Effects of Sulfate Attack on Local Atomic Structure of Alkali-Activated Slag Cement

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Introduction

- Cement accounts for up to 8% of the world's CO_2 emissions [1]
- Alkali-activated cement (AAC) is an environmentally sustainable alternative to ordinary Portland cement (OPC).
- AAC can reduce OPC CO_2 emissions by up to 97% [1]

Portland cement

Limestone → Calcination (rotary kiln) → CO_2 → Grinding → CO_2 → Hydration with water → Portland cement

Alkali-activated cement

Industrial byproducts (e.g. slag) → Hydration with alkaline substance → Alkali-activated cement

Reuse waste, reduce landfill usage, reduce disposal cost

Up to 97% reduction in CO_2 [1]

To promote use of AAC, its material properties are studied:
- Strength – already proven to be strong enough [1]
- Resistance to chemical attacks has been established [2,3,4]

AAC in use in Melbourne, Australia

Source: http://www.zeobond.com/projects-swan-st-retaining-wall.html

AAC versus OPC

AAC has better --
- Mechanical strength
- Freeze-thaw cycle resistance
- Warm temperature resistance

AAC has similar or lower cost compared to OPC [1]

Sulfate Attack on Cement

- Sulfates in seawater, soil, and sewage degrade cement

Concrete bridge exposed to sulfate

Source: https://www.pexels.com/photo/grey-concrete-bridge-above-water-under-blue-sky-77630/

Concrete structure damaged by sulfate

Source: http://www.spec-net.com.au/press/1111/cem_091111.htm

Previous research on sulfate attacks on AAC

- Analyzed sulfate effects on appearance, physical strength, and microstructure of AAC
- AAC more resistant than Portland cement [2, 4, 5, 6, 7]
- Na_2SO_4 attack had a negligible effect on AAC [3]
- $MgSO_4$ extensively degraded AAC with gypsum formation [3]

Novel contributions of this study

- First study of effects of sulfate attack on nanostructure of cement
  - Sulfate attack begins at nanoscale
  - Critical to understand fundamental degradation mechanisms
- First study to investigate varying concentrations of sulfates

A novel computer program for PDF analysis

- Identifies atom-atom correlations from the data
- Generates graphs
- Creates tables with important data points for analysis
- Handles multiple sample groups
- Handles large data sets with millions of data points

$$2SO_4^{2-} + Ca_4Al_2(OH)_{12}\cdot SO_4\cdot 6H_2O + 2Ca^{2+} \rightarrow Ca_6Al_2(OH)_{12}(SO_4)_3\cdot 26H_2O$$

- Eq. 1 (Na_2SO_4 & C-S-H)
- Yields ettringite

$$SO_4^{2-} + Ca^{2+} + 2H_2O \rightarrow CaSO_4\cdot 2H_2O$$

- Eq. 2 (Na_2SO_4 & C-S-H)
- Yields gypsum

$$Mg^{2+} + SO_4^{2-} + Ca(OH)_2 + 2H_2O \rightarrow Mg(OH)_2 + CaSO_4\cdot 2H_2O$$

- Eq. 3 ($MgSO_4$ & C-S-H)
- Yields gypsum

X-ray Pair Distribution Function (PDF) analysis

- Enables nanoscale analysis of disordered materials such as cement
- Shows the probability of finding two particles (atoms) that are a certain distance apart (in angstroms)
- The sine Fourier transform from the total scattering function measured using the 2D image plate detector is used to obtain the PDF [8]

$$G(r) = \frac{2}{\pi}\int_{Q=Q_{max}}^{Q=Q_{max}} Q[S(Q)-1]\sin(Qr)\,dQ$$

$$Q = \frac{4\pi\ sin\theta}{\lambda}$$

Methods

Experimental Design

Control
- Dry
- Immersed in distilled water
  - differentiate between effects caused by sulfate and water

Na_2SO_4
- Immersed in solutions of Na_2SO_4
- 1% wt.
- 5% wt.
- 10% wt.

$MgSO_4$
- Immersed in solutions of $MgSO_4$
- 1% wt.
- 5% wt.
- 10% wt.

Each of the 8 subgroups had 6,000 data points for a total of 48,000 data points in PDF analysis

Step 1

Synthesize NaOH-activated slag cement samples, grind into powder, and immerse in sulfate solutions

Step 2

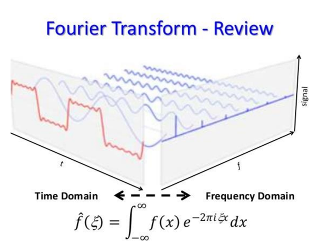
After two weeks, dry and crush the samples and load into capillary tubes

Step 3

Source: https://www.anl.gov/photos/advanced-photon-source

Test samples in beamline at Advanced Photon Source particle accelerator at Argonne National Laboratory

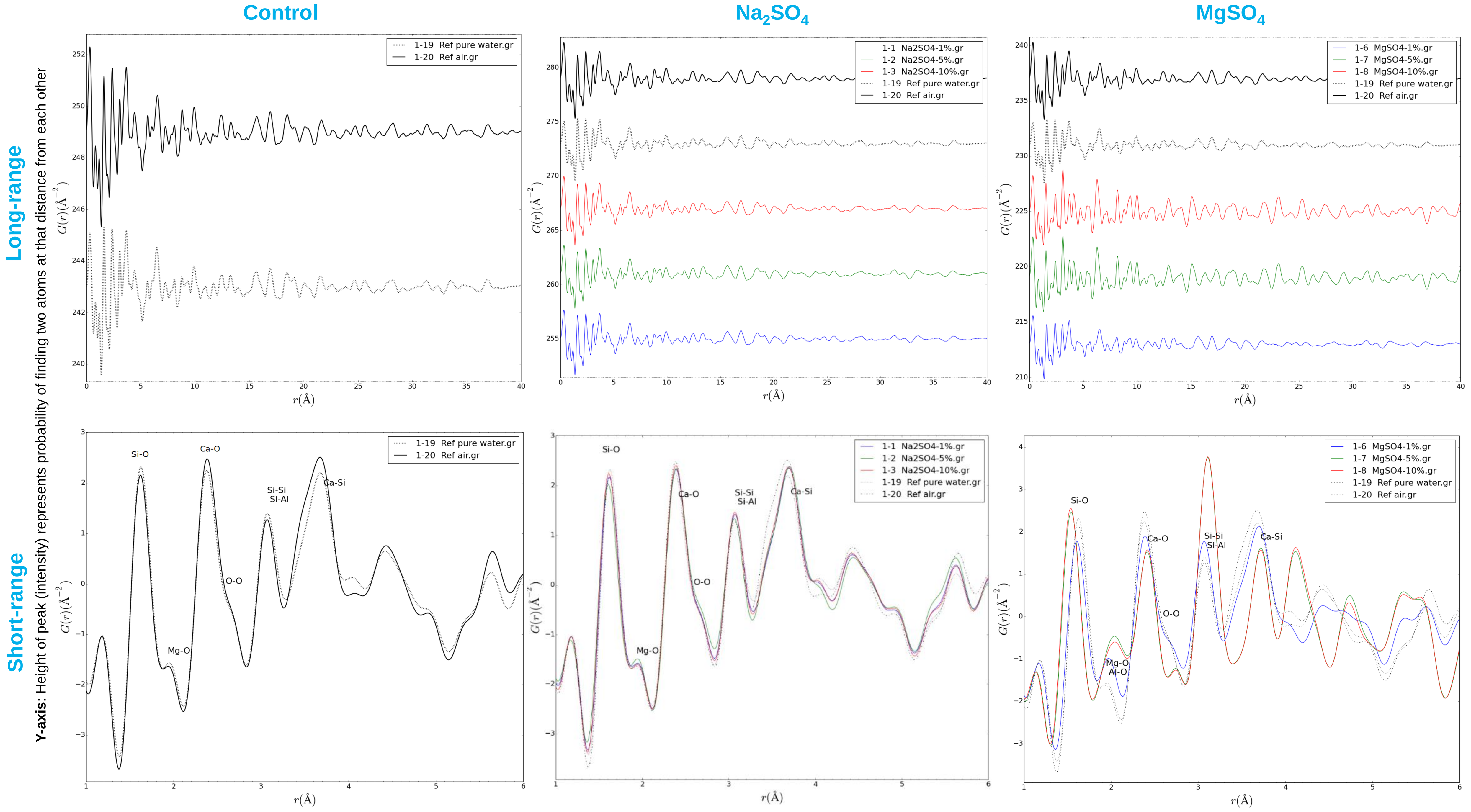
Step 4



Source: https://www.slideshare.net/aarthi2991/sparse-fourier-transform

Process and analyze data using Fourier transform and PDF analysis

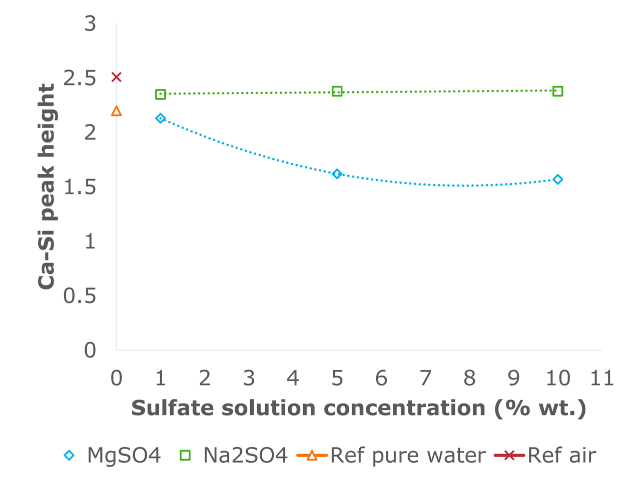
Results and Discussion



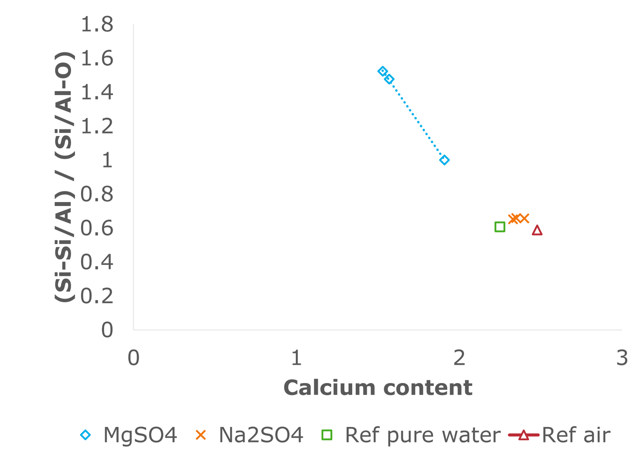
X-axis: Location along x-axis represents atom-atom distance (bond length)

- Lack of discernible peaks indicates that material is disordered
- Each peak indicates an atom-atom correlation
- If a peak moves compared to the control samples, it indicates that this particular atomic bond has changed

Quantitative Analysis of Atom-Atom Correlations



- Higher Ca-Si peak intensities imply greater amount of CASH gel
- Na_2SO_4: no change in amount of Ca-Si peak intensity
- $MgSO_4$: Decrease of Ca-Si peak height, indicating decrease in amount of CASH



- Effect of amount of calcium on degree of polymerization of the CASH gel
- Higher concentrations of $MgSO_4$ lead to lower Ca levels and higher Si-Si : Si-O ratio, indicating higher degree of polymerization of CASH gel

Summary of Results from PDF analysis

Group	Level	Long Range (6- 40 Å)	Short Range (< 6 Å)
Control	Dry	Disordered	No change
	Wet	Disordered Similar to dry	Calcium aluminosilicate hydrate (CASH) gel leached Ca^{2+} ions
Na_2SO_4	1% wt.	Disordered	No change
	5% wt.	Disordered	No change
	10% wt.	Disordered	No change
$MgSO_4$	1% wt.	Disordered	No change
	5% wt.	Ordered	Gypsum formation Higher Polymerization
	10% wt.	Ordered	Gypsum formation Higher Polymerization Effects similar to 5%

Conclusion

- Na_2SO_4 attack had insignificant effect on AAC
- $MgSO_4$ 5% wt. & 10% wt. solutions led to gypsum formation
- Increasing concentrations of $MgSO_4$ result in increasing degree of polymerization
- Negligible differences between 5% wt. and 10% wt. $MgSO_4$

Applications:

- NaOH-activated slag cement is suitable for use in environments containing Na_2SO_4
- NaOH-activated slag cement is suitable in environments with ≤ 1% wt. $MgSO_4$ concentration
- Increased use of AAC will reduce CO_2 emissions, reduce landfill usage and disposal cost, and reuse waste

Future research:

- Find threshold concentration value (between 1% to 5%) at which increasing $MgSO_4$ concentration does not further affect the cement
  - AAS concrete would be suitable for use in environments with $MgSO_4$ exposure concentrations below this threshold value

References

1. Provis, J.L and Bernal, S.A. Geopolymers and Related Alkali-Activated Materials. Annu. Rev. Mater. Res. 2014. 44:299-327
2. Bakharev T, Sanjayan JG, Cheng YB (2002) Sulfate attack on alkali-activated slag concrete. *Cem Concr Res* 32(2):211-216
3. Ismail I et al. (2013) Microstructural changes in alkali activated fly ash/slag geopolymers with sulfate exposure. *Materials and Structures* 46:361-373
4. Rodriguez E, Bernal S, Mejía de Gutiérrez R, Puertas F (2008) Alternative concrete based on alkali-activated slag. *Mater Constr* 58(291):53-67
5. Deja J, Malolepszy J (2003) Some aspects of alkali activated slag binders durability. *Ann Chimie* 28:51-58
6. Kukko H, Mannonen R (1982) Chemical and mechanical properties of alkali-activated blast furnace slag (F-concrete). *Nord Concr Res* 1:16.1-16.16
7. Douglas E, Bilodeau A, Malhotra VM (1992) Properties and durability of alkali-activated slag concrete. *ACI Mater J* 89(5):509-516
8. T.Egami, S.J. Billinge, *Underneath the Bragg Peaks*: Structural Analysis of Complex Materials, Pergomon, Elmsford, NY, 2003

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