The damage in cement pastes exposed to NaCl and $CaCl_2$ solutions

Chunyu Qiao, Prannoy Suraneni and Jason Weiss

Presented by Chunyu Qiao, November 2017

Outline

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- Overview
  - Basics of Chemical Reaction: Calcium oxychloride (Ca-Oxy)
  - Phase Diagram Development: $Ca(OH)_2$-$CaCl_2$-H_2O system
- Experimental Methods
  - Low temperature differential scanning calorimetry (LT-DSC)
  - Thermogravimetric Analysis (TGA)
  - Ball-on-Three-Balls Test Method (B3B)
- Damage of cement paste exposed to NaCl and $CaCl_2$ solutions
  - Damage of cement paste in NaCl solutions
  - Damage of cement paste in $CaCl_2$ solutions
- Summary and Conclusions

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SP18

Overview

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- Calcium chloride ($CaCl_2$) can react with calcium hydroxide ($Ca(OH)_2$) 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, Afm.
- $CaCl_2$ solutions: Other than FS, $CaCl_2$ reacts with $Ca(OH)_2$ in cementitious materials.
  - Calcium oxychloride forms due to reaction with $Ca(OH)_2$.

$$3Ca(OH)_2 + CaCl_2 + 12H_2O \rightarrow 3Ca(OH)_2 \cdot CaCl_2 \cdot 12H_2O$$

Calcium Oxychloride

Phase Diagram For $CaCl_2$-H_2O

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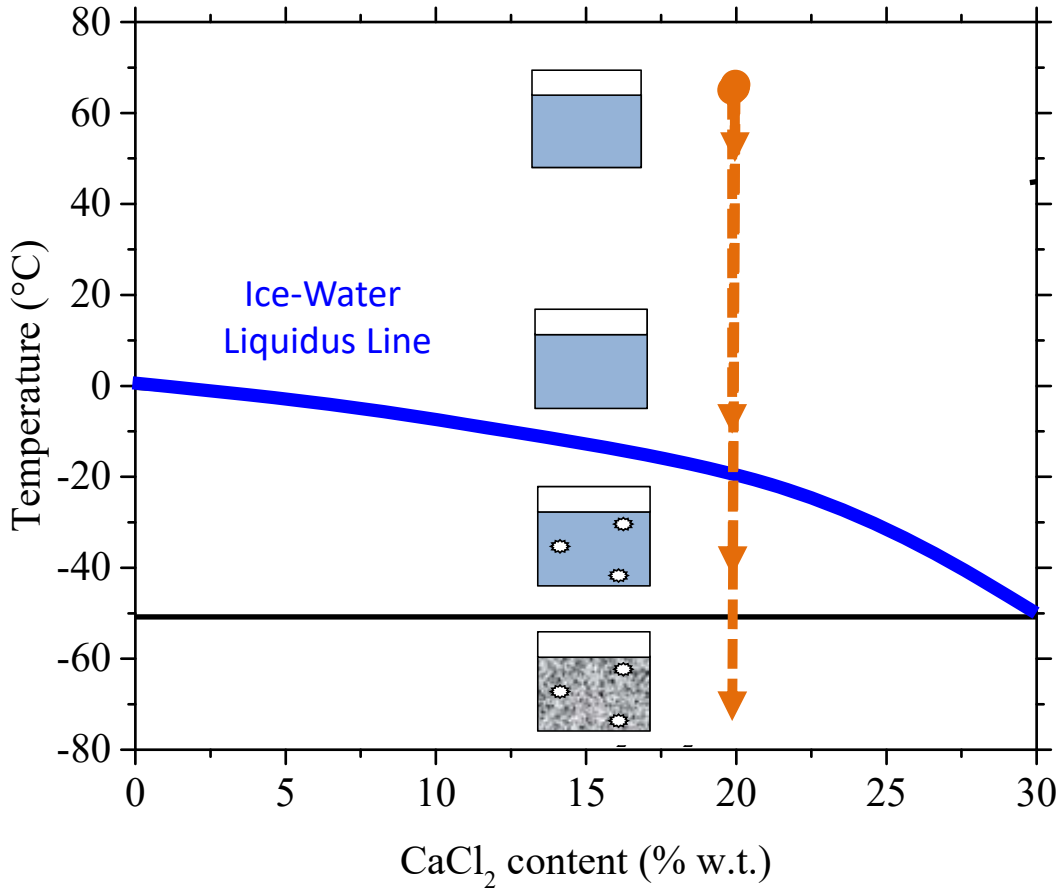
- $CaCl_2$-H_2O phase diagram is well known.
- Ice forms as the temperature goes below the liquidus line.
- All solution solidifies below the eutectic temperature.



Phase Isopleth For $Ca(OH)_2$-$CaCl_2$-H_2O

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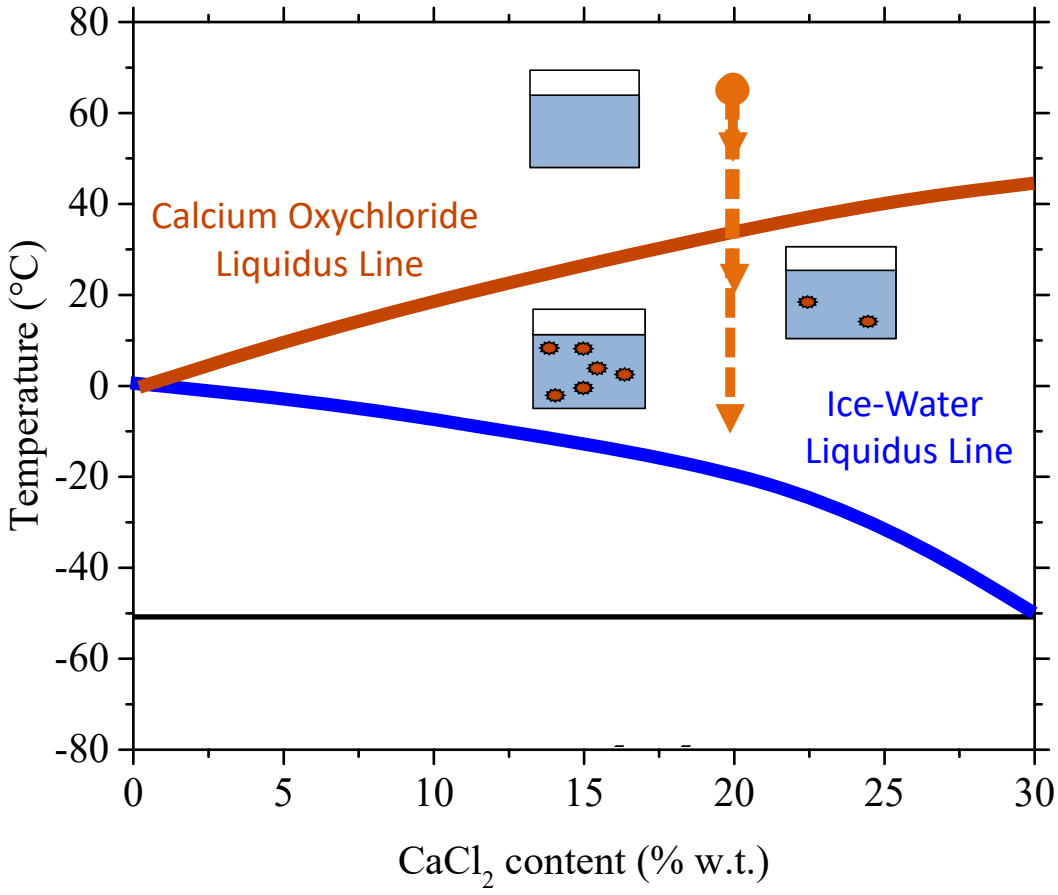
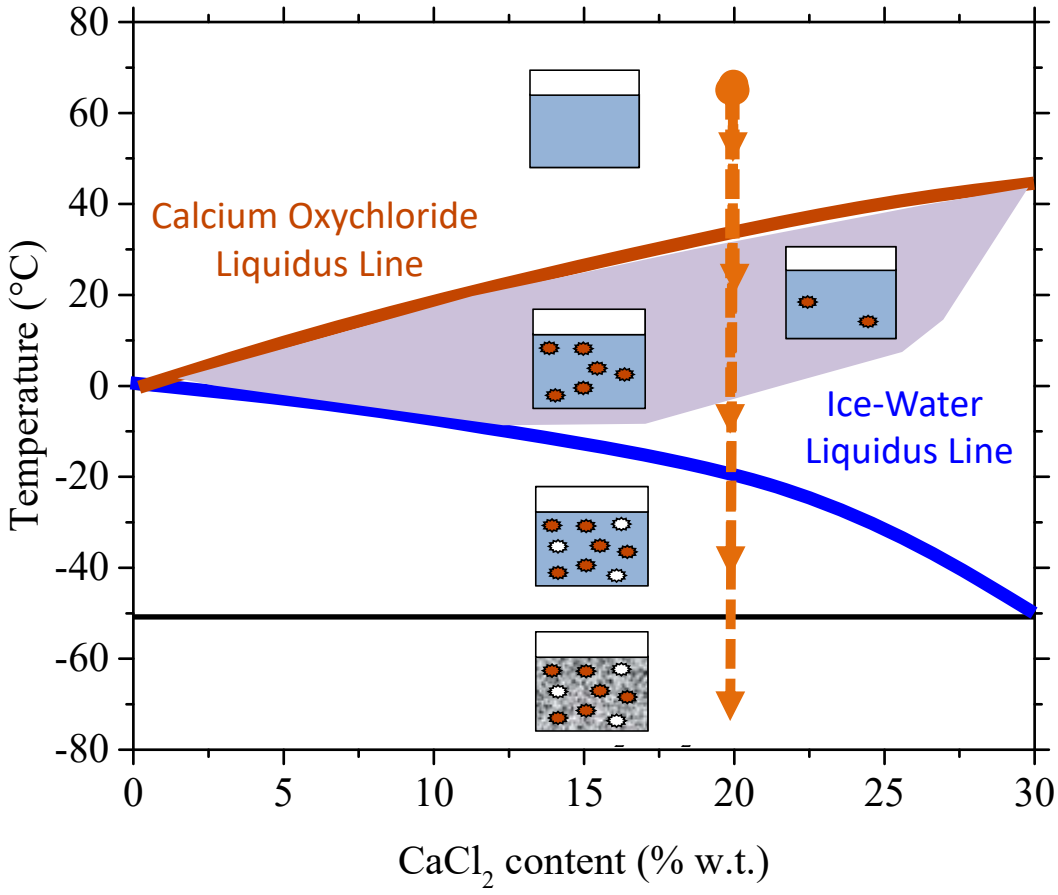
- When the solution contains $Ca(OH)_2$, a new phase is able to form: calcium oxychloride.
- Calcium oxychloride forms when the temperature goes below Ca-Oxy liquidus line.



Farnam et al. 2015; Qiao et al. 2017

Phase Isopleth For $Ca(OH)_2$-$CaCl_2$-H_2O

- 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.



Qiao et al. 2017

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LT-DSC: Quantification of Ca-Oxy

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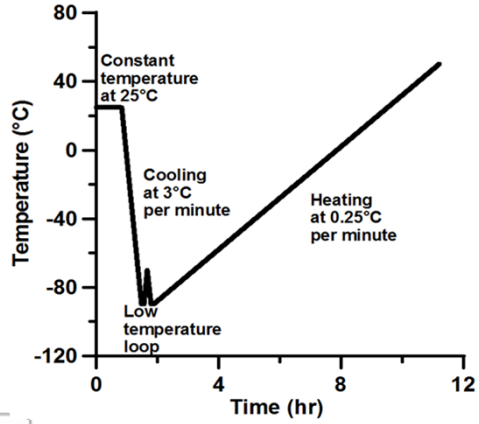
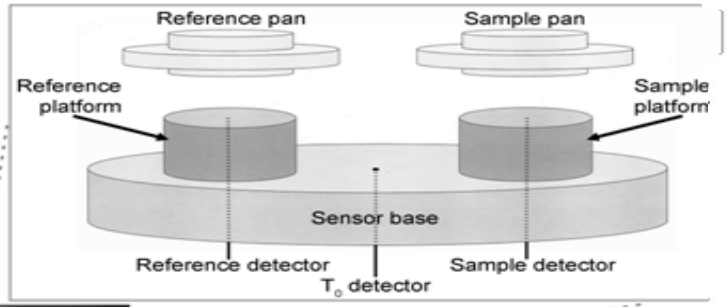
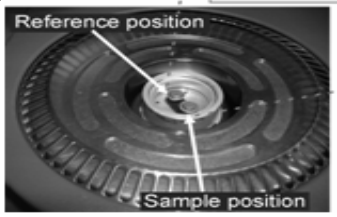
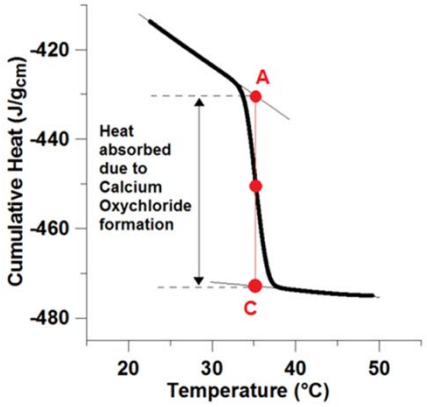
- Cement paste is ground and placed in a salt solution.
- Pan is moved into the cell.
- The temperature is decreased from 25 °C to -90 °C, then sample is then re-heated.
- Heat flow is measured and used to detect phase changes.









(Monical et al., 2016)

TGA: Quantification of FS

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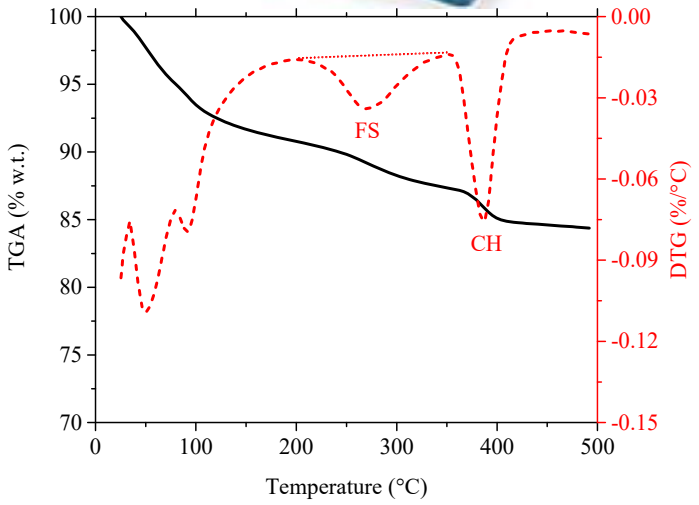
- Cement paste after exposure to NaCl solution is ground.
- The temperature is increased from 23 °C to 500 °C.
- Mass loss is measured and used to quantify the amount of Friedel's salt formed:

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



(Qiao et al, 2017, submitted)

B3B: Strength Reduction in Cement Pastes

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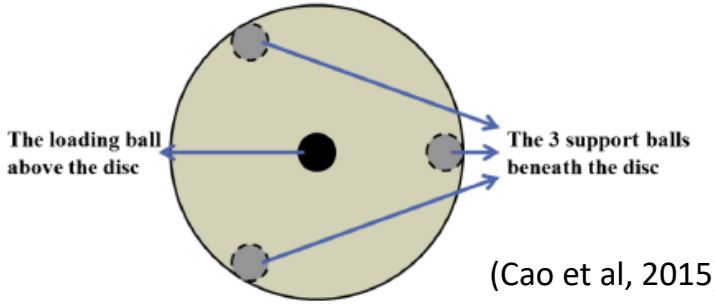
- Dimension: 50.8 mm in diameter with a thickness of 2.6 ± 0.2 mm.
- Conditioning:
  - Heating at 50 °C in varying NaCl and $CaCl_2$ solutions for a week;
  - Cooling in a 5 °C chamber for 2 days;
  - Heating back to 50 °C for 1 day.
- Flexural strength (Borger et al., 2004):
  - $\sigma = f(\alpha, \beta, \nu)\frac{F}{t^2}$



(Cao et al, 2015)

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NaCl solutions: Friedel's salt

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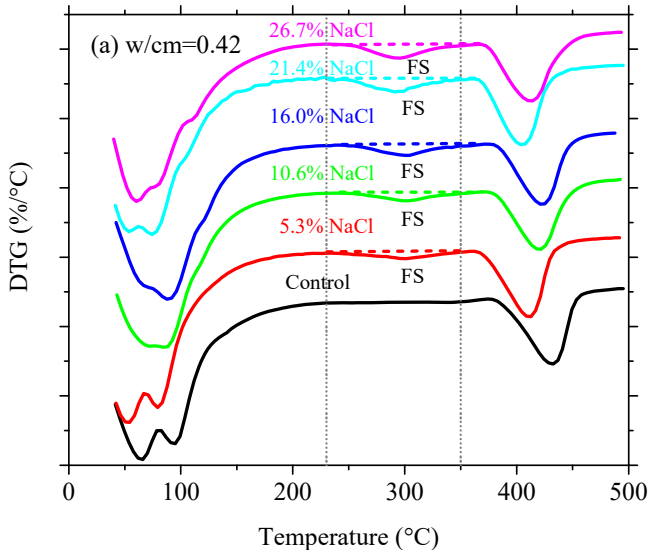
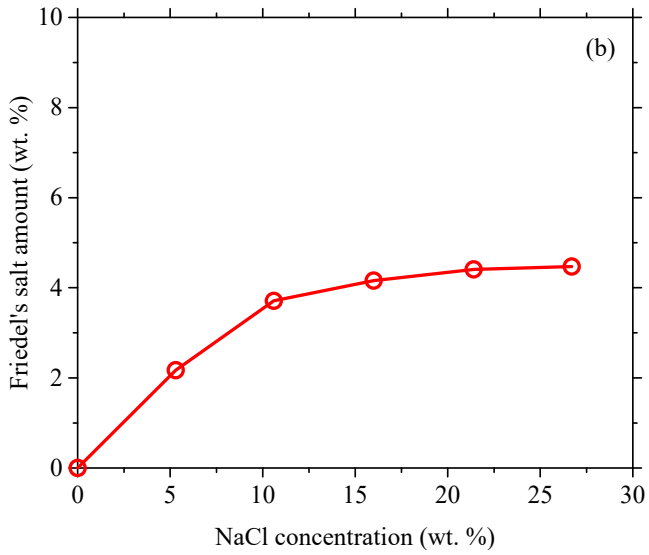
- As NaCl concentration increases, the amount of formed Friedel's salt increases.





(Qiao et al., 2017, submitted)

NaCl solutions: Friedel's salt

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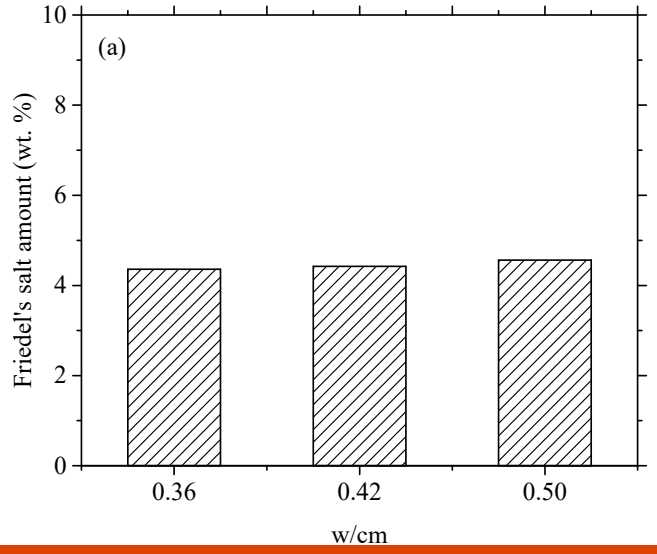
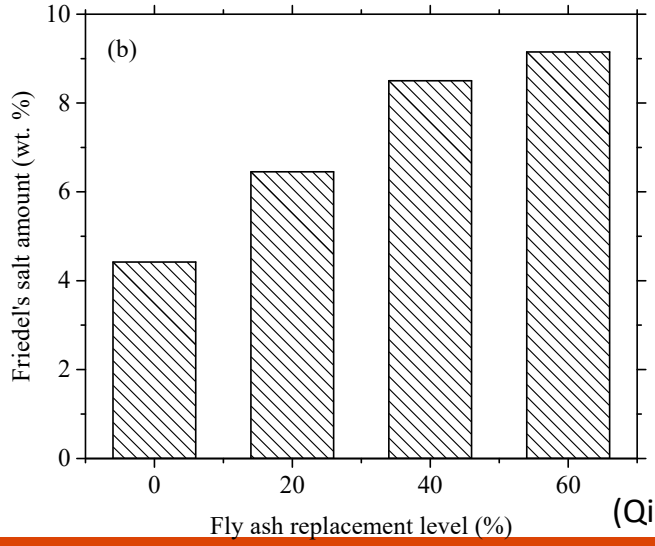
- Similar amounts of FS formed in plain cement paste with varying w/cm.
- As fly ash replacement levels increases, the amount of FS increases.





(Qiao et al., 2017, submitted)

NaCl solutions: Flexural strength

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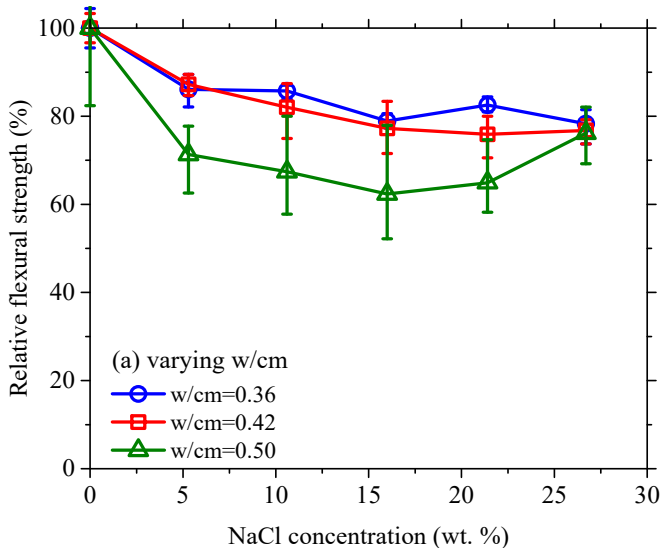
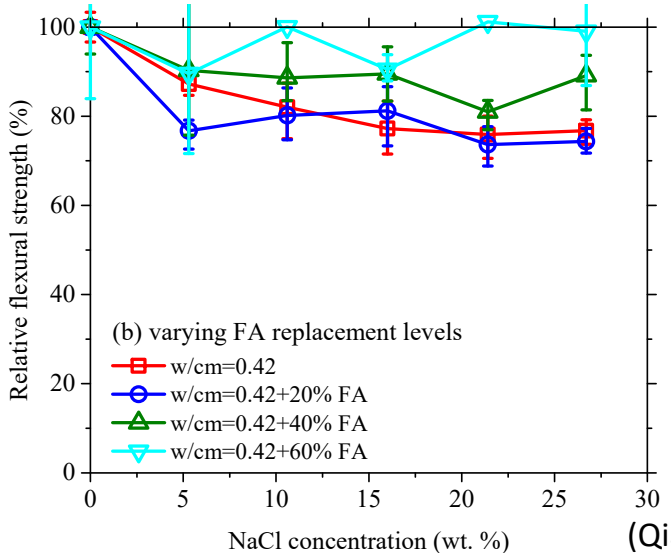
- As w/c increases, the flexural strength reduction increases.
- As fly ash replacement level increases, the flexural strength reduction decreases.





(Qiao et al., 2017, submitted)

NaCl solutions: Flexural strength

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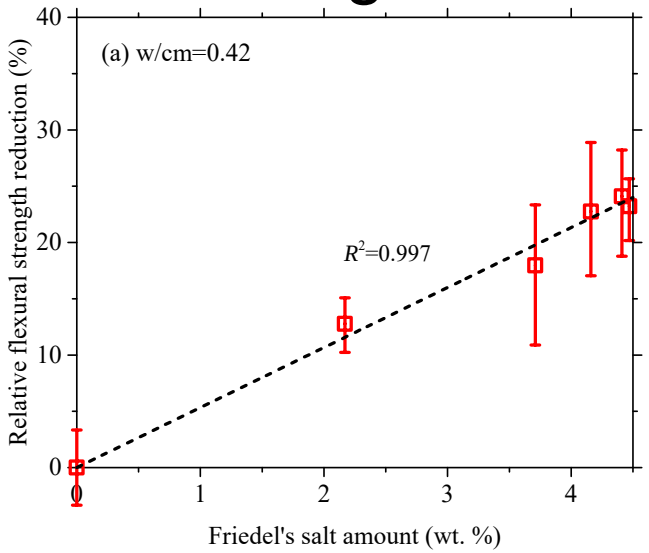
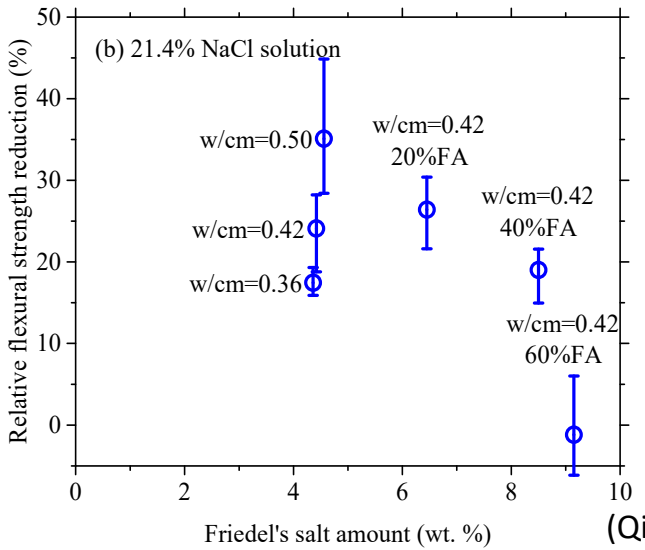
- In the same cement paste, the strength reduction is linearly related to the amount of formed FS.
- In the same NaCl solution, there is no clear relationship between strength reduction and the amount of FS.





(Qiao et al., 2017, submitted)

$CaCl_2$ solutions: Ca-Oxy

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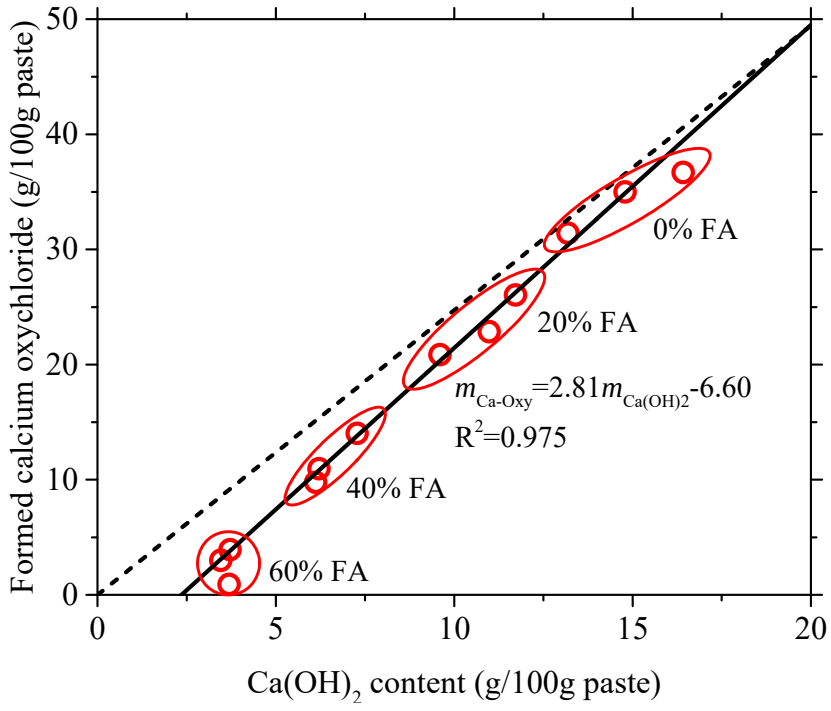
- As the fly ash replacement level increases, the $Ca(OH)_2$ content decreases.
- Linear relationship between the measured amounts of $Ca(OH)_2$ & calcium oxychloride.



(Qiao et al., 2017, submitted)

$CaCl_2$ solutions: Flexural strength

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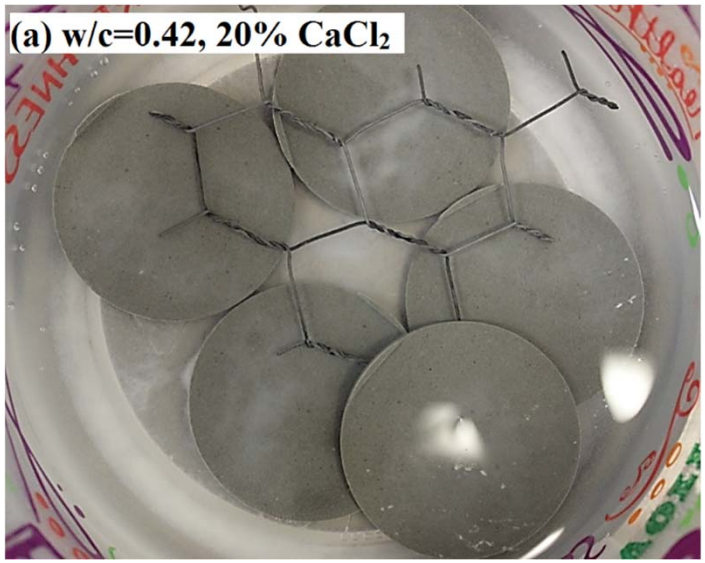

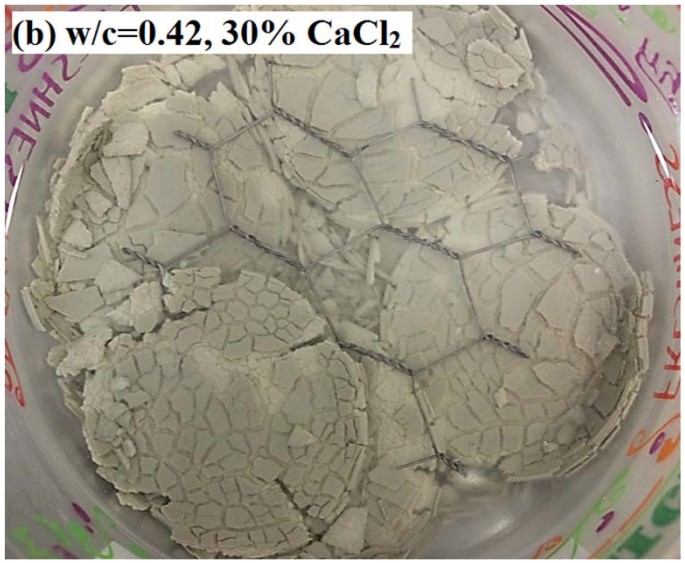

(Qiao et al., 2017, submitted)

$CaCl_2$ solutions: Flexural strength

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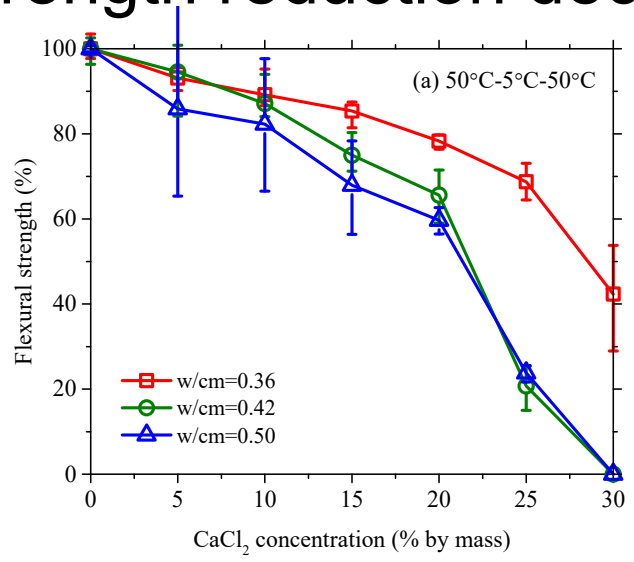
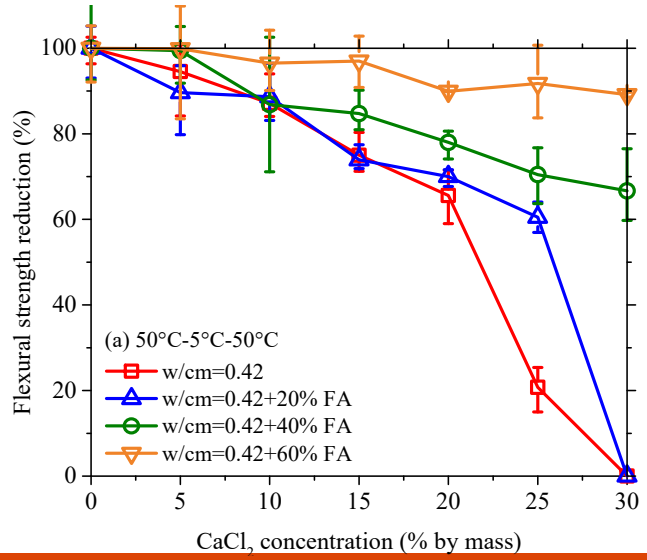
- As w/cm increases, the flexural strength reduction increases.
- As fly ash replacement levels increases, the flexural strength reduction decreases.





More damage than in NaCl solutions!

(Qiao et al., 2017, submitted)

$CaCl_2$ solutions: Flexural strength

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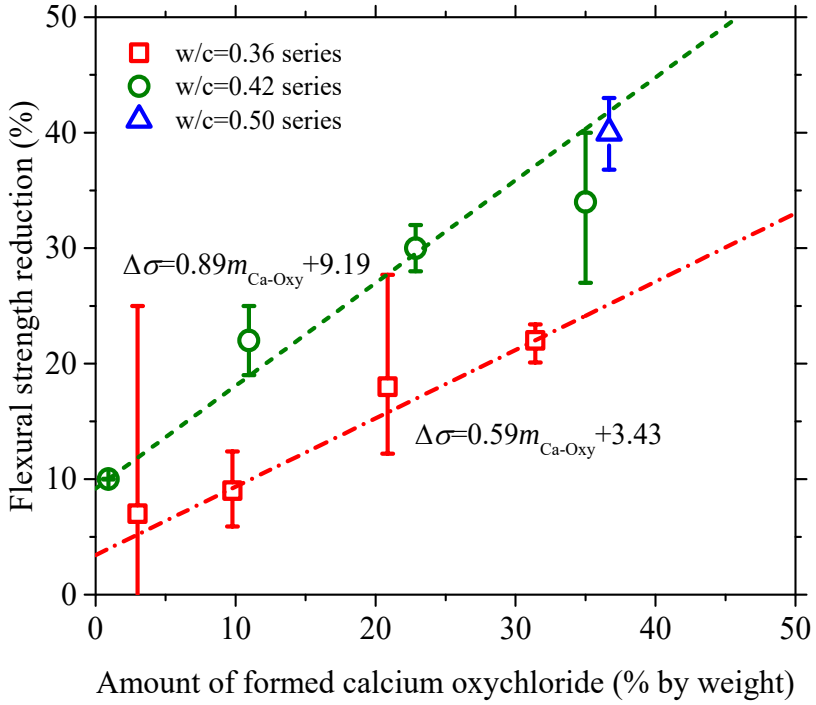
- Volume of calcium oxychloride takes up 303% that of $Ca(OH)_2$
- Damage is not only due to the volume change, but also related to the crystallization pressure.
- Fitted line does not pass through the origin, may be due to the formation of Friedel's salt and Kuzel's salt, or leaching.



(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.

References

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- Farnam, Y., Dick, S., Wiese, A., Davis, J., Bentz, D., and Weiss, J., "The influence of calcium chloride deicing salt on phase changes and damage development in cementitious materials". *Cement and Concrete Composites*, 2015. 64: p. 1-15
- Qiao, C., Suraneni, P., and Weiss, J., "Phase diagram and volume change of the $Ca(OH)_2$-$CaCl_2$-H_2O system for varying $Ca(OH)_2/CaCl_2$ molar ratios". *Journal of Materials in Civil Engineering*, 2018. 30(2): p. 04017281
- Monical, J., Unal, E., Barrett, T., Farnam, Y., and Weiss, W.J., "Reducing joint damage in concrete pavements". *Transportation Research Record: Journal of the Transportation Research Board*, 2016. 2577: p. 17-24

References

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- Qiao, C., Suraneni, P., and Weiss, J., "Damage in cement pastes exposed to NaCl solutions". *Construction and Building Materials*, 2018. Under Review
- Cao, Y., Zavaterri, P., Youngblood, J., Moon, R., and Weiss, J., "The influence of cellulose nanocrystal additions on the performance of cement paste". *Cement and Concrete Composites*, 2015. 56: p. 73-83
- Qiao, C., Suraneni, P., and Weiss, J., "Flexural strength reduction of cement pastes exposed to CaCl2 solutions". *Cement and Concrete Composites*, 2018. 86: p. 297-305

Thank you! Questions?

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http://cce.oregonstate.edu/deicing-salt