Chemical Characterization of Lime-Based Binders in Historic Buildings of Latvia

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Abstract. The aim of this research is to investigate the chemical composition of stone materials of several local historic buildings with a purpose of elaboration of restoration strategy, including the choice of restoration materials. Most of the examined mortars are lime-based hydraulic mortars, characteristic of the architecture of 19th/20th century. Pure aerial lime binders show reduced compatibility with historic materials, that is why lime binders with pozzolan additive (cement) are an appropriate choice for restoration. In order to examine the changes of hydraulicity (i.e. the property of binders to harden when exposed to water) of perspective restoration binders, a series of blended lime–cement mixtures were synthesized with growing content of cement (up to 10 % by weight). A significant relationship between cement content and hydraulic properties has been shown.

1. Introduction
Principal factor of the sustainability of historic monuments is usage of compatible materials. In the conservation practice, both lime binders and cement binders often display incompatibility with historic mortars [1], [2], [3]. Cement binders have high content of soluble salts, low vapor permeability, high modulus of elasticity, while lime binders show low mechanical strength, slow hardening and low water resistance. To avoid these disadvantages, a wide range of materials and their combinations are recommended – hydraulic lime, Roman cement, lime with pozzolan additive etc. [4], [5], [6], [7], [8], [9]. It has been observed that substitution of a small percentage of lime by cement (below 10% in mass) does not modify the microstructure of the mortar and the mixture can be formulated in order to meet the requirements for conservation mortars [3]. Overall, the choice of material for each object must be based on the knowledge about the original material.

Scientific investigation of several mortars from local historic buildings (Vingrotaju Str. 1 (Riga), Daugavpils Fortress, the banks of the River Aleksupite (Kuldiga) etc. (total of 13 samples)) was...
carried out at the laboratory of the Institute of Silicate Materials of Riga Technical University in order to characterize authentic materials and elaborate conservation plans. The results of analysis of the chemical composition of historic mortars allow indicating the original components of mortar, providing necessary information for the choice of the most compatible restoration materials. Binders used for restoration are recommended to contain hydraulic components (associated with soluble Al$_2$O$_3$ and SiO$_2$). Matching composition and compatible properties to historic binders can be achieved by using lime-cement mixtures. A range of aerial lime – white cement binders were synthesized with growing cement content (up to 10 %); their composition was then determined.

2. Materials and methods

The historic mortar samples examined in this research are characterized in table 1.

| Sample No. | Location | Sample characterization |
|------------|----------|-------------------------|
| 1          | Bank of the River Aleksupite in Kuldiga | Mortar with crushed brick particles |
| 2          | The right bank of the River Aleksupite in the niche near Pasta Street in Kuldiga | Mechanically strong mortar with crushed brick particles |
| 3          | Vault under the bridge of Skolas Street in Kuldiga | Mechanically strong mortar with crushed brick particles |
| 4          | Daugavpils Fortress, 1$^{st}$ coast lunette | Corroded mortar with high content of sulphates and chlorides |
| 5          | Daugavpils Fortress, 1$^{st}$ coast lunette | White disintegrated plaster with high content of sulphates and chlorides |
| 6          | Daugavpils Fortress, 1$^{st}$ coast lunette | Mechanically strong cement plaster on the surface of white lime plaster of decor |
| 7          | Vingrotaju Street 1 in Riga | White mechanically strong plaster |
| 8          | Vingrotaju Street 1 in Riga | White mechanically strong mortar for cladding bricks |
| 9          | Vingrotaju Street 1 in Riga | Disintegrated grey mortar joints corroded by sulphates |
| 10         | Belfry of Aleksander Nevsky Church on Brivibas Street 56 in Riga | White, old corroded mortar under cement layer |
| 11         | Professional school on Saules Street 15 in Ventspils | Greyish corroded plaster |
| 12         | Miesnieku Street 13 in Riga | Mechanically strong two layered part of a decor |
| 13         | Puzes Church near Ventspils | White calcitic lime plaster |

The chemical composition of historic mortars as well as synthesized lime-cement binders was characterized through classical (wet) chemical analysis (according to EN 196-2 [10]). The mineralogical phases of mortar samples were determined by means of differential thermal and thermogravimetric (DTA/TG) analysis (SETARAM SETSYS Evolution – 1750) and X-Ray diffraction (XRD) analysis (Rigaku Ultima + with CuK$_\alpha$ radiation at scanning interval 0-60° (2θ) and speed 2°/min). Classical chemical analysis comprised determination of loss of ignition, CaO, MgO, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, Na$_2$O, K$_2$O and part insoluble in HCl. From the data of chemical analysis, the type of binder, its original components, modulus of hydraulicity and aggregate/binder ratio were determined. Size distribution of aggregate was analyzed after dissolving a sample in 10 % HCl, elution, drying and sieving [11].
For the synthesis of lime-cement binders with growing cement content (0, 2, 4, 8 and 10 %), mixtures of slaked lime (Ca(OH)$_2$) with sand (aggregate size 0-4 mm) and white Portland cement (CEM I 52,5 R) were used.

3. Results and discussion

By means of chemical analysis it was determined that most of the analyzed binders are based on dolomitic or calcitic lime with different levels of hydraulicity. The results of chemical and granulometric analysis are shown in table 2, table 3 and table 4.

The amount of hydraulic components is of great importance, providing mechanical strength and water resistance, and it is strongly connected with the grade of deterioration: historic binders with higher content of soluble SiO$_2$ and Al$_2$O$_3$ were found to be in a better condition and are mechanically stronger. It can be featured by using modulus of hydraulicity (m) (Equation 1) [12].

\[
m = \frac{\%(\text{CaO+MgO})}{\%(\text{SiO}_2+\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3)}
\]  

(1)

The modulus of hydraulicity expresses the ratio between basic and acid oxides in mortar. If m>9, it is a pure lime binder, but if m<1.7 – the binder can be considered to be Roman cement. The modulus of hydraulicity of hydraulic lime is 1.7-9 [12].

All samples with m > 6 are observed as corroded and most of them also suffering from migrating salts and moisture.

Hydraulic nature of the examined mortars dated to 19th/early 20th century (or earlier) can be attributed to raw materials with high content of clay used in the binder production. The dehydroxylated clays acted as a pozzolan which imparts early strength to the mortar. In mortars with crushed brick additive, compounds of hydraulic type occur at the brick matrix interface [13].

Pure lime mortars without hydraulic additives are weaker attached to the original surface. As an example of unconformity between old and new (without hydraulic components) building materials, rendering of Puze Church (sample N° 13) can be mentioned (figure 1). The usage of the aerial lime binder with no hydraulic additives (m = 43.0) for the restoration of the façade has led to fast and intensive decay and pealing of exterior surfaces in the exposure to outdoor conditions.

Figure 1. Church of Puze, Latvia (sample N° 13).
| Component                        | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Sample 7 | Sample 8 | Sample 9 | Sample 10 | Sample 11 | Sample 12 | Sample 13 | Accuracy, [± absol. %] |
|----------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|------------------|
| Loss of ignition at 1000°C       | 16.03    | 25.04    | 21.78    | 27.29    | 27.04    | 14.21    | 13.20    | 11.44    | 30.60    | 8.62      | 10.10     | 14.13     | 44.05     | 0.3               |
| Sand and gravel                  | 61.84    | 49.56    | 47.92    | 41.84    | 52.61    | 62.73    | 68.81    | 72.12    | 35.44    | 80.46     | 72.87     | 45.23     | 11.45     | 0.5               |
| CaO                              | 15.21    | 13.94    | 21.32    | 16.04    | 12.09    | 16.56    | 9.59     | 10.01    | 19.37    | 7.03      | 8.05      | 24.92     | 42.20     | 0.5               |
| MgO                              | 2.78     | 7.35     | 2.41     | 9.60     | 7.90     | 0.72     | 3.76     | 2.86     | 9.43     | 1.96      | 3.38      | 3.36      | 1.71      | 0.5               |
| Soluble SiO₂                     | 0.96     | 1.70     | 2.28     | 1.36     | 0.31     | 1.17     | 2.80     | 2.26     | 1.61     | 0.68      | 4.20      | 6.04      | 0.37      | 0.3               |
| Al₂O₃                            | 1.71     | 1.52     | 2.72     | 1.20     | 0.89     | 2.13     | 1.05     | 0.97     | 1.08     | 0.45      | 0.76      | 4.09      | 0.44      | 0.3               |
| Fe₂O₃                            | 0.96     | 0.50     | 1.08     | 0.65     | 0.33     | 0.53     | 0.34     | 0.28     | 0.56     | 0.19      | 0.38      | 1.07      | 0.21      | 0.1               |
| Total                            | 99.36    | 99.50    | 99.45    | 97.92    | 98.17    | 98.05    | 99.55    | 99.71    | 97.77    | 99.37     | 99.74     | 98.84     | 100.4     | -                 |
| CaO/MgO ratio (modulus of hydraulicity) | 4.6   | 5.7       | 4.0       | 8.0       | 13.1     | 4.5       | 3.2       | 3.7       | 8.9       | 6.8        | 2.1        | 2.5        | 43.0       | -                 |
| Aggregate/binder ratio           | 1:2      | 1:1.5     | 1:1.5     | 1:1.4     | 1:2.3     | 1:2.7     | 1:3.8     | 1:4.4     | 1:1       | 1:4.4      | 1:1.7      | 1:4        | 1:0.8      | 1:0.3            |
Table 3. Calculated parameters of the binder in historical mortars from chemical analysis, weight %.

| Sample Component | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  | Accuracy, [± absol. %] |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----------------------|
| CaO              | 68.8| 54.9| 70.4| 51.9| 51.8| 71.8| 53.4| 60.9| 57.0| 64.4| 47.1| 61.4| 90.3| 0.5                   |
| MgO              | 12.6| 28.4| 7.9 | 31.0| 33.8| 3.1 | 20.9| 17.4| 27.8| 17.9| 19.8| 8.3 | 3.8 | 0.5                   |
| Soluble SiO2     | 4.5 | 6.7 | 7.5 | 4.4 | 1.3 | 6.1 | 15.6| 13.7| 4.7 | 6.2 | 24.5| 14.9| 0.8 | 0.5                   |
| Al2O3            | 7.7 | 6.0 | 8.9 | 3.9 | 3.8 | 9.2 | 5.8 | 5.9 | 3.2 | 4.1 | 4.4 | 10.1| 1.0 | 0.5                   |
| Hydr. compounds  | 15.9| 14.7| 20.0| 16.4| 6.5 | 18.6| 23.2| 21.3| 9.5 | 12.1| 31.1| 27.6| 2.2 | -                     |
| Type of binder   |     |     |     |     |     |     |     |     |     |     |     |     |     |                       |
| b                |     |     |     |     |     |     |     |     |     |     |     |     |     |                       |

a) Hydr. compounds = (SiO2 + Al2O3 + Fe2O3).

b) SH = strongly hydraulic; WH = weakly hydraulic; NH = non-hydraulic; C/L = calcitic lime; DL = dolomitic lime; C/L = cement with lime addition; C = cement.

Table 4. Recalculated aggregate size distribution, weight %.

| Particle size, mm | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | Accuracy, [± absol. %] |
|-------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|-----------------------|
| > 0.7             | 26.1| 38.8| 28.2| 44.0| 32.8| 9.5| 30.2| 31.2| 11.2| 14.8| 14.8| 14.8| 0.5                   |
| 0.5-0.7           | 44.6| 31.2| 32.7| 28.8| 31.1| 48.0| 36.2| 48.9| 60.1| 45.1| 45.1| 45.1| 0.5                   |
| 0.2-0.5           | 16.8| 15.7| 15.8| 10.8| 15.5| 24.5| 17.5| 11.9| 23.4| 21.3| 21.3| 21.3| 0.5                   |
| 0.16-0.2          | 3.1 | 5.3 | 6.2 | 5.3 | 6.9 | 5.3 | 8.5 | 3.8 | 2.4 | 6.7 | 6.7 | 6.7 | 0.5                   |
| <0.16             | 9.4 | 9.0 | 17.1| 11.1| 13.7| 12.7| 7.6 | 4.2 | 2.9 | 12.1| 12.1| 12.1| 0.5                   |
| Total             | 100.0| 100.0| 100.0| 100.0| 100.0| 100.0| 100.0| 100.0| 100.0| 100.0| 100.0| 100.0| 0.5                   |
In the selected historic mortar samples, XRD showed carbonates as the main crystalline phases formed by the carbonation of lime. In dolomitic mortars two forms of magnesium hydrogen carbonates were also detected – hydromagnesite \((4\text{MgCO}_3\cdot\text{Mg(OH)}_2\cdot4\text{H}_2\text{O})\) and nesquehonite \((\text{MgCO}_3\cdot3\text{H}_2\text{O})\) (figure 2). Calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH), which are among the main hydrated phases formed at room temperature after pozzolanic reaction, were not observable by means of XRD, which could be due to their decomposition caused by aging of the mortar as well as low crystallinity [14].

![Figure 2. Example of XRD pattern of historic dolomitic mortar (sample N^\circ 4).](image)

Thermal analysis (DTA/TG) showed common basic thermo effects in the selected samples attributed to quartz inversion (573°C) and decomposition of carbonates (in figure 3 - calcite) (650-900°C). Dolomitic lime-based mortars show endothermic reaction at 350-450°C temperature attributed to dissociation of Mg(OH)_2 (figure 3). At the temperature range of 480-620°C the dissociation of uncarbonated portlandite (Ca(OH)_2) takes place [15]. Broad peaks indicate weight loss of the absorbed water in the temperature range from 60 to 180 °C and of the water bound to hydraulic components in the temperature range from 200 to 600 °C [16].
The investigation of the change of the modulus of hydraulicity (m) of cement-lime mixtures approved that hydraulicity is contributed to the amount of added cement, allowing choosing the best matching composition for each object. In table 5, it can be seen that the modulus of hydraulicity of the lime binder without cement additive is very high (m=9.9) meaning low hydraulicity, but if cement content reaches 10 %, modulus decreases to 2.0. Beginning with 4 % cement additive, binder can be considered as strongly hydraulic. XRD data approve this coherence (figure 4) – the XRD patterns of the synthesized lime-cement mixtures after 2 months hardening show presence of cement mineral (calcium silicate – larnite (2CaO·SiO$_2$)), if the content of cement in the binder is 4 % or higher. These minerals (calcium silicates and calcium aluminates) are responsible for hydraulic activity, forming hydrates while hardening. Hydrates of cement minerals – calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH) – are mostly amorphous [14] and for the determination of the presence of these phases such methods as DTA and SEM-EDS can be used.

The amount of soluble Al$_2$O$_3$ and SiO$_2$ (indicative of hydraulic components) is increasing with the content of cement in the binder (table 6).
Table 5. The results of chemical analysis of aerial lime-white cement mixtures, weight %.

| Content of cement in mixture Component | 0   | 2   | 4   | 8   | 10  | Accuracy, [± absol. %] |
|--------------------------------------|-----|-----|-----|-----|-----|-----------------------|
| Loss of ignition at 400°C            | 0.93| 1.00| 1.30| 1.09| 1.80| 0.20                  |
| Loss of ignition at 1000°C           | 13.10| 13.07| 12.83| 12.63| 11.53| 0.20                 |
| Insoluble residue in HCl (sand and gravel) | 62.42| 61.40| 57.29| 57.76| 56.61| 0.30                 |
| CaO                                  | 20.56| 21.45| 21.12| 20.14| 20.03| 0.50                  |
| MgO                                  | 0.11| 0.00| 0.00| 0.00| 0.00| 0.30                  |
| Soluble SiO₂                         | 1.58| 2.07| 4.96| 4.11| 4.28| 0.50                  |
| Soluble Al₂O₃                        | 0.11| 0.30| 1.15| 4.48| 5.27| 0.30                  |
| Fe₂O₃                                | 0.39| 0.41| 0.46| 0.47| 0.53| 0.10                  |
| Total                                | 99.20| 99.70| 99.11| 99.78| 100.05| -                     |
| Binder to filler ratio               | 1:3.3| 1:3.1| 1:2.5| 1:2.5| 1:2.3| -                     |
| m (modulus of hydraulicity)         | 9.9| 7.7| 3.2| 2.2| 2.0| -                     |
| Type of binder                       | Weakly hydraulic binder | Weakly hydraulic binder | Strongly hydraulic binder | Strongly hydraulic binder | Strongly hydraulic binder | - |

Table 6. Calculated composition of the binder according to chemical analysis, weight %.

| Content of cement in mixture Component | 0   | 2   | 4   | 8   | 10  | Accuracy, [± absol. %] |
|--------------------------------------|-----|-----|-----|-----|-----|-----------------------|
| CaO                                  | 87.5| 86.8| 78.1| 69.7| 66.5| 0.8                   |
| MgO                                  | 0.5| 0.0| 0.0| 0.0| 0.0| 0.0                   |
| Soluble SiO₂                         | 6.7| 8.4| 15.3| 15.1| 16.2| 0.8                   |
| Soluble Al₂O₃                        | 0.5| 1.2| 4.0| 14.2| 16.5| 0.8                   |
| Fe₂O₃                                | 1.6| 1.6| 1.6| 1.5| 1.6| 0.5                   |

Figure 4. XRD pattern of aerial lime-white cement mixture with 4 % cement content.
Thermal analysis allows detecting hydraulic components (hydrated cement minerals), which are often hard to detect by XRD because of their poorly crystalline structure. Two endothermic peaks in the region 100-125 °C and 150–310 °C illustrate the loss of absorbed water and endothermic dehydration of pozzolanic hydrated products, calcium silicate hydrates and calcium aluminate hydrates, respectively (figure 5) [14]. As the cement-lime ratio increases in the mixtures, the mass loss attributed to total bound water of the pozzolanic reaction compounds also increases. Endothermic peak at 480°C can be attributed to dissociation of portlandite (Ca(OH)$_2$) and 650-900°C – to calcite (CaCO$_3$) [15]. Two endothermic minimums of calcite dissociation peak could occur due to 2 types of calcite origin in material: primary calcite – formed by the calcination of lime, and secondary – formed after the hydrolysis process of cement mineral alite.

![Figure 5. DTA curve of the mixture with 10 % of cement (after 2 months of hardening).](image)

4. Conclusions
The choice of materials used for restoration purposes is based on the results of research on the historic materials. The basic aspects for the choice of the binder, filler and additives (if necessary) are the data obtained during visual observation, chemical and granulometric analysis, XRD and DTA/TG analysis.

Hydraulicity plays an important role in the durability of mortars. Most of the examined samples from historic buildings in Latvia are based on dolomitic or calcitic lime with hydraulic properties, achieved by pozzolan additives or natural admixture of clay.

Lime binders with Portland cement additive can be used in restoration as an appropriate material. The cement-lime mortars described in this study presented the increase of hydraulicity, which is needed in the restoration of historic masonries.

This study helps finding adequate proportions of pozzolan additive (white cement) in the restoration binders, in order to achieve desirable hydraulic nature of the binder, at the same time avoiding undesired changes of the hardened properties (for example, excessive improvement of the mechanical strength), which might cause incompatibility with the original materials.
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