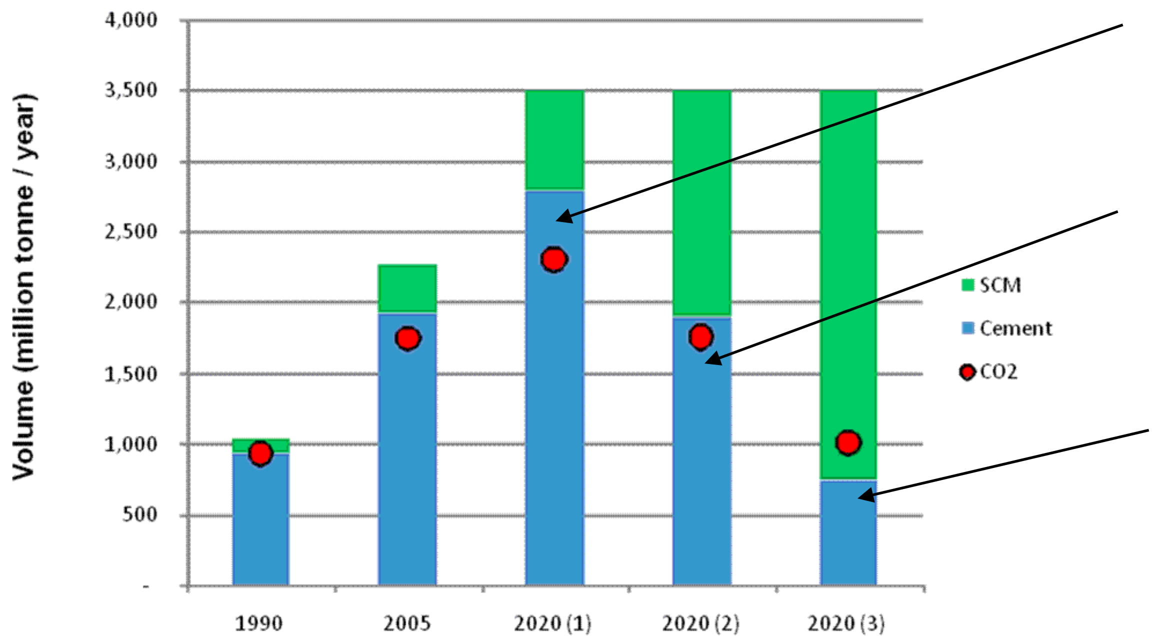
SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

UNIVERSITY OF ABERDEEN

Activation of aluminosilicates - some chemical considerations

Donald E Macphee and Ines Garcia Lodeiro

High volume SCM binders – a case for hybrid AA-OPC systems



Not sustainable

Just possible with OPC concrete (OPC normally in excess to provide adequate strength development)

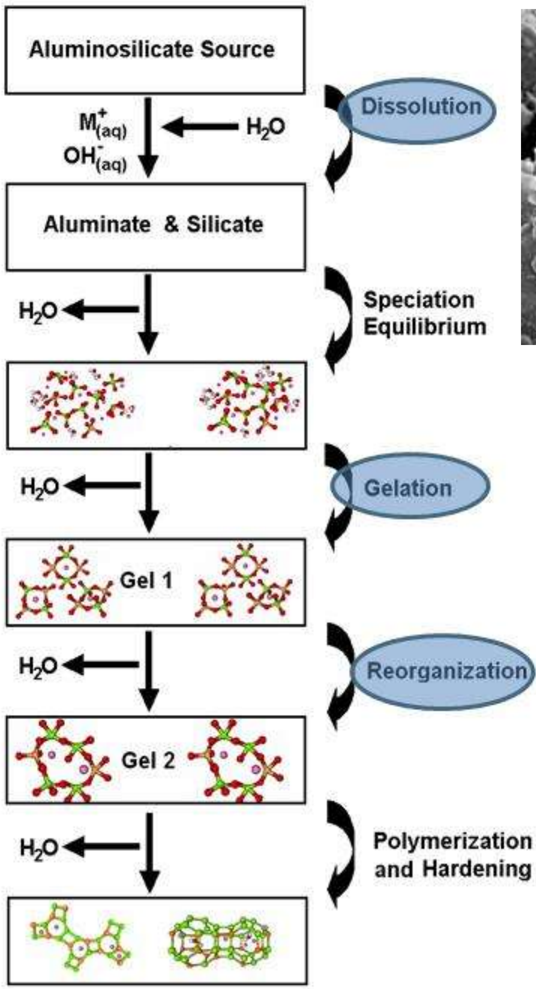
insufficient OPC to activate the SCM

- **1990 and 2005 values** are actual global quantities of cement and SCM used
- **Predicted scenarios for 2020** *(Mehta, P K, Sustainability of the Concrete Industry – Critical Issues, March 29, 2007, Washington DC)*

  (1) Continuing at present rate but with increased use of SCMs to 20% by mass of binder
  (2) CO_2 levels to be kept at 2005 levels
  (3) CO_2 levels to be reduced to 1990 levels

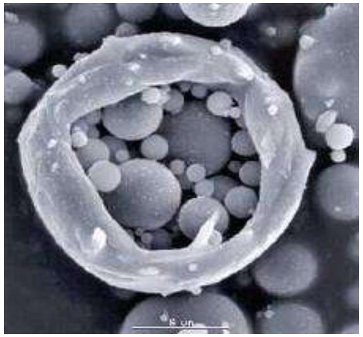
…. use of additional alkali as a *secondary activator* for excess SCM?

Cement Reactions

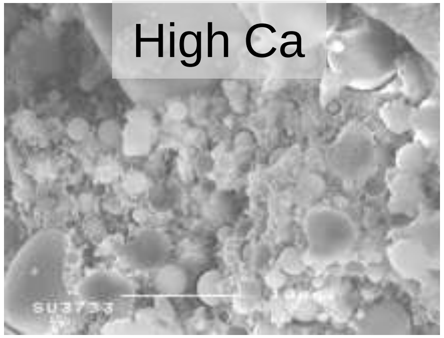


P. Duxson, et al, J. Mat. Sci. 42, 2917-33, (2007)

PFA + 8M NaOH (85ºC 20 hrs)

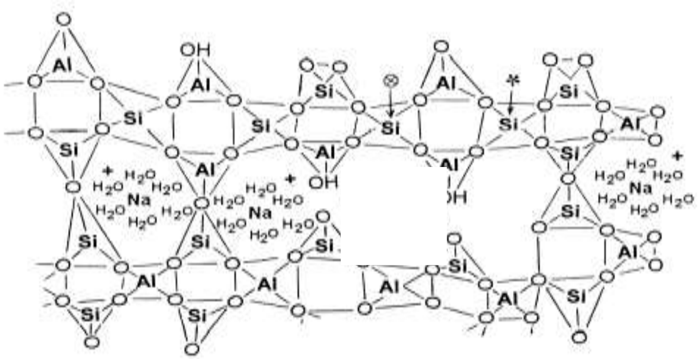


PFA



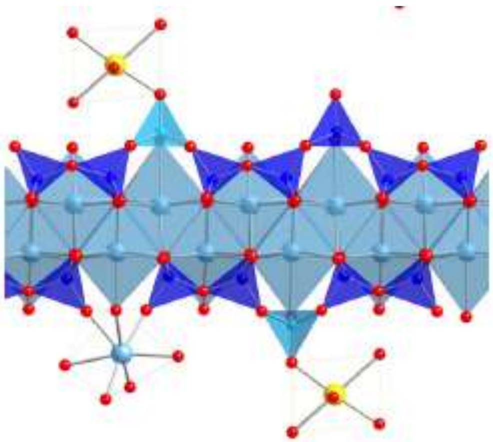
5:4 PFA:OPC 90 days at 20ºC

Precipitation (but as what?)



N-A-S-H

/. F. F. Barbosa and K. J. D. Mackenzie, Materials Research Bulletin, 38 (2003) 319-331.



C-A-S-H

I.G. Richardson, C&CR, 34 (2004) 1733-1777.

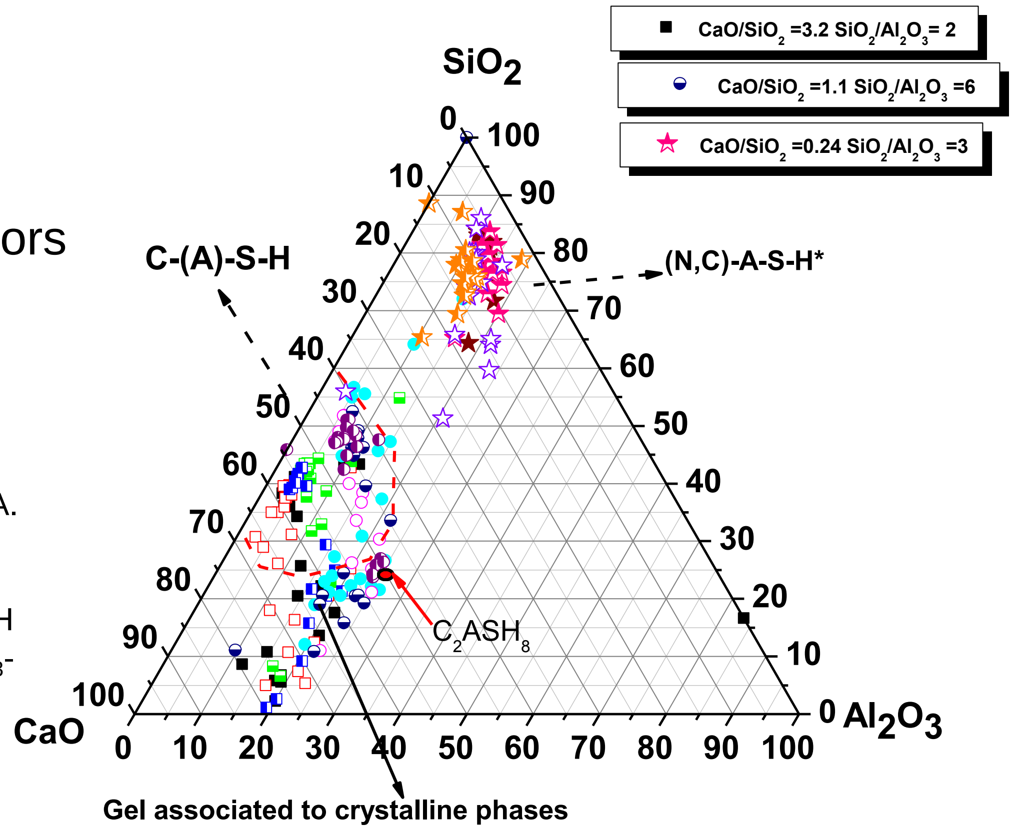
Characterisation of phase relations in the systems Na_2O-CaO-SiO_2-Al_2O_3-H_2O

Nanocem core project:

- precipitation from soluble precursors
- direct mixing of pre-formed gels

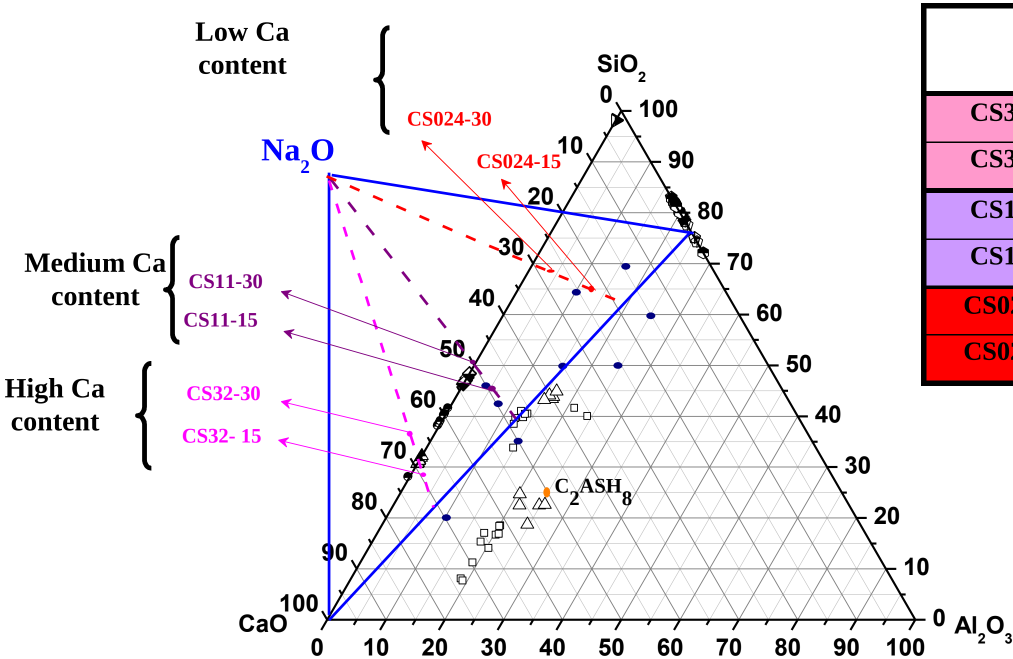
Garcia-Lodeiro, I., Palomo, A., Fernandez-Jiminez, A. and Macphee, D.E.

'Compatibility studies between N-A-S-H and C-A-S-H gels. Study in the Ternary Diagram Na_2O-CaO-Al_2O_3-SiO_2-H_2O.', ***Cement and Concrete Research***., (*in press*, 2011)

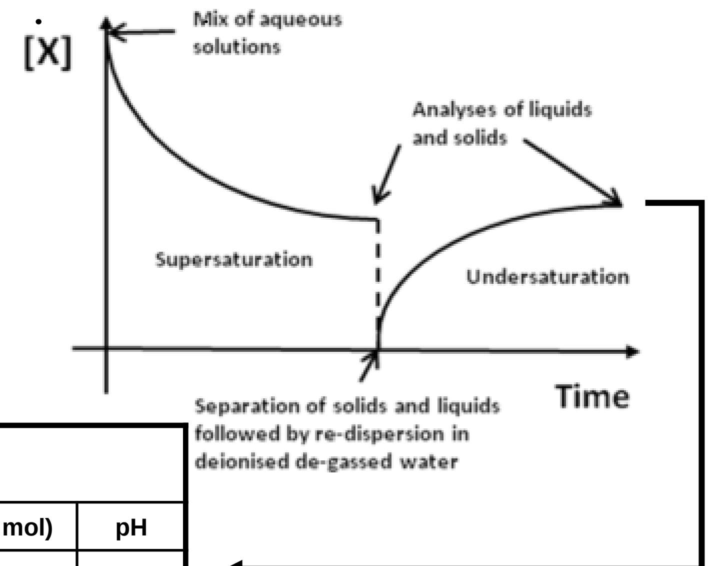


THE INDUSTRIAL-ACADEMIC RESEARCH NETWORK ON CEMENT AND CONCRETE

Precipitation/solubility approach → equilibria conditions



	NaOH *mmol* (% Na_2O)	$Ca(OH)_2$ *mmol* (% CaO)	$Al(OH)_3$ *mmol* (% Al_2O_3)	SiO_2 *mmol (aerosi* (% SiO_2)
CS32-15	8.00 (15 %)	16.00 (59.95 %)	3.34 (6.26 %)	5.01 (18.79 %)
CS32-30	19.44 (30 %)	16.00 (49.36 %)	3.34 (5.16 %)	5.01 (15.48 %)
CS11-15	12.26 (15 %)	16.00 (39.15 %)	4.68 (11.46 %)	14.05 (34.39 %)
CS11-30	29.76 (30 %)	16.00 (32.25 %)	4.68 (9.43 %)	14.05 (28.32 %)
CS024-15	37.15 (15%)	16.00 (12.92 %)	44.63 (18.02 %)	66.94 (54.06 %
CS024-30	90.22 (30%)	16.00 (10.64 %)	44.63 (14.84 %)	66.94 (44.52 %



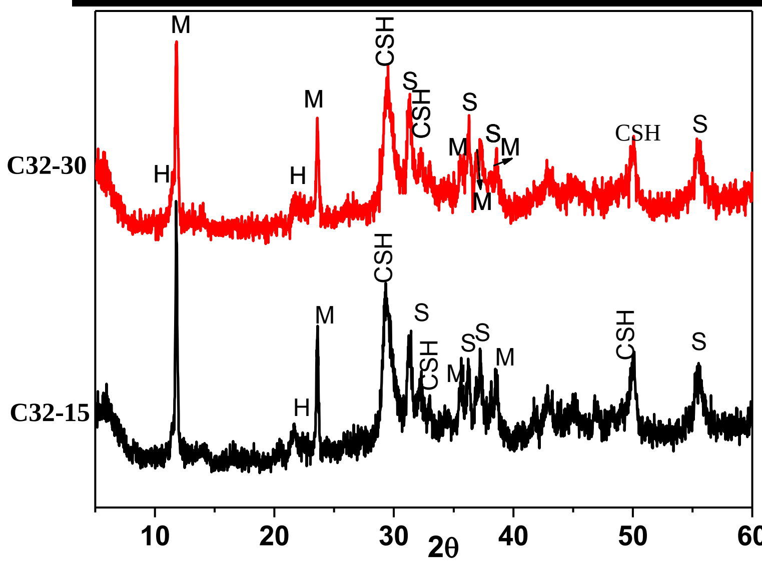
- Focus of discussion on undersaturation approach

e.g.

	Solid Composition	Aqueous				
CS11-15(S)		**Ca^{2+}(mmol)**	**Si^{4+}(mmol)**	**Al^{3+}(mmol)**	**Na^{+}(mmol)**	**pH**
		0.45	5.64	0.089	20.49	11.91
	Phases identified (XRD)	***Strätlingite, hemicarboaluminate, monocarboaluminate, C-S-H gel***				

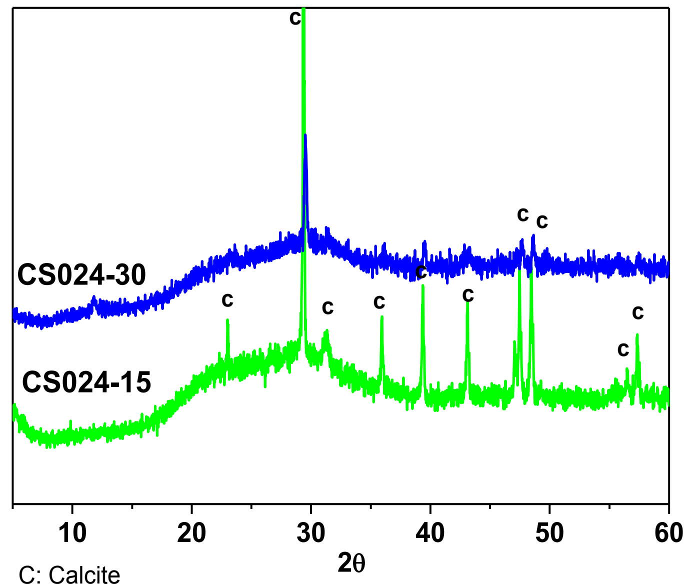
GEL CHARACTERIZATION: XRD

HIGH Ca CONTENT (CaO/SiO_2=3.20; SiO_2/Al_2O_3=2)



H: Hemicarboaluminate; M: Monocarboaluminate; CSH:C-S-H gel; S:Gehlenite hydrate

LOW Ca CONTENT (CaO/SiO_2=0.24; SiO_2/Al_2O_3=3)

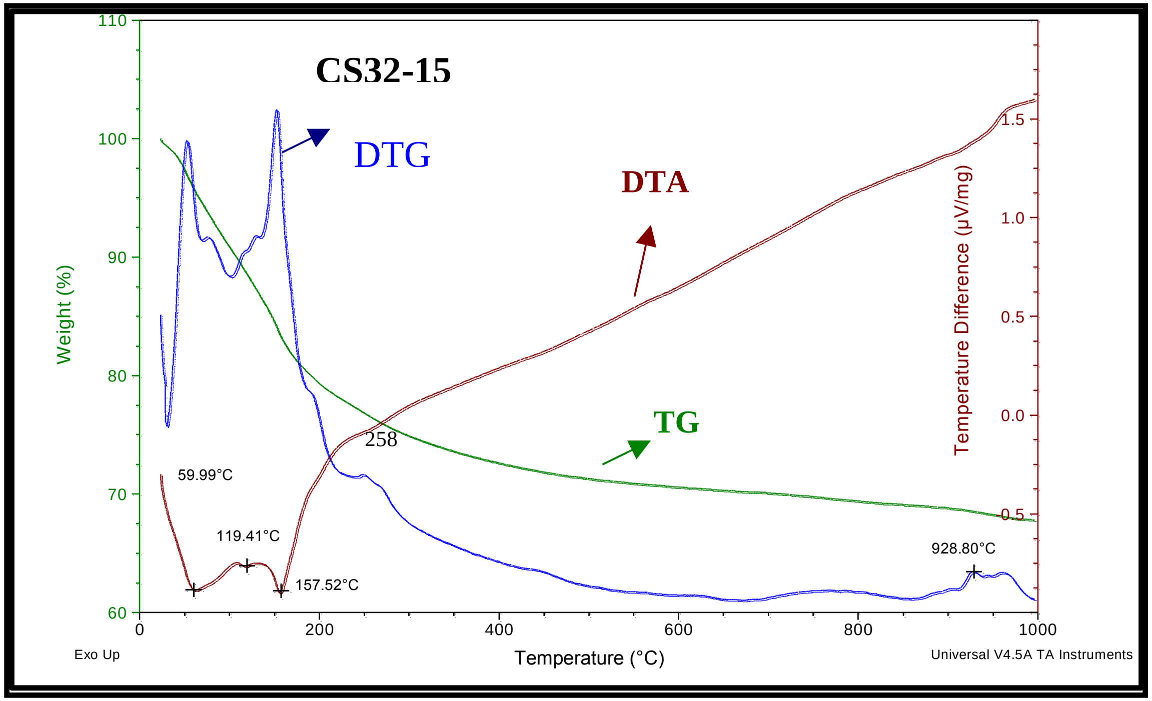


C: Calcite

High Ca Content: carboaluminates, strätlingite and C-S-H gel

Low Ca Content: amorphous halo (2θ 20-35º), calcite

GEL CHARACTERIZATION: DTA/TG



DTA (endotherms)

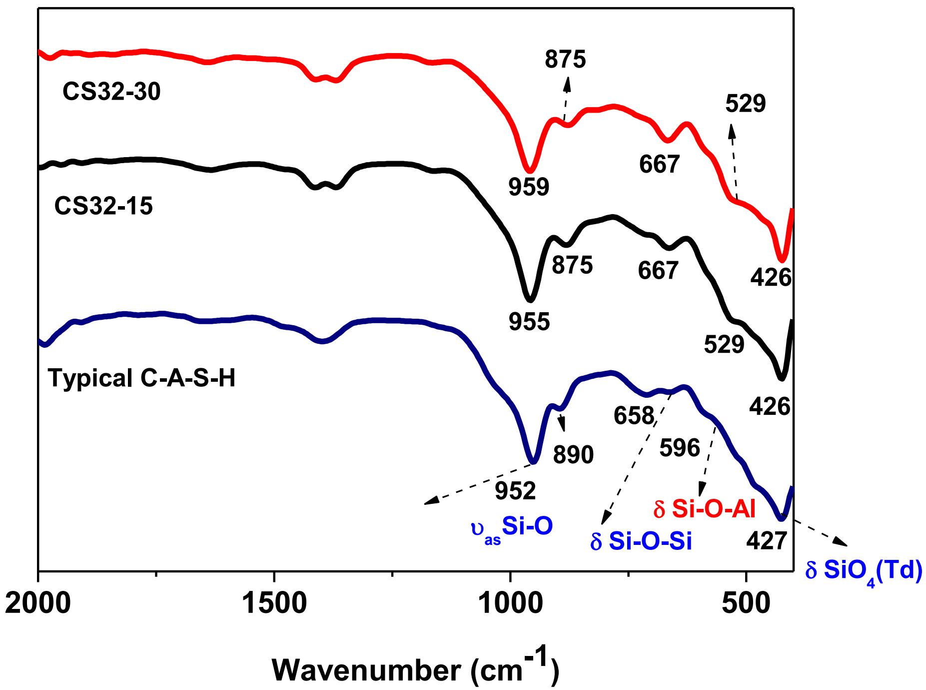
- 60-150ºC: loss of evaporable water in gel
- >150ºC: loss of bound water in calcium aluminosilicates or carboaluminates

Note: no decarbonation peaks

[1] *F. Cassagnabére et.al, Cem. Con. Res. 39 (2009) 1164-1173*

GEL CHARACTERIZATION: FTIR

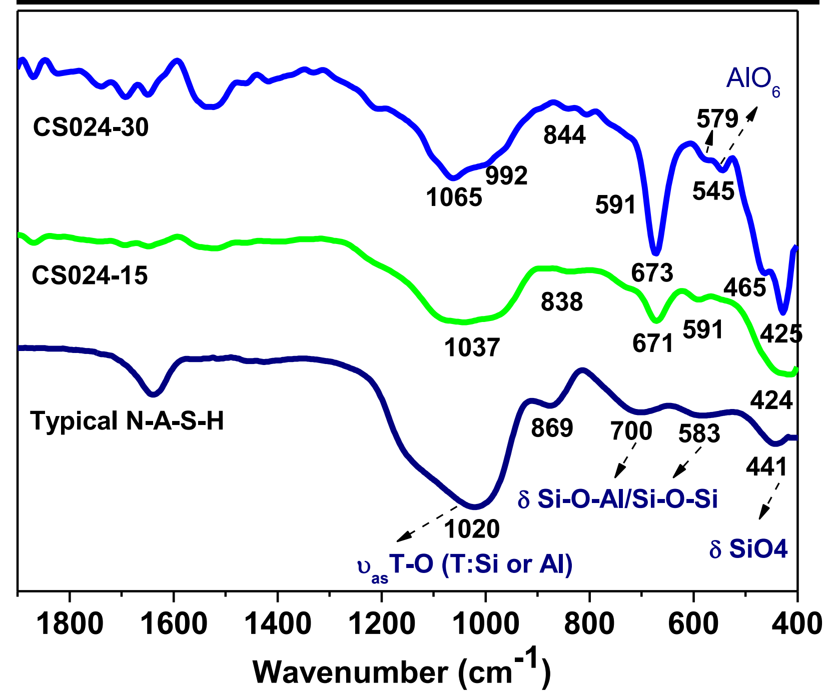
HIGH Ca CONTENT (CaO/SiO_2=3.2 ; SiO_2/Al_2O_3= 2)



Spectra representative of C-A-S-H like gels structures [1]

[1] Ping Yu, *et.al* , J. Am. Ceramic. Soc. 82, 3 (1999), 742

LOW Ca CONTENT (CaO/SiO_2=0.24; SiO_2/Al_2O_3=3)



Spectra representative of N-A-S-H-like gel structures[2]

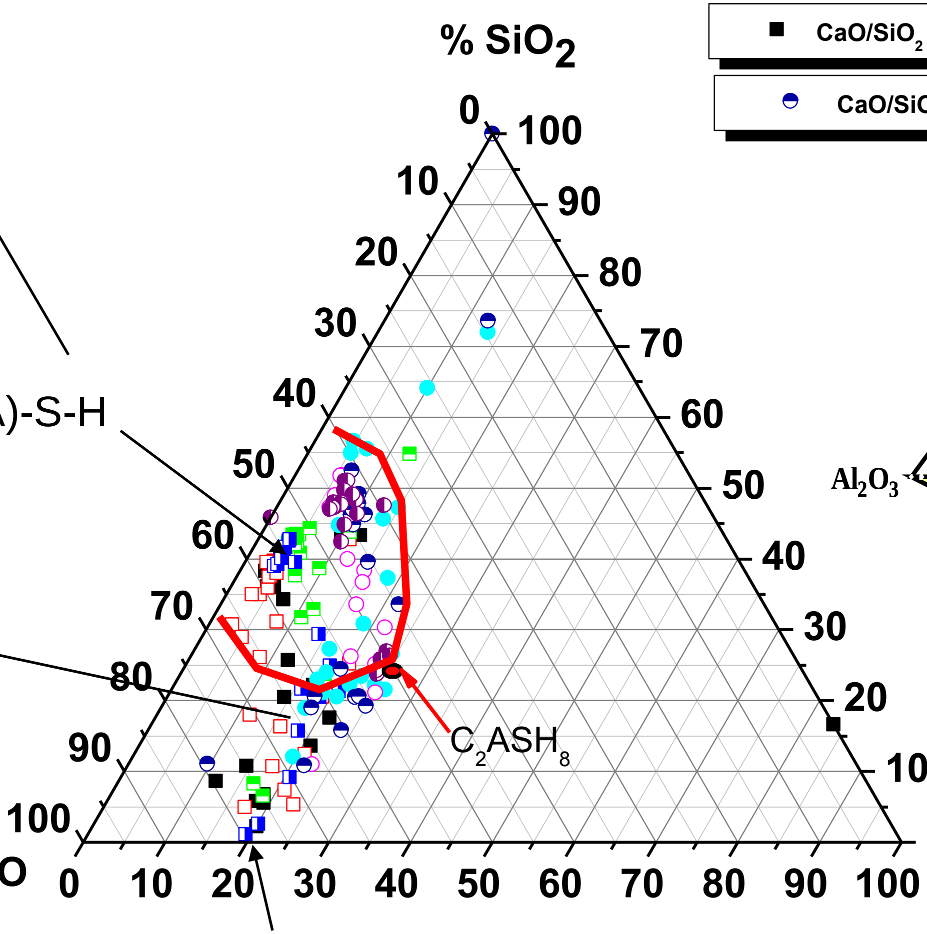
[2] A. Fernández-Jiménez *et. al*., Micr. Mes. Mater., 86, (2005).

GEL CHARACTERIZATION: TEM/EDX

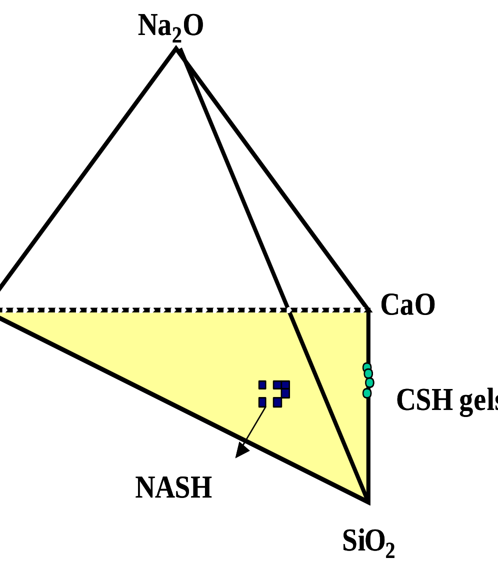
C-(A)-S-H

C_2ASH_8

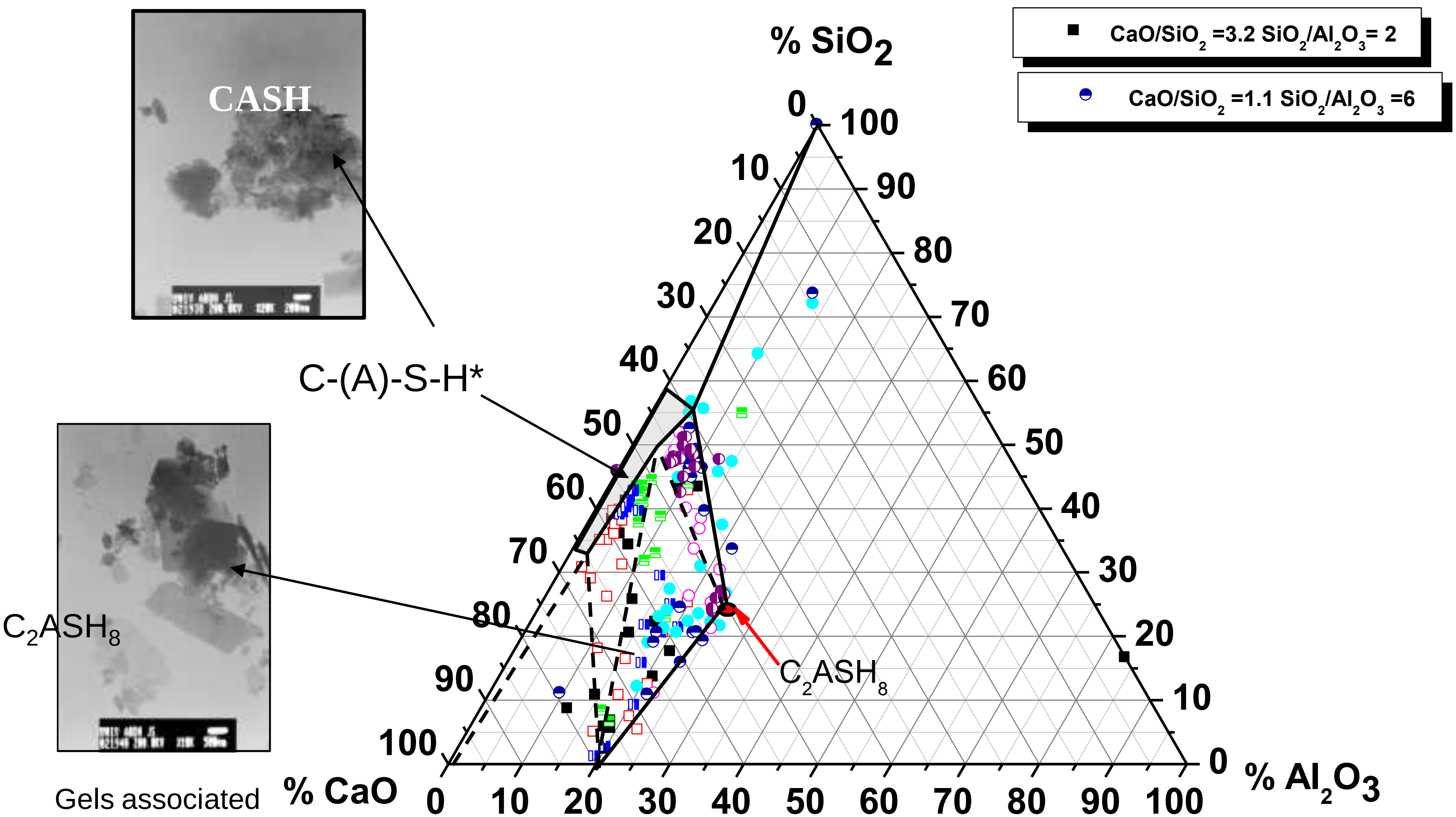
Gels associated with crystalline phases



mono-carboaluminate
hemi-carboaluminate



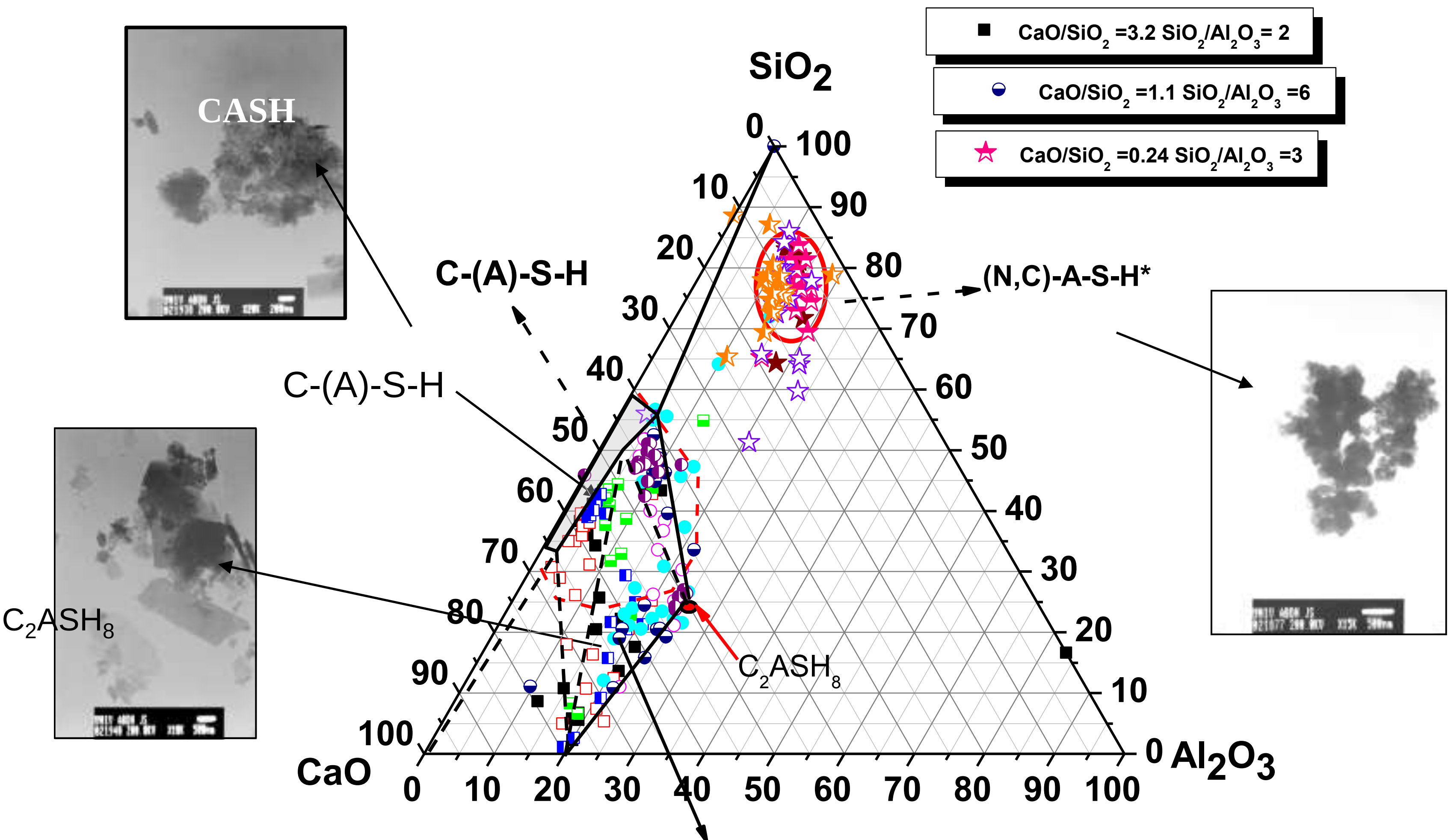
GEL CHARACTERIZATION: TEM/EDX



Gels associated with crystalline phases

*X. Pardal, I. Pochard, A. Nonat, "Experimental study of Si-Al substitution in calcium-silicate-hydrate (C-S-H) prepared under equilibrium conditions", *Cem. Con. Res*. 39 (2009) 637-64

GEL CHARACTERIZATION: TEM/EDX

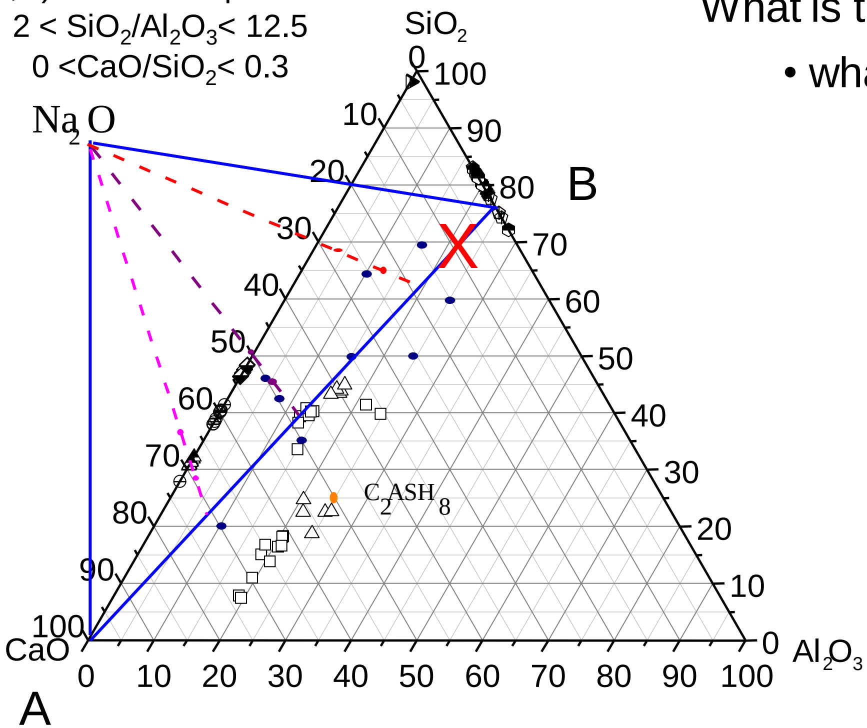


Phase characteristics

Different clusters of composition depending on the initial mixture characteristics:

- C-A-S-H gels (compositional limits and tentative phase field boundaries established)
- (N,C)-A-S-H gels

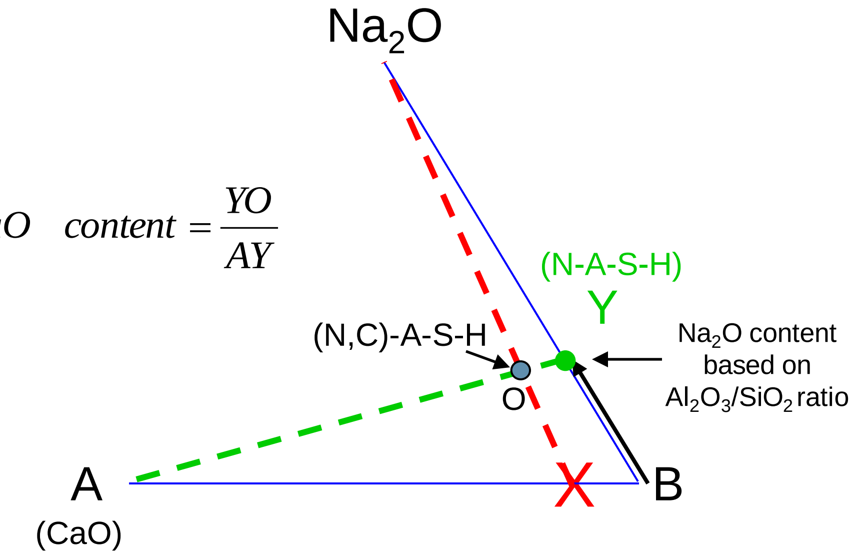
(N,C)-A-S-H Composition:
$2 < SiO_2/Al_2O_3 < 12.5$
$0 < CaO/SiO_2 < 0.3$



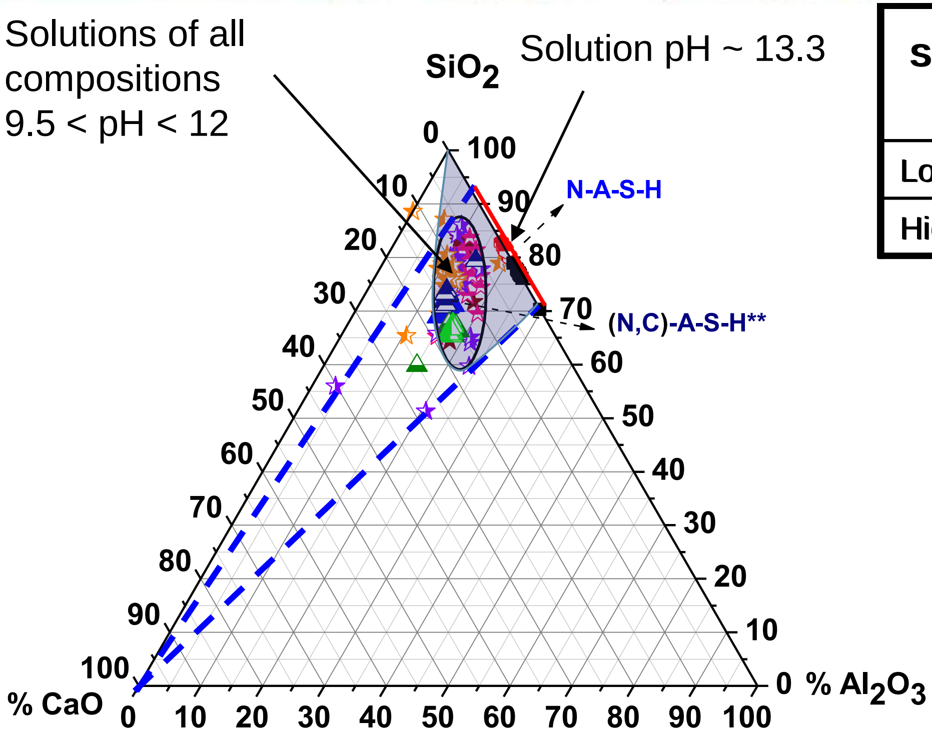
What is the nature of the (N,C)-A-S-H gel?

- what is the relative Na and Ca content of the gel?
  - application of the lever rule!

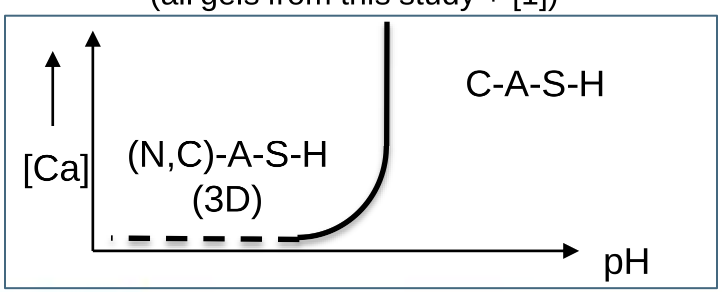
$$CaO \quad content = \frac{YO}{AY}$$



(N,C)-A-S-H: Importance of pH



Gel compositions – low CaO gels
(all gels from this study + [1])



SiO_2/Al_2O_3 limit	CaO Content (mol %)	IEC (equiv/100 mols)	Ca as % of capacity
Low	14	42	67
High	7	14	100

Why does Ca content not promote C-A-S-H?

At low system pH (in the presence of Ca):

- N-A-S-H – behaves like a zeolite (ion exchange)?
- Ca displaces Na by ion exchange mechanisms until available Ca is exhausted
  - *at the higher SiO_2/Al_2O_3 ratio limit, IX sites on the N-A-S-H gel are saturated with Ca*
  - *at the lower SiO_2/Al_2O_3 ratio limit and at the low Ca loading used, only 67% of the sites are saturated with Ca assuming zeolite behaviour*
    - *balance of charge provided by Na^+*

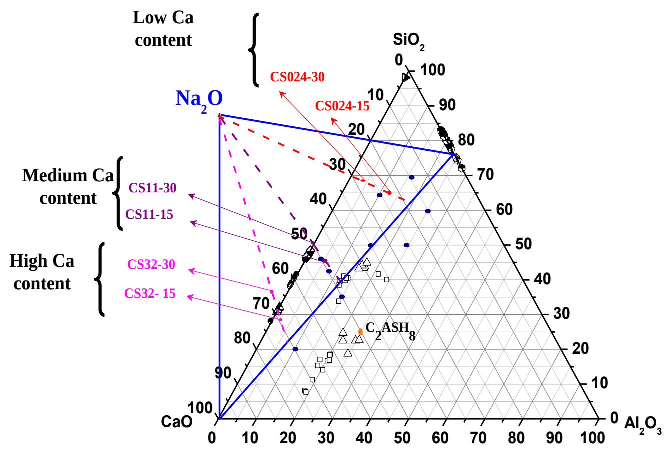
At high system pH:

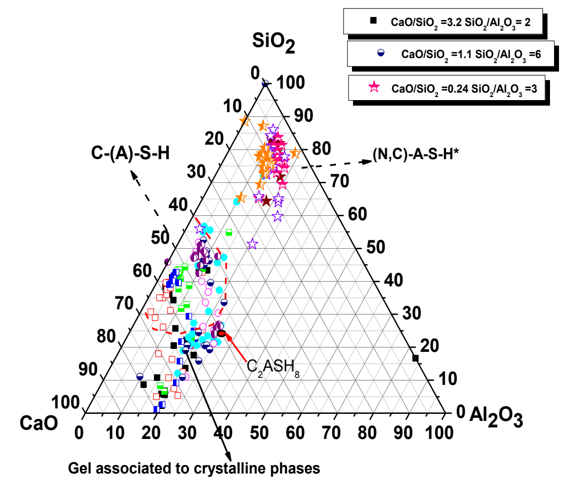
- C-A-S-H precipitation is favoured in the presence of Ca (pH > 12)

Lodeiro, IG, Fernandez-Jimenez, A, Palomo, A, Macphee, DE, 'Effect of Calcium Additions on N–A–S–H Cementitious Gels', *J Amer Ceram Soc (Feb 2010)*

Characterisation of phase relations in the systems Na_2O-CaO-SiO_2-Al_2O_3-H_2O

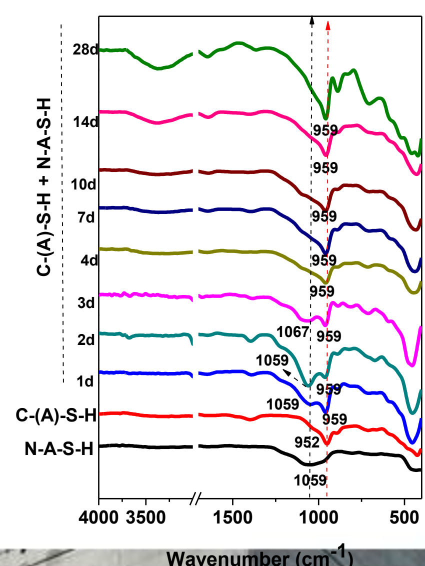
PRECIPITATION FROM SOLUBLE PRECURSORS APPROACH

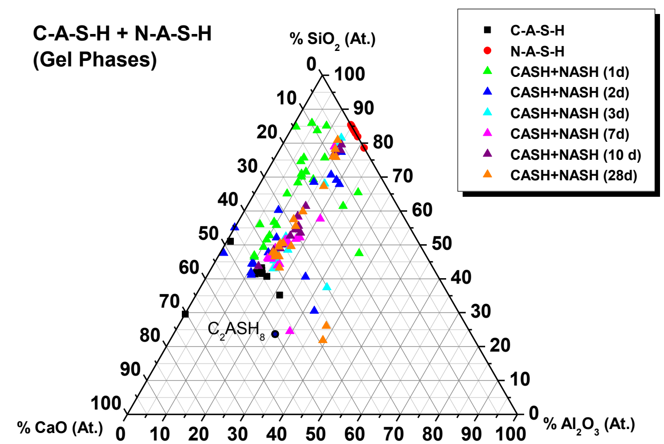




DIRECT MIXING OF PRE-FORMED GELS

FTIR STUDY: C-(A)-S-H+N-A-S-H

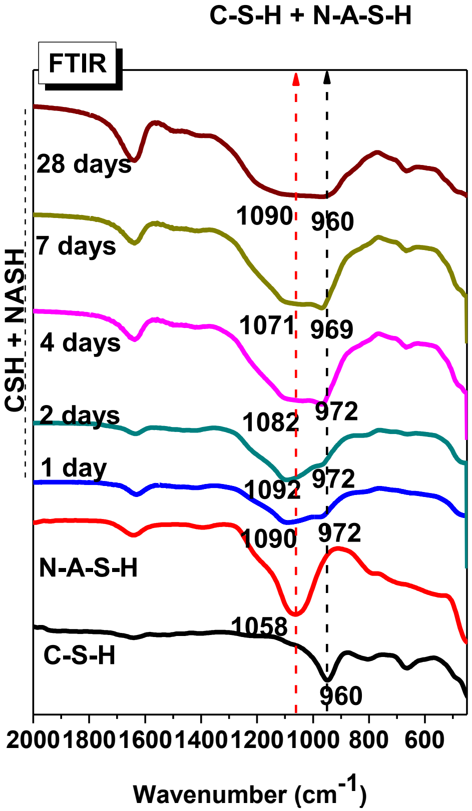


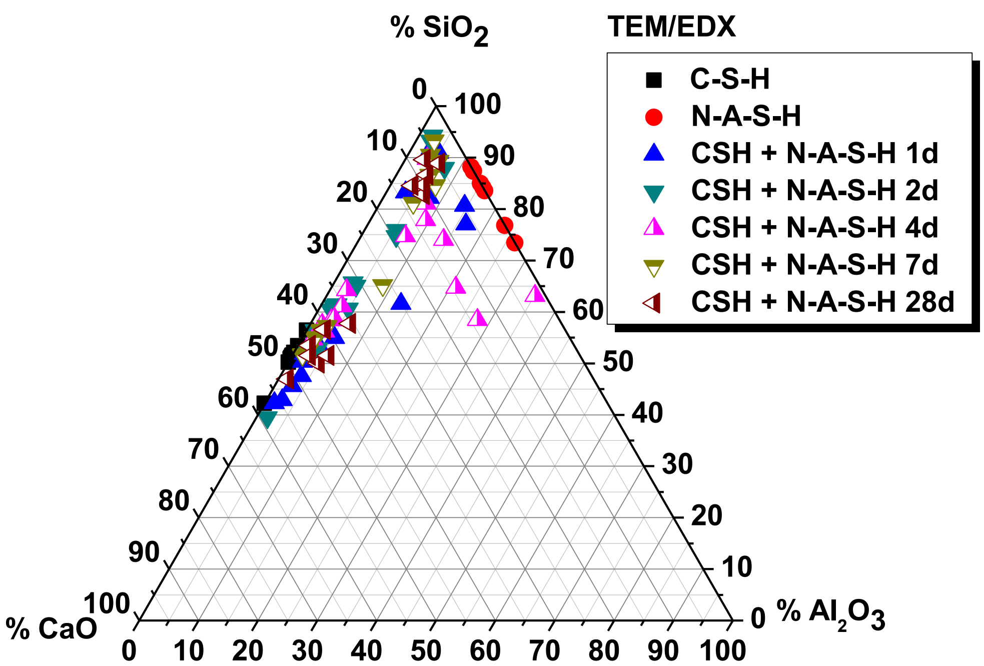


Direct mixing of C-S-H and N-A-S-H gels.

50:50 (w/w) mixture of dried gels dispersed in water (water/solid ratio = 30)

C-S-H + N-A-S-H



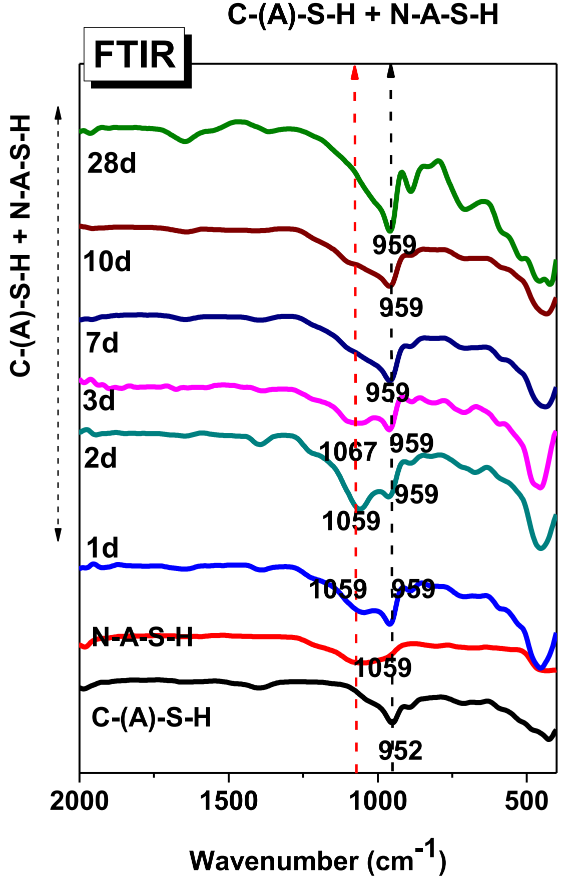


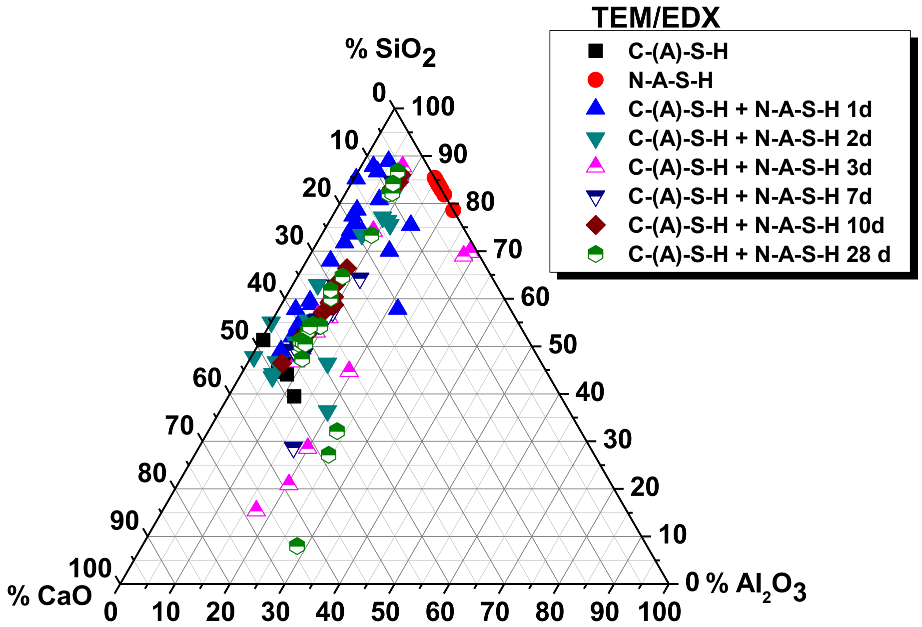
- Tendency towards C-A-S-H characteristics with time
- co-existence of C-A-S-H and N-A-S-H gels

Direct mixing of C-A-S-H and N-A-S-H gels

50:50 (w/w) mixture of dried gels dispersed in water (water/solid ratio = 30)

C-(A)-S-H
+
N-A-S-H



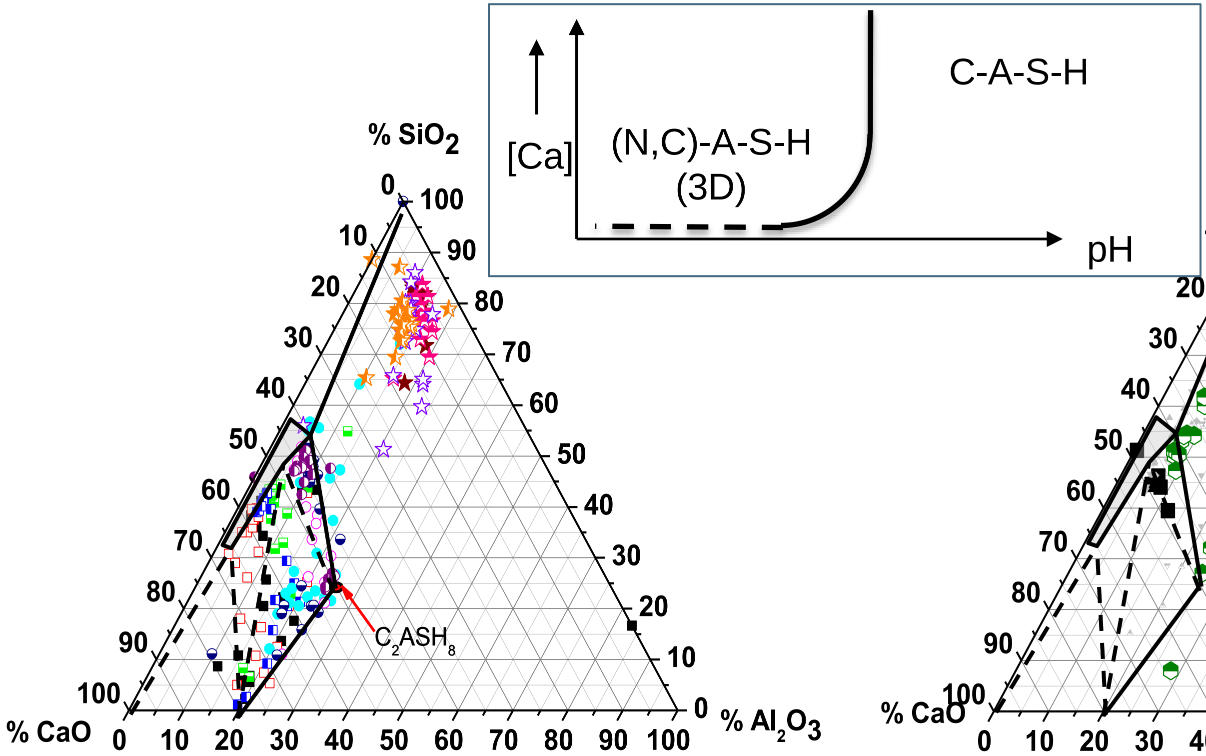


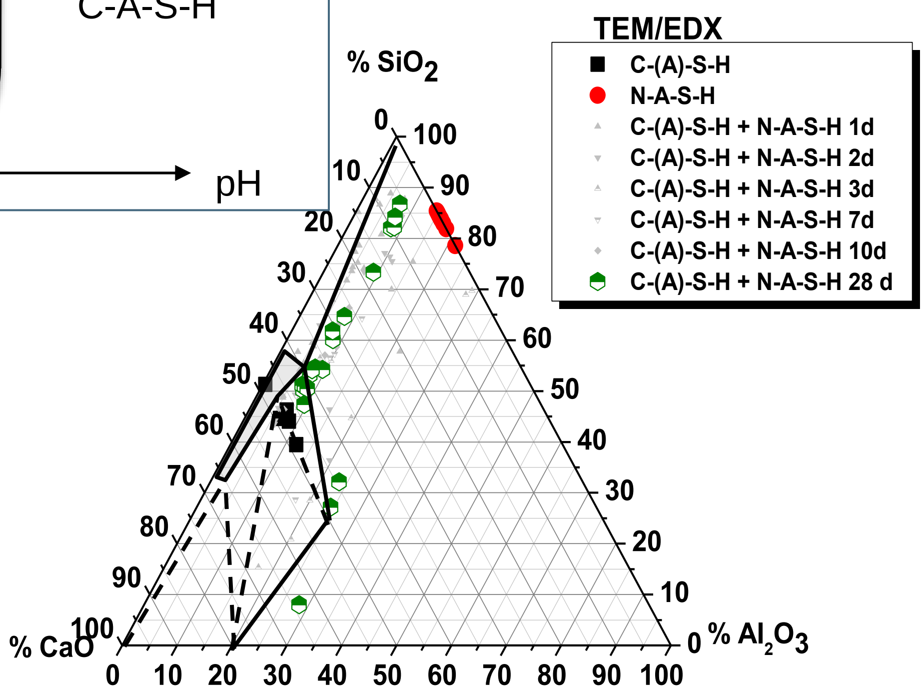
- Tendency towards C-A-S-H characteristics with time
- co-existence of C-A-S-H and N-A-S-H gels

CONSOLIDATION OF SOLUBILITY AND COMPATIBILITY DATA

Solubility/precipitation approach

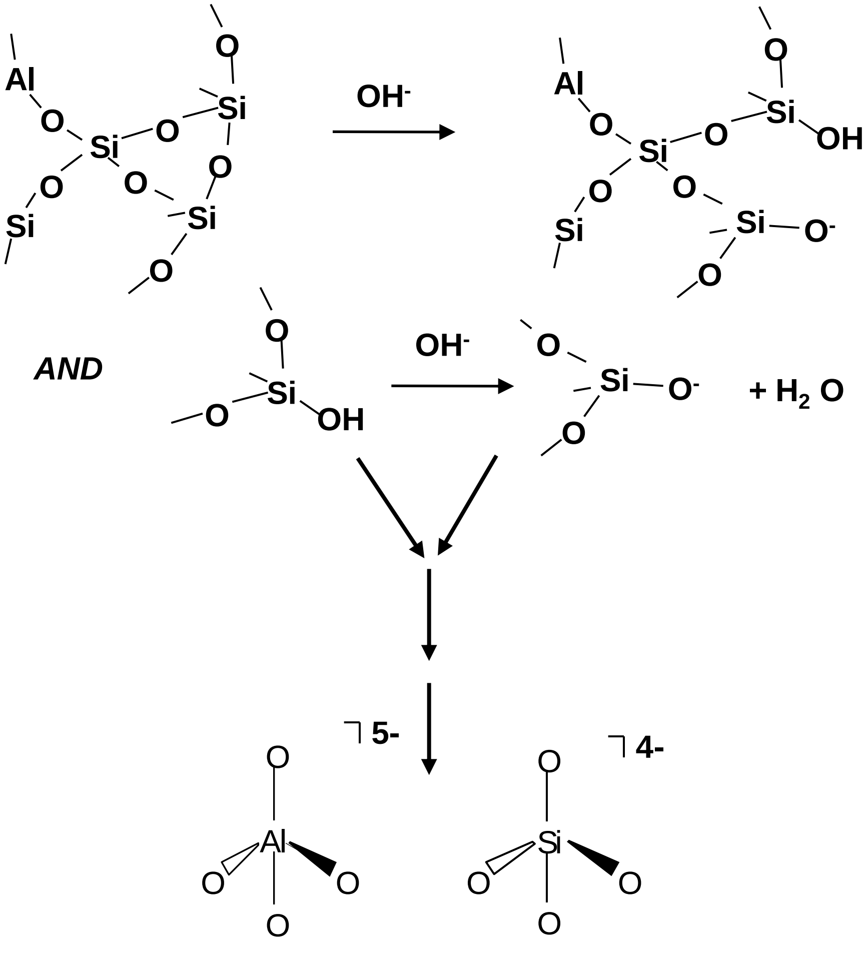
Gel compatibility approach





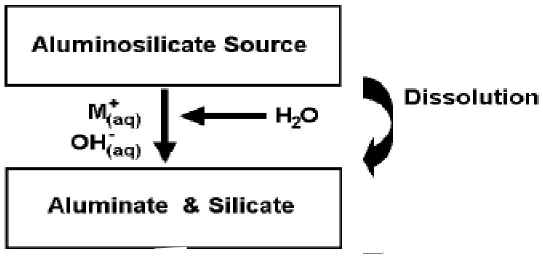
Slower approach to equilibrium

Activation of SCMs – some fundamental chemistry

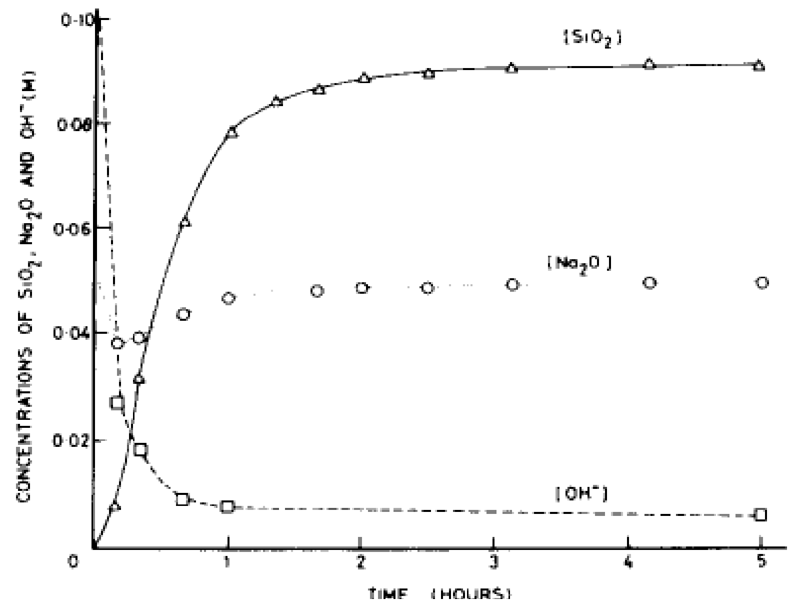


monomeric units

- Hydrolysis



Dissolution step – a net consumer of OH^-



Solution compositions following action of NaOH on silica gel

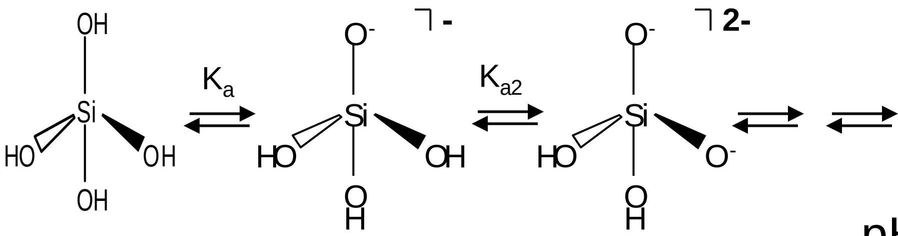
LS Dent Glasser and N Kataoka, Cem Concr Res, 11, 1, (1981)
LS Dent Glasser and N Kataoka, Cem Concr Res, 12, 321, (1982)

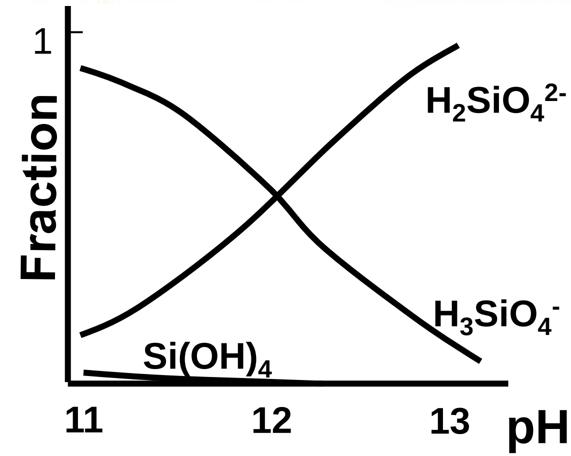
Chemical Speciation

Silicate is a weak acid…..

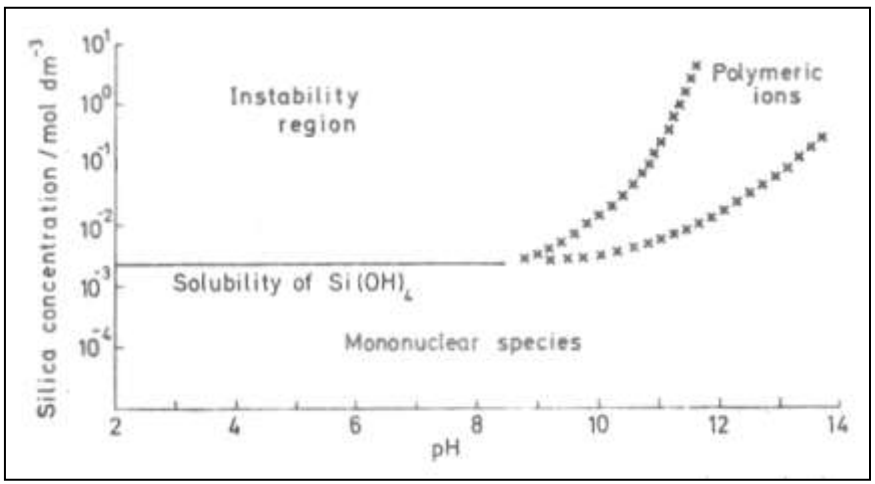
$$H_4SiO_4\,(Si(OH)_4) \Leftrightarrow H^+ + H_3SiO_4^- \qquad K_a = 10^{-9.8}$$

$$H_3SiO_4^- \Leftrightarrow H^+ + H_2SiO_4^{2-} \qquad K_{a2} = 10^{-12.16}$$

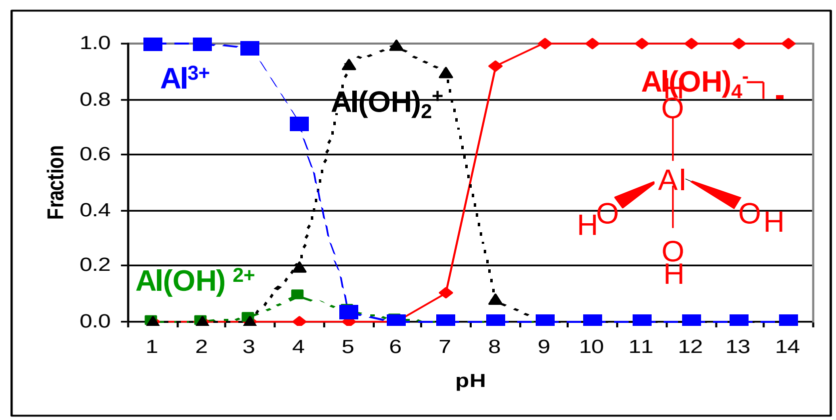




…….. and so is aluminate!

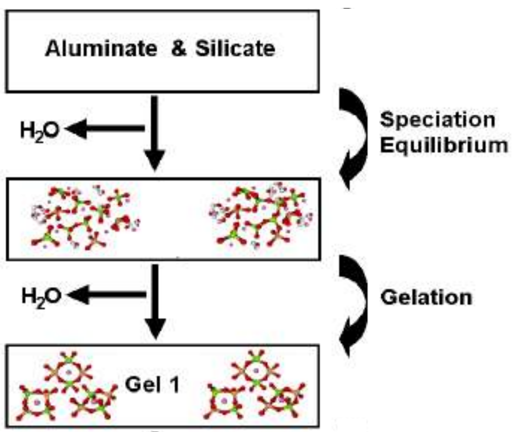


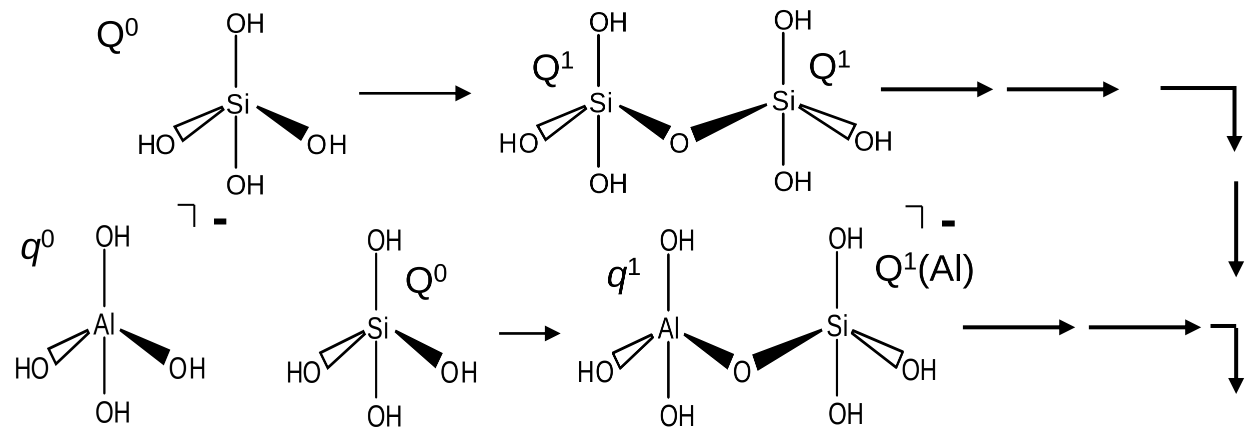
D Barby, *et al*, in 'The Modern Inorganic Chemicals Industry,' ed. R. Thompson, The Chemical Society, London, 1977.

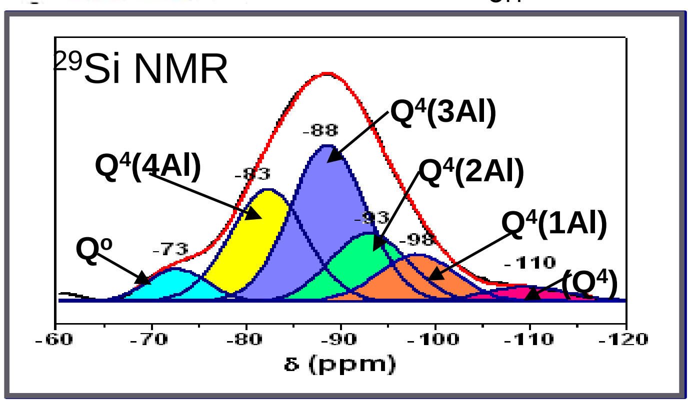


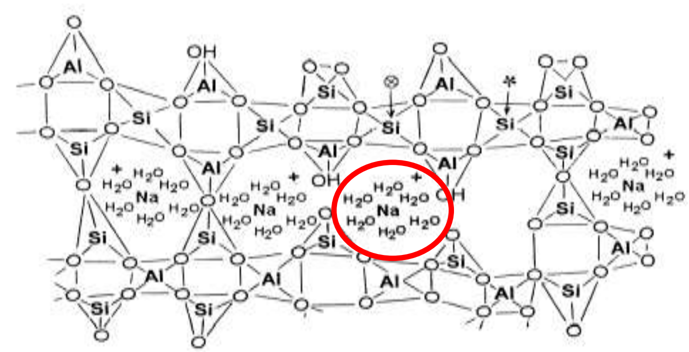
- **at cement-relevant pH, silicates and aluminates are predicted to be monomeric but only *partially* deprotonated**

Precipitation - formation of siloxane and sialate linkages (gel formation)







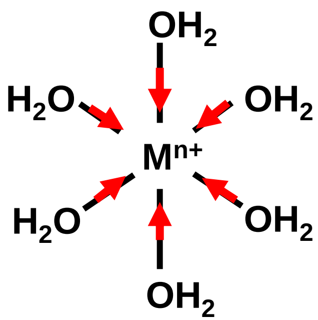


Barbosa, VFF, et al, ***Int. J. Inorg. Mats.****, 2, 309-17, (2000)*

What factors influence degree of condensation?

- **availability of reactive species (rate of hydrolysis and diffusion characteristics)**
- ***local*** **pH**
- **presence and characteristics of cations**

Effect of counter ions – cation hydrolysis

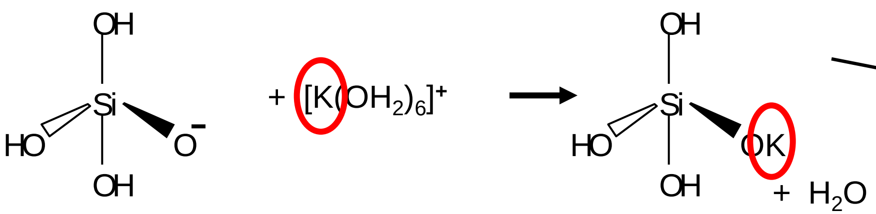


• cation charge density (Z/r) → polarisability

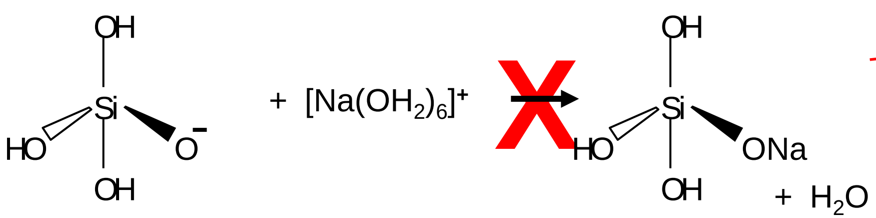
	Li^+	Na^+	K^+
Radius A°	0.68	0.97	1.33
Z/r	1.47	1	0.75
ΔH^o_{hydn}/kJmol^{-1}	-519	-406	-322

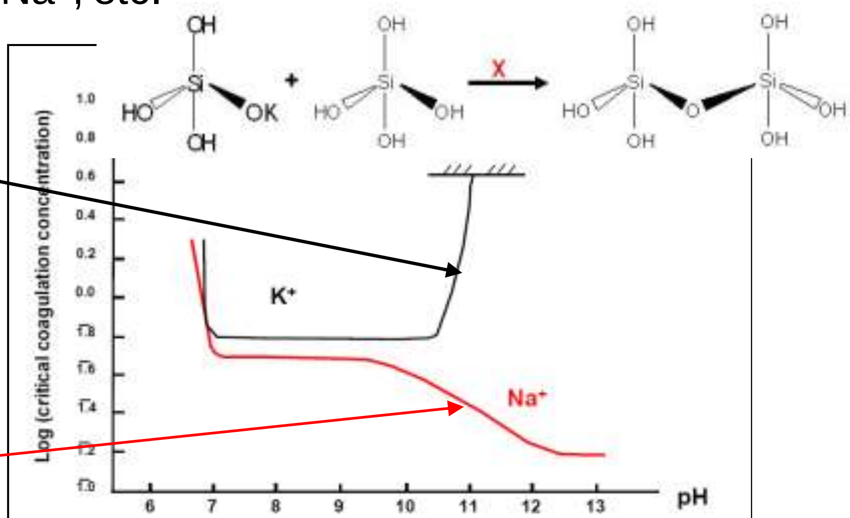
• K^+ less strongly hydrated than Na^+, etc.

• silicate species are negatively charged



For $Na^+_{(aq)}$



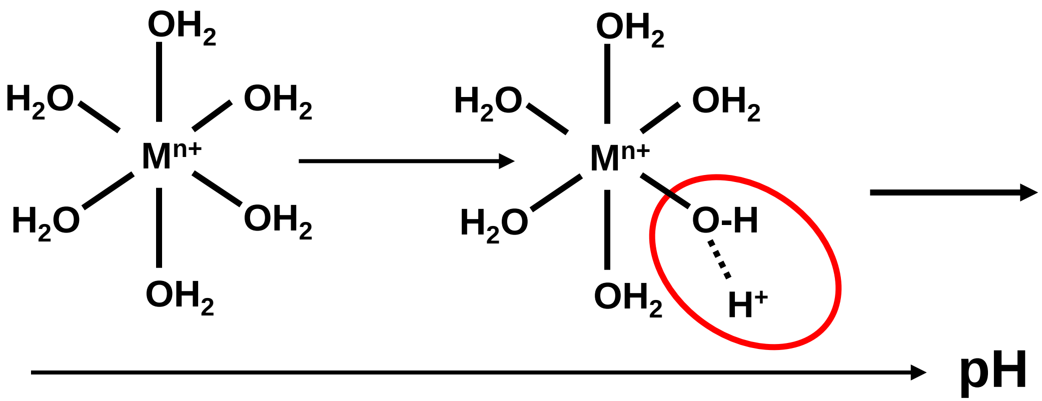


Critical concentrations of KCl and NaCl for coagulation of silica sols

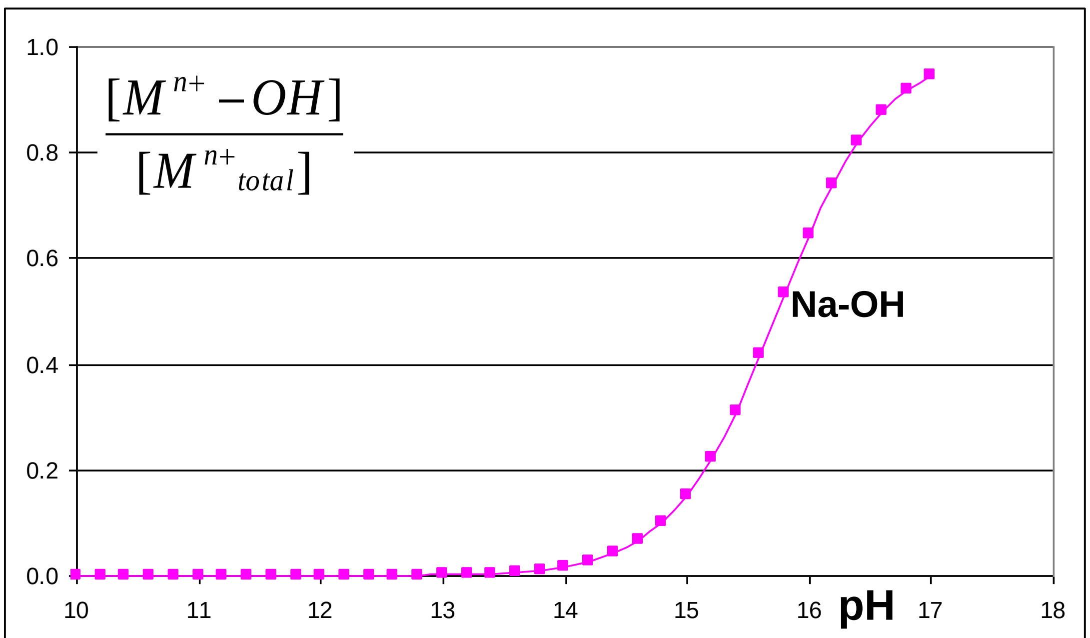
J Depasse and A Watillon, J. Coll. and Int. Sci., 33, 430, (1970)

http://www.pharmacorama.com/en/Sections/Elements-Water.php

Further Hydrolytic Effects

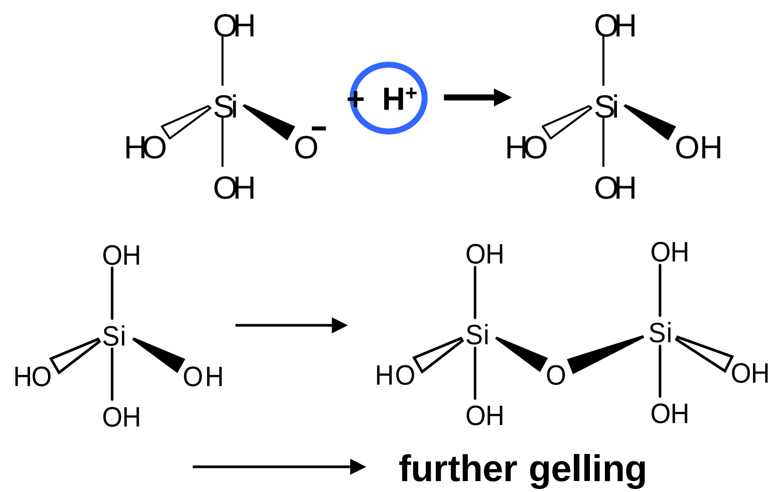


$$[MOH(OH_2)_5]^{(n-1)+} + H^+$$



e.g. for Na^+

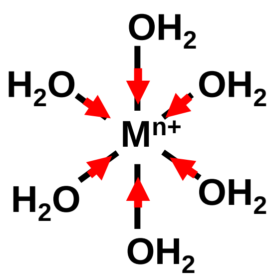
$NaOH(OH_2)_5 + H^+$

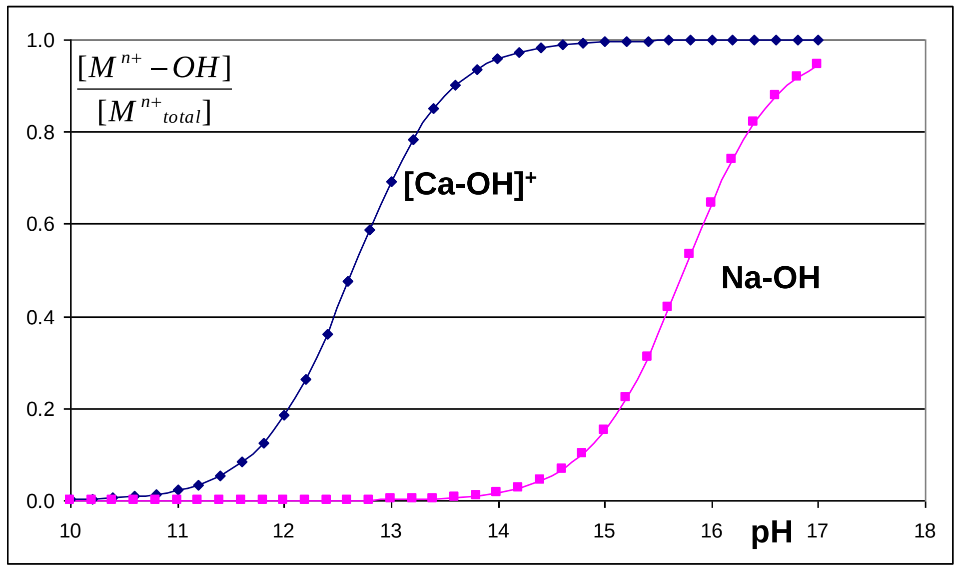


Alkaline earths – even better as complexing cations

Ca^{2+} even more acidic than Na^+

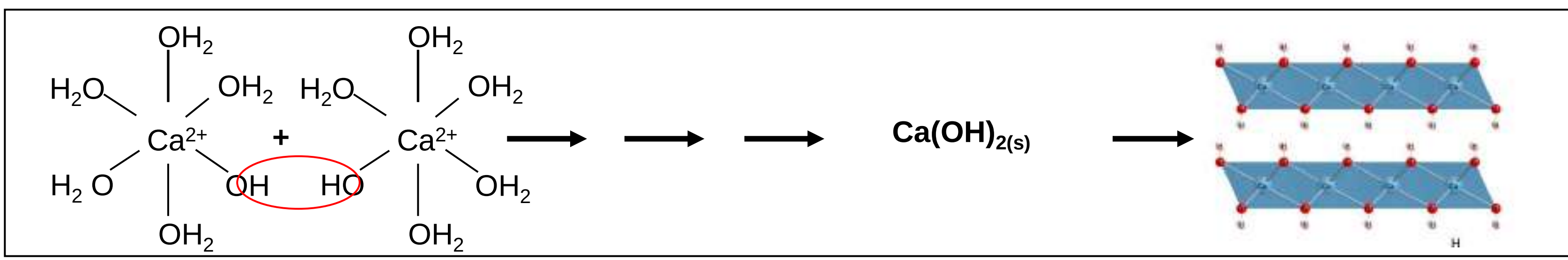
- dissociates at lower pH
- lower solubility in alkaline conditions





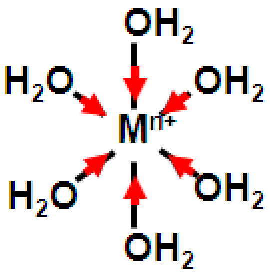
	Na^+	Mg^{2+}	Ca^{2+}
Radius A°	0.97	0.66	0.99
Z/r	1	3	2
ΔH^o_{hydn}/kJmol^{-1}	-406	-1921	-1577

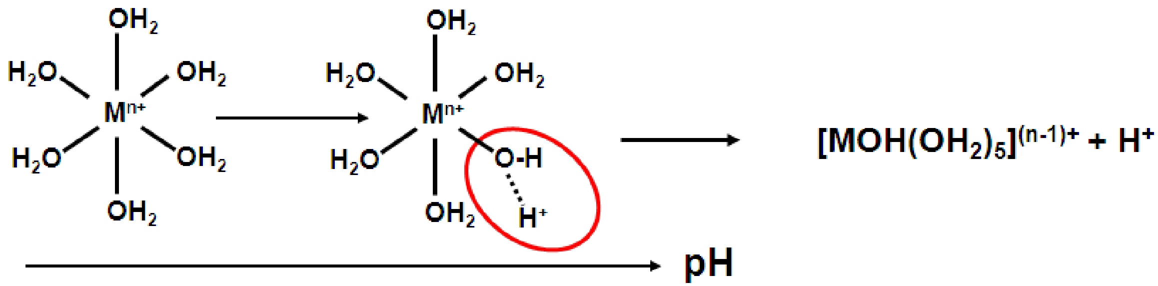
http://www.pharmacorama.com/en/Sections/Elements-Water.php



C-A-S-H or N-A-S-H?

Hydrolysis effects





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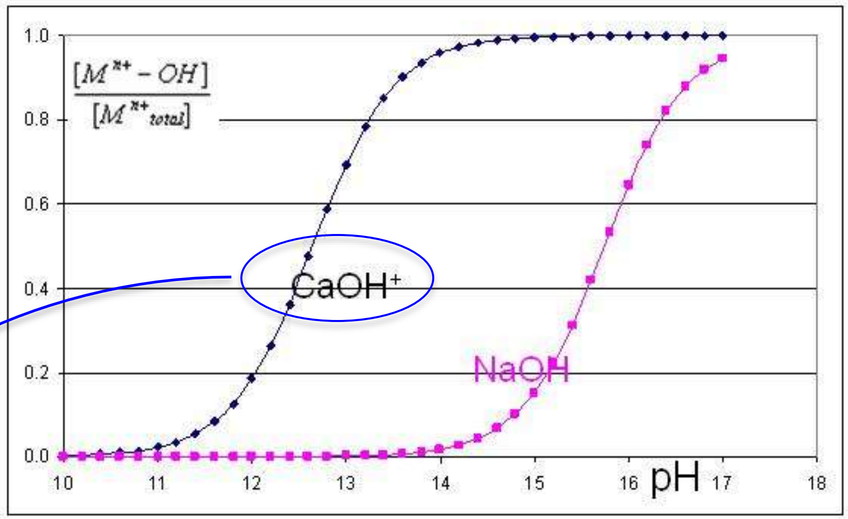
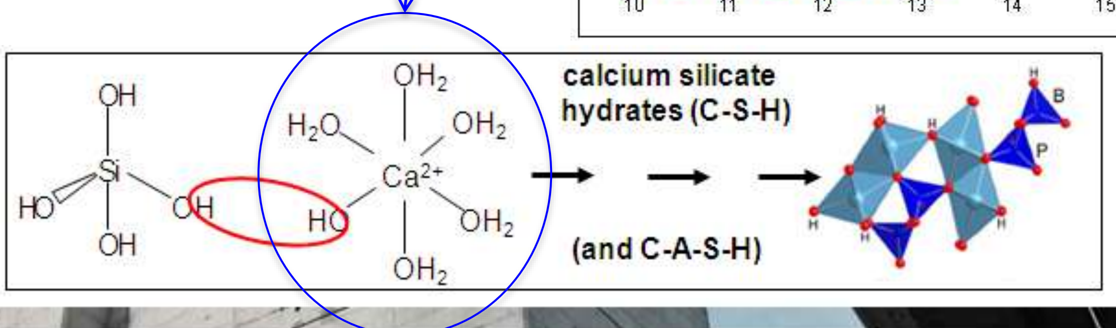
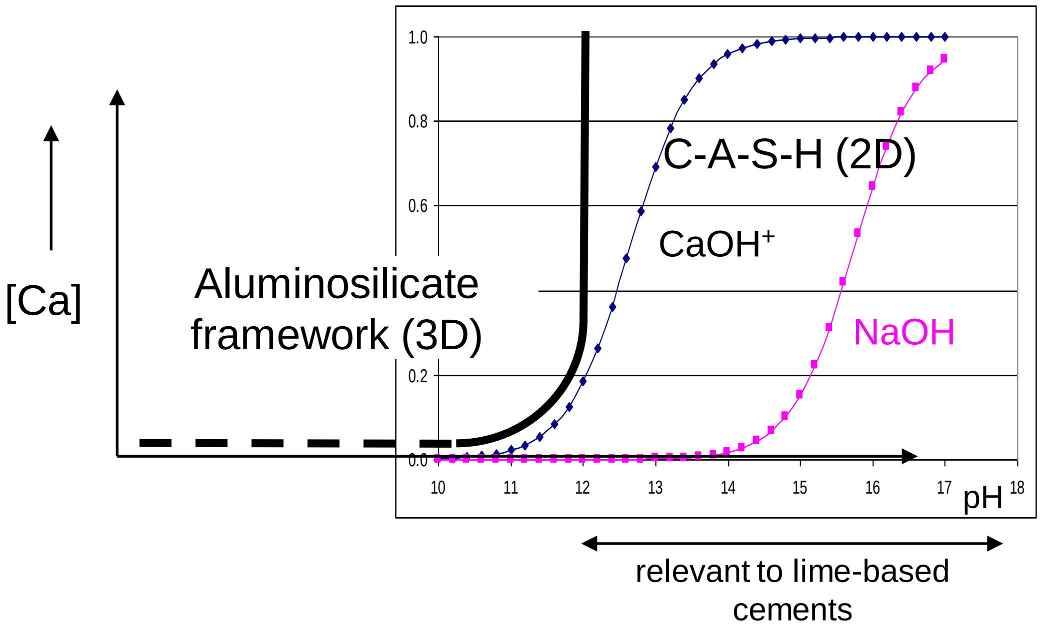


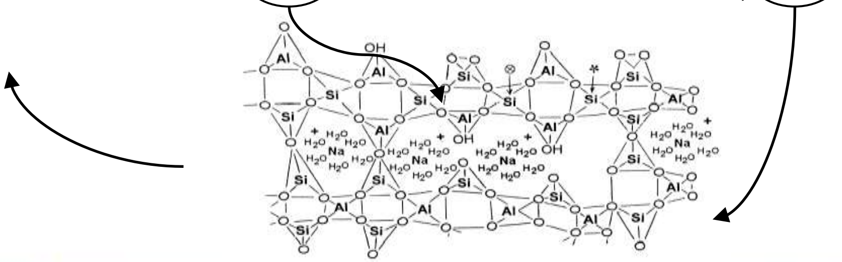


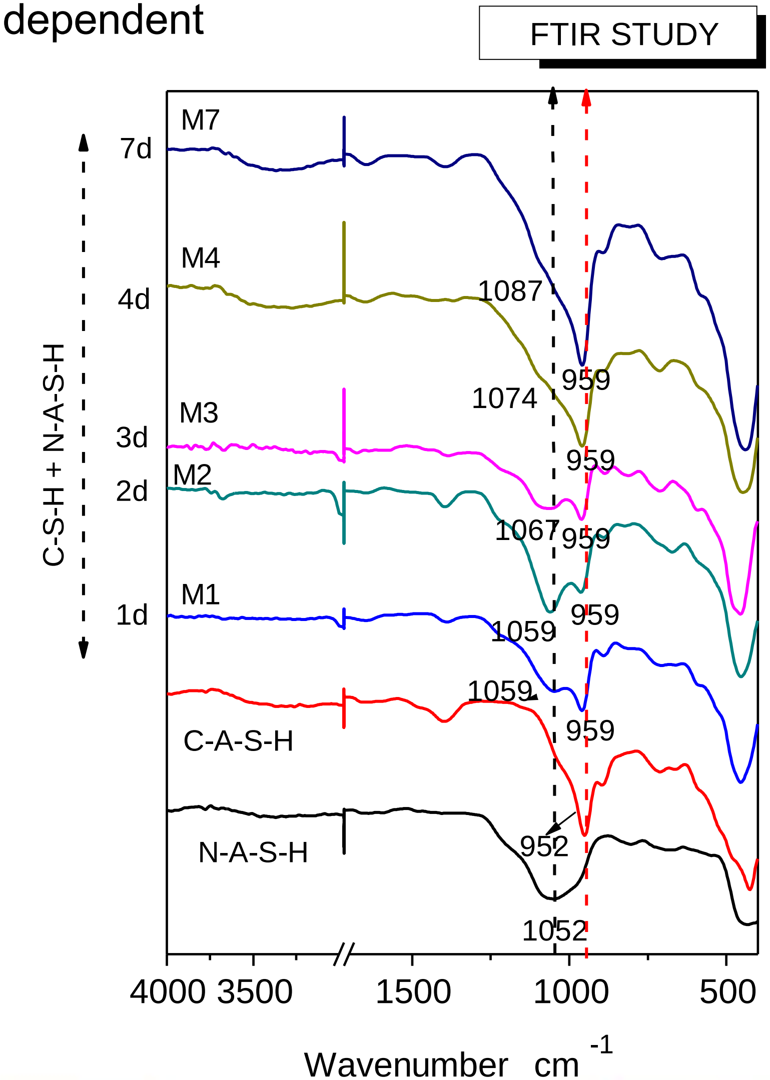
N-A-S-H or C-A-S-H?

- stability of 'NASH structure' in the presence of Ca is pH dependent
- pozzolanic behaviour is expected at high enough pH

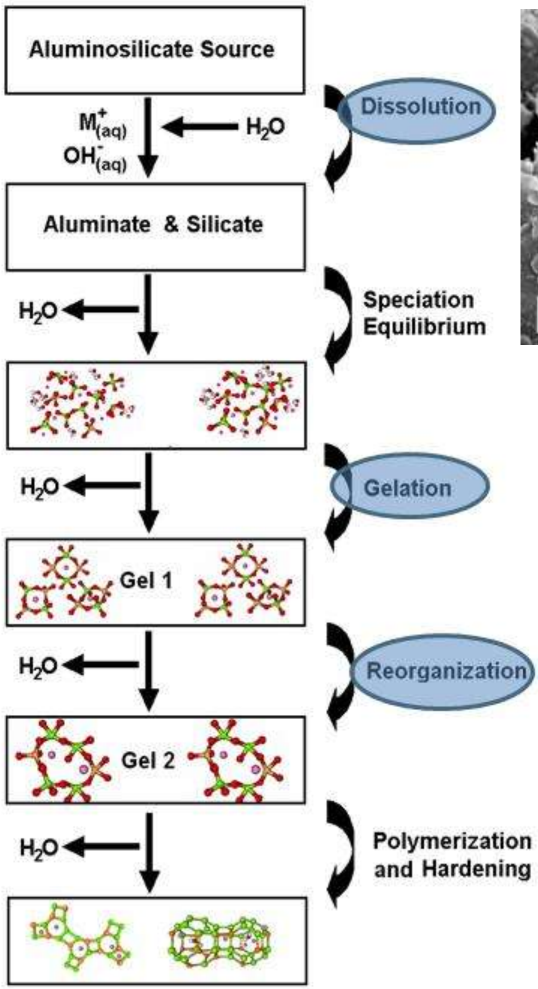


C-A-S-H ⇄ Ca^{2+}, $H_nSiO_4^{(4-n)-}$, $Al(OH)_4^-$, OH^-

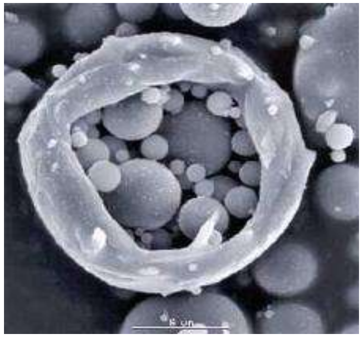


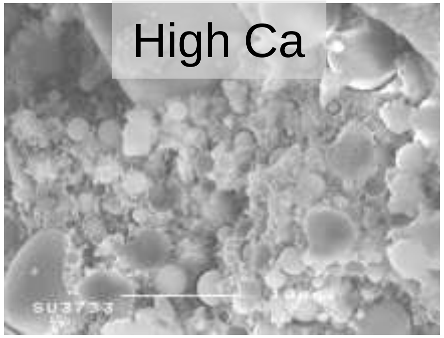


Cement Reactions



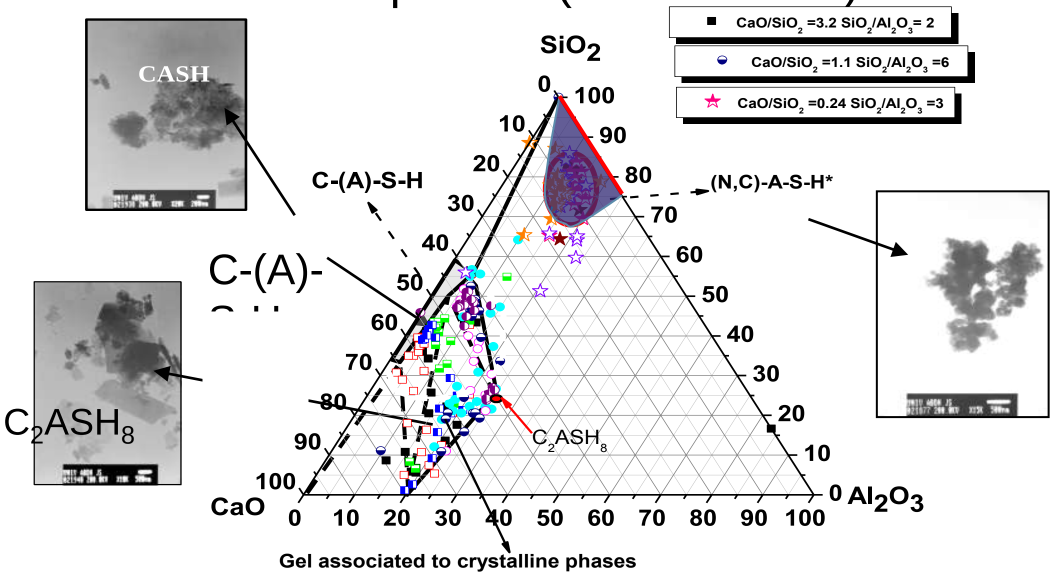
P. Duxson, et al, J. Mat. Sci. <u>*42*</u>*, 2917-33, (2007)*





PFA + 8M NaOH (85ºC 20 hrs) PFA 5:4 PFA:OPC 90 days at 20ºC

Precipitation (but as what?)



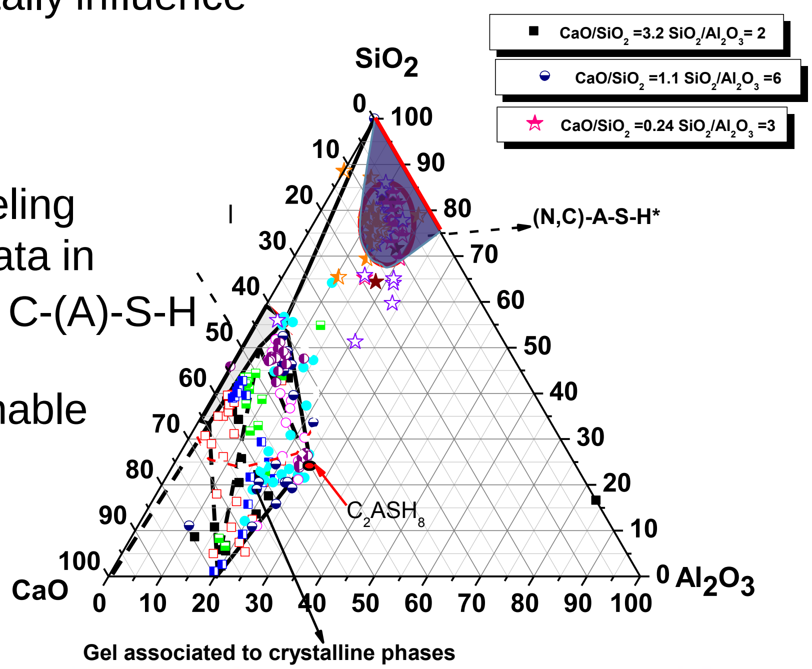
Gartner, E.M. and Macphee, D.E., 'A Physico-Chemical Basis for Novel Cementitious Binders', ***Cement and Concrete Research***, (*in press, 2011)*)

Summary of Outcomes:

- equilibrium phase relations proposed for the partial $Na_2O.CaO.Al_2O_3.SiO_2.H_2O$ system at 25°C
- new solubility data for several phase assemblages arising in the $Na_2O.CaO.Al_2O_3.SiO_2.H_2O$ system at 25°C
- distinction between (N,C)-A-S-H and C-A-S-H phases and conditions of stability identified
- cation polarisaility/pH effects fundamentally influence precipitation/gelation

Opportunities:

- to build on current thermodynamic modeling capability by integrating new solubility data in existing databases
- to extend the characterisation of the $Na_2O.CaO.Al_2O_3.SiO_2.H_2O$ system to enable predictions of phase relations in more lime deficient regions (to understand implications of higher SCM additions)



SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

UNIVERSITY OF ABERDEEN

Activation of aluminosilicates - some chemical considerations

Donald E Macphee and Ines Garcia Lodeiro

centre

SMART-PRO²