Thermodynamic modelling of cementitious systems

Lecture and hands-on computer simulations
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Online course 2020
Preliminary programme: 15:00 h to ≈ 16:30

Download and read the slides before each session

Tuesday, 25. Aug 2020: 02 First modelling, single systems
Wednesday, 26. Aug 2020: 03 Process
Thursday, 27. Aug. 2020: 04 Database
Friday, 28. Aug. 2020: 05 Hydration modelling + Introduction to self studying exercises

Monday, 31. Aug. 2020: 06 Durability
Tuesday, 1. Sept. 2020: self studying excercises
Wednesday, 2. Sept. 2020: self studying excercises
Thursday, 3. Sept. 2020: Student presentations
Friday, 4. Sept. 2020: Student presentations

Friday, 4. December 2020: Hand in short reports of individual modelling project
1 Introduction cement chemistry

2 GEMS / Single calculations
3 Process calculations

...
Introduction cement chemistry 1

- Cement production
- Hydration of Portland cement
- Effect of limestone
Portland cement (PC) production

- **Limestone** (CaCO₃)
- **Clay + Sand** (Si, Al, Fe-oxides)

Rotary kiln

- Increasing temperature ~ 1500°C

- Clinker + Gypsum

Ordinary Portland cement (OPC)
Rotary kiln
Rotary kiln

Fast cooling,
else:
$C_3S \rightarrow C_2S + C$ (free lime)
CO₂ in OPC production ((CaO)₃SiO₂)

Reduction of CaCO₃

Mass flow

Data from Gartner (2004) CCR 34, 1489-1498
cement paste:
  OPC 
  water

mortar:
  + sand

concrete:
  + gravel 
  = concrete
Portland cement: CEM I 42.5 N

**Chemical analysis**

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.7</td>
</tr>
<tr>
<td>CaO</td>
<td>62</td>
</tr>
<tr>
<td>CaO\text{free}</td>
<td>0.6</td>
</tr>
<tr>
<td>MgO</td>
<td>1.4</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.95</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.10</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.1</td>
</tr>
</tbody>
</table>

**Phases**

<table>
<thead>
<tr>
<th>Phase</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite C₃S</td>
<td>58</td>
</tr>
<tr>
<td>Belite C₂S</td>
<td>10</td>
</tr>
<tr>
<td>alum. C₃A</td>
<td>7.6</td>
</tr>
<tr>
<td>ferrite C₄AF</td>
<td>7.5</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>3.6</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>4.8</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>1.6</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Small amounts of titanium, manganese, phosphate and chromium

Bogue calculations
Chemical reactions

**Alite** (C₃S) + water → C-S-H + portlandite

(CaO)₃SiO₂ + 5.3H₂O → Ca₁.₇SiO₂(H₂O)₄ + 1.3Ca(OH)₂
C₃S + 5.3H → C-S-H + 1.3CH

**Belite** (C₂S) + water → C-S-H + portlandite

(CaO)₂SiO₂ + 4.3H₂O → Ca₁.₇SiO₂(H₂O)₄ + 0.3Ca(OH)₂
C₂S + 4.3H → C-S-H + 0.3CH

**Aluminate** (C₃A) + anhydrite (C₅) + water → ettringite

(CaO)₃Al₂O₃ + 3CaSO₄ + 32H₂O → (CaO)₃(CaSO₄)₃Al₂O₃.32H₂O
C₃A + 3Cs + 32H → C₆As₃H₃₂

**Aluminate** (C₃A) + calcite (Cc) + water → monocarbonate

(CaO)₃Al₂O₃ + CaCO₃ + 12H₂O → (CaO)₃(CaCO₃)Al₂O₃.12H₂O
C₃A + Cc + 12H → C₄AcH₁₂

AFt + AFm contain a lot of water -> high volume
What is cement?

«Minute Cement»
Video from John Rossen and Arnaud Muller (EPFL)

https://www.youtube.com/watch?v=L4OLBNXMdHk
Hydration of PC: TGA

- gypsum/hemihydrate
- unhydrated
- ettringite
- C-S-H
- calcium monocarbonate
- AFm / hydrotalcite
- Ca(OH)$_2$
- CaCO$_3$

Temperature [°C]: 0 - 1000

Relative weight [%]: 100 - 0

Diff. relative weight [%/K]: -0.15 - 0.00
Hydration of PC: XRD

- ettringite
- portlandite
- gypsum
- ferrite

Counts / -

2-theta / °

unhydrated

1 year

28 d

1 d
6 Hours

- Pores
- Hydrates
- Clinker
24 Hours

ettringite

Acc.V  Spot Magn  Det  WD  Exp
20.0 kV  3.0  1250x  GSE 10.0  1  2.3 Torr
Hydration of PC: Pore solution

CaSO₄ depleted

[mM]

OH⁻
Na
K
Ca
S
Si
Al

[days]
Modelling of Hydration

clinker

C-S-H  Portlandite  Ettringite
What is needed to model hydration?

1 Portland cement

Multi-component input

I Clinkers
$\text{C}_3\text{S}$ $\text{C}_2\text{S}$ $\text{K}_2\text{O}$
$\text{C}_3\text{A}$ $\text{C}_4\text{AF}$ $\text{Na}_2\text{O}$
$\text{CaO}$ $\text{MgO}$

II Other solids
$\text{K}_2\text{SO}_4$ $\text{Na}_2\text{SO}_4$
$\text{Hemihydrate}$ $\text{Anhydrite}$
$\text{Calcite}$

III Water
$\text{H}_2\text{O}$

Hydrated OPC

C-S-H
portlandite
monosulfate
monocarbonate
ettringite
hydrotalcite

Thermodynamic modeling
2 Thermodynamic databases

PSI/Nagra TDB
- Aqueous phase (Ca$^{2+}$, Ca(OH)$^+$, ...)
- Gaseous phase (e.g. CO$_2$ (g), ...)
- Minerals (calcite, gypsum, portlandite, ...)

Cemdata07, 18
- AFm
- SO$_4$-AFm
- OH-AFm
- CO$_3$-AFm
- hemicarb.
- strätlingite
- Al-AFm
- Fe-AFm

- AFt
- SO$_4$-AFt
- CO$_3$-AFt
- thaumasite
- Fe-AFt
- Al-AFt

- hydrogarnet

- C-S-H
- High Ca C-S-H
- tobermorite
- SiO$_2$

Data based on solubility measurements at different temperatures + solid phase characterisation

Recent additions: Cl$_2$, I$_2$, CrO$_4$, NO$_3$, NO$_2$-AFm, M-S-H, zeolites, C-A-S-H, relative humidity
What is needed to model hydration?

3 Reactivity of anhydrous phases

based on empirical data, measured data, dissolution rates,…

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

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

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

All parameters (\(K, N\)) from Parrot and Killoh (1984)
Modelled pore solutions

Lothenbach, Winnefeld (2006), CCR 36, 209-226
Al-, SO₄- and CO₃-hydrates

C₃A + 3gypsum ⇌ 3CaO·Al₂O₃·3CaSO₄·32H₂O

Lothenbach, Winnefeld (2006), CCR 36, 209-226
Modelled Ca- and Si-Hydrates

Lothenbach, Winnefeld (2006), CCR 36, 209-226
Portland cement (without calcite)

Lothenbach ea (2008), CCR 38, 1162-1186
Portland cement (without calcite)

Lothenbach ea (2008), CCR 38, 1162-1186
Portland cement (with 4% calcite)

Volume [cm$^3$/100 g cement] vs. Hydration time [days]

- **Porosity**
- **Chemical shrinkage**
- **Pore solution**

Materials:
- Calcite
- Hydrotalcite
- Monocarbonate
- Ettringite
- C-S-H
- Gypsum
- C4AF
- C2S
- C3S

Angles 2θ (degrees) CuKα:
- 1 day
- 7 days
- 1 year

Lothenbach ea (2008), CCR 38, 1162-1186
Influence of limestone on PC

More Volume ⇔ higher strength

- 30
- 20
- 10
- 0

Influence of limestone on PC

- 70
- 60
- 50
- 40
- 30
- 20
- 10
- 0

Influence of limestone on PC

- 80
- 70
- 60
- 50
- 40
- 30
- 20
- 10
- 0

Influence of limestone on PC

- 5.0% Al2O3
- 4.2% Al2O3
- 4.4% Al2O3
- De Weerdt, 2010
- De Weerdt, 2011a
- De Weerdt, 2011b

5.3 wt% Al2O3

Damidot ea 2011 CCR 41; Lothenbach ea 2008
Influence of limestone on PC

More Volume ⇔ higher strength

- ettringite
- monosulfate
- hemicarbonate
- monocarbonate
- portlandite
- calcite

More Volume

Higher strength

1 day

7 days

1 year

Ettringite

C₄AF

C-S-H

Angles 2θ (degrees) CuKα
Effect of limestone on pore solution

Weeks to years:
Limestone increases sulfate concentration
lowsers aluminium concentrations
=> Low Al, faster reaction of clinker, glasses, slag, ...

Lothenbach ea 2008, CCR 38
Influence of limestone on PC blended with fly ash (FA): CEM II/B-V

Limestone effect more pronounced if more Al$_2$O$_3$ present: «synergistic effect»

wt% Al$_2$O$_3$
PC: 5.3
FA: 24.0
PC+FA: 11.8
reacted: 6.7

De Weerdt ea 2011, CCR 41; Damidot ea 2011, CCR 41
Influence of limestone on strength

OPC: 6% Al$_2$O$_3$

Blending of OPC with fly ash and limestone
Al$_2$O$_3$-content: Fly ash 24% ↔ OPC 6%

more Al$_2$O$_3$ => «synergistic» effect

\[ \text{De Weerdt et al., 2010, 2011} \]

=>$\text{Calcined clay + limestone}$
Conclusions

PC
• High pH, portlandite
• High Ca/Si C-S-H

Limestone
• Positive effect
• MS+Cc => AFt+Mc
• Accelerates slag and alite reaction

Questions?