Applications of the X-Ray Fluorescence Spectroscopy (XRF) on Chloride Binding Isotherms

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Research Questions:

• How does the x-ray fluorescence spectroscopy (XRF) measure chloride concentration for chloride binding isotherms?

• How does the XRF method compare to the Titration method for this analysis?
Introduction

Objectives:

• To develop a protocol to accurately analyze chloride in solutions for chloride binding isotherms using the XRF
Introduction

The Basics of XRF:

• Non-destructive analytical technique that determines the chemical composition of any material
Introduction

The Basics of XRF:

• Excites the material with a primary x-ray source
• Measures the emitted fluorescent or secondary x-ray and its intensity

Image taken from www.projects.library.villanova.edu
Introduction

Chloride Binding

• Environmental exposure of concrete to salts
• 2 types of chlorides in concrete:
  • Free: chloride ions in solution
  • Bound: chloride ions that react with mineral phases in cement paste
    • Calcium oxychloride

\[ 3\text{Ca(OH)}_2 + \text{CaCl}_2 + 12\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O} \]
Introduction

Chloride Binding

Calcium Hydroxide (Portlandite) from cement matrix

\[ 3\text{Ca(OH)}_2 + \text{CaCl}_2 + 12\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O} \]

Image taken from www.explorecivil.net
Introduction

Chloride Binding

Calcium Chloride from deicing salts

\[3\text{Ca(OH)}_2 \rightarrow \text{CaCl}_2 + 12\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}\]
Introduction

Chloride Binding

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Introduction

Chloride Binding

• Importance:
  • Damage in concrete due to the formation of calcium oxychloride
XRF for Chloride Binding Solutions:

- Sample Preparation of Solutions (Cody)
- Titration analysis of chloride concentration (Cody)
- Calibration of XRF (Marisol)
- Sample Preparation of Solutions for XRF (Marisol)
- XRF analysis of chloride concentration (Marisol)
Methodology

XRF for Chloride Binding Solutions:

Sample Preparation of Solutions:

• Mix 4 g of powdered cement paste with 10 mL of CaCl₂ solution
• 14 cement mixtures
• CaCl₂ at 18 different concentrations
• Three temperatures: 5°C, 23°C, 38°C
• Cement exposure to CaCl₂ solution for 6 weeks
Methodology

XRF for Chloride Binding Solutions:

Sample Preparation of Solutions:

- Top solution extracted
- Measure the chloride concentration of extracted solution with titration and with XRF
Methodology

XRF for Chloride Binding Solutions:

- **Sample Preparation for XRF**
  - Solution sample preparation with Mylar film
  - Time of preparation: 5 minutes

- **Calibration**
  - Calcium chloride (>99% purity) known solutions at different concentrations

- **Analysis**
  - Time of analysis: 3 minutes
Methodology

XRF for Chloride Binding Solutions:

- Analysis of bound chlorides versus calcium chloride initial concentration
- Bound chloride = difference between initial concentration of CaCl₂ and free chlorides in solution tested

**Figure 1:** Difference between isotherms due to the formation of calcium oxychloride

Figure taken from “Effects of temperature on the chloride binding of Portland cement pastes exposed to CaCl₂ Solutions” by Wei, Tao and Weiss
Results

XRF for Chloride Binding:

![Chloride Binding Isotherm for Mixture 1 at 5°C](image)

**Figure 2:** Chloride concentration results from the titration versus the XRF method
Results

XRF for Chloride Binding:

<table>
<thead>
<tr>
<th>Initial CaCl₂ Concentration</th>
<th>Chloride Concentration</th>
<th>% Difference</th>
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<tr>
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</tr>
<tr>
<td>12.5</td>
<td>0.291</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Results

XRF versus Titration:

\[
y = 1.0572x \quad R^2 = 0.99837
\]

**Figure 3:** Chloride concentration results from the titration versus the XRF method
Conclusion

Solutions for Chloride Binding:

• XRF can be used to produce chloride binding isotherms
• There is a good 1:1 linear correlation between both methods’ results (titration and XRF)

Advantages of XRF:

• Less time testing for chloride concentration
• Can detect other elements (Na, K, etc)
Acknowledgements

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Questions?