Interaction of the NNP replaced cementitious systems with different types of chlorides

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Raikhan Tokpatayeva, Alberto Castillo and Jan Olek

Purdue University

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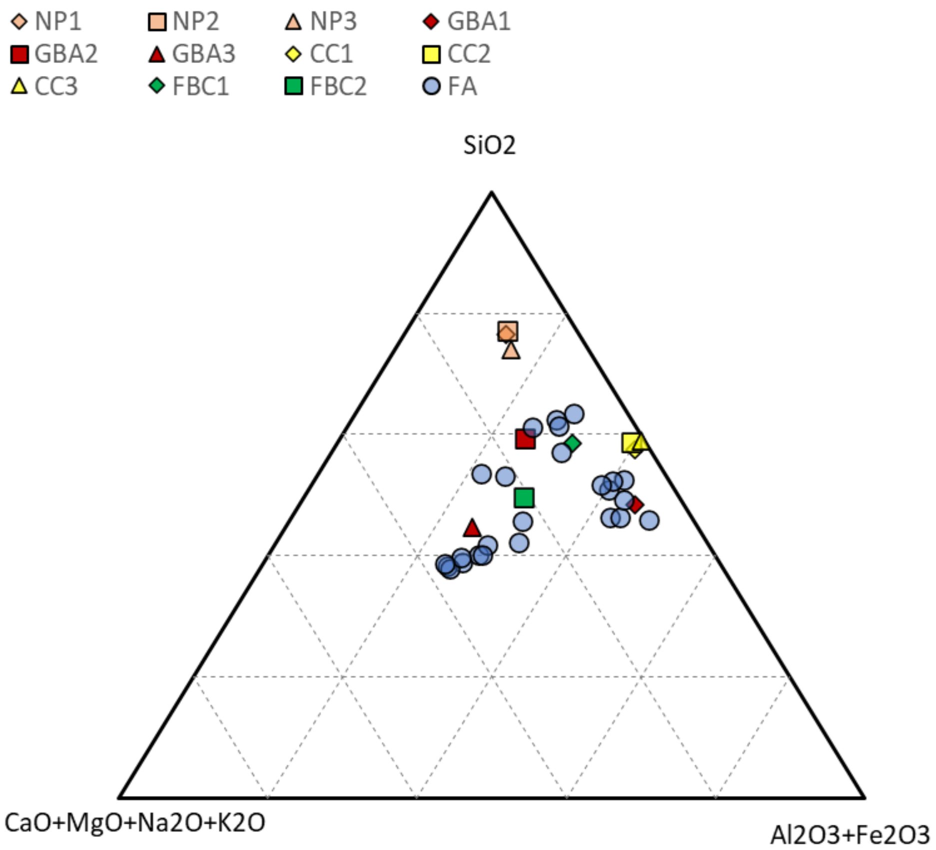
Outline

- Characteristics of the raw NNPs
- Experimental setup
- Analytical results
- Summary

Characteristics of NNPs

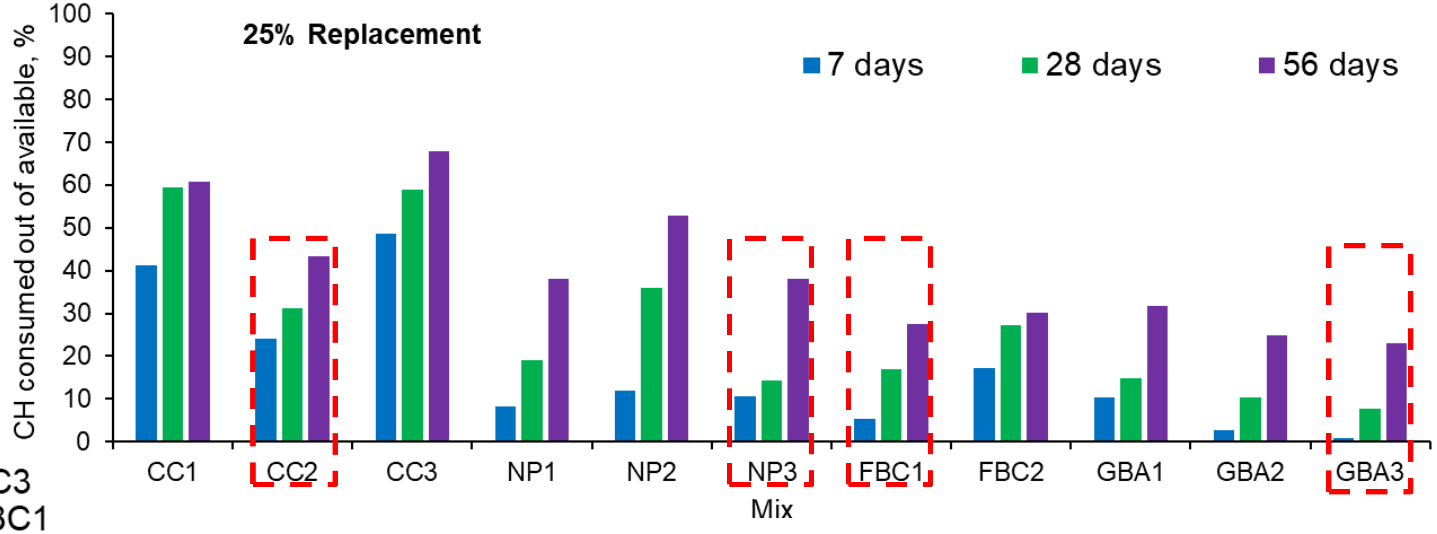
	CC1	CC2	CC3	NP1	NP2	NP3
Crystalline phases	Muscovite, quartz, hematite, anatase	Muscovite, quartz, hematite, anatase	Muscovite, quartz, kaolinite, anatase	-	-	Quartz, albite
Amorphous phase amount, %	49.5	56.2	55.6	100	100	47.1

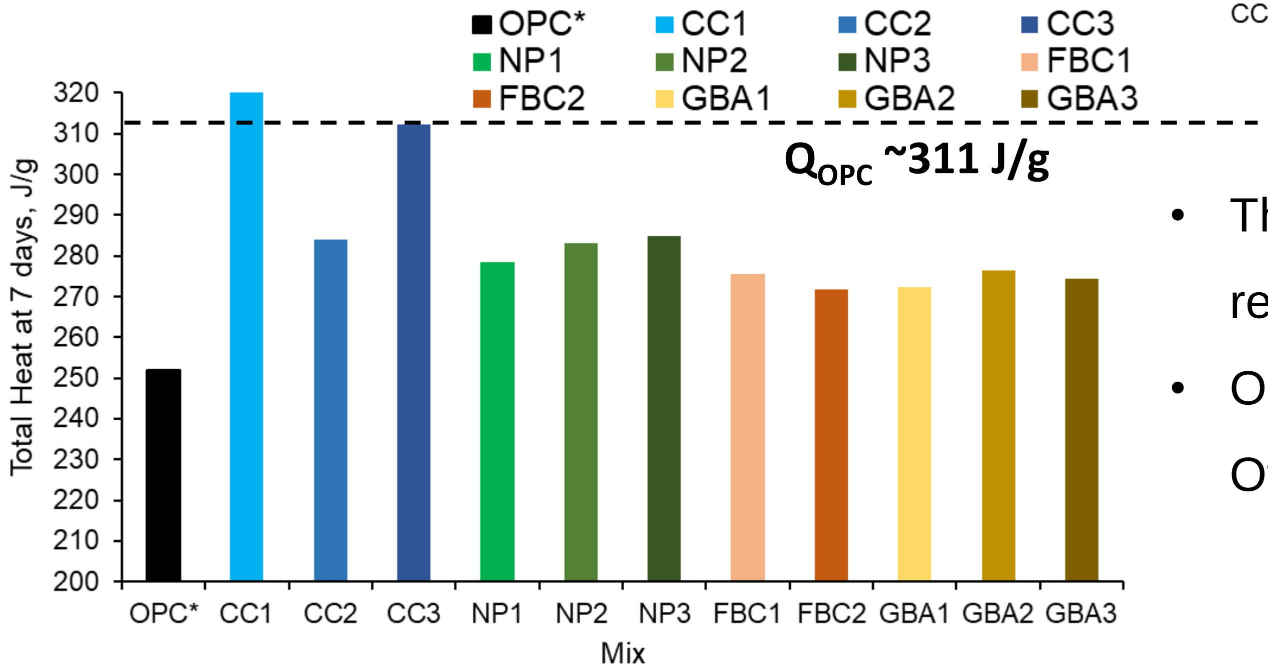
	FBC1	FBC2	GBA1	GBA2	GBA3
Crystalline phases	Muscovite, quartz, hematite, anatase, anhydrate	Muscovite, quartz, hematite, anatase, anhydrate	Quartz, mullite, hematite, magnetite	Quartz, albite anorthite	Quartz, anorthite, akermanite, augite, diopside
Amorphous phase amount, %	41.7	57.9	77.1	67.3	52.7



Courtesy of PenState group

Pozzolanic reactivity of NNPs in cementitious system : $Ca(OH)_2$ consumption





- The paste samples were prepared with w/cm = 0.42 25% replacement level.
- OPC* paste samples were prepared with inert filler (ground Ottawa sand).

Experimental Setup

- **Objectives** – to study the chemical interaction of paste samples with 25% by wt. replacement of cement by NNPs and exposed to various chloride solutions. The exposure regime is following the ASTM C672 scaling test temperature regime (up to 50 temperature cycles of -20°C to + 20°C).

- The samples will be analyzed (DSC, XRD) for presence of chloride-containing phases

Salt solutions

- 3% wt. NaCl
- 3% wt. $CaCl_2$
- 3% wt. $MgCl_2$

Control

- Plain OPC paste (w/c=0.42) cured at 100% RH and 23°C.
- At the age of 28-days ground and sieved through 80 µm sieve.

NNP samples

- Pastes with 25% replacement of OPC with NNPs, cured at 100% RH and 23°C
- At the age of 28-days, ground and sieved through 80 µm sieve.

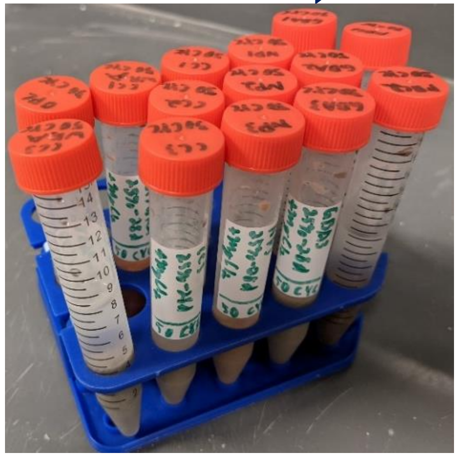
Experimental Setup

Slurry

Paste powder

Chloride solution

1:5 by wt.



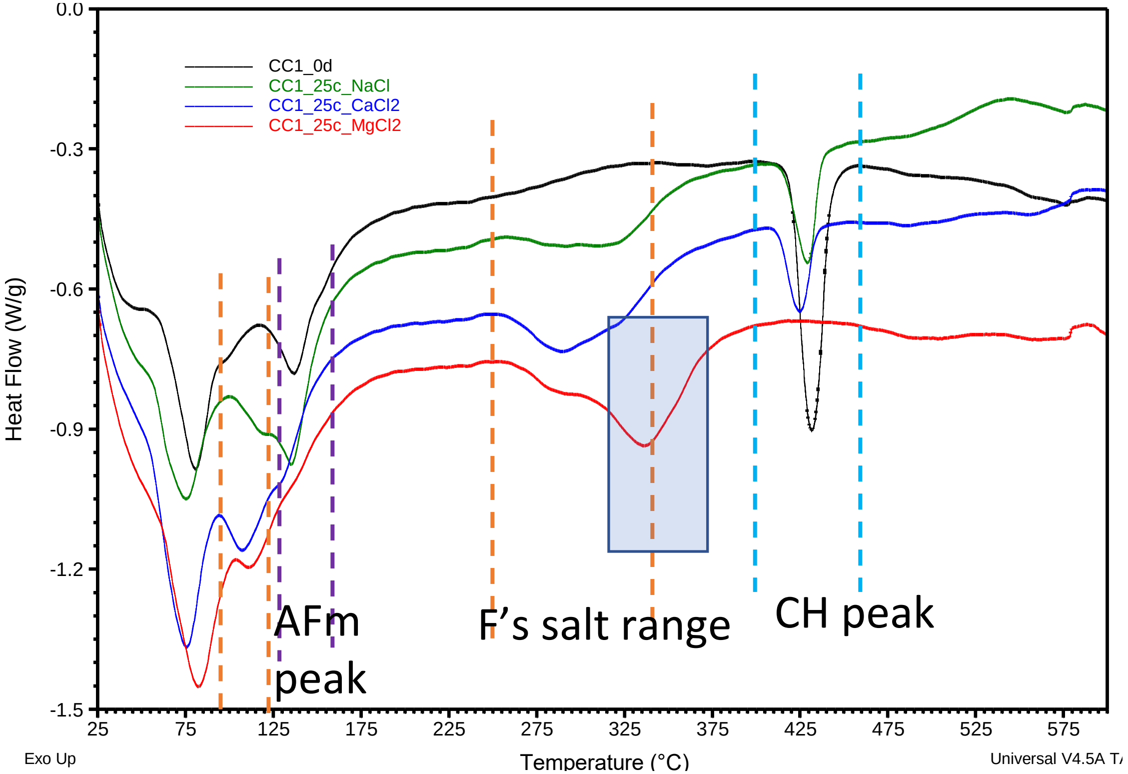
25 and 50 scaling test regime temp. cycles (-20ºC to +20ºC)

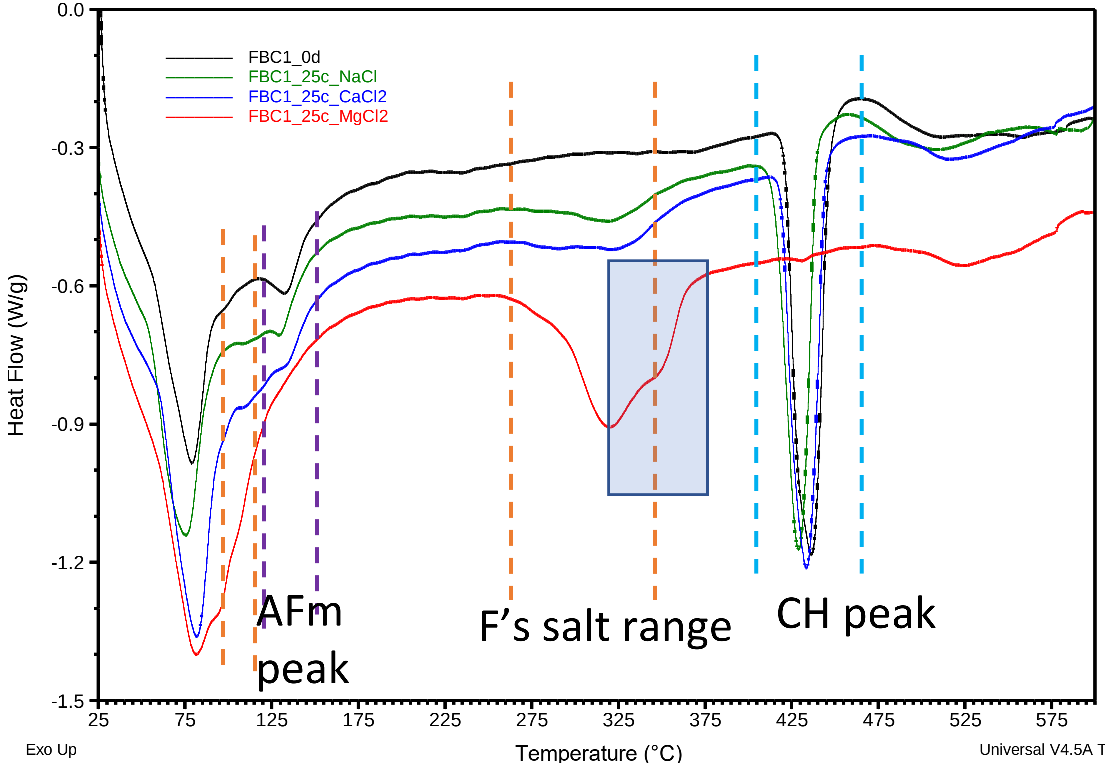
Solids

Solvent exchange (4 days) and drying in desiccator under the vacuum for 3 days

DSC, XRD

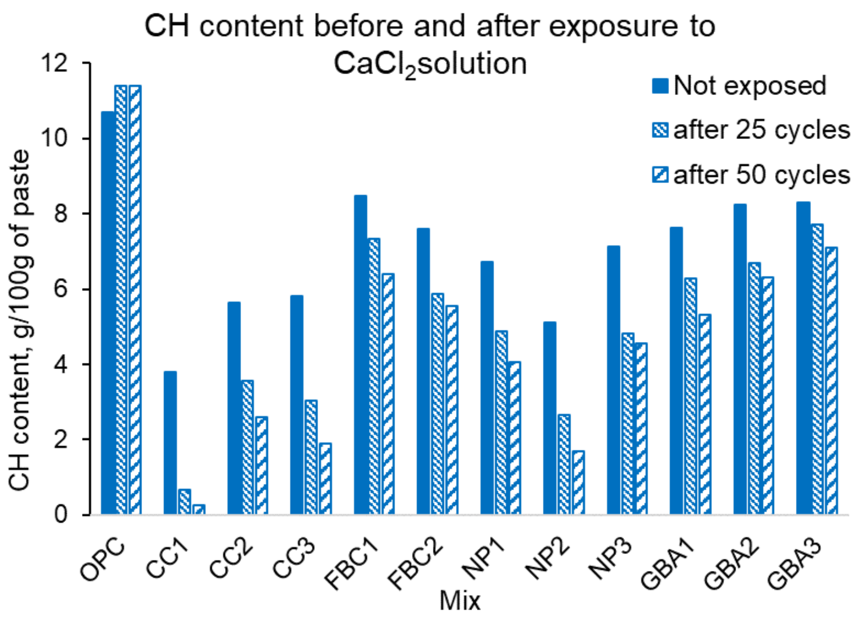
Analytical results: DSC curves

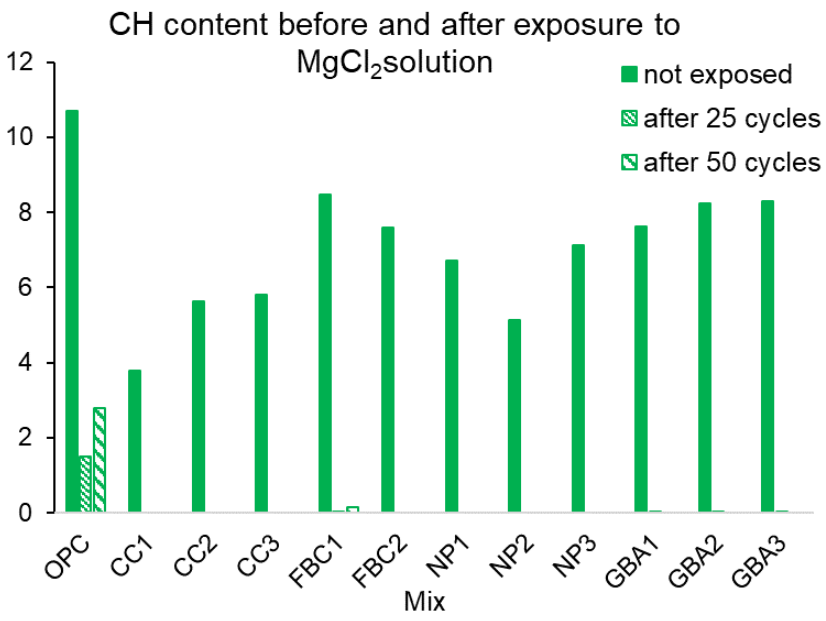


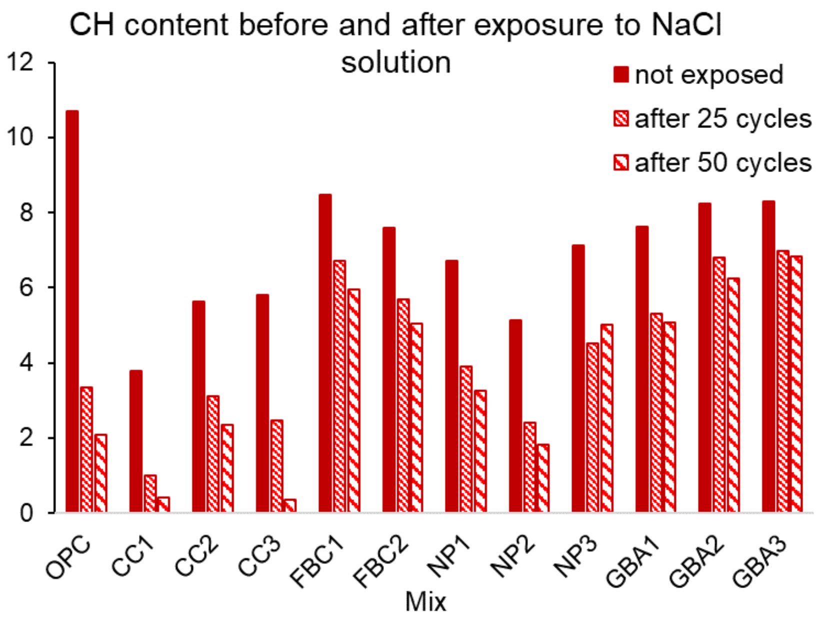


- In all cases, after exposure to chloride solutions a peak appears in the range of 250-375°C (Friedel's salt, $C_3A{\cdot}CaCl_2{\cdot}10H_2O$ [$Ca_2Al(OH)_6]Cl{\cdot}2H_2O$]), while the peak at around 120-150°C (AFm) becomes smaller (or almost disappears).
- Peak appearing in temperature range 320-400°C in $MgCl_2$ system– likely brucite/M-S-H overlapping with FS
- In all paste samples, the peak belonging to CH peak disappeared upon exposure to $MgCl_2$ solution.

Quantification of $Ca(OH)_2$ (CH)

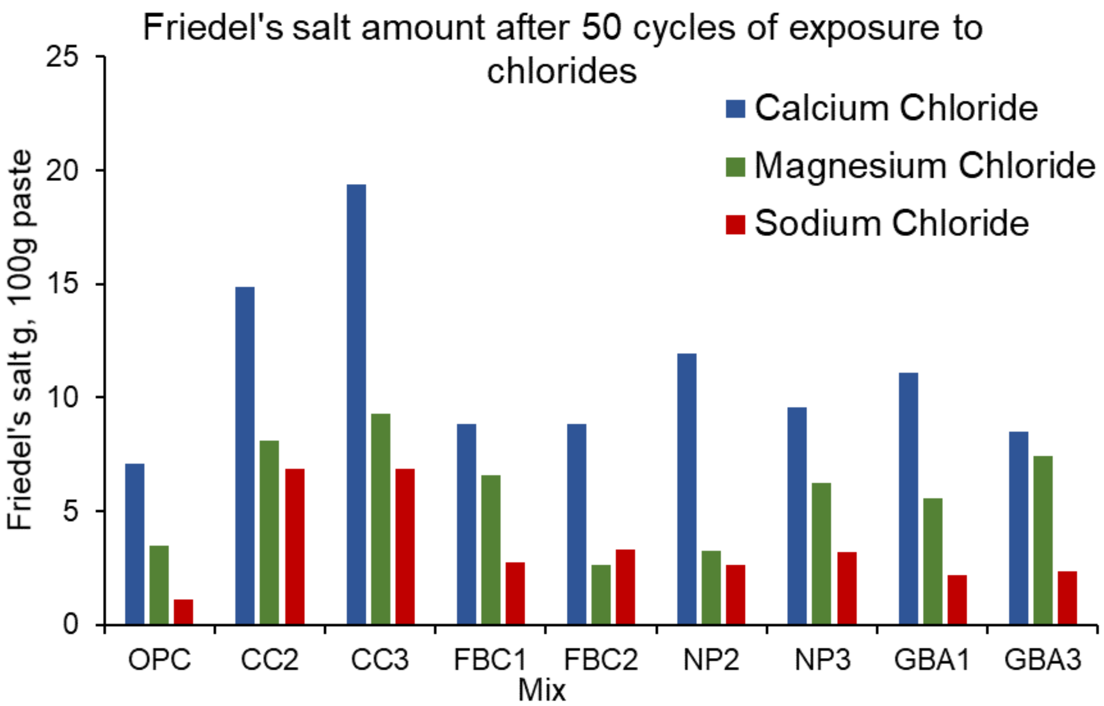


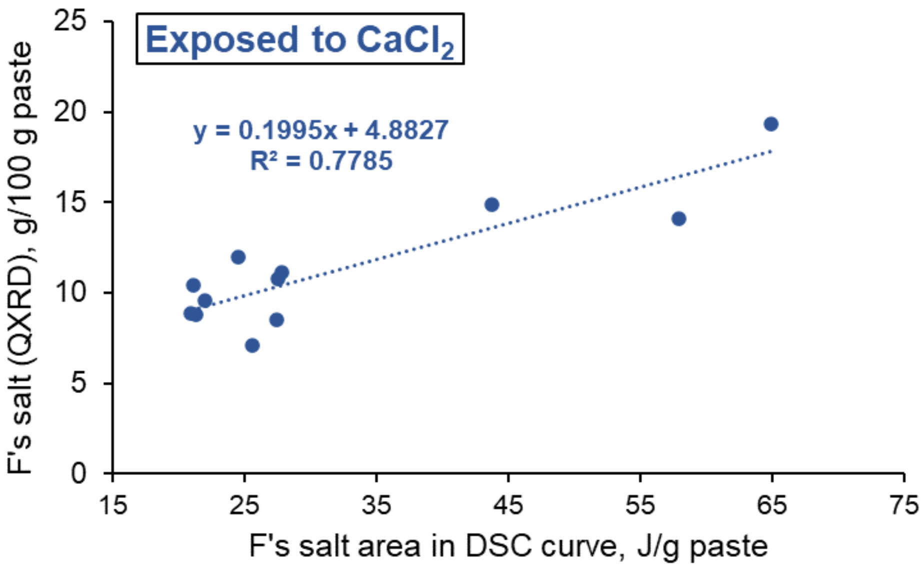




- Almost in all cases, decrease of CH amount was observed.
- In all paste samples, except plain OPC mix, the CH disappeared upon exposure to $MgCl_2$ solution.

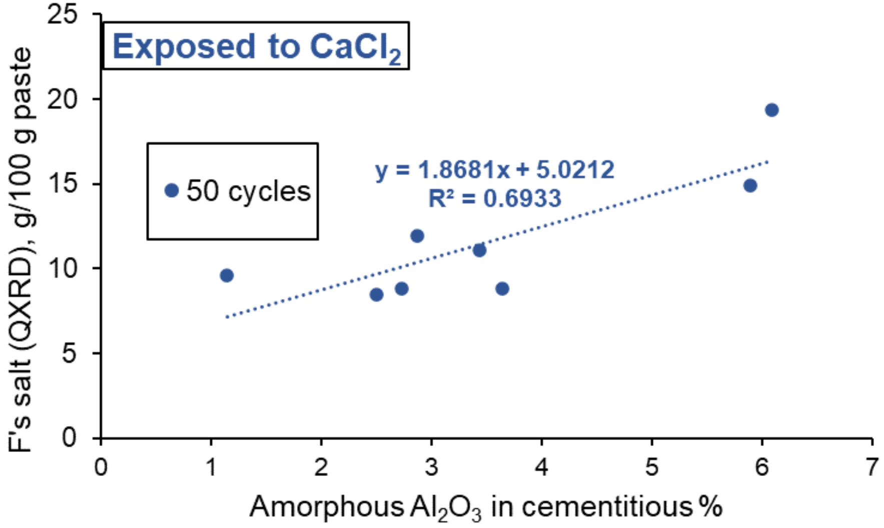
Quantification of Friedel's salt (FS) amount

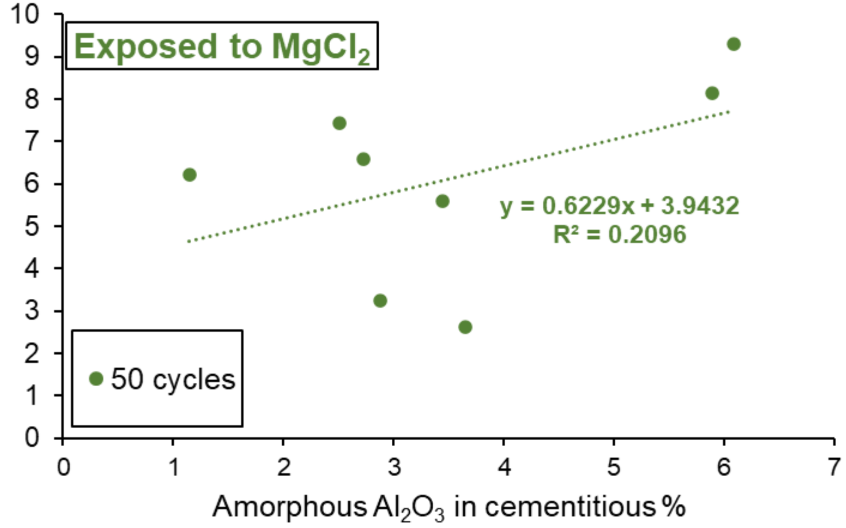


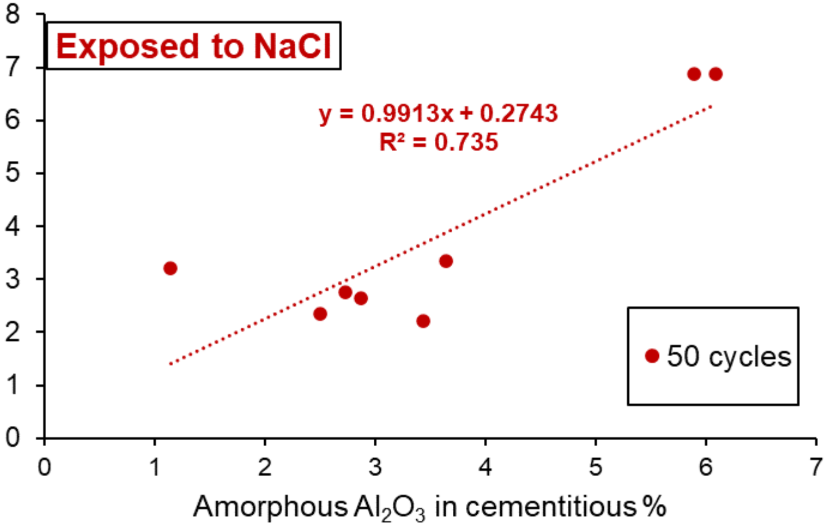


- Almost in all samples, the amount of formed FS appeared to be in trend of $CaCl_2$ > $MgCl_2$ >NaCl.
- The highest amount of FS was determined in CC blended samples.
- A good correlation was observed between QXRD and DSC results.

Correlation of Friedel's salt amount with amorphous Al_2O_3 contributed by NNPs

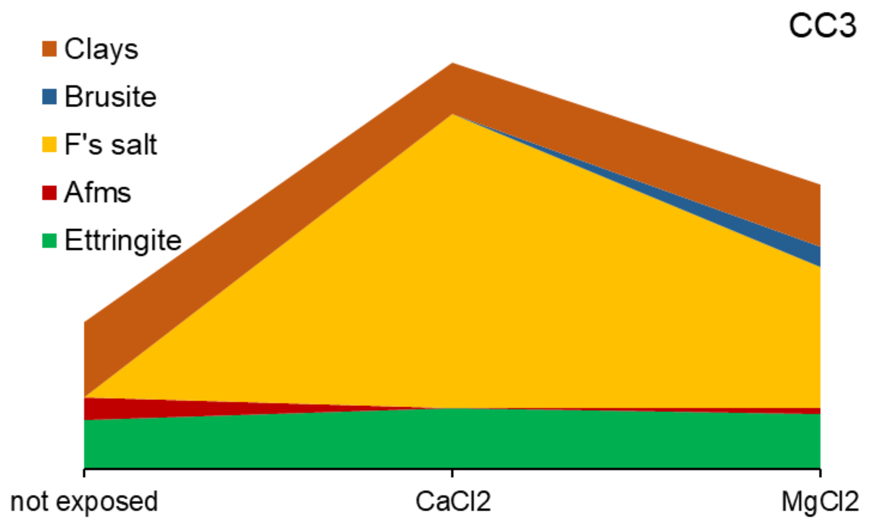


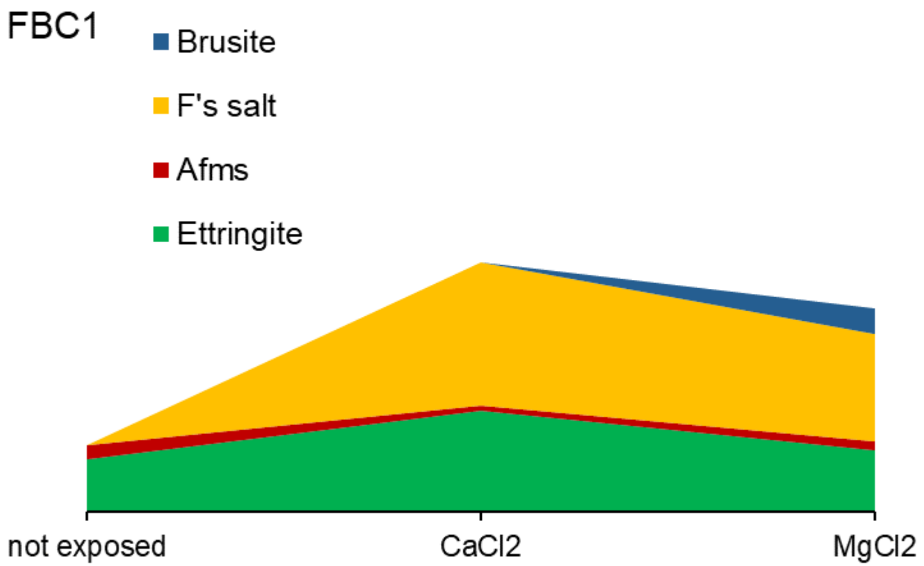


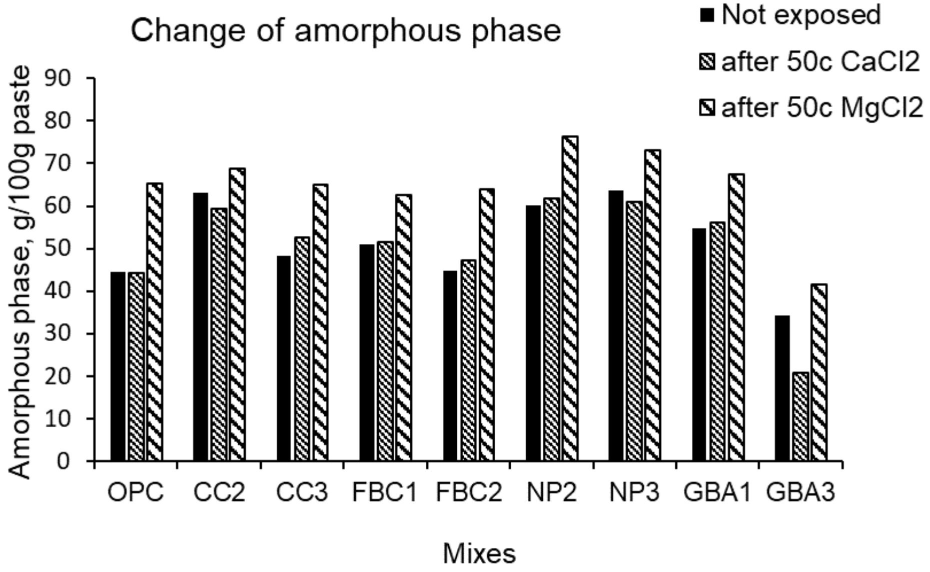


- Amorphous Al_2O_3 content in NNPs showed a good correlation with FS formed upon exposure to $CaCl_2$ and NaCl solutions.

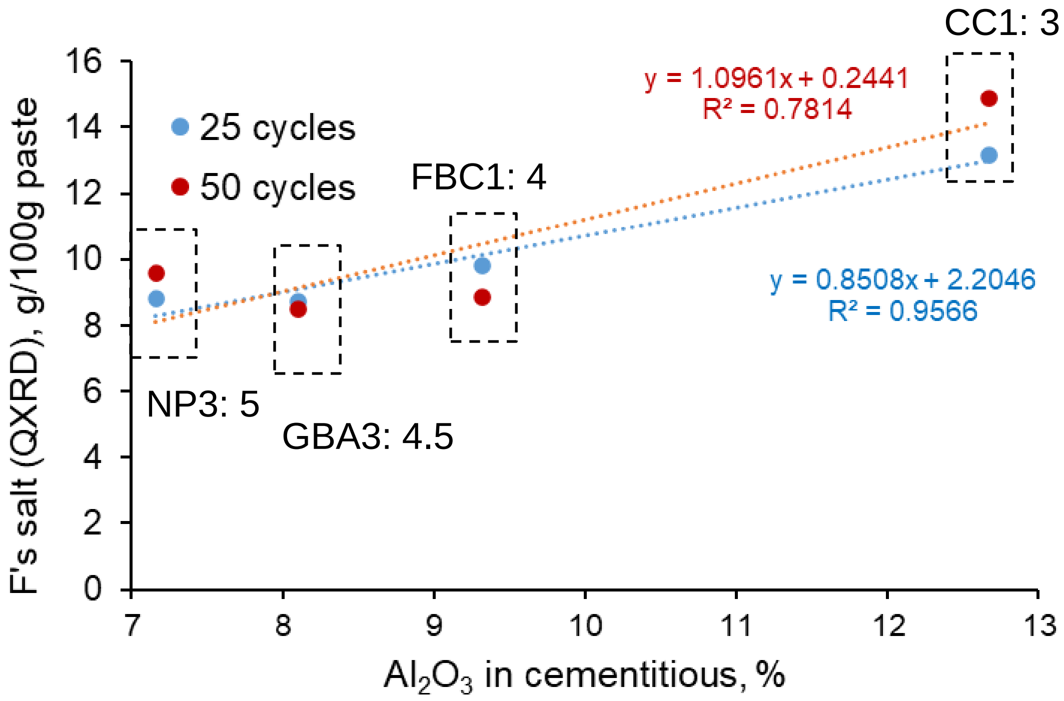
Some features observed in QXRD analysis

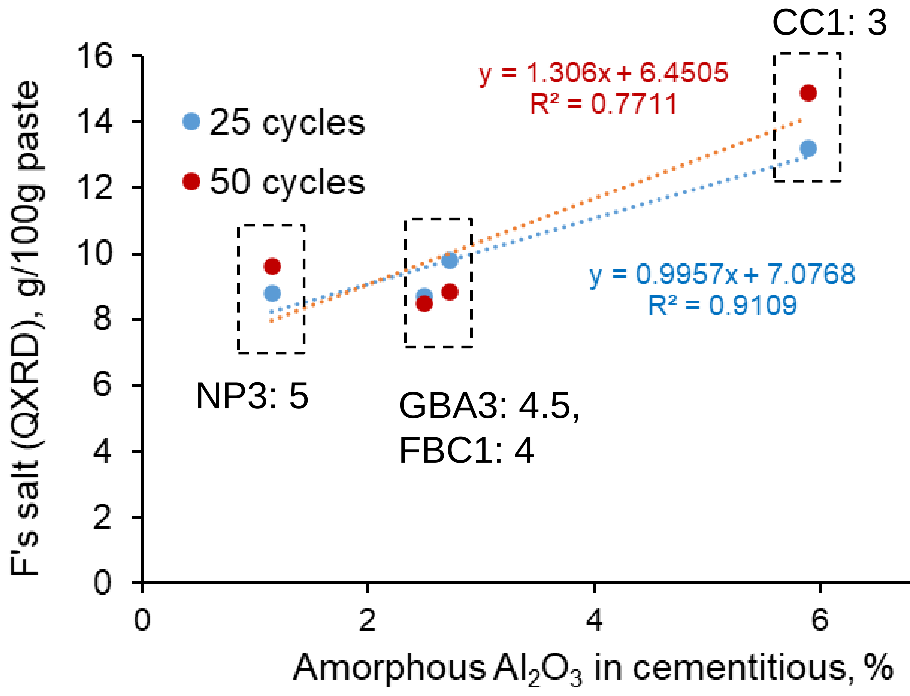






Correlation between scaling test and Friedel's salt amount





- Amorphous Al_2O_3 content in NNPs showed better correlation with ranking in the results of Scaling test (ASTM C672 scaling test temperature regime – up to 50 temperature cycles of -20°C to + 20°C, exposure to 3% wt. $CaCl_2$ solution).

Summary

- Calcined clays blended mixes demonstrated highest amount of Friedel's salt formation.
- For almost all mixes, the least amount of Friedels's salt appeared to be in case of exposure to sodium chloride solution.
- Upon exposure to all chloride solutions, the decrease of CH was observed. In samples submerged in $MgCl_2$ solution, the CH almost disappeared.
- During interaction with chloride solutions, in CC mixed samples, the clay amount was found to be decreased (especially, CC3 mix).
- In samples exposed to $CaCl_2$ solution, the increase of ettringite was observed, whereas the decrease of Afm phases took place.
- Good correlation was determined between amorphous alumina content of the NNPs and amount of Friedel's salt formed in case of $CaCl_2$ and NaCl solutions.
- The samples interacted with $MgCl_2$ showed increase of amorphous phase in all mixes.
- As analysis showed, the amount of formed Friedel's salt upon exposure to $CaCl_2$ solution can be correlated to the Scaling test results.

Acknowledgements

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