



The damage in cement pastes exposed to NaCl and CaCl_2 solutions

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Presented by Chunyu Qiao, November 2017



Outline

- Overview
 - Basics of Chemical Reaction: Calcium oxychloride (Ca-Oxy)
 - Phase Diagram Development: $\text{Ca}(\text{OH})_2\text{-CaCl}_2\text{-H}_2\text{O}$ system
- Experimental Methods
 - Low temperature differential scanning calorimetry (LT-DSC)
 - Thermogravimetric Analysis (TGA)
 - Ball-on-Three-Balls Test Method (B3B)
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 - Damage of cement paste in NaCl solutions
 - Damage of cement paste in CaCl_2 solutions
- Summary and Conclusions



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Overview

- Calcium chloride (CaCl_2) can react with calcium hydroxide ($\text{Ca}(\text{OH})_2$) to form calcium oxychloride.
- This reaction, which is expansive in volume, causes damage, usually seen at the joint.



Slide 4

SP18 I would change "such as joint damage" to "usually seen at the joints" or something like that. Maybe say or have in the slides that this is a huge problem, lots of damage, premature deterioration, etc. Maybe mention that salt is only part of the damage as FT is also part of the damage.

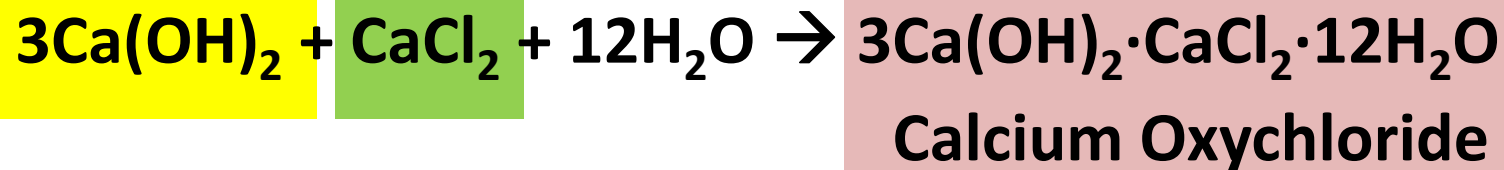
Suraneni, Prannoy, 2017-11-14

Reactions between cement paste and salt solutions



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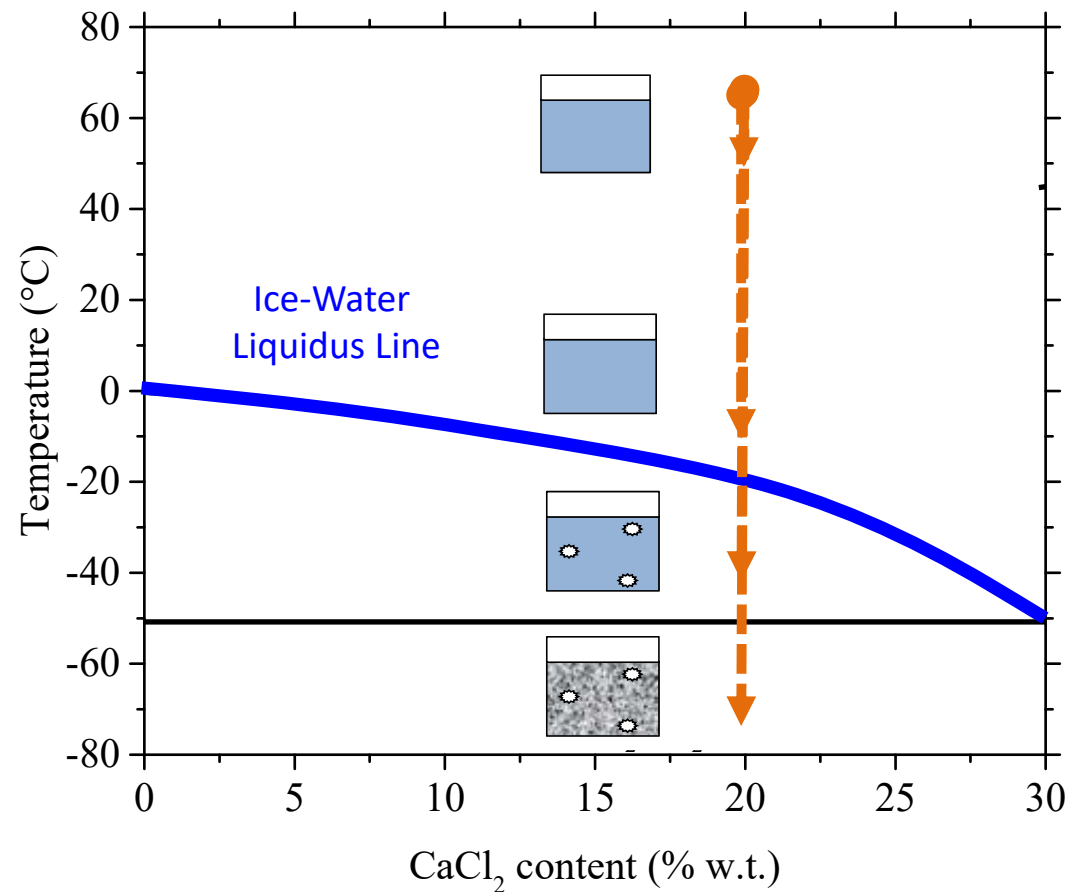
- NaCl solutions: Friedel's (FS) and Kuzel's salt (KS) form due to the reaction with C_3A , $A_{f,m}$.
- $CaCl_2$ solutions: Other than FS, $CaCl_2$ reacts with $Ca(OH)_2$ in cementitious materials.
 - Calcium oxychloride forms due to reaction with $Ca(OH)_2$.



Phase Diagram For $\text{CaCl}_2\text{-H}_2\text{O}$

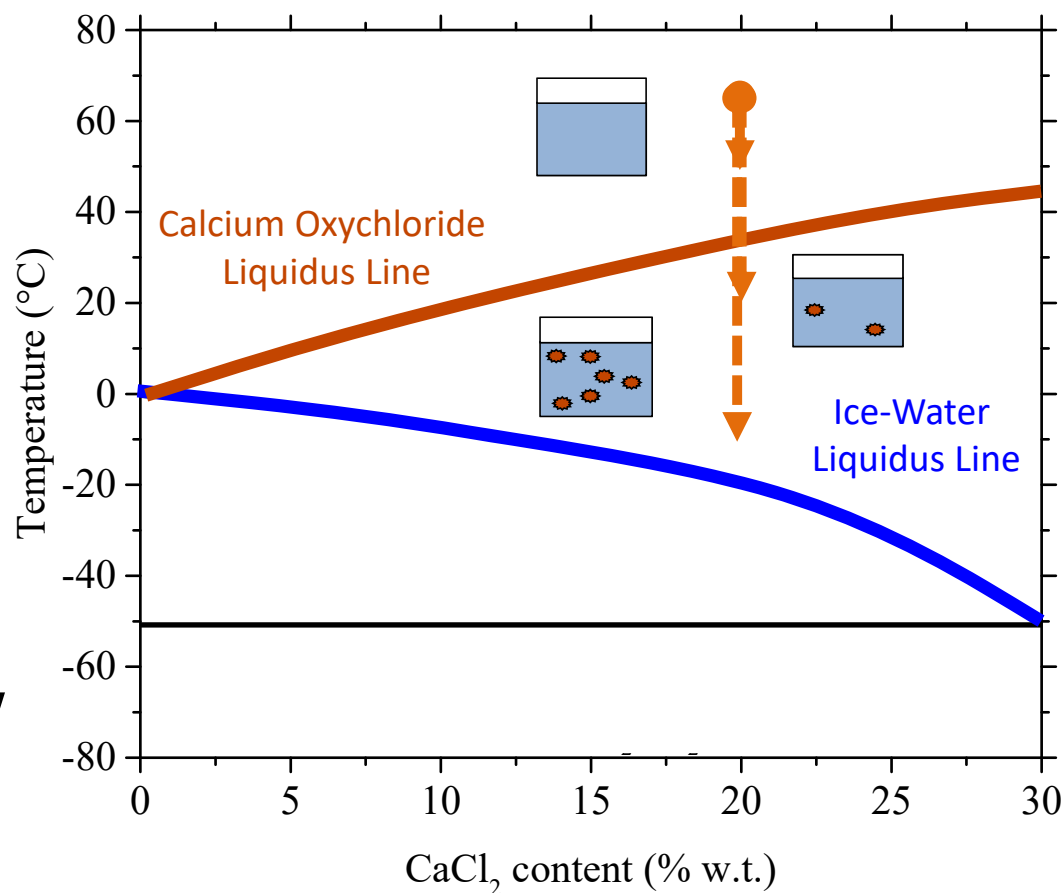


- $\text{CaCl}_2\text{-H}_2\text{O}$ phase diagram is well known.
- Ice forms as the temperature goes below the liquidus line.
- All solution solidifies below the eutectic temperature.



Phase Isopleth For $\text{Ca}(\text{OH})_2\text{-CaCl}_2\text{-H}_2\text{O}$

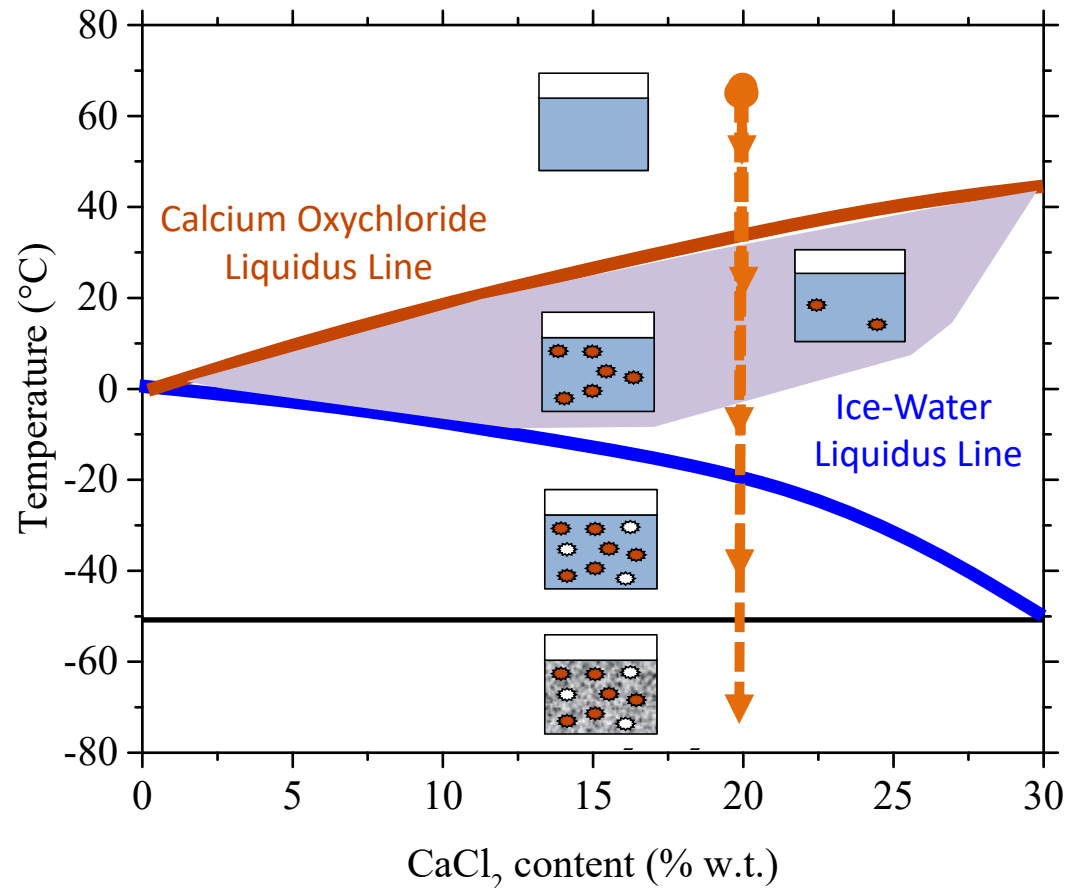
- When the solution contains $\text{Ca}(\text{OH})_2$, a new phase is able to form: calcium oxychloride.
- Calcium oxychloride forms when the temperature goes below Ca-Oxy liquidus line.



Farnam et al. 2015; Qiao et al. 2017

Phase Isopleth For $\text{Ca(OH)}_2\text{-CaCl}_2\text{-H}_2\text{O}$

- When the solution contains Ca(OH)_2 , a new phase is able to form: calcium oxychloride.
- This phase has some implications on the performance of the system.





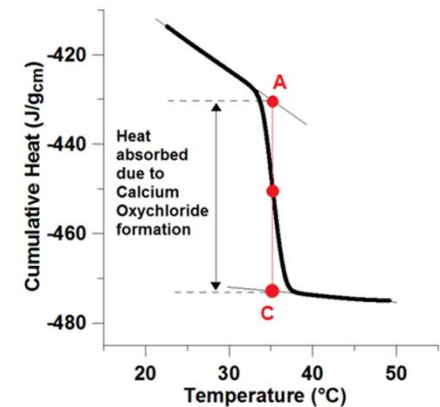
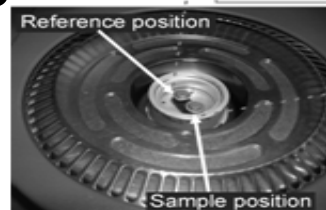
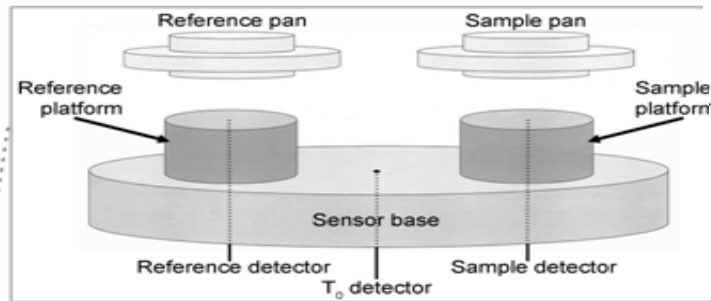
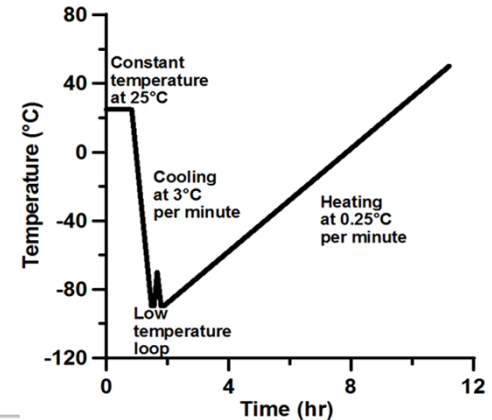
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LT-DSC: Quantification of Ca-Oxy

- Cement paste is ground and placed in a salt solution.
- Pan is moved into the cell.
- The temperature is decreased from 25 °C to -90 °C, then sample is then reheated.
- Heat flow is measured and used to detect phase changes.



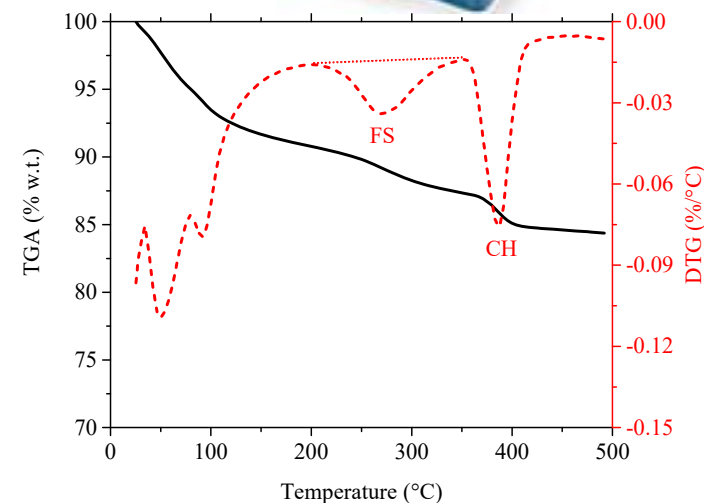
(Monical et al., 2016)



TGA: Quantification of FS

- Cement paste after exposure to NaCl solution is ground.
- The temperature is increased from 23 °C to 500 °C.
- Mass loss is measured and used to quantify the amount of Friedel's salt formed:

$$m_{FS} = \frac{M_{FS}}{6M_{H_2O}} m_{H_2O}$$

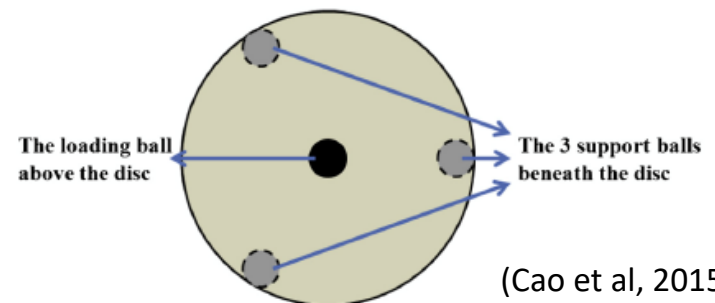


(Qjao et al, 2017, submitted)

B3B: Strength Reduction in Cement Pastes

- Dimension: 50.8 mm in diameter with a thickness of 2.6 ± 0.2 mm.
- Conditioning:
 - Heating at 50 °C in varying NaCl and CaCl₂ solutions for a week;
 - Cooling in a 5 °C chamber for 2 days;
 - Heating back to 50 °C for 1 day.
- Flexural strength (Borger et al., 2004):

$$\sigma = f(\alpha, \beta, \nu) \frac{F}{t^2}$$



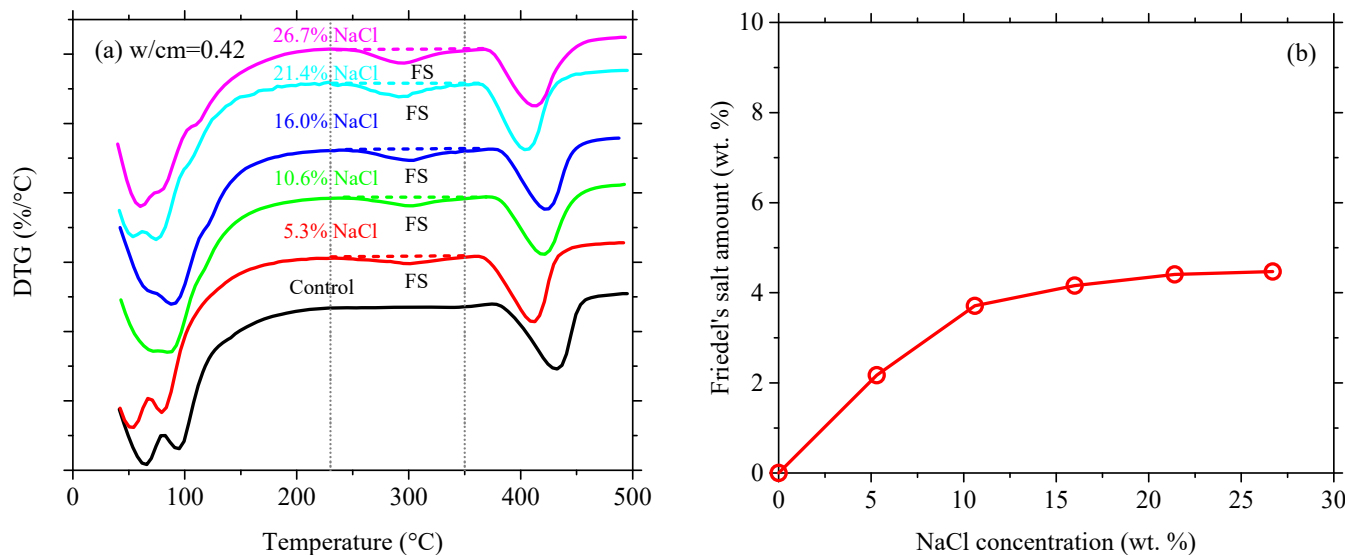


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NaCl solutions: Friedel's salt

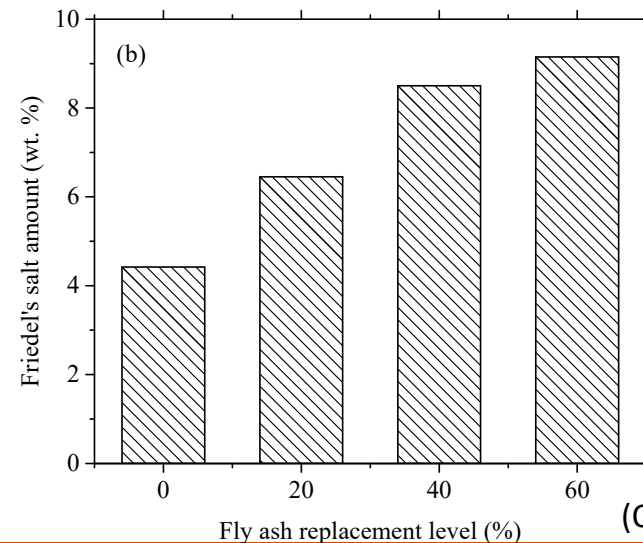
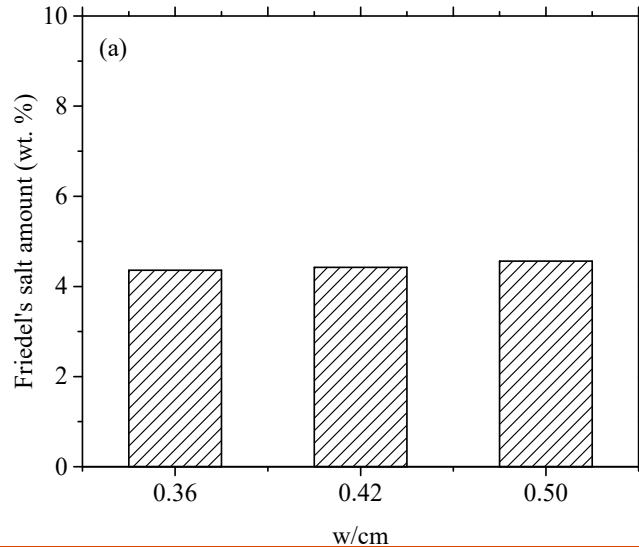
- As NaCl concentration increases, the amount of formed Friedel's salt increases.



(Qiao et al., 2017, submitted)

NaCl solutions: Friedel's salt

- Similar amounts of FS formed in plain cement paste with varying w/cm.
- As fly ash replacement levels increases, the amount of FS increases.

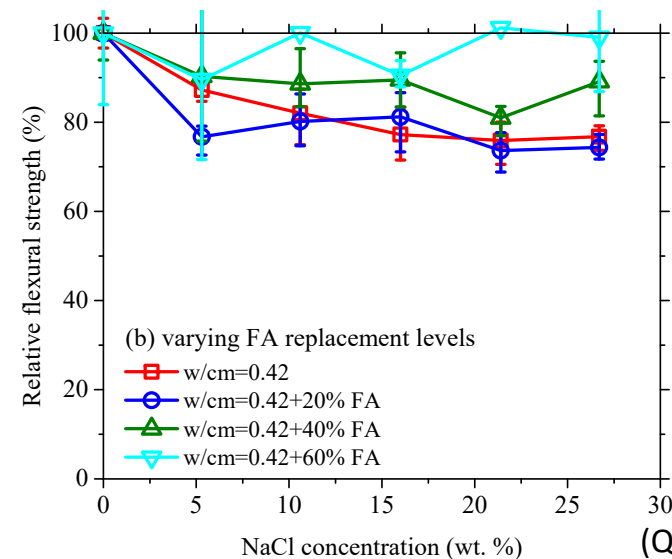
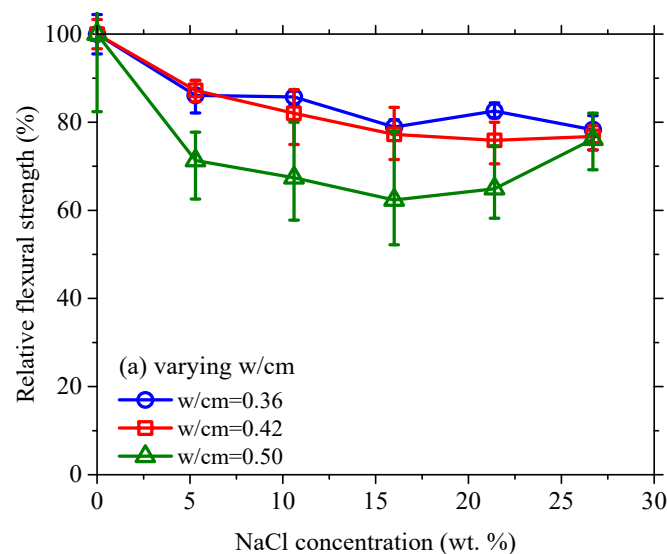


(Qiao et al., 2017, submitted)

NaCl solutions: Flexural strength



- As w/c increases, the flexural strength reduction increases.
- As fly ash replacement level increases, the flexural strength reduction decreases.

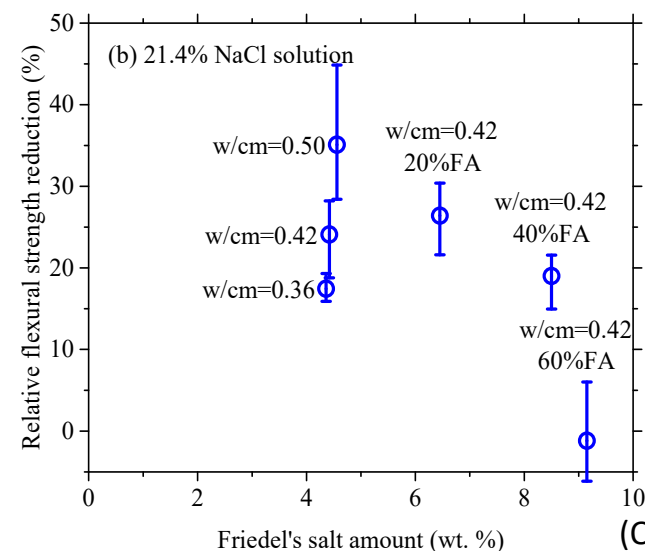
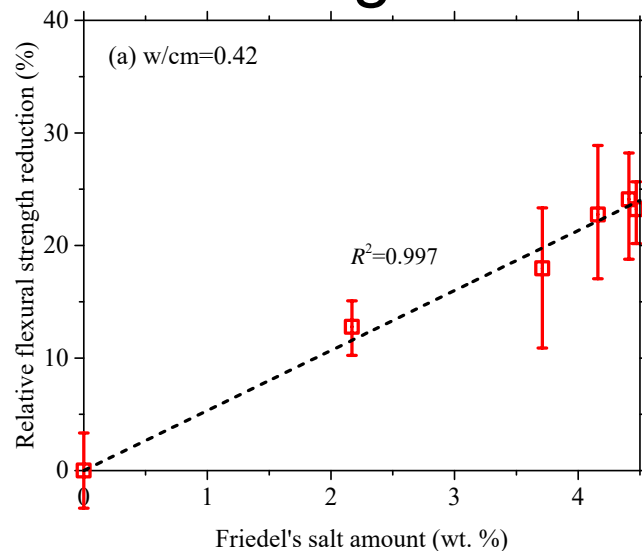


(Qiao et al., 2017, submitted)

NaCl solutions: Flexural strength



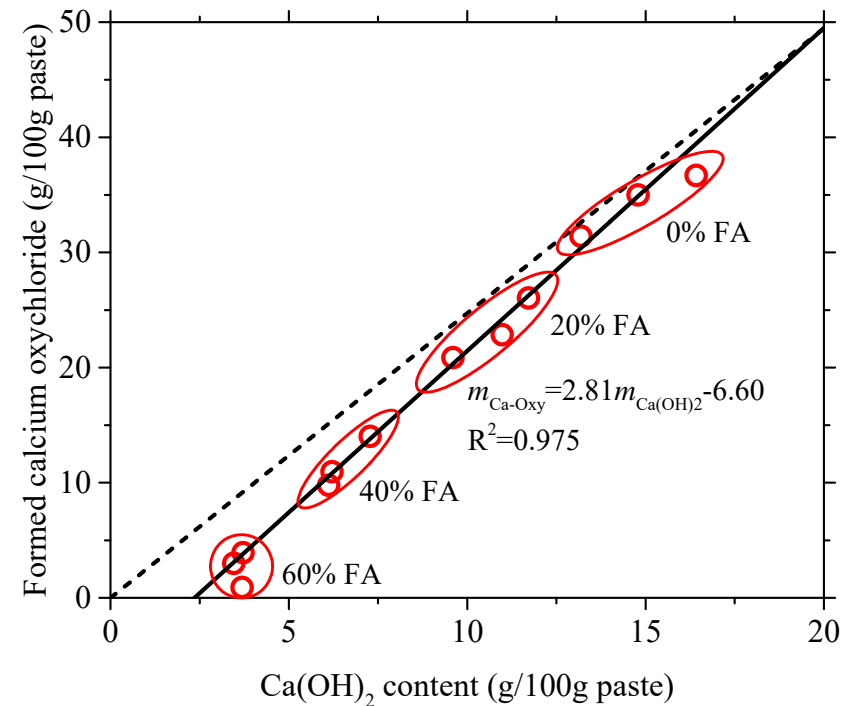
- In the same cement paste, the strength reduction is linearly related to the amount of formed FS.
- In the same NaCl solution, there is no clear relationship between strength reduction and the amount of FS.



(Qiao et al., 2017, submitted)

CaCl₂ solutions: Ca-Oxy

- As the fly ash replacement level increases, the Ca(OH)₂ content decreases.
- Linear relationship between the measured amounts of Ca(OH)₂ & calcium oxychloride.

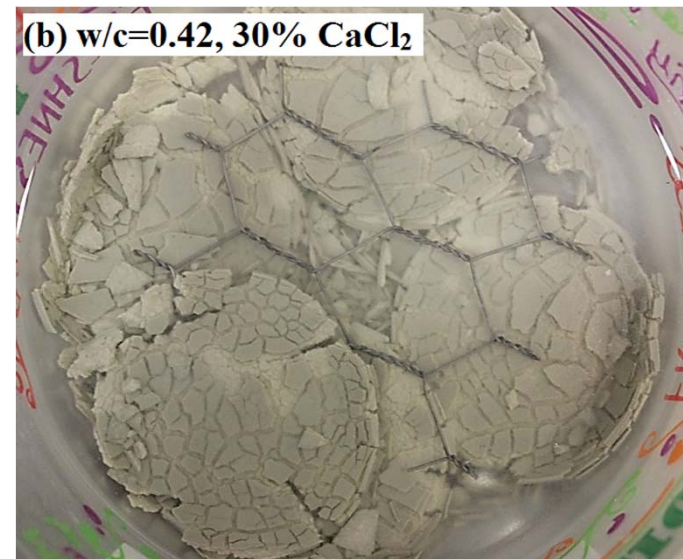
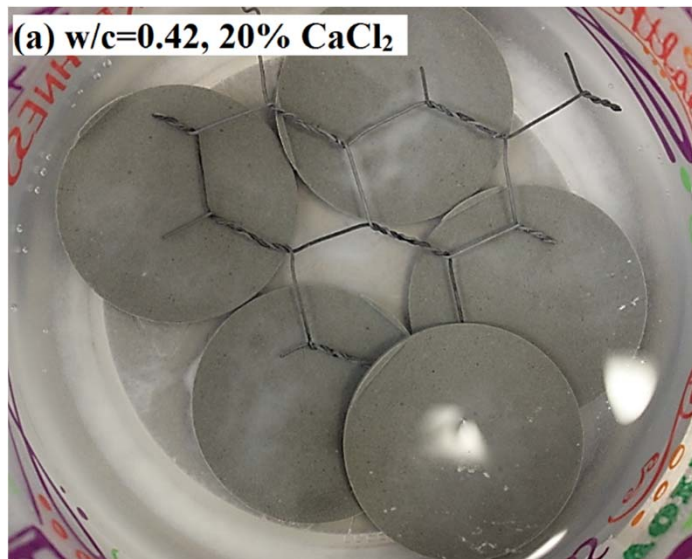


(Qiao et al., 2017, submitted)

CaCl₂ solutions: Flexural strength



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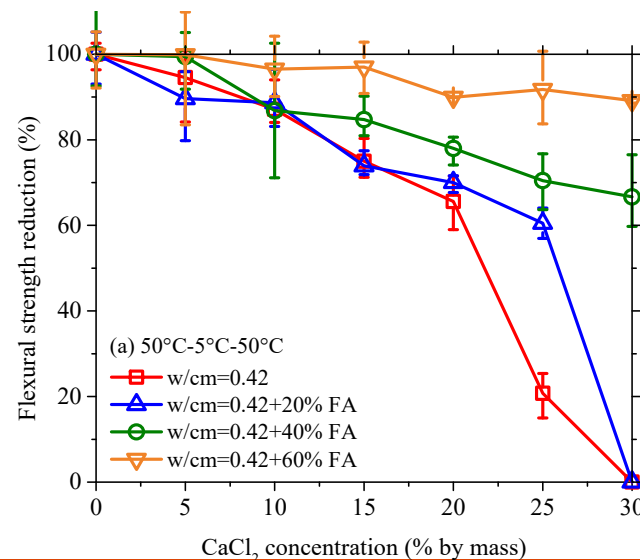
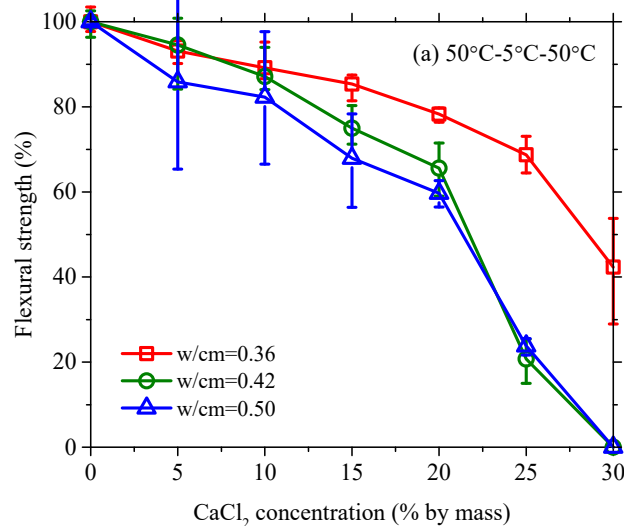


(Qiao et al., 2017, submitted)

CaCl₂ solutions: Flexural strength



- As w/cm increases, the flexural strength reduction increases.
- As fly ash replacement levels increases, the flexural strength reduction decreases.



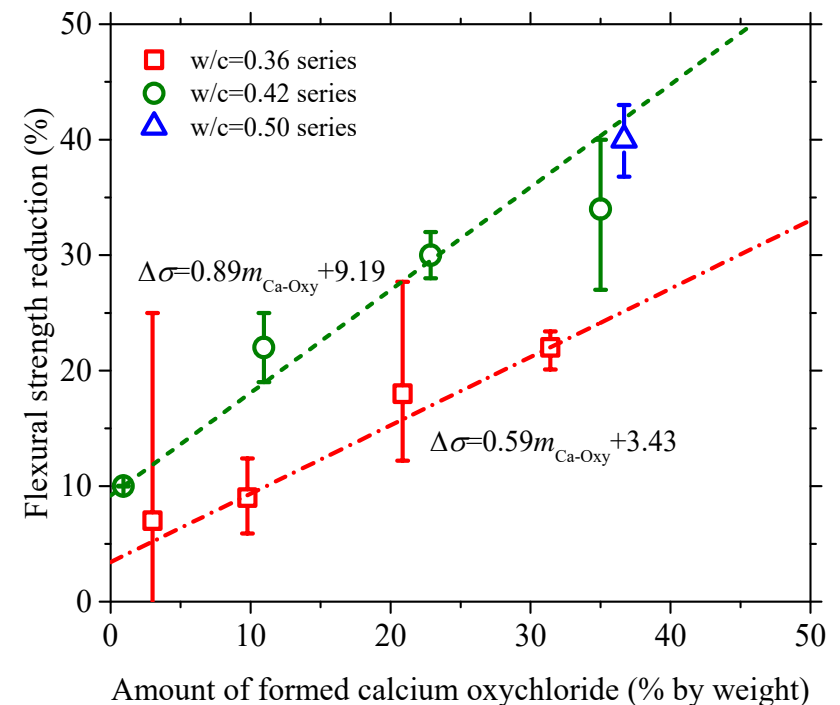
More damage than in NaCl solutions!

(Qiao et al., 2017, submitted)

CaCl₂ solutions: Flexural strength



- Volume of calcium oxychloride takes up 303% that of Ca(OH)₂
- Damage is not only due to the volume change, but also related to the crystallization pressure.
- Fitted line does not pass through the origin, may be due to the formation of Friedel's salt and Kuzel's salt, or leaching.



(Qiao et al., 2017, submitted)



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Summary and conclusions



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- Formed Friedel's salt causes damage in cement paste exposed to NaCl solutions.
- Formed calcium oxychloride results in additional damage in cement pastes exposed to CaCl_2 solutions.
- Strength reduction increases as w/cm increases.
- Strength reduction decreases as fly ash replacement level increases.
- It is important to address the thermal history of cementitious materials when analyzing the damage.

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Thank you! Questions?
Email: Jason.Weiss@oregonstate.edu
<http://cce.oregonstate.edu/deicing-salt>

The screenshot shows a web browser window with the URL cce.oregonstate.edu/deicing-salt. The page title is "Deicing Salt - Concrete Pavement Interaction Bibliography". The page content includes a list of bibliographic references and a "NOW HIRING!" section.

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