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

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@CementsAtShef
Traditional and non-traditional cements

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

Increasing Ca content
- Portland-based cements
- Calcium aluminate/sulfoaluminate-based cements

Increasing alkali content
- Alkali activated cements
- Geopolymer cements
- Mg-based cements
- Super-sulfated cements

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

Most important: Designing materials that are fit for purpose!

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)

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$_2$CO$_3$ produced using the Solvay process
How does it happen?

- Dissolution of solid aluminosilicate source
- Rearrangement and exchange among dissolved species
- Silicate species in activating solution

Gel nucleation

High Ca (medium-high Mg)
- Layered double hydroxides
- C-A-S-H gel

Low Ca (low Mg)
- N-A-S-(H) gel
- Crystalline zeolites

Solidification, hardening and strength development

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

NordTest chloride migration – low penetration

- Alkali-activated (AA) slag
- AA 75:25 slag:fly ash
- AA 50:50 slag:fly ash
- PC

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

Some remaining open questions...

- 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

\[
G_m = \left[ \sum_{n_1} \sum_{n_2} \sum_{n_3} \cdots \sum_{n_s} \left( y^{n_1}_{i_1} y^{n_2}_{i_2} y^{n_3}_{i_3} \cdots y^{n_s}_{i_s} \right) \right] C_{i_1 i_2 i_3 \cdots i_s} + R^s T \left[ \sum_{i_1} \left( y^{i_1}_{i_1} \ln y^{i_1}_{i_1} \right) + \sum_{i_2} \left( y^{i_2}_{i_2} \ln y^{i_2}_{i_2} \right) + \sum_{i_3} \left( y^{i_3}_{i_3} \ln y^{i_3}_{i_3} \right) + \cdots + \sum_{i_s} \left( y^{i_s}_{i_s} \ln y^{i_s}_{i_s} \right) \right] + G_m^E
\]

\[
\frac{(CaO)_{a'}(SiO_2)_{b'}(Al_2O_3)_{c'}(Na_2O)_{d'}(H_2O)_{e'}}{(CaO)_{a'}(SiO_2)_{b'}(Al_2O_3)_{c'}(Na_2O)_{d'}(H_2O)_{e'}} \xrightarrow{K_{so}} \frac{d'Ca^{2+}_{aq}}{b'SiO_3^{2-}_{aq} + 2c'AlO_2^{−}_{aq} + 2d'Na^{+}_{aq} + 2(d' - b' + c' - d')}OH^{−}_{aq} + (b' + c' + e' - b' - c')H_2O(l)
\]

CNASH ss

CaO

Ca/(Al+Si) = 0.67
Al/Si = 0.26

Ca/Si = 0.67

Ca/(Al+Si) = 1
Al/Si = 0.25

SiO₂

Ca-heulandite

Na-analcime

Natrolite

OH-AFm series, 2[Ca₂Al₂(OH)₆]²⁺[2(OH)²⁺H₂O] monosulfate, 2[Ca₃Al₂(OH)₆]²⁺[SO₄]²⁻H₂O;

OH-garnet series

hydrogarnet series

[Ca₃Al₂(SiO₄)₃(OH)₆]ₖₐₐ, 1.5 ≤ y ≤ 3

CaO
Al₂O₃

katoïte (y = 3) [Ca₃Al₂(OH)₁₂]

strätlingite

hydrogarnet series

[Ca₃Al₂(SiO₄)₃(OH)₆]ₖₐₐ, 1.5 ≤ y ≤ 3

CaO

Ca/(Al+Si) = 1
Al/Si = 0.25

Ca/Si = 1.5

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CNASH ss
Phase and volume stability

Blast furnace slag + Na$_2$SiO$_3$ activator

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

Validation of CNASH_ss: AAS (C-M-N-K-S-A-S-H) system

AAS pore solution chemistry described accurately

Literature data for pore solutions extracted from cements made of BFS with NaOH·mH₂O or Na₂O·rSiO₂·mH₂O; reaction extents estimated where needed

Controlling shrinkage?

Blast furnace slag + Na$_2$SiO$_3$ activator

Slag chemistry and durability

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<th>Before indicator</th>
<th>After indicator</th>
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<td>SP – GBFS</td>
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</tbody>
</table>

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

S.A. Bernal et al., *Cement & Concrete Research*, 57(2014):33-43
Can we predict this?

Blast furnace slag + Na$_2$SiO$_3$ activator

Important differences depending on Mg-Al LDH phase...

In an Na$_2$CO$_3$-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.

How does CLDH work?

In a slag-based binder activated by \( \text{Na}_2\text{CO}_3 \):

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

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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 \(\sim 1.6\)

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...

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  - Ms Xinyuan Ke


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