Feasibility of Calcined Marl as an Alternative Pozzolanic Material

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Tone Østnor

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Introduction:

- 5-7% of global CO$_2$-emissions today derive from cement industry.
- Most effective way to reduce these emissions is the use of supplementary cementitious materials.
- The right choice of the material is mainly a question of availability.

Marl is clay with high amounts of CaCO$_3$, rendering it unsuitable for the clay industry. But can it be made reactive?
Approx. mineralogical composition of the ”marl” in %:

<table>
<thead>
<tr>
<th></th>
<th>Smectite</th>
<th>Kaolinite</th>
<th>Illite</th>
<th>Calcium Carbonate</th>
<th>Quartz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marl</td>
<td>50</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

Chemical composition of the ”marl” in %:

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marl</td>
<td>48.6</td>
<td>18.6</td>
<td>10.8</td>
<td>12.7</td>
<td>2.9</td>
<td>0.7</td>
<td>2.4</td>
<td>0.2</td>
<td>0.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Calcination of the marl:
IBU-Tec Germany → small rotary kiln (7m), 45 min retention time, 700-1000 °C (50 °C steps)

Milling of the marl:
UVR-FIA GmbH Germany, discontinous drum mill to d₅₀ ≤ 10 µm
28 days compressive of mortars:
Standard procedure NS-EN 196-1

20 % replacement of OPC by calcined marl:

- 20% SØ-800:
  - 12% higher strength than reference mortar

- with 20 % metakaolin*:
  - only 3% strength increase

* Commercial Metakaolin (Metaver N) from Newchem
Phase transformations during calcination between 700 - 1000 °C

Kaolinite: AS$_2$H$_2$
Calcite - Cc
Smectite/Illite
amorphous phase
Gehlenite - C$_2$AS
at 850 °C
Anorthite – CAS$_2$
Wollastonite - CS
Diopside – CMS
FT-IR:

OH-stretching region

- **Si-O stretching**
- **Al-O-Si deformation**
- **Si-O-Si deformation**

**complete dehydroxylation of clay**

- **Al-Al-OH deformation band disappears**
- **complete dehydroxylation of octahedral layer**

Decomposition of **calcite**

- **not complete:**
  - ~5% left (TG/DTG)

**Significant structural changes in the clay mineral structure**

**Decreasing content of octahedral cations:**

**Al-NMR:**

- **Al(VI) → Al(IV)**

Transmittance [%] vs. wavenumber [cm⁻¹]

- **raw**
- **650 °C**
- **800 °C**

**CO₃²⁻ stretching/bending modes**
Mössbauer Spectroscopy:

Søvind Marl:

\[ 4 \text{Fe}^{2+} + \text{O}_2 \rightarrow 4 \text{Fe}^{3+} + 2 \text{O}_2^- \]

Oxidation of iron:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe(^{2+}) [%]</th>
<th>Fe(^{3+}) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw-clay</td>
<td>23</td>
<td>77</td>
</tr>
<tr>
<td>calcined clay</td>
<td>7</td>
<td>93</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe(^{2+})</th>
<th>Fe(^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Isomer shift</td>
<td>Quadrupole splitting</td>
</tr>
<tr>
<td>raw clay</td>
<td>1.12</td>
<td>2.20</td>
</tr>
<tr>
<td>Calcined clay</td>
<td>0.95</td>
<td>1.90</td>
</tr>
</tbody>
</table>

Main coordination change:
- Fe\(^{2+}\)(VI) \(\rightarrow\) Fe\(^{2+}\)(IV)
- Fe\(^{3+}\)(VI) \(\rightarrow\) Fe\(^{3+}\)(V)
+ changes in the ligand structure

Both iron species originally in octahedral coordination \(\rightarrow\) substitution for Al\(^{3+}\) and Mg\(^{2+}\) in octahedral layer of clay minerals

EPMA:

Coccoliths in Søvind Marl:

Calcined marl:

Feasibility of Calcined Marl as an Alternative Pozzolanic Materials

[1] Young & Henriksen (2003), Rev. Min. & Geoch. 54, 189-215

X

Weight %_X:

<table>
<thead>
<tr>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.1</td>
<td>44.4</td>
<td>24.0</td>
<td>10.3</td>
<td>1.8</td>
<td>1.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

800 °C:
Pozzolanic activity
Calcium hydroxide consumption by thermal analysis:

- Paste with marl/lime ratio of 1/1 mixed with alkaline solution (0.158 M, KOH/NaOH = 2/1, pH = 13.2)
- Curing for 28 days and 6 month at 20 and 38°C
- TGA/DTG was used to calculate the calcium hydroxide content
- Reduction in calcium hydroxide decomposition peak in range 400-500°C relative to reference was taken as “pozzolanic activity”

<table>
<thead>
<tr>
<th></th>
<th>Marl/Lime = 1/1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 °C</td>
</tr>
<tr>
<td>CH at 0 days [%]</td>
<td>47.1</td>
</tr>
<tr>
<td>CH at 28 days [%]</td>
<td>19.8</td>
</tr>
<tr>
<td>Consumed CH [%] 0-28 days</td>
<td>58.0</td>
</tr>
<tr>
<td>Consumed lime [g] per gram clay</td>
<td>0.52</td>
</tr>
<tr>
<td>CH at 6 month [%]</td>
<td>15.1</td>
</tr>
<tr>
<td>Consumed CH [%] 0-6 month</td>
<td>67.9</td>
</tr>
<tr>
<td>Consumed lime [g] per gram clay</td>
<td>0.60</td>
</tr>
</tbody>
</table>

After 28 days comparable to the lime consumption of metakaolin
XRD: Søvind Marl/lime 1/1 cured at 20 °C:

- Quartz
- Calcite
- Lime = calcium hydroxide
- monocalcium-aluminate hydrate
- hemicalcium-aluminate hydrate

Fe-substituted carbo-aluminate hydrate

TG/DTG:
- C-S-H
- Signs of Katoite

27Al-MAS-NMR:
- Al(IV) → Al(VI)
- Al (V) incorporation in C-S-H phases
- Al substitution for Ca in C-S-H
SEM (Polished cross section of samples embedded in epoxy resin)

20 °C

1 C-S-H

2 Clay

38 °C

3 AFm

4 glass

WDX_1: Ca: 26.1, Si: 10.8, Al: 4.5
2: Ca: 29.1, Si: 5.2, Al: 1.4
3: Ca: 21.8, Si: 4.6, Al: 11.1, Fe: 4.4
4: Ca: 15.2, Si: 8.9, Al: 6.3, Fe: 3.5
Industrial Scale Production Test:

Compressive strength of mortars with 20, 35, 50, 65 % (volume) replacement of OPC by calcined marl

<table>
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<tr>
<th>Replacement</th>
<th>Superplasticizer (%)</th>
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<tbody>
<tr>
<td>20 % repl.</td>
<td>0.18</td>
</tr>
<tr>
<td>35 % repl.</td>
<td>0.35</td>
</tr>
<tr>
<td>50 % repl.</td>
<td>0.52</td>
</tr>
<tr>
<td>65 % repl.</td>
<td>0.91</td>
</tr>
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</table>
Conclusions:

- Calcined Marl can be made an efficient pozzolanic material by calcination and be considered as “industrial pozzolan” within the standard EN 197-1.

- 50% replacement of Portland cement by marl calcined at optimum temperature gave the same 28 days strength as reference with 100% cement. → it may be feasible to make portland pozzolan cements (CEM VI/B).

- Significant structural changes in the clay minerals (XRD, FT-IR, 27Al-NMR).

- Mössbauer spectroscopy is applicable to document structural changes increasing the clay reactivity.

- Formation of Ca-enriched reactive glass phase from reaction of clay minerals and decomposing coccoliths.

- Due to some remaining calcite upon calcination carboaluminate hydrates were the main hydration products formed in marl/lime pastes besides C-S-H and C-A-(S)-H.
Thank you for your attention

Acknowledgements:

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