Blended lime-cement mortars for conservation purposes: Microstructure and strength development

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ABSTRACT: Blended lime-cement mortars are commonly used in conservation practices even though they may show lack of adequate strength and durability for certain cement-lime compositions. This paper focuses on understanding the hardening reactions and their influence on the strength development, microstructure and porosity for the cement-lime mortars in various compositions. Mortars composed of 30%, 50% and 70% cement replacement with lime hydrate and lime putty by mass were studied. Cement hydration has been found to contribute to the early stage strength development while carbonation is mostly favoured after 3 days and contributes to the strength development until 180 days. The degree of carbonation is much more pronounced with increasing lime content and porosity of the mortars and the reaction is still in progress at 90 days. All the blended mortars revealed lower compressive and flexural strength than that of the reference cement mortar due to their lower cement content and higher porosity. Long-term compressive strength development has been achieved after 180 days while flexural strength for certain mortar compositions does not increase beyond 28 days. Unlike cement mortar, the mortars blended with lime hydrate and lime putty exhibit an elastic-plastic deformation before failure occurs, which is preferred for repair mortars to adapt to differential settlements and to allow more deformation under critical stresses in the masonry.

1 INTRODUCTION

Since ancient times, lime based binders such as high calcium lime, lime with pozzolana and hydraulic lime have been successfully used in construction and have proven their long-term durability. Towards the end of the 19th century, development in the building industry and increase in the construction needs encouraged the search for stronger mortars with more rapid hardening. This eventually induced the development of the Portland cement which became a dominant binder in the construction industry after that period. This has inevitably led to the replacement of lime based binders with the cement in conservation practices, which has resulted in serious damaging mechanisms related to the incompatibility of cement in chemical, physical and mechanical properties when used together with ancient building materials. There exist evidences that stronger mortars can reduce the durability of the masonry whereas mortars with low compressive strength like lime mortars can increase the durability of the masonry in the long-term (Van Hees et al., Van Balen et al. 2005). In spite of this, addition of cement to lime based mortars is still a common practice in most of the conservation works in order to promote the hardening reaction by cement hydration, to shorten the construction time and to increase the strength of the mortar. However, certain mortar compositions with lime and cement may cause lack of strength development and durability. The main objective of this study is, therefore, to investigate the influence of the cement addition on the strength development, porosity and microstructure of the lime mortars, and to understand the hardening reactions. This will provide fundamental insight while defining the compatibility requirements for repair mortars.

Literature concerning the hydration of cement in the presence of additional lime is quite limited. Researches have been mainly devoted on understanding the influence of lime addition on the hydration of tricalcium aluminate (Collepardi et al. 1978, Kuzel & Pollmann 1991) as well as on porosity, microstructure and strength development of various cement-lime mortar compositions (Sebaibi et al. 2006, Mosquera et al. 1996).
Apart from cement hydration, carbonation reaction contributes to the strength development of the cement-lime mortars, which is generally neglected. Therefore, in this study special emphasis is given on understanding hardening reactions and their influence on the strength development, porosity and microstructure of the cement-lime mortars using lime hydrate and lime putty as a partial replacement of cement in varying ratios.

2 RESEARCH PROGRAMME

2.1 Materials

Portland cement (CEM I 52.5 N), commercial lime hydrate and lime putty were used as binders for mortars. The lime hydrate is composed of 83.22% calcium hydroxide content with a Blaine specific surface area of 19,464 cm²/g and a mean value of its particle size distribution of 4.40 µm. The lime putty was produced at the laboratory through slaking quicklime (0–50 mm) in 1:3 quicklime-water ratio. The putty was then stored in hermetically sealed containers to promote its aging under water. The lime putty used in the mortars was aged for one year and contained 60% water by mass. It is composed of 83.47% calcium hydroxide with a Blaine specific surface area of 21,739 cm²/g.

2.2 Mortar compositions

Cement was partially replaced by lime hydrate and lime putty in 30%, 50% and 70% by mass of the total binder (Table 1 and Table 2). Reference cement (C_ref), lime hydrate (L) and lime putty (LP) mortars were studied as well for the comparison of the data. The mortars were prepared using standard quartz sand with maximum grain size of 2 mm (EN 196-1). Binder/sand ratio of the mortars is 1:3 by mass. Due to higher specific surface area of calcium hydroxide particles than cement, more water was required in cement-lime hydrate and cement-lime putty mortars to reach similar workability (125–130 mm) with the reference cement mortar, which was measured by the flow table test (EN 1015-3). The water content increased with increasing lime content in the mortar composition. Considering the cement-lime putty mortars, additional water was required only for the C7LP3 and C5LP5 mortars as the water content available in the lime putty used was adequate to gain the required workability for the C3LP7 mortar.

2.3 Methods

Hardening of the mortars was studied using standard mortar prisms (40 × 40 × 160 mm) which were prepared in accordance with the European standard (EN 196-1). Mortars were cured at the standard laboratory conditions (20°C, 60% R.H.) for 180 days. The progress of hardening was studied by means of mechanical strength test and thermal analysis. The mechanical strength tests were carried out by compressive strength and three-point bending using the standard mortar prisms at 3, 7, 28, 60, 90 and 180 days of hardening (EN 196-1). For thermal analysis the mortar specimens were first gently ground in order to separate sand grains from the binder fraction and then vacuum dried at 0.025 mbar. After that, the sample was sieved through 112 µm sieve to obtain the binder fraction which was ground further for thermal analysis. This analysis was carried out using a Netzsch STA 409 PC DSC-TGA system in static nitrogen atmosphere at a temperature range between 20-1000°C with a controlled heating rate 10°C/min. Porosity of the mortars at 90 days has been studied with total porosity (EN 1936) and pore size distribution using Mercury Intrusion Porosimetry (Micromeritics AutoPore IV 9500). Microstructure of the mortars was studied using Philips XL 30S FEG Scanning Electron Microscope (SEM) coupled with X-Ray Energy Dispersive System. The analysis was carried out on the fresh fractured surfaces coated with gold after the samples were dried at 45°C.

3 RESULTS

3.1 Porosity

Bulk density and total porosity of the mortars are given in the Table 3, and their cumulative pore size
Table 3. Bulk density and total porosity of the mortars at 90 days.

<table>
<thead>
<tr>
<th>Mortar</th>
<th>Bulk density (g/cm³)</th>
<th>Total porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cref</td>
<td>2.19</td>
<td>16.78</td>
</tr>
<tr>
<td>L</td>
<td>1.86</td>
<td>28.72</td>
</tr>
<tr>
<td>LP</td>
<td>1.71</td>
<td>33.50</td>
</tr>
<tr>
<td>C7L3</td>
<td>2.05</td>
<td>18.50</td>
</tr>
<tr>
<td>C5L5</td>
<td>1.96</td>
<td>22.39</td>
</tr>
<tr>
<td>C3L7</td>
<td>1.87</td>
<td>27.21</td>
</tr>
<tr>
<td>C7LP3</td>
<td>1.98</td>
<td>19.19</td>
</tr>
<tr>
<td>C5LP5</td>
<td>1.81</td>
<td>28.23</td>
</tr>
<tr>
<td>C3LP7</td>
<td>1.70</td>
<td>35.18</td>
</tr>
</tbody>
</table>

Figure 1. Cumulative pore size distribution of the mortars.

distribution is given in the Figure 1. The bulk density decreases and the total porosity increases with increasing lime content in the mortars compositions.

Cement-lime hydrate mortars show a higher volume of pores with a diameter between 0.1 µm and 1 µm than those of the reference cement mortar (Figure 1). The volume of the pores within this diameter range increase with increasing lime content in the mortar composition. Volume of pores with a diameter less than 0.1 µm increased as well. Cement-lime putty mortars indicated higher volume of pores than the cement-lime hydrate mortars for the same percentage of cement replacement.

3.2 Hardening reactions by thermal analysis

The first derivative of the weight loss (DTG) recorded during thermal analysis of the reference cement mortar is represented in Figure 2. This technique allows following the progress of hydration and carbonation reactions qualitatively. Evolution in the peaks of hydrated phases can be seen at temperatures around 110°C due to the dehydration of the C-S-H phase and around 160°C due to the dehydration of the AFm phase. The peak observed at around 480°C indicates the decomposition of calcium hydroxide. Another peak recorded at temperatures between 600–800°C derives from the decomposition of the calcium carbonate.

In comparison with the hydration reaction of the reference cement mortar, DTG thermographs of the blended mortars are represented in Figure 3. Peaks observed are similar with those of the reference cement mortar with some differences in the intensities.

3.3 Mechanical strength of the mortars

Compressive and flexural strength development of the mortars is given in Figure 4 and Figure 5 respectively. While the reference cement mortar yielded the highest strength values at all stages, these values became lower as cement was partially replaced with lime hydrate and lime putty at 30%, 50% and 70% by mass respectively. Cement-lime hydrate mortars indicated higher strength values than the cement-lime putty mortars for the same amount of replacement. Their compressive strength values increased gradually until 180 days while no considerable increase was recorded after 28 days in the flexural strength of the C7L3, C5L5, and C7LP3 mortars.

Lime hydrate (L) and lime putty (LP) mortars yielded the lowest strength values of all blended mortars except for the C3LP7 mortar which has revealed flexural strength values lower than that of the LP mortar at all stages.

In Figure 6, stress-strain diagram obtained from the compressive strength testing of the reference cement mortar (C_ref) and cement-lime (C5L5) mortar at 90
days is given. Although these results are influenced by the set-up conditions of the testing machine to some extent, stiffness and deformation of the mortars can be estimated. The stiffness decreases with increasing lime content in the mortar composition. In comparison to the cement mortar, the cement-lime mortars reveal more deformation and withstand a measurable post-failure load before the failure occurs due to their plastic
behaviour. This particular behaviour is much more pronounced for the lime mortars and cement-lime mortars with 70% lime content.

3.4 Microstructure

Partial replacement of cement by calcium hydroxide has led to the modification of the microstructure of the mortars to some extend. Reference cement mortar is characterized by a microstructure composed of reticular amorphous and needle-like C-S-H phase where calcium hydroxide crystals are locally embedded (Figure 7). The most distinguishing feature between the microstructure of the reference cement mortar and cement-lime mortars is the presence of calcium hydroxide crystals in the latter (Figure 8). They are present individually or as clusters embedded within the hydrated matrix. These calcium hydroxide crystals indicated corroded edges where amorphous C-S-H phase has precipitated subsequently and has grown towards the surrounding matrix (Figure 10 and Figure 11).

Plate-like crystals which probably belong to the AFm phase were observed locally in the hydrated matrix (Figure 9). With increasing lime content in the mortar composition, less amorphous C-S-H phase is observed and the microstructure becomes more porous with more calcium hydroxide crystals, plate-like crystals and needle-like crystals (Figure 12).

4 DISCUSSION

Partial replacement of cement with lime hydrate and lime putty has resulted in lower compressive and
Figure 11. A detailed SEM micrograph showing the formation of amorphous C-S-H on the edges of the calcium hydroxide crystals.

Figure 12. SEM micrograph of the hydrated matrix of the C3L7 cement-lime hydrate mortar at 90 days.

Flexural strength values for the blended mortars in comparison with the strength of the reference cement mortar (Figure 4 and Figure 5). Strength values become lower respectively with 30%, 50% and 70% replacement of cement with lime hydrate and lime putty by mass. This is related with both decreasing cement content and increasing water/binder ratio in the composition of these blended mortars, which has resulted in an increase in their porosity. With decreasing cement content and increasing calcium hydroxide content, an increase in the volume of pores with diameters less than 1 µm is observed (Figure 1). C3L7 and C3LP7 mortars, which have 70% replacement of cement with lime hydrate and lime putty, revealed total porosity values that are very close to the porosity values of the L and LP mortars respectively. The cement-lime putty mortars revealed higher porosity than that of the cement-lime hydrate mortars for the same amount of replacement. This can explain their lower strength values than those of the cement-lime hydrate mortars. Considering C3LP7 mortar having 70% cement replacement with lime putty, increase in the volume of pores is much more pronounced than the rest of the mortars especially for the pore diameters between 10 µm and 0.6 µm as well as those less than 0.3 µm.

30% replacement of cement with lime hydrate has resulted in 38.4% reduction in the compressive strength of the reference cement mortar while it is 56.3% reduction in case of replacement with lime putty at 180 days. The reduction in the flexural strength is 23.6% for cement-lime hydrate mortar and 46.8% for the cement-lime putty mortar. Further replacement of the cement at 70% has led to extremely lower compressive and flexural strength values. This is much more pronounced for C3LP7 mortar as its flexural strength value (0.45 N/mm²) is even lower than that of the LP mortar (0.8 N/mm²). Therefore, the mortar composition with 30% cement and 70% lime putty does not improve the strength of the mortar in comparison with the LP mortar. This is not the case for C3L7 mortar as it has higher compressive and flexural strength values than those of the L mortar and LP mortar but quite lower than those of C5L5 and C7L3. However, its compressive strength does not increase beyond 60 days as well as its flexural strength beyond 28 days.

Thermal analysis results indicated that hardening reactions responsible for the strength development of the blended mortars are cement hydration and carbonation reaction (Figure 3). The latter is expected due to the presence of additional calcium hydroxide in the mortar compositions from the beginning. This is clearly seen in the DTG thermographs with the increase in the intensity of the calcium carbonate peak at temperatures between 600°C and 800°C. Degree of carbonation increases in time and with increasing calcium hydroxide content in the mortar composition as well as increasing porosity which favours the diffusion of the carbon dioxide into the core where calcium hydroxide is still present to carbonate (Van Balen & Van Gemert 1994). Cement hydration is mostly complete within 28 days as the intensity of the peaks of the hydrated phases does not increase beyond that period. These phases are C-S-H and AFm which are the same with those of the reference cement mortar. The presence of these phases has been verified by SEM analysis. Microstructure of the reference cement mortars is composed of reticular amorphous and needle-like C-S-H phase where calcium hydroxide crystals are locally embedded (Figure 7). Hydrated microstructure of the blended mortars is characterized by clusters of calcium hydroxide crystals that are surrounded by amorphous C-S-H phase (Figure 8) and locally formed AFm crystals (Figure 9). These calcium hydroxide crystals indicated corroded edges where amorphous C-S-H phase formed subsequently.
(Figure 10 and Figure 11). With increasing lime content in the mortar composition, the microstructure becomes more porous with less amorphous C-S-H phase and more calcium hydroxide crystals as well as hexagonal plates and needles (Figure 12). These plate-like and needle-like crystals are assumed to belong to the AFm phase due to the peak observed at around 160°C in the DTG thermographs (Figure 3).

In the literature, hexagonal hydro-aluminate plates were reported to be formed during the hydration of the tri-calcium aluminate in the presence of lime (Collepardi et al. 1978, Taylor 1990). Their formation in our mortar compositions is not clear from the DTG thermographs as the hexagonal hydro-aluminates reveal dehydration peaks between 100°C and 200°C, which is the same dehydration range for the C-S-H and AFm phases, and therefore their presence can be masked.

With decreasing cement content in the mortars composition less hydrated phases and more calcium carbonate phase are observed (Figure 3). At 3 days of hardening, hydrated phases can already be seen in the thermographs but the peak of the calcium carbonate evolves in time. This shows that the cement hydration takes place at the very early stage while the carbonation reaction becomes effective after 3 days and continues until 90 days. Therefore, the cement hydration contributes to the early stage strength development until 28 days. In the meantime, carbonation reaction continues and contributes to the strength development until 90 days. This is quite clear from the compressive strength development of the mortars but the flexural strength of all cement-lime hydrate mortars and only C7LP3 mortar does not increase beyond 28 days.

In comparison to the reference cement mortar, stiffness decreases with increasing lime content in the composition of the blended mortars, which enhances their physical and mechanical compatibility with ancient mortars. The cement-lime mortars indicated a reasonable plastic behaviour and more deformation than the reference cement mortar. Similar to the self-healing ability of lime mortars, cracks occurring due to the deformation can be healed by either dissolution precipitation cycles of calcite or carbonation reaction of the calcium hydroxide that is still available in the matrix. However, the influence of formation of calcium carbonate crystals on the initially hydrated phases and its consequence on the strength development and durability of the blended mortars should be considered well.

5 CONCLUSIONS

Hardening of the cement-lime mortars occurs as a result of combined cement hydration and carbonation. Cement hydration contributes to the early stage strength development while carbonation is mostly favoured after 3 days and proceeds gradually until 180 days. Degree of the carbonation is much more pronounced with increasing lime content and porosity of the mortars. The cement-lime mortars have revealed lower compressive and flexural strength than the reference cement mortar due to lower cement content and higher porosity of the blended mortars. Long-term compressive strength development has been achieved after 180 days while flexural strength for certain mortar compositions does not increase beyond 28 days. Further replacement of the cement at 70% with lime putty does not improve the strength of the mortar in comparison with the LP mortar while this is not the case when lime hydrate is used. Unlike the reference cement mortar, the cement-lime mortars exhibit an elastic-plastic deformation which enables them to adapt to differential settlements and more deformation under critical stresses in the masonry. Considering the mortar compositions and hardening reactions, compatibility of the lime-cement mortars should be further evaluated in terms of physical, mechanical and durability requirements for conservation purposes.

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REFERENCES


