Lecture 4: Aluminates and Microstructure

Cement Chemistry and Sustainable Cementitious Materials

Professor Karen Scrivener, FREng

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- Part 1: reaction of aluminate phases

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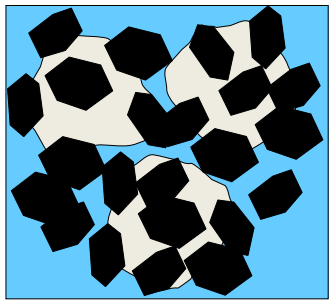
C_3A



C_3A + **water**

Rapid reaction
large platey hydrates

Stiffening
Flash set

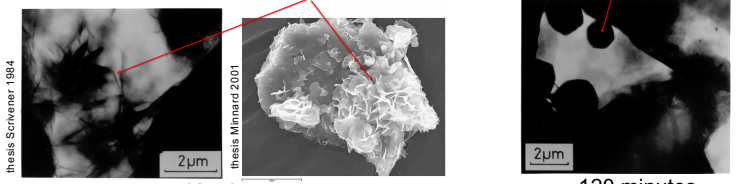
3

Hydration C_3A without sulfate

C_3A + H → C_4AH_{10} + C_2AH_8 → C_3AH_6

"metastable" AFm phases

hydrogarnet



10 minutes

120 minutes

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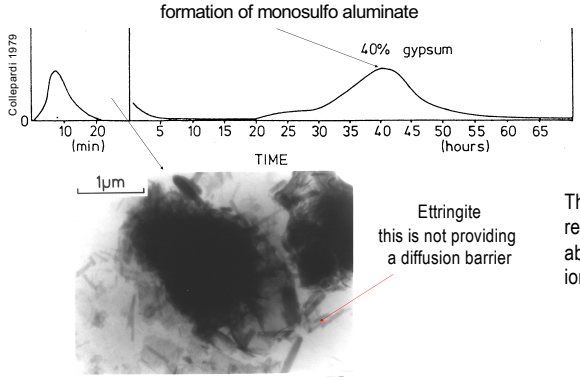
$C_3A + CaSO_4H_x$



The slowing down of the reaction is linked to absorption of sulfate ions on C_3A surface

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$C_3A + CaSO_4H_x$

$$C_3A + 3C\bar{S}H_2 + 26H \Rightarrow C_3A.3(C\bar{S}).H_{32}\,(\text{ettringite})$$

Reaction is through solution

$$6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O$$

$$\Rightarrow C_3A.3(C\bar{S}).H_{32}\,(\text{ettringite})$$

Hypotheses of "topochemical" formation of ettringite are nonsense

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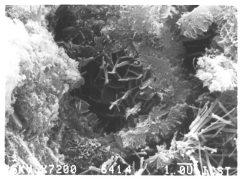
Exhaustion of sulfate

$$2C_3A + C_3A.3(C\bar{S}).H_{32} + 4H \Rightarrow 3C_3A.C\bar{S}.H_{12}$$

Calcium monosulfo aluminate
"AFm"



Paste at 7 days
Formation of monosulfo
inside C-S-H shell.
Ettringite remains outside grain

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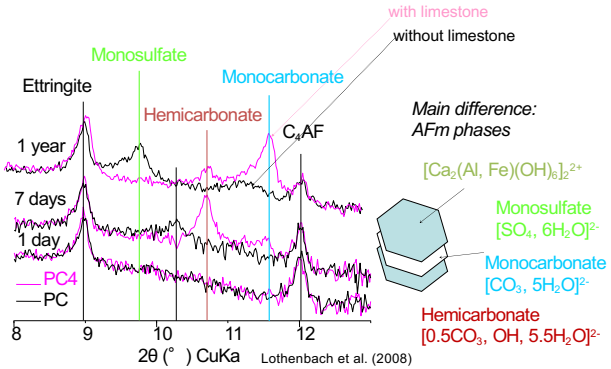
AFm phases: effect of limestone addition



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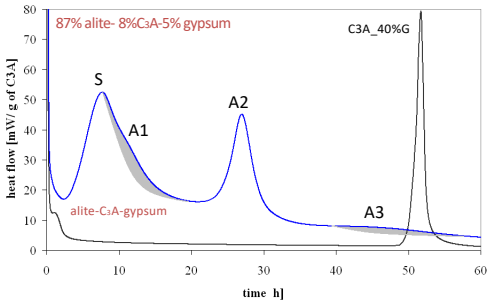
Mixture of Ailite and C3A



- Multiple aluminate peaks when hydration occurs in the presence of alite

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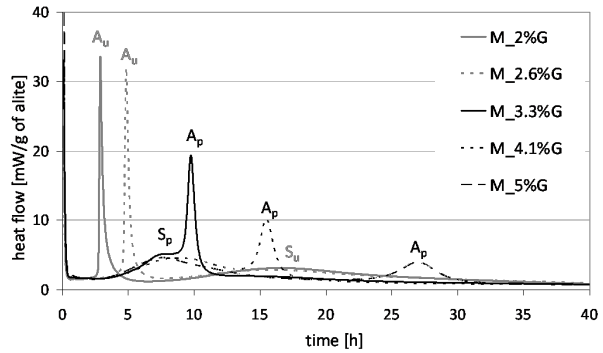
Sufficient gypsum to ensure aluminate reaction after silicate



Silicate reaction reduced if aluminate reaction occurs first,

Undersulfation, can be exacerbated with admistures

Quennoz and Scrivener 2013

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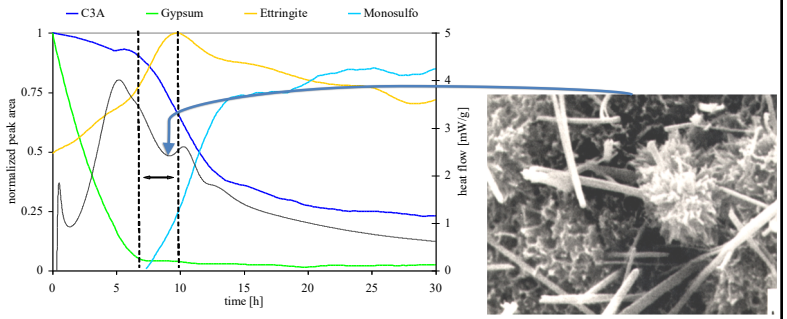
Multiple aluminate peaks

- Peak A1 → second formation of ettringite
  [Scrivener, 1984]



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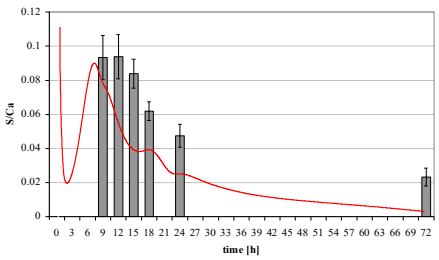
Desorbtion of sulfate from C-S-H

- Reaction of C_3A with sulfate ions desorbed form C-S-H



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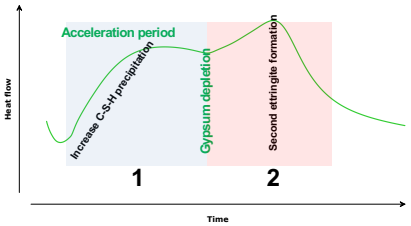
Mechanism of sulfate balance in cements



1. Sulfate gets adsorbed in the C-S-H surface.
   If the rate of C-S-H precipitation is increased, sulfate adsorption also increase
   i. Finer material hydrate quicker, consuming more sulfate per unit time
   ii. The addition of **more nucleation surface** (fillers) affect the **C-S-H precipitation rate** and therefore the sulfate balance, but the effect is **independent of the chemical composition** of the filler (in particular, of the Al content)
2. As hydration keeps going, gypsum is depleted, triggering the **desorption of sulfate from C-S-H** which then reacts with aluminates to form ettringite (second ettringite formation)

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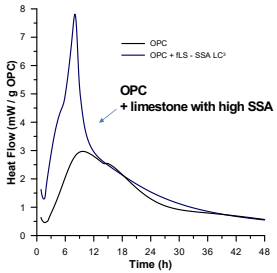
What controls sulfate demand ?

More related to rate of C-S-H formation than overall amount of aluminate?



Fine limestone increase rate of reaction of alite by filler effect
(more in Wednesday's lecture)
More C-S-H formed – more sulfate absorbed
Earlier depletion

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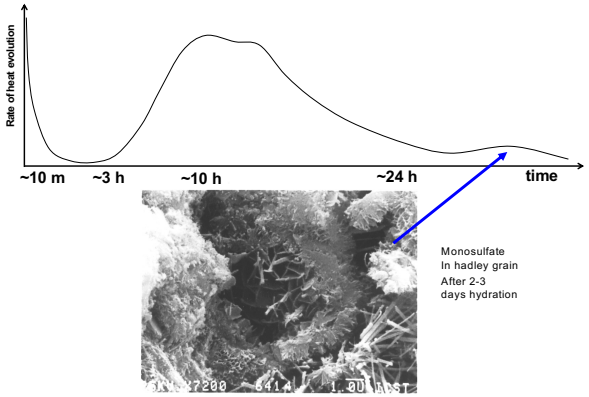
Afm peak (mono sulfate or carbonate)



Monosulfate
In hadley grain
After 2-3
days hydration

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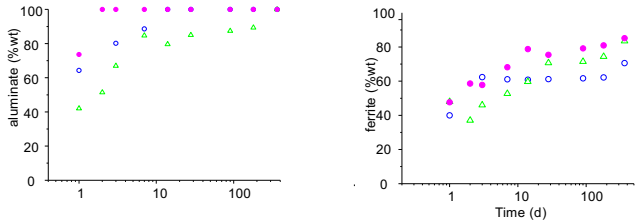

Both aluminate AND ferrite react initially

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Development of Microstructure during Hydration

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- For a properly regulated cement
  (enough rapidly soluble calcium sulfate added),
- hydration and structure development is dominated by the reaction of C_3S

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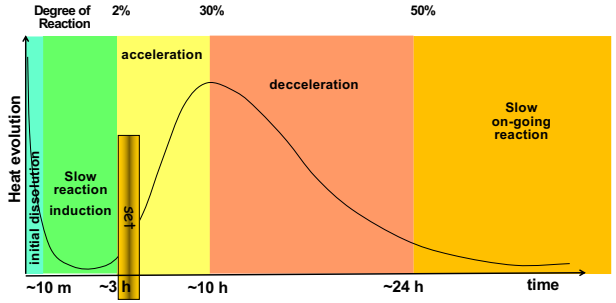
Reaction of silicates



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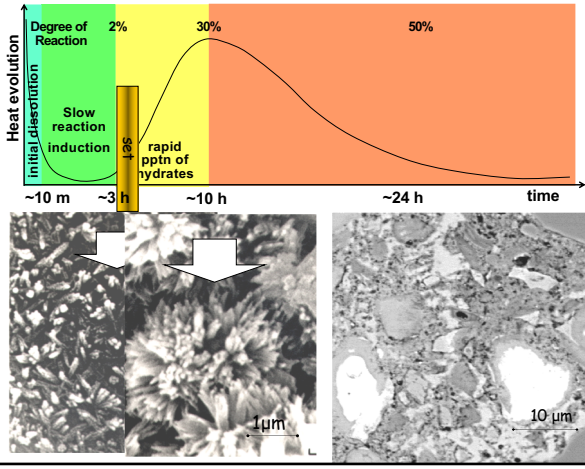

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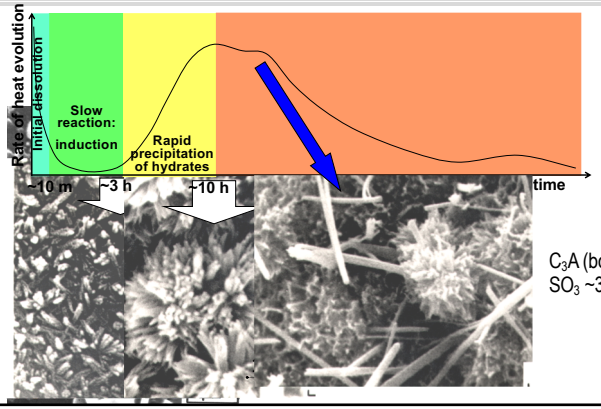
Reaction of Portland cement:



C_3A (bogue) ~8% ;
SO_3 ~3%

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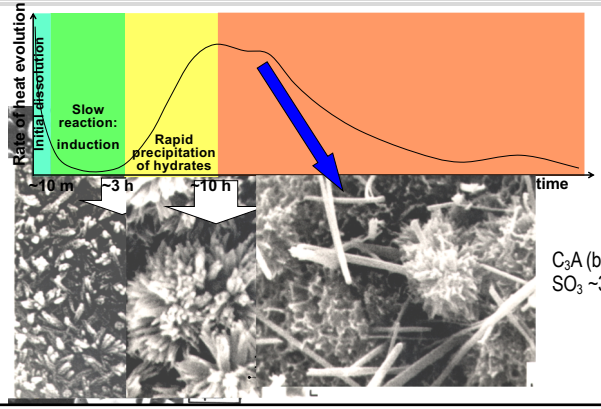
Reaction of Portland cement:



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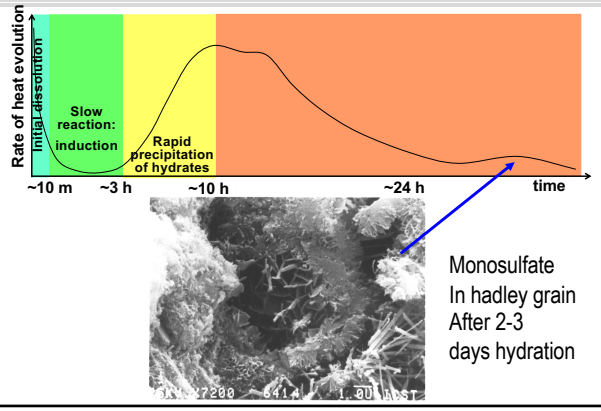
22



Monosulfate
In hadley grain
After 2-3
days hydration

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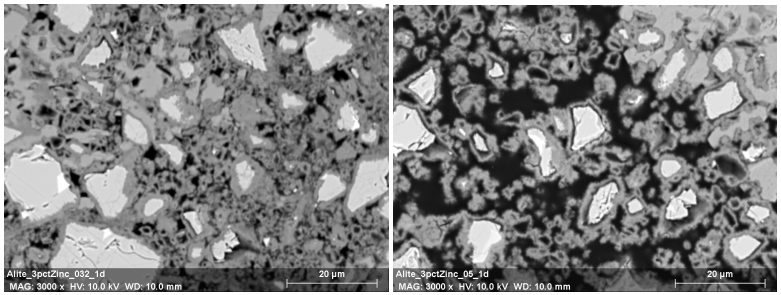
Filling space



w/c = 0.32 **w/c = 0.5**

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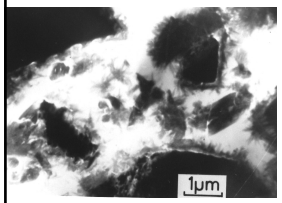
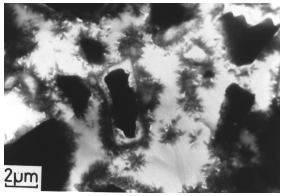
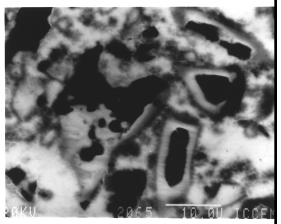
Formation of Hadley grains (thesis Scrivener 1984)



5hrs cement paste: ion thinned section



12hr cement paste: ion thinned section



18 hr cement paste:
SEM/BSE, inverse contrast

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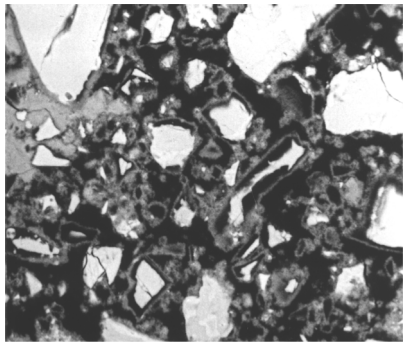

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Separated Shells ("Hadley" Grains)

- The "shell" of hydrates formed during the main heat evolution peak becomes separated from the underlying reacted grain, simply because the growth of the outer product is faster than the inner product at early ages
- Product is forming at the ends of the "needles"
- Inner product starts forming once the growth of the outer needles slows down

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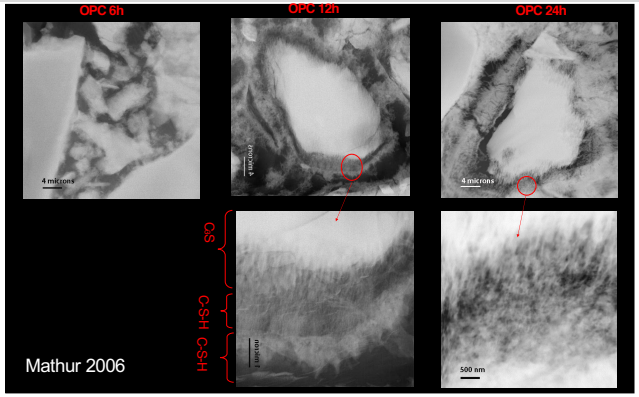
TEM studies



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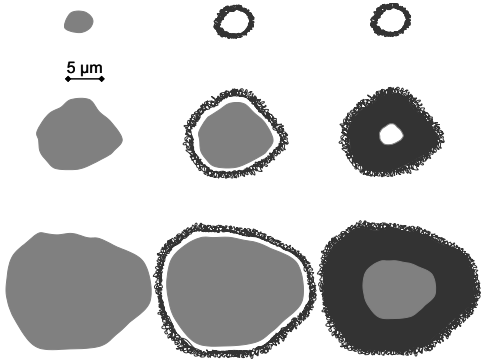

The eventual evolution of these "Hadley" grains depends on the size of the grain.
Large ones the gap fill in, small ones remain empty

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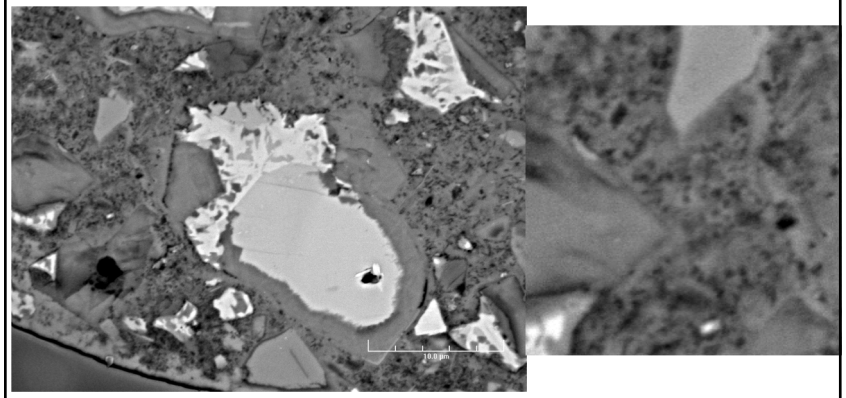

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Overview, Scrivener 1984

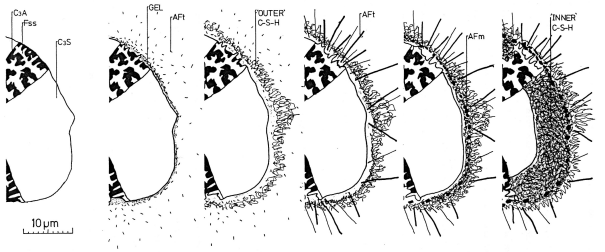

FIG. 6.1 Microstructural Development ion of Portland Cement

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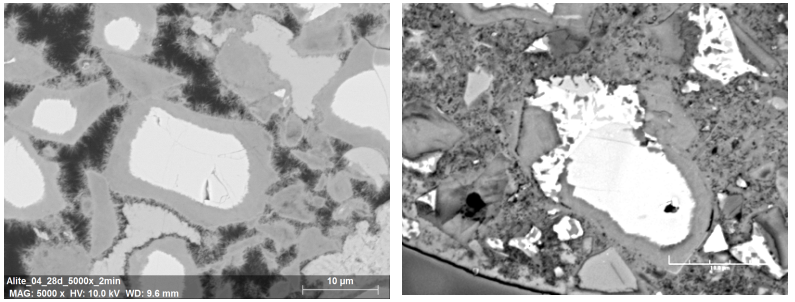
Alite ≠ Portland cement



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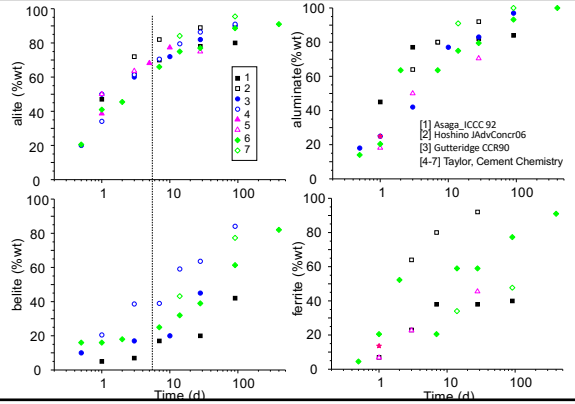
Reaction of different phases



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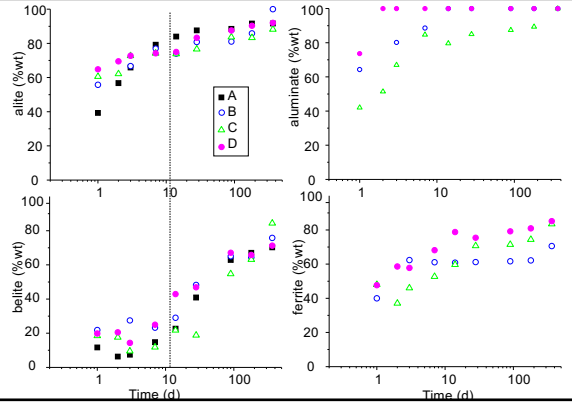
PhD Kocaba 2010



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- Belite:-
  little reaction before 10 days (thermodynamics)
- Aluminate:
  fast, but slowed by ferrite in grey cements
- Ferrite:
  slow but significant

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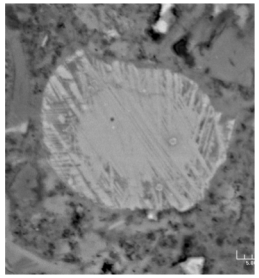
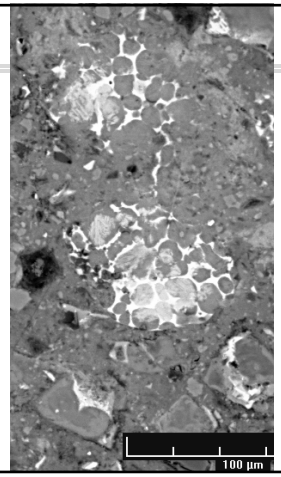
Reaction of Belite





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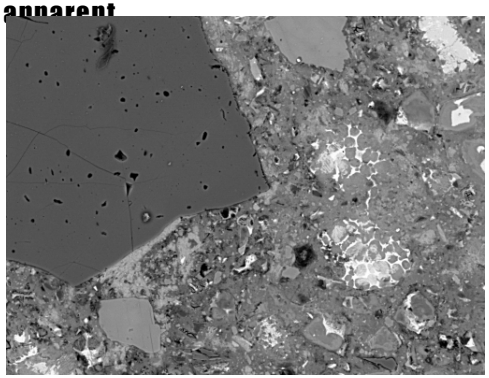
Old concrete, only belite and ferrite apparent



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Reaction of ferrite phase

- XRD shows reaction but in BSE appears unreacted
- Probable that A and C “leach” out leaving Fe “relic” of ferritic siliceous hydrogarnet

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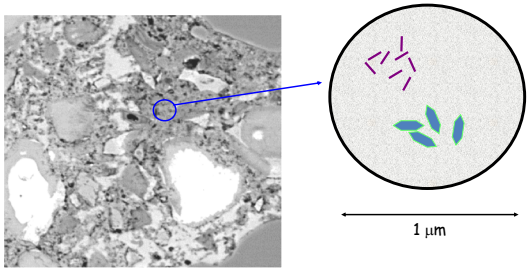
Aluminates in hardened cement paste



Intermixing of ettringite and/or
Monosulfate at submicron scale

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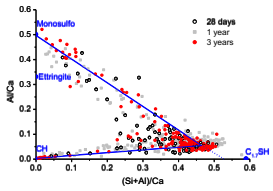
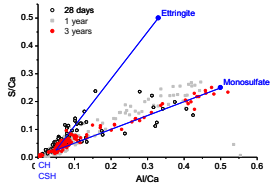
EDS analyses



28 days. Formation of C-S-H, CH
ettringite and then monosulfate

$$2C_3A + C_3A.3C\overline{S}H_{32} + 4H \rightarrow 3C_3A.C\overline{S}H_{12}$$



1, 3 years. Further formation of C-S-H, CH
Reaction of ettringite into monosulfate

thesis Lamberet 2005

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Summary

- Presence of sulfate modifies reaction of aluminate (& ferrite) phase
- Small initial reaction, then induction period which should be longer enough to allow silicate to react.
- When sulfate exhausted in solution, second burst of aluminate reaction with formation of ettringite from sulfate absorbed on C-S-H
- Monosulfate (or monocarbonate forms) typically after a few days
- Hadley grain formation
- Belite reaction only significant after about 10 days (inhibited by alite reaction)
- Ferrite reacts to poorly crystalline ferritic siliceous hydrogarnet
- Aluminate phases mainly finely dispersed in C-S-H

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