Structure formation in alkali-activated binders for development of sustainable construction materials

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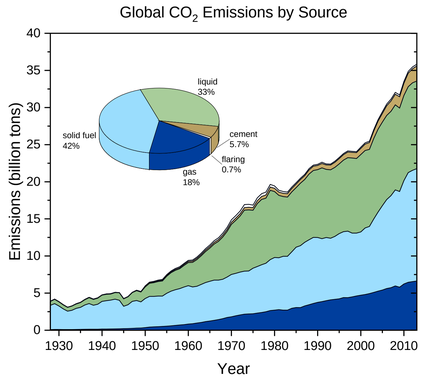
Motivation

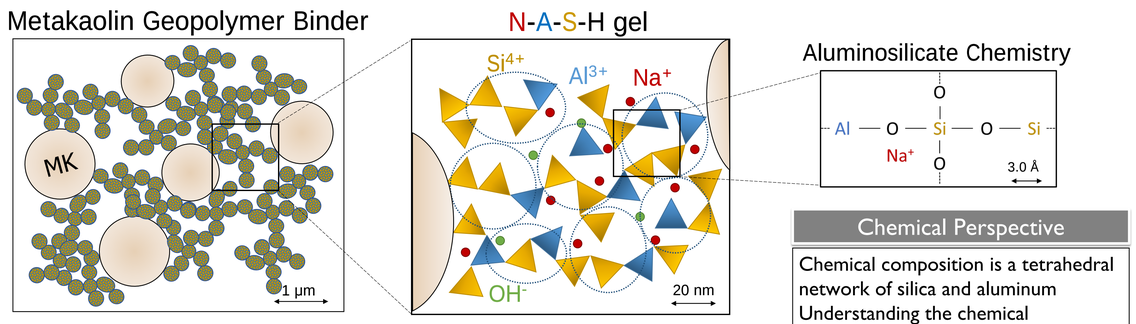
Reducing cement-related CO_2 emissions



- Cement production contributes a significant amount to CO_2 emissions **(2B tons**/ 6% of all emissions)
- Geopolymers eliminate the two main sources of cement related CO_2 emissions (by-product from calcining and kiln fuel combustion)
- Potential to **reduce emissions up to 80%**

Chart adapted from *'Our World in Data'*
T.A. Boden, G. Marland, and R.J. Andres. 2017. Global, Regional, and National Fossil-Fuel CO2 Emissions.

Material Scales



Polymer Perspective

Reactive clay grains ~ 1 μm
Reaction product, fractal particle network bridging reactive surfaces
Metakaolin tends to have a less variable composition than aluminosilicates like slag and fly ash

Colloidal Perspective

Primary particles ~30 nm
The binder 'gel' can be synthesized **without** the clay precursor
Stoichiometric composition is relatively unknown, material is heterogeneous and amorphous

Chemical Perspective

Chemical composition is a tetrahedral network of silica and aluminum
Understanding the chemical composition is necessary for building a kinetic mechanism

N-A-S-H gel advantages
(a model system)

- No diffusion kinetics
- No large grain particles (dominate/confound scattering)
- More control over chemical composition

Research Goal and Hypothesis

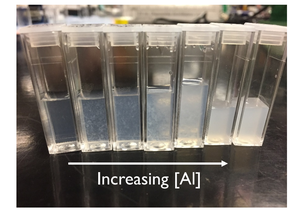
Question: How is gelation related to chemical composition?

Hypothesis:

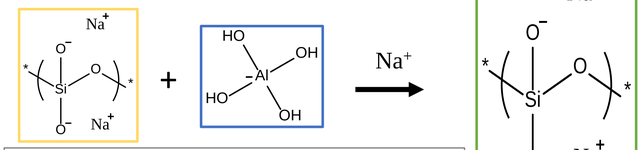
- There exists a critical concentration of aluminum necessary for percolation

Assumptions

- N-A-S-H gel formation mechanism is the same as in the binder (after dissolution, reaction below)
- Extent of reaction can be simulated with addition of limiting reactant, aluminum



Proposed Polycondensation Reaction[1-2]



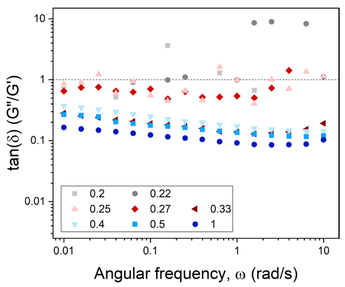
A step-growth polymerization with f=4 (functionality)

Extent of reaction $p = 1 - \frac{[Al]}{[Al]_0}$ Stoichiometric imbalance $r = \frac{[Al]_0}{[Si]_0}$

$+ n\ H_2O$

Gel Transition as a Function of Aluminum Concentration

Percolation



Qualitatively, samples with **Al>0.25** exhibit G'>G"

Flory-Stockmayer Gelation Theory[2-3]

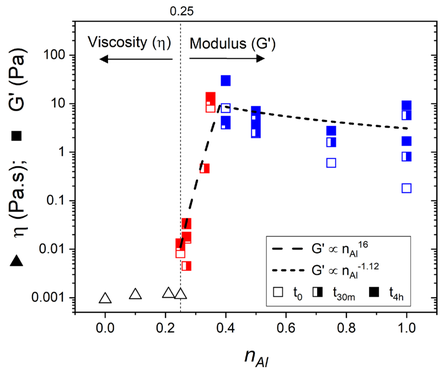
$$\underbrace{p * r}_{\text{P(Si-O-Al)}} + \underbrace{\frac{m*p}{r}}_{\text{P(Si-O-Si)}} = \underbrace{\alpha_c}_{\text{P(branched gel)}} = \underbrace{\frac{1}{f-1}}_{\text{Percolation Condition}}$$

- Gel conversion point $p_c = \frac{r}{(f-1)(r^2+m)}$
- Estimating m=0.46 (from NMR[6]) yields

$$p_c = 0.24 = \frac{Al_{rxd}}{Al_0}$$

- This value agrees well with the onset of rapid increase in storage modulus seen in rheology data

Rheological Characterization

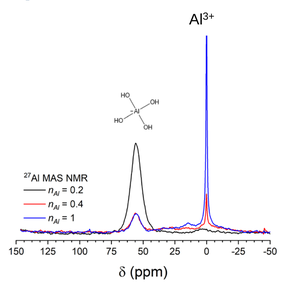


Rheology indicates **two gel phases** dependent on aluminum concentration above an initial percolation threshold

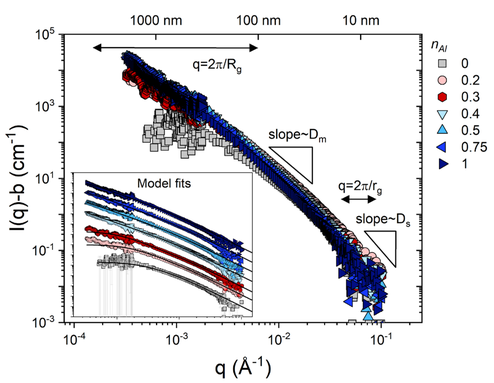
Chemical Composition

- NMR shows a saturation of tetrahedral aluminum (compared to free aluminum) above n_{Al} = 0.4
- This effect may be pH driven [5]
  - pH (n_{Al} < 0.2) > 9
  - pH (n_{Al} > 0.4) < 4

Future work can separate the effects of pH and n_{Al} by using a different free aluminum source

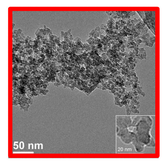


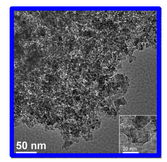
Structure and Fractal Dimension



Grey squares: sodium silicate solution (pre- N-A-S-H gel)
Data fit to a mass-surface fractal model [6-7]

Initial N-A-S-H gel, Al<0.25
D_m ~ 2.5 | R_g ~ 100 nm





Saturated N-A-S-H Gel, Al>0.40
D_m ~ 2.0 | R_g > 10 μm

Mass fractal dimension (D_m) transition from **~2.5 (DLA)** to **~2.0 (RLCA)**

- Initial structure: diffusion limited **monomer-cluster** aggregation.
  - Free Al and Si ions are added to the growing network via step-growth polymerization, strong bonds are formed (modulus increases)
- Saturated gel: reaction limited **cluster-cluster** aggregation
  - Reaction is inhibited, existing clusters may aggregate with weak bonds (modulus plateau)

Aggregate size (R_g) increases with aluminum concentration (there may be a maximum cluster size outside the range of our measurements)
Surface fractal dimension (D_s) value of 3 is constant
Primary particle size (r_g) is polydisperse but relatively constant (5-15 nm)

Conclusions

1. **Polymer gel point:** Polymer physics predicts a concentration of 0.24 moles aluminum relative to 2 moles silica which agrees with rheological gel percolation
2. **Two gel phases:** Scaling of storage modulus suggests formation of two distinct gel phases based on aluminum concentration with a transition at n_{Al} = 0.4
3. **Mass Fractal Dimension:** Transitions between 2.0 (DLA) and 2.5 (RLCA) between the initial and saturated gel phases; cluster size (R_g) increases with aluminum
4. **Inhibition of network growth:** NMR indicates a saturation of tetrahedral Al at n_{Al} = 0.4 consistent with transitions in modulus scaling and fractal dimension regimes
5. **Future work:** constant pH experiments could show whether pH is inhibiting the reaction

Quantifying the relationship between chemistry, structure, and physical properties of N-A-S-H gel formation will guide the formulation of advanced geopolymer cements.

References

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Acknowledgements

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