Hydration products of SCM blended cements

Data collection

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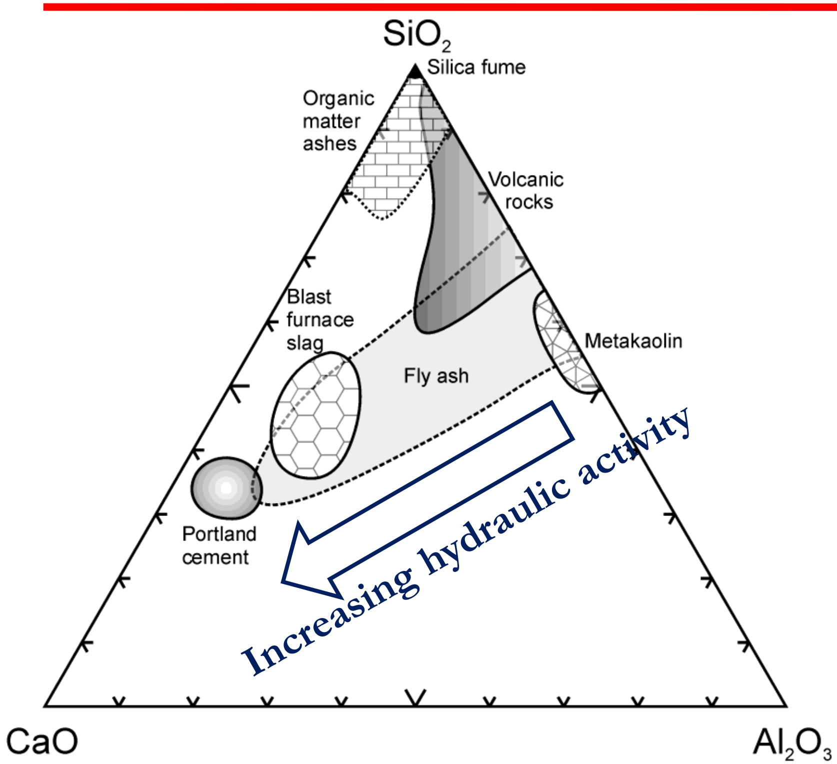
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

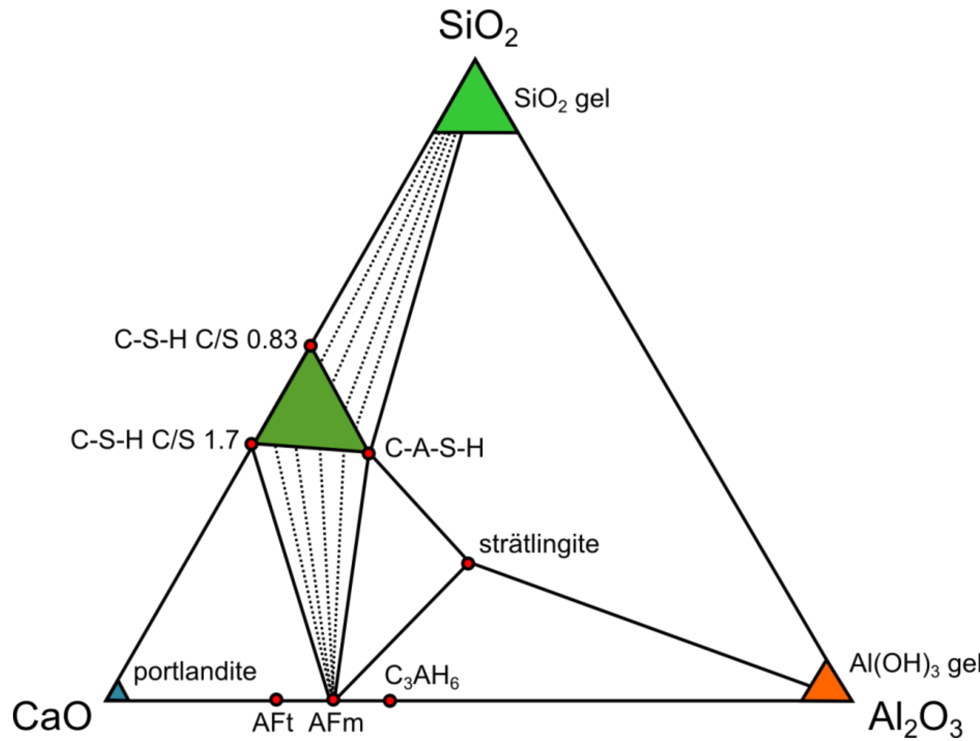
Outline

- Overview of hydrate assemblages in blended cements
- Hydration products in blended cements
  - C-A-S-H
  - AFt phases
  - Layered double hydroxides
    - AFm phases: SO_4^{2-} – CO_3^{2-} - OH^-
    - Al:Si; strätlingite
    - Mg:Al; hydrotalcite (-like) phases
  - Hydrogarnets
  - Metal hydroxides
- Summary and outcome

Hydrate assemblage overview



Ternary diagram (wt%) of the major SCM groups and Portland cement



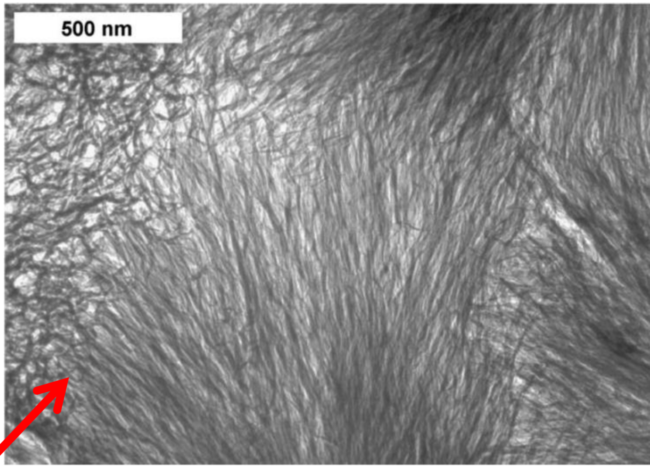
Ternary diagram (wt%) of cement hydration products (cf. Lothenbach et al. 2011)

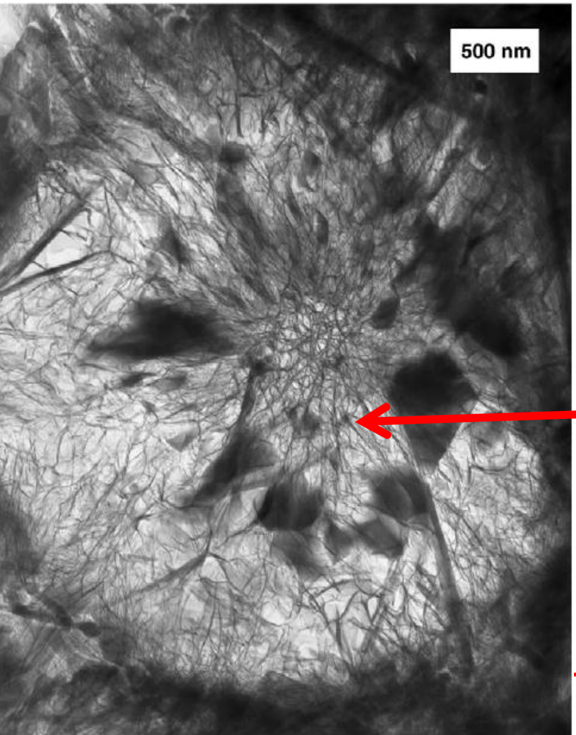
Similar hydration products as in OPC, composition and proportions change depending on:

1. **Overall compositional change**: CaO:(Al_2O_3-SiO_2), Al_2O_3:SiO_2, Al_2O_3:(SO_4^{2-}-CO_3^{2-} -X^{m-}),...
2. **SCM reactivity**: rate of release of constituents compared to hydration of PC components

C-(A)-S-H in blended cements

- Occurrence: morphology and microstructure
  - Outer product:
    - Fibrillar morphology linked to high Ca:Si
    - Foil-like morphology at low Ca:Si and high Al content
  - Inner product:
    - LD: coarse, wavy infill of relict particles
    - HD: fine texture, intermixed with LDH phases



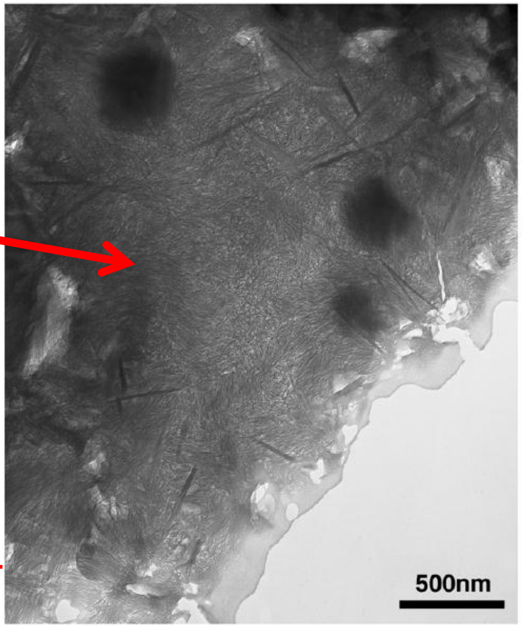


TEM examples

50% slag paste OP [Richardson, 2004]

50% slag paste IP [Taylor et al., 2010]

Reacted FA particle [Giraõ et al., 2010]



C-(A)-S-H in blended cements

- Impact of SCM addition on C-A-S-H composition
  - Data collection for real systems

Reference	System						C-A-S-H					
		SCM %	T	Age	Curing	w/b	Ca/Si	Ca/(Al+Si)	Al/Si	MCL	Ip Morphology	Op Morphology
	OPC	0	20	1y, 26y	water	0.4	1.7-1.8		0.05	3.3-5.0	Fine	fibrillar
Taylor et al 2010	OPC-Slag	10	20	20y	water	0.4	1.6		0.12	6.7	Fine	fibrillar to foil (increasing slag content)
Taylor et al 2010	OPC-Slag	90	20	20y	water	0.4	1.18		0.18	14.3	Fine	fibrillar to foil (increasing slag content)
Girao et al 2010	OPC-FA	30	55	1 mth	water		1.57		0.2	15.6	low density foil fibrillar in FA	foils and fibrils
Love et al 2007	OPC-MK	20	25	1 day	water	0.55			0.06	2.8		fibrils
Love et al 2007	OPC-MK	20	25	1 mth	water	0.55	1.43	1.14	0.25	11	Fine	foils and fibrils
Richardson 2000	OPC-SF	>50	40	3 mth	water	0.7	0.7-0.8			8.5	20% SF fine >50% SF: foil	foil-like
Rayment 1982	OPC-FA	20	20	8 d	water	0.5	1.55	1.38	0.12			

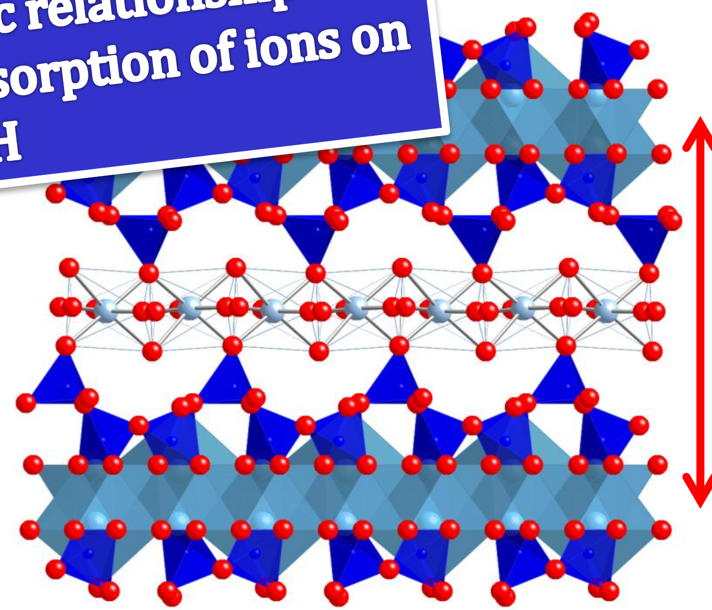
[J. Rossen]

  - GGBFS: lowers (slightly) Ca:Si, increases Al:Si
  - Pozzolans: lowers Ca:Si, increases Al:Si (except SF)
  - Compositional changes depend on **SCM%** and **age**

C-(A)-S-H in blended cements

- Impact of SCM addition on C-A-S-H atomic structure
  - Most likely defect tobermorite models for C-S-H of low Ca:Si typically found in blended cements (Richardson, 2004)
  - Decrease of Ca/(Si+Al) leads to chain polymerisation
  - Incorporation of Al[4] predominantly in bridging sites
  - Al[5] and Al[6] may substitute Ca in interlayer (NMR
  - Limite
    - Mg
    - Fe
    - Sulfate
    - Alkalies
  - Difficulties in distinguishing structural incorporation from fine-scale intermixing and adsorption

Lack of thermodynamic relationships describing incorporation/sorption of ions on C-(A)-S-H



14 Å

[Bonaccorsi et al., 2005]

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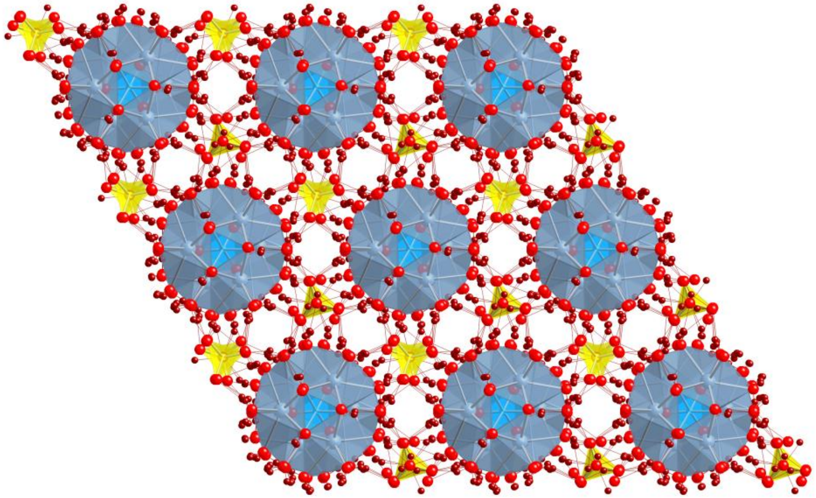
AFt phases

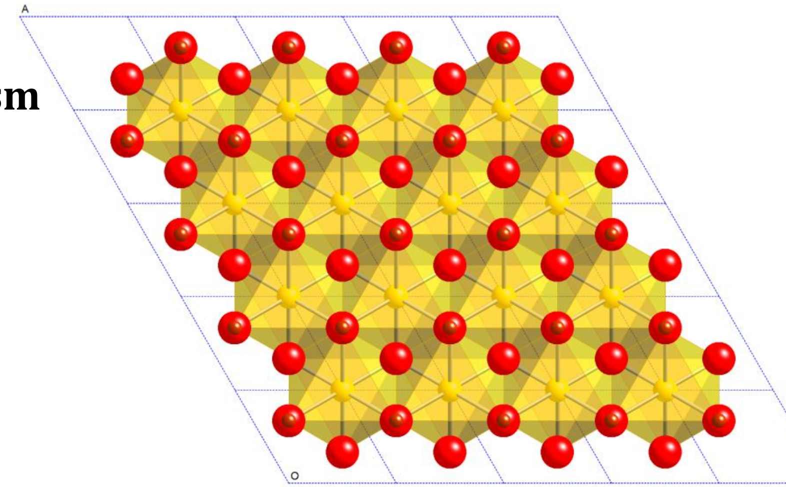
- $[Ca_3(Al,Fe)(OH)_6 \cdot 12H_2O]_2 \cdot X_3 \cdot xH_2O$
  - X is divalent anion
- Occurrence
  - Ettringite forms early on in blended cements
  - Transforms into AFm phases depending on sulfate and carbonate activity
- No systematic changes in composition reported for blended cements
  - Solid solution 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)

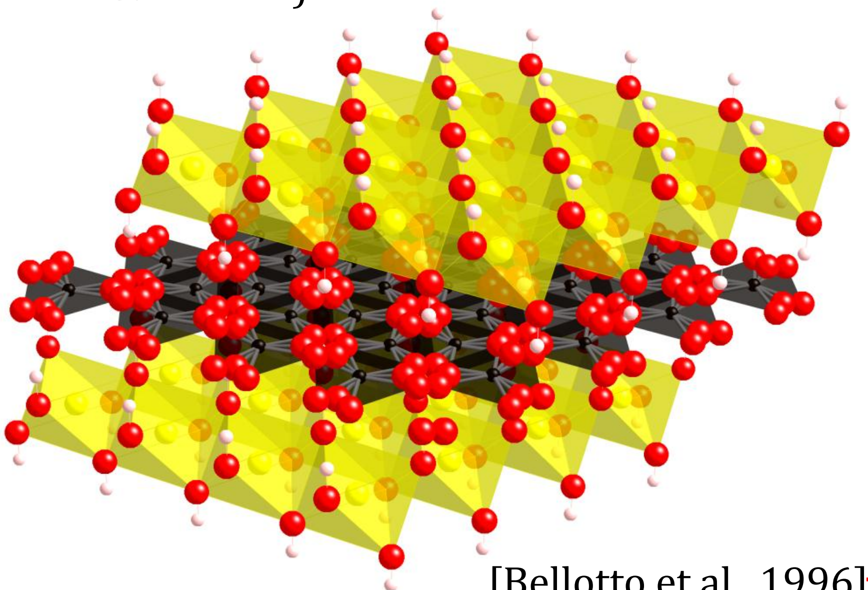


[Hartman & Berliner, 2006]

Layered double hydroxides

- LDH – hydrotalcite supergroup nomenclature
  (Mills et al., IMA report 2012)
  - $[(M_{1-x}^{2+}M_x^{3+})(OH)_2]^{x+}$ 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)





[Bellotto et al., 1996]

«Proposal of compact notation for synthetic LDH phase for use by chemists as alternative to the widespread misuse of mineral names» (Mills et al., 2012)

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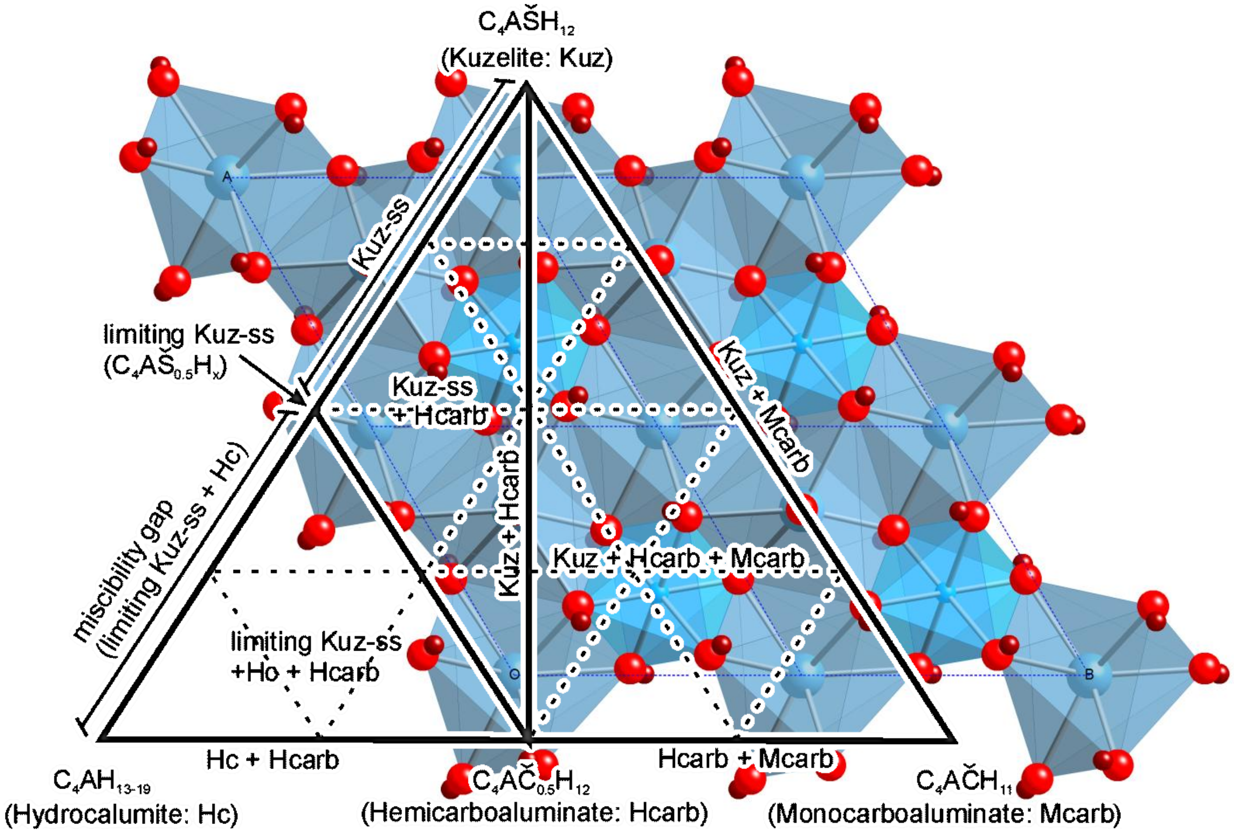
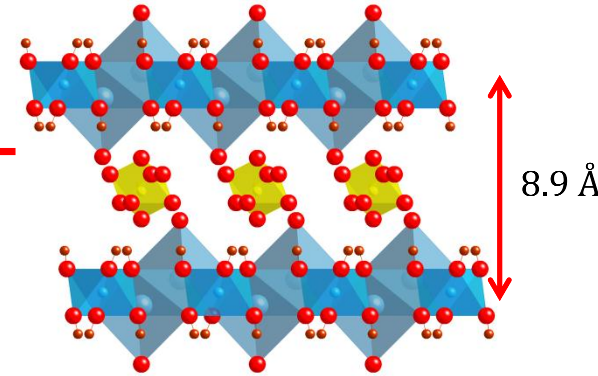
Layered double hydroxides

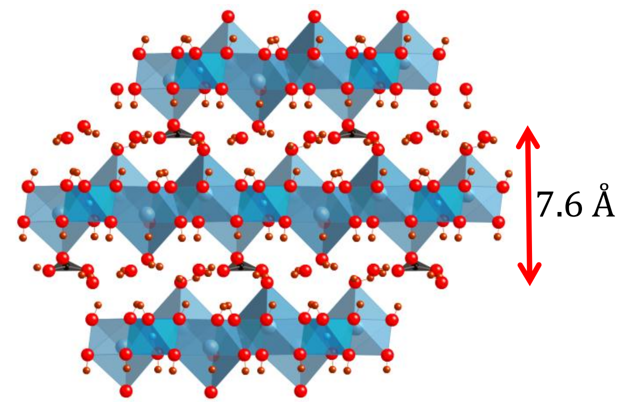
- LDH in cement: AFm phases
  - Distorted brucite layer, Ca:Al 2:1
  - AFm-SO_4^{2-} – CO_3^{2-} – OH^-
  - Limited solid solution between end-members



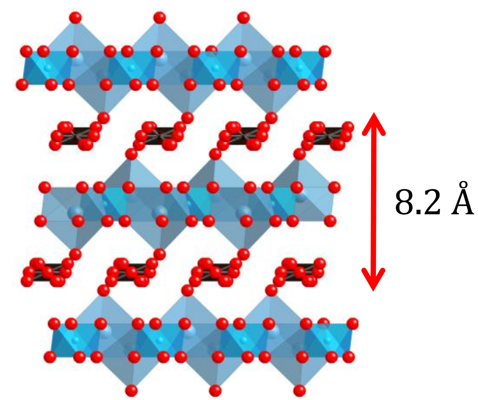
[Matschei et al., 2007]



[Allmann, 1977]



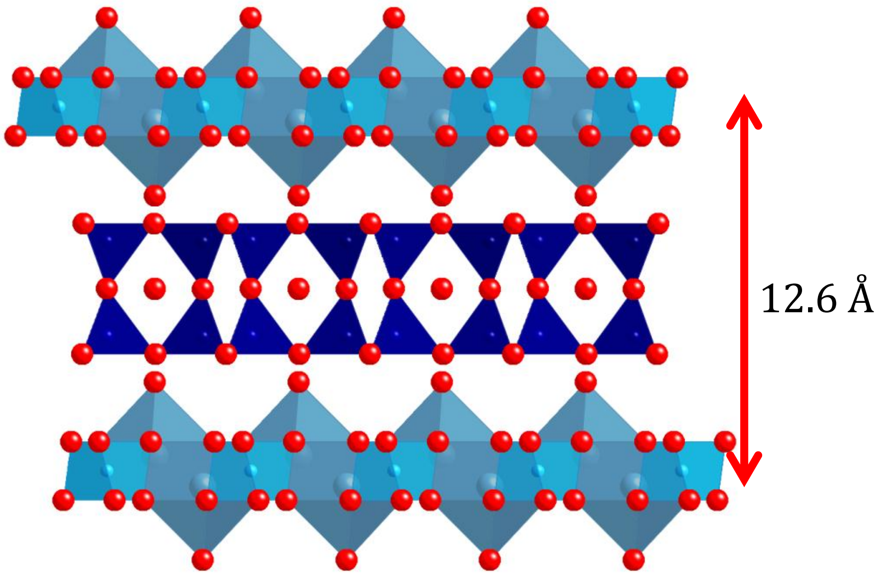
[Francois et al., 1998]



[Rumcevski et al., 2012]

Layered double hydroxides

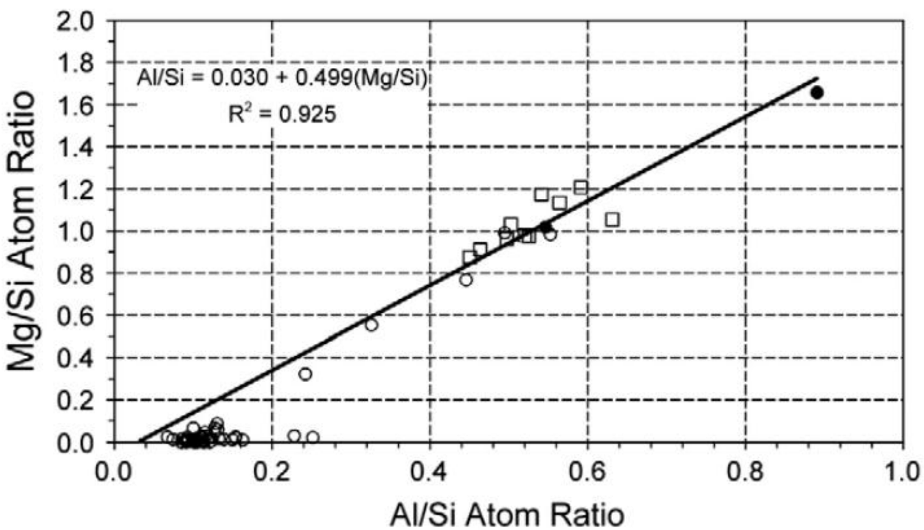
- Compositional solid solution
  - Strätlingite (hydrated gehlenite)
    - $(Al, Si)_2OH_8$ groups in interlayer
    - Conditions of formation and solubility not well constrained
    - Occurrence
      - Low SO_3/Al_2O_3 ratio (MK, Class C FA)
      - Absence of CH



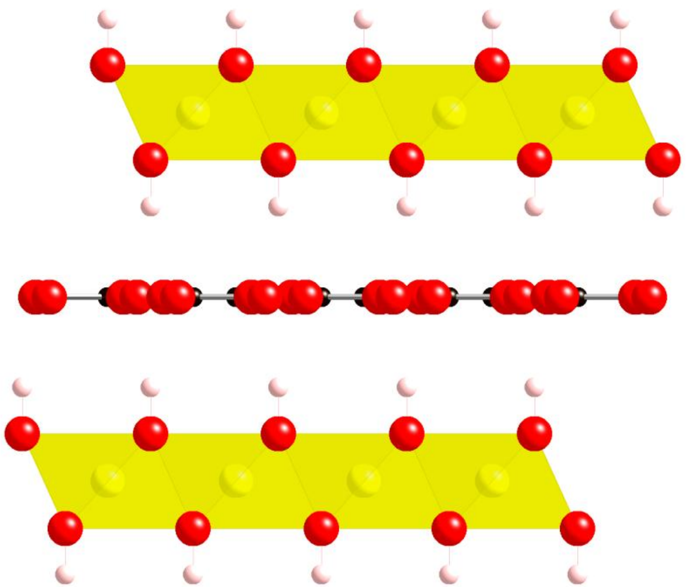
[Rinaldi et al., 1990]

Layered double hydroxides

- Compositional solid solution:
  - Mg – hydrotalcite-like phases:
    - Mg:Al ratio 2:1 (quintinite) or 3:1 (hydrotalcite)?
    - Variable anion content, most selective for CO_3^{2-}
    - Intimately mixed with C-A-S-H in SCM Ip



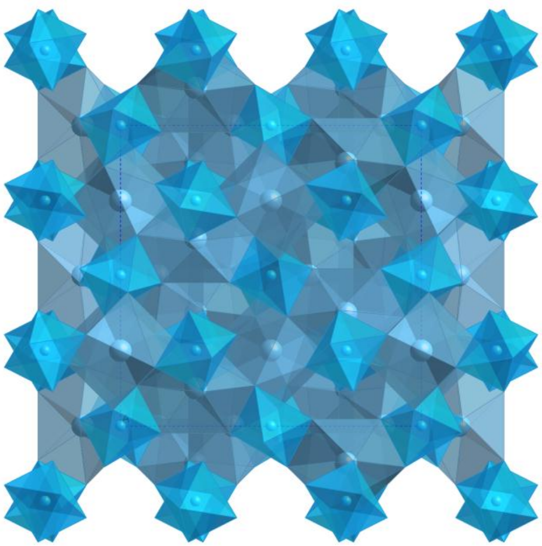
TEM-EDX of 50% slag – OPC systems
[Taylor et al., 2010]



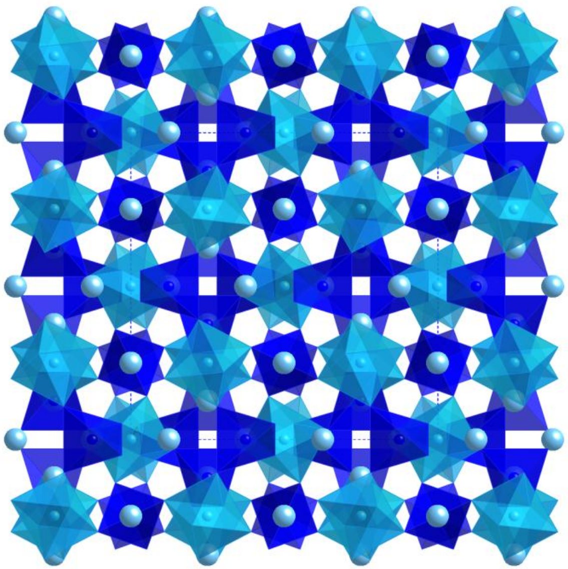
[Bellotto et al., 1996]

Hydrogarnets

- Occurrence, composition and structure
  - 3Ca:Al katoite
  - Si[4] connects Al[6] in siliceous hydrogarnet
  - Thermodynamically stable phase in many blended cements
  - Forms slowly at low T (high E_a?)
  - Occurs in high T cured cements and old cements



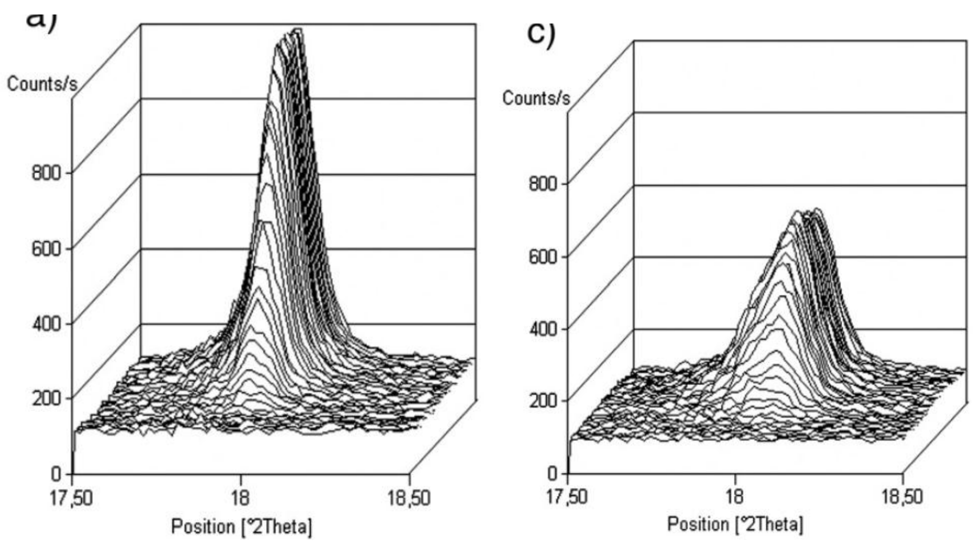
Hydrogarnet
[Cohen-Addad et al., 1964]



Siliceous hydrogarnet
[Sacerdoti & Passaglia, 1985]

Metal hydroxides

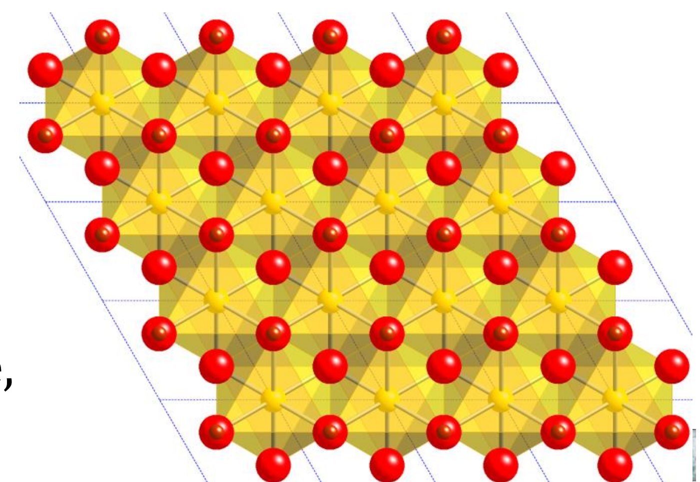
- Portlandite
  - Consumption in pozzolanic reaction
  - Change in crystallite size during consumption



OPC PC-SF

[Korpa et al., 2008]

- Brucite
  - Not easily identified (TG)
  - Forms simultaneously with ettringite, when sulfate availability is high



Summary

- Hydration product assemblages are largely similar to OPC, however SCM changes:
  - Proportions of the hydration products
  - Composition of hydration products
    - **C-A-S-H**: lower C/S, more polymerized, Al incorporation
      - More data needed that describe solid solution/sorption in function of C-A-S-H properties and (pore) solution composition
    - **AFt and LDH** phases: few *in situ* data for blended cements
      - General assumption that compositional variation is limited or similar to synthetic systems at thermodynamic equilibrium
- Fine-scale **intergrowth/intermixing** often interferes with hydrate characterisation in real blended cements, many data derive from simplified synthetic systems

Projected outcomes

- Papers summarizing knowledge on hydrate assemblages in blended cements already exist (Richardson, 2004; Lothenbach et al., 2011)

- Need for guidelines in characterisation of blended cements hydrate assemblages

- Review documenting
  - **XRD** identification table
  - Characteristic **TGA** weight loss intervals
  - Solid state **NMR** chemical shifts
  - …

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