Inorganic Polymers: Novel Cement-Free Binders for Transportation Infrastructure

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Presentation Outline

• Motivation for research

• Molecular design strategy (MDS)
  – Fly ash screening to elucidate composition-property relations as a function of solid/solution chemistry
  – Reaction characterization and manipulation
  – Simulation platform development

• Summary and Next Steps
**Motivation for Research**

**CO₂ Pressure on Construction Industry:** Reducing, and bringing new efficiencies to cement use would address this issue

- Develop alternatives to OPC, which can be produced in substantial quantities
- Develop new platforms which can precisely predict evolutions of reactions/properties in alternative binder materials
- Address technological limitations which limit deployments of alternative binders

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Sant et al. (2015) | 2015 World of Coal Ash Conference, Nashville, TN | Slide 3 of 32
Motivation for Research

- Use fly ashes (Class C and Class F) as a precursor
- Choice is based on the widespread availability of ashes
- Good “benchmark” as a raw material: other options include clays: kaolins, etc.
- There is value to beneficial use rather than disposal
Long-Standing Issues with Inorganic Polymers

• **# 1**: High pH and heat curing to develop suitable properties
• **# 2**: Lack of reaction control, thus accelerated setting and loss of workability
• **# 3**: Highly amplified chemical shrinkage and risk of cracking
• Solution require understanding of fundamental chemistry: i.e., composition, kinetics and the thermodynamics of reactions

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Compositional Banded Inorganic Polymers

- Limited empirical data of “well-performing” systems
- Need to understand the correlation between initial composition and properties
- Need to understand the reactivity of precursors, in relation to solution chemistry as this impacts the compositions of products

Formula: \( \text{M}_n \left[ (\text{SiO}_2)_z \text{AlO}_2 \right]_n - w \text{H}_2\text{O} \)

Duxson and Provis, JACeRS 2008
Composition-Property Relationships

- Effects of temperature and pH of activator examined
- 5 fly ashes were selected: 4 low and 1 high CaO content
- NaOH: 4 M, 6 M and 8 M
- Curing: 25, 45 and 85°C
- w/s = 0.45 (mass basis)
- Strength: 3 and 7 days
- Can we isolate composition-property relations?

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Effects of Temperature and pH

Strength increased between 3 and 7 days for all samples. Across all NaOH concentrations, lower concentrations of OH, strength developed is proportional to temperature relationship fails for higher concentrations of NaOH. The samples cured at 45°C showed best strength; crystalline
Analyses of Strength vs. Composition Trends

Strength can be cast againstwick and glassy oxide content
ghly non-linear trend noted
identify trends: (a) apply
tern recognition methods,
carry out regression
alysis, and select functions
t fit majority of dataset
ore work is needed, but
imum around 12% CaO ?
Sharp drop in strength for $O_2 > 45\%$ (mass basis)

$O_2/Al_2O_3$: Non-linear, but it may be so that optimum is around 4.0-to-5.0 general, increasing the pH betters only slightly, which suggests that this is less linked to FA reactivity, and perhaps more to composition
Network Modifiers in Glasses

crystalline glass has random networked structure of silicate tetrahedra. Network modifying elements with low valence (e.g., Na, Mg, K, Ca) break up this structure. This results in a higher degree of atomic disorder in the glass network. More non-bridging oxygens, NBOs, are produced. Aluminum can occupy the tetrahedral coordination sites held by silicon and produce NBOs. Results in consumption...
Parameters to Describe Network Order

A single parameter to describe glass networks must take into account both the network modifiers and network formers. This has been attempted using \{M/Al\}, where M (i.e., Na+K) is the network modifier and Al is a network former. Another compositional indicator is:

\[
\text{Network Modifier Ratio, } N_r = \frac{2n_{Ca} + n_K + 2n_{Mg} + n_{Na}}{\sum n}
\]

This equation quantifies the network modifiers in the system in relation to the overall composition.
Silicate glasses, when $\text{Al}_2\text{O}_3$ ranges between [0-to-$M_2\text{O}$]: hardness increases with $\text{Al}_2\text{O}_3$ because the Al atoms assume the non-bridging oxygen (NBO) created by alkalis when $\text{Al}_2\text{O}_3 > M_2\text{O}$, all NBOs are consumed – hardness decreases following a rigidity reversal.

This appears to be true also for systems examined herein.

**Increasing Al**

4/8 M NaOH, 38°C, 28 days

**Glassy M$_2$O/Al$_2$O$_3$ (Molar Ratio)**
For low-calcium FAs, strength increases with increasing NMC: linearly up to ≈40%. Higher N_r indicates more ordered glassy structure and, hence, more reactive FA. For NMC > 40%, non-linear and non-monotonous links which need further work.
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Summary and Next Steps
Partial progress of reactions is driven by solution rates or precursors. Abundances of species released will control formation of the end products (drates; that evolve with time). Solution and precipitation are correlated steps: one linked to the other. Parameters: disorder in solids, and the solution chemistry (pH and $U_s$). Multistep reactions: stepwise progress...
VSI: Overview of the Method

Combination of optical and interferance microscopy provides a resolution limited by the size of the optical elements, here around 500 nm (objective resolution). The interferance microscopy is limited by the sensitivity to track interference changes (beam split) ≈ 0.2 nm. The wView 8200 optical profiler can further expand the typical image field: 1000s of µm².
solution: Tracking the Surface Topography

8 hours of solvent contact
recursors: Dissolution of Amorphous SiO\textsubscript{2}

- Dissolution rates (DR) in good agreement with literature studies
- "Reversal" reported in various studies – DR increases on both sides of the IEP (isoelectric point)
- Addition of neutral salts (e.g., NaCl) enhances dissolution rates
Precursors: Dissolution of Crystalline Al$_2$O$_3$

Measured the dissolution of crystalline alumina (corundum) at several different pHs, and agreement with other studies face charge (and dissolution rate) reversal between $9 < \text{pH} < 10$. At pH $< 9$, Al exists as Al$^{3+}$/Al(OH)$^{2+}$ species which are resistant to hydrolysis; low dissolution rates. At pH $> 9$, Al exists as Al(OH)$_4^{-}$ species which do hydrolyze easily; enhancing phase dissolution.
Dissolution Rates: Measure of Reactivity

Class C

Order of Reactivity
1. Am. SiO₂
2. Class C Ashes
3. Class F Ashes
4. Crys. SiO₂/Crys. Al₂O₃

Dissolution Rates
- BP Fly Ash
- NV Fly Ash
- ML Fly Ash
- LS Fly Ash
- CC Fly Ash
- MR Fly Ash
- WP Fly Ash
- BC Fly Ash

Am. SiO₂
Crys. SiO₂
Mechanical truss: slender, but rigid members which link together at joints

Simple analogy: joints = atoms, and slender members = atomic bonds
For a central atom, determine the number of permissible BS and BB constraints by assessing the radial and angular excursions of each neighboring atom (MD simulations).
Outcomes of rigidity theory show that atomic constraints and dissolution rates closely linked to the instability of the network in water. A critical number of constraints below which phases and fly ashes would be reactive is a powerful indicator that FAs can be intrinsically non-reactive. How do we enhance...
Reaction Regulation for Enhanced Reactivity

When brought in proximity to each other, some surfaces dissolve at the expense of others, preferentially related to electrochemical similarities of surfaces, and can be measured using surface forces apparatus (SFA) when DDL’s overlap can be used to favor/enhance dissolution at lower pH.

- Amorphous Alumina
  - EC-SFA Measurements
  - Exponential Fit

Single nanoparticle between symmetric muscovite mica surfaces. pH = 10.0
Dissolution Manipulation via “Applied Potential”

“Work in Progress”

- pH = 10 (0.1 mM NaOH)
- P = 1 atm
- T = 25°C
- Applied potential (V) measured between Au and Ag/AgCl electrodes
- “Surface height change rate” measured with ellipsometry as the difference in height between initial height ($h_0$) and height at 24 hours ($h_{24\text{ hours}}$) of dissolution
- Dissolution rate increases with the applied voltage

-a-sized silica particle in contact with gold (Au) electrode. Dissolution of silica enhances exponentially with applied potential as described by Butler–Volmer equations.
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Modeling of Reactions in Inorganic Polymers

... to understand the nature and composition of IP hydrates... reactions via a GEMS: minimization of the Gibbs free energy of a complex system...ic input: Kinetics (dissolution/precipitation rates), thermodynamics (ion-association, solubility constants, phase assemblage)...

\[
\Delta G_i = \Delta H_i - T \Delta S_i
\]
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Summary and Conclusions

Composition-property linkages are complex, but have been elucidated for a range of systems. Need to better understand how composition of the hydrates influences these trends. Dissolution rates of pure phases, and fly ashes have been quantified. Dissolution rates are correlated with the atomic order of the network which via the parameter “nc” and fly ash reactivity are being studied as to enhance fly ash reactivity. A thermodynamic platform is being built to simulate the progress of reactions, and the role of additives.
Acknowledgements

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