Lime Addition Effect on Corrosion of Reinforced Mortar

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ABSTRACT

This study aims to investigate the effect of lime addition in cement mortar on corrosion resistance of carbon and galvanized steel reinforcements. Mixed mortars were studied containing three contents of lime (6.7, 13.3, and 26.3 wt.%). The water retention, incorporated air, and compression strength of reinforced mortars were determined. Immersion tests were performed using the reinforced mortars consisting of 12 cycles of immersion in a solution of 3.5% (wt/v) sodium chloride and drying in a stove at 60°C. Electrochemical impedance spectroscopy was used to monitor reinforcement corrosion after cyclic tests. These measurements were repeated after 36 months of the cyclic immersion testing. After the cyclic immersion tests in a saline solution, the polarization resistance of carbon and galvanized steel reinforcement increased as the lime content in mortar increased, demonstrating the protective effect of lime. After 36 months, the polarization resistance of steels in mixed mortars with the highest lime content was the lowest. For the carbon and galvanized steel in cement and mixed mortars, the polarization resistance increased after 36 months of the cyclic test.

Keywords: Lime. Mortar. Reinforcement corrosion. Electrochemical impedance spectroscopy.

1. INTRODUCTION

Studies focusing on materials used in Cultural Heritage conservation projects are increasingly relevant [1-3]. Heritage buildings have been built with mud/clay bricks and lime-based mortars since quite early historical times, as confirmed by traces of ancient constructions in Palestine and Turkey dating back to 12,000 B.C [1]. Autogenous self-healing in lime-based mortars is a well-known phenomenon related to the deposition of calcite in cracks in mortars with high lime content [1]. Aerial lime-based mortars are recommended by many experts to restore the ancient buildings due to their compatibility with ancient building materials [4]. The lime–cement mortars could reduce the disadvantages presented by both lime-based mortars and cement-based mortars [5,6]. García-Cuadrado et al. [7] studied the fracture behaviour of lime–cement masonry mortars prepared with various fractions of lime and cement. One possibility that has arisen with the use of mixed mortar is related to the effect of lime addition on the corrosion resistance of the reinforcement. The reinforcement corrosion depends on the concrete–reinforcement interfacial condition which depends on the mortar used [8].

Sébaïbi et al. [9] studied the effect of various slaked limes on the microstructure of a lime–cement–sand mortar. Several papers are found about admixtures and properties of lime-based mortars [10-15]. However, on our best knowledge, literature about corrosion resistance of carbon and galvanized reinforcements in a mixed mortar is scarce.

Thus, this study aims to investigate the effect of adding lime in mortar, seeking thus greater resistance to corrosion of reinforcing carbon and galvanized steel associated with an economic feasibility. The technique of electrochemical impedance spectroscopy was used to evaluate the corrosion resistance of reinforcements after partial immersion tests in a saline environment. After three years of the immersion tests, new electrochemical tests were performed to evaluate the effect of time on the reinforcement corrosion.
2. MATERIALS AND METHODS

The mortars were prepared according to the composition shown in Table 1. The CPIII 40 RS cement (sulfate resistant and with addition of a blast furnace slag), which showed a compression strength of 45 MPa at 28 days, CH-I hydrated lime which consists of calcium and magnesium hydroxides, and quartz sand were utilized. The characterization of hydrated lime provided by manufacturer is shown in Table 2. The galvanized steel shows a 366 g/m² of zinc (51µm of thickness). The carbon steel CA-50 showed yield strength of 500 MPa. The reinforcements were covered with electrical tape and leaving a length of 5 cm uninsulated inside the prismatic specimen. The exposed area of reinforcement in mortar was 7.854 cm². The exposed ends of the armour were sealed with tape.

The water/cement ratio was determined for the consistency of 260 ± 5 mm, and the tests with started with a content of 16 wt.% of water of the total weight of solids, for each mixture (Table 1).

Table 1: Composition of samples

<table>
<thead>
<tr>
<th>Mortar</th>
<th>Trace (wt.% of cement, lime, sand)</th>
<th>Lime concentration (wt.%)</th>
<th>Water/cement ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>High content of lime</td>
<td>1:2:5:6</td>
<td>26.3</td>
<td>2.67</td>
</tr>
<tr>
<td>Medium content of lime</td>
<td>1:1:6</td>
<td>13.3</td>
<td>1.62</td>
</tr>
<tr>
<td>Low content of lime</td>
<td>1:0.5:6</td>
<td>6.7</td>
<td>1.35</td>
</tr>
<tr>
<td>Without lime</td>
<td>1:0:6</td>
<td>0</td>
<td>1.31</td>
</tr>
</tbody>
</table>

The wires of a carbon or galvanized steel with a diameter of 5.00 mm were used. The identification of moulds according to the mixture and the type of frame was made considering the lime content: H (high), M (medium), L (low), W (no lime) and the type of armour: G (galvanized), A (carbon steel). The characterization of hydrated lime is shown in Table 2.

Table 2: Characterization of hydrated lime

<table>
<thead>
<tr>
<th>Characterization</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total non-volatile base oxides</td>
<td>≥ 90%</td>
</tr>
<tr>
<td>Insoluble waste</td>
<td>≤ 8%</td>
</tr>
<tr>
<td>Total not-hydrated oxides</td>
<td>≤ 10%</td>
</tr>
<tr>
<td>Moisture</td>
<td>≤ 0.5%</td>
</tr>
<tr>
<td>Retained on # 30 sieve (0.600 mm) sieve</td>
<td>≤ 0.5%</td>
</tr>
<tr>
<td>Retained on #200 sieve (0.075 mm)</td>
<td>≤ 10%</td>
</tr>
<tr>
<td>Water retention</td>
<td>≥ 75%</td>
</tr>
<tr>
<td>Incorporation of sand</td>
<td>≥ 3%</td>
</tr>
<tr>
<td>Plasticity</td>
<td>≥ 110%</td>
</tr>
</tbody>
</table>

2.1 Water retention

A cylindrical cast steel (100 mm in diameter and 25 mm in height - internal measures) was weighed with a resolution of 0.1 g (mass registration: Mm). Similarly, 12 dry filter paper discs (85 g/cm² and 110 mm diameter) were weighed with a resolution of 0.01 g (mass registration: Mse). The mould was filled with mortar (using a spatula) into ten layers to form a small excess (subsequently crushed by the blade of the spatula). Moulds with mortar were weighed with a resolution of 0.1 g (mass registration: Mma). Under the surface of the mortar two gauze screens (surgical type, with 110 mm edge), the set of 12 filter paper disks and a rigid plate (110 mm diameter, 5 mm thick, one face having machining smooth) were placed. Subsequently, a weight of 2 kg (consisting of metal solid cylinder with 110 mm diameter) was placed on the rigid plate. After 2 minutes of application of the load, the weight of 2 kg and the rigid board were removed. The set of filter papers were removed and immediately weighed in the balance with a resolution of 0.01 g (mass registration Mf). The amount of water retention ratio was calculated by the following equation:
Ra = \[1 - (M - M_{\text{se}}) \times \frac{100}{AF (M_{\text{ma}} - M_{\text{m}})}\]  

Where:
- Ra: water retention
- AF: factor water / fresh mortar: \(AF = \frac{M_{\text{w}}}{M + M_{\text{w}}}\)
- M_{\text{w}}: total mass of water added to the mix in g
- M: mortar mass industrialized or mass sum of the anhydrous components in the case of work mortar, g
- M_{\text{se}}: mass of the dried disc in g
- M_{\text{ma}}: mass of the mould with mortar in g
- M_{\text{m}}: mass of the empty mould in g

### 2.2 Incorporated air

For determination of entrained air content, the most common method used is based on Boyle’s law for determining the air content by the ratio of pressure and volume at a given temperature (manometric method). In this method, the employee meter comprises a measuring hood and a sealing system. Its principle of operation consists in introducing water to a certain height on the known volume sample of mortar and applying a predetermined air pressure by means of a small pump on the water. The determination consists in reducing the air volume of the mortar sample, by observing the amount of water penetrating under the applied pressure, and this amount is calibrated in terms of the percentage of air voids in the mortar sample. Thus, the device directly provides the air volume of the sample.

### 2.3 Compression strength

Four cylindrical specimens (5 cm x 10 cm) by age with freshly prepared mortar having the pattern consistency index were prepared. The specimens were kept for 48 hours in the mould (in a humid chamber with a relative humidity of 95%) and then demoulded; samples were immersed in water (inside the camera) to the age of the test (except in the case of mortars with lime that after demoulded were kept outdoor lab until the age test). Prior to the compression test, the specimen was capped with Sulphur and its diameter was measured with callipers in two orthogonal positions in its middle third, recording the average in millimetres. After the axial rupture test, specimens were press-calculated individual resistance (each sample breaking load divided by the area of the sample section, expressed in MPa) and the average strength (average of individual resistors, expressed in MPa).

### 2.4 Electrochemical measurements and immersion tests

The open circuit potential was measured using the samples as received (after 12 hours immersion in water), and after 12 cycles of immersion in a saline solution and drying. The equipment used was the Omnimetra PG-29, the reference electrode was Ag/AgCl, and the counter electrode was an austenitic stainless-steel plate. Immersion tests were performed consisting of 12 cycles of immersion in a solution of 3.5 (wt./v)\% of NaCl and drying in a stove at 60°C. In each cycle, the sample was partially immersed in a saline solution for two days and dried in a stove at 60°C for five days. The measurement was performed after the immersion stage.

Electrochemical Impedance Spectroscopy (EIS) was performed immediately after the immersion tests, using a AUTOLAB 30 potentiostat, and the data acquired by the FRA for Windows v. 2.3 of Eco Chemie B. V. The frequency range used was from 100 kHz to 10 mHz, with amplitude of 20 mV. These measurements were repeated after 36 months of immersion testing to determine the effect of time on the corrosion resistance of reinforcement. Measurements of open circuit potential and electrochemical impedance spectroscopy were repeated using the potentiostat Princeton Versastat 3. Data were acquired by using the VersaStudio software. The impedance results were treated using the ZsimpWin software.

For the characterization of corrosion products of reinforcements, X-ray diffraction was performed, using an Empyrean Philips - Panalytical diffractometer, CuKα radiation and graphite monochromator crystal. The analysis method relies on a comparison of the values of the interplanar spacing and intensities of the peaks in the diffractograms of the samples and a reference sample using the default PDF-2 database ICDD - International Centre for Diffraction Data. The pattern of the ICDD PDF-2 database used for the identification of crystalline phases was copper (Cu) - ICDD # 85-1326. The characterization of corrosion products was
performed after 12 cycles of the immersion and drying tests.

The finished diameter of the reinforcement was measured after 12 cycles of immersion and drying, immersing the sample in the pickling solution of 3.5 g of hexamethylenetetramine dissolved in 500 mL of hydrochloric acid (density = 1.19 g/cm³), and the volume made up to 1 liter. The pickling was performed for 10 minutes according to the ASTM G1-90 standard, using a hydrochloric acid solution 1:1 with 3.5 g/L hexamethylenetetramine. The reinforcements were washed with distilled water, dried and the diameter of wire was measured until constant value. The reduction of the reinforcement diameter is an auxiliary technique to evaluate the reinforcement corrosion.

3. RESULTS AND DISCUSSIONS

A higher water/cement ratio, as observed for the sample with higher lime content, tends to generate higher porosity and benefit from the entry of aggressive agents to the reinforcement steel and cement itself [16]. Lime mortars have higher water retention capacity than the cement mortar as shown in Table 3. This result is due to a higher fineness, high specific surface, and greater adsorption capacity of its particles of lime mortar with a formation of a gel on the surface of the particles up to 100% water depending on the particle volume [4].

Table 3: Incorporated air and water retention of mixed mortars

<table>
<thead>
<tr>
<th>Mortar Lime concentration (wt.%)</th>
<th>Water/cement ratio</th>
<th>Incorporated air (%)</th>
<th>Water retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High lime content (26.3)</td>
<td>2.67</td>
<td>3.4</td>
<td>96.6</td>
</tr>
<tr>
<td>Medium lime content (13.3)</td>
<td>1.62</td>
<td>4.2</td>
<td>98.3</td>
</tr>
<tr>
<td>Low lime content (6.7)</td>
<td>1.35</td>
<td>5.8</td>
<td>98.8</td>
</tr>
<tr>
<td>Without lime (0)</td>
<td>1.31</td>
<td>6.1</td>
<td>91.4</td>
</tr>
</tbody>
</table>

Lime mortars showed lower values of incorporated air than the cement mortar. Carvalho Jr [17] reported values of incorporated air in the range of 4-10% for mixed (cement and lime) mortars. A higher incorporated air content can contribute with entry of aggressive gaseous agents to concrete such as oxygen and carbon dioxide. However, the analysis should be made considering the sample pore structure. Compression strength results of mortars are shown in Table 4. Compression strength is influenced primarily by the nature of the binder, nature of the aggregates, proportion binder/aggregate, water/cement ratio of the fresh mixture and the execution technique of coating.

Table 4: Compression strength of mixed mortars

<table>
<thead>
<tr>
<th>Mortar Lime concentration (wt.%)</th>
<th>Compression strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 days</td>
</tr>
<tr>
<td>Without lime (0 wt.%)</td>
<td>2.28</td>
</tr>
<tr>
<td>Low lime content (6.7 wt.%)</td>
<td>2.39</td>
</tr>
<tr>
<td>Medium lime content (13.3 wt.%)</td>
<td>2.07</td>
</tr>
<tr>
<td>High lime content (26.3 wt.%)</td>
<td>0.68</td>
</tr>
</tbody>
</table>

The highest compressive strength obtained after 28 days of curing time are for samples without lime or with a lower lime content; the lime addition in mortar reduced the compressive strength of the samples.
which could lead the generation of cracks, affecting the stability and durability of structures. Cement significantly improves compressive strength of mortar [6]. However, the deleterious effect on the compressive strength was more evident in the case of adding 26.3 wt.% of lime in mortar corresponding to the highest content of lime [4].

The obtained values of corrosion potential of carbon and galvanized steel reinforcements in cement and mixed mortars were shown in Table 5 and Table 6. For galvanized reinforcements in concrete, the first mechanism of zinc corrosion occurs in the beginning when the system is still wet, or the hardening process has not reached 95% of the solidification of the matrix [18]. This is usually in a timeframe of 48 hours. When the system is still wet and highly alkaline, the zinc is attacked by a combination of hydroxyl ions and calcium.

\[ \text{Zn} + 2 \text{OH}^- + \text{Ca}^{2+} = \text{CaZnO}_2 + \text{H}_2 \]  

The formation of calcium zincates occurs due to the amphoteric character of zinc. The calcium zincates improve the adhesion between the zinc and the matrix. However, if the reaction occurs too fast, the hydrogen that is formed (H₂) reduces significantly the strength of the composite as a spongy layer is formed around the wire, which is detrimental to the properties of reinforced mortar.

Before the cyclic test, there is an increase in corrosion potential of carbon steel and galvanized steel with the lime addition in mortar (Tables 5 and 6). This result demonstrates the beneficial effect of lime on corrosion resistance of steel. In the case of lime addition on mortar, carbon dioxide gas is necessary for curing the mortar with calcium oxide in masonry. The CO₂ improves the passivation of zinc region and contributes to increase the corrosion resistance of galvanized steel. For the galvanized steel, low lime content was sufficient to increase the open circuit potential of reinforcement. For the carbon steel, the effect of lime addition on corrosion potential was significant for medium and high contents of lime in mortar.

**Table 5:** Results of Ecorr of galvanized reinforcements in cement and mixed mortars.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ecorr ((\text{mV})_{\text{Ag/AgCl}}) (before cyclic test)</th>
<th>Ecorr ((\text{mV})_{\text{Ag/AgCl}}) (immediately after cyclic test)</th>
<th>Ecorr ((\text{mV})_{\text{Ag/AgCl}}) (after 36 months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without lime</td>
<td>-910 ± 54</td>
<td>-890 ± 71</td>
<td>-379 ± 34</td>
</tr>
<tr>
<td>Low lime content</td>
<td>-650 ± 32</td>
<td>-770 ± 69</td>
<td>-417 ± 25</td>
</tr>
<tr>
<td>Medium lime content</td>
<td>-710 ± 50</td>
<td>-780 ± 54</td>
<td>-459 ± 31</td>
</tr>
<tr>
<td>High lime content</td>
<td>-735 ± 58</td>
<td>-760 ± 61</td>
<td>-448 ± 36</td>
</tr>
</tbody>
</table>

**Table 6 – Corrosion potential of carbon steel reinforcement**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ecorr ((\text{mV})_{\text{Ag/AgCl}}) (before cyclic test)</th>
<th>Ecorr ((\text{mV})_{\text{Ag/AgCl}}) (after cyclic test)</th>
<th>Ecorr ((\text{mV})_{\text{Ag/AgCl}}) (after 36 months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without lime</td>
<td>-484±38</td>
<td>-610±43</td>
<td>-451±31</td>
</tr>
<tr>
<td>Low lime content</td>
<td>-458±32</td>
<td>-650±52</td>
<td>-487±29</td>
</tr>
<tr>
<td>Medium lime content</td>
<td>-300±40</td>
<td>-620±37</td>
<td>-473±38</td>
</tr>
<tr>
<td>High lime content</td>
<td>-283±25</td>
<td>-560±50</td>
<td>-464±37</td>
</tr>
</tbody>
</table>

For the galvanized steel reinforcement in mortar with low lime content, and for all samples of carbon steel reinforcement, after cyclic immersion in a saline solution, the corrosion potential reduced indicating the deleterious effect of chlorides in this medium.

After 36 months of the cyclic test, the corrosion potential of all samples became higher than the corrosion potential measured immediately after immersion tests. This result can be due to the increase of alkaline content in mortar. Lime mortars have autogenous self-healing properties due to dissolution, transport and re-precipitation of calcium compounds [1].

But after 36 months of the cyclic tests in a saline solution, the highest corrosion potentials were obtained for the reinforcement in mortar without lime for the galvanized and the carbon steel reinforcements.
The results of electrochemical impedance spectroscopy are shown in Table 7. Figures 1 and 2 show Bode diagrams for carbon and galvanized steel reinforcement after 36 months of immersion tests, respectively.

**Table 7**: Polarization resistance of carbon and galvanized steels in cement and mixed mortars after cyclic tests.

<table>
<thead>
<tr>
<th></th>
<th>Carbon steel</th>
<th>Galvanized steel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_p$ (Ω cm$^2$)</td>
<td>$R_p$ (Ω cm$^2$)</td>
</tr>
<tr>
<td>(after cyclic tests)</td>
<td>(after 36 months)</td>
<td>(after cyclic tests)</td>
</tr>
<tr>
<td>Without lime</td>
<td>10</td>
<td>190</td>
</tr>
<tr>
<td>Low lime content</td>
<td>15</td>
<td>174</td>
</tr>
<tr>
<td>Medium lime content</td>
<td>13</td>
<td>148</td>
</tr>
<tr>
<td>High lime content</td>
<td>18</td>
<td>55</td>
</tr>
</tbody>
</table>

**Figure 1**: Bode diagram for carbon steel reinforcement after 36 months of immersion tests.
After cyclic tests, the carbon steel showed the highest corrosion potential (Table 6) and polarization resistance (Table 7) for the mortar with the highest lime content. The lime addition was beneficial to the corrosion resistance of reinforcements. After cyclic tests, the corrosion potential of galvanized steel was higher for the mortar with lime addition than the cement mortar as shown in Table 5, and the polarization resistance was the highest for galvanized steel in mortar with the highest lime content.

However, after 36 months, the polarization resistance of steel in mortars with the highest lime content was the lowest. In the beginning of project, the best corrosion behaviour was observed for carbon and galvanized steel in mortars with high content of lime. After 36 months of moulding, the highest corrosion resistance of reinforcement was obtained in mortars without lime fouling by mortars with the addition of low and medium lime concentrations.

For the carbon and galvanized steels in mortar, the polarization resistance and corrosion potential increased with time for all samples as shown in Tables 5 to 7. The alkaline content of mortars increased after 36 months of the cyclic test.

After the cyclic tests, the mortars were broken, the final diameters of reinforcements were measured, and mortars were analysed by using X-ray diffraction (XRD) to identify the phases present. The initial diameter of wire was 5 mm. The results of measurement of the final diameter of reinforcements after cyclic tests are shown in Table 8.

**Table 8:** Final diameter of carbon and galvanized steel reinforcements in cement and mixed mortars.

<table>
<thead>
<tr>
<th>Samples without and with lime</th>
<th>Diameter of carbon steel (mm)</th>
<th>Diameter of galvanized steel (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without lime (0%)</td>
<td>4.0 ± 0.2</td>
<td>4.5 ± 0.2</td>
</tr>
<tr>
<td>Low content (6.7 wt.%)</td>
<td>4.6 ± 0.3</td>
<td>4.7 ± 0.3</td>
</tr>
<tr>
<td>Medium content (13.3 wt.%)</td>
<td>4.5 ± 0.3</td>
<td>4.6 ± 0.2</td>
</tr>
<tr>
<td>High content (26.3 wt.%)</td>
<td>4.3 ± 0.2</td>
<td>4.5 ± 0.1</td>
</tr>
</tbody>
</table>
For the carbon steel reinforcements, after the cyclic immersion tests, the final diameter of reinforcement was lower for the cement mortar. This result agrees with the smaller value of the polarization resistance obtained for the carbon steel reinforcement in this condition. The other values of the final diameter of reinforcements obtained by using a gravimetric method are similar.

The phases identified by using XRD were SiO2: 2.4524, 2.4562, 2.2808, 1.8174, 1.6713, 1.5411, 1.3716, 1.1837, 1.1527 (peak values in Å); FeOOH-lepidocrocite: 2.4593, 1.9266, 1.6214; FeO (OH)-tetragonal: 2.2859, 1.3752, 1.1573; Fe2O3: 2.5327, 2.5100, 1.4520; β-FeOOH - akaganeite: 3.333, 2.6344, 2.5502, 1.9540, 2.2952; portlandite, Ca(OH)2: 4.9063, 2.6270, 1.9262, 1.6864 1.4475, 1.2091; CaCO3: 3.8537, 2.8435, 2.2840, 1.9122, 1.8749, 1.2180, 1.1864, 1.1534. The SiO2 and portlandite are usual phases in mortars and concrete [19]. The akaganeite is an iron corrosion product which is formed in environments containing chlorides [20].

In galvanized reinforced mortars, ZnO: 2.4760, 1.6260, 1.3790, 1.4770, 1.1527; Zn2O3: 2.4709, 1.6864, 1.3790, 1.4770, 1.1527; Zn(OH)2: 2.2859, 1.3752, 1.1573; FeOOH (akageneite). In galvanized reinforced mortars, ZnO and Zn(OH)2 were found besides lepidocrocite, akageneite, FeO(OH)-tetragonal, and Fe2O3.

After 36 months of the cyclic test, the polarization resistance of steel in mortars with the highest content of lime was the lowest. The polarization resistance and corrosion potential increased after 36 months of the cyclic tests, were: FeOOH (akageneite). The reinforcements showed a best corrosion behaviour in cement mortar than in blended mortars fabricated with steelmaking slags [20].

5. BIBLIOGRAPHY


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