Materials of the Future: Engineering Zero Carbon Cements Entirely from Industrial Waste

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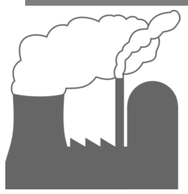
Introduction



Cement plants – major emitters of CO2
- 1 ton cement ~ 1 ton CO2

Concrete – most consumed material in the world after water

7% of global CO_2 emissions

4.1 Billion Metric Tons CO_2 Annually

At the same time, globally, we have mountains of industrial waste

Steel Production: 250 Mt Ground Granulated Blast Furnace Slag

Coal burning: 750 Mt Fly Ash

Problem: By 2050, 68% of world population will be urban (UN). Infrastructures, steel, and electricity will be in high demand. A sustainable cement is needed and waste needs to be managed.

Geopolymers

Using solely waste material and an alkaline solution, geopolymer can be synthesized.

Cement

Water

Conventional concrete

Aluminosilicate Source (slag, fly ash, etc.)

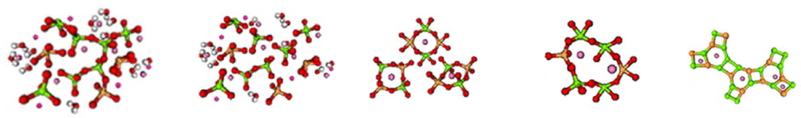
Alkaline Solution (ex. NaOH)

Geopolymer

- ✓ Eliminate cement and associate CO2
- ✓ Utilize waste material to alleviate landfilling

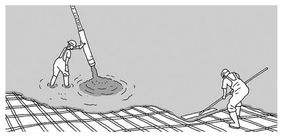
Material design challenges

Once combined



1. Hydrolysis causes breaking of bonds
2. Aluminate and Silicate Species appear and solution becomes supersaturated
3. Oligomers form condensed networks
4. And continues
5. Until polymerizes and hardens

- Degree of polymerization depends on how many  units form.
- Polymerization impacts rheology and early hardening/setting properties → impacts workability (ease of casting)
- Workability is important for constructability!
  - Lack of rheological studies for geopolymers



Experimental program

Goal: Determine influence of key components of geopolymers (slag and activator) on rheological and setting properties.

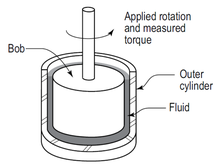
	Fly Ash (%)	GGBS (%)	Molar Ratio (SiO_2/Na_2O)	Na_2O (%)	Water/Binder Ratio
Control	50	50	1.5	3	0.375
Activator-rich	50	50	1.5	5	0.375
Ca-rich	25	75	1.5	3	0.375

where GGBS is ground granulated blast furnace slag and molar ratio of SiO_2 to Na_2O is in the alkaline solution.

Settings times determined through Vicat tests:
- Measure of time for casting
- Based on ASTM Standard C191

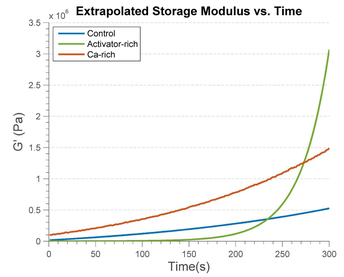
Vicat Apparatus

Shear rheological protocols:
- Small amplitude oscillatory shear – storage modulus
  - measure of degree of polymerization
  - Applied strain amplitude – $1x10^{-4}$
- Dynamic flow curve – dynamic and static yield stress; viscosity
  - measure of pumpability, compactibility, stability
  - Applied max strain rate – 100 1/s

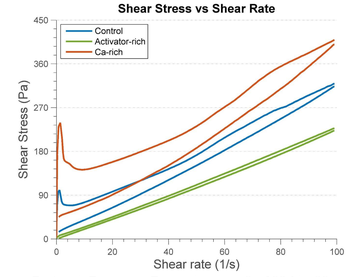


Rheological apparatus
Part of HAAKE MARS Rheometer

Results

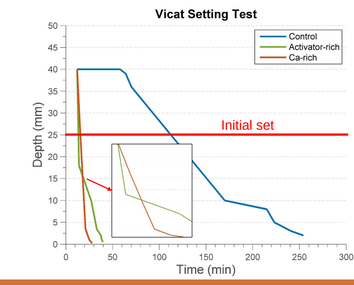


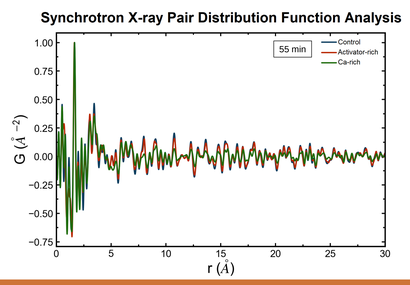
Protocol: Sinusodial strain, $\gamma_0=10^{-4}$, f = 1 hz



Protocol: Ramp up, Ramp down, $\dot{\gamma}$=0 - **100** 1/s, 30s each

	Viscosity (Pa-s)	Dynamic Yield stress (Pa)	Static Yield Stress (Pa)
Control	3.0	3.8	100.5
Activator-rich	2.2	0	5.9
Ca-rich	3.6	17.9	239.0





Discussion

- Rheological tests help characterize cement workability so that we can optimize composition to achieve good surface finish, pumping pressure, formwork pressure, and minimal segregation.
- Higher slag content increased viscosity and yield stress, which can improve stability but can lead to poor surface finish if not well controlled.
- Higher activation decreased viscosity and yield stress, which can facilitate casting by lowering pumping pressure and consolidation energy, but might lead to segregation if not well controlled.
- Although initially very fluid, mixes with high activation exhibited sudden and rapid stiffening/setting, which must be controlled to avoid premature setting during casting. This behavior can be tied to its effect on gel development, which is shown in the local structure given by the pair distribution function (PDF).
- As activation and slag influence rheology, in addition to meeting strength requirements, their content should be controlled to meet workability requirements for the application at hand.

Future work: TEM of geopolymer, more mixes, and analysis of calcium role.

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