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

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

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.
- When a sufficient concentration of chlorides reaches the surface of the embedded reinforcing bars, **chloride-induced corrosion** is initiated.
Irrespective of how chlorides enter the concrete, chlorides can exist in concrete in two forms: Free and bound chlorides.
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).
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.
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.
The disassociation of bound chlorides is an **unfavorable mechanism** because it increases available chloride ion concentration, leading to an increased risk of corrosion.

We hypothesize 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

- Cementitious Materials
  - Type I/II ASTM C150
  - GGBF SASTM C989
- Salt Solution and Concentration
  - NaCl
  - CaCl₂
  - MgCl₂
- 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.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>LOI</th>
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<td>OPC</td>
<td>19.24</td>
<td>3.80</td>
<td>2.75</td>
<td>59.05</td>
<td>1.50</td>
<td>2.49</td>
<td>0.17</td>
<td>0.60</td>
<td>9.90</td>
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<tr>
<td>Slag</td>
<td>31.40</td>
<td>15.70</td>
<td>0.40</td>
<td>37.70</td>
<td>8.60</td>
<td>2.50</td>
<td>–</td>
<td>–</td>
<td>0.60</td>
</tr>
</tbody>
</table>

- Reagent-grade solids: NaCl, CaCl₂, and MgCl₂. 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

- Titrator
- pH Meter
- Environmental Chamber
- Vacuum Oven
- Microscope
- XRD
- TGA

Pastes
Methodology: Chloride Binding

Salt Type
NaCl
CaCl₂
MgCl₂

Preparing exposure solutions

Stock Solution (2M)

0.1M 0.3M 0.5M 0.7M 1M 2M

Chloride binding

14 days exposure
X2 replicates

Bound Chlorides = \[
\frac{[C_i - C_f] \times V \times 35.45}{m_{paste}}
\]

(mg Cl/ g paste)

Titration

Result

C_i (mol/l)

C_f (mol/l)
Methodology: Chloride Desorption

Chloride Binding

Two weeks exposure to salt solution

Chloride Desorption

Two weeks exposure to acid + salt solution

\[ C_l_{released} = \left( c_d - c_f \right) \times V_f \times 34.45 \]

\[ m_{dry} \]

Papers

- 

- Chloride Binding

- pH Measurement

- Titration

- Result

\[ C_f \text{ (mol/l)} \]

\[ C_d \text{ (mol/l)} \]
Two weeks exposure to salt solution

Two weeks exposure to acid + salt solution

+5 ml HNO₃

+10 ml HNO₃

+15 ml HNO₃

+20 ml HNO₃

+25 ml HNO₃

Chloride Binding

Chloride Desorption

Methodology: Chloride Desorption

NaCl

CaCl₂

MgCl₂

NaCl

CaCl₂

MgCl₂

Binding Test

Desorption Test
Results: Chloride Binding

- **Bound chlorides (mg/g paste)**
- **Free chloride concentration at equilibrium (M)**

[Graphs showing fitted Langmuir isotherm for different types of cement (OPC, Slag 25%, Slag 50%) with data points for MgCl₂, CaCl₂, and NaCl.]
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.
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 Al2O3 leading to formation of higher Afm.
iii) The formation of higher Friedel's salt.
Results: Phase Composition After Exposure to Brine Solutions

Intensity (n.u.)

2theta (degrees)

Intensity

2theta (degrees)

Intensity

2theta (degrees)
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)

<table>
<thead>
<tr>
<th>Paste system</th>
<th>Salt type</th>
<th>Cl(^{-}) concentration (M)</th>
<th>Temperature Range (℃)</th>
<th>( m_{H_2O} ) (%)</th>
<th>( m_{Fs} ) (%)</th>
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<tbody>
<tr>
<td>OPC</td>
<td>NaCl</td>
<td>0.7</td>
<td>270-390</td>
<td>0.56</td>
<td>3.04</td>
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<td>340-400</td>
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<td>5.89</td>
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<td>260-390</td>
<td>0.97</td>
<td>5.04</td>
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<tr>
<td>CaCl(_2)</td>
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<td>MgCl(_2)</td>
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<td>8.88</td>
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<td>260-400</td>
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<td>6.63</td>
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<tr>
<td>CaCl(_2)</td>
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<td>5.88</td>
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<td>MgCl(_2)</td>
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<td>2</td>
<td>260-410</td>
<td>2.48</td>
<td>12.89</td>
</tr>
</tbody>
</table>
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!
The incorporation of **slag** resulted in the highest amount of **Friedel’s salt** among the all binders.

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

<table>
<thead>
<tr>
<th></th>
<th>NaCl</th>
<th>CaCl$_2$</th>
<th>MgCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>90%</td>
<td>92%</td>
<td>86%</td>
</tr>
<tr>
<td>Slag</td>
<td>90%</td>
<td>72%</td>
<td>58%</td>
</tr>
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</table>

Release of bound chloride at pH=9
Results: Visual Inspection

(a) pH > 12

(b) 3 < pH < 12

(c) pH > 10
Results: influence of GGBFS on pH, chloride binding, and desorption

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Total bound chloride</th>
<th>Released bound chloride (at 5 ml and 10 ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG25 compared to OPC</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td>SG50 compared to OPC</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
</tr>
</tbody>
</table>
- 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 MgCl₂ and CaCl₂ 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


Thanks For Listening!

Questions?
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Paper 1

Paper 2