The role of Al in alkali-activated slag cements

Betoniyhdistys, 13/03/24

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Calcium silicate hydrates (C-S-H) from OPC

OPC systems form calcium silicate hydrate **C-S-H,** nano-crystalline, with underlying atomic structure similar to 14 Å tobermorite.

- Increasing incorporation of SCMs will form **C-A-S-H** alongside C-S-H.

C-A-S-H contains defects such as:

- Vacancies
- Al for Si substitution on the dreierketten chain
- **Cross-linking** of adjacent dreierketten chains

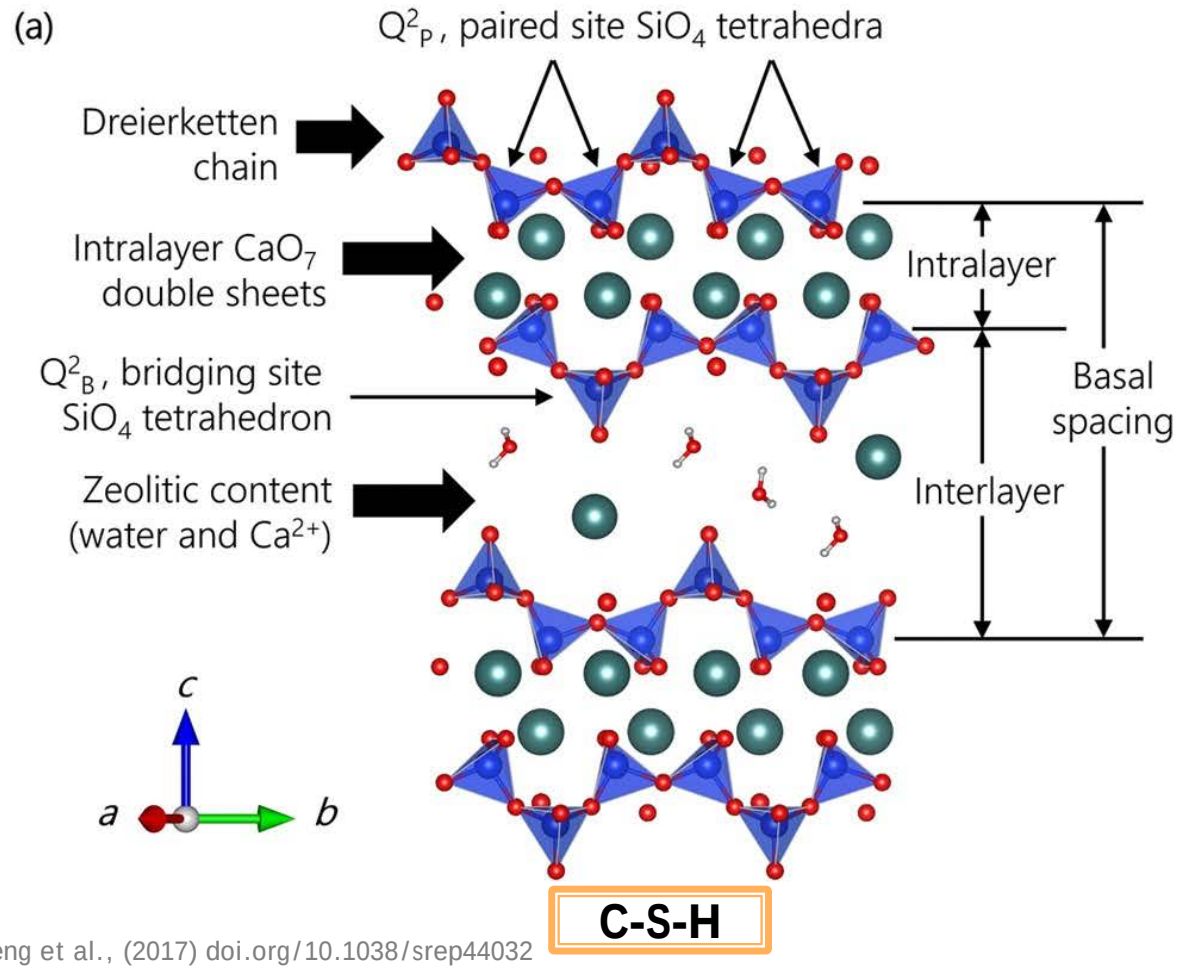
Cross-linking happens at:

- High temperatures
- In presence of **alkali-activator**

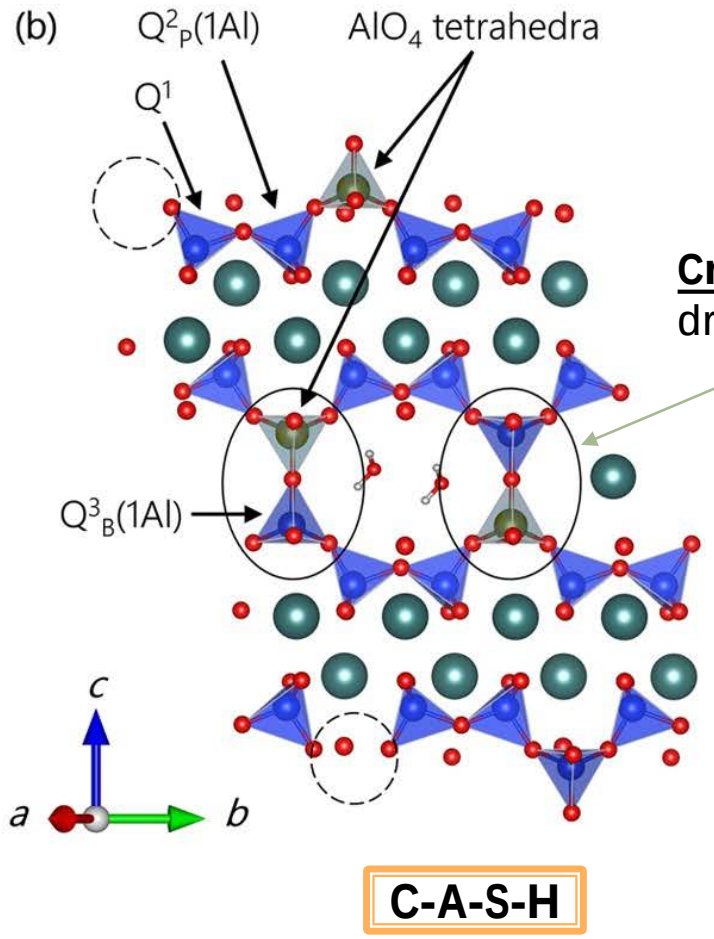
Al-incorporation typically decreases C-A-S-H crystallinity.

Geng et al., (2017) doi.org/10.1038/srep44032

Calcium silicate hydrates (C-S-H) from OPC



C-S-H



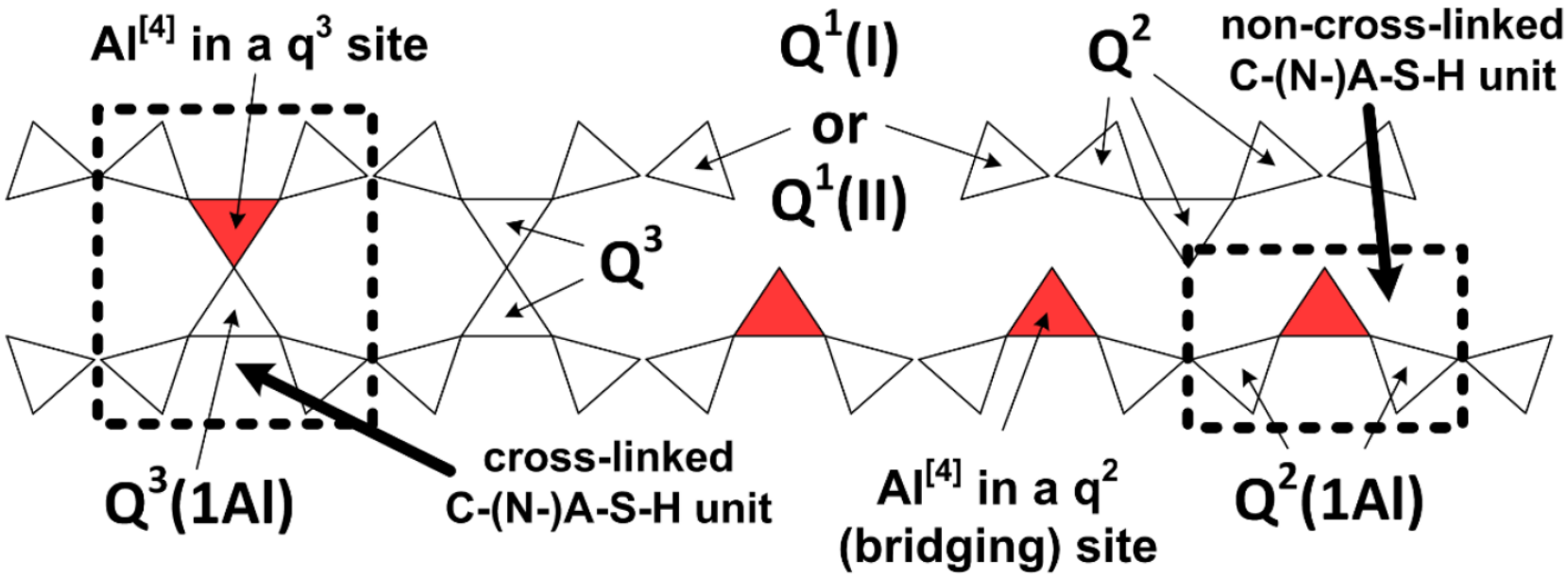
C-A-S-H

Cross-linking of adjacent dreierketten chains

Geng et al., (2017) doi.org/10.1038/srep44032

Role of Al in alkali-activated slags

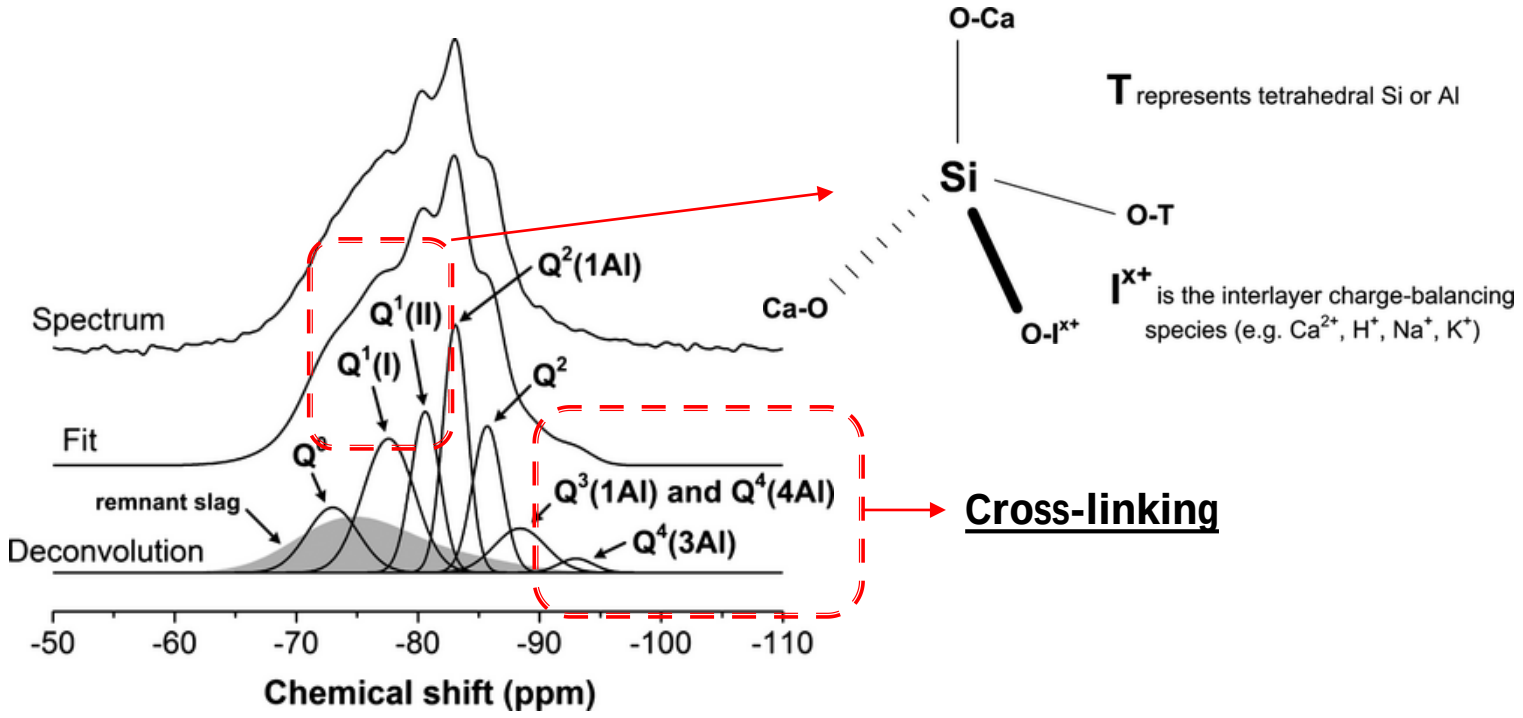
- Key role of Al in alkali-activated slags forming as main reaction product C-A-S-H is increasing gel **cross-linking.**



- The processes of **incorporation of Al and alkalis (Na^+)** in C–S–H gels are directly related but dependent on the Ca/Si ratio.
- Calcium (alkali) aluminosilicate hydrate (C–(N-)A–S–H) gels are formed in systems that are rich in both Al and alkalis and lower calcium concentrations.

Myers et al., (2014) doi.org/10.1111/jace.13360
L'Hôpital et al., (2016) doi.org/10.1016/j.cemconres.2016.03.009

Characterisation of C-A-S-H - solid state NMR



Cross-linking

^{29}Si NMR of C-A-S-H

Myers et al., (2014) doi.org/10.1111/jace.13360

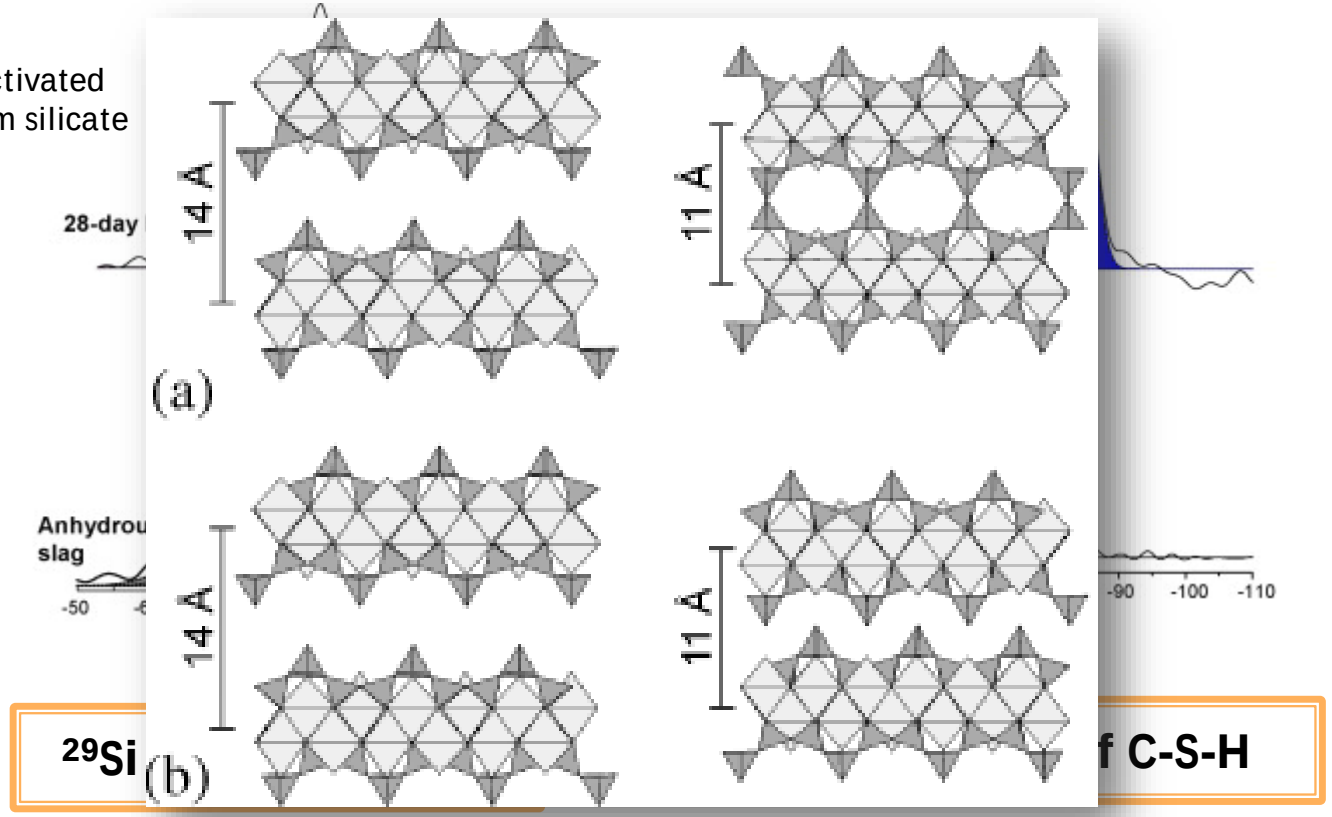
Characterisation of C-A-S-H - solid state NMR

GGBFS activated with sodium silicate

co-existence of:

- tobermorite **14 Å**, with a chain length of **11**
- tobermorite **11 Å**, with a chain length of **14** tetrahedra.

Very densely packed structure



Tobermorite structure
doi:10.1111/j.1551-2916.2005.00116

- tobermorite **14 Å** mean chain length of **5**
- jennite (two tetrahedra)

Puertas et al., (2011) doi:10.1016/j.jeurceramsoc.2011.04.036

Limitations and secondary products formed with Al

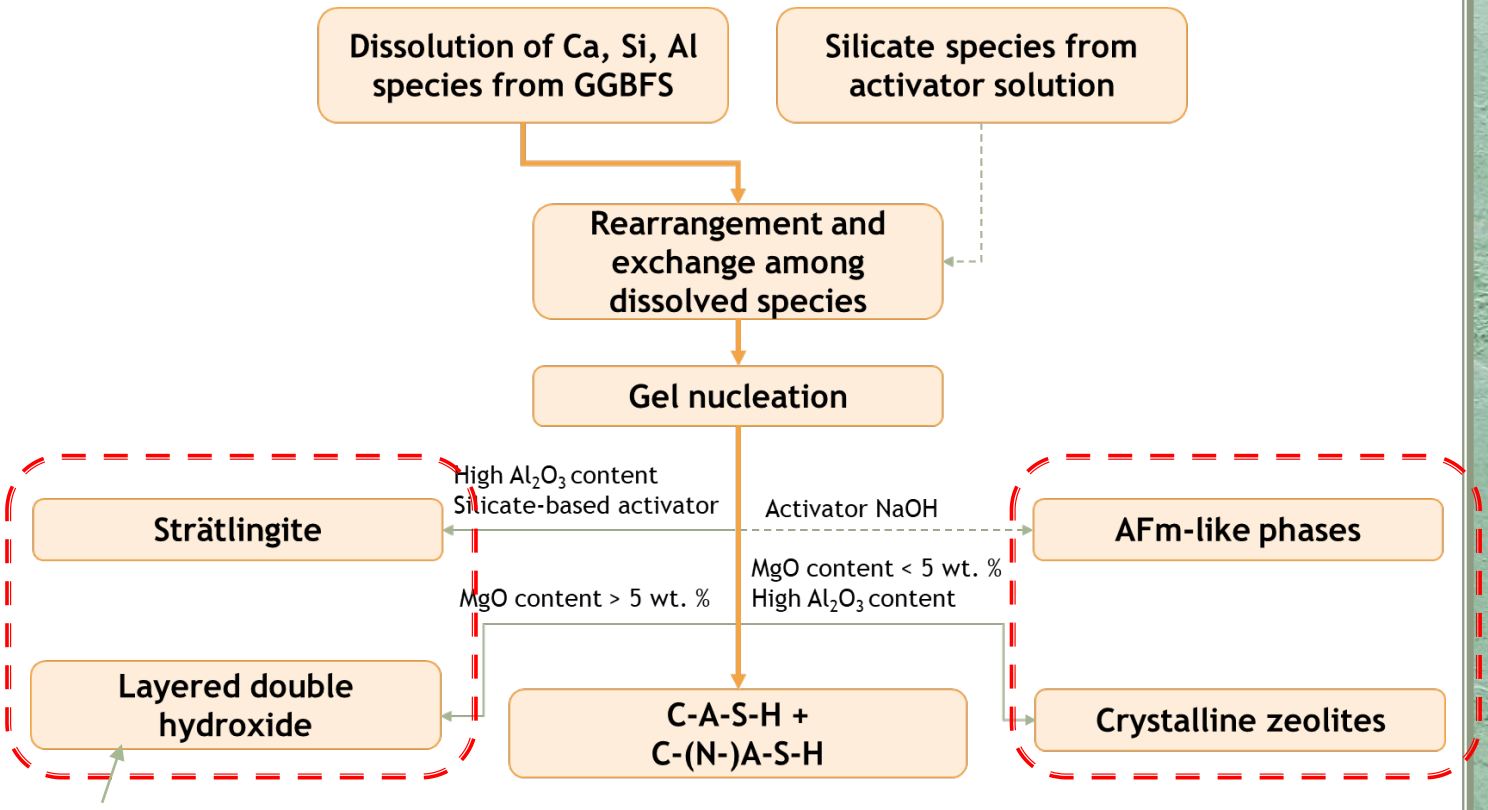
Al uptake into the C–A–S–H gel is beneficial but **restricted** by:

- The chain structure of the tobermorite-like gel.
- Avoidance of Al–O–Al bonds.

When maximum uptake of Al is reached, Al-rich **secondary reaction products** are formed. These:

- Often contain higher concentrations of Al compared to the C-A-S-H gel itself.
- Are competitive reactions with the formation of C-A-S-H..

High Al concentration accelerates precipitation rates, **increasing the crystallinity** of reaction and secondary products.

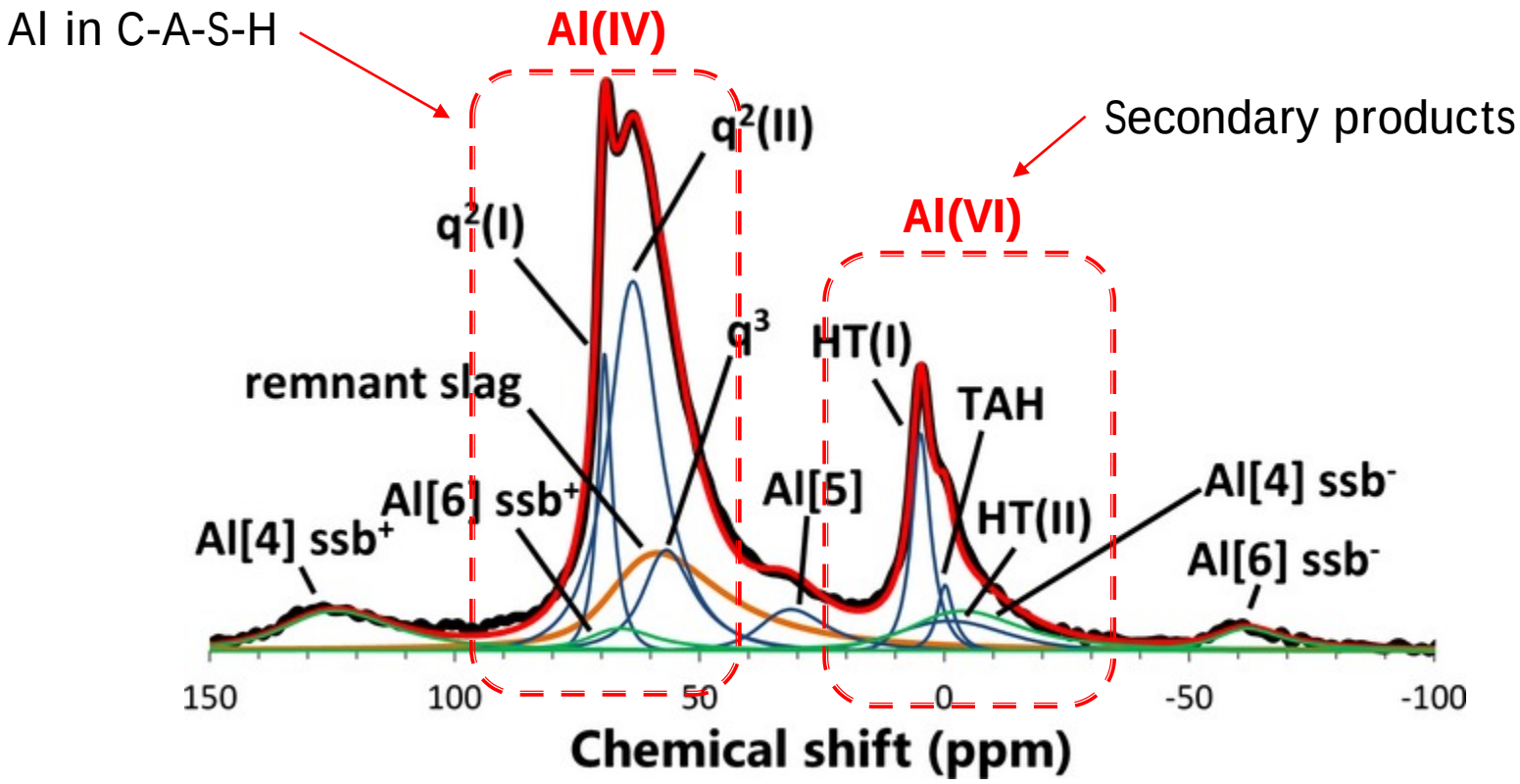


Hydrotalcite-type structure
$Mg_{1-x}Al_x(OH)_2(CO3)_x \cdot nH_2O$

All secondary products are strictly dependent on chemistry of GGBFS and nature of activator but all contain Al.

Provis (2013) doi:10.1617/s11527-013-0211-5

^{27}Al solid state NMR



^{27}Al NMR of C-A-S-H

Myers et al., (2014) doi.org/10.1111/jace.13360

Conclusions

- The gel type formed by alkali-activated slag is **C-A-S-H**.
- The presence of Al leads to an **increased degree of gel cross-linking**, higher density and packing of the gel structure with respect to C-S-H.
- There is a **limit of Al incorporation** due to the tobermorite-like structure and avoidance of Al-O-Al linkages.
- The excess Al will participate to the formation of **secondary products**, such as layer double hydroxides, strätlingite, AFm phases, or zeolites, based on
  - The chemistry of the GGBFS.
  - The nature of the alkaline solution.

Thank you for your attention! Questions?

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