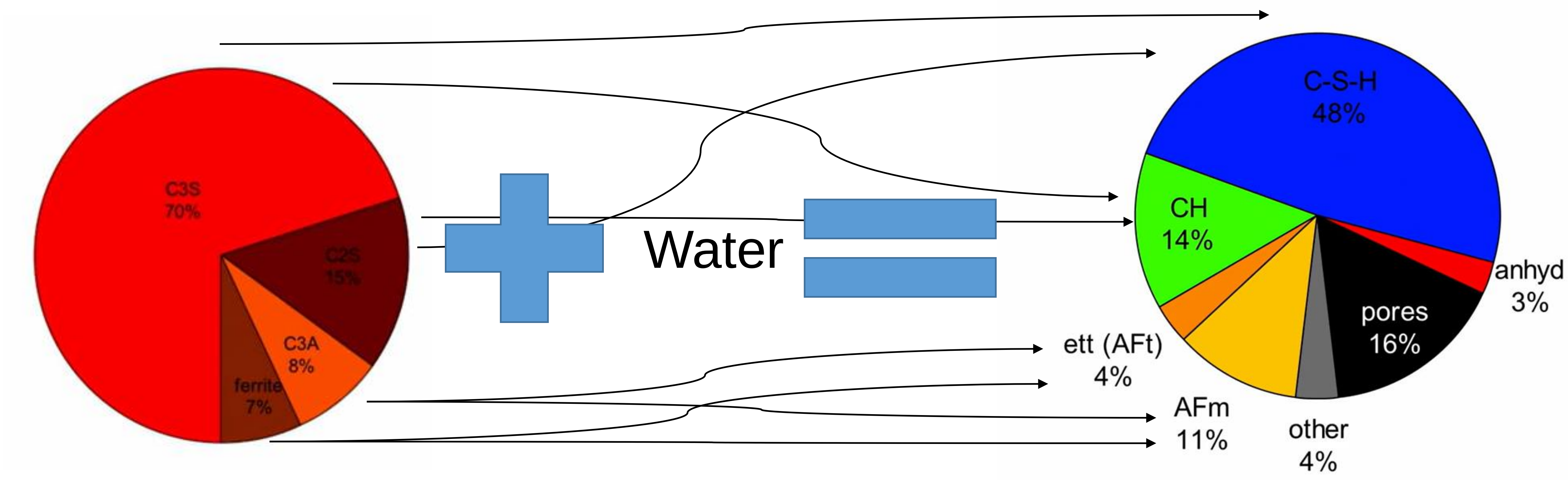
2. Hydration process of Cement

- In this section we will consider the Hydration process of the cement.
- Hydration of cement refers to the action done on the cement by the water that is added to the cement.
- This cement reacts with water and forms hydrates.
- We will use the notations defined in Cement chemistry which can be referred in this slide.
- In reference to the same slide , it is known to us the main 4 phases of cement.

- Filling of spaces dictates the development of the properties of the cement which is related to volume.
- Generally, $(W/C)_{wt.}$ of cement = 0.5

  = 0.5 gm of Water/ 1 gm of Cement
- Since we know that $\rho_{water} = 1\ (gm/cm^3)$ and $\rho_{cement} = 3\ (gm/cm^3)$.
- Thus, this translates that 60% of water and 40% of cement is present during hydration of cement as per volumetric dimension.
- Now after hydration, we have 80% hydrates and remaining 20% of water as pores. These hydrates gives the adhesiveness, strength and bridges the gap between grains and the water.

Hydration process in a nutshell



Composition of cement before the hydration process

Composition of cement after the hydration process

- The phases of cement such as Alite ,Belite ,Aluminates and Ferrites dissolves in the water, then they form these different ions like

  Ca^{2+} , $H_2SiO_4{}^{2-}$, $Al(OH)_4$, OH^- , $SO_4{}^{2-}$

- Then these ions combine in different proportions to give us the hydrate phases.

Results :-

- Silicates C_3S and C_2S forms Calcium Hydroxide and C-S-H.
- Aluminate and Ferrite forms the AFm and the AFt phases.

Structure of Hydrated products:-

- *CSH :-*
- Calcium Silicate Hydrate (C_x-S_x-H_x ratio not defined)
- Nano Crystal
- Multiple morphologies
- ~50-60% of the hydrated product

1. Atomic Structure-

- Analyzed through Silicone NMR
- Ca/Si ratio = 0.7-1.5 for Synthetic C-S-H

- The structure of C-S-H resembles Tobermorite (natural mineral found in Scotland).
  - Layers of Ca-O in series on both sides.
  - On these layers we have tetrahedral of $Si\text{-}O_2$ (Silicates) in chain.
  - Silicone being in the centre.
  - Oxygen surrounds it in Tetrahedral shape.
  - Interlayer – which contains water & calcium ions or alkaline ions.

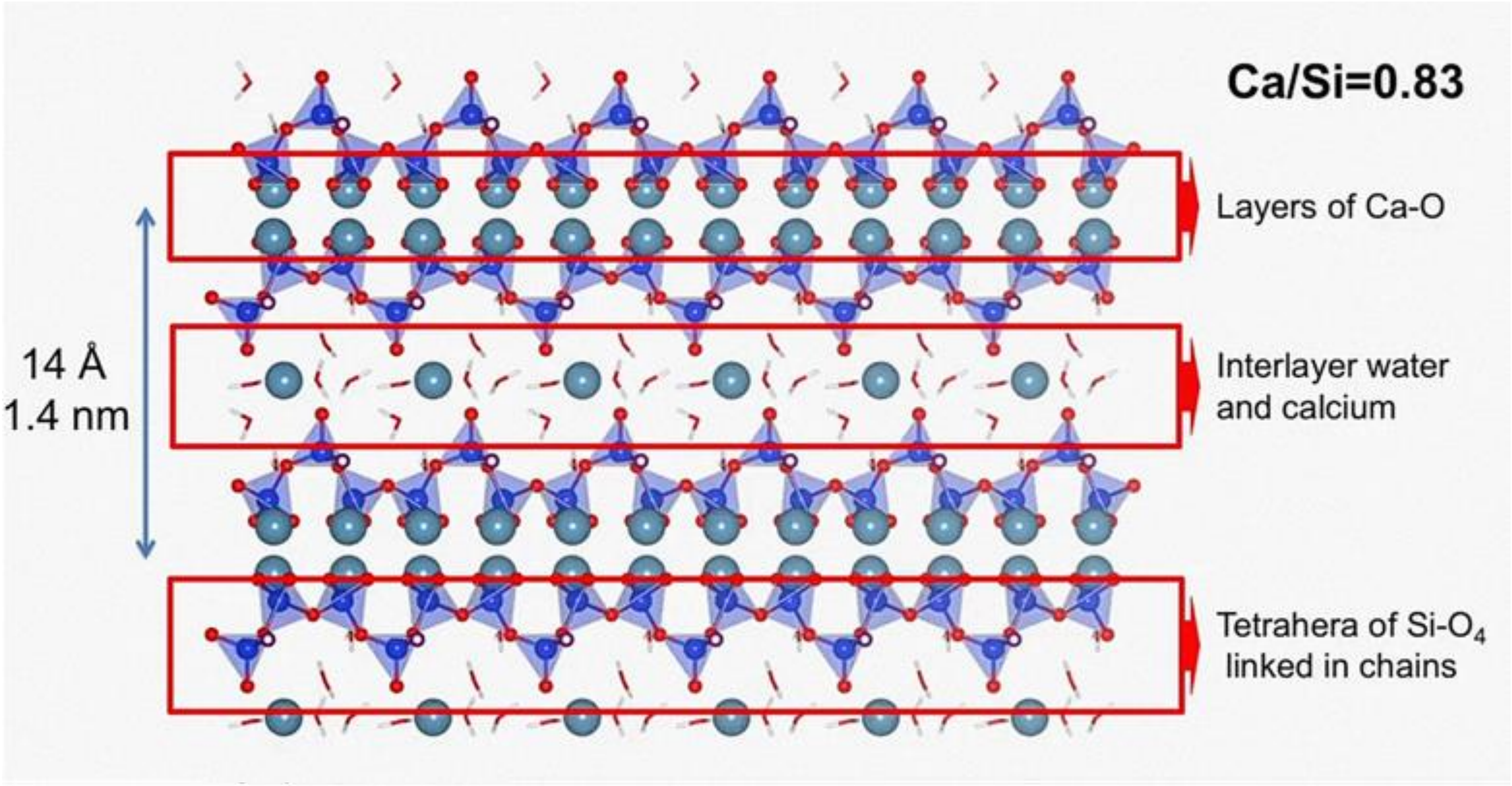


Fig – Structure of C-S-H (based on tobermorite)

Ways to vary C/Si ratio (to make artificial CSH) :-

- 1) Missing bridging tetrahedral – (defects)
  - Full chains of silicone hydroxides are removed. Ca/Si becomes 0.9
- 2) Calcium replacing two terminating hydroxides –
  - The hydrogen in hydroxide ions in the full chain is replaced by one calcium. Ca/Si becomes 1.38
- 3) Calcium ions in interlayer – (addictives)
  - The interlayer of tobermorite is added w/ calcium ions. Ca/Si becomes 1.5

- Combination of these three methods is defect & addictive mechanism.
- Structure has random organization of these defects.

- ***Meso Structure of C-S-H :-***

1)

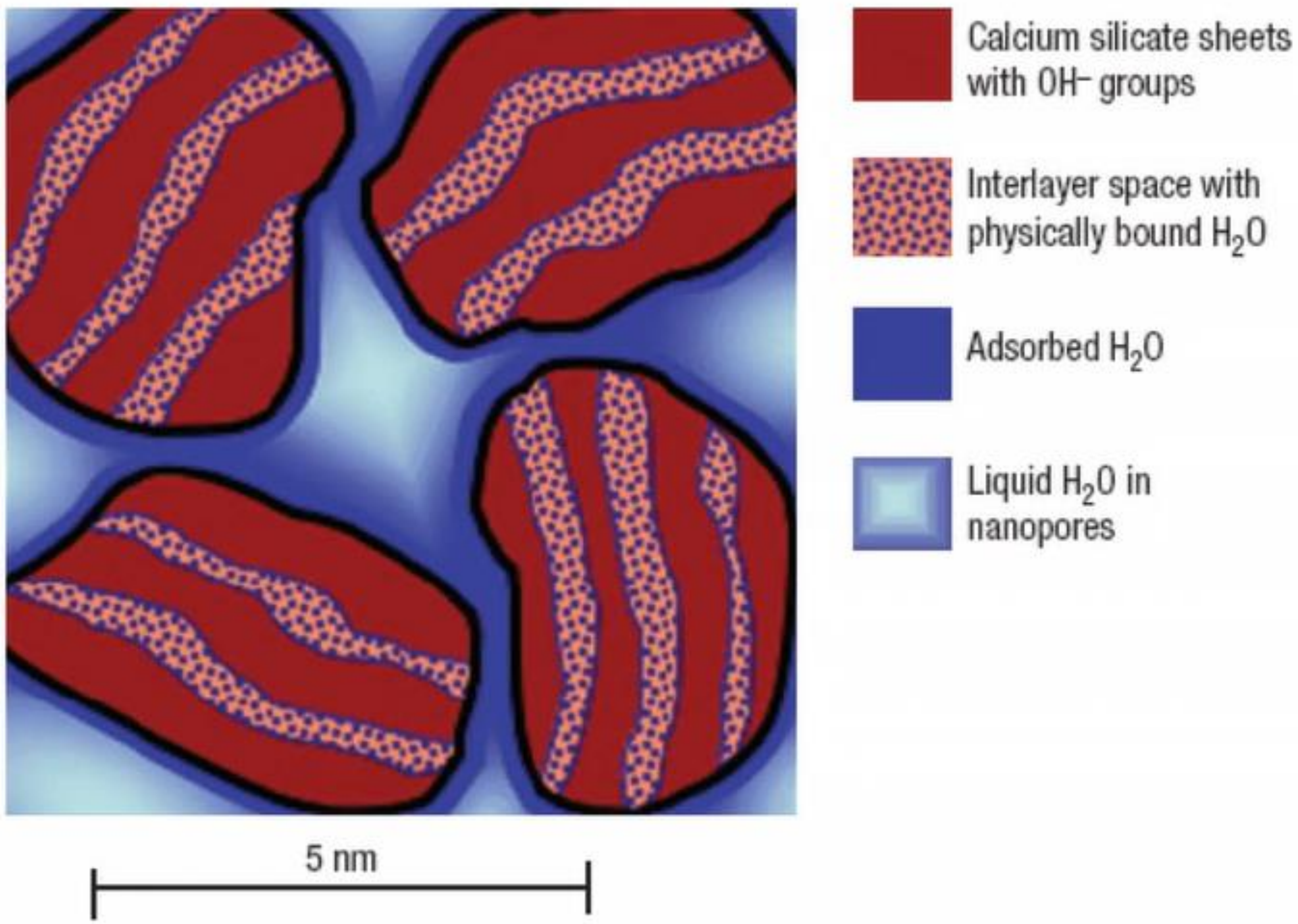


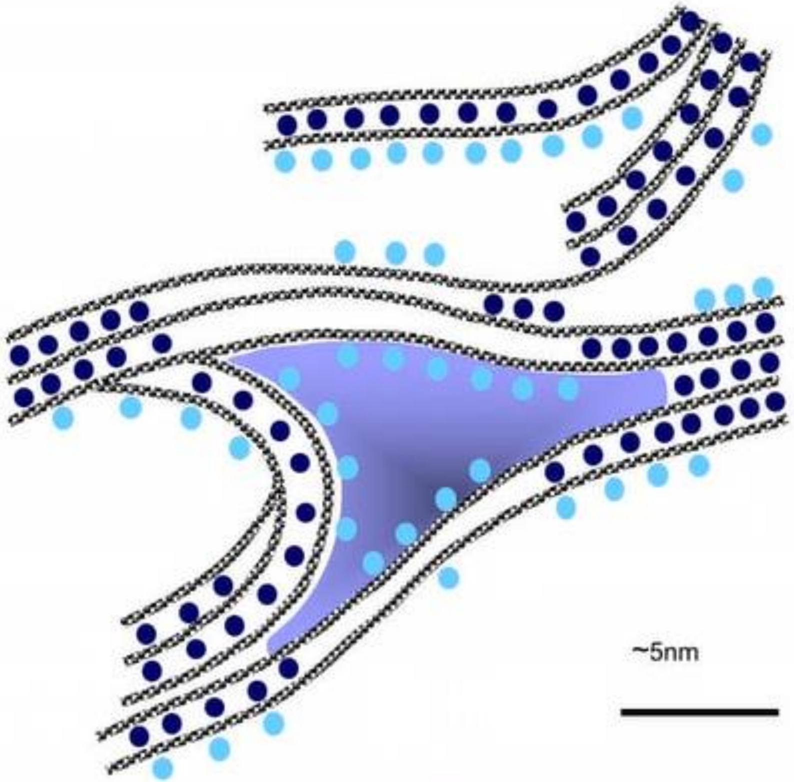
Fig:- Jenning's model
Colloidal model of CSH

Little areas of CSH are discrete particles which are not linked together.

And these discrete nanoparticles are made up of 4-5 layers of the CSH.

2)

Fig :- Feldman-Serada model
Sheet's model



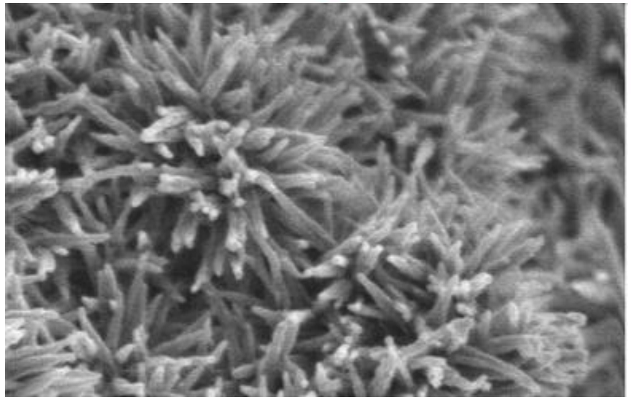
In this model we have nanocrystalline regions where

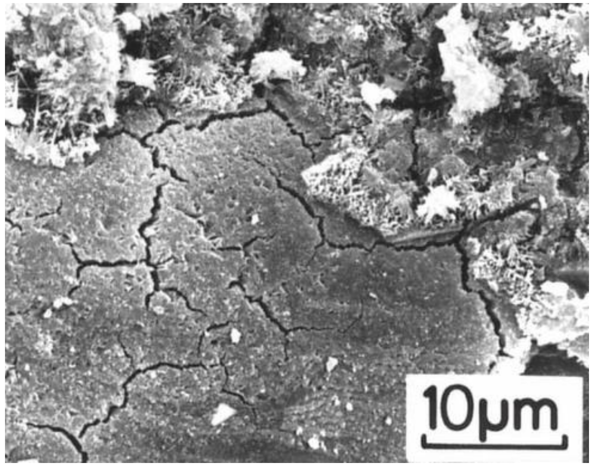
the layers of CSH are aligned these layers extend from one nanocrystalline region to another.

Microstructure :-

Early/Outer
Late/Inner

High density/Low density





Calcium aluminate hydrates :-

In hydrated products composition , we can see that

CSH + CH ≡ 65%

And AFm + AFt ≡ 20~25% (Which is 1/4th volume of total hydrated products.

Aluminate Hydrates in **hydration** can be described in :-

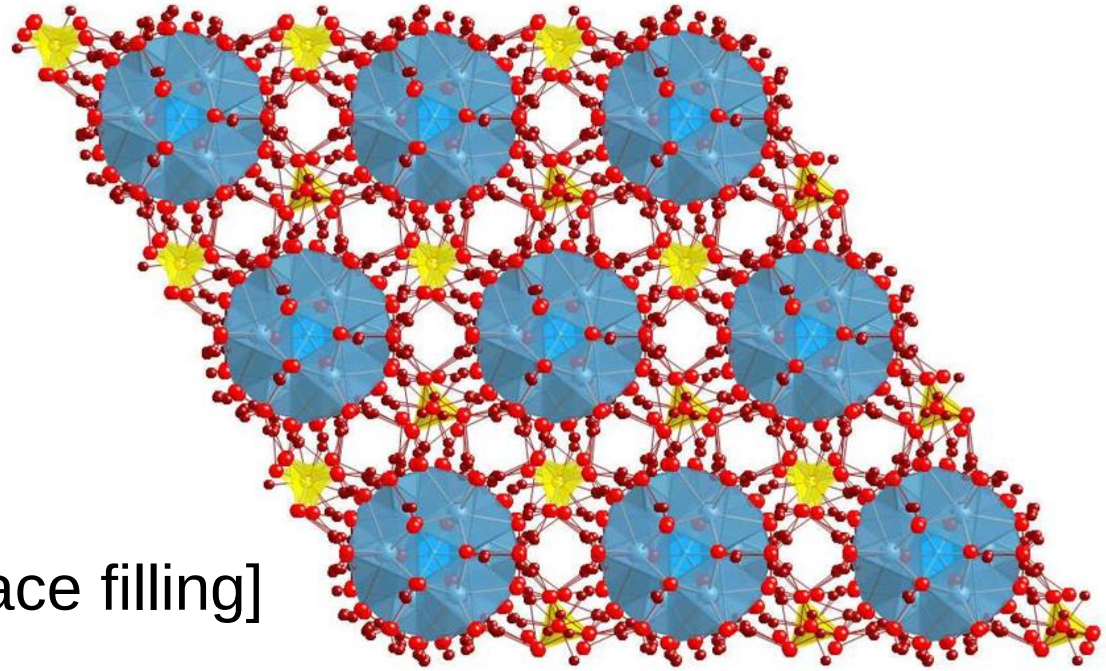
- 1. AFt [Aluminate Ferrite Tri] :-
    - Ettringite ($C_3A.3CS.H_{32}$)
- 2. AFm [Aluminate Ferrite Mono]
- 3. Hydrogarnets

Ettringite or AFt phase:-

- AFt = Aluminate Ferrite Tri ➔ which means Aluminate or Ferrite ions
- $[Ca_3(Al/Fe)(OH)_6.12H_2O]_2.X_3.\,x\ H_2O$
  - X is a divalent anion
- It has crystal structure.
- It forms early during hydration.
- It may form later depending on

the sulfate and CO_3 activity.

- High water content
- Low density ($1.8/cm^3$) [Good space filling]

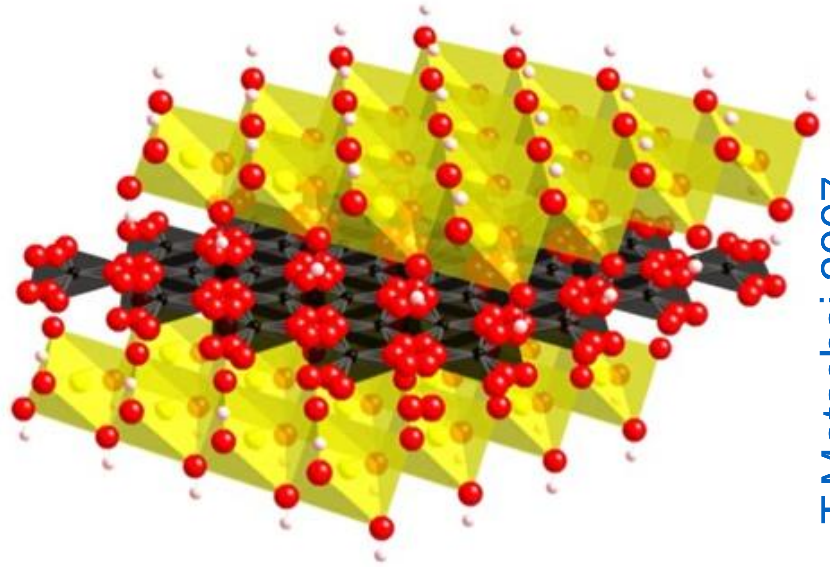


(Hartman & Berliner, 2006)

AFM phases : Subset of Layered double hydroxides

- LDH – hydrotalcite supergroup nomenclature
- Part of larger group of hydrates.
- Layers of M^2 & M^3 ions and between the layers OH^{-1} anions.
- 8 groups within this LDH supergroup :-
  - Hydrotalice group (M^{2+}:M^{3+} =3:1)
  - Quintinite group (M^{2+}:M^{3+} =2:1)
  - *Hydrocalumite group*

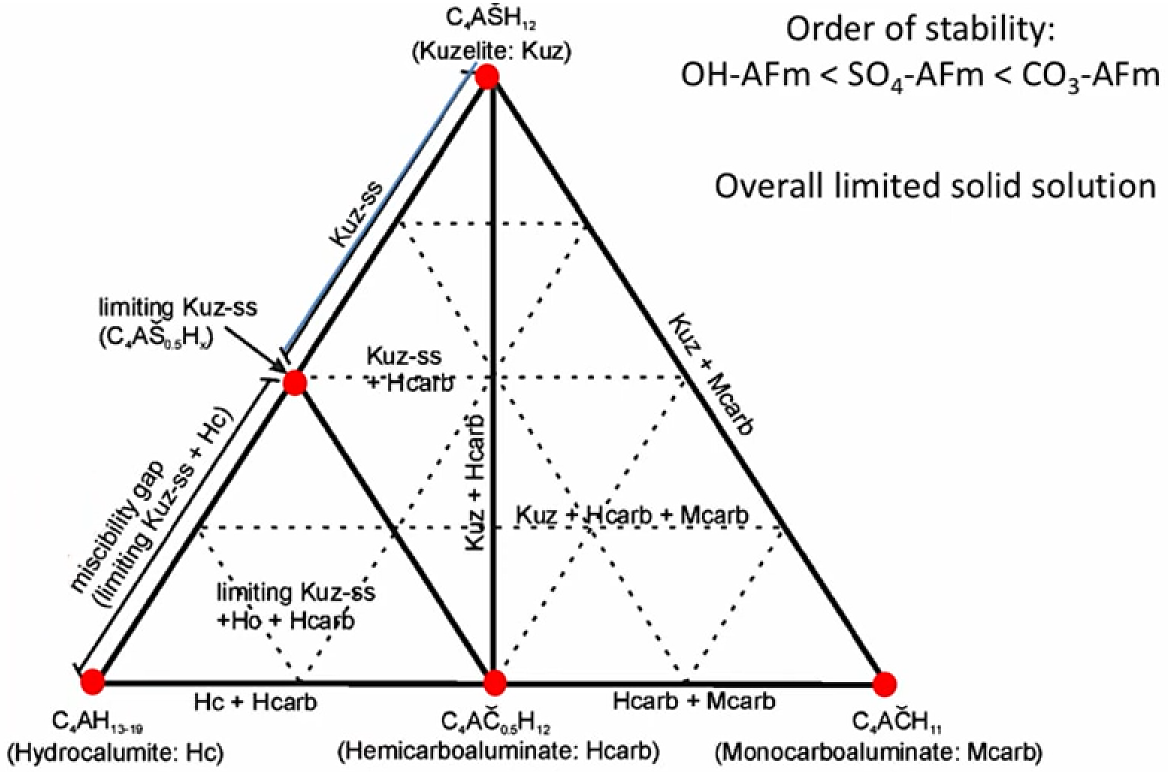
    (M^2 =Ca^{2+} ,M^3=Al^{3+}, Ca:Al = 2:1)



T.Matschei 2007

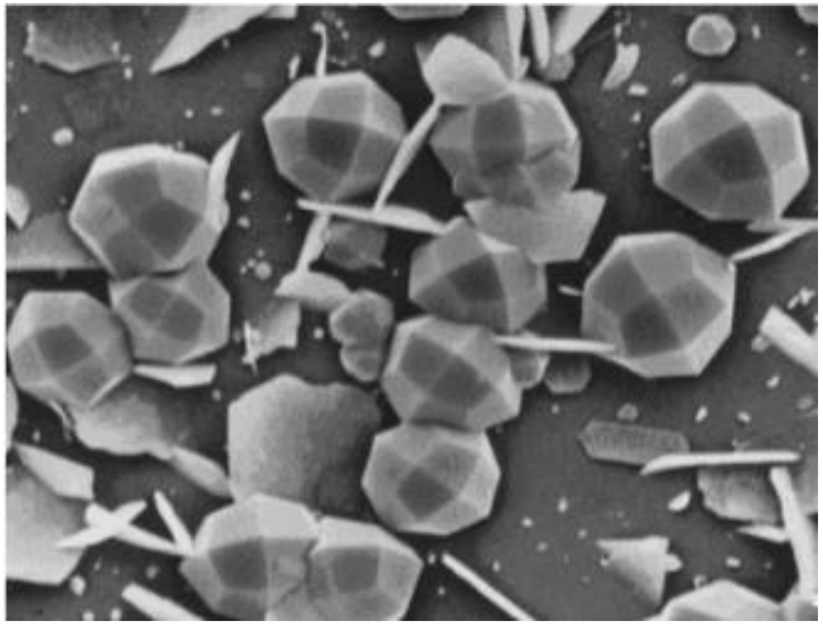
AFm Solid Solutions

- Solid solutions are possible if the subtitutable ions have:
  - Similar charge,size or geometry



Hydrogarnets

- C_3AH_6 : katoite
- $C_3(A,F)S_xH_{6-2x}$: siliceous hydrogarnet
- Solid solutions
  - $Al^{3+} \leftrightarrow Fe^{3+}$
  - $SiO_2^0 \leftrightarrow 2\ H_2O$
- Low water content
  - **High density**: 2.5 g/cm3
  - Less space filling



Kinetics of Hydration **:-**

- **Why Study Kinetics of Hydration?**
  - Controls early strength development
  - Influences workability, setting time, and durability
  - Critical for optimizing admixtures and curing conditions
- **Phases of Hydration:**
  - Initial Reaction (Pre-induction)
  - Induction/Introduction Period
  - Acceleration
  - Deceleration
  - Steady-State or Diffusion-Controlled Phase

Introduction Period :-

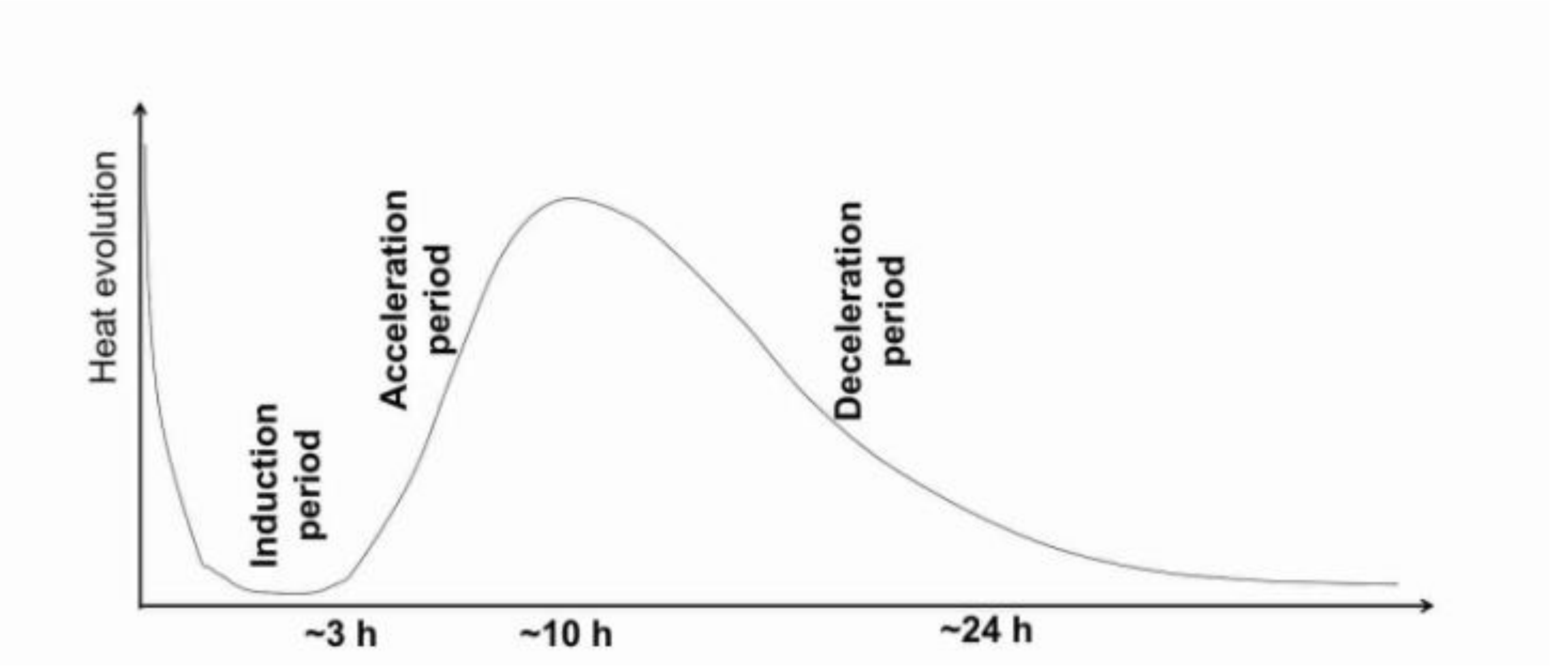
- The **induction period** is a slow reaction phase after initial cement-water contact (first few hours).
- Hydration reactions temporarily slow down before accelerating.
- Formation of a **protective gel layer** (ettringite & C-S-H) around cement grains.
- **Supersaturation** of ions (Ca^{2+}, OH^{-}) delays further dissolution.
- This determines **workability time** (critical for concrete placement).
- Ends when **accelerated hydration** begins (setting starts).

- (insert graph)

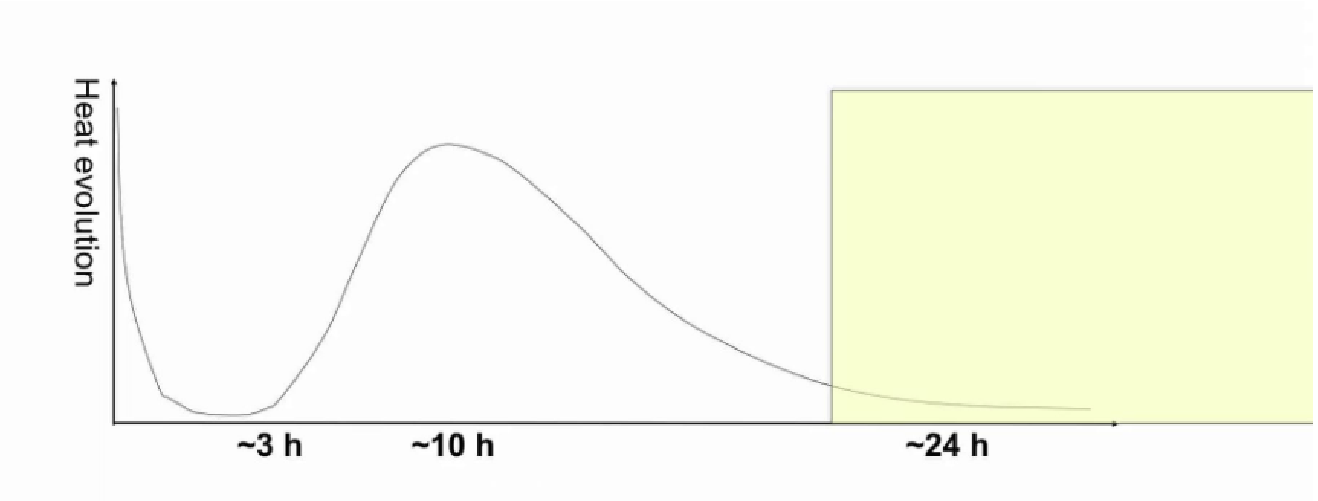
Main theories of Hydration Kinetics

- 1. Protective Layer Theory **(Le Chatelier, 1882)**
  - A semi-permeable barrier forms on cement grains, slowing water penetration.
  - Later disrupted by osmotic pressure or crystallization forces.
- 2. Delayed Nucleation Theory **(Stein & Stevels, 1960s)**
  - Slow initial nucleation of C-S-H due to low supersaturation.
  - Acceleration occurs once critical nuclei density is reached.
- 3. Electrochemical Theory **(Powers & Brownyard, 1940s)**
  - Focuses on ionic diffusion and charge barriers.
  - Hydration resumes when the electrical double layer breaks down.

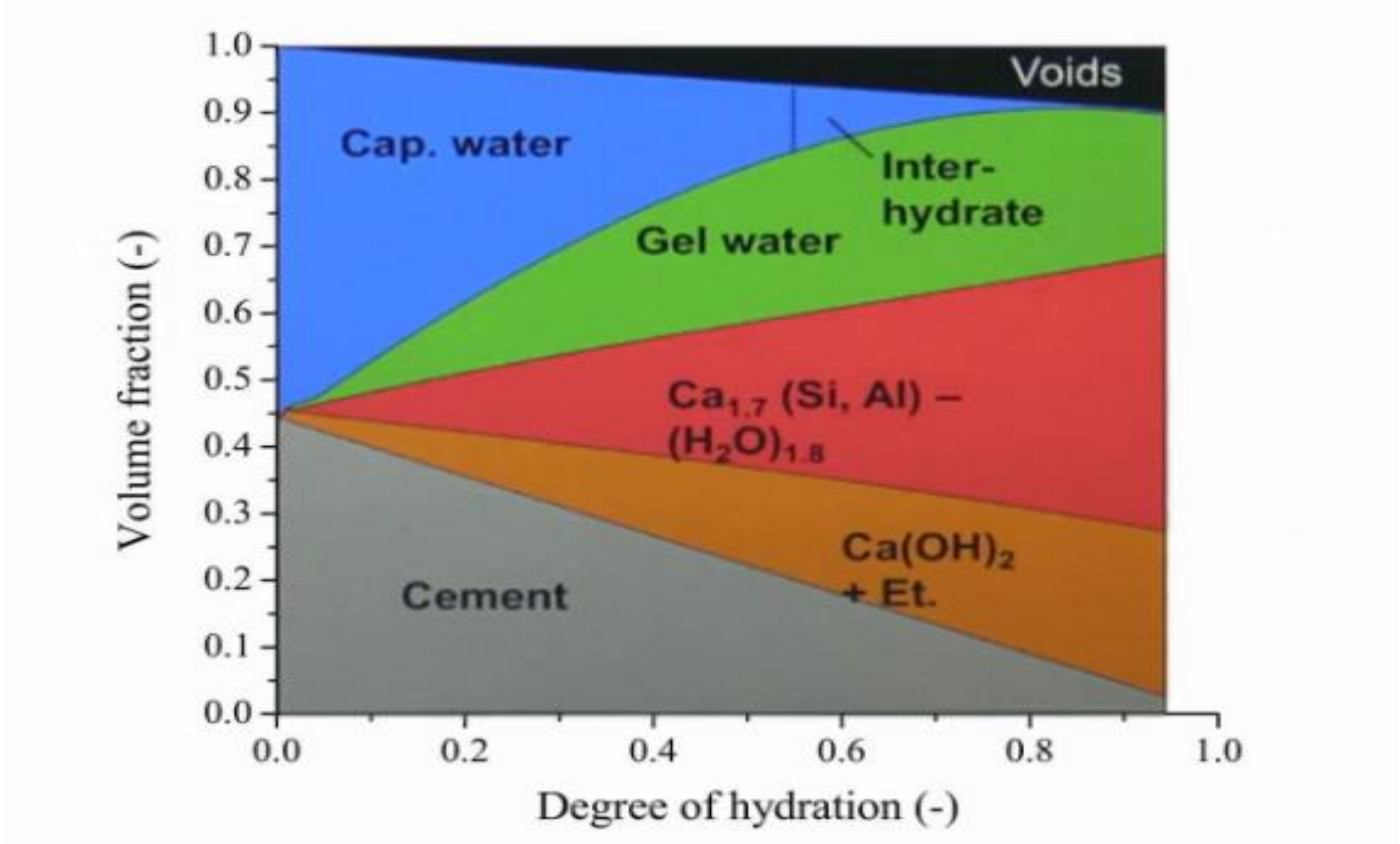
- Hydration curve
- Three major periods.
  - Induction Period
    - (Heat generated, slows down because of formation of protective membrane.
  - Main Hydration Peak
    - Effected by majorly Nucleation and then the growth of CSH.
    - Peak can be predicted by Avrami Equation or Mic model.



- After the main peak
  - Water evolves later here.
  - Capillary pores formation slows down.
  - In the longer term, space fillin -g plays an important role up to a few days.
  - Densification of C-S-H is obse- rved over time.
  - Very slow kinetics after a few days of this period (III).

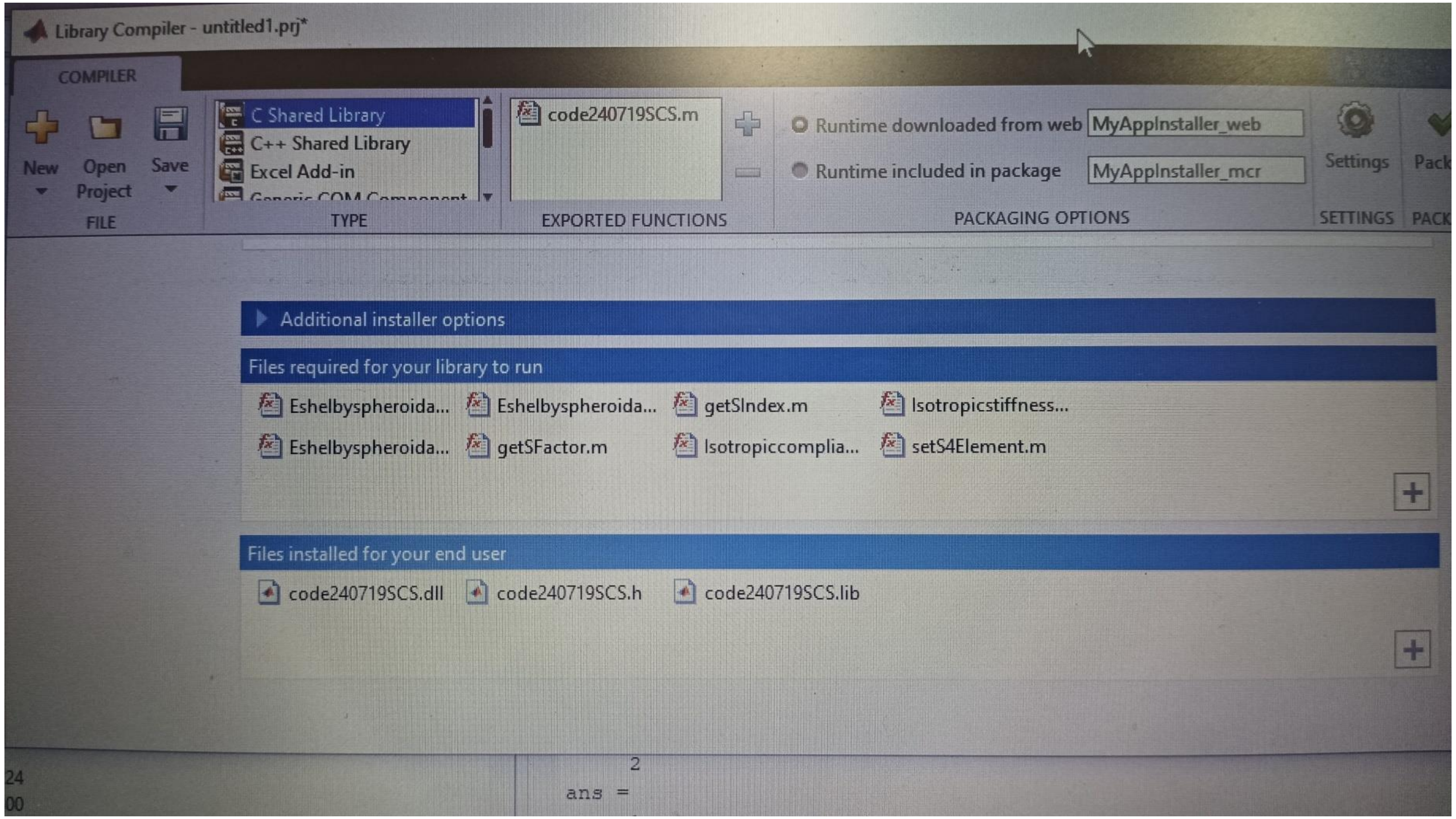


- Pictorial representation of Degree of hydration and Volume fraction :-



Python Interface for MATLAB Program:-

- During the Internship, I also made a Python interface for MATLAB Program.
- Cause :-
  - Since MATLAB is a paid software, it is not possible for every researcher to have this program onboard. But, Python is an open source program and very fast when compared with MATLAB.
  - Although, writing a program from scratch might be an option, but MATLAB provides an "add on" which facilitates users to share there programs with wider audience, without sharing the actual code and MATLAB.
  - This add on (MATLAB Compiler SDK), turns the MATLAB code into a Python/C++ script, whichever is desirable.



All these files are requirement, and this is the Add On (Matlab Compiler SDK) which helps to convert, all these dependent files and convert it into an runable Python Script (on MATLAB Runtime Compiler).

- Now this script, can be edited, and manipulated to complete it’s task. In my case, I used **Pandas** for data Input - Output, **Matplotlib** for plotting the graph & **Numpy** for numerical operations.
- Further you can publish this, which will leave you with 3 following files:

Name	Size	Packed	Type	Modified	CRC32
..			File folder		
ConcreepPython.py	5,828	1,934	Python File	01-08-2024 06:...	FAA1AC...
MCR.exe	7,848,448	1,178,531	Application	31-07-2024 08:...	761C3E51
Readme.txt	1,126	653	Text Document	01-08-2024 05:...	8834F87B

- Go the MCR which is **MATLAB Compiler Runtime** (it’s a completely free software provided by MATLAB , **R_2023_B** version specifically).
- Add the MCR win32/64 to the PATH directory and then run the code. [For Example :- C:\Program Files\MATLAB Runtime\R2023b\runtime\win64]

- Install the setup.py file which will be installed with MCR.exe
- Execute the script, ConcreepPython.py with required data set.

```
5. Variables in order=
        1.Tstart
        2.Tmin
        3.Tmax
        4.b_power
        5.b_log
        6.nu_matrix
        7.V_capillary
        8.V_c3s
        9.V_c2s
        10.V_c3a
        11.V_c4af
        12.V_gypsum
        13.V_port
        14.V_ettr
        15.V_ms
        16.V_FH3
        17.V_hydrogarnet
        18.V_mc
        19.V_hc
        20.V_calcite
        21.V_AS2
        22.V_csh
```

data - Notepad

File Edit Format View Help

```
Tstart=0
Tmin=0.001
Tmax=30
b_power=20
b_log=10
nu_matrix=0.24
V_capillary=0.5
v_c3s=0.0560
v_c2s=0.0196
v_c3a=0.0118
v_c4af=0.0261
v_gypsum=0.4011
v_port=0.56472
v_ettr=0.0255
v_ms=0.0567
v_fh3=0.0000
v_hydrogarnet=0.0188
v_hc=0.0000
v_mc=0.0000
v_calcite=0.0066
v_as2=0.000013
v_csh=0.4573
```

Sample data.

• The script will run, and return an JPEG image, of the graph and an Excel file which contains the plotting points.