COMPARATIVE STUDY OF ALTERNATIVE BINDERS FOR CONCRETE SEALING STRUCTURES IN ROCK SALT

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The safe disposal and long-term management of radioactive wastes have become key factors for the current society, as well as for future generations. In Germany, especially the salt-containing ‘Zechstein’ formations are considered to be suitable for this purpose, due to their low permeability. The long-term sealing function of a barrier is mainly determined by stress-strain interactions between the host rock and the sealing structure, especially at early ages after construction, as well as the permeability with respect to gases and liquids at later ages.

Despite significant progress that has been made with research on specific cements (e.g. magnesium oxychloride cement (MOC) and blended Portland cements (low-pH cements), there is still room for improvement, e.g. in terms of heat evolution during hydration and shrinkage.
Studied Binder Systems

Low-pH Cements
- Ordinary Portland Cement (OPC)
- Supplementary Cementitious Materials (SCMs)

Opus Caementitium
- Slaked Lime + Pozzolan

Alkali-Activated Materials (AAMs)

One-Part (OP)
- Silica + Alkaline Activator (solid)

Two-Part (TP)
- Aluminosilicate + Alkaline Activator (liquid)

Hybrid Cements
- OPC + SCMs + Alkaline Activator (solid)

+ water
### Starting Materials and Sample Nomenclature

<table>
<thead>
<tr>
<th>Class</th>
<th>TP AAM</th>
<th>OP AAMs</th>
<th>Low-pH</th>
<th>Opus</th>
<th>Hybrid</th>
<th>OPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>F1</td>
<td>O1</td>
<td>O2</td>
<td>M2 (REF)^1</td>
<td>R1</td>
<td>H1</td>
</tr>
<tr>
<td>Solids (b)</td>
<td>Fly Ash (FA)</td>
<td>Silica Fume</td>
<td>OPC</td>
<td>Slaked Lime</td>
<td>OPC</td>
<td>Slag</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sodium Aluminate</td>
<td>Slag</td>
<td>Trass</td>
<td>Slag</td>
<td>Na₂CO₃</td>
</tr>
<tr>
<td>Liquids (b)</td>
<td>Sodium Silicate-sln</td>
<td>NaOH-sln</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water (w/b)</td>
<td>0.55*</td>
<td>0.5</td>
<td>0.4</td>
<td>0.41</td>
<td>0.63</td>
<td>0.4</td>
</tr>
<tr>
<td>Aggregates (A)</td>
<td>Rock Salt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*(liquids(b)+w)/solids(b)

\[ w+b=\text{paste} \quad w+b+A=\text{mortar} \]

^1 DBE 2004 (Unterlagen-Nr.: P 192)
Isothermal Calorimetry (pastes)
(20°C)

<table>
<thead>
<tr>
<th>Class</th>
<th>Sample (pastes)</th>
<th>Heat of reaction (7d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAMs</td>
<td>F1</td>
<td>54.9</td>
</tr>
<tr>
<td></td>
<td>O1</td>
<td>45.9</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>48.4</td>
</tr>
<tr>
<td>Opus</td>
<td>R1</td>
<td>38.9</td>
</tr>
<tr>
<td>Hybrid</td>
<td>H1</td>
<td>154.3</td>
</tr>
<tr>
<td>low-pH (REF)</td>
<td>M2</td>
<td>125.4</td>
</tr>
<tr>
<td>OPC</td>
<td>OPC</td>
<td>317.6</td>
</tr>
</tbody>
</table>

Low Heat ≤ 270 J/g (DIN EN 197-1)
Isothermal Calorimetry (pastes) (20°C)

0 initial dissolution
1 main hydration (CSH; CH)
2 sulfate depletion
3 AFt to AFm transformation
4 SCM reaction

dissolution, condensation of N-A-S(-H), hydration → no peaks
Strength Development of the AAM-based Mortars

(Curing at 23°C/50% r.H. or 40 °C/35% r.H.)

- at 23 °C comparably low early strength of the AAMs, but highest final compressive strength for F1
- at 40 °C acceleration (early strength) and increase of the final compressive strength
- at 40 °C decrease of the final flexural strength for O2
Microstructure of the AAM-based Mortars (Curing at 23°C/50% r.H. or 40 °C/35% r.H.)

**XRD**

\[
\begin{align*}
H &= \text{halite} \\
A &= \text{anhydrite} \\
q &= \text{quartz} \\
C &= \text{calcite} \\
M &= \text{mullite} \\
G &= \text{gibbsite} \\
M &= \text{mirabilite} \\
AFm &= \text{Friedel` s salt}
\end{align*}
\]

No major differences, except a slightly increased dissolution rate of the rock salt impurities

**Optical Microscopy (UV-mode)**

Introduction of cracks due to increased drying shrinkage (air humidity), → decreased flexural strength (O2)
Conclusions and Future Work

- Calorimetry (low heat of reaction) and strength development of the AAMs indicate promising reaction kinetics at room temperature.
- Improved compressive strength of the AAMs at 40 °C demonstrates an accelerated reaction and presumably an increased degree of reaction (higher dissolution rate of the solid starting materials of the paste).

Next steps:
- Isothermal calorimetry of the AAMs at elevated ambient temperature.
- Temperature increase (semi adiabatic calorimetry) and shrinkage of the AAMs under sealed conditions, as expected in-situ.
- Adjustments of the hybrid cements with respect to the heat of reaction, chemical durability of the AAMs and hybrid cements (Ph.D. project).
THANK YOU FOR YOUR KIND ATTENTION