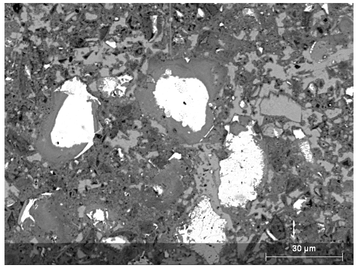


Part 2: Hydration: Overview and hydrates

Cement Chemistry and Sustainable Cementitious Materials

Professor Karen Scrivener, FREng

1

Cement chemistry: Nomenclature

As cement is composed of oxides a particular notation is used to shorten chemical formulae

Calcium oxide or lime:	$CaO = C$
Silicon dioxide or silica:	$SiO_2 = S$
Aluminium oxide or alumina:	$Al_2O_3 = A$
Iron oxide:	$Fe_2O_3 = F$
"sulfate":	$SO_3 = \bar{S}$ or $\$$
Water:	$H_2O = H$

2

Examples

Tricalcium silicate or alite: $Ca_3SiO_5 = C_3S$

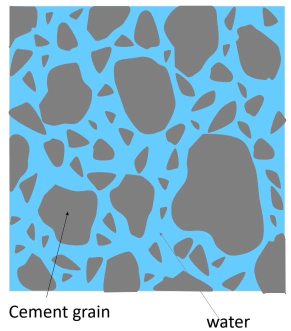
Ye'elimite: $Ca_4Al_6SO_{16} = C_4A_3\$$

Calcium silicate hydrate: $Ca_XSiH_YO_{(X+2+Y)} = C\text{-}S\text{-}H$

Hyphens indicate variable ratios of lime silica and water

3

How cement works:

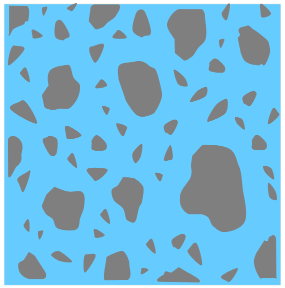


We mix the grey cement powder with water.

To start with the grains are just floating about in the water and we can cast the concrete into moulds

4

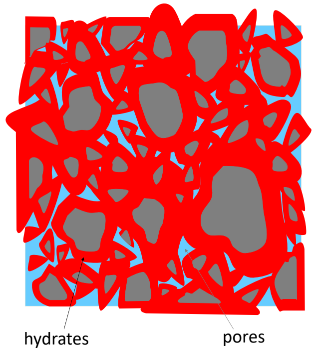
How cement works:



The cement grains dissolve in the water

5

How cement works:

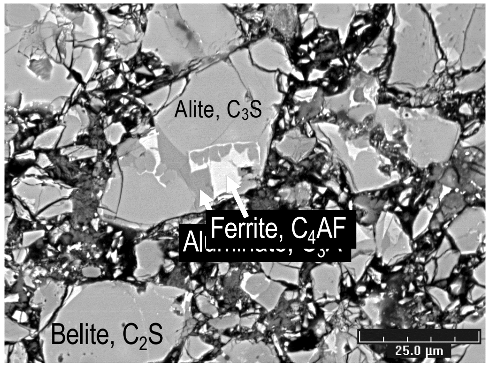


The cement grains dissolve in the water

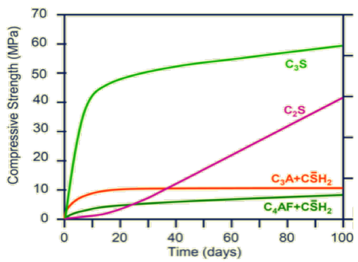
And then precipitate *Hydrates* – new solids which have higher volume and hold the grains together: creating a rigid solid

6

Real cement



- Rough, angular grains
- Multi phase grains
- 4 main phases



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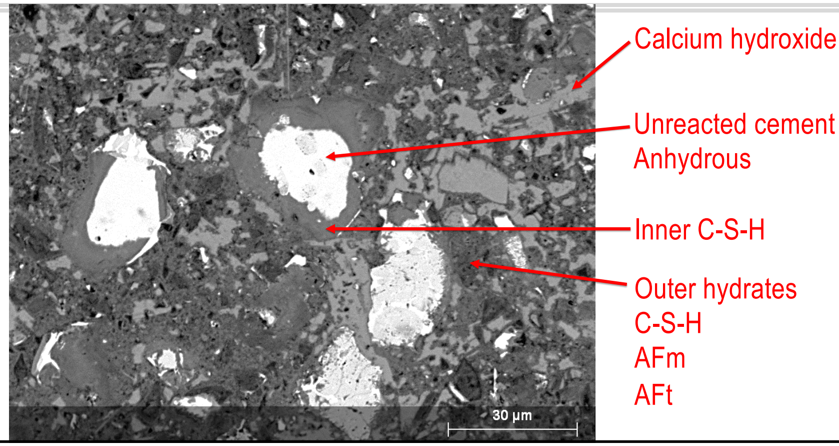
Hydrated cement paste



8

Volume changes are critical

The ratio between cement and water are usually expressed by weight
For example a typical water to cement ratio (w/c) for concrete is 0.5:
for each gram of cement 0.5 gram of water is added.

But the development of properties is controlled by
the filling of space related to volumes.

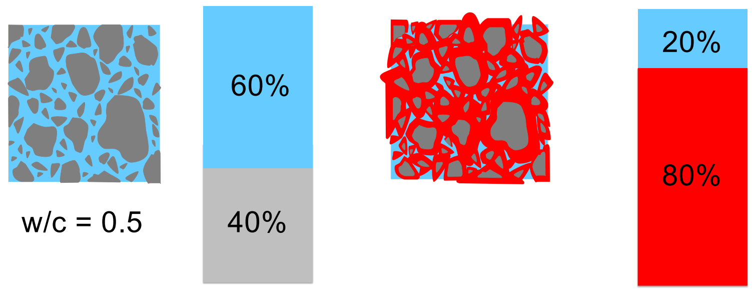
How does a w/c of 0.5 in weight translate into volumes?

Given the density of cement is around 3 (g/cm^3),
calculate the relative volumes of cement and water just after mixing.

9

Volume changes

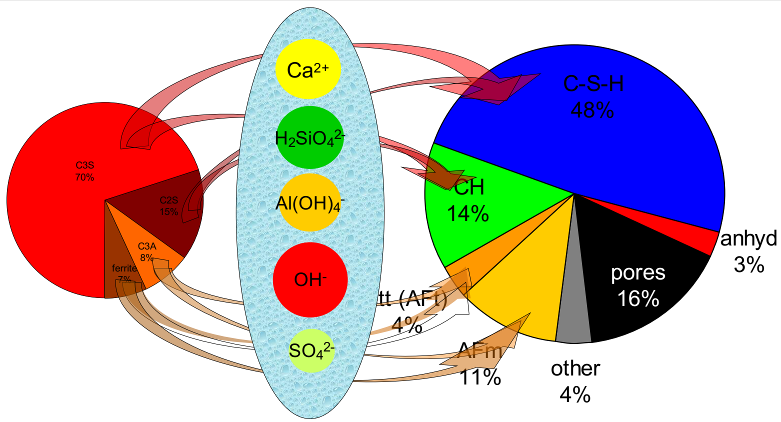
During hydration:
Solid volume doubles



100% hydration

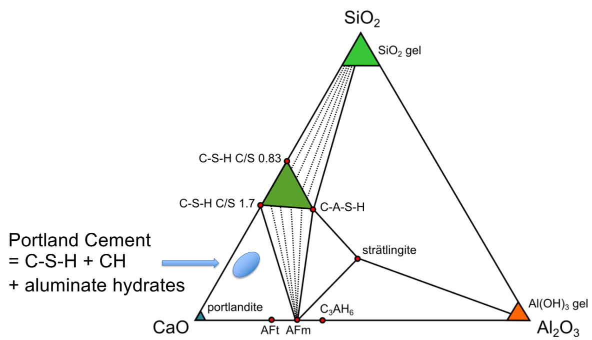
10

Phases present – mature paste



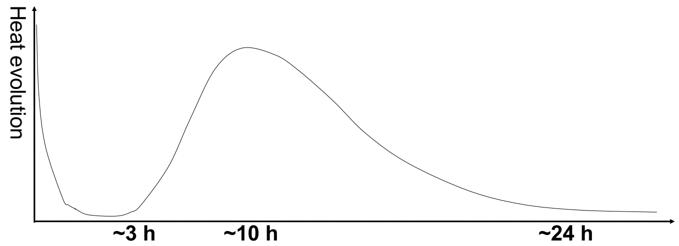
11

Hydrates overview



12

Kinetics of reaction



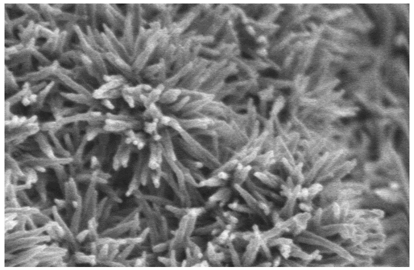
13

Summary

- Hydration involves reaction of cement with water
- This increases the volume of solid, bridging space between the grains and forming a solid
- Essential aspect is volume change
- Silcates: C_3S and C_2S form calcium hydroxide and C-S-H
- Aluminate and Ferrite lead to formation of AFt and AFm phases

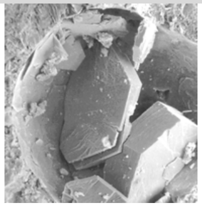
14

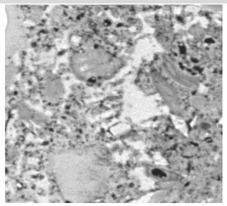
C-S-H



15

Hydration of calcium silicates : C_3S and C_2S

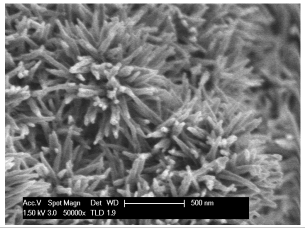




calcium hydroxide
Hydrated lime
portlandite
$Ca(OH)_2$
CH

} crystalline Hexagonal morphology

~ 10-20% of hydrated paste



calcium silicate hydrate
C-S-H

Nano crystalline
multiple morphologies

~ 50-65% of hydrated paste

16

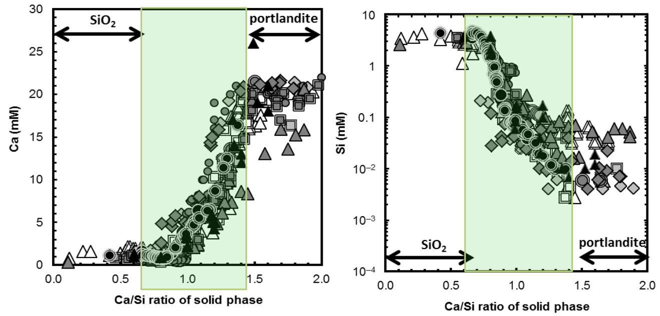
C-S-H

- "atomic" structure and composition
- "meso" structure
- "microstructure / morphology"

17

Definite phase, reproducible behaviour

Variable calcium to silicate ratio, depending on composition of solution



Ca/Si =
0.7 to 1.5
for "synthetic" C-S-H

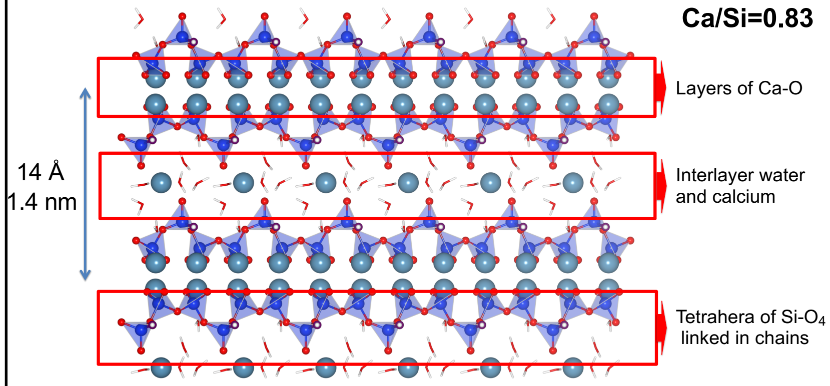
1.7-2 PC pastes

Lothenbach, Nonat (2015) CCR

18

Structure based on natural mineral tobermorite

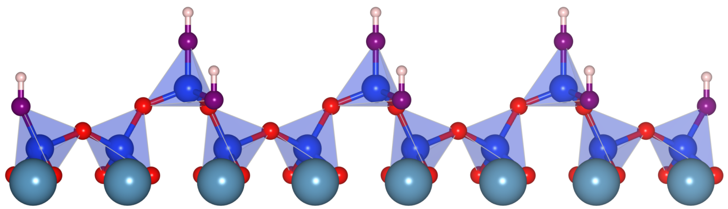
Ca/Si=0.83



Images by Aslam Kunhi Mohamed

19

Ways to vary C/S

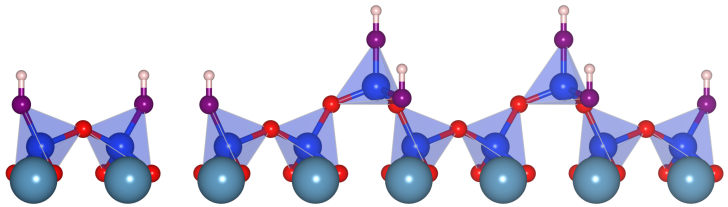


Ca/Si= 0.727

Full chains, terminating hydroxides

20

Ways to vary C/S

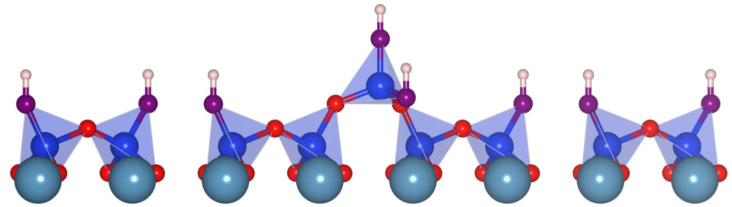


Ca/Si= 0.8

Missing bridging tetrahedra

21

Ways to vary C/S

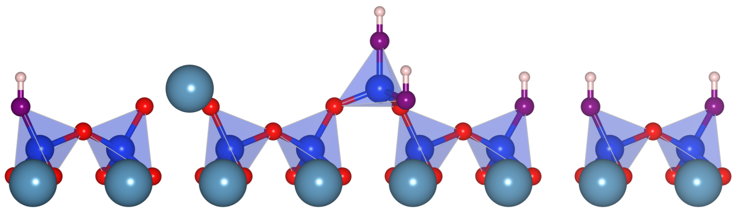


Ca/Si= 0.9

Missing bridging tetrahedra

22

Ways to vary C/S

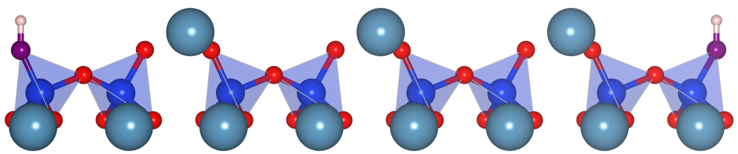


Ca/Si= 1.0

Calcium replacing two terminating hydroxides

23

Ways to vary C/S

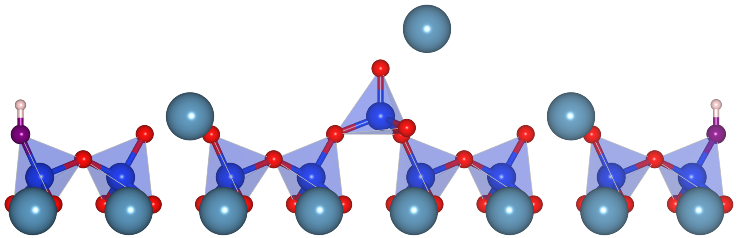


Ca/Si= 1.38

Calcium replacing two terminating hydroxides

24

Ways to vary C/S

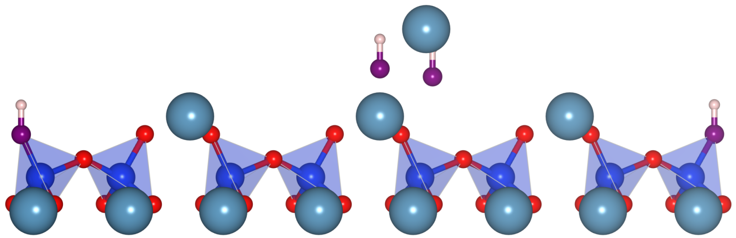


Ca/Si= 1.22

Calcium in interlayer

25

Ways to vary C/S



Ca/Si= 1.5

Calcium in interlayer

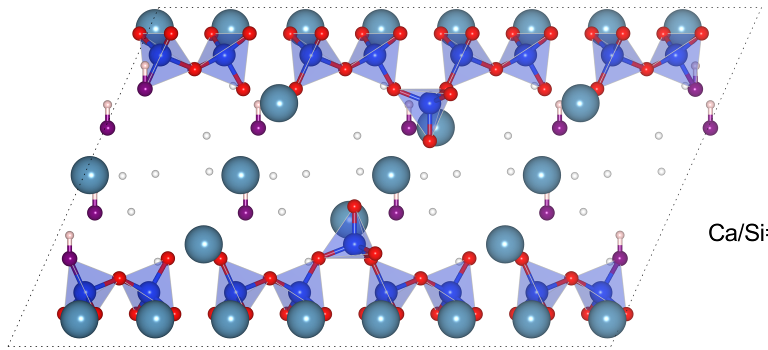
26

3 mechanisms

- Missing bridging tetrahedral
- Calcium replacing terminating hydroxides
- Calcium in interlayer

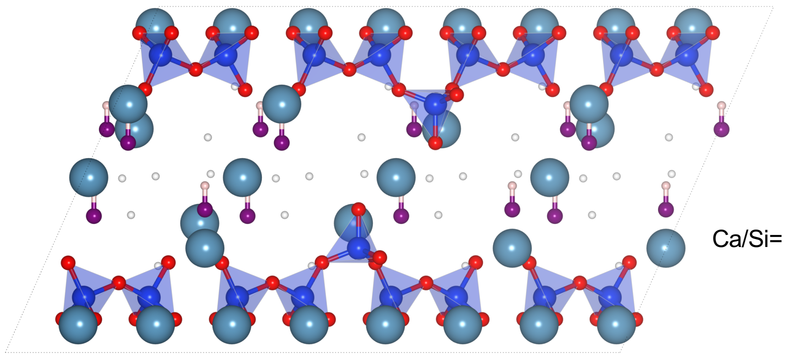
- No unique way to get a given C/S
- Structure probably has random organisation of these defects:
  - One reason for low crystallinity by X-rays

27



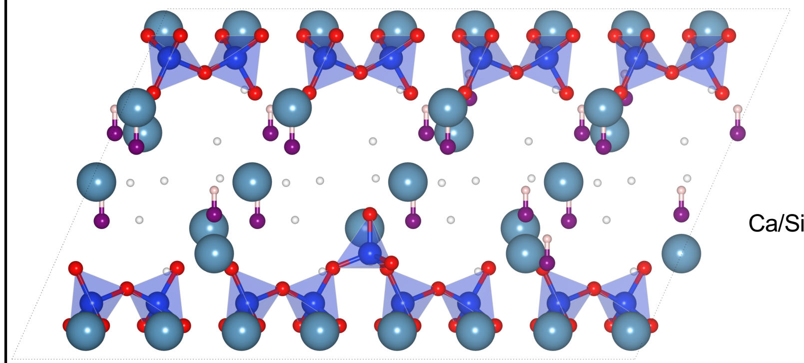
Ca/Si= 1.44

28



Ca/Si= 1.72

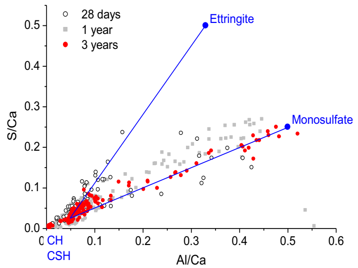
29

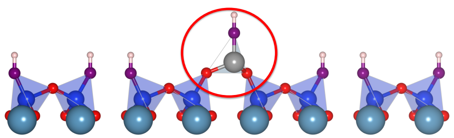


Ca/Si= 1.94

30

C-S-H: Si substitution by Al





OPC pastes: Al/Ca ~ 0.05; Al/Si ~ 0.1
Higher with Al rich SCMs

Location in bridging sites

31

C-S-H

- “atomic” structure and composition
- “meso” structure
- “microstructure / morphology”

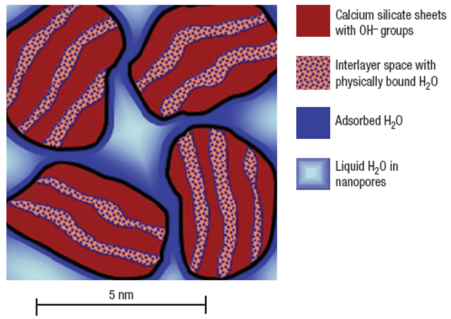
32

Experimental Evidence

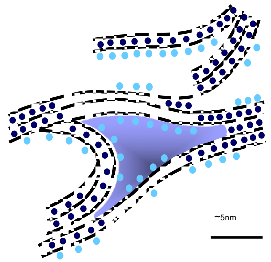
- No long range order
- "intrinsic" porosity of 26-28% (Powers)
  - "gel porosity"
  - Scattering experiments (neutron, X-ray) and proton NMR indicate "characteristic size" of about 4-5 nm

33

Two schools of thought



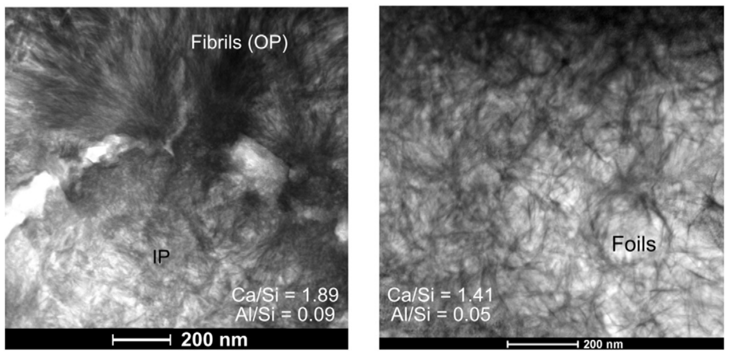
"Jennings" model
Discreet colloidal nanoparticles



"Feldman-Serada" model
Linked nanocrystalline regions

34

C-S-H in cements

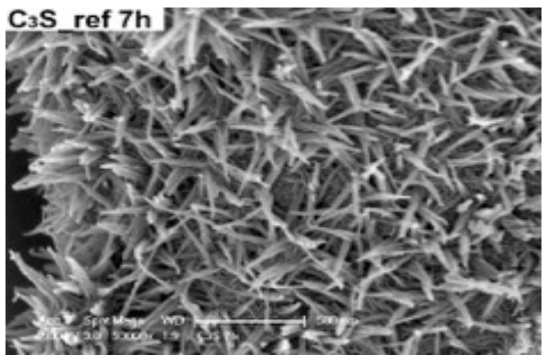


(a) Plain cement (PC), 90 days, 20°C
(b) PC 10SF, 90 days, 20°C

Rossen ea (2015) CCR 75

35

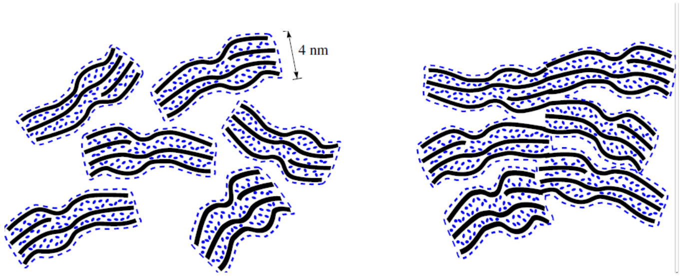
SEM morphology "needles"



36

Meso structure

- Two interpretations of nanocrystalline nature
- The main open question is whether they are discrete or linked by sheets



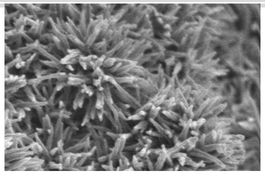
37

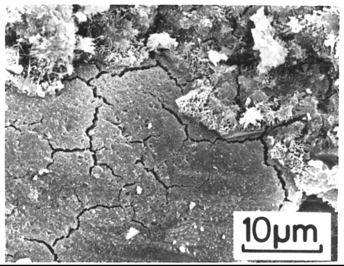
C-S-H

- “atomic” structure and composition
- “meso” structure
- “microstructure / morphology”

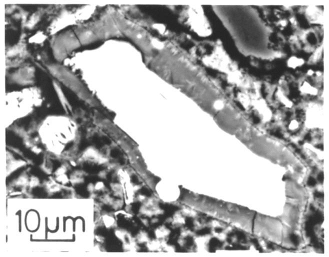
38

Two microstructurally distinct forms





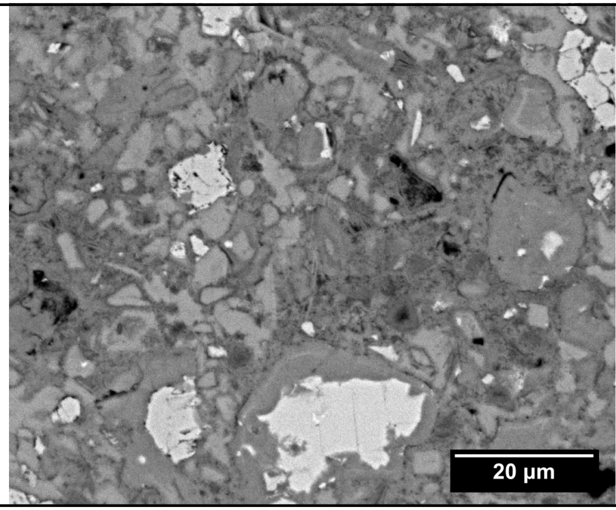
“Outer” or “early”
“inner” or “late”



Also “high density” and “low density”

Some debate as to whether this is analogous to inner and outer

39

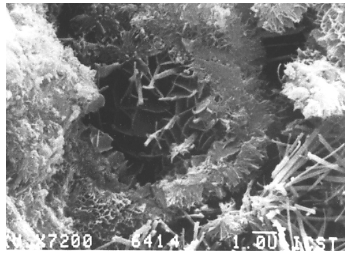


40

C-S-H summary

- Atomic level structure fairly well understood:
  - CaO sheets with chains (dimers) of SiO_4 tetrahedra attached
  - Al substitutes for Si, in bridging sites
- Meso level structure less clear
  - Nanocrystallites or nanocrystalline regions with characteristic scale of about 5nm
- Microstructure
  - Outer, formed early through solution
  - Inner formed later

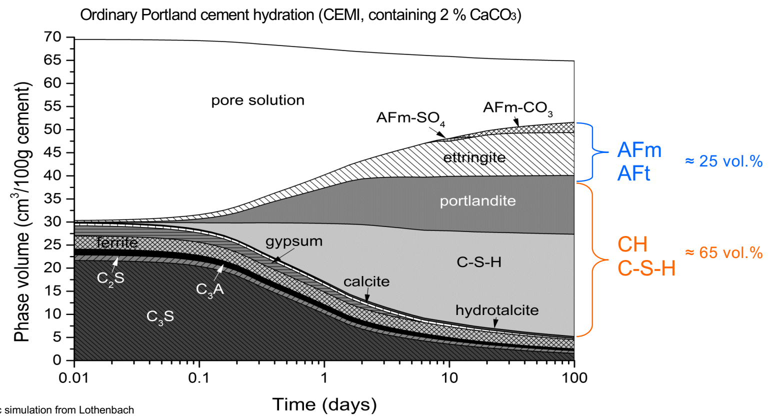
41



Aluminate Hydrates

42

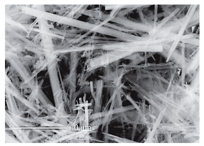
Aluminate hydrates make up a about ¼ of volume



Thermodynamic simulation from Lothenbach

43

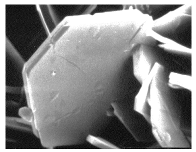
Calcium aluminate hydrates: overview



ettringite

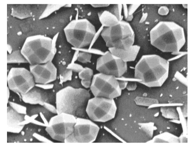
$C_3A.3C\$.H_{32}$

AFt – *aluminate ferrite tri*



AFm

aluminate ferrite mono

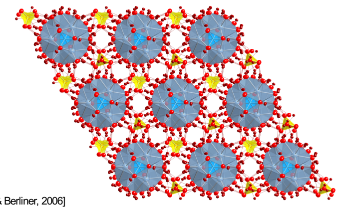


hydrogarnet

44

Ettringite or AFt phases

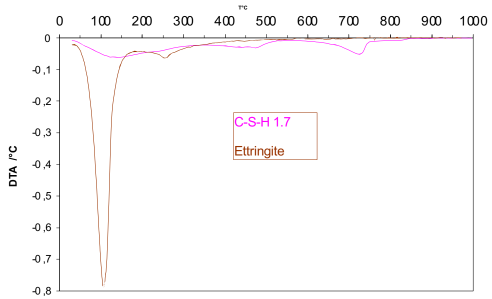
- $[Ca_3(Al,Fe)(OH)_6 \cdot 12H_2O]_2 \cdot X_3 \cdot xH_2O$
  - X is divalent anion
- Ettringite forms early on in blended cements
- Some may later transform into AFm phases depending on sulfate and carbonate activity
- No systematic changes in composition reported for blended cements
  - Solid solution between **(Al, Fe)**[6], miscibility gap 0.3<Al/(Al+Fe)<0.6 (Möschner et al., 2009)
  - Incomplete solid solution between **CO_3-SO_4**: ettringite stabilisation of AFt-CO_3 at low T (Matschei & Glasser, 2010)
- Ettringite
  - High water content
  - Low density: 1.8 g/cm^3
  - Good space filling



[Hartman & Berliner, 2006]

45

Decomposition of Ettringite and C-S-H in same range

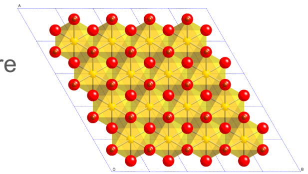


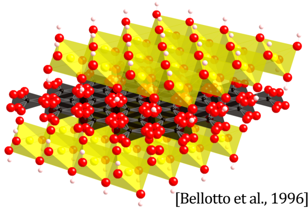
46

AFm phases: a subset of layered double hydroxides

- LDH – hydrotalcite supergroup nomenclature (Mills et al., IMA report 2012)
  - $[(M^{2+}_{1-x}M^{3+}_{x})(OH)_2]^{x+}$ layers
  - **Anions** in interlayer, stacking leads to **polytypism**
  - 8 groups within hydrotalcite supergroup
    - Hydrotalcite 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)**

AFm phases



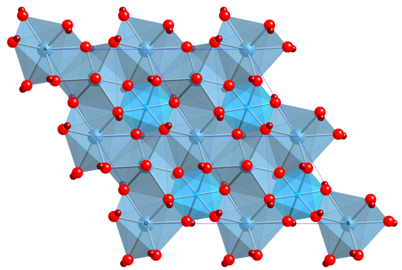


[Bellotto et al., 1996]

47

AFm phases

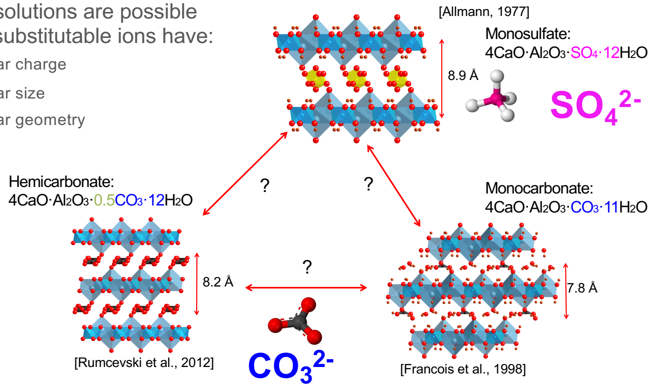
- LDH in cement: AFm phases
  - Main layer is a distorted brucite layer, Ca:Al 2:1
  - AFm-SO_4^{2-} – CO_3^{2-} – OH^-
  - What is extent of solid solution?



48

AFm solid solutions

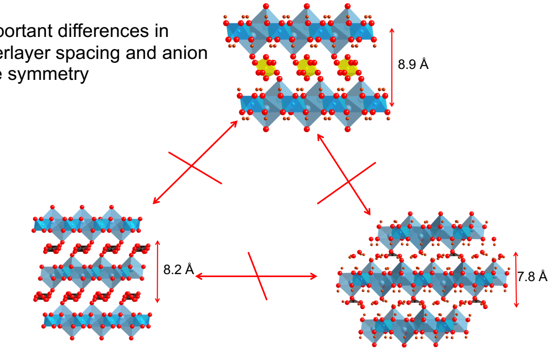
- Solid solutions are possible if the substitutable ions have:
  - Similar charge
  - Similar size
  - Similar geometry



49

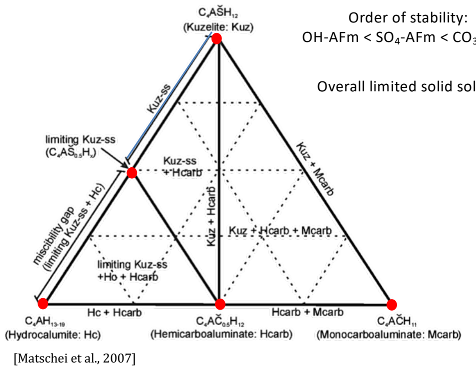
AFm solid solutions: SO_4-AFm – CO_3-AFm ?

Important differences in interlayer spacing and anion site symmetry



50

AFm phases: CO_3 – SO_4 – OH- phase diagram

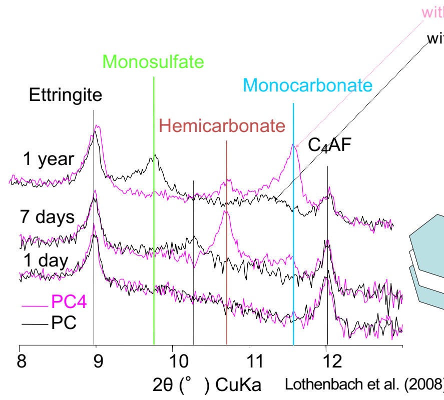


Order of stability:
OH-AFm < SO_4-AFm < CO_3-AFm

Overall limited solid solution

51

AFm phases: effect of limestone addition



Main difference: AFm phases

$[Ca_2(Al, Fe)(OH)_6]_2^{2+}$

Monosulfate $[SO_4, 6H_2O]^{2-}$

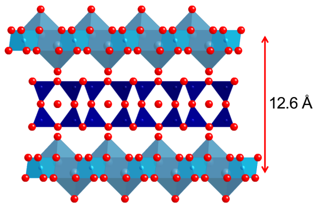
Monocarbonate $[CO_3, 5H_2O]^{2-}$

Hemicarbonate $[0.5CO_3, OH, 5.5H_2O]^{2-}$

52

Strätlingite

- Compositional solid solution
  - Strätlingite (hydrated gehlenite)
    - $AlSi(OH)_8^-$ groups in interlayer
    - Conditions of formation and solubility not well constrained
  - Occurrence
    - Low SO_3/Al_2O_3 ratio (MK, Class C FA)
    - Absence of CH



[Rinaldi et al., 1990]

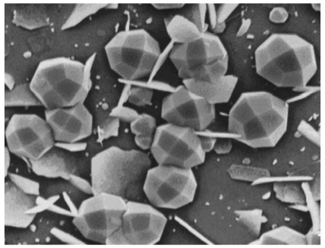
53

Hydrogarnets

C_3AH_6 : katoite

$C_3(A,F)S_xH_{6-2x}$ siliceous hydrogarnet

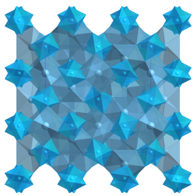
- Solid solutions
  - $Al^{3+} \leftrightarrow Fe^{3+}$
  - $SiO_2^0 \leftrightarrow 2\ H_2O$
- Low water content
  - **High density**: 2.5 g/cm^3
  - Less space filling


Pöllmann (2012)

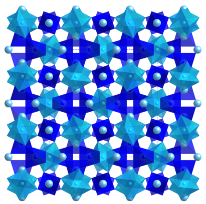
54

Hydrogarnets

- Si[4] connects Al[6] in siliceous hydrogarnet
- Thermodynamically predicted phase in many blended cements
- Location of most of iron in mature pastes


Hydrogarnet
[Cohen-Addad et al., 1964]

$C_3AS_xH_{6-2x}$


Siliceous hydrogarnet
[Sacerdoti & Passaglia, 1985]

55

Summary

- Aluminate containing hydrates constitute an important part of the hydrate assemblage (~ 25 vol.% in mature pastes)
- They contribute to space filling (strength development) in the same way as C-S-H and portlandite
- Ettringite can be substituted, but fairly pure in Portland pastes
- AFm phases solid solution is important; limestone favours carboaluminates
- Hydrogarnet forms only at long ages (high temperatures)

56