Expansive Binders in the Portland Cement - Calcium Aluminate Cement - Calcium Sulfate System

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The volume increase during the hardening of expansive binders in the Portland cement - calcium aluminate cement - calcium sulfate system is conditioned by a careful correlation between the ettringite formation and the evolution of the hardening structure. The volume change and mechanical characteristics of this type of binders are influenced by parameters such as: the composition and fineness of the components, portland cement/expansive admixture and calcium sulfate/calcium aluminate cement ratios, the nature of the calcium sulfate source and the curing conditions. This paper presents the influence of the components dosage on the kinetics of the hydration processes and on the nature and quantity of formed hydrates, as well as on the volume change and hardening processes of expansive cement. The portland cement/expansive addition ratio used in this project was in the range of 75/25...85/15 and the calcium sulfate/calcium aluminate cement between 0.55 and 0.80. The calcium sulfate source was natural gypsum as well as anhydrite obtained by gypsum calcination for 4 h at 400°C. A good correlation was observed between the volume increase and the mechanical properties of the investigated expansive binders. The initial curing of the specimens in water (2 days) followed by 4 days of curing in humid atmosphere (R.H. 85%) determines a bigger volume increase as compared to the samples cured 6 days in humid atmosphere. The expansive binders with anhydrite content develop higher mechanical strength and permit an easier control of the expansive processes as compared to those containing gypsum.

Keywords: expansive binders, calcium sulfate, ettringite, hydration and hardening

The shrinkage of the hardened cement or concrete may represent a major disadvantage for special applications such as railroads, highway and subway tunnels, mine galleries or pipe swears. Therefore, expansive and shrinkage compensating cements are generally used with good results for this type of special applications. This type of cements is also used for the production of prestressed concrete elements with positive economic effects – suppression of the pre-tension of reinforcement prior to concrete casting.

The expansive and shrinkage compensating cements can be classified as unitary cements (such as sulfoaluminate cements) or blended cements which contain Portland cement (main component) and expansive admixtures (usually mixtures of calcium aluminate cement and calcium sulfate). The expansion is determined by the formation of ettringite - 3CaO.Al2O3.3CaSO4.31H2O [1-6].

In order to obtain expansive cement of good quality it is compulsory to correlate the speed of the hydration and hardening processes of Portland cement with the expansive agent (ettringite) formation, in the first 3-7 days. The speeds of these two processes may be influenced by the composition and fineness of binder’s components, through the solubility of the compounds from which the ettringite is formed, especially of the materials containing AlO and CaSO, as well as the curing conditions – humidity and temperature [7-10].

The main objective of the research work presented in this paper was to asses the influence on the hydration, hardening and expansive processes of several parameters such as: expansive mixture/Portland cement and calcium sulfate/calcium aluminate cement ratios and nature of calcium sulfate – gypsum or anhydrite.

Experimental part
Two types of normal Portland cements (P1 and P2) and calcium aluminate cement (CAC) with the main characteristics presented in table 1 were used. As source for calcium sulfate, gypsum (96.5% CaSO4.2H2O) and anhydrite (95.58% CaSO4) were used. The anhydrite was obtained by the calcination of gypsum at 400°C for 4 h.

The binders were obtained by the dry mixing in a laboratory ball mill (Pulverisette) of the Portland cement, calcium aluminate cement and gypsum or anhydrite. The binders were denominated as follows: P1 or P2, depending on the Portland cement composition (table 1) and G for gypsum or A for anhydrite admixtures. The gypsum and anhydrite dosage was performed according to their content in anhydrous CaSO4. The values of expansive admixture/Portland cement ratio were in the range 15/85..25/75 and for calcium sulfate/CAC ratio in the range 0.55...0.8.

The hydration processes were assessed by TG&DTG and XRD analysis, on pastes with a water to binder ratio of 0.4. The development of the hardening structure was assessed by compressive strength tests on micro specimens (15x15x60 mm³) of mortar with binder/aggregate = 1/3 and water/binder=0.5, compacted by vibration (2 min). The mortar specimens were cured the first 24 h in the mould, followed by two alternative curing methods:
- 6 days in humid atmosphere (R.H. =85%) followed by dry curing (in air);
- 2 days in water, the next 4 days in humid atmosphere R.H. =85% followed by dry curing (in air).

The length changes of the mortar specimens at different ages were assessed by length measurement using an electronic micrometer.

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Table 1
MAIN CHARACTERISTICS OF PORTLAND CEMENTS AND CALCIUM ALUMINATE CEMENT

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Portland cement (P1)</th>
<th>Portland cement (P2)</th>
<th>Calcium aluminate cement (CAC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L.O.I. %</td>
<td>-</td>
<td>0.14</td>
<td>0.78</td>
</tr>
<tr>
<td>SiO₂, %</td>
<td>21.03</td>
<td>20.77</td>
<td>6.80</td>
</tr>
<tr>
<td>Al₂O₃, %</td>
<td>4.59</td>
<td>6.35</td>
<td>53.42</td>
</tr>
<tr>
<td>Fe₂O₃, %</td>
<td>3.55</td>
<td>3.88</td>
<td>10.11</td>
</tr>
<tr>
<td>CaO, %</td>
<td>62.42</td>
<td>65.03</td>
<td>28.56</td>
</tr>
<tr>
<td>MgO, %</td>
<td>1.31</td>
<td>1.90</td>
<td>0.70</td>
</tr>
<tr>
<td>Na₂O, %</td>
<td>0.75</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>K₂O, %</td>
<td>0.80</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>SO₃, %</td>
<td>3.24</td>
<td>n.d.</td>
<td>0.10</td>
</tr>
<tr>
<td>Lime saturation factor LSF</td>
<td>0.89</td>
<td>0.96</td>
<td>-</td>
</tr>
<tr>
<td>C₃S, %</td>
<td>51.21</td>
<td>58.64</td>
<td>-</td>
</tr>
<tr>
<td>Specific surface area (cm²/g)</td>
<td>2595</td>
<td>3450</td>
<td>3287</td>
</tr>
</tbody>
</table>

Table data n.d. not determined

Results and discussions
The XRD analysis of pastes (water/binder = 0.4) hardened 1, 3, 7 and 28 days, shows the progressive consumption of the anhydrous phases and the formation of some crystalline hydrates – portlandite, ettringite and solid solutions (3CaO.Al₂O₃.CaSO₄.12H₂O - 4CaO.Al₂O₃.13H₂O).

The influence of the value of expansive mixture to P1 Portland cement ratio on the formation of ettringite in binders with CaSO₄/CAC = 0.6 is presented in figure 1. As expected, the intensity of the 9.7 Å ettringite peak, increases with the increase of the expansive admixture content. The maximum value of the 9.7 Å ettringite peak is achieved after 3 days of hydration and corresponds to the disappearance of gypsum XRD peaks. Forwards the intensity of the XRD ettringite peaks decreases and the patterns of sulfataminate hydrate solid solutions appear on the diffractograms.

The influence of the value of the CaSO₄/CAC ratio, for compositions with expansive admixture/Portland cement ratio = 20/80, is presented in figure 2. For the sample with CaSO₄/CAC = 0.65 the highest value of the intensity of ettringite XRD peak (9.7 Å) is recorded after 7 days of hydration; meanwhile, for the samples with smaller values of this ratio the maximum value of the intensity was recorded after 3 days. This delay in the process of ettringite formation is due to the increase of the sulfate content in the samples with higher values of the CaSO₄/CAC ratio.

For the specimens with P1 Portland cement, characterized by a smaller specific surface area (2595 cm²/g) and lime saturation factor (0.89) as compared with the P2 cement, the increase of the CaSO₄/CAC ratio from 0.55 to 0.65 determines only small alterations of the amount of formed ettringite. For the composition with CaSO₄/CAC = 0.6 prepared with P2 cement (LSF = 0.96 and specific surface area of 3450 cm²/g) the intensity of the ettringite XRD peak is sensible higher and recorded already after 1 day of hydration. The smaller fineness of the P1 cement (as compared with P2) and the smaller amount of C₃S (the main compound which by hydration forms Ca(OH)₂) determines, at a first sight, a slower development of the hydration processes. This behaviour suggests a more important influence of the low Ca(OH)₂ content as compared with the CaSO₄/CAC ratio on the ettringite formation, in the initial stage of hydration.

The influence of the sulfate source (anhydrite or gypsum) on the intensity of ettringite XRD peak (9.7 Å) is presented in figure 3 and 4. The lower solubility of anhydrite (as compared with gypsum) reduces the rate of the ettringite formation process; thus the higher value of the intensity of ettringite XRD pattern from 9.7 Å is recorded after 3-7 days of hydration for compositions with anhydrite and after 1-3 days for the compositions with gypsum.

The diagrams presented in figure 3 and 4 suggest different relationships between the ettringite formation process and the value of CaSO₄/CAC ratio vs. hydration time.

In the first 24 h of hydration, the increase of the calcium sulfate content delays the hydration-hydrolysis processes of Portland cement and consequently hinders the formation of ettringite. After longer hydration times (3, 28 days) the
increase of the CaSO4/CAC ratio favours the formation of greater amounts of ettringite in the specimens.

The evolution vs. time of the Ca(OH)2 content (determined from the mass loss recorded on TG curves between 440-530°C) of pastes based on Portland cement P2 and different values of CaSO4/CAC ratio is presented in figure 5.

For the same value of CaSO4/CAC ratio, the amount of Ca(OH)2 formed in the pastes hydrated 1 and 7 days, is higher for the compositions with anhydrite as compared with those containing gypsum. After 28 days of hydration the difference becomes irrelevant. This evolution is in good agreement with the smaller delaying effect on the Portland cement hydration process induced by anhydrite as compared with gypsum, as well as the smaller rate of the ettringite formation process in the anhydrite compositions [11].

The influence of the value of expansive admixture to Portland cement ratio on the amount of chemically bound water in hydrates, for compositions with CaSO4/CAC=0.6, is shown in figures 6-8.

The amount of chemically bound water in Ca(OH)2 increases with the increase of the Portland cement amount in the studied compositions, opposite to the chemically bound water in other hydrates (ettringite, AFm and C-S-H) that increases with the increase of the expansive admixture amount. This correlation is more important at early ages (1 day) but is still noticeably after 7 days of hydration and suggests a predominance in a first stage of the process of ettringite formation over the calcium silicates hydration. After 28 days of hydration (fig.8), the amount of chemically bound water in hydrates is quasi-similar and the influence of the expansive admixture/Portland cement ratio can be noticed only for Ca(OH)2.

The compressive strength values assessed on specimens based on P1 Portland cement are presented in figure 9. The increase of the CaSO4/CAC ratio determines, in general, increases of compressive strength. For CaSO4/CAC = 0.55, the compressive strength increases with the increase of the Portland cement amount. For higher values of the CaSO4/CAC ratio (0.60 and 0.65) the higher values of compressive strength are achieved in the binders with 20% expansive admixture.

The influence of the nature of the calcium sulfate source (gypsum or anhydrite) on the compressive strength development of expansive binders with P2 Portland cement, is presented in figure 10 and 11. As it can be seen, for the binders with gypsum (fig. 10) the increase of the CaSO4/CAC ratio determines a small increase of the compressive strength values at early ages (1 day). On the contrary, at longer curing times, the increase of the CaSO4/CAC ratio reduces the compressive strength values, especially for values over 0.7. The maximum value of the compressive strength in the systems with anhydrite (fig. 11) is achieved for the composition with CaSO4/CAC ratio of 0.65. For similar CaSO4/CAC ratios, the expansive binders with anhydrite have higher compressive strength as compared with those containing gypsum.
Length changes (measured on the longer side of the mortar prisms -15x15x60 mm\(^3\)) are presented in figure 12. Length changes are the result of two opposite processes:
- an expansion process determined by the ettringite formation in the system;
- a contraction process determined by the drying shrinkage of mortar.

The magnitude of these two processes is influenced by the value of CaSO\(_4\) to CAC ratio, type of calcium sulfate source, value of expansive admixture/Portland cement ratio, Portland cement characteristics and curing conditions [1, 5,11,12].

The influence of the Portland cement characteristics on the length changes, presented in figure 12 for compositions with CaSO\(_4\)/CAC = 0.60, shows a good correlation between the ettringite formation process and length changes.

P1 cement with a lower value of the specific surface area and smaller C. S content (as compared with cement P2) has a slower rate of hydration, therefore the amount of ettringite formed at early ages is small (fig. 2). For compositions with CaSO\(_4\)/CAC ratio 0.55, after an initial expansion (recorded after 3-7 days of hardening) the specimens length (volume) decreases. For the compositions with higher values of the CaSO\(_4\)/CAC ratio (0.60 and 0.65), the specimens length increases, due to the expansive process, are more important as compared with the contraction phenomena; therefore the final deformation of the specimens is expansion.

The influence of the CaSO\(_4\)/CAC ratio and calcium sulfate source (gypsum-G or anhydrite-A) on the length changes of mortar specimens based on Portland cement P2 is presented in figure 13.

As expected the mortar specimen expansion increases with the increase of the sulfate content in the expansive binder; it has to be noted that even for CaSO\(_4\)/CAC = 0.8 the sulfate content is not sufficient for the complete conversion of the calcium aluminate phases in ettringite. The more important length changes recorded for the binders with gypsum as compared with those containing the same amount of anhydrite can be explained by the higher solubility of gypsum (fig. 3 and 4).

The influence of the expansive admixture/Portland cement ratio on the length changes of the mortar specimens, is presented in figure 14, for binders with P1 with expansive admixture/Portland cement = 0.6, shows a good correlation between the ettringite formation process and length changes.
The influence of Portland cement characteristics (P1 and P2) on the length changes (ΔL) of mortar specimens based on binders with expansive admixture/Portland cement ratio of 20/80 and CaSO4/CAC ratio in the range 0.55-0.65, cured in humid atmosphere.

The influence of CaSO4/CAC ratio and sulfate source on the length changes (ΔL) of mortar specimens based on P2 Portland cement. The correlation between these two parameters is almost linear.

The curing in water for 2 days of the mortar specimens (after demoulding) favors the ettringite formation (hydrate with a high amount of crystallization water) as well as the hydration process of Portland cement (fig. 15).

The decrease of the value of expansive admixture/Portland cement ratio increases the magnitude of the second process (hydration and hardening of Portland cement) and specimens contraction is recorded after 28 days. For the specimens with higher values of expansive admixture/Portland cement ratio a higher quantity of ettringite is formed and the expansion phenomenon determines the specimens destruction.

Conclusions

The main hydrates formed at the hardening of expansive binders in the Portland cement-calcium aluminate cement–gypsum/anhydrite system are: ettringite, portlandite, C-S-H and solid solutions (3CaO.Al2O3.CaSO4.12H2O – 4CaO.Al2O3.13H2O).

The rate of ettringite formation is higher in the compositions with gypsum as compared with those containing anhydrite.

For the specimens with gypsum content, the maximum amount of ettringite is formed after 1-3 days and for the specimens with anhydrite after 3-7 days.

The amount of hydrates formed depends on the characteristics of the components (portland cement composition and fineness, calcium sulfate source) and dosage, as well as the curing conditions.

The increase of the calcium sulfate content has a delaying effect on the hydration process at early ages (first day); this effect is more important for the compositions with gypsum, as compared with those containing anhydrite, and modifies also the rate of ettringite formation; for longer hydration times the increase of the CaSO4/CAC ratio favours the formation of bigger amounts of ettringite.

The length (volume) changes of the mortar specimens at different ages are in good correlation with the amount of different type of hydrates formed. The higher values of the expansion were recorded for the binders with gypsum content (as compared with those of anhydrite) and are due to its higher solubility and consequently the formation of a bigger amount of ettringite.

The compressive strength increases, in general, with the increase of portland cement content; the increase of calcium sulfate amount in the expansive admixture decrease the strength values developed after 1-3 days of hydration.

References

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