Multi-Parameter Study of Sulfate Attack in Blended Cement Materials

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Objectives

- Durability and sustainability for concrete
- Role of fly ash in concrete durability
- Introduction to sulfate attack phenomenon
- Macro-scale experiments
- Micro-scale experiments
- Modeling of sulfate attack
Why is studying the durability of concrete important?

- Concrete is the 2\textsuperscript{nd} consumed material per capita in the world (Note: water is 1\textsuperscript{st})

- ASCE recently estimated that $1.6$ trillion is needed over a 5-year period to bring the nation's infrastructure to a good condition.

- The rehabilitation and renovation required is due to a lack of serviceability of many structures, caused by structural damages and/or durability faults.
Sustainable construction and green concrete!

In up-coming constructions, attention must be paid to sustainability issues:

• To implement more efficient use of resources in concrete production, including re-used materials and by-products. This will help in less cement consumption (less energy used, less CO$_2$ produced).

• To develop construction techniques for low-energy and long-lasting concrete materials and structures (stronger and more durable).
History of pozzolanic materials

- Most probably, Romans were the first to use volcanic ash to harness the power of pozzolans.

- In fact, the term “pozzolan” is derived from the name of an Italian city — Pozzuoli — that is regarded as the birthplace of ash concrete technology.

- Famous Roman structures such as the Pantheon and Coliseum, as well as many roads, are still standing over 2,000 years. They had volcanic ash in their structural material.
What is fly ash?

- Fly ash is a by-product of coal-fired electric and steam generating plants.

- Over 70 million tons of fly ash was produced in 2001, but only 30% of it was used in various applications.

- Fly ash is a pozzolan: a siliceous and/or aluminous material, which in exposure to water, reacts and shows cementitious properties.

- Fly ash has higher SiO$_2$ and Al$_2$O$_3$ and lower CaO, compared to cement.
How can fly ash affect durability?

- Fly ash can improve the microstructure of concrete in both physical and chemical ways:
  - **Physical**: fly ash particles are much finer than cement and they have spherical geometry, so they fill out the micro-pores of the cement paste and provide a denser microstructure.
  - **Chemical**: fly ash participates in Pozzolanic reactions which require the consumption of more calcium hydroxide (CH) and production of more CSH gel which provides more strength and finer structure.
  - Because of improved microstructure, concrete with fly ash is more resistance to the transport of moisture and chemical ions (such as sulfates and chlorides).
What is sulfate attack?

- Sulfates mostly from soil, ground or wastewater (external attack)

- Chemical reactions between sulfates ($\text{SO}_4^{2-}$) and calcium aluminates ($\text{C}_3\text{A}$) in cement.

- These reactions can generate expansive products (such as ettringite crystals) which cause internal pressure and cracking of the material.

- Also, due to the consumptions of cement paste constituents, the stiffness of the materials reduces and the bond between cement and aggregates falls apart.

Cracks appeared on an exposed sample
Experimental program: Fly ash compositions and properties

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<th>Lab Code</th>
<th>Cement</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>C1</th>
<th>C2</th>
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ASTM C 1012

• Standard test
  1x1x11 in. (25x25x280 mm) mortar specimens
  Exposed to Na$_2$SO$_4$ solution (50 g/L) for more than 6 months

• Modified (accelerated) test
  0.4x0.4x4 in. (10x10x100 mm) specimens
  Exposure time can be reduced
Standard vs. modified test
Expansions could be enhanced in a shorter time

![Graphs showing expansion for standard and modified bars](image-url)
Paste vs. Mortar (effect of ITZ)

Comparison of 12 months expansion values from paste and mortar mixtures

ITZ: Interfacial Transition Zone
Microstructural studies (SEM-EDS)

SEM images and EDS spectra for reaction products from sulfate attack

Concentration profile of sulfate ions in 25×25 mm (1×1 in)

Formation of Ettringite

\[ Ca_6Al_2(OH)_{12}(SO_4)_3 \cdot 26H_2O \]
Modeling Sulfate Attack

Diffusion of sulfate ions from the solution

Reaction of sulfates with calcium aluminates

Formation of reaction products (ettringite)

Volumetric changes and volumetric strains

Cracking of cement paste and stiffness reduction

Macroscopic expansion of paste/mortar bars

Modeling steps and major affecting parameters for external sulfate attack
Ionic diffusion is the predominant transport mechanism in most chemical attack cases for cement based materials.

\[
\frac{\partial C(x,t)}{\partial t} = D_0 \frac{\partial^2 C(x,t)}{\partial x^2} + R(C)
\]

\[
\frac{C}{C_0} = 1 - 4 \sum_{m=0}^{\infty} \frac{1}{\pi} \frac{1}{m!} \sin(\lambda x) \left[ k + \nu \exp(-(k + \nu)t) \right]
\]
Reaction and volumetric changes

• The result of reaction between sulfates and C$_3$A is formation of delayed ettringite which has a lot more water molecules and consequent volume change.

\[ C_3A + 3C\overline{SH}_2 + 26H \rightarrow C_6\overline{ASH}_{32} \]

\[ \Delta V = \sum_i V_i = \sum_i \pm \frac{a_i M_i}{\rho_i} \]

\[ \Delta V_{\text{reacted}} = \Delta V \cdot S_{\text{reacted}} \]

\[ \epsilon_v = \epsilon_v(t) = \frac{\Delta V_{\text{reacted}}}{V_{\text{specimen}}} \]
Model vs. Experiments

**ASTM C 1012 - Paste Standard Test (25x25x280 mm)**

Modeling vs. Experiment

- Control: $D=8 \times 10^{-13}$
- $E_s = 9$ GPa  
- $E_i = 20$ GPa

- 30% Class F: $D=4 \times 10^{-13}$
- $E_s = 12$ GPa  
- $E_i = 22$ GPa

**ASTM C 1012 - Expansion of Mortar Specimens**

Modeling vs. Experiment

- Control (Experiment)
- $w/cm = 0.6$
- $c = 0.7$
- $k = 10^{-7}$  
- $f_p = 2$ MPa
- $E_i = 13$ GPa
- $E_s = 22$ GPa

- 30% Class F: $D=2 \times 10^{-12}$
- Control (Experiment)nn
- $w/cm = 0.6$
- $c = 0.7$
- $k = 10^{-7}$  
- $f_p = 2$ MPa
- $E_i = 13$ GPa
- $E_s = 22$ GPa
Conclusions

- Sulfate attack on cement based materials was reviewed and the effectiveness of fly ash was studied.

- Modified size specimens provided faster results compared to the standard size specimens in ASTM C 1012.

- Formation of ettringite crystals was observed using SEM and the diffusion fronts was examined using EDS techniques.

- A Diffusion-reaction based model was developed and used to predict the damage from sulfate attack and the positive effect of fly ash addition on the damage control was modeled.
THANK YOU FOR YOUR ATTENTION

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