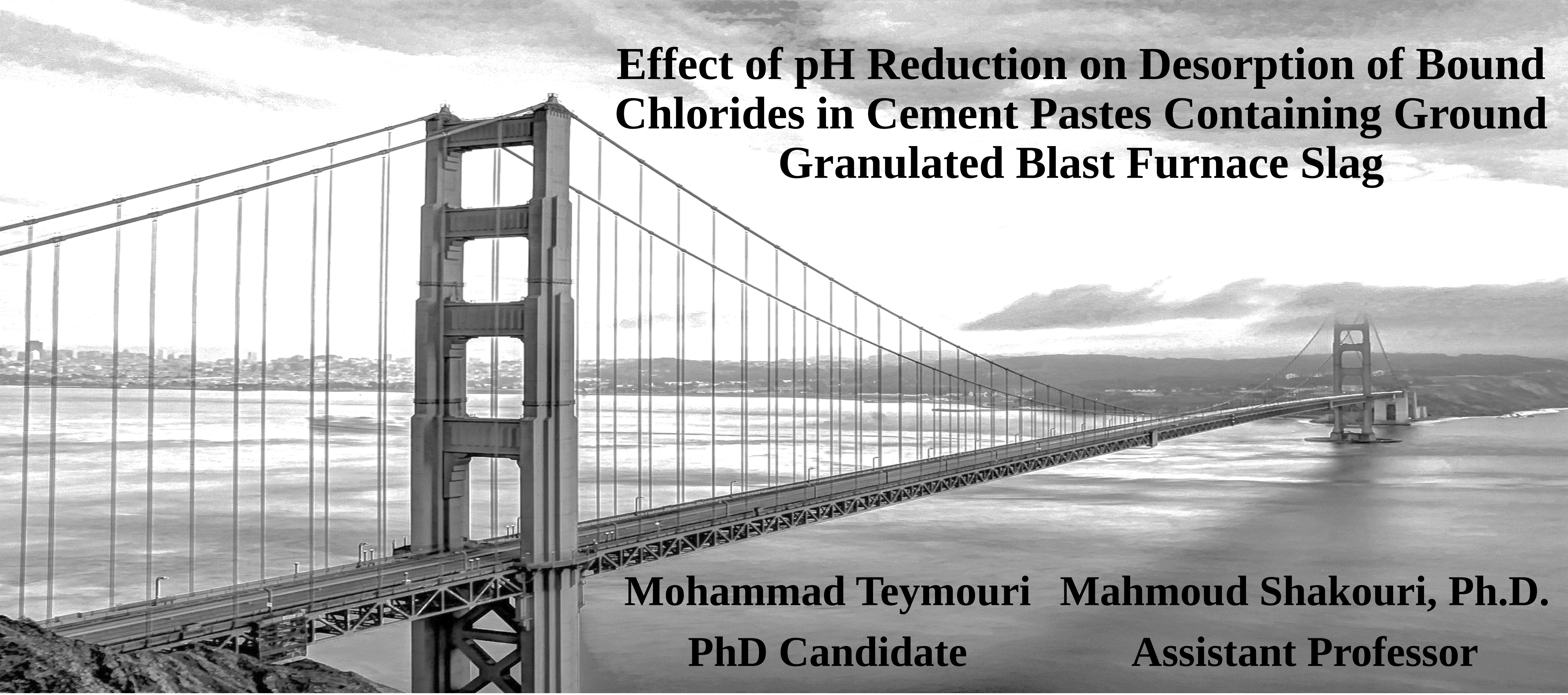

Effect of pH Reduction on Desorption of Bound Chlorides in Cement Pastes Containing Ground Granulated Blast Furnace Slag

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SCA SLAG CEMENT ASSOCIATION

aci CONCRETE CONVENTION

aci Foundation

Acknowledgment

aci Foundation

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Thanks to the Slag Cement Association for the recognition and their generosity in providing me with a travel grant.

Table of Contents

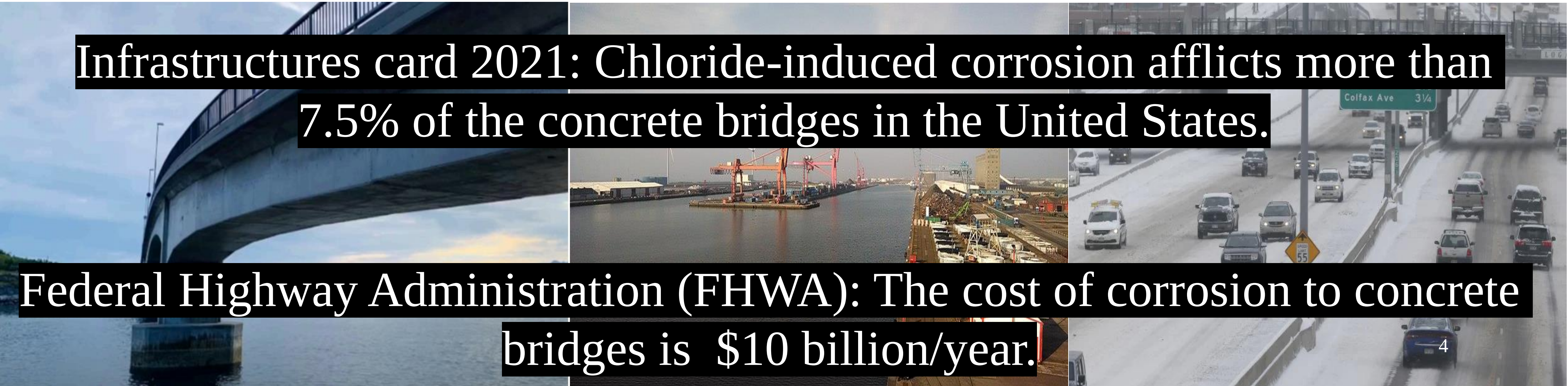
Background

- What is chloride-induced corrosion and why it is important to investigate?

BRIDGES

MARINE STRUCTURES

ROADWAYS

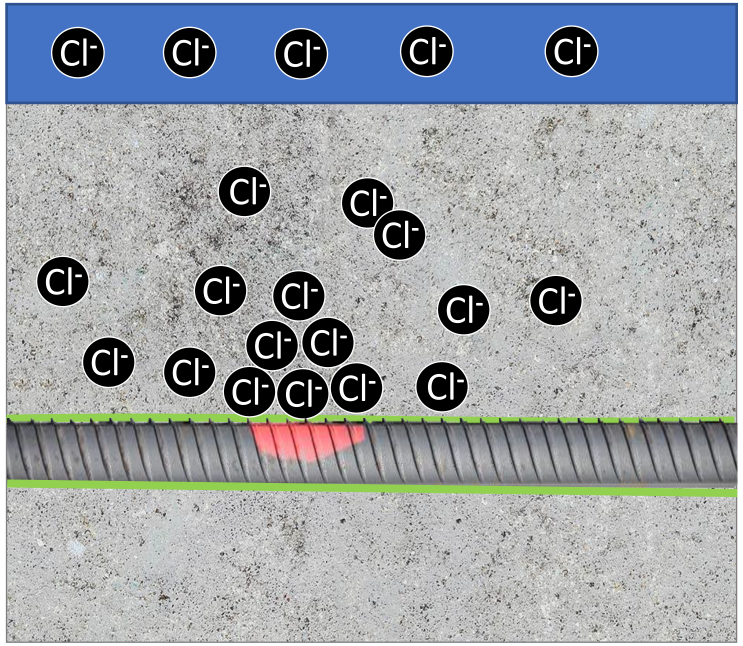


Infrastructures card 2021: Chloride-induced corrosion afflicts more than 7.5% of the concrete bridges in the United States.

Federal Highway Administration (FHWA): The cost of corrosion to concrete bridges is $10 billion/year.

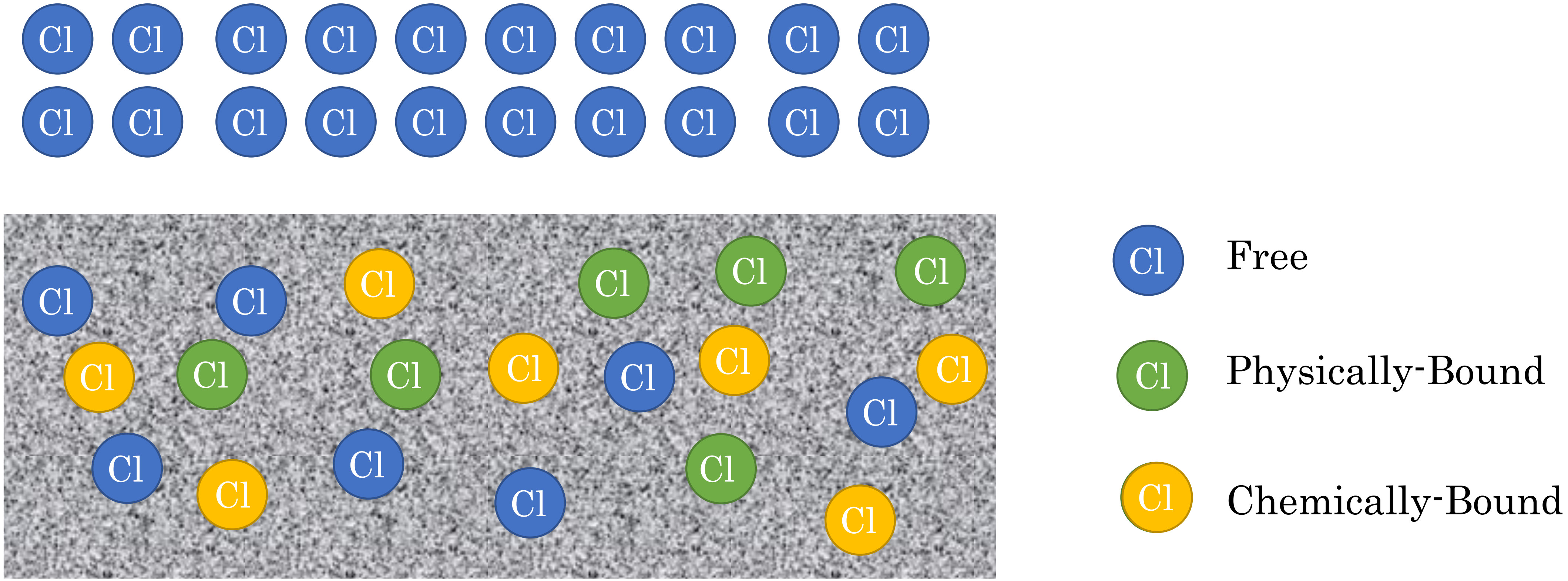
Background

- When a sufficient concentration of chlorides reaches the surface of the embedded reinforcing bars, **chloride-induced corrosion** is initiated.



Chloride Binding

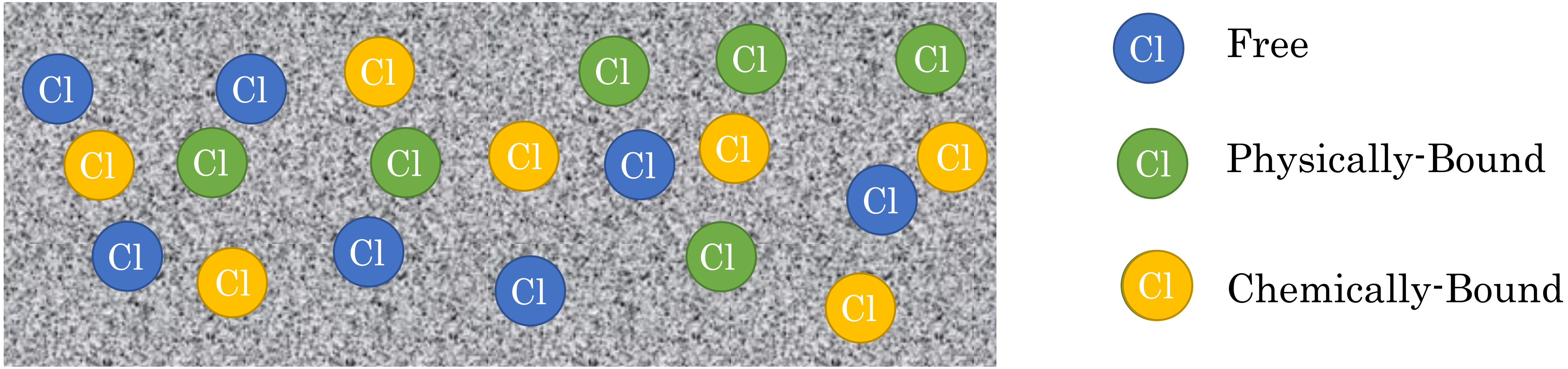
Irrespective of how chlorides enter the concrete, chlorides can exist in concrete in two forms: Free and bound chlorides.



Chloride Binding

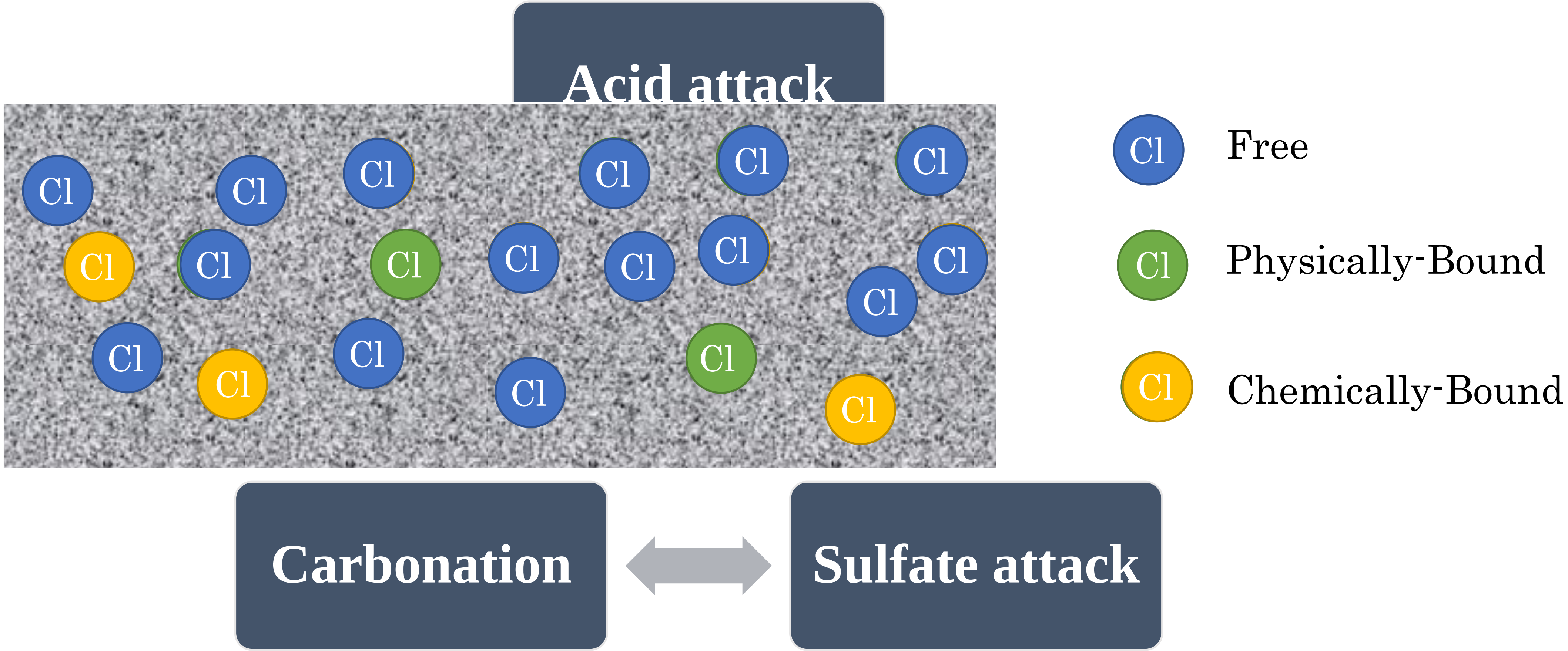
What is chloride binding?

Chlorides ions can be **physically** adsorbed onto the surface of cement hydrates, especially (C–S–H) and can **chemically** bind to form **Friedel's salt (Cl-AFm)** (C3A.CaCl2.10H2O).



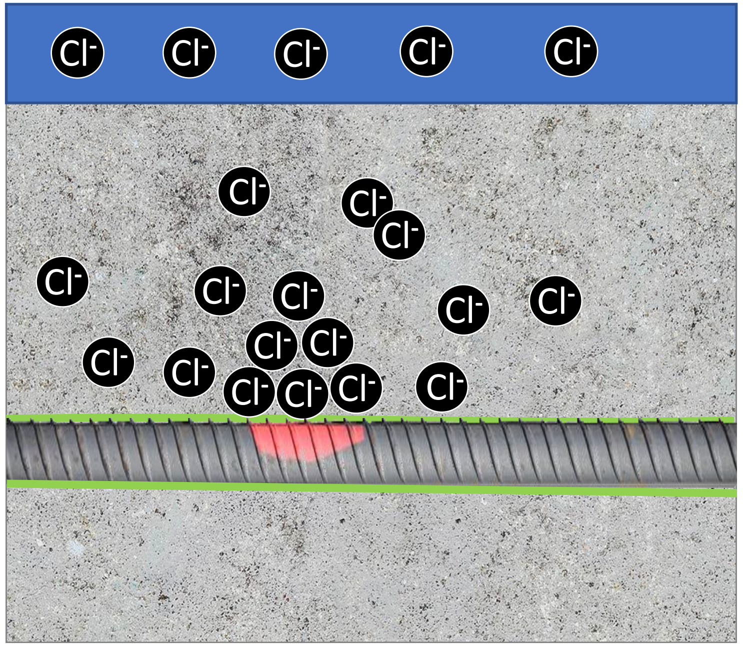
Disassociation of Bound Chloride

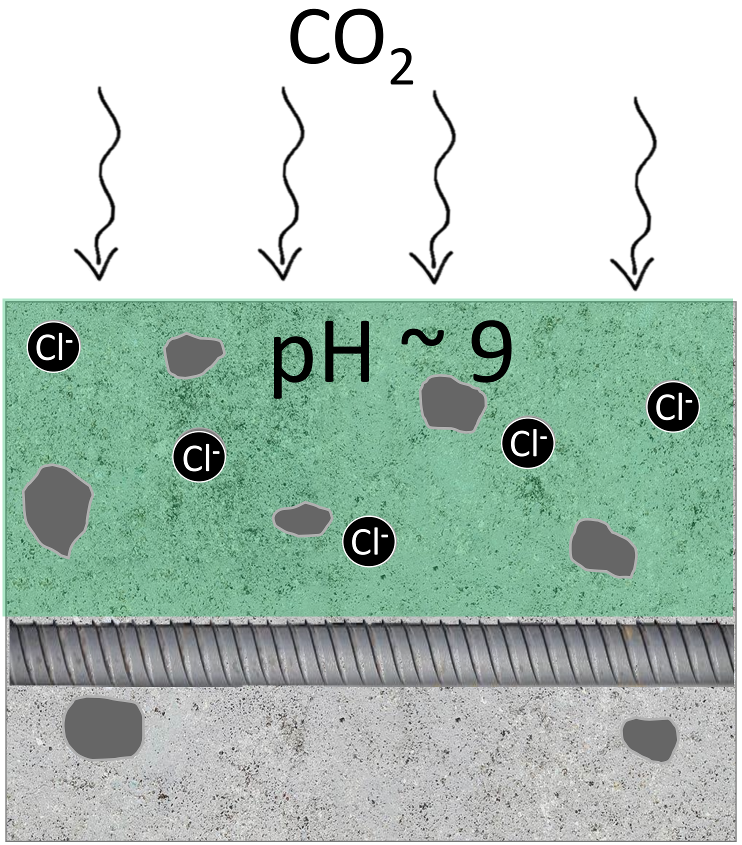
Under certain circumstances (carbonation, sulfate attack, acid attack) and as a result of a drop in the pH of the concrete, bound chlorides can disassociate from the hydration products, leading to an increased risk of corrosion.



Disassociation of Bound Chloride

- What is disassociation of bound chloride (Chloride Desorption)?
- The process by which the chlorides separate from the concrete matrix and become free ions in the pore water within the concrete.





Disassociation of Bound Chloride

- The disassociation of bound chlorides is an unfavorable mechanism because it increases available chloride ion concentration , leading to an increased risk of corrosion.

- We hypothesis that cementitious systems that develop a strong bond with chlorides are more durable in low-pH and release fewer chlorides into the concrete pore solution.

Objectives

1. Investigate the kinetics of chloride desorption mechanisms
2. Assess impacts of pH reduction on chloride disassociation
3. Evaluate the impact of binder salt type on chloride desorption

Methodology: Experimental Design

- Tests
  - Cementitious Materials
    - Type I/II ASTM C150
    - GGBF SASTM C989
  - Salt Solution and Concentration
    - NaCl
    - $CaCl_2$
    - $MgCl_2$
  - Samples Preparation
    - Disk-shaped molds
    - W/C= 0.4
    - 56 days curing
  - Chloride Measurement Tests
    - Chloride binding test
    - Reduction of pH
    - Chloride desorption test
  - Analytical Test
    - XRD
    - TGA
    - pH Monitoring
    - Visual observation

Methodology: Sample Preparation

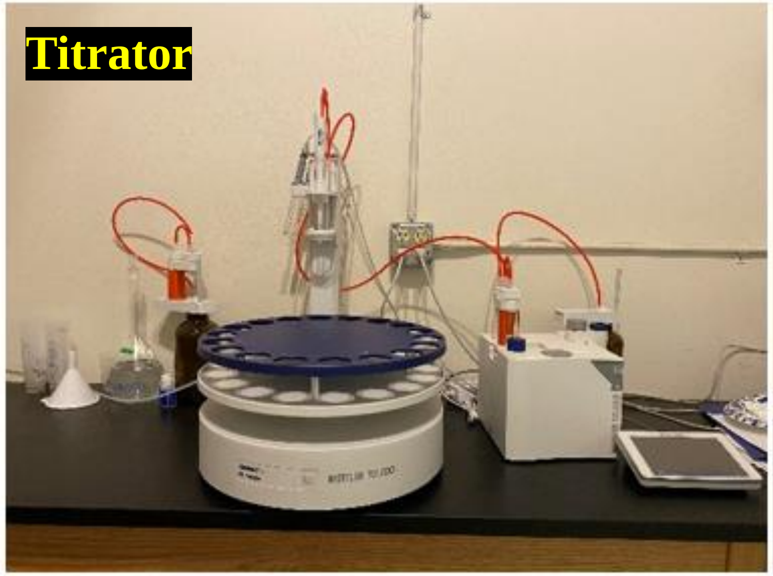
- Materials: Type I/II cement and slag (25% and 50%).
- Curing inside an environmental chamber at 25°C and RH of 95% for 56 d.

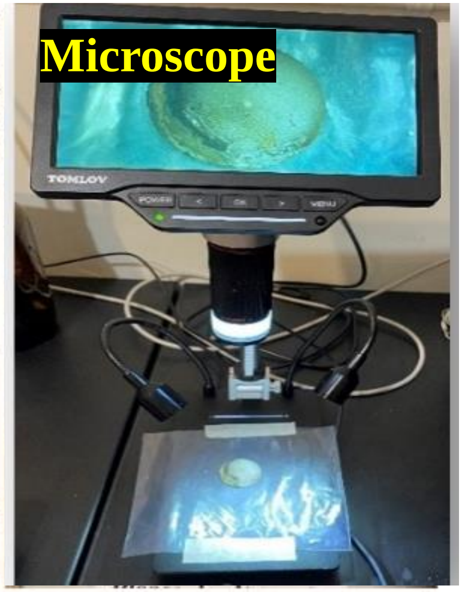
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
OPC	19.24	3.80	2.75	59.05	1.50	2.49	0.17	0.60	9.90
Slag	31.40	15.70	0.40	37.70	8.60	2.50	–	–	0.60

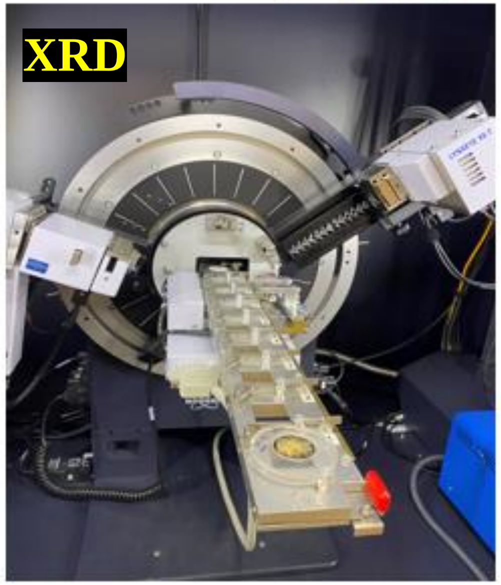
- Reagent-grade solids: NaCl, $CaCl_2$, and $MgCl_2$. Exposure solutions at six concentrations. 0.1, 0.3, 0.5, 0.7, 1, and 2 mol/L.
- Nitric acid

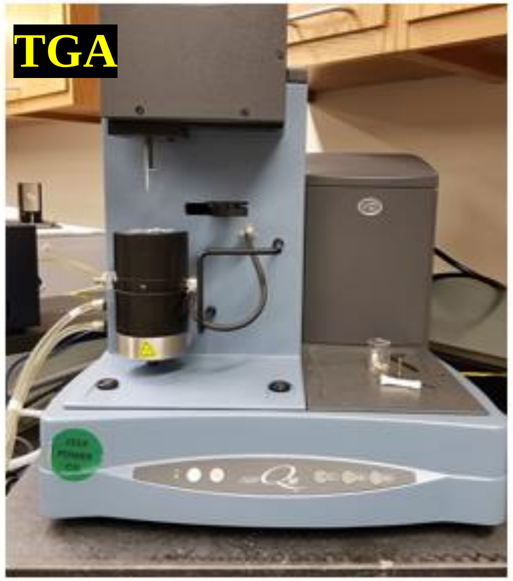
(1 M acid solutions was used to reduce pH)

Methodology: Equipment









Methodology: Chloride Binding

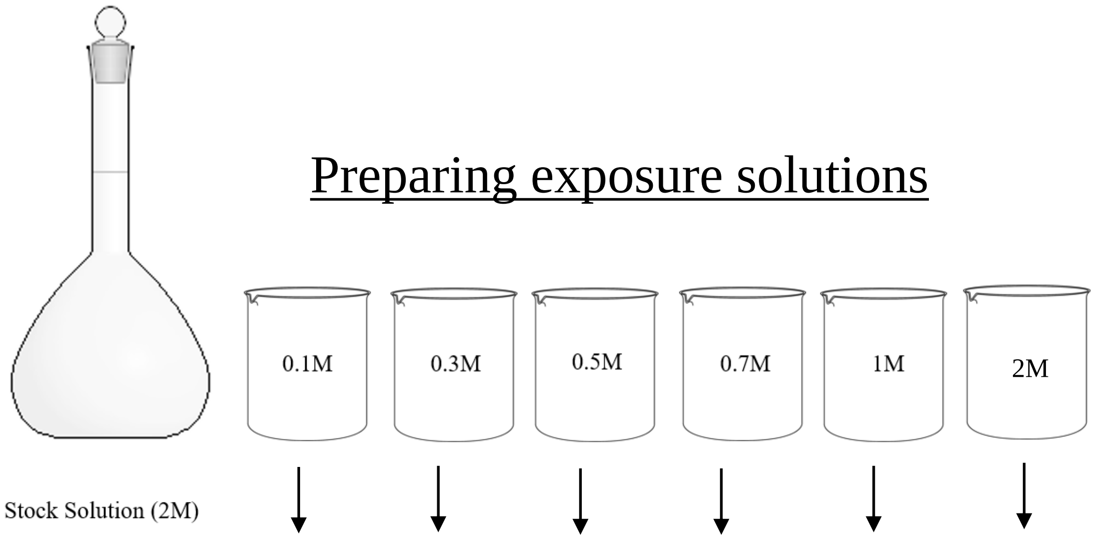
Salt Type

NaCl

$CaCl_2$

$MgCl_2$

Preparing exposure solutions



Chloride binding

14 days exposure
X2 replicates

Titration

Result

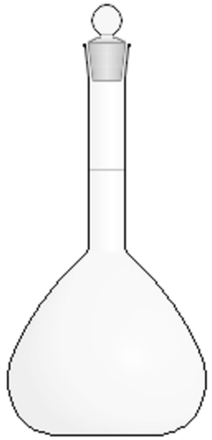
C_i (mol/l)

C_f (mol/l)

Bound Chlorides = (mg Cl/ g paste)

$$\frac{\left[C_i - C_f\right] \times V \times 35.45}{m_{paste}}$$

Methodology: Chloride Desorption



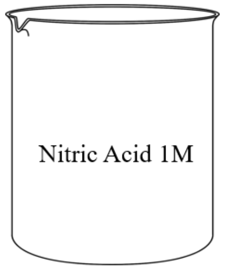
Stock Solution (2M)

<u>Chloride Binding</u>

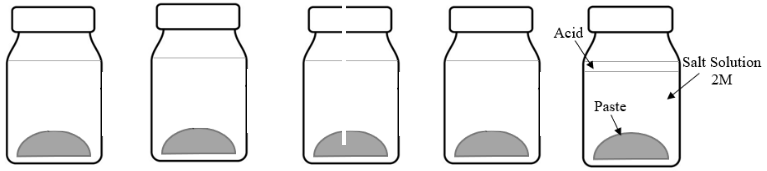
<u>Two weeks exposure to salt solution</u>

↓ ↓ ↓ ↓ ↓

<u>Chloride Desorption</u>



Acid



+5 ml HNO_3	+10 ml HNO_3	+15 ml HNO_3	+20 ml HNO_3	+25 ml HNO_3

<u>Two weeks exposure to acid + salt solution</u>

<u>pH Measurement</u>

<u>Titration</u>

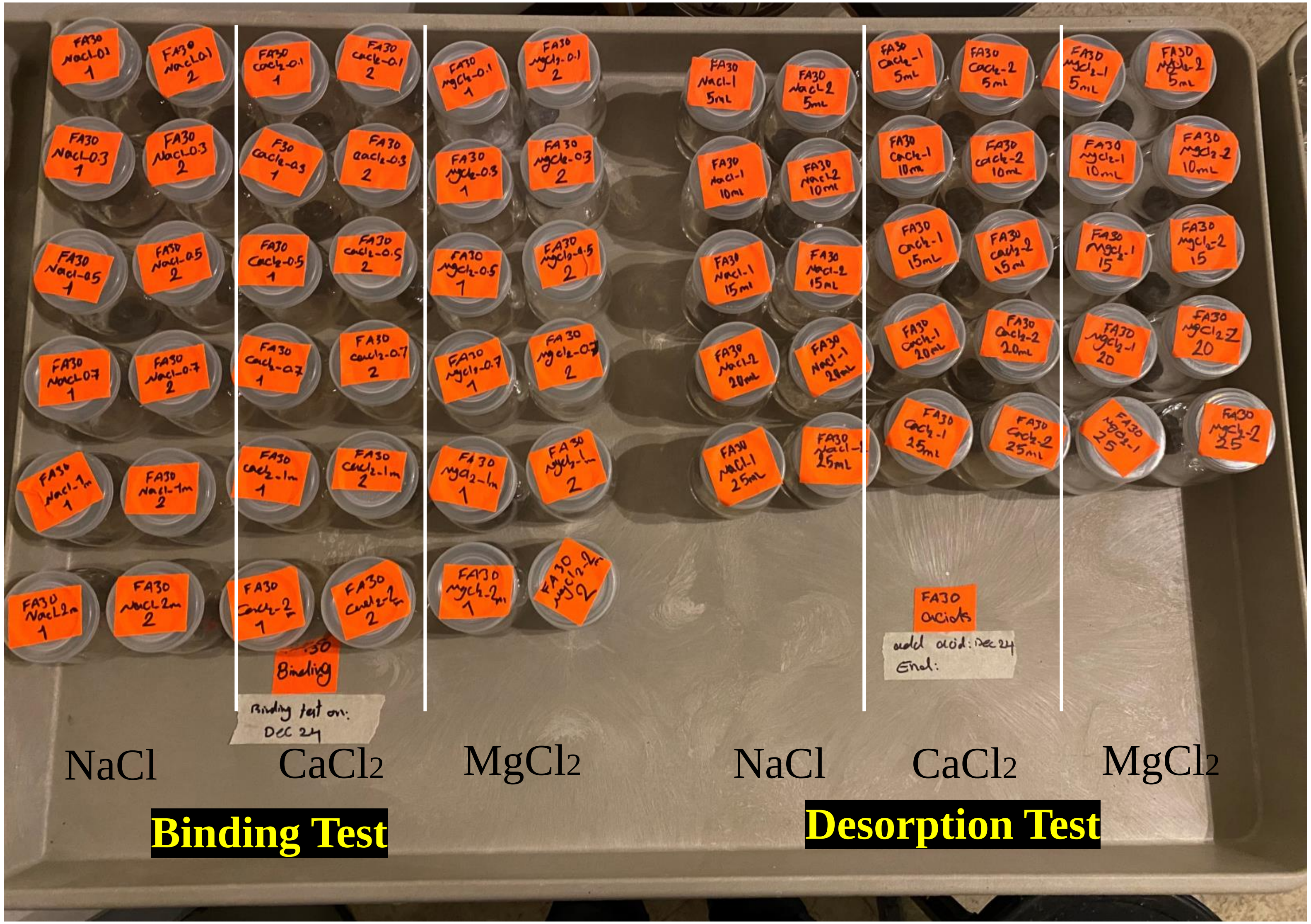
<u>Result</u>

C_f (mol/l)

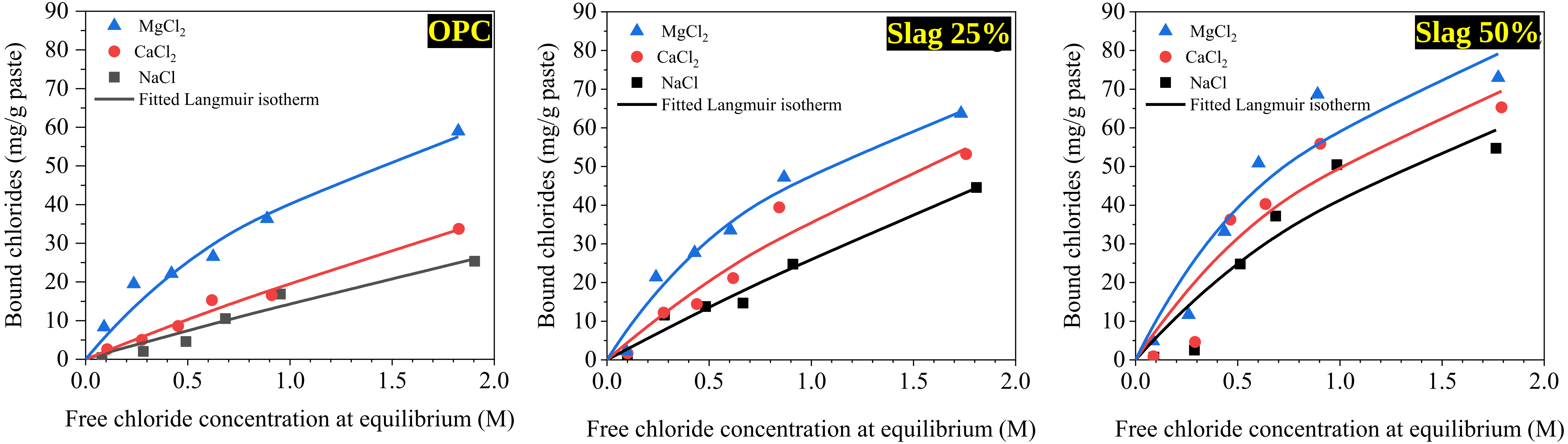
C_d (mol/l)

$$Cl_{b\ released} = \frac{(c_d - c_f) \times V_f \times 34.45}{m_{dry}}$$

Methodology: Chloride Desorption



Results: Chloride Binding



Results: Chloride Binding

- Which solutions had the lowest and highest chloride binding capacity?

$MgCl_2$ showed higher binding, in the decreasing order of $MgCl_2 > CaCl_2 > NaCl$.

- pH of brine solution (NaCl has pH of >12) which impacts the solubility of Friedel's salt (chemical chloride binding) formation compared to $CaCl_2$ and $MgCl_2$.

- Ca in $CaCl_2$ increase Ca/Si ratio in C-S-H, enhancing binding of chloride.

- Exposure to $MgCl_2$ resulted in formation of M-S-H, increasing porosity of the pastes.

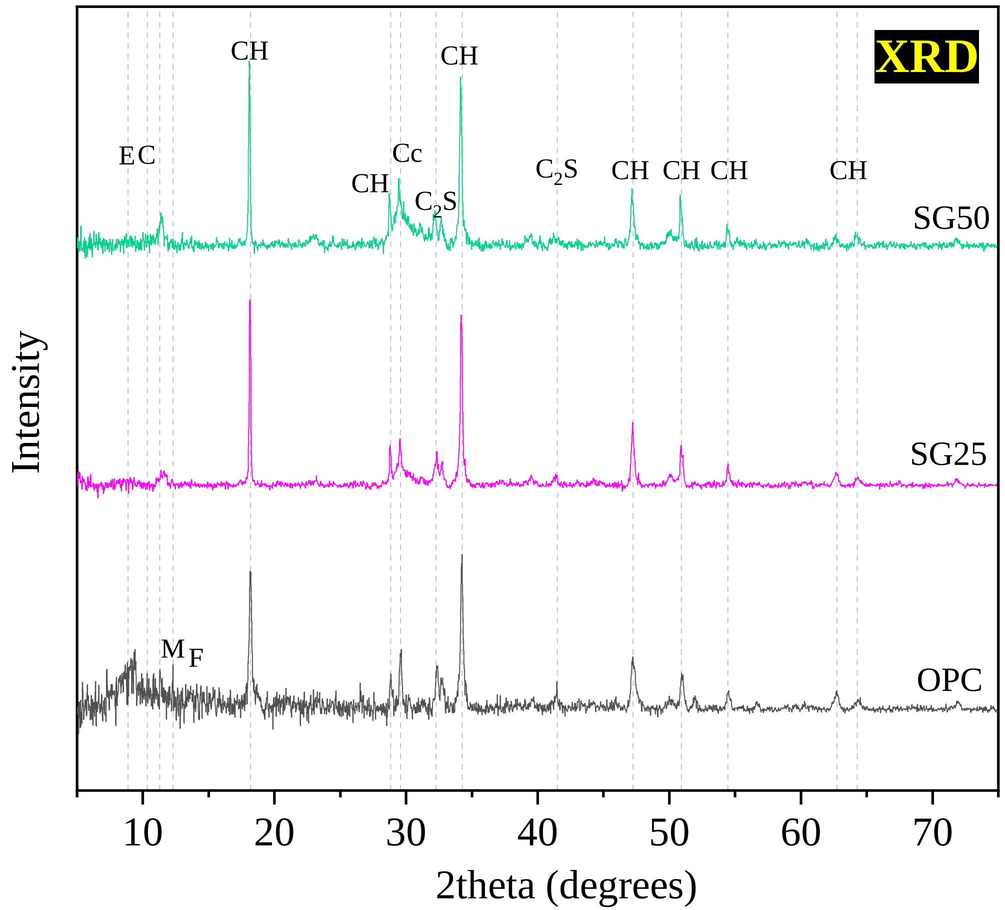
Results: Chloride Binding

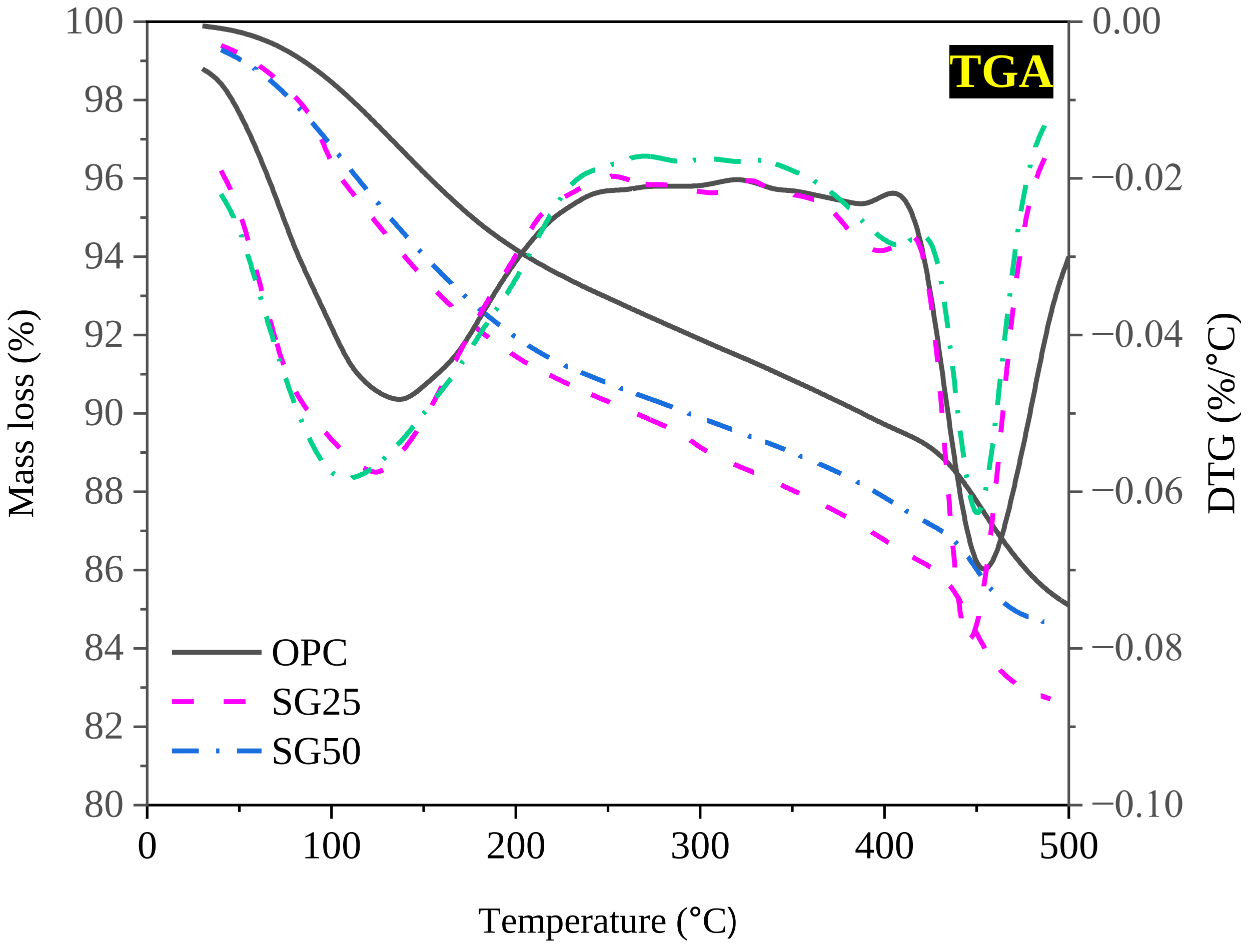
- Which pastes had the lowest and highest chloride binding capacity?

Slag is most favorable, in the decreasing order of slag50% > slag25% > OPC.

i) The formation of more C-S-H
ii) Presence of higher Al_2O_3 leading to formation of higher Afm.
iii) The formation of higher Friedel's salt.

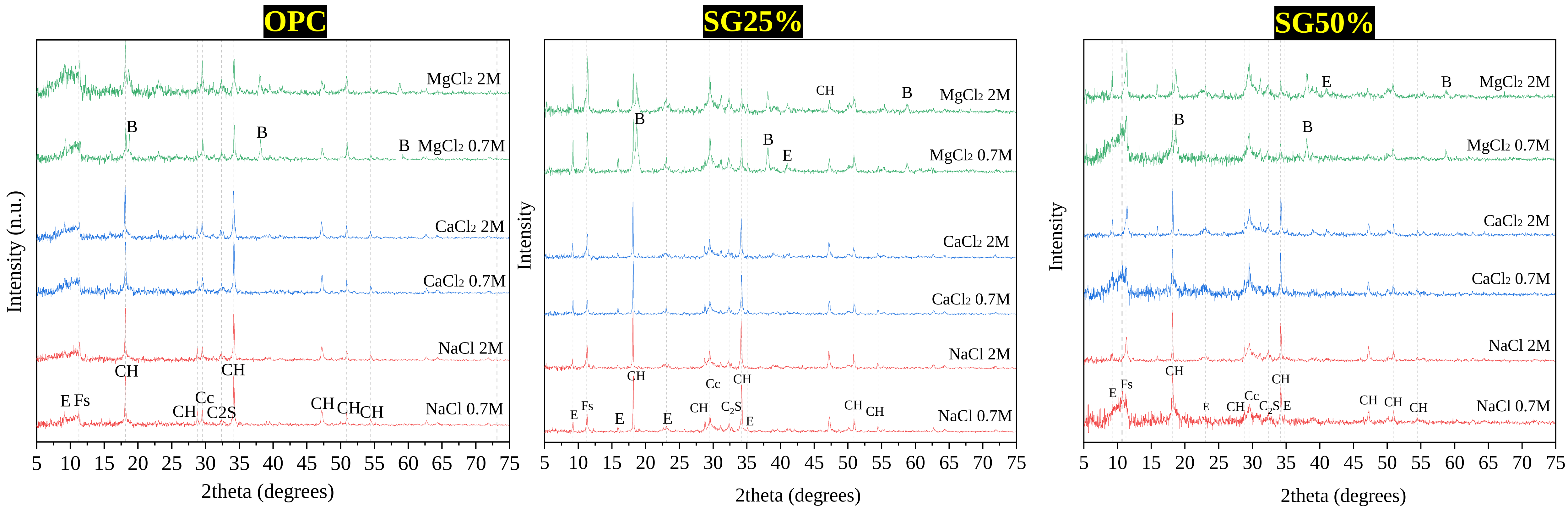
Results: Phase Composition Before Exposure



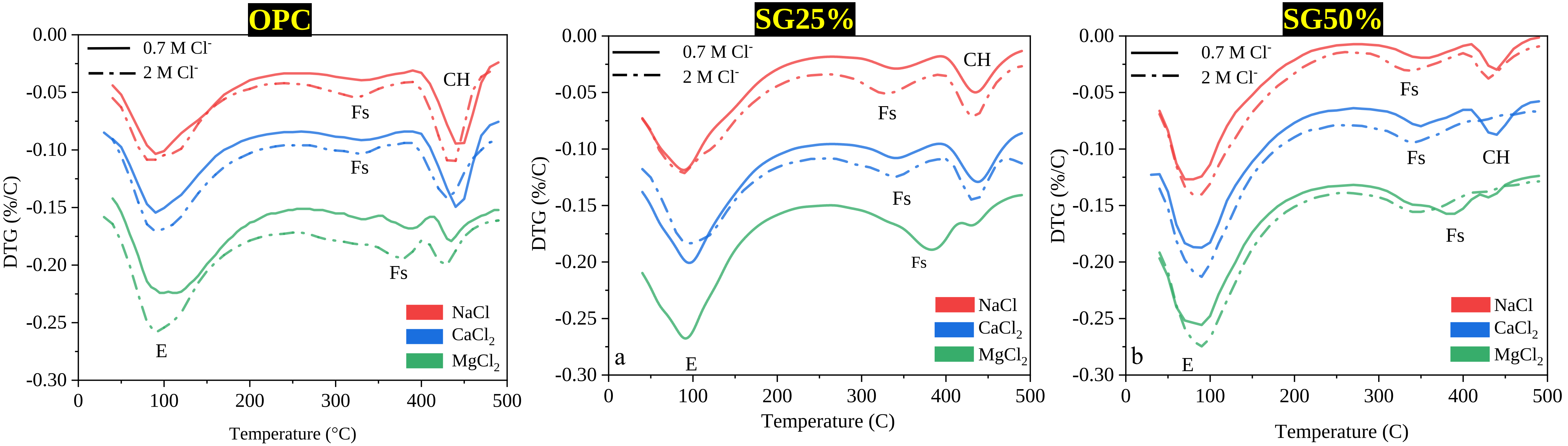


The XRD patterns of hydrated pastes. (b) Mass loss and DTG curves of hydrated pastes (E: Ettringite, C: C4AF, M: Monocarbonate, F: Ferrite, CH: portlandite, Cc: Calcite, C2S: Belite).

Results: Phase Composition After Exposure to Brine Solutions



Results: Phase Composition After Exposure to Brine Solutions



Results: Phase Composition After Exposure to Brine Solutions

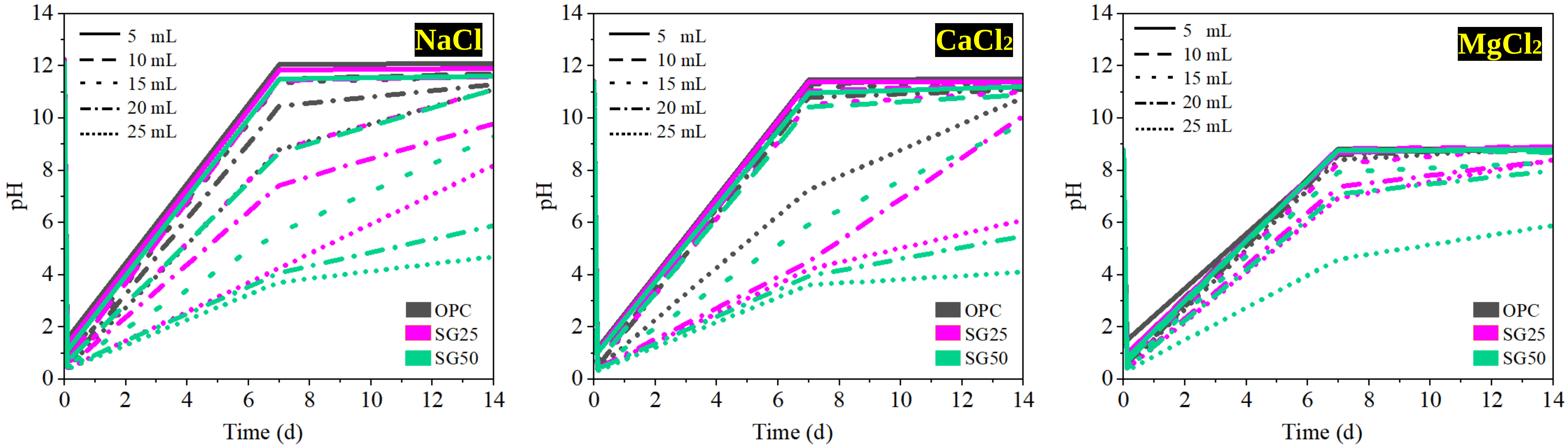
- The mass fraction of Friedel's salt in paste samples:

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

m_{Fs} is the mass fraction of Friedel's salt
m_{H_2O} is the mass loss (wt. %) of the main layer of water obtained from the TGA test,
M_{FS} molar mass of Friedel's salt (561.3 g/mol)
M_{H_2O} molar mass of water (18.02 g/mol)

Paste system	Salt type	Cl^- concentration (M)	Temperature Range (°C)	m_{H2O} (%)	m_{Fs} (%)
OPC	NaCl	0.7	270-390	0.56	3.04
		2	240-390	0.8	4.14
	$CaCl_2$	0.7	270-380	0.6	3.1
		2	270-380	0.66	3.41
	$MgCl_2$	0.7	355-410	0.84	4.39
		2	340-400	1.6	5.89
SG25	NaCl	0.7	270-390	0.77	4.01
		2	260-390	0.97	5.04
	$CaCl_2$	0.7	270-390	0.77	4.01
		2	260-400	0.9	4.69
	$MgCl_2$	0.7	350-410	1.71	8.88
		2	-	-	-
SG50	NaCl	0.7	280-410	0.67	3.49
		2	260-400	1.28	6.63
	$CaCl_2$	0.7	270-400	0.81	4.23
		2	250-410	1.13	5.88
	$MgCl_2$	0.7	330-410	1.39	7.21
		2	260-410	2.48	12.89

Results: Evolution of pH after adding different volumes of acid

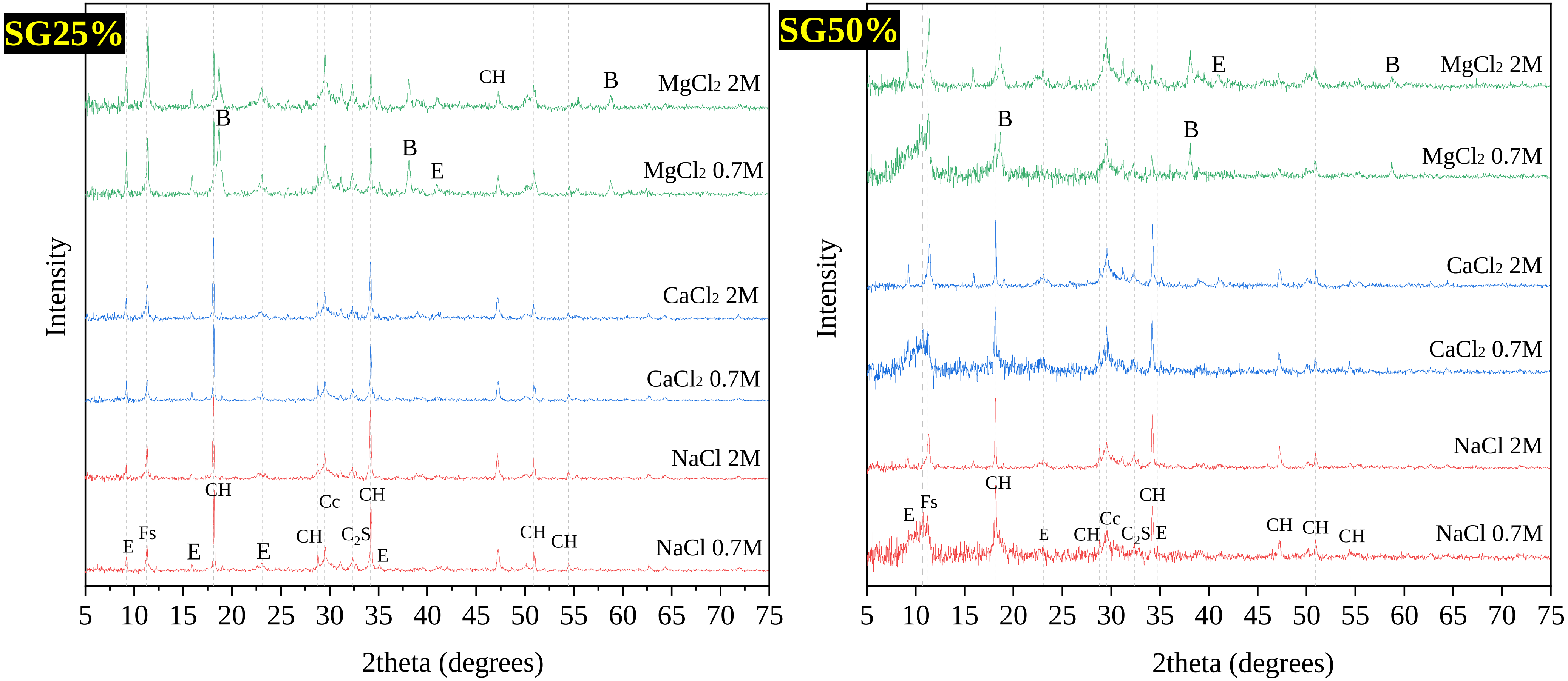


For a fully carbonated concrete, the pH range is around 9.

Lower than that barley can be found in the real case scenarios!

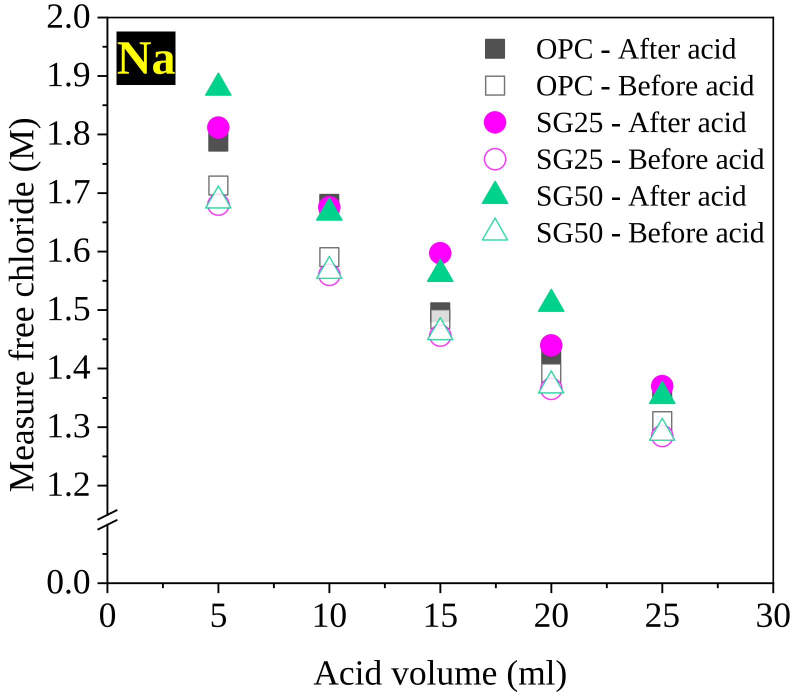
Results: XRD & TGA (Before Exposure to Salt Solutions)

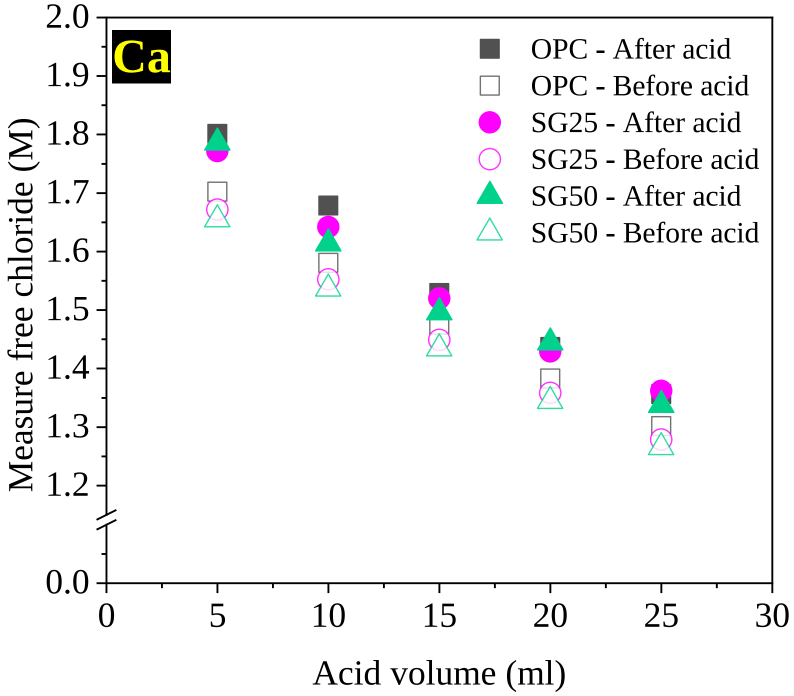
- The incorporation of **slag** resulted in the highest amount of Friedel's salt among the all binders.

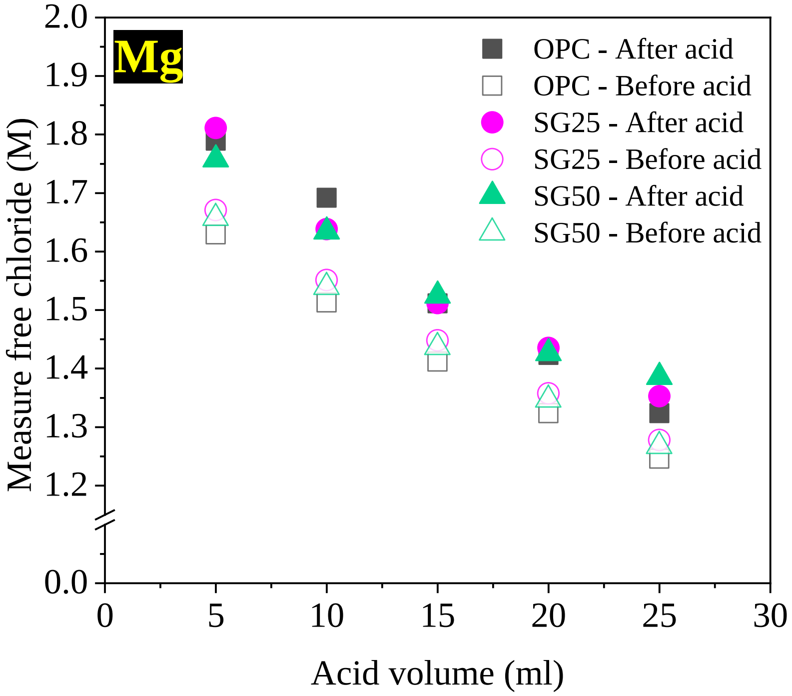


Results: Chloride Desorption

- The amount of measured free chloride after pH reduction increased compared to the samples without acid, regardless of binder and cation types.







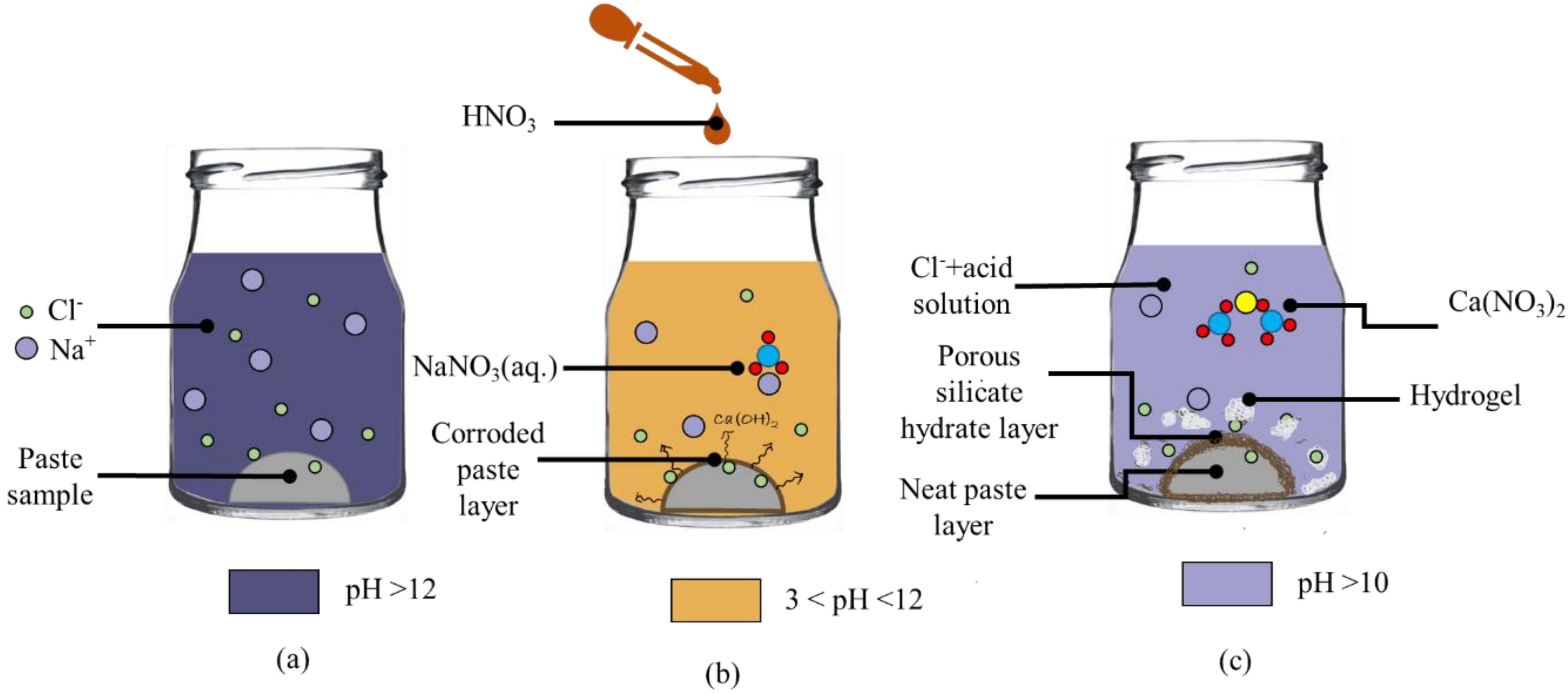
Results: Chloride Desorption

Percentage of released bound chloride: The bound chloride content **before** acid addition was compared to those measured **after** adding acid.

	$NaCl$	$CaCl_2$	$MgCl_2$
OPC	90%	92%	86%
Slag	90%	72%	58%

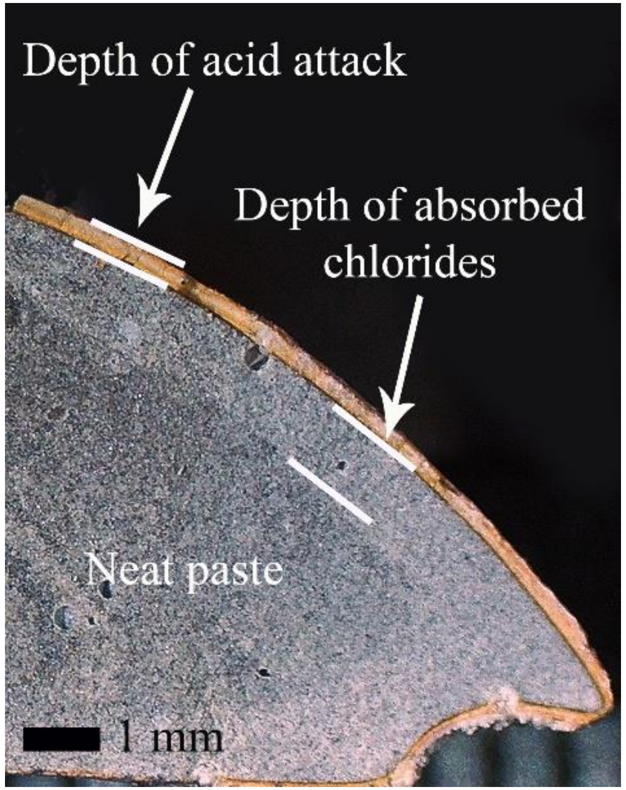
Release of bound chloride at pH=9

Results: Visual Inspection



Results: influence of GGBFS on pH, chloride binding, and desorption

	pH	Total bound chloride	Released bound chloride (at 5 ml and 10 ml)
SG25 compared to OPC	↓	↑	↓
SG50 compared to OPC	↓	↑	↓



Conclusion

- Chloride desorption phenomenon should be considered in the service life modelling of concrete structure.

- Incorporation of slag inhibited chloride desorption and led to the retention of more bound chlorides when the pH decreased.

- Increased slag replacement levels reduced the released bound chloride percentage, particularly in $MgCl_2$ and $CaCl_2$ solutions compared to OPC.

- The chloride desorption in blended pastes was influenced by the cation in the order

Mg > Ca > Na.

Limitation of Study

- Using pure salt solutions
- Using dried paste samples

Ongoing Work

- Commercial brine solutions
- Wet–dry or freeze-thaw cycles
- Incorporating corrosion inhibitors

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Thanks For Listening!

Questions?

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Paper 1

Paper 2