# Alkali-Activated and Geopolymer Cements: Design from Atoms to Applications

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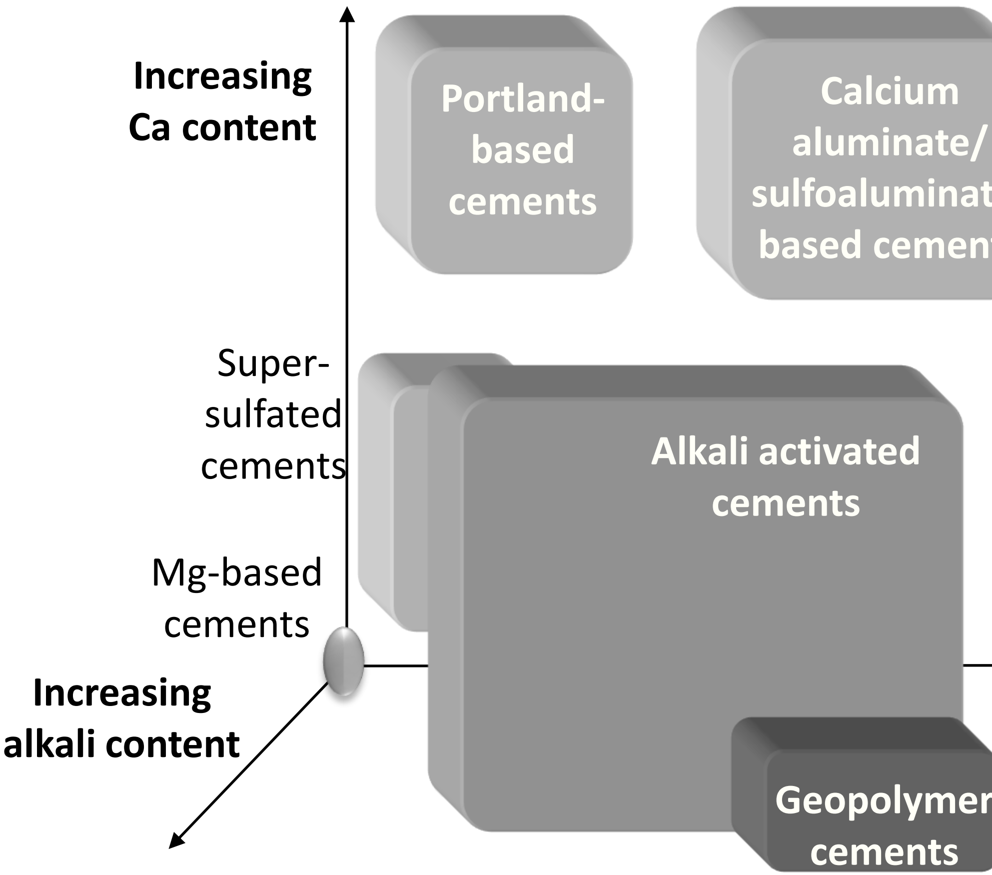
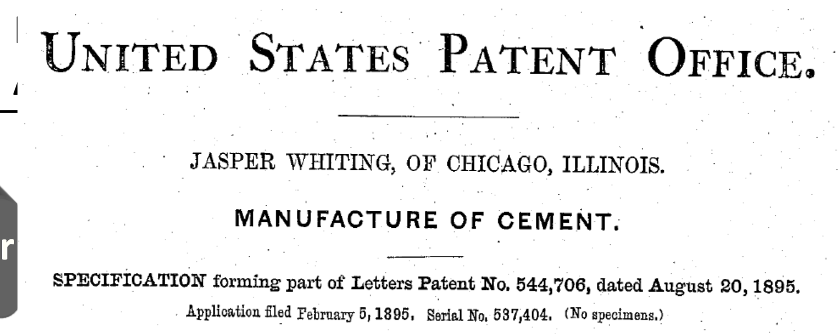
# Traditional and non-traditional cements

**Moving from a single universal cement to an array of cement types**




J. Whiting, U.S. Patent 544,706, 1895 – alkali-activated slag



UNITED STATES PATENT OFFICE.

JASPER WHITING, OF CHICAGO, ILLINOIS.

MANUFACTURE OF CEMENT.

SPECIFICATION forming part of Letters Patent No. 544,706, dated August 20, 1895.

Application filed February 5, 1895. Serial No. 537,404. (No specimens.)

**Most important: Designing materials that are fit for purpose!**



Adapted from: J.L. Provis & J.S.J. van Deventer (eds.), State of the Art Report of RILEM TC 224-AAM, 2014

# Why alkali activation?

- Common SCMs are less reactive than clinker, reaction with water is slow

  → Chemical activation needed

- High-volume blended cements use PC clinker as activator – but it is not optimised for this task!
  - Clinker components & gypsum balanced to give optimal rheology, reaction & strength when used alone
  - If another material dominates, this is no longer optimal

**→ Why not use a purpose-designed alkali activator instead?**

# e.g. Brisbane West Wellcamp Airport (Wagners; Australia)

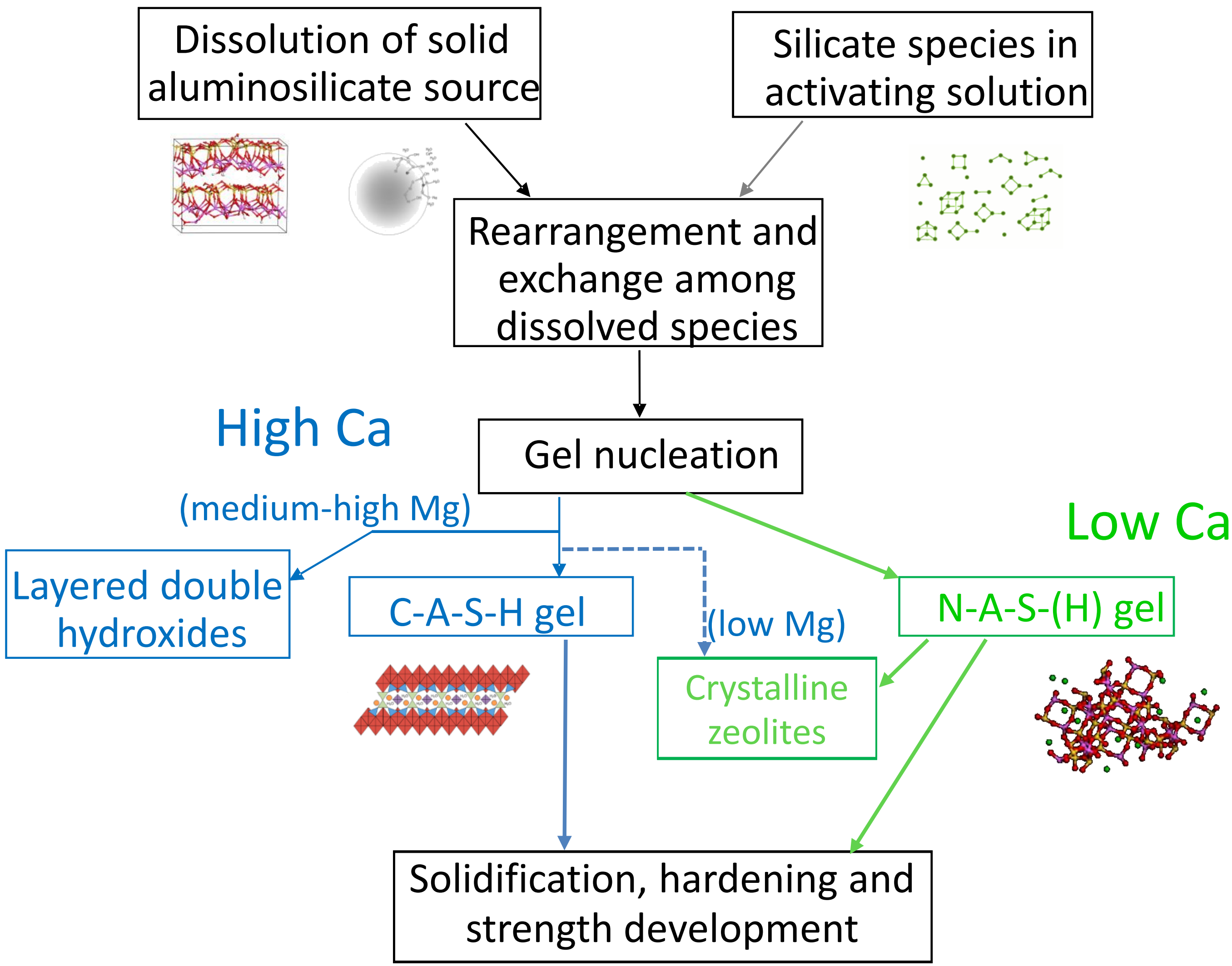

http://australianaviation.com.au/wp-content/uploads/2015/11/Lenn-Bayliss-First-747-8-to-Wellcamp-Airport-Monday-23-November-2015-2.jpg

http://www.engineersaustralia.org.au/portal/news/brisbane-west-wellcamp-airport-world%E2%80%99s-greenest

# Some comments on "sustainability"

- Many studies calculate net $CO_2$ savings for alkali-activated binders cf. Portland cement
  - Values range from 9 to 97% savings
  - Very few studies specific to an application or location, and few take care with reference concrete
- Realistic value probably ~40-80% in most locations and applications
- ~90% of environmental footprint of an alkali-activated binder is from the activator (!)
  - Particularly if Na silicate is sourced from $Na_2CO_3$ produced using the Solvay process

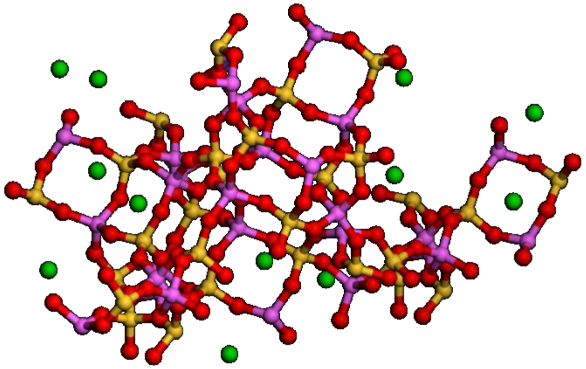
# How does it happen?



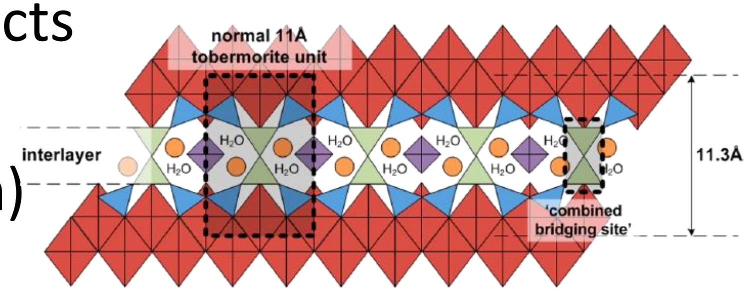

J.L. Provis & S.A. Bernal, *Annual Review of Materials Research*, 2014, 44: 299–327

# Gel chemistry

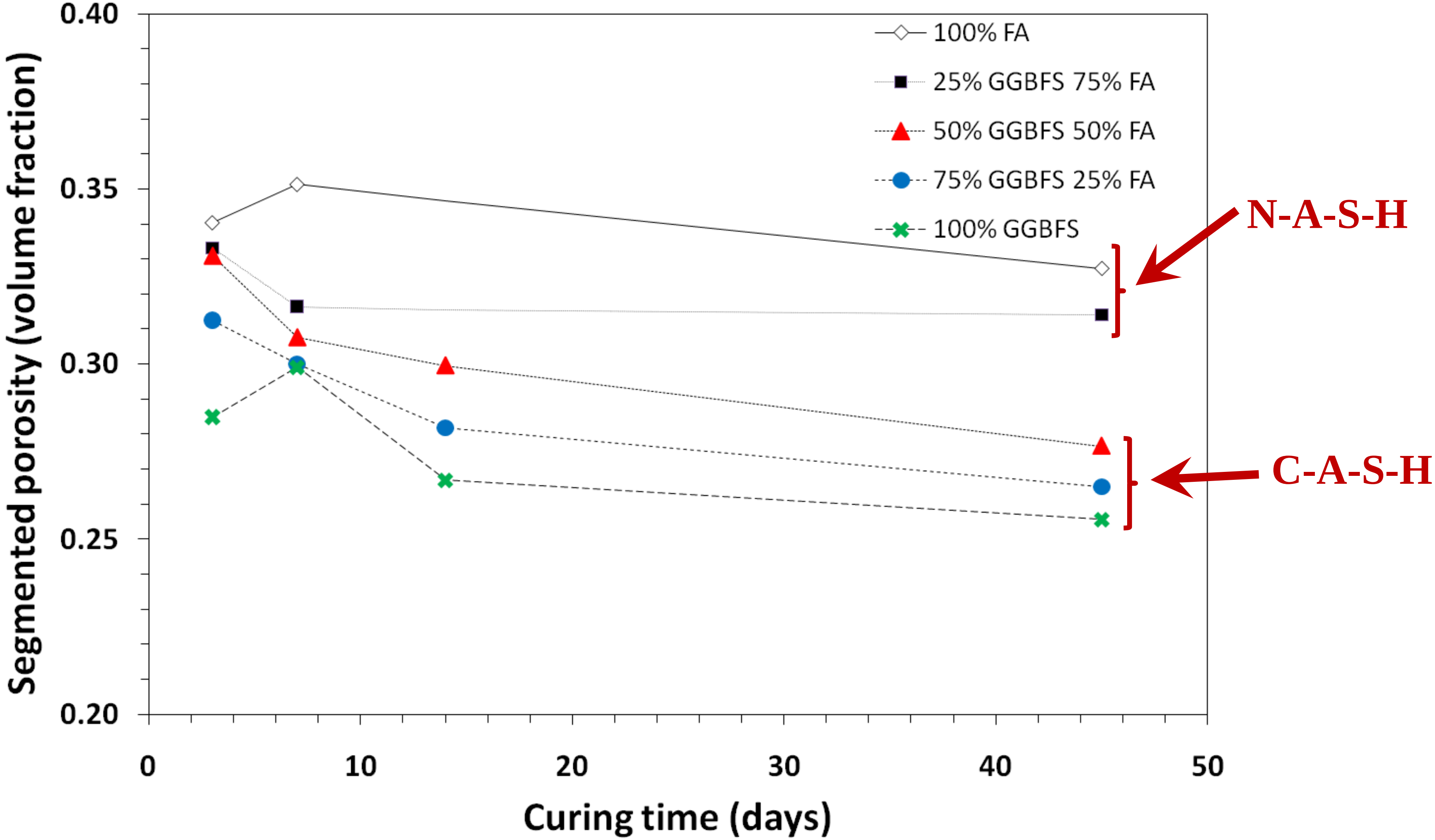
- Alkali activation with low calcium – N-A-S-(H) (‘geopolymer’) gel
  - Fly ash, metakaolin precursors
  - Pseudo-zeolitic structure, sometimes minor crystalline inclusions
  - Little chemically bound water



- Alkali activation with more calcium – C-A-S-H type gel
  - Low C/S ratio, high Al content, generally more cross-linked than PC hydration products
  - Secondary phases mostly layered double hydroxides (hydrotalcite/AFm)
  - Some bound water (space-filling)



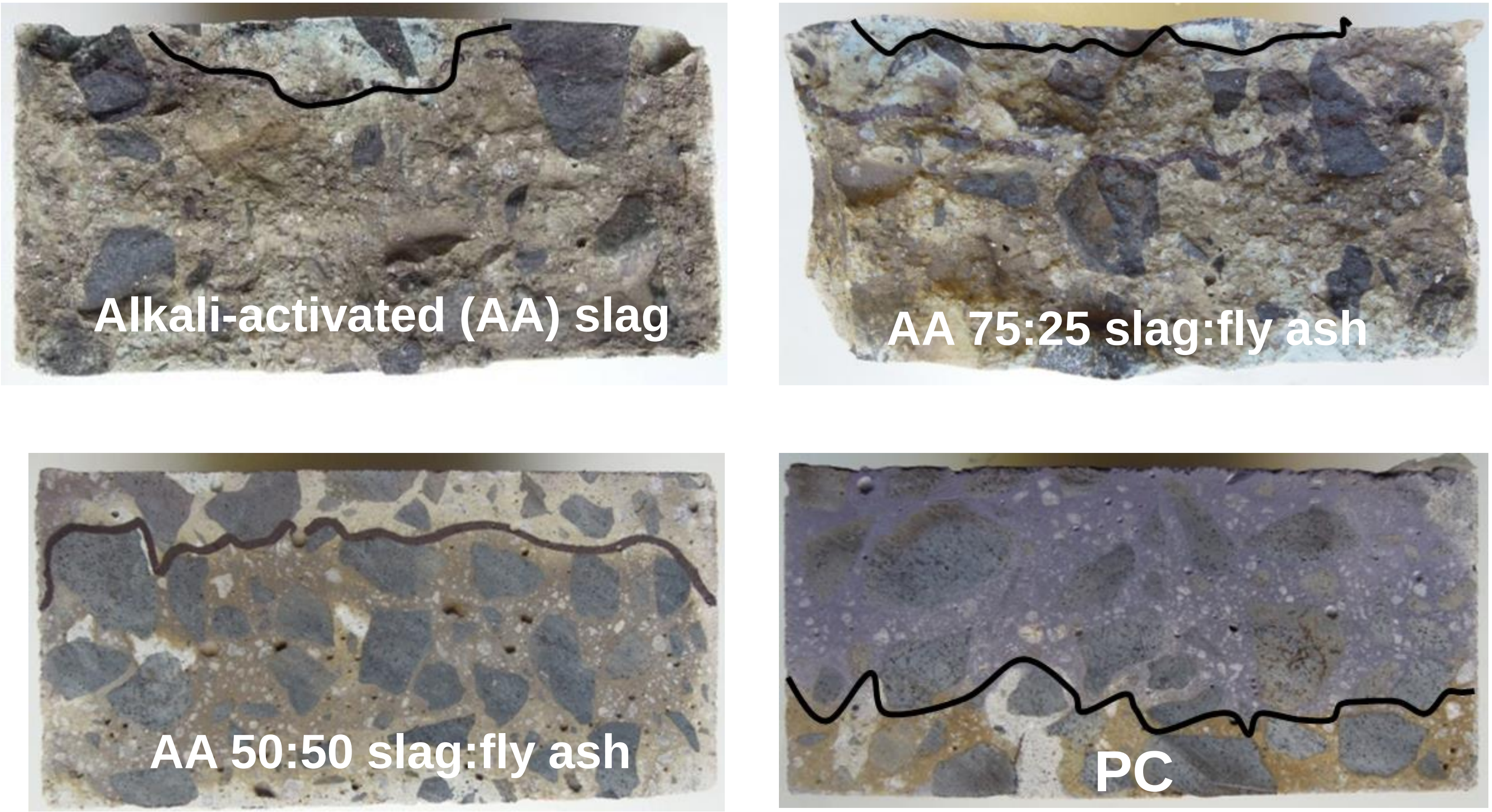
# Differences in space-filling character






Data from X-ray μCT (APS 2-BM-B): J.L. Provis et al., *Cem. Concr. Res.*, **2012**, 42(6):855-864.

# NordTest chloride migration – low penetration




(all concretes of comparable 56-day strength, & similar total pore volume according to ASTM C642)



I. Ismail et al. *Constr Build Mater* 48 (2013):1187-1201.

# Some remaining open questions…

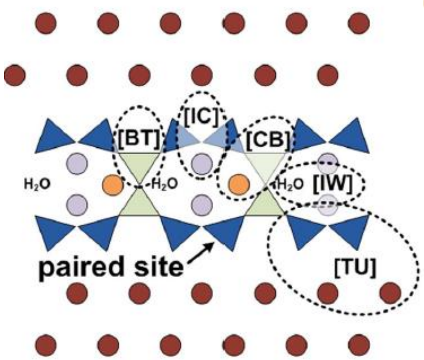
- Can C-A-S-H and N-A-S-H gels really coexist in a stable state?
- What happens to the water in the gel, and can we control this?

  →How does this influence properties in service?

**Best available approach: Linking experimental characterisation with thermodynamic modelling**

(…only for C-A-S-H so far, no model for N-A-S-H yet)

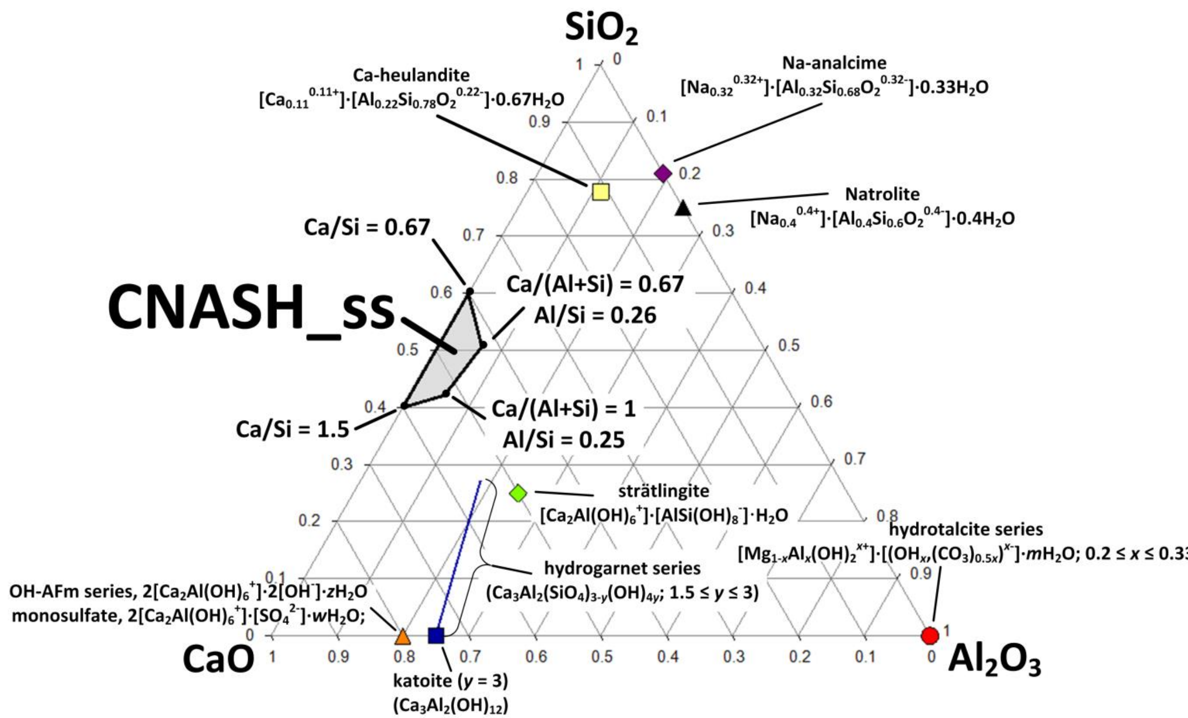
# Thermodynamic modelling




$$G_m = \left[\sum_{n_1}\sum_{n_2}\sum_{n_3}\cdots\sum_{n_s}\left(y_{i_1}^{n_1} y_{i_2}^{n_2} y_{i_3}^{n_3}\cdots y_{i_s}^{n_s}\right)\cdot {}^{o}G_{i_1 i_2 i_3 \cdots i_s}\right] +$$

$$R^*T\left[\mathrm{I}\sum_{i_1}\left(y_{i_1}\ln\left(y_{i_1}\right)\right) + \mathrm{II}\sum_{i_2}\left(y_{i_2}\ln\left(y_{i_2}\right)\right) + \mathrm{III}\sum_{i_3}\left(y_{i_3}\ln\left(y_{i_3}\right)\right) + \cdots + \zeta\sum_{i_s}\left(y_{i_s}\ln\left(y_{i_s}\right)\right)\right] + G_m^E$$

$$(\mathrm{CaO})_{a'}(\mathrm{SiO_2})_{b'}(\mathrm{Al_2O_3})_{c'}(\mathrm{Na_2O})_{d'}(\mathrm{H_2O})_{e'(s)} \overset{K_{so}}{\longleftrightarrow} d'\mathrm{Ca}^{2+}{}_{(aq)} + b'\mathrm{SiO_3^{2-}}{}_{(aq)} + 2c'\mathrm{AlO_2^{-}}{}_{(aq)} + 2d'\mathrm{Na}^{+}{}_{(aq)} + 2(a'-b'-c'+d')\mathrm{OH}^{-}{}_{(aq)} + (b'+c'+e'-a'-d')\mathrm{H_2O}_{(l)}$$

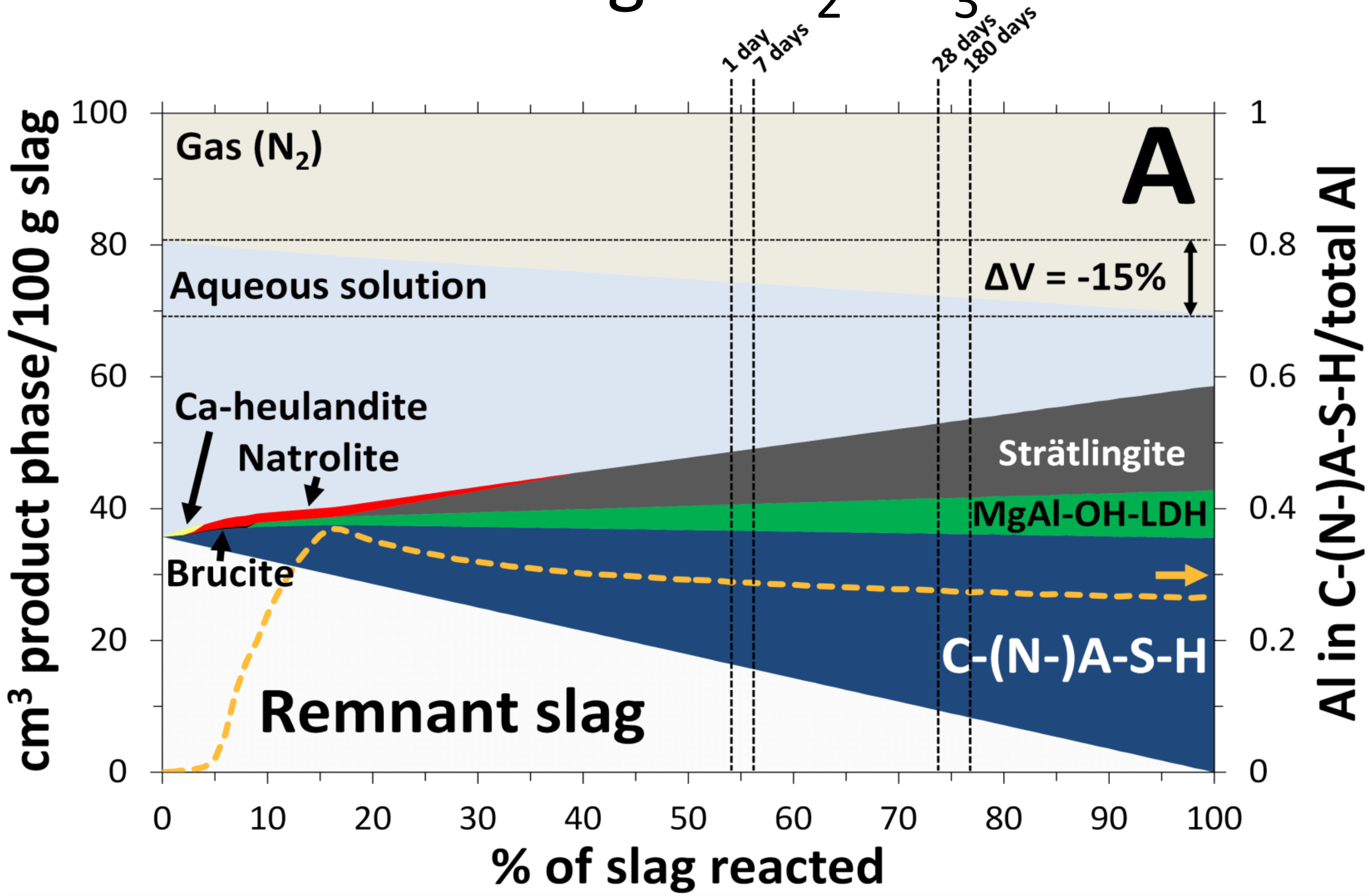



R.J. Myers et al. *Cement & Concrete Research* 66(2014):27–47

The University Of Sheffield.

# Phase and volume stability

## Blast furnace slag + $Na_2SiO_3$ activator



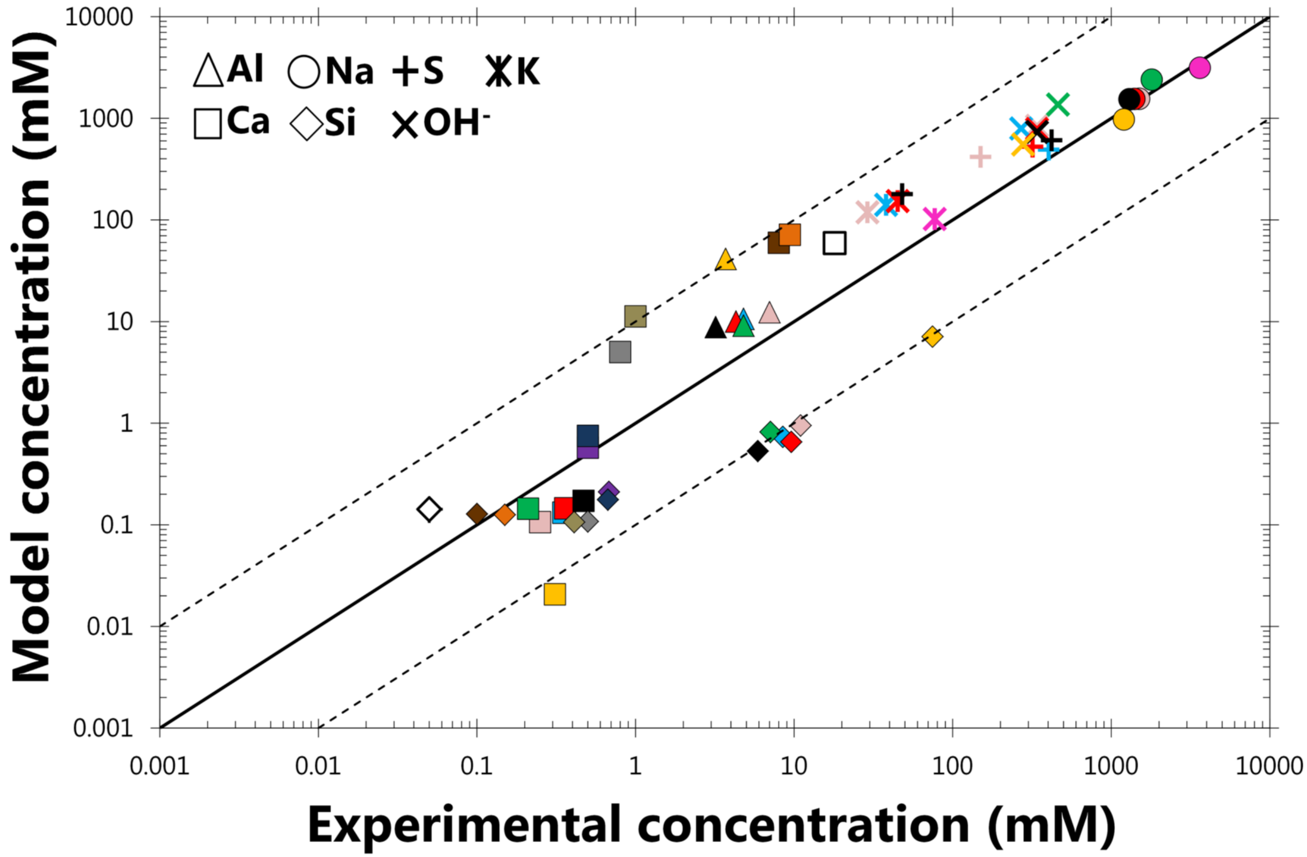

CNASH_ss model has a more dense C-(N-)A-S-H gel than previous work just based on C-S-H



R.J. Myers et al. *Applied Geochemistry*, 61: 233–247

# Validation of CNASH_ss: AAS (C-M-N-K-S-A-$\bar{S}$-H) system

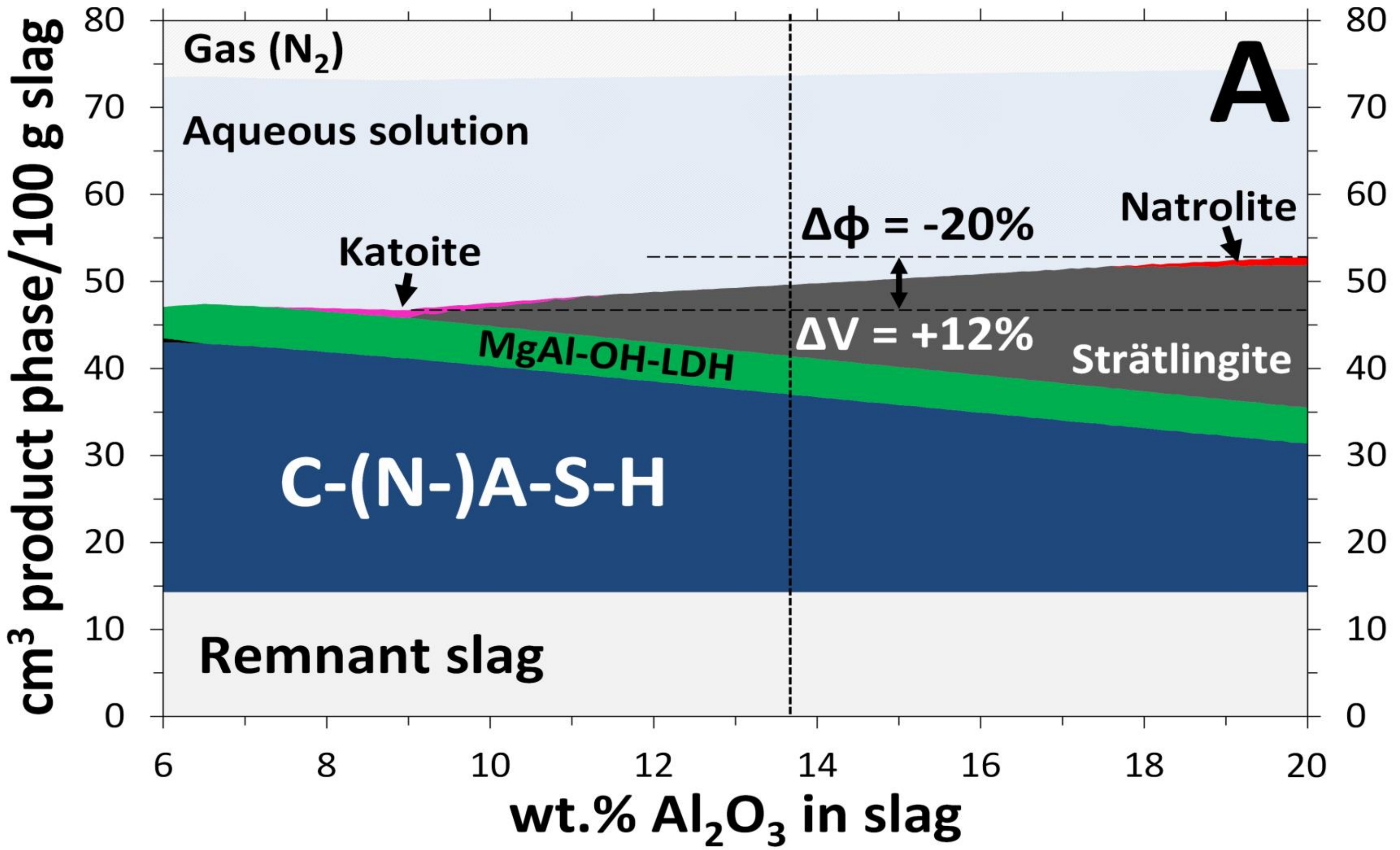
## AAS pore solution chemistry described accurately




*Literature data for pore solutions extracted from cements made of BFS with $NaOH \cdot mH_2O$ or $Na_2O \cdot rSiO_2 \cdot mH_2O$; reaction extents estimated where needed*

# Controlling shrinkage?

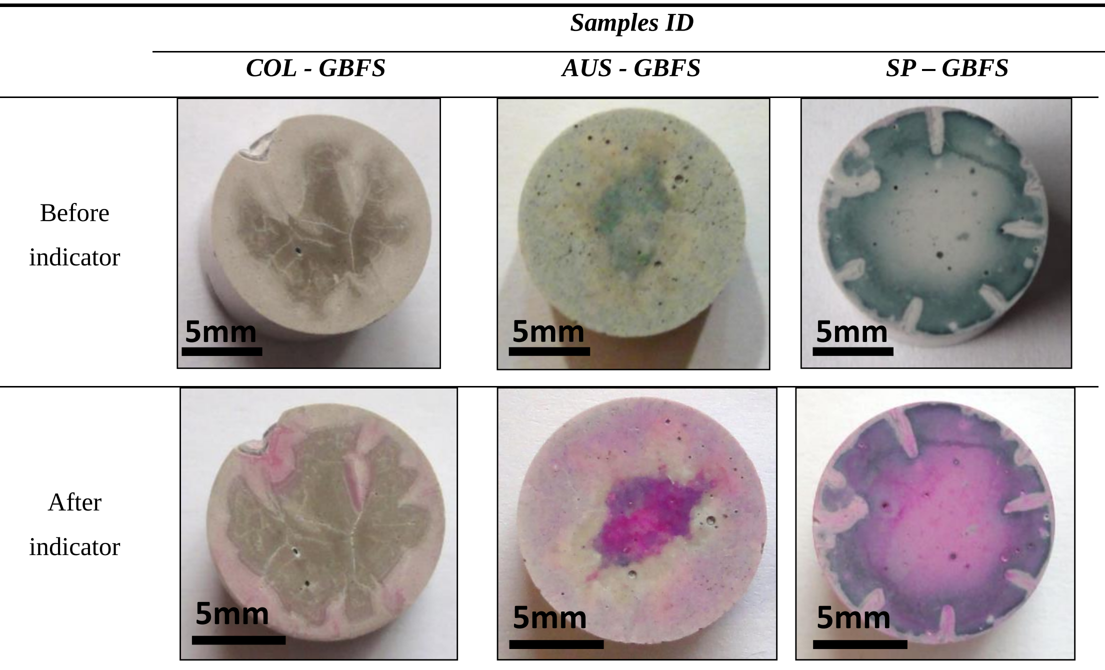
## Blast furnace slag + $Na_2SiO_3$ activator

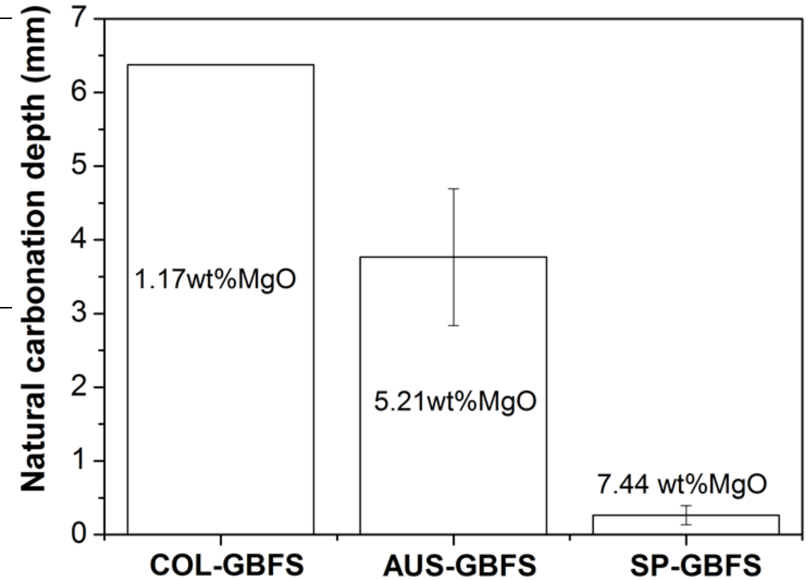





R.J. Myers et al. *Applied Geochemistry*, 61: 233–247

# Slag chemistry and durability

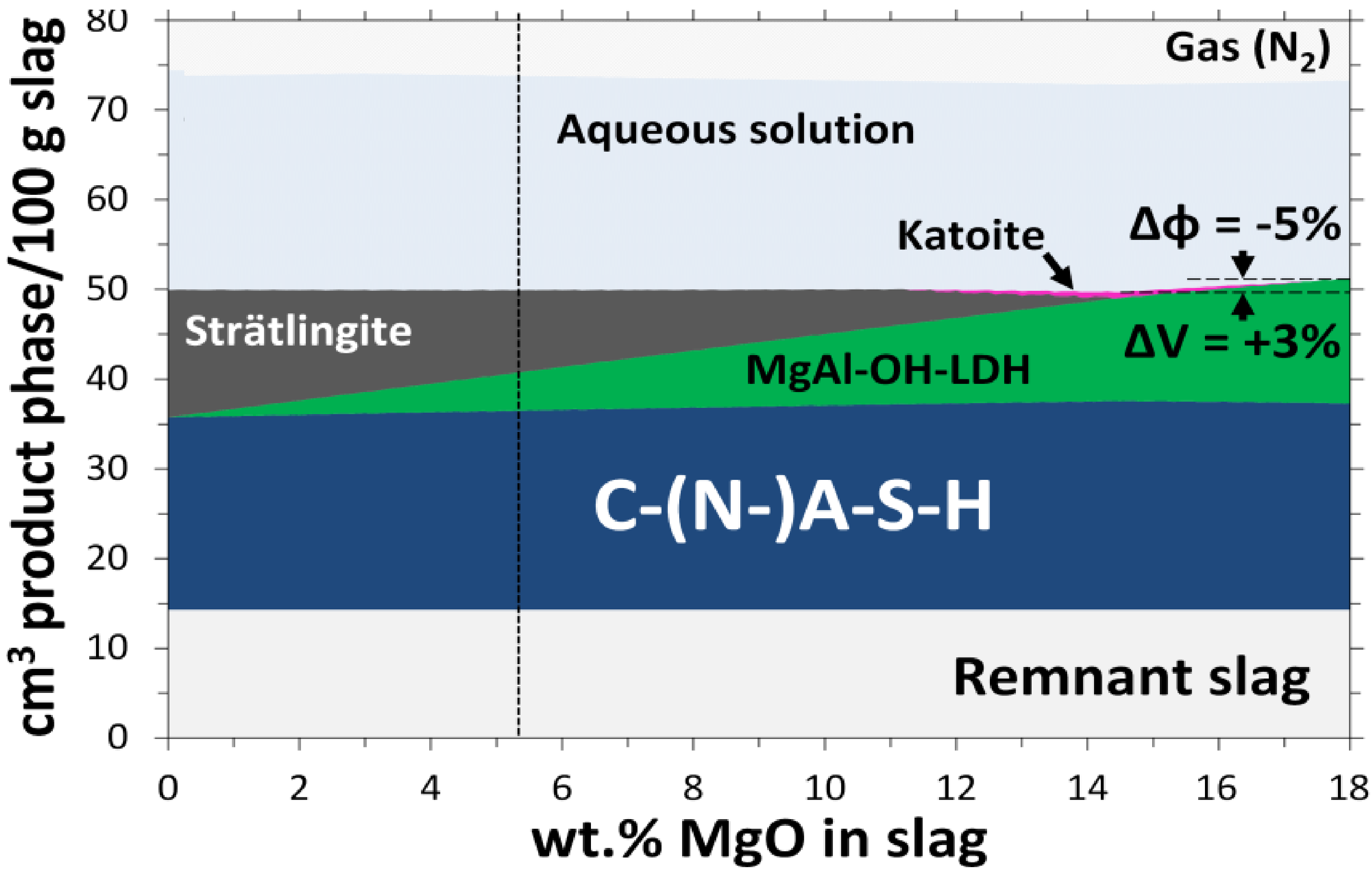



**→ Slag chemistry plays an important role in determining the performance of alkali-activated slag binders**

# Can we predict this?

## Blast furnace slag + $Na_2SiO_3$ activator



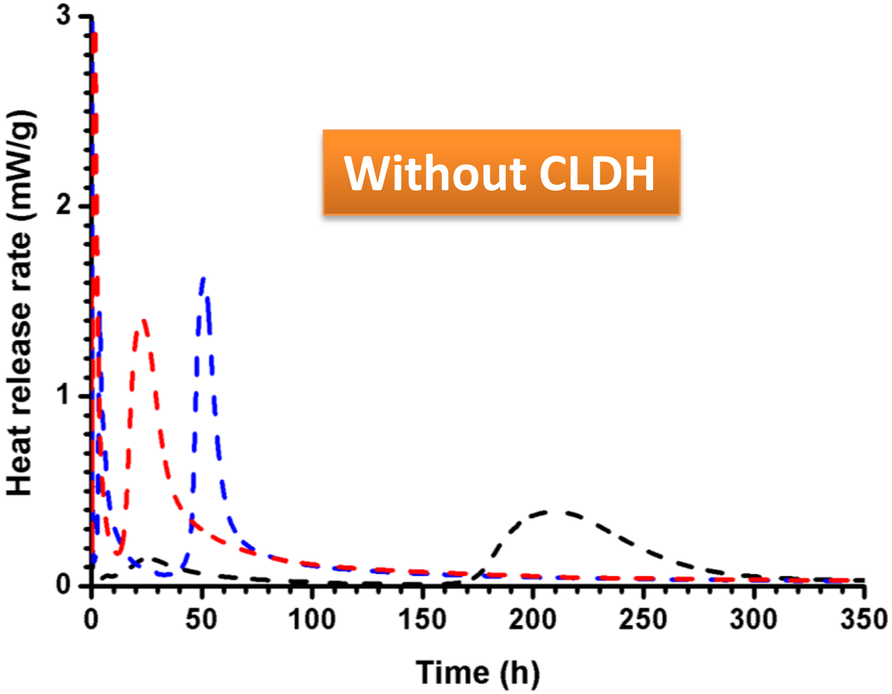

Important differences depending on Mg-Al LDH phase…

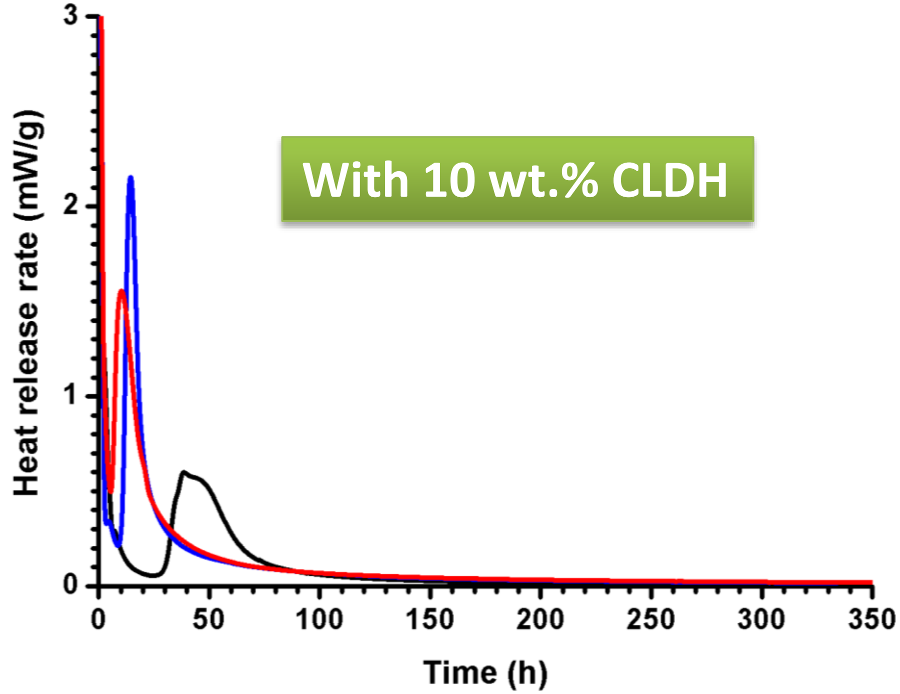


R.J. Myers et al. *Applied Geochemistry*, 61: 233–247

# Accelerating carbonate activation

**Adding calcined layered double hydroxide (CLDH) (hydrotalcite, 500°C)**




- In an $Na_2CO_3$-activated binder system, slags containing higher levels of MgO react much more rapidly
- Incorporation of 10 wt.% CLDH in sodium carbonate activated slag pastes accelerates the reaction, enabling setting within 24 hours.

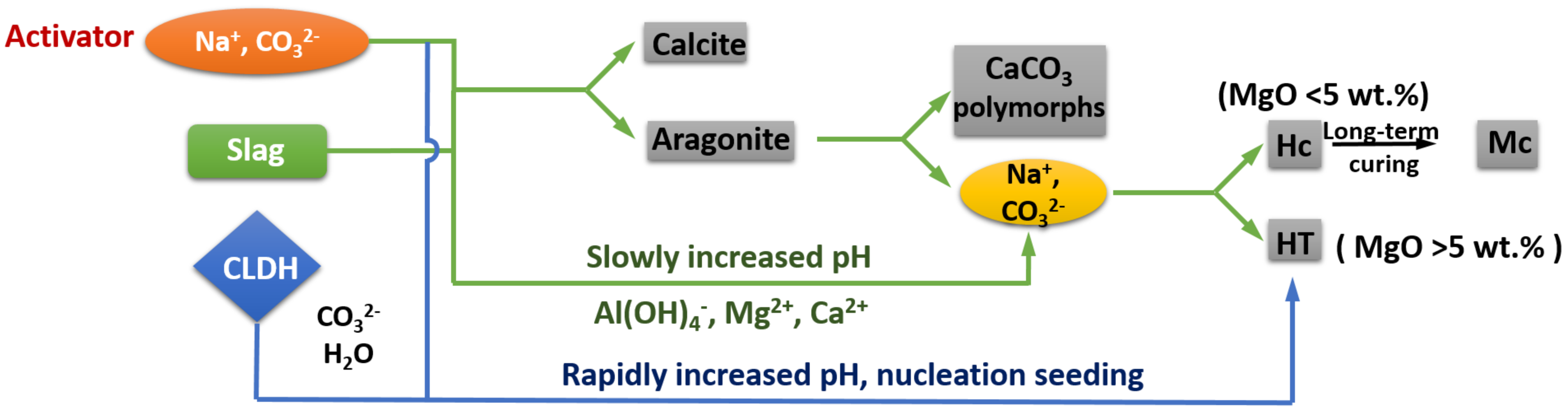


X. Ke et al. 2016. *Cement and Concrete Research*, 81, 24-37.

# How does CLDH work?

In a slag-based binder activated by $Na_2CO_3$:

- Accelerated consumption of carbonate ions
- Increasing the pH of the activator
- Hydrotalcite nucleation seeding

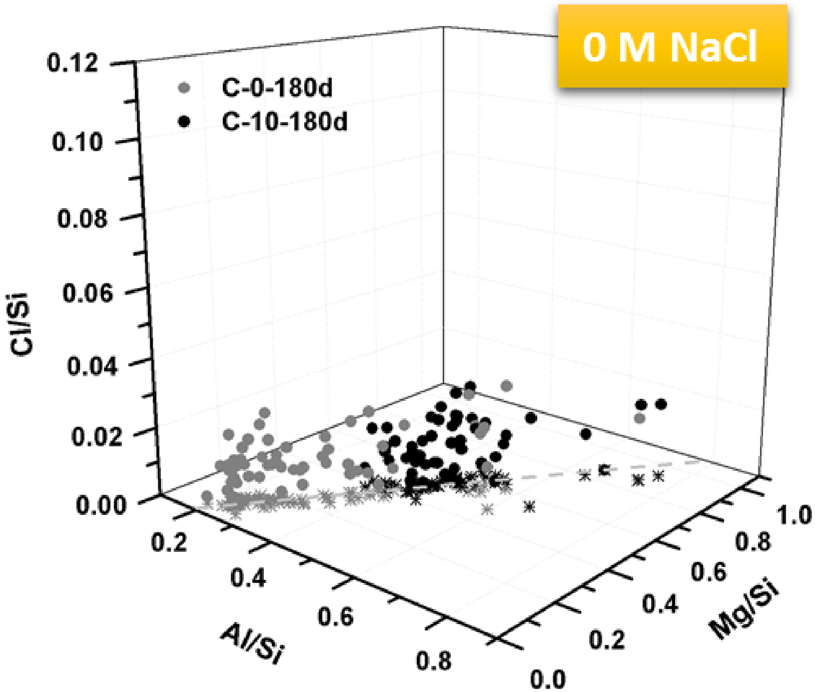


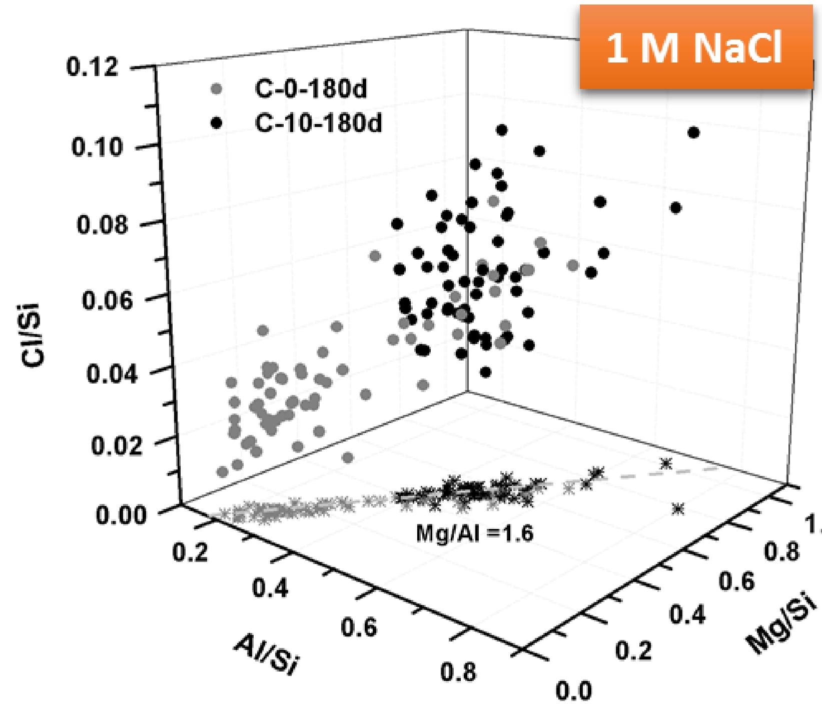



X. Ke et al. 2016. *Cement and Concrete Research*, 81, 24-37.

# Increasing chloride binding

## Before and after chloride exposure (slag M06), data from SEM-EDX




- Close correlation between Cl/Si ratio and Mg/Si ratio
- Higher Mg/Si ratio is related to LDH regions, these selectively bind $Cl^-$
- Mg/Al ratio of LDH phase is ~1.6



X. Ke. PhD (Sheffield), in progress.

# So – what is really needed?

- Most important – the right application (!)
- Material (and application) must be 'sustainable'
  - Financially and environmentally
  - Reliable and sufficient volume supply of raw materials? Activator?
  - Mix design must be efficient – admixtures??
- Material must be durable
  - Replacement/repair is expensive – design for durability at both cement and concrete levels, including creep (?)
- Material must be robust

# With many thanks…


- Cements@Sheffield group!
  - Dr Susan Bernal
  - Dr Rupert Myers (now at Yale)
  - Dr Idawati Ismail (now at U. Malaysia Sarawak)
  - Ms Xinyuan Ke
- Collaborators/discussions/materials: RILEM TC 247-DTA, UniMelb, EMPA, Southeast U., Hohai U., Hunan U. Tech., UFRGS, CEA, APS, U. Laval
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