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Influence of firing temperature on the chemical properties of hydraulic dolomitic binder

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The synthesis of a binder from the mixture of dolomite flour and clay is investigated. The main anticipated usage of the binder is for the restoration of historical dolomitic Roman cement objects. During the 19th/20th century, in the territory of Latvia dolomitic Roman cement was the main hydraulic binder applied for the construction of buildings. It was processed in Riga since 1865 by firing the local raw material dolomitic marlstone below its sintering temperature (800–900 °C) and by fine milling. Because of its fast setting and good water resistance, the material was used mostly for decorative elements of facades. However, since the middle of the 20th century its production has been stopped. With the aim to provide a compatible material for restoration needs, compositions from dolomite flour and clay were investigated as a perspective raw material for the synthesis of a low-temperature hydraulic binder. Mixtures from two types of clay and dolomite flour in powder state were synthesized. Clay content in the compositions varied from 13 to 30 %. Samples were prepared by mixing the raw materials, semi-dry pressing and firing at 750–950 °C. The study gives an insight into the chemical processes that occur during the synthesis of a binder from a mixture of clay and dolomite flour. Thermochemical processes in the obtained binder depending on production temperature and clay type were compared by using the XRD analysis and a full chemical analysis.

Key words: binder, dolomite flour, hydraulic components, XRD, chemical analysis.

Introduction

Roman cement was a widely used binder in all Europe in the 19th/20th century. It was obtained from marlstone – a rock containing 15–40 % of clay and 60–85 % of carbonates (limestone or dolomite). The process was simple – the marlstone was fired at low temperatures (800–1200 °C) and ground to a fine powder state, thus obtaining a hydraulic binder that did not slake in contact with water [1, 2, 3].

Because of geological differences, in distinction from the other parts of Europe where calcitic Roman cement was mostly applied, on the territory of Latvia beginning with the 1860s the dolomitic Roman cement was produced. It was obtained by firing the locally sourced dolomitic marlstone below the sintering temperature (800–900 °C) and grinding it to a floury fineness [4]. The dolomitic Roman cement was used in the construction of several significant historical buildings of Latvia of the late 19th / early 20th centuries [5]. The advantages of the Roman cement were a 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 [1, 6, 7].

Since the middle of the 20th century the producing of dolomitic Roman cement has been stopped. Still there is a need for a compatible binder for restoration purposes.

With the aim to provide a compatible material for restoration needs, compositions from dolomite flour and clay were investigated as a perspective raw material for the synthesis of a low-temperature hydraulic binder. The formation of hydraulic components – 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 this binder.

Materials and methods

The binder was obtained from a range of mixtures by using two types of pulverized clay and dolomite flour. The components of each mixture are given in Table 1. The chemical composition of the raw materials was determined using a classical chemical analysis. The results are summarized in Table 2.

Table 1. Composition of experimental mixtures, wt.%

Composition designation	Quaternary clay (Spartaks deposit, Latvia)	Devonian clay (Liepa deposit, Latvia)	Dolomite flour (Kranciems quarry, Latvia)
U2	24	-	76
A1	-	13	87
A2	-	24	76
A3	-	30	70

Table 2. Chemical composition of the raw materials, wt.%

Component \ Sample	Quaternary clay (Spartaks deposit)	Devonian clay (Liepa deposit)	Dolomite flour (Kranciems quarry)	Error, ± absolute %
LOI at 400 °C	1.70	1.34	0.60	0.30
LOI at 1000 °C	11.62	3.31	38.87	0.30
SiO_2	49.52	71.22	8.47	0.50
CaO	9.04	0.37	27.88	0.50
MgO	3.48	0.96	17.83	0.50
Al_2O_3	14.84	14.58	4.92	0.50
Fe_2O_3	5.07	4.17	0.58	0.10
Na_2O	0.50	0.06	0.11	0.01
K_2O	3.39	3.21	0.21	0.01
TiO_2	0.51	0.69	-	0.01
Total	99.67	99.91	99.47	-

*LOI – loss of ignition

Specimens were prepared by weighing the required amounts of raw materials – clay and dolomite flour – and homogenizing the mixture in dry state. Plate-like samples (56×26×6 mm) were shaped under the pressure of 20 MPa (by adding 10 wt.% water), dried and fired in the temperature range of 750–950 ºC in 50 ºC steps, with the holding time of 2 hours at each temperature.

The thermo-chemical processes in the synthesized binder, depending on the firing temperature and clay content in the mixture, were analyzed using the XRD (X-ray diffraction) analysis (*Rigaku Ultima* + with CuK_α radiation at a scanning interval 5–60° (2θ) and speed 2°/min, interpretation according to the data base *PDF-4+* 2014), as well as a full chemical analysis (according to EN 196-2: 2013). The amount of active oxides – soluble SiO_2 and R_2O_3 (Al_2O_3 and Fe_2O_3) – in the binder were determined by dissolving the sample in a 5 % HCl solution.

Results and discussion

The hydraulicity of a binder can be characterized by using the hydraulicity modulus (Eq. 1) [8].

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

The lower is the modulus, the higher is the hydraulicity of a binder. The general classification states that for lime binders m = 1.7–9.0 but for the Roman cement < 1.7 [8]. However, in comparison with calcitic binders, the dolomitic Roman cement does not fully conform to this classification, and a dolomitic binder with the modulus higher than 1.7 can achieve the properties of Roman cement [9]. In Table 3 one can see that all synthesized compositions closely match the composition of the historical dolomitic Roman cement and are highly hydraulic (m = 2.39–3.21). The amount of released CO_2 (10–14 %) may be attributed to the presence of undissociated carbonates. This value is close to the amount of carbonates in the historic dolomitic Roman cement as it is described in the literature [9] where it is considered as advisable for gaining a higher mechanical strength.

It must be taken into account that the insoluble residue (IR) contains not only sand but also unreacted clay minerals, because the temperature of 800 °C is too low for them to fully dissociate.

Table 3. Comparison of the chemical compositions of synthesized binders (firing temperature 800 °C), wt.%

Component \ Sample	Composition U2	Composition A2	Composition A1	Historical dolomitic Roman cement [10]	Error, ± absolute %
LOI at 400 °C	0.46	0.50	0.54	5.39	0.10
LOI at 1000 °C	12.45	10.58	13.91	4.90	0.20
IR	29.46	25.28	17.16	18.10	0.50
SiO_2	8.08	8.08	6.90	5.66	0.50
CaO	29.75	27.06	30.26	34.24	0.50
MgO	18.28	17.65	21.66	24.14	0.50
Al_2O_3	9.61	9.20	8.01	5.65	0.50
Fe_2O_3	1.68	1.40	1.27	1.31	0.20
Na_2O	0.05	0.07	0.06	-	0.01
K_2O	0.73	0.71	0.71	-	0.01
Total	100.55	100.53	100.48	99.39	-
CaO/MgO	1.63	1.53	1.40	1.42	-
m	2.48	2.39	3.21	4.63	-

*LOI – loss of ignition; IR – insoluble residue; m – modulus of hydraulicity.

The XRD studies (Fig. 1) showed that the main crystalline phases in the synthesized binder after firing in the temperature range 750–950 °C 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 detected at temperatures above 850 °C, but for undissociated calcite ($CaCO_3$) the temperature was lower than 850 °C.

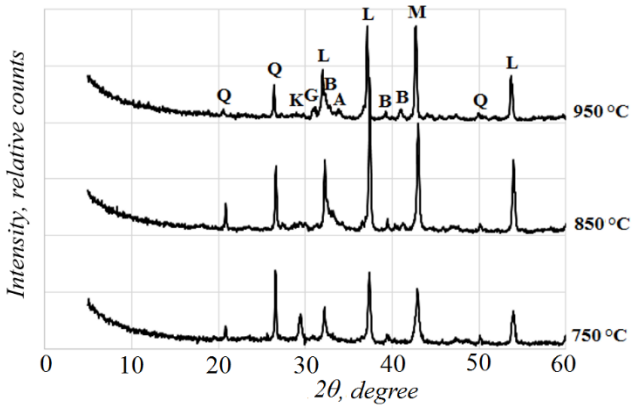

Fig. 1. XRD patterns of composition A1 fired at a temperature of 750, 850 and 950 °C (Q – quartz (01-076-9281, hkl – 100), L – calcium oxide (00-048-1467, hkl – 220), K – calcite (00-005-0586, hkl – 104), M – periclase (00-045-0946, hkl – 200), G – gehlenite (00-035-0755, hkl – 211), B – belite (00-033-0302, hkl – 002), A – tricalcium aluminate (00-008-0005, hkl – 440)).

Changes of the relative intensity of dominant crystalline phases depending on the firing temperature of the synthesized binder were determined by measuring the height of characteristic XRD maximums of each phase in equal conditions. As the mass of a sample, the particle size and the settings of the diffractometer stood unchanged, and changes of the maximum intensity can be attributed to changes of the amount of a phase in a sample.

According to data obtained from the XRD analysis, the free CaO crystallization reached the maximum at 850 °C (Fig. 2).

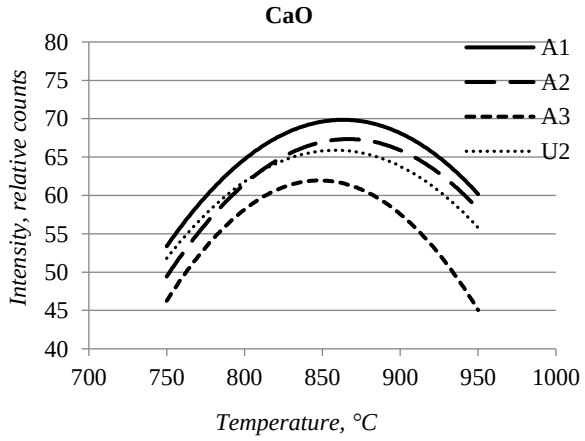

Fig. 2. The relative changes of CaO crystallization intensity depending on the firing temperature.

The intensity of MgO crystallization increased with temperature (Fig. 3), and up to 950 °C there was no decrease of its intensity, which could be attributed to the involvement in the formation of new phases. As the dissociation of dolomite and the release of MgO had ended at approximately 800 °C, it can be concluded that at higher temperatures the gain of diffraction maximums is due to the increase of crystallinity.

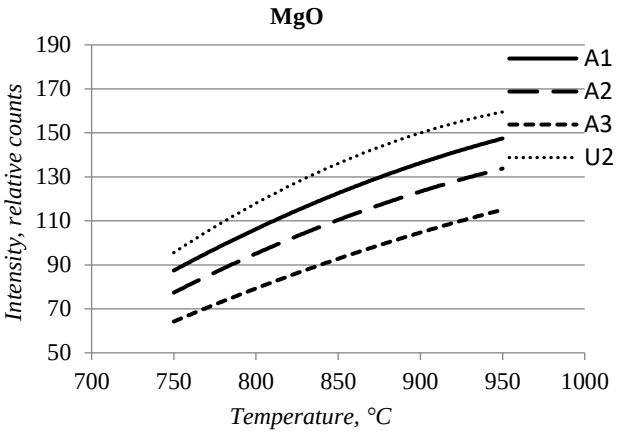

Fig. 3. Relative changes of MgO crystallization intensity depending on the firing temperature

The crystallization intensity of hydraulic components – dicalcium silicate ($2CaO \cdot SiO_2$) and tricalcium aluminate ($3CaO \cdot Al_2O_3$) – increased with increasing the temperature (Fig. 4 and Fig. 5).

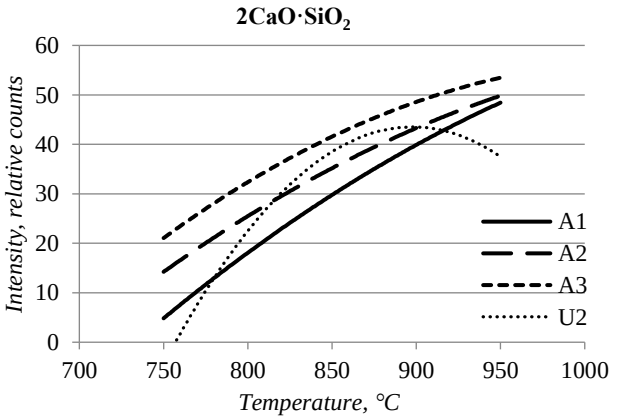

Fig. 4. Relative changes of the $2CaO \cdot SiO_2$ crystallization intensity depending on the firing temperature

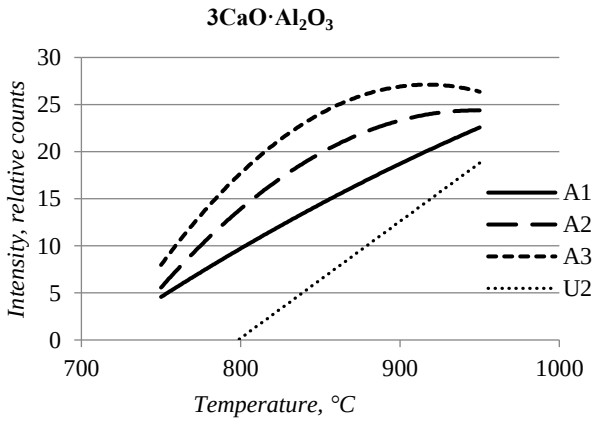

Fig. 5. Relative changes of the $3CaO \cdot Al_2O_3$ crystallization intensity depending on the firing temperature

In compositions where Devonian clay was used (A1, A2 and A3), their formation was detected by XRD beginning with 750 °C. In the composition U2, the formation of $3CaO \cdot Al_2O_3$ started beginning with 800 °C, but of $2CaO \cdot SiO_2$ – between 750 °C and 800 °C. Higher amounts of hydraulic components had formed in the compositions with a higher clay admixture.

The obtained amount of cement minerals at an equal burning temperature was higher in compositions where more clay was added. For example, in composition A1 (13 % of clay) the crystallization intensity of cement minerals at 850 °C was the same as in the composition A2 (24 % of clay) at 800 °C. This means that a higher clay additive allows to use a lower firing temperature, at the same time obtaining the needed amount of cement minerals providing an economic advantage.

Hydraulic components in a binder are of great importance, providing for the mechanical strength and water resistance of the mortar. The amount of active SiO_2, Al_2O_3 and Fe_2O_3 in the synthesized binder after firing was measured by dissolving the binder in a highly diluted HCl. It can be assumed that active SiO_2, Al_2O_3 and Fe_2O_3 participate in the formation of hydraulic components (cement minerals – $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$). When these oxides are bound in the clay mineral structure they are insoluble, but when the clay minerals dissociate, they turn into an active, soluble state. In Figs. 6 and 7 one can see that the amount of active SiO_2 and Al_2O_3 in all compositions increases with increasing the firing temperature. The increase can be attributed to the clay structure decomposition and the formation of new phases – calcium silicate and calcium aluminate which are hydraulically active.

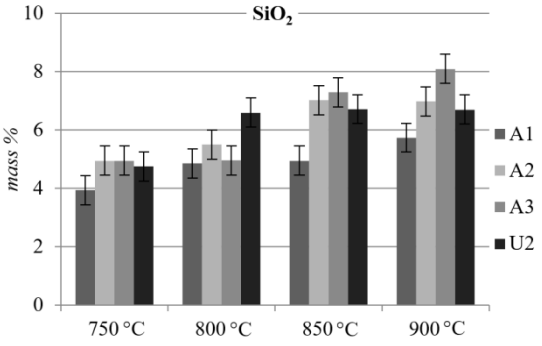

Fig. 6. The amount of active SiO_2 in the obtained binder, depending on the firing temperature

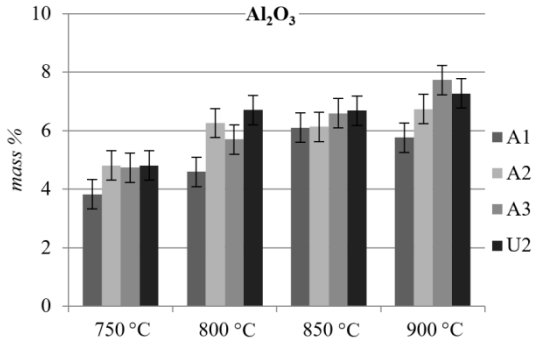

Fig. 7. The amount of active Al_2O_3 in the obtained binder, depending on the firing temperature

The amount of Fe_2O_3 was very low, and its increase was not detected (Fig. 8). A correlation could be established that in all compositions regardless of the firing temperature the approximate ratio $SiO_2 : R_2O_3$ was about 1 : 1.

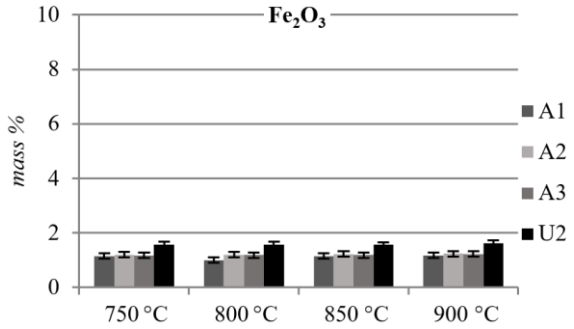

Fig. 8. The amount of active Fe_2O_3 in the obtained binder, depending on the firing temperature

Al_2O_3 was found to be transformed into the active state more easily than SiO_2. The increase of the amount of active Al_2O_3 was detected already at 800 °C, but of SiO_2 – at 850 °C.

Conclusions

A hydraulic low-temperature binder was obtained from a mixture of dolomite flour and clay. The binder's main anticipated usage was for the restoration of historical objects. The chemical and mineralogical composition of the binder closely conformed with the historical dolomitic Roman cement.

An increased clay additive allows to reduce the firing temperature, thus giving an economical advantage. For example, in the composition A2 (24 % of clay) the crystallization intensity of hydraulic components at 800 °C was the same as in the composition A1 (13 % of clay) at 850 °C.

The hydraulic properties of the binder are provided by hydraulically active minerals $2CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ which are formed already at 800–850 °C, but in the series when the Devonian clay is used – even at 750 °C. It is essential that at these temperatures gehlenite and other phases that are not hydraulically active are not yet formed.

The amount of the active oxides that participate in the formation of hydraulic components increased with higher firing temperatures. Based on the chemical and mineralogical analysis, 800–850 °C was chosen as the optimal firing temperature.

The usage of a mixture of clay and dolomite flour instead of the natural dolomitic marlstone can provide a better homogeneity, and in this way the composition of a binder can be precisely predicted.

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DEGIMO TEMPERATŪROS ĮTAKA HIDRAULINĖS DOLOMITINĖS RIŠAMOSIOS MEDŽIAGOS CHEMINĖMS SAVYBĖMS

S a n t r a u k a

Šiame darbe iš dolomitmilčių ir molio mišinio buvo sintetinta rišamoji medžiaga, skirta istoriniams dolomitinio romancemenčio objektams restauruoti. XIX–XX a. Latvijos teritorijoje dolomitinis romancementis buvo pagrindinė hidraulinė rišamoji medžiaga, naudojama pastatams statyti. Nuo 1865 m. Rygoje ši medžiaga gaminta degant vietines žaliavas – dolomitinį mergelį – žemiau jo sukepimo temperatūros (800–900 °C) ir smulkiai malant. Tačiau dėl greitos rišimosi trukmės ir atsparumo vandeniui, gauta rišamoji medžiaga daugiausia buvo naudojama fasadų dekoratyviniams elementams restauruoti. Nuo XX a. vidurio šis gamybos būdas buvo sustabdytas. Todėl siekiant gauti medžiagą, tinkančią restauravimo darbams atlikti, buvo tiriamos dolomitmilčių ir molio mišinių sudėtys kaip galima žaliava hidraulinės rišamosios medžiagos žematemparatūrei sintezei. Iš dviejų skirtingų molio atmainų ir dolomitmilčių miltelių buvo paruošti mišiniai, kuriuose molio kiekis sudaro 13–30 %. Iš žaliavų mišinio pusiau sauso presavimo būdu suformuoti bandiniai buvo degti 750–950 °C. Atlikti tyrimai suteikia duomenų apie cheminius procesus, vykstančius rišamosios medžiagos sintezės metu. Termocheminiai procesai, vykstantys gaunant šią rišamąją medžiagą, atsižvelgiant į degimo temperatūrą ir molio atmainas, tirti atliekant XRD ir cheminę analizes.

Reikšminiai žodžiai: rišamoji medžiaga, dolomitmilčiai, hidrauliniai komponentai, XRD (RSDA), cheminė analizė.