Micro-spectroscopic investigations of the Al and S speciation in hardened cement paste

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Layout

- Introduction
- Materials and methods
- Al and S speciation in cementitious materials
  - Al speciation
    - References
    - Micro-spectroscopic studies
  - S speciation
    - References
    - Micro-spectroscopic studies
- Conclusions
Background

**Waste package (cement & steel)**

**Cement** – important component of the engineered barrier system of the repositories for low- (L/ILW) and intermediate-level wastes (ILW)

Hardened cement paste: ~ 20 wt%
Example: Ni uptake by cement

- Combination of BSE (SEM) with µ-XRF/XAS
- Information on the morphology and the chemical composition of phases on the same spot

BSE-image

Ni spot

Portlandite

Inner CSH

Outer CSH

Belite

µ-XRF/LUCIA

Si

µ-XRF/ALS

Ni, Ca

µ-XRF/LUCIA

Al

Example: Ni uptake by cement

Combination of BSE (SEM) with µ-XRF/XAS

Information on the morphology and the chemical composition of phases on the same spot

BSE-image

Ni spot

Portlandite

Inner CSH

Outer CSH

Belite

µ-XRF/LUCIA

Si

µ-XRF/ALS

Ni, Ca

µ-XRF/LUCIA

Al
Motivation

- X-ray absorption fine structure (XAFS) spectroscopy as complementary tool to XRD for cement phase characterization?

- In situ identification of single cement phases with micro-scale resolution in hardened cement paste?

- Identification of uptake-controlling cement phase in connection with metal cation and anion binding in hardened cement paste?
**Hardened Cement Paste (HCP)**

**Sulphate-resisting cement: CEM I 52.5 N HTS**

**Clinker phases in non hydrated cement wt%:**
- **Alite**: $3\text{CaO} \cdot \text{SiO}_2$ 61
- **Belite**: $2\text{CaO} \cdot \text{SiO}_2$ 18
- **Aluminate**: $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ 3.9
- **Ferrite**: $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ 5.8
- **Calcite**: $\text{CaCO}_3$ 3.7
- **Gypsum, Anhydrite**: $\text{CaSO}_4$ 3.6
- **Others**: ≤ 4

**Hydration products in wt% (w/c = 0.4; 1 y hydration):**
- **Calcium silicate hydrate** (C-S-H) ~49
- **Portlandite** ~20
- **Calcium aluminates** (AFt, AFm) ~19
- **Hydrotalcite** ~2
- **CaCO$_3$** ~2
- **Minor phases** (Fe, Mn oxides) <1
- **Non-hydrated clinker minerals** ~8

*Lothenbach & Wieland 2006*
Materials

- **References**
  - S: Gypsum CaSO₄
  - Al: Aluminate C₃A
  - Al: Ferrite C₄AF
  - Al/S: Ettringite, Fe-Ettringite
  - Al/S: AFm (C₄AH₁₃), Monosulfate, Monocarbonate
  - Al: Hydrogarnet, Si-Hydrogarnet
  - Al: Hydrotalcite

- **Cement**
  - CEM I 52.5 N **HTS** (Lafarge, France)

- **Hardened cement pastes (HCP)**
  - HTS cement hydrated at 5°, 20°, and 50° for 28 days
Sample Preparation for Micro and Bulk XAS Studies

**Cement**

1. Hydration
2. 5°/20°/50°
3. Dry, impregnate, cut, polish

**Thin sections of HCP**

- \( \mu \)-XRF/XAS @ Lucia/SLS
  - Beamsize: \( \sim 5 \times 5 \ \mu m^2 \)

**References Clinkers (<63\( \mu m \))**

- „Bulk“-XAS @ Lucia/SLS
Sample Preparation

- Powder materials

- Thin sections

Note: Probed volume at the given energy: \(~5 \times 5 \times 1 \, \mu m^3\)
X-ray Absorption Fine Structure (XAFS) Spectroscopy

Detection methods

\[
\frac{I_0}{I} = e^{\mu x}
\]

Transmitted beam

Fluorescence
X-ray photons

Incident X-ray beam

Spectra - regions

XANES
EXAFS
Edge

Photon - Matter interaction
X-ray Absorption Fine Structure (XAFS) Spectroscopy

X-ray Absorption Near Edge Structure; XANES

Extended X-ray Absorption Fine Structure, EXAFS

$E_0$: photoelectron threshold energy

Al K: $E_0 = 1559.6$ eV

S K: $E_0 = 2472$ eV

Relative Energy [eV]

S

Interference of Si edge@1839 eV with the Al EXAFS

limited structural information on the chemical environment
XANES Data Analysis

- **Features**
  - XANES range: to an energy of about 50 eV above the edge
  - XANES states: Excited electron populate higher unoccupied states
    
    *(unoccupied bound states and low-lying continuum states in complex ions etc.)*

  - XANES regime: electronic and geometric structure
    - multiple-scattering events
    - average valence of absorber atom

- **Experimental consistency checks**
  - Same reference measured on different campaigns
  - Same compounds prepared by different groups
  - Spectra of similar compounds
Reproducibility

Si-Hydrogarnet:  - Two campaigns in June 2007 and April 2008 at the Lucia beamline@SLS

![Graph showing normalized absorbance vs energy for Si-Hydrogarnet in June 2007 and April 2008.](image-url)
Variability in C₃A

C₃A: - XANES data of C₃A prepared in different laboratories

![Graph showing normalized absorbance vs. energy for C₃A from different laboratories: C₃A_PSI (red solid line) and C₃A_TM (blue dashed line). The graph is annotated with energy values in keV and normalized absorbance values ranging from 0 to 2.5. The data is from Matschei et al. 2007.]
Consistency of AFt Spectra

Fe-ettringite: - Spectrum of Al/Fe-ettringite-ss
- Spectrum calculated based on ettringite
Aluminium speciation
HTS Modelling

5 °C

Lothenbach et al. 2007
Lothenbach et al. 2007
HTS Modelling

50 °C

Lothenbach et al. 2007
References - Hydrogarnets

Si-hydrogarnet: $C_3ASH_4$

Hydrogarnet: $C_3AH_6$

Graph showing normalized absorbance vs. energy in keV for Si-hydrogarnet and Hydrogarnet.
References - Ettringite

Ettringite:  
\[ \text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot26\text{H}_2\text{O} \]

Al/Fe-Ettringite-ss:  
\[ \text{Ca}_6(\text{Al/Fe})_2(\text{SO}_4)_3(\text{OH})_{12}\cdot26\text{H}_2\text{O} \]

[Graph showing normalized absorbance vs. energy in keV]
AFm - $\text{C}_4\text{AH}_{13}$: $\text{Ca}_4\text{Al}_2(\text{OH})_{14} \cdot 6\text{H}_2\text{O}$
AFm - Monocarbonate: $\text{Ca}_4\text{Al}_2\text{CO}_3(\text{OH})_{12} \cdot 5\text{H}_2\text{O}$
AFm - Monosulfate: $\text{Ca}_4\text{Al}_2\text{SO}_4(\text{OH})_{12} \cdot 6\text{H}_2\text{O}$
Ettringite: \( \text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O} \)
AFm - C\text{A}_4\text{H}_{13}: \( \text{Ca}_4\text{Al}_2(\text{OH})_{14} \cdot 6\text{H}_2\text{O} \)
AFm - Monosulfate: \( \text{Ca}_4\text{Al}_2\text{SO}_4(\text{OH})_{12} \cdot 6\text{H}_2\text{O} \)
References - XANES data

⇒ Shift of 3 eV between clinker minerals and secondary phases
References - XANES data
Conclusions

δ **Possible:**
- Clinker minerals - AFt/AFm - Hydrogarnets - Hydrotalcite

δ **Difficult:**
- AFm - C₄AH₁₃ against AFm - Ca monocarbo/sulfoaluminates
- AFt (Ettringite) against AFm-type phases

δ **Impossible:**
- AFm - Ca monocarboaluminate and Ca monosulfoaluminate
Clinkers

Cem 4234: - Portland cement *(Lothenbach et al. 2008)*
HTS 2000/2004: - Cem I 52.5 N HTS (Lafarge, France)
Clinkers

Linear combination: - 40 % C₃A and 60 % C₄AF based on chemical analyses
MicroXRF maps - Elemental distribution

- **Al**
  - Low
  - High

- **S**
  - Low
  - High

- **Si**
  - Low
  - High

- **Mg**
  - Low
  - High
HTS 20° 28 d

Spot 1: high Al, medium Si
Spot 2: high Al, medium Si
Spot 3: high Al, low Si
Spot 4: medium Al, high Si
Spot 5: high Al, medium Si
Spot 6: high Al, low Si
Spot 7: high Al, high Si
Spot 8: high Al, low Si
Spot 9: high Al, low Si
Spot 10: low Al, high Si
Spot 11: low Al, low Si
Spot 1: high Al, low S
Spot 2: medium Al, low S
Spot 3: low Al, high S
Spot 4: high Al, medium S

Spot 5: medium Al, low S
Spot 6: high Al, low S
Spot 7: high Al, low S
Spot 8: medium Al, medium S
XANES HTS 5° 28d

Normalized Absorbance (a.u) vs. Energy [keV] for spots 1 to 8, showing peaks corresponding to Si-Hydrogarnet, Ettringite, and C₃A phases.
Spot 1: high Al, low Si
Spot 2: medium Al, medium Si
Spot 3: medium Al, low Si
Spot 4: high Al, medium Si
Spot 5: low Al, medium Si
Spot 6: medium Al, low Si
Spot 7: high Al, low Si
Spot 8: low Al, medium Si
Spot 9: high Al, medium Si
Spot 10: high Al, medium Si
Spot 11: high Al, medium Si
Spot 12: high Al, low Si
**XANES HTS 50° 28d**

- **Energy** [keV] range: 1.56 to 1.66
- **Normalized Absorbance (a.u)**
- **Spots**: 1 to 12
- **Materials**:
  - Si-Hydrogarnet
  - Ettringite
  - $\text{C}_3\text{A}$

Graphs showing absorbance curves for different spots and materials.
Principal Components Analysis (PCA)

PCA

- Analyse a set of spectra to see if they can be represented as linear combination of a smaller number of spectra (abstract components)

\[ D = C \times R \]

\((m \times r) \times (m \times n) = (n \times r)\)

- D: Data matrix which is factored into its components
- C: Factor loading matrix
- R: Factor-score matrix

Target transformation

- Determine which real reference can make up the abstract component
- SPOIL – number which measures the degree to which replacing an abstract component with the real reference would increase the fit error

- SPOIL < 1.5: reference is an excellent candidate for a component
- SPOIL 1.5 - 3: reference is a good candidate for a component
- SPOIL 3 - 4.5: reference is a fair candidate for a component
- SPOIL 4.5 - 6: reference is a poor candidate for a component
Principal Components Analysis

» HTS 20° 28d
- 4-5 components (total of 11 XANES spectra - SPOIL < 4.5)
- $C_3A/AFm(C_4AH_{13})/Ettringite/AFm-Monosulfate/Hydrotalcite/Si-Hydrogarnet$

» HTS 5° 28d
- 3 components (total of 8 XANES spectra SPOIL < 4.5)
- $C_3A/AFm(C_4AH_{13})/Ettringite/AFm-Monosulfate/(AFm-Monocarbonate)$
  Hydrotalcite/Si-Hydrogarnet

» HTS 50° 28d
- 3 components (total of 12 XANES spectra – SPOIL < 4.5)
- $C_3A/AFm(C_4AH_{13})/Ettringite/AFm-Monosulfate/(AFm-Monocarbonate)$
  Hydrotalcite/Si-Hydrogarnet
Aim:
- XANES spectra as linear combination of reference spectra
- Minimum number of components according to PCA
- References selected based on the results from PCA/Target transformation

Procedure:
- Linear combination tool in Athena (Iffefit)
- Residual: \( R = \frac{\sum (\text{data} - \text{fit})^2}{\sum (\text{data})^2} \times 100\% \)
- Fit: excellent for \( R \leq 0.5 \); fair for \( R > 0.5 \)
HTS 5° 28 d

Spot 5 (R = 0.67)  Spot 8 (R = 0.21)
<table>
<thead>
<tr>
<th>Spot</th>
<th>C\textsubscript{3}A</th>
<th>C\textsubscript{4}AF</th>
<th>Ettringite</th>
<th>AFm</th>
<th>Hydro-talcite</th>
<th>Res %</th>
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<tbody>
<tr>
<td># 1</td>
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<td>25 %</td>
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<tr>
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<td>0.31</td>
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<tr>
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<td>54 %</td>
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<td>46 %</td>
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<td>0.21</td>
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### Linear Combination HTS 20°

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<th>Spot</th>
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<tr>
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<tr>
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<tr>
<td># 7</td>
<td>71 %</td>
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<td>2% 27 %</td>
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<td>0.65</td>
</tr>
<tr>
<td># 8</td>
<td>68 %</td>
<td></td>
<td>23 % 9 %</td>
<td>0.2 %</td>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td># 9</td>
<td>51 %</td>
<td></td>
<td>26 % 11 %</td>
<td>12%</td>
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<tr>
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## Linear Combination HTS 50°

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<th>C$_4$AF</th>
<th>Ettringite</th>
<th>AFm</th>
<th>Hydro-talcite</th>
<th>R</th>
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<td>0.36</td>
</tr>
<tr>
<td># 3</td>
<td>71 %</td>
<td>24 %</td>
<td>5 %</td>
<td></td>
<td></td>
<td>0.77</td>
</tr>
<tr>
<td># 4</td>
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<td>38 %</td>
<td>8 %</td>
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</tr>
<tr>
<td># 5</td>
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<td>55 %</td>
<td>33 %</td>
<td>12 %</td>
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<tr>
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<tr>
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<td>32 %</td>
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<td></td>
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<td>0.41</td>
</tr>
</tbody>
</table>
Sulfur speciation
Sulfur - References

Normalized Absorbance vs. Energy [keV]

- CaSO$_4$
- Ettringite
- Ca monosulfoaluminate
HCP Sample

HTS-50C: HTS cement 2004 hydrated at 50° for 28 d

Ettringite or Monosulfate Formation?
MicroXRF Maps

- **Si**
  - Silver spot
  - High: 8, 10, 9
  - Low: 6, 4, 5

- **Al**
  - Silver spot
  - High: 8, 10, 9
  - Low: 6, 4, 5

- **S**
  - Silver spot
  - High: 8, 10, 9
  - Low: 6, 4, 5

- **Mg**
  - Silver spot
  - High: 8, 10, 9
  - Low: 6, 4, 5
HTS 50° 28 d
Linear combination

Spot 2 \((R = 0.23)\)

Spot 6 \((R = 0.33)\)

<table>
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<tr>
<th>Energy [keV]</th>
<th>Model</th>
<th>Experimental Data</th>
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</tr>
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<td>2.48</td>
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<tr>
<td>2.52</td>
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### Linear Combination HTS 50°

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<tr>
<th>Spot</th>
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<th>Ettringite</th>
<th>Monosulfate</th>
<th>Res %</th>
</tr>
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<td># 1</td>
<td>32 %</td>
<td>68 %</td>
<td></td>
<td>0.76</td>
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<td>38 %</td>
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<td>0.23</td>
</tr>
<tr>
<td># 3</td>
<td>14 %</td>
<td>86 %</td>
<td></td>
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</tr>
<tr>
<td># 4</td>
<td>24 %</td>
<td>76 %</td>
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<td>0.37</td>
</tr>
<tr>
<td># 5</td>
<td>16 %</td>
<td>84 %</td>
<td></td>
<td>0.37</td>
</tr>
<tr>
<td># 6</td>
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<td></td>
<td>0.33</td>
</tr>
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<td>38 %</td>
<td>62 %</td>
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<td>0.46</td>
</tr>
<tr>
<td># 10</td>
<td>35 %</td>
<td>65 %</td>
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</table>
Conclusions

Micro-spectroscopic approach to phase identification
- Allows cement phases to be identified with micro-scale resolution
- Requires good quality data (references, spectra from single spots) as single cement phases have to extracted from complex mixtures

Al speciation
- High content of C₃A at hot spots
- C₃A and ettringite as dominating Al species in cement paste hydrate for 28 days at 5°
- C₃A, ettringite and AFm phases present in cement paste hydrated for 28 days at 20° and 50°

S speciation
- Predominantly Ca monosulfoaluminate and some ettringite is observed in cement paste hydrated for 28 days at 50°
- Presence of Ca monosulfoaluminate consistent with thermodynamic modelling
- More sensitive with regards to distinction of ettringite and monosulfate
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T. Matschei          L. Aimoz
G. Möschner          K. Rozov

**Beamline**
Lucia @ SLS/PSI

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