Hydration of “low pH” cements

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Objectives

- Hydration of
  - OPC: CEM I 42.5 HS
  - ESDRED: CEM I 42.5 N + 40% silica fume + accelerator
  - LAC: CEM III/B 42.5 L + 10% nanosilica

Cementitious materials used in field experiments
- composition of the pore solution
- mineral composition of the cement matrix
- comparison
Cement-Clay interface

Side view

Top view

EDZ
ESDRED
OPC
LAC
OPA
### OPC: CEM I 42.5 R HS

(g/100g)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Value</th>
<th>Type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>58.8</td>
<td>alite</td>
<td>31</td>
</tr>
<tr>
<td>SiO₂</td>
<td>20.6</td>
<td>belite</td>
<td>36</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.9</td>
<td>aluminate</td>
<td>1.6</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.2</td>
<td>ferrite</td>
<td>16</td>
</tr>
<tr>
<td>MgO</td>
<td>4.6</td>
<td>MgO</td>
<td>4.6</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.27</td>
<td>CaCO₃</td>
<td>3.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.75</td>
<td>CaSO₄</td>
<td>5.1</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.4</td>
<td>Na₂O</td>
<td>0.22</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.5</td>
<td>K₂O</td>
<td>0.27</td>
</tr>
<tr>
<td>CaO&lt;sub&gt;free&lt;/sub&gt;</td>
<td>0.71</td>
<td>Na₂SO₄</td>
<td>0.12</td>
</tr>
<tr>
<td>LOI</td>
<td>2.3</td>
<td>K₂SO₄</td>
<td>0.89</td>
</tr>
</tbody>
</table>

w/c = 0.8
Hydration (Lothenbach and Winnefeld, 2006)

alite ($C_3S$), belite ($C_2S$)
aluminate($C_3A$), ferrite $C_4AF$
Modeling - Dissolution


\[ R_t = \frac{K_1}{N_1} (1 - \alpha_t)(-\ln(1 - \alpha_t))^{(1-N_1)} \]

\[ R_t = \frac{K_2 \times (1 - \alpha_t)^{2/3}}{1 - (1 - \alpha_t)^{1/3}} \]

\[ R_t = K_3 \times (1 - \alpha_t)^{N_3} \]

All parameters \((K_i, N_i)\) from Parrot and Killoh (1984)

\(\alpha\): degree of hydration

Cement specific input: surface area, w/c
## Thermodynamic Modeling

### Cements

**I clinkers (slowly soluble)**
- $\text{C}_3\text{S}$
- $\text{C}_2\text{S}$
- $\text{C}_3\text{A}$
- $\text{C}_4\text{AF}$
- $\text{K}_2\text{O}$
- $\text{Na}_2\text{O}$
- $\text{MgO}$

**II soluble solids**
- $\text{K}_2\text{SO}_4$
- $\text{Na}_2\text{SO}_4$
- gypsum
- hemihydrate
- anhydrite
- $\text{CaO}$
- calcite

**III water**
- $\text{H}_2\text{O}$

### Thermodynamic modeling

- $\text{Ca}^{2+}$
- $\text{CaOH}^+$
- $\text{CaSO}_4^0$

Speciation in solution:
- Portlandite
- C-S-H
- Ettringite
- AFm
- Hydrotalcites, ...

**Diagram:**
- Ettringite
- Portlandite
- C-S-H
- Ettringite
- AFm
- Hydrotalcites, ...
Modeling – Volume of solids

![Graph showing the volume of solids over time for various materials such as gypsum, hydrotalcite, calcite, ettringite, monocarbonate, portlandite, C-AF, C-S, C₃S, and C-S-H. The graph plots cm³/100 g cement against time in days, ranging from 0.01 to 1000 days.]
ESDRED: 60% CEM I + 40% silica fume  
5% alkali free accelerator

<table>
<thead>
<tr>
<th></th>
<th>CEM I 42.5 N (g/100g)</th>
<th>silica fume (g/100g)</th>
<th>alkali-free accelerator</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>61.6</td>
<td>2.1</td>
<td>&lt;</td>
</tr>
<tr>
<td>SiO₂</td>
<td>21.9</td>
<td>93.3</td>
<td>&lt;</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.8</td>
<td>0.2</td>
<td>16</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.5</td>
<td>0.1</td>
<td>&lt;</td>
</tr>
<tr>
<td>MgO</td>
<td>1.9</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.25</td>
<td>&lt;0.01</td>
<td>0.2</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.99</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.0</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.4</td>
<td>0.02</td>
<td>15</td>
</tr>
<tr>
<td>LOI</td>
<td>2.3</td>
<td>3.1</td>
<td>2.5</td>
</tr>
<tr>
<td>dissolved organic carbon</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

→ 0.16 mmol

+ CaSO₄ (0.32)
+ CaO (0.64)
→ C₆A₃H₃₂

→ 0.18 mmol
$$A + $ + 2C$ + 4C \rightarrow C_6A_3H_{32}$$

XRD

Ettringite
Hemicarbonate
Monocarbonate
Portlandite
Hemicalcium carbonate
C-S-H
Anhydrite
Alite
Hemicarbonate

XRD chart showing the evolution of different compounds over time. The chart includes peaks for Ettringite, Hemicarbonate, Monocarbonate, Portlandite, Hemi-carbonate, C-S-H, Anhydrite, Alite, and Alite/belite. The chart is labeled with time intervals such as 360 days, 56 days, 7 days, and 1 day.
Reactivity of SiO$_2$

- Si-NMR
dissolution of silica fume
SiO$_2$ [%] = 17 + 23e$^{-0.05t}$
Composition of the pore solution

The graph depicts the concentration of various ions and DOC over time, with the x-axis representing time in days and the y-axis showing concentration in mol/l. The ions and DOC are indicated by different symbols and colors on the graph.
Composition of the pore solution

K, Na => in C-S-H
Low C/S => more K, Na in C-S-H

pH (360 days) 11.3

Composition of the pore solution:
- K, Na in C-S-H
- Low C/S => more K, Na in C-S-H

Graph showing the composition over time with mol/l values:
- K
- OH
- Na
- Ca
- S
- Al
- Si

pH (360 days) 11.3

Al, Ca, K, Na, S, Si concentrations over time.
alkali uptake

![Graph showing alkali uptake with silica fume concentration and Na + K concentration on the x-axis and y-axis, respectively. The graph includes data points for different silica fume concentrations and Na + K values, with error bars indicating variability. The x-axis is labeled as silica fume [g/100 g] and ranges from 0% to 50%, and the y-axis is labeled as Na + K [mM] and ranges from 0.01 to 1000. The graph includes a legend with symbols for silica fume and Na + K.](image-url)
The graph represents the dissolution of silica fume as a function of pH. The x-axis shows the time in days, while the y-axis depicts the concentration of silica fume in g/100 g. The graph includes data points for initial amount of silica fume and pH, with various concentrations of silica fume shown, ranging from 0% to 50%. The pH values are marked on the right side of the graph, ranging from 11.0 to 13.5.
Modeling ESDRED hydration

Portland cement hydration
• similar to OPC system
• 1st hour increased dissolution of clinker
  (Paglia et al., 2004; XRD)
• silica fume dissolution according to NMR data
decreases at low pH values

Problems
- Alkali (K) and Al-uptake in C-S-H not well known
- strätlingite or Al-in C-S-H?

EDS: 0.08 Al/Si in C-S-H
Modeling - relative mass of solids

(mass refers to total solid, including hydrated)

- pH > 13
- pH ≤ 12.5
- pH 11.3

Experimental:
Portlandite 1-7 days
Hemi-/Monocarbonate: 1-28 days

Time (days)

Mass of solids:
- C-S-H
- Hydrotalcite
- Portlandite
- Aluminate
- Ferrite
- Calcite
- Silica fume
- Belite
- Alite
- Pore solution

Mass of solids per 100 g of cement hydrated.
pH measured

Models – Volume of solids

Al/Si = 0.08

C-(Al)-S-H

calcite

hydrotalcite

monocarbonate

ettringite

portlandite

silica fume

C_A_S_H
Thaumasite formation possible

\[ \text{eff saturation index} = \frac{1}{n} \log \frac{\text{IAP}}{K_{s0}} \]

\( n = \text{number of ions} \)
Strong dependency on silica fume dissolution

Al/Si = 0.08
Summary - ESDRED

- Mix of OPC with SiO₂
- 0-2 days: similar to OPC
- >2 days: SiO₂:
  - no (temporary small amount) portlandite
    - low pH buffering capacity
  - pH decreases, no further SiO₂ reaction

- Hydration products
  - C-S-H (low C/S), ettringite
  - hydrotalcite, calcite, hemi-/monocarbonate

- pH decreases with time (11.3 after 1 year)

- Solution dominated by Ca, K, Na, OH, DOC

- Longterm unclear (ettringite <-> thaumasite ?)
  - potential for stratlingite, Si-hydrogarnet or thaumasite
**LAC: 90% CEM III/B + 10% Nanosilica**

<table>
<thead>
<tr>
<th></th>
<th>Portland cement</th>
<th>slag (g/100g)</th>
<th>Nanosilica</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>66</td>
<td>41</td>
<td>&gt;99.8</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>17</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>4</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>5</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.1</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.7</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>SO$_3$</td>
<td>3.2</td>
<td>0.8 (as S(-II))</td>
<td></td>
</tr>
<tr>
<td>LOI</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ w/b = 1.1 \]

(contains ~74% slag)
XRD

- Ettringite
- Hemicarbonate
- Mono-carbonate
- C-S-H

Graph showing XRD patterns over time:
- Unhydrated sample
- 1 h hydration
- 7 days hydration
- 1 day hydration
- > 1 day hydration
- 360 days hydration

Peaks for:
- Alite
- Alite/belite
- C3A
- Gypsum
dissolution of nanosilica

\[ NS = 0.1 \times 10^{-0.25t} \]

initial amount of nanosilica

[Graph showing the dissolution of nanosilica over time with a fitted equation and data points.]

nanosilica [g/100]

0% 10% 20% 25%

time [days]

0.01 0.1 1 10 100 1000
Selective dissolution with EDTA

dissolution of slag

\[
\text{slag [\%]} = 51 - 8\times\log(\text{time})
\]

Initial slag content of LAC

Time [days]

Slag [g/100 g unhydrated LAC]
Composition of the pore solution

OPC

slag
nano silica

Time (days)

mol/l

K

OH⁻

Na

HS⁻

SO₄²⁻

Ca

Si

Al

Ca

Si

Al
Sulfur speciation

\[ S_{\text{tot}} \]
\[ \text{SO}_4 \]
\[ \text{HS}^- \]
\[ \text{SO}_3 \]
\[ \text{S}_2\text{O}_3 \]

Detection limit

\[ \text{mol/l} \]

Time (days)

EMPA Materials Science & Technology
Modeling LAC hydration

Portland cement hydration
• according to OPC system
• nanosilica dissolution according to NMR data
• slag dissolution according to selective dissolution

Problems
➤ Alkali (K) and Al-uptake in C-S-H not well known
➤ strätlingite or Al-in C-S-H?
LAC modelled

Al/Si = 0.08

C-A-S-H

calcite
ettringite

hydrotalcite

stratlingite

gypsum

nanosilica

unhydrated clinker

slag

Materials Science & Technology
Summary - LAC

- Slag with OPC and SiO$_2$
- 0-1 days: similar to OPC,
- >1 days: slag + SiO$_2$:
  - Reducing conditions (HS-)
  - no portlandite
  - pH decreases
- Main hydration products
  - C-S-H (low C/S), ettringite -> strätlingite?
- pH decreases with time (12.3 after 1 year)
- Solution dominated by Ca, K, Na,OH and HS$^-$. 
Comparison: hydrates after 1 year

Graph showing the comparison of hydrates after 1 year with different materials. The graph includes peaks for ettringite, C-S-H, portlandite, and alite/belite. The x-axis represents 2-theta in degrees, and the y-axis represents counts. The materials are labeled LAC (Ettringite), ESDRED, and OPC.
Comparison: different pore solutions

**pH values**

- OPC CEM I HS
- LAC 90% CEM III/B 10% nanosilica
- ESDRED: 60% CEM I 40% silica fume accelerator
Conclusions

- **OPC**
  - hydration consistent with previous hydration studies
  - pH = 13.3 after 12 months

- **ESDRED (CEM I + 40 % SiO₂)**
  - Initially similar to OPC
  - Silica fume dissolution proceeds slowly
  - C-S-H: Initially C/S ~ 1.5, after 10 days ↓ (final C/S ~ 0.9)
  - Portlandite consumed after 10 days
  - Alkali and pH ↓ (after 12 months: pH = 11.3)

- **LAC (CEM III/B + 10% SiO₂)**
  - Initially similar to OPC
  - HS⁻ increases with time – reducing conditions
  - pH = 12.3 after 12 months
Conclulsion 2: SCM

- Reactivity of slag, silica fume
  -> depends on hydrate assemblage
- Al and alkali uptake in C-S-H!
- No portlandite, strätlingite formation
- Thaumasite formation possible

- Thermodynamic models for Al-alkali-C-S-H missing