Impact of the Conditions of Ettringite Formation on Ternary Systems Performance

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Impact of the Conditions of Ettringite Formation on Ternary Systems

- Normally, calcium aluminat cement does not include sulfate and its derivatives.

- Addition of calcium sulfate or anhydrite to the calcium aluminate cement results C-A-H hydrate to the ettringite structure partially or totally.

- Range of ettringite formation may depend on amount of calcium sulfate.

- As a binder, ettringite has a strong and long-lasting structure.
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- Stability of ettringite depends on kinetic and thermodynamic parameters.

- These parameters:
  - Temperature,
  - Moisture,
  - Carbonation resistance,

- During the hydration process, matrix having low permeability follows a different way when compared with permeable matrix.

- Ettringite formation is crucial for repair mortars which are formed by minimum amount of water to produce flexible structure.
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- Ettringite hydration products in ternary systems have a strong effect on setting time.

- Generally high dosage of ettringite amount contributes to dimensional stability.

- However, too much amount of ettringite does not mean that this structure provides stability in all circumstances.

- Adjustment of water/ cement ratio and formulation is important for final products’ dimensional stability.
The formation of ettringite results from mixing CAC and calcium sulphate in the following way;

\[ 3CA + 3C\bar{s}H_x + (38 - 3x)H \rightarrow C_3A.3C\bar{s}.H_{32} + 2AH_3 \]

For anhydrite \( x=0 \), for hemihydrite \( x=0.5 \) and for calcium sulphate \( x=2 \)

If amount of calcium sulfate is far below the stochiometric ratio, non-reacted calcium aluminate reacts with ettringite and produces calcium monosulfoaluminate as seen below.

\[ 6CA + C_3A.3C\bar{s}.H_{32} + 16H \rightarrow 3C_3A.C\bar{s}.H_{12} + 4AH_3 \]
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- Formation of ettringite highly depends on solubility. The change in ettringite formation can be observed by two ways with the addition of lime.

- **With small lime addition**  ➔ By adding lime not exceeding dosage %3 in the total binder (CAC+Sulfate). There is still some aluminium ions in the solution and ettringite precipitation is strongly accelerated due to the large impact of the calcium concentration on the supersaturation value.
With high percentage of lime addition (e.g. %10) ➔ No alumina is observed in the bulk solution. Almost instantaneous precipitation occurs because all alumina available at the surface of the cement grains, reaction takes place here and it slows down further dissolution of the anhydrous phases. Therefore, the overall rate of reaction is significantly slows down.

** This situation indicates necessity to optimize of PC amount in ternary mix that includes lime
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- Figure indicates the composition ratio of two mixtures having different range of binders.

<table>
<thead>
<tr>
<th>Mortar Composition*</th>
<th>n1</th>
<th>n2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica Sand %</td>
<td>65,8</td>
<td>55,8</td>
</tr>
<tr>
<td>Hydraulic Binder %*</td>
<td>33,0</td>
<td>43,0</td>
</tr>
<tr>
<td>Lithium Carbonate%</td>
<td>0,1</td>
<td>0,1</td>
</tr>
<tr>
<td>Sodium Gluconate %</td>
<td>0,1</td>
<td>0,1</td>
</tr>
<tr>
<td>Water /Solid Ratio %</td>
<td>13,3</td>
<td>15,4</td>
</tr>
<tr>
<td>Water/Binder Ratio %</td>
<td>40,0</td>
<td>35,7</td>
</tr>
</tbody>
</table>

*n1 calcium sulfate alpha hemihydrate, n2 calcium sulfate beta hemihydrate
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- Calcium aluminate cement, calcium sulfate and portland cement limits are indicated in figure below.

<table>
<thead>
<tr>
<th>Binder Composition</th>
<th>CAC</th>
<th>Calcium Sulfate</th>
<th>PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max, %</td>
<td>75</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>Min, %</td>
<td>49</td>
<td>15</td>
<td>35</td>
</tr>
</tbody>
</table>
As seen in figure, we maximize the strength when we increase simultaneously the calcium sulfate and portland cement in the binder composition.

At a given Plaster/ CAC ratio, for a small portland cement addition, first there is a slight improvement of the strength, but if portland cement addition is continued, then we get a decrease or almost no effect.
As shown in figure, the plaster/CAC ratio has a direct impact on the amount of ettringite formed at 28 days.

Increase in the plaster/CAC ratio results in an increase in strength and amount of ettringite formation.
This figure shows that the portland cement rich mortars contain less $\text{AH}_3$ in their microstructure after 28 days, which is consistent with the theoretical mechanisms defined by hydration reaction equations.
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<table>
<thead>
<tr>
<th>n</th>
<th>CAC, %</th>
<th>Calcium Sulfate, %</th>
<th>PC, %</th>
<th>Ettringite*DS C, J/g</th>
<th>Compressive Strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75</td>
<td>25</td>
<td>0</td>
<td>102</td>
<td>89.5</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
<td>20</td>
<td>5</td>
<td>106</td>
<td>92.7</td>
</tr>
<tr>
<td>3</td>
<td>63</td>
<td>25</td>
<td>13</td>
<td>132</td>
<td>95.1</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td>145</td>
<td>39</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>15</td>
<td>35</td>
<td>130</td>
<td>81.4</td>
</tr>
</tbody>
</table>
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- From the compositions given in figure, we confirm that the highest ettringite content results from highest plaster+ portland cement dosages.

- There are some cracking observed on the hardened samples. These microcracks are propably due to expansion resulting from the formation of large amount of hydrates in a dense microstructure.
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Conclusions

According to the results in this research;

- Theoretical model used for formation of ettringite explains the observations made when designing mortars based on binder compositions. Because of close relationship between formation of ettringite and setting time & workability, it is too important to make optimization according to rate of formation and amount of it.

- Different amount of binder compositions provide wide range of usage properties such as rapid setting and hardening, rapid drying, size variation control, final strength in the most demanding applications.
We highlight the key role of both calcium sulfate /calcium aluminat cement ratio and the portland cement content on the ettringite capacity and as a consequence on the final performance of the mortar. But too much portland cement (eventually hydrated lime) increase the probability to make calcium monosulfoaluminate and in some cases may only give a poor strength development.
For Further Information…

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