RIGA TECHNICAL UNIVERSITY
Faculty of Material Science and Applied Chemistry
Institute of Silicate Materials

Inta KIRILOVICA
Student of the Doctoral Program "Chemical Technology"

THE SYNTHESIS OF HYDRAULIC BINDER SUITABLE FOR RESTORATION OF DOLOMITIC ROMAN CEMENT OBJECTS

Summary of the Doctoral Thesis

Scientific supervisor:
Dr. sc. ing.
Linda KRAGE

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OFFICIAL REVIEWERS

Assoc. prof., *Dr. habil. sc. ing.* Visvaldis Svinka
Institute of Silicate Materials, Riga Technical University, Latvia

Assoc. prof., *Dr. geol.* Girts Stinkulis
Chair of Bedrock Geology, University of Latvia, Latvia

Assoc. prof., *Dr.* Roman Kozłowski
Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Poland

DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Engineering Sciences is my own and does not contain any unacknowledged material from any source. I confirm that this Thesis has not been submitted to any other university for the promotion to other scientific degree.

Inta Kirilovica ……. (Signature)

Date: ……

The Doctoral Thesis has been written in Latvian and comprises an introduction, three chapters (literature review, methodological part, experimental part), conclusions and bibliography with 93 reference sources. It has been illustrated by 73 figures, 10 tables and 27 equations. The volume of the present Doctoral Thesis is 129 pages, including 6 appendices.

ACKNOWLEDGEMENTS

I would like to express sincere gratitude to my supervisor Linda Krage for the time she invested helping to formulate the direction of research. Tremendous gratitude to Inta Vitina and Lauma Lindina for their enthusiasm, encouragement, approval and a helping hand in the work process. Without their experience and thorough knowledge the research would not be possible.

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OVERVIEW OF THE DOCTORAL THESIS

Topicality

In the early 20th century, dolomitic Roman cement was one of the dominant binders used for the construction of buildings that are now a significant cultural heritage of Riga. As the production of the material was discontinued in the middle of the 20th century, the knowledge of dolomitic Roman cement manufacturing and properties has been lost. Nevertheless, there is a need of compatible material for restoration purposes that is not currently commercially available.

As the traditional raw material of dolomitic Roman cement – dolomitic marlstone – has become difficult to obtain, the range of raw materials is widened by synthesizing a compatible binder from mixture of dolomite flour and clay.

Such binder would be the closest compatible binder for the restoration of historical dolomitic Roman cement objects. The raw materials were chosen from economic and ecological perspectives, because these materials – clay and dolomite flour – are locally sourced; besides, the dolomite flour is a by-product in the manufacturing process.

The Aim

The aim of the Thesis is the synthesis of hydraulic binder in system clay – dolomite, which based on compatible chemical and physical properties would be suitable for restoration purposes of historical dolomitic Roman cement objects.

The Tasks

To reach the aim, the following tasks have been set out:

- To identify and gather data from literature about Roman cement, its manufacturing and properties and, in particular, about the dolomitic Roman cement;
- To synthesize a low-temperature hydraulic binder in a system clay – dolomite;
- To characterize the ongoing physico-chemical processes during the hardening of hydraulic binders;
- To identify the chemical and mineralogical composition of synthesized binder after firing and after hydration, as well as the physical and mechanical properties;
- To evaluate the impact of the firing temperature and the content of clay to the binder composition;
- To evaluate the suitability of synthesized binder for restoration purposes.

Scientific Novelty

The novelty of the Doctoral Thesis is concerned with the synthesis of new binder from mixture of dolomite flour and clay, which is compatible with dolomitic Roman cement. The properties of obtained binder are investigated, assessing the compatibility of materials. As the traditional raw material of dolomitic Roman cement – dolomitic

marlstone – has become difficult to obtain, the range of raw materials is widened by synthesizing a compatible binder from mixture of dolomite flour and clay.

The influence of the firing temperature on the activity of the synthesized binder and hydraulic component production has been established. Wider explanation is given on a late-stage hardening process of binder synthesized from dolomite flour and clay, proving the significant role of MgO hydration and carbonation products in strength gain.

Practical Significance

The practical significance is concerned with the synthesis of binder for restoration purposes that is compatible with dolomitic Roman cement and based on its physical and chemical properties is suitable for the restoration of significant architectural heritage objects of $19^{th}/20^{th}$ century, where dolomitic Roman cement was as a binder. As there are no commercially available binders that are compatible with dolomitic Roman cement, the range of materials is widened by synthesizing a hydraulic, highly porous, low-temperature binder from local raw materials – dolomite flour and clay. The developed synthesis technology gives economic and ecological advantage, comparing with other similar materials, as the raw material – dolomite flour – is a by-product in the manufacturing process; furthermore, low firing temperature (800 °C) reduces the power consumption required to obtain binder.

Approbation

The results of the Thesis have been approbated in 10 full text publications (2 of them indexed in data bases *SCOPUS* or *Web of Science*) and 16 international and local scientific conferences, seminars and congresses. On the basis of the research, LV patent has been received.

Thesis Statements to Be Defended

1. It is possible to obtain a low-temperature hydraulic binder from dolomite flour and clay, which is chemically, mineralogically and physically compatible with the historical dolomitic Roman cement.
2. The MgO hydration and carbonation products are of great importance, providing the mechanical strength of binder obtained from dolomite flour and clay.
3. Increased clay content in the mixture of raw materials contributes to the formation of hydraulic components – $2CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ – in the binder that is synthesized from clay and dolomite flour.
4. Increased hydration activity of the binder can be achieved by reducing the firing temperature.

CONTENT OF THE THESIS

Literature Review

The theoretical part of the Doctoral Thesis contains information about hydraulic binders, i.e., such binders, which can harden not only in the air, but also in the presence of water, and are moisture-resistant. Their role in restoration is discussed. The information is given about Roman cement – significant historical hydraulic binder, its production and properties. Separate chapter is dedicated to the description of dolomitic Roman cement in Latvia, and also to the differences between calcitic and dolomitic binders.

Roman cement was a binder widely used in Europe in $19^{th}/20^{th}$ century. It was obtained from marlstone – rock containing 15 % to 40 % clay and 60 % to 85 % carbonates (limestone or dolomite). The process was simple – marlstone was burnt at low temperatures (800 °C to 1200 °C) and ground to a fine powder state, thus obtaining a hydraulic binder that did not slake in contact with water [1].

In comparison with other parts of Europe, where calcitic Roman cement was mostly applied, in the territory of Latvia from 1860s dolomitic Roman cement was produced. It was obtained by burning locally sourced dolomitic marlstone below the sintering temperature (800 °C to 900 °C) and grinding it to a floury fineness. Dolomitic Roman cement was used in the construction of several significant historical buildings of Latvia of the late 19^{th} / early 20^{th} century [2]. The advantages of Roman cement were very short setting time (approx. 15 min), which was useful for making casts, high porosity (approx. 30 %), high water-resistance and excellent weather-resistance, because of which it was usable in facades [3].

Since the middle of the 20^{th} century, the manufacturing of dolomitic Roman cement has been stopped; still there is a need for a compatible binder for restoration purposes.

One of the main principles of restoration is the use of material that is compatible with the original material and matches its current antiquated condition [4]. Despite its wide application in construction, Portland cement is not suitable for the purposes of restoration due to its high density and incompatible chemical, mineralogical and physical properties. Meanwhile, pure air lime binders that show good compatibility with altered historical materials cannot be used in facades because they are not water-resistant (they have low hydraulicity) [5].

Hydraulic binders, for example, hydraulic lime (natural or artificial), Roman cement, Portland cement, can harden not only in the air, but also in the presence of water, and are moisture-resistant. The formation of cement minerals – dicalcium silicate ($2CaO \cdot SiO_2$) and tricalcium aluminate ($3CaO \cdot Al_2O_3$) – by the reaction between active SiO_2, Al_2O_3 and free CaO is an important prerequisite for obtaining hydraulic properties in these binders. For a long time, builders have tried to obtain hydraulic binders by adding pozzolan (disperse materials that contain active SiO_2 or Al_2O_3) to fired lime. In 1796 J. Parker patented Roman cement – hydraulic binder, which does not require addition of hydraulic additives [1].

The hydraulicity of binders is usually described using the modulus of hydraulicity:

$$m = \frac{\%(CaO+MgO)}{\%(Al_2O_3+Fe_2O_3+SiO_2)} \quad (1)$$

The Doctoral Thesis provides an overview of the physical and chemical processes during the hardening of dolomitic binders that set them apart from limestone binders of similar type. The hardening process of dolomitic binders starts with the hydration of MgO and formation of $Mg(OH)_2$. Then hydrated binder absorbs CO_2, which then is chemically bonded in carbonate phases in the system $MgO\text{-}CO_2\text{-}H_2O$. The carbonation of $Mg(OH)_2$ is always incomplete due to its low solubility [6]. In carbonation process, depending on environmental conditions and curing time, various types of magnesium carbonate hydrates are formed, for example, hydromagnesite ($4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$), nesquehonite ($MgCO_3 \cdot 3H_2O$), minerals from hydrotalcite group, and others [7], [8], [9].

As the traditional raw material of dolomitic Roman cement – dolomitic marlstone – has become difficult to obtain (the deposits have been exhausted and are mostly underwater) and, furthermore, it is hard to achieve constant chemical composition, the experimental synthesis of low temperature hydraulic binder using locally sourced raw materials – dolomite flour and clay – is performed.

Materials and Methods

At the beginning of methodical part, the preparation of the samples is described. Five various mixtures using two types of pulverized clay and dolomite flour were designed, and the composition of each mixture is given in Table 1.

Table 1

Composition of Experimental Mixtures, Mass %

Composition designation	Quaternary (carbonatic) clay, Spartaks clay deposit	Devonian (non-carbonatic) clay, Liepa clay deposit	Dolomite flour, Ltd. *Saulkalne-S*, Kranciems deposit
U1*	13	-	87
U2	24	-	76
A1	-	13	87
A2	-	24	76
A3*	-	30	70

* Compositions that were excluded from most part of further studies due to their unsatisfactory properties.

The scheme of preparation of samples is shown in Fig. 1. Specimens were prepared by weighing the required amounts of raw materials – clay and dolomite flour – and homogenizing the mixture in dry state. Before the mixing clay and dolomite flour were already grained to a size less than 0.2 mm. Samples were shaped under the pressure of 20 MPa (by adding 10 mass % water), dried and fired. Two forms of samples were shaped – small plate-like (56 mm x 26 mm x 6 mm) samples for determination of

the chemical and mineralogical composition of fired material, and cylindrical samples (h = 3 cm, d = 3.5 cm) in order to obtain a larger quantity of binder for the preparation of mortar samples. Prepared samples were fired in the temperature range of 750 °C to 1000 ºC in 50 ºC steps (heating rate – 7 °/min), with the holding time of 2 hours at each temperature. According to the same procedure also dolomitic marlstone (from Dzukste, Latvia) was fired. The firing samples were grained and sieved, until the size of particles was smaller than 0.2 mm. The binder was then mixed with water to make cubic mortar samples without aggregate (water/binder ratio 0.65, dimensions 4 cm x 4 cm x 4 cm). As a setting retarder 0.6 % citric acid (related to the weight of the binder) was used. The samples were demolded after 1 day and kept in a moist atmosphere (RH 90 % to 100 %) for 7 days, but further hardening took place in laboratory environment (in air). Specimens from the commercial product – calcitic Roman cement *Prompt* (France) – were prepared taking into account the same conditions.

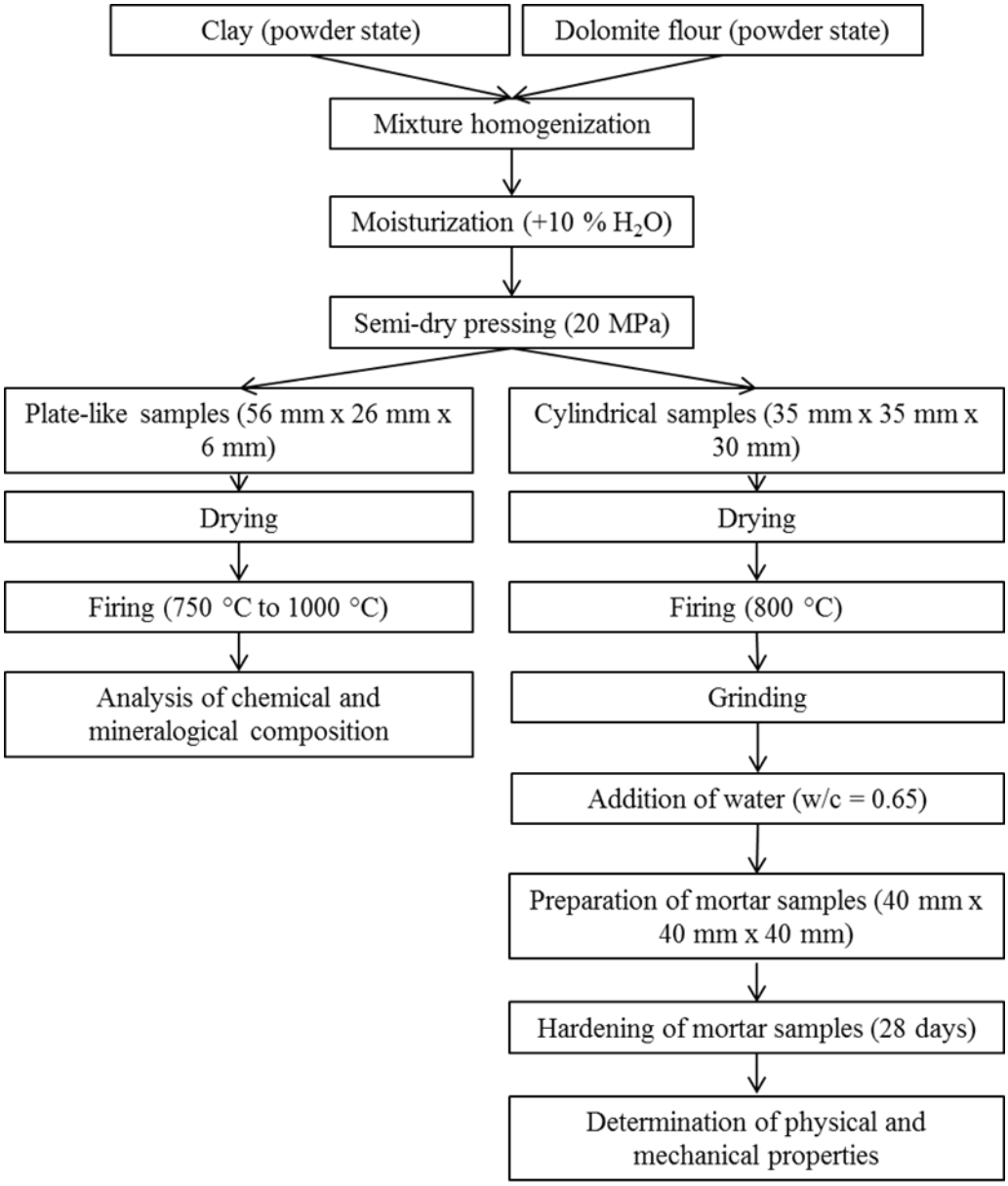

Fig. 1. The scheme of synthesis.

Full chemical analysis of raw materials, synthesized binder, as well as samples of historical mortars, and the determination of the amount of active (soluble) SiO_2 and Al_2O_3 in the synthesized binder were carried out according to LVS EN 196-2:2013. The amount of active CaO + MgO was detected by titration (according to LVS EN 459-2:2011).

In order to detect the phase composition, the following methods were used: 1) X-ray diffraction analysis (XRD) (*Rigaku Ultima* + with CuKα radiation at a scanning interval 5° to 60° (2θ) and speed 2 °/min); 2) differential thermal analysis (DTA) (*SETARAM SETSYS Evolution* – 1750, using corundum crucibles, at a 10 °C/min heating rate, under air atmosphere, from ambient temperature to 1100 °C).

After the binder was mixed with water, the setting time was determined. The pore size distribution of hardened mortar samples was measured with mercury porozimeter *Pore Master 33 Quantachrome Instruments.* The frost resistance, water absorption, drying rate and forced water absorption were also determined. Compressive strength was measured with mechanical press (loading rate 0.5 MPa/s to 1.0 MPa/s). The changes of the structure and composition of hardened mortar samples during the hardening were investigated by using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) (*Hitachi TableTop Microscope TM3000* and a field emission scanning electron microscope *FEI Nova NanoSEM 650*).

Results and Discussion

In the experimental part of the Doctoral Thesis, the synthesis of hydraulic binder in system clay–dolomite flour is studied. Based on compatible chemical and physical properties, it would be suitable for restoration purposes of historical dolomitic Roman cement objects. The influence of clay content in compositions and of firing temperature on the physico-chemical properties and mineralogical composition of obtained material is estimated. The physical and mechanical properties, as well as the hydration process of the synthesized binder are investigated.

Characterization of Historical Mortars

In order to identify the properties of local historical mortars, at the beginning of experimental part of the Doctoral Thesis chemical and mineralogical investigation of several local historical mortar samples (total 13 samples) was performed. The aim was to characterize original materials in order to evaluate the conformity of restoration materials and to develop a restoration strategy.

It was found that most of the binders of analyzed mortars were dolomitic or calcitic lime with different levels of hydraulicity. The amount of hydraulic components in a binder is of great importance, providing mechanical strength and water resistance. It is strongly concerned with the grade of deterioration of mortars. It was ascertained that historical mortars with higher content of active SiO_2 and Al_2O_3 were in better condition and mechanically stronger. The XRD analysis in samples of historical mortars as main crystalline phases showed carbonates that were formed as a result of

lime carbonation. In dolomitic lime based binders also two forms of magnesium carbonate hydrates were recognized – hydromagnesite ($4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$) and nesquehonite ($MgCO_3 \cdot 3H_2O$). The DTA curves of investigated historical dolomitic mortar samples clearly indicate their hydraulic nature (two broad endothermic thermal effects in a temperature range of 100 °C to 300 °C).

Raw Materials

For the synthesis of a hydraulic binder for restoration purposes local raw materials were chosen: Quaternary (carbonatic) clay from the Spartaks deposit (Latvia), Devonian (non-carbonatic) clay from the Liepa deposit (Latvia) and dolomite flour from the Kranciems quarry (Ltd. *Saulkalne-S*, Latvia).

The full chemical composition of the raw materials was determined by the classical (wet) chemical analysis. Local dolomitic marlstone – potential natural raw material for dolomitic Roman cement – was also investigated. According to the results of the chemical analysis, the content of carbonates ($CaCO_3$ + $CaCO_3 \cdot MgCO_3$) in Quaternary clay reached 24 wt%, while in Devonian clay it was just 6 wt%. Dolomite flour from the Kranciems quarry contained 88 wt% carbonates (mostly dolomite) and 12 wt% impurities, such as quartz and clay minerals. The dominant clay mineral in both types of clay was illite. The content of carbonates in the sample of dolomitic marl was 80 wt%, while the rest 20 wt% were clay minerals and quartz.

Synthesized Binder after Firing

The chemical composition of synthesized binder (compositions A1, A2, U2), as well as of calcitic Roman cement *Prompt*, which is one of closest matching alternatives for the Roman cement restoration purposes, was determined. Comparing obtained results with the data of the chemical composition of historical dolomitic Roman cement from literature [2], in Table 2 it can be seen that all synthesized compositions closely match the composition of historical dolomitic Roman cement and are highly hydraulic (*m* is 2.39 to 3.21).

Table 2

Chemical Composition of Binder, Mass %

	Composition U2 (fired at 800 °C)	**Composition A2 (fired at 800 °C)**	**Composition A1 (fired at 800 °C)**	Historical dolomitic Roman cement (Riga) [2]	Calcitic Roman cement *Prompt* (800 °C to 1200 °C) (France)	Error, ± absolute %
LOI at 400 °C	**0.46**	**0.50**	**0.54**	-	1.36	0.30
LOI at 1000 °C	**12.45**	**10.58**	**13.91**	10.70	8.70	0.30
IR	**29.46**	**25.28**	**17.16**	-	7.82	0.50
SiO_2 (sol.)	**8.08**	**8.08**	**6.90**	14.72	13.88	0.50
CaO	**29.75**	**27.06**	**30.26**	36.74	47.88	0.50
MgO	**18.28**	**17.65**	**21.66**	22.26	1.61	0.50
Al_2O_3	**9.61**	**9.20**	**8.01**	8.56	10.70	0.50
Fe_2O_3	**1.68**	**1.40**	**1.27**	2.70	2.77	0.20
Na_2O	**0.05**	**0.07**	**0.06**	-	0.05	0.02

K_2O	**0.73**	**0.71**	**0.71**	-	0.88	0.02
SO_3	-	-	-	-	3.70	0.30
Total	**100.55**	**100.53**	**100.48**	95.68	99.35	-
CaO/MgO	**1.63**	**1.53**	**1.40**	1.65	29.74	-
SiO_2 (sol.) + Al_2O_3 + Fe_2O_3	**19.37**	**18.68**	**16.18**	25.98	27.35	
m	**2.48**	**2.39**	**3.21**	2.27	1.81	-

LOI – loss of ignition; IR – insoluble residue; *m* – modulus of hydraulicity ($m = \frac{CaO+MgO}{SiO_2+Al_2O_3+Fe_2O_3}$)

The XRD studies showed that main crystalline phases in the synthesized binder after firing were quartz (SiO_2), calcium oxide (CaO), magnesium oxide – periclase (MgO), dicalcium silicate – belite ($2CaO \cdot SiO_2$) and tricalcium aluminate ($3CaO \cdot Al_2O_3$). Gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) was formed if the temperature were higher than 850 °C. Undissociated calcite ($CaCO_3$) was detected when firing temperature was lower than 850 °C. In Fig. 2 the composition of synthesized series of binder (A1, A2, U2) after firing at 800 °C is compared.

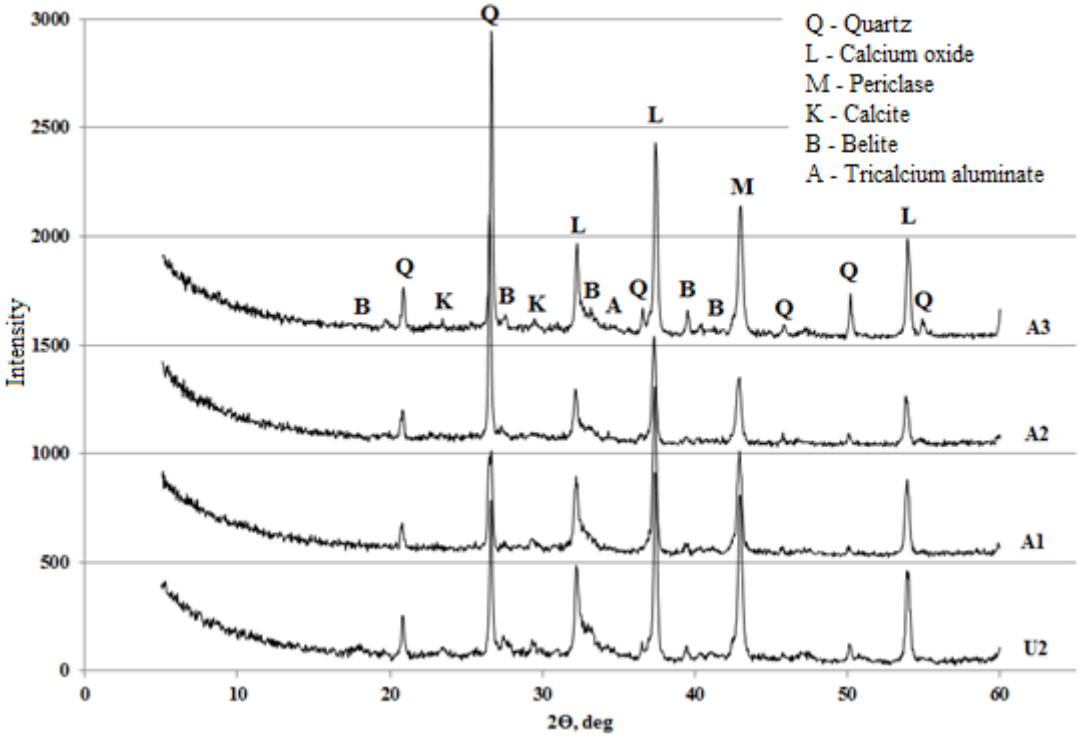

Fig. 2. The XRD patterns of synthesized binder after firing at 800 °C.

The changes of relative intensity of dominant crystalline phases depending on the firing temperature of the synthesized binder (as well as of the dolomitic marl, fired at the same temperatures) were determined by measuring the height of characteristic XRD maxima of each phase in equal conditions after firing in 5 different temperatures in the range of 750 °C to 950 °C.

According to XRD data, the amount of free CaO reached the maximum at 850 °C. The intensity of MgO crystallization increased with temperature, and till 950 °C there was not observed a decrease of its intensity that could be attributed to the involvement in the formation of new phases. The DTA data showed that dissociation of dolomite

and release of MgO had ended at approximately 770 °C. It leads to conclusion that at higher temperatures the gain of diffraction maxima is due to the increase of crystallinity.

The intensity of crystallization of cement minerals – tricalcium aluminate (C_3A) and dicalcium silicate (C_2S) – increased with increasing temperature (Fig. 3). In compositions A1, A2 and A3 their formation was detected by XRD beginning with 750 °C, but in composition U2 and in dolomitic marl (DM) their crystallization was observed beginning with 800 °C. More cement minerals (C_3A and C_2S) have formed in the compositions with higher clay admixture (composition A3 with 30 % clay).

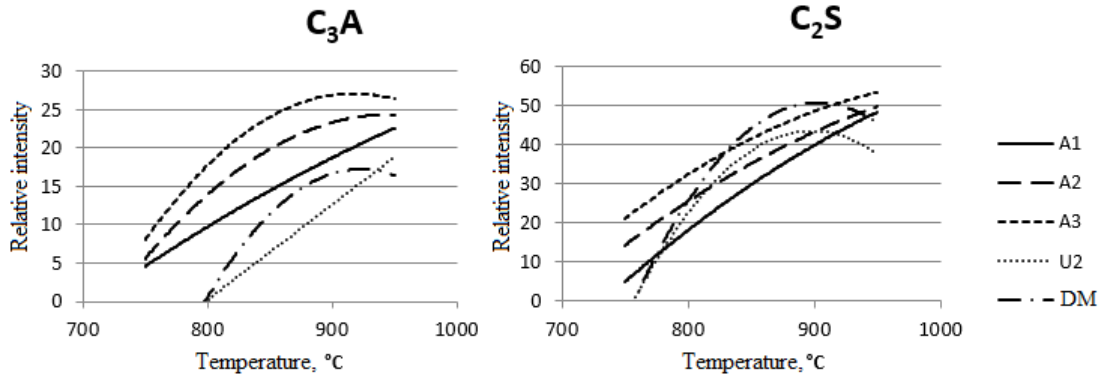

Fig. 3. The changes of relative amount of C_3A and C_2S in the synthesized compositions (measured by XRD) depending on firing temperature.

The obtained amount of cement minerals at equal burning temperature is higher in compositions, where more clay is added. For example, in composition A1 (13 % clay) the crystallization intensity of cement minerals at 850 °C is the same as in composition A2 (24 % clay) at 800 °C. It means that increased clay additive allows reducing the firing temperature, providing an economic advantage.

By the titration method it was determined that the amount of free (active) CaO + MgO in the synthesized binder reaches maximum (23 % to 31 %) at 800 °C to 850 °C.

The amount of active SiO_2, Al_2O_3 and Fe_2O_3 was measured by dissolving binder in a highly diluted HCl. It can be assumed that active SiO_2, Al_2O_3 and Fe_2O_3 participate in the reaction of cement mineral formation. While these oxides are bonded in the clay mineral structure, they are insoluble, but, when the clay minerals are dissociated, they turn into an active, soluble state. The amount of active SiO_2 and Al_2O_3 in all compositions increases with increased firing temperature, but the amount of active Fe_2O_3 is very low and does not change depending on the temperature. Correlation could be established that in all compositions regardless of the firing temperature the approximate ratio $SiO_2 : (Al_2O_3 + Fe_2O_3)$ is about 1 : 1.

Synthesized Binder after Hydration

For the investigation of changes of phase composition during the hydration, XRD method was used. In all compositions there are similar crystalline hydration products after 28 days of hardening – portlandite ($Ca(OH)_2$), brucite ($Mg(OH)_2$), calcium aluminate hydrates (mostly $4CaO \cdot Al_2O_3 \cdot 13H_2O$), and other (unhydrated) phases –

quartz (SiO_2), periclase (MgO), calcite ($CaCO_3$), belite ($2CaO \cdot SiO_2$) and gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$).

As calcium silicate hydrates (C-S-H) are Roentgen-amorphous, the hydration of $2CaO \cdot SiO_2$ can be represented by a decrease in the amount of dicalcium silicate itself (Fig. 4). The hydration of $2CaO \cdot SiO_2$ is slow and XRD studies show the presence of unhydrated C_2S in the material even after 3 months of hydration. Contrary, the C-A-H is formed as soon as in 1 hour from the addition of water, and full hydration is achieved after 1 month. The fast hydration of calcium aluminate is responsible for the quick setting of mortar.

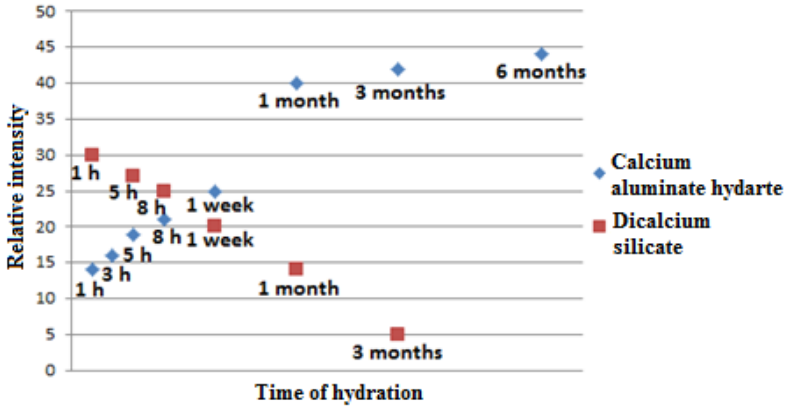

Fig. 4. Formation of calcium aluminate hydrate and decrease of dicalcium silicate in the synthesized binder A2 (fired at 800 °C) depending on the time of hydration (determined by XRD).

Newly formed crystalline phases were observed in the synthesized binders after 1 year of hardening that was not detected in samples hardened for 3 months. By using XRD analysis it has been found that the new phases are artinite ($MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$) and hydrotalcite type compound (general formula $Mg_{1-x}(Al, Fe)_x(OH)_2 \cdot [A^{n-}]_{x/n} \cdot mH_2O$, where $[A^{n-}] = OH^-$, Cl^-, SO_4^{2-}, CO_3^{2-}, H_2O [8]) with formula $Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$.

The changes in the amount of crystalline phases during the hydration depending on firing temperature (850 °C to 1000 °C) in composition U2 were investigated by using XRD method (Fig. 5). Each phase changes were investigated separately. In the samples that were fired at lower temperature (850 °C, 900 °C) the amount of $Ca(OH)_2$ was increasing faster than in samples that were fired at higher temperature. This illustrates that more active CaO is obtained at a lower temperature. The amount of MgO was decreasing during the hydration. This was a slow process, and after 28 days unhydrated MgO still remained in samples. In comparison with samples fired at higher temperatures, MgO that was formed at 850 °C was very active and it hydrated especially fast in the first week. This indicates the transition of MgO to inactive form at 900 °C. During the hydration the amount of $Mg(OH)_2$ increased inversely proportional to the amount of MgO. As the amount of MgO in the samples fired at 850 °C was fast decreasing, but the formation of $Mg(OH)_2$ was not detected by XRD, it could be concluded that amorphous hydration products are formed, such as magnesium oxyhydrate ($MgO \cdot Mg(OH)_2 \cdot mH_2O$) [10]. There is also a chance that rapid

further carbonation of formed $Mg(OH)_2$ appeared, and magnesium carbonate hydrates were formed that could not be detected by using XRD because of low state of crystallinity. The hydration of MgO was delayed in the samples that were fired at temperatures higher than 900 °C. In the samples fired at 900 °C to 950 °C the formation of $Mg(OH)_2$ occurred after 3 days, but at 1000 °C – after 7 days. The hydration of belite ($2CaO \cdot SiO_2$) was slow, especially, if the samples were fired at high temperature (950 °C, 1000 °C). In that case, after 28 days of hydration a large amount of unhydrated mineral remained. If the firing temperature of samples were lower, the hydration of belite would be faster.

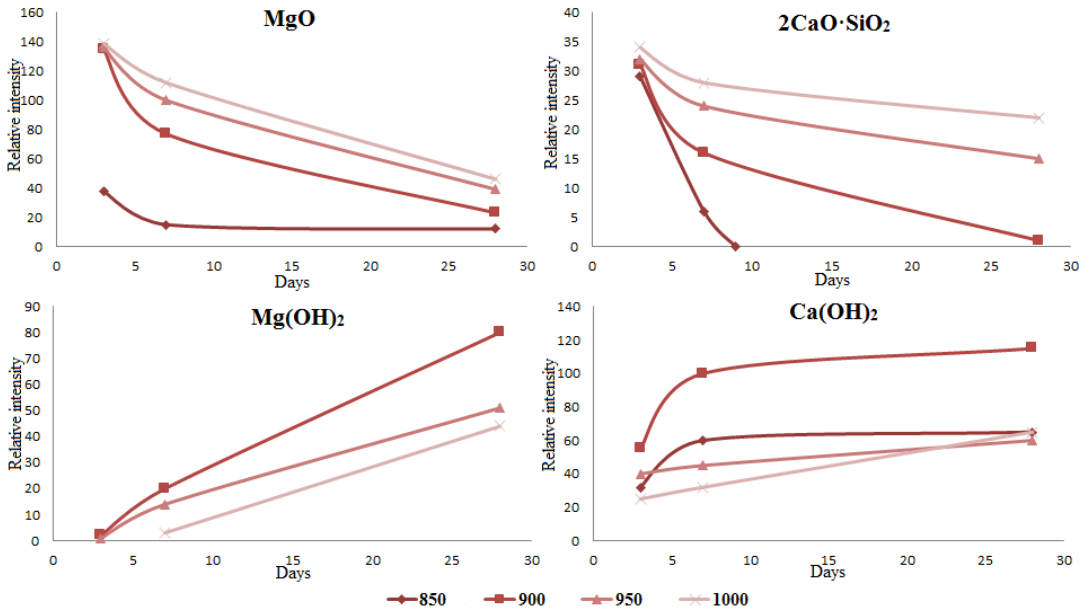

Fig. 5. The changes in the amount of crystalline phases – MgO, $Mg(OH)_2$, $Ca(OH)_2$ and $2CaO \cdot SiO_2$ – in the composition U2 during the hydration (measured by XRD).

Thermographic studies of synthesized binder samples after 2 months of curing showed two broad endothermic thermal effects at 135 °C and 220 °C (Fig. 6) that corresponded to the decomposition of calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H), respectively [8], [11]. At the same temperature range (120 °C to 400 °C) thermal effects could also appear that were related to the dehydration of Mg carbonate hydrates as well as decomposition of undissociated clay minerals [12], [13]. Thus, it can be concluded that in such a complicated system, as it is in this case, the overlapping of thermal effects can occur. The rest of thermal effects, which were observed in all compositions, corresponded to the decomposition of $Mg(OH)_2$ (400 °C to 410 °C) and $Ca(OH)_2$ (approx. 510 °C), the quartz transition (573 °C) and dissociation of $CaCO_3$ (approx. 800 °C).

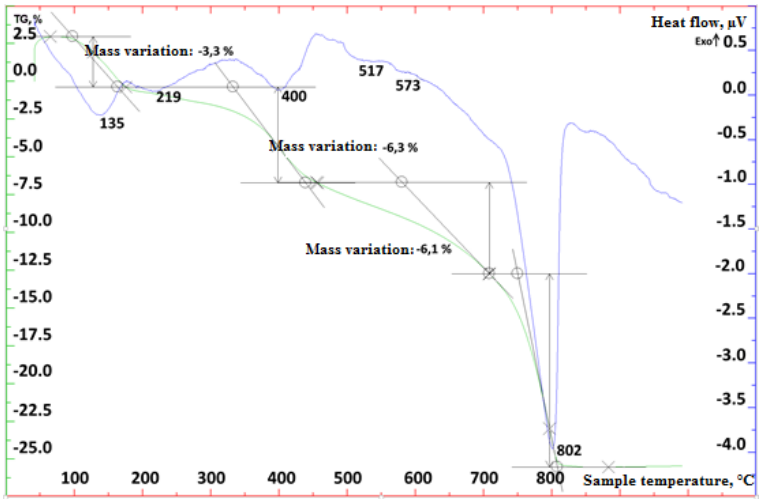

Fig. 6. DTA curve of the composition U2 after 2 months of hydration.

The structural changes of binder (compositions A1 and U2) during the hardening process of the material were investigated by using SEM analysis in every 7 days for 3 months. The shortened statement of results can be seen in Fig. 7. The samples were prepared by firing the compositions at 800 °C, grinding, and adding water to the grout consistency (no aggregate or setting retarder was used).

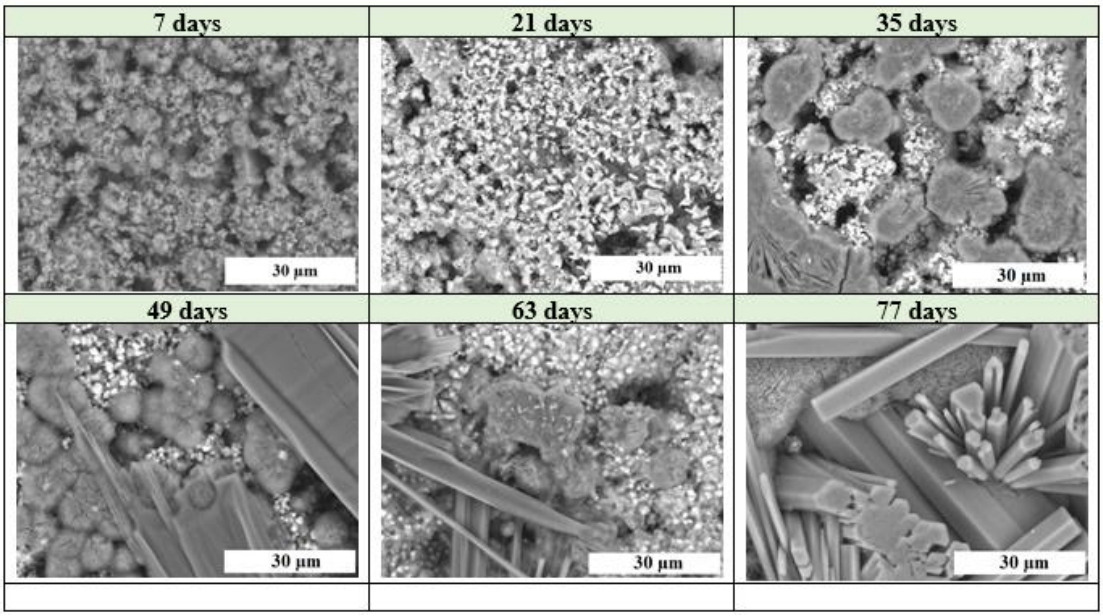

Fig. 7. The structural changes in synthesized binder (composition A1) during the hardening (measured by SEM, 2000x magnification).

During the first month of hydration, fine crystals were growing and agglomerating on the surface of samples. When the curing time reached 5 weeks, monolithic, hexagonal, prism-type crystals were appearing on the surface of sample of composition A1 (Fig. 8: A), and also rosette-type crystalline structures were grown in the pores (likely, hydromagnesite) (Fig. 8: B). The structure of sample U2 was still finely-grained after 5 weeks of hydration. The formation of gel-like C-S-H was observed beginning with 1 month curing time.

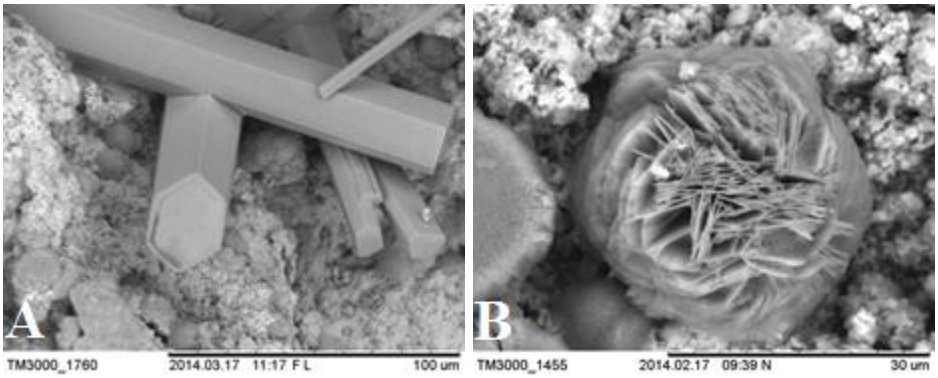

Fig. 8. A: Prism-type hexagonal crystals (1000x magnification); B: Rosette-type crystalline structure (3000x magnification).

The SEM images showed intense intergrowth of the prismatic crystals. After 12 weeks the surface of sample A1 was almost fully covered by the network of prism-like monolithic crystals (Fig. 9). Such structure can be the reason of the excellent durability and increased mechanical strength, comparing to calcitic binders. Due to the monolithic structure of the prismatic crystals, they act as a holding network, which increases the bonding strength of binder.

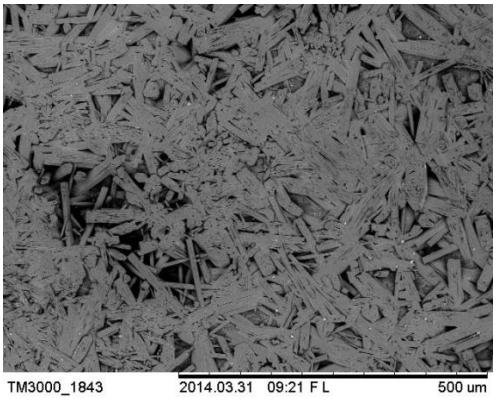

Fig. 9. SEM micrograph of composition A1 after 11 weeks of hardening (200x magnification).

SEM/EDS method was used to determine the phase composition (curing time 6 and 14 weeks). Mostly phases with high content of Mg (also Ca) in different zones were identified by EDS. All across the surface as dominating elements Mg and O were detected. The amount of Si was low, and Al was found rarely. It led to a conclusion that as a result of carbonation the surface was covered mostly with hydration and carbonation products of CaO and MgO, which were intensively grown together, forming phases with variable and complex composition, and Si and Al containing compounds were beneath the surface. After 6 weeks of hardening the newly-formed prismatic crystals contained only Mg and O, but after 14 weeks (as in Fig. 10) their elemental composition could be characterized by approximate mass ratio Mg : C : O = 2 : 1 : 6.

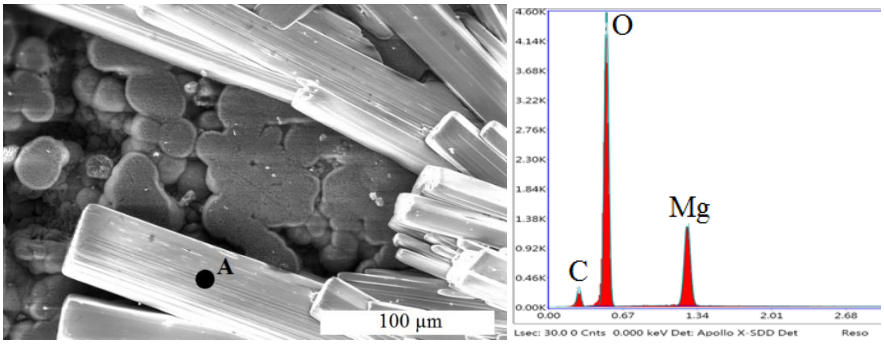

Fig. 10. The SEM micrograph of composition A1 after 14 weeks of hardening, and the EDS spectrum of spot A.

Judging from the prismatic, hexagonal crystal structure and elemental composition (estimated main component mass ratio Mg : C : O = 2 : 1 : 6), the crystals may be carbonation product of brucite – hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$).

The porosity, pore size distribution and pore structure are one of the most important properties that affect the water permeability of mortar. That is the reason why they are significant, considering the compatibility of materials in restoration. It is important that the restoration material must have similar porosity with original material. Compatible porosity and pore size distribution provide free moisture flow through the materials (historical and restoration), thus reducing the risk that a damage zone could form in the interaction surface between materials because of water or salt crystallization [4].

Restoration mortar must meet the following prerequisites to be considered compatible with the original [14]:

- porosity equal or higher than original;
- strength equal or lower than original;
- lower density and better moisture permeability than original;
- sufficient durability.

According to the *ROCEM* research, the diameter of pores from samples of historic Central Europe Roman cement mortars is in the range of 0.04 µm to 3.1 µm [4]. The mercury porosimetry test indicated that after 4 months of hardening the pore size distribution in the synthesized samples was wide and similar to that of historic Roman cement mortars (approximately 0.01 µm to 5 µm). It allowed considering that the synthesized binder would provide free migration of the moisture through the original and restoration material. The pore size distribution of calcitic Roman cement *Prompt*, cured at the same conditions, was narrow (0.03 µm to 0.1 µm), and there were no large pores found that could impact the migration of water. The measured frost resistance of synthesized binder of all compositions was higher than 10 cycles.

The free water absorption of the synthesized compositions reached 28 % to 32 % and it was completed as early as in 1 hour. The water absorption of calcitic Roman cement *Prompt* was lower – 23 %, and the uptake rate was slower – samples were fully saturated just after 24 hours.

As the porosity of historical Roman cement mortars is high (30 vol% to 40 vol%) [1], [8], the restoration mortar should reach the same values or higher. The mortar samples of synthesized binder could be characterized as highly porous (porosity of samples without aggregate – 40 % to 43 %; with aggregate (1 : 2.5) – 35 %). In comparison, porosity of calcitic Roman cement *Prompt* was lower (without aggregate – 34 %; with aggregate (1 : 2.5) – 29 %).

The compressive strength of synthesized binder samples was 4 MPa to 8 MPa after 7 days of hardening and 8 MPa to 10 MPa – after 28 days (Fig. 11). It was equivalent to compressive strength values of historical dolomitic Roman cement from Sloka (Latvia) (4 MPa to 7 MPa and 10 MPa to 12 MPa, respectively), given in literature [2]. Compositions, where Devonian clay was used (A1 and A2), reached higher compressive strength. Comparing the synthesized binder compositions, the highest strength after 1 month was presented by the samples with the lowest clay content (composition A1, containing 13 % clay).

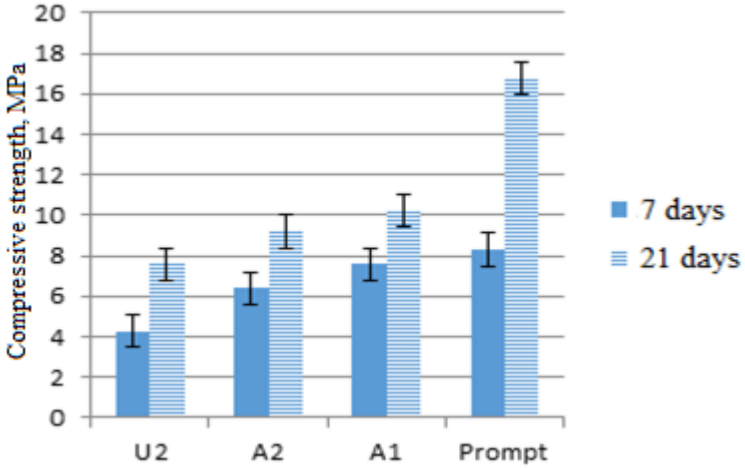

Fig. 11. The compressive strength of binder samples after hardening for 7 and 28 days.

As the hardening of material results from two different mechanisms (carbonation in the air and hydration with the water), the curing conditions are very important. It must be ensured that the initial curing takes place in a high humidity, but later the air access must be provided (samples must not be placed in water) in order to allow the carbonation.

The summary of characteristic physical and mechanical properties of binder is given in Table 3. The synthesized material is deemed suitable for restoration purposes based on its properties similar to historical dolomitic Roman cement mortars: high porosity (40 % to 43 %) and water absorption (28 % to 32 %), low density (1.32 g/cm^3 to 1.38 g/cm^3), high compressive strength (8 MPa to 10 MPa after 28 days), good durability (frost resistance – more than 10 cycles), fast setting (once water has been added setting starts between 3 minutes to 30 minutes), high hydraulicity (modulus of hydraulicity (Eq. (1)) = 2.39 to 3.21) and finally, its light brown color.

Table 3

Summary of Physical and Mechanical Properties of Roman Cement Samples

	A1_800	A2_800	U2_800	Calcitic Roman cement *Prompt* (800 °C to 1200 °C) (France)	Historical dolomitic Roman cement (Riga) [2]
Raw materials	13 % non-carbonatic clay; 87 % dolomite flour	24 % non-carbonatic clay; 76 % dolomite flour	24 % carbonatic clay; 76 % dolomite flour	Calcitic marlstone	Dolomitic marlstone
Firing temperature, °C	800	800	800	800 to 1200	800
Start of setting, min	3	30	15	7	45 to 70
End of setting, min	16	>180	180	12	150 to 240
Compressive strength after 7 days, MPa	8	6	4	8	4 to 7
Compressive strength after 28 days, MPa	10	9	8	17	10 to 12
Water absorption, %	28	32	32	23	-
Porosity, %	40	43	43	34	-
Apparent density, g/cm^3	1.38	1.33	1.32	1.49	-
Pore size, μm	0.01 to 1.00	0.01 to 5.00	0.01 to 7.00	0.03 to 0.10	-
Color	Light brownish-yellow	Light red	Light brownish-red	Brownish-yellow	-

CONCLUSIONS

1. A hydraulic low-temperature binder with properties that closely conform to historical dolomitic Roman cement has been obtained and investigated. Binder main anticipated usage is aimed at the restoration of historical objects.
2. Optimal mixtures of raw materials for the synthesis of binder have been defined:
   - A1: 87 % dolomite flour + 13 % Devonian clay (Liepa deposit);
   - A2: 76 % dolomite flour + 24 % Devonian clay (Liepa deposit);
   - U2: 76 % dolomite flour + 24 % Quaternary clay (Spartaks deposit).
3. The firing temperature of the mixtures of raw materials – 750 °C to 1000 °C, optimal firing temperature – 800 °C to 850 °C.
4. Increased clay additive allows reducing the firing temperature. For example, in composition A2 (24 % clay) the crystallization intensity of cement minerals at 800 °C is the same as in composition A1 (13 % clay) at 800 °C.
5. A full chemical analysis of raw materials, synthesized binder and historical mortars has been performed. The phase composition of synthesized binder after firing, as well as after hydration and hardening has been determined by using DTA and XRD. The investigation of the changes in microstructure of binder during hardening is based on the results of SEM and EDS data.
6. The binder obtained from mixture of dolomite flour and clay is characterized by high mechanical strength (8 MPa to 10 MPa after 28 days), which is achieved due to its specific structure. It is composed of the lime-type structure ($Ca(OH)_2$, $Mg(OH)_2$, $CaCO_3$) and amorphous and crystalline hydration products such as calcium silicate hydrates, calcium aluminate hydrates, $Mg(OH)_2$ carbonation products that have tight intergrowth with the carbonate phases. The prismatic crystals of Mg carbonate hydrates act as a holding network, improving the bonding and increasing the strength.
7. The strength of the material has been determined by two processes – the hydration of hydraulic components and carbonation of $Mg(OH)_2$ and $Ca(OH)_2$.
8. The hydraulic properties and hardening of the binder are provided by hydraulically active minerals – $2CaO \cdot SiO_2$ (C_2S) and $3CaO \cdot Al_2O_3$ (C_3A), which are formed already at 800 °C to 850 °C, but in the series when Devonian clay is used – even at 750 °C. It is essential that at these temperatures gehlenite and other phases, which are not hydraulically active, have not been formed yet. In comparison with calcitic binders, the hydration of MgO and further carbonation are of great importance in the hardening process of synthesized binder.
9. Physico-mechanical properties of hardened mortar samples have been determined – pore size distribution (0.01 μm to 5 μm), frost resistance (> 10 cycles), water absorption (28 % to 32 %), open porosity (40 % to 43 %), compressive strength (8 MPa to 10 MPa after 28 days).
10. The synthesized Roman cement type binder is more appropriate for restoration purposes, comparing with commercially available calcitic Roman cement *Prompt*

(produced in France), because it forms more porous, less dense, more “breathable” mortar for the restoration of historical objects.

11. Synthesized binder is fast setting. The setting of all series of obtained binder fired at 800 °C starts at less than 30 minutes.
12. The obtained binder is characterized by high open porosity (40 % to 43 %), which conforms to the porosity of historical Roman cement samples (30 % to 40 %), thus providing free water and moisture migration through the materials, which is one of the most important factors of the compatibility of materials in restoration.
13. The obtained results about the formation of Mg containing crystalline phases and hydraulic components during long-time hardening can explain the longevity or degradation of many historical objects.

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