

Investigation of Physical and Chemical Properties of Low-temperature Hydraulic Binder from Latvia's Raw Materials

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A necessity of compatible material to historical romancement for restoration needs has led to research of artificially made binders from mixtures of clay and dolomite. Low temperature hydraulic binder or so called dolomitic romancement synthesis of mixture composed from local Quaternary period clay and dolomite (both in powder state) in mass ratio 24:76 is discussed in this paper. The chemical composition of the raw materials was analyzed. Specimens were prepared by homogenizing the mixture of requisite amounts of clay and dolomite in dry state and shaping samples measuring 56x26x6 mm by semidry pressing. After firing at temperatures between 650 and 1050°C crystalline phases formed in samples were determined by XRD. Afterwards, water was added to the samples and formation of new crystalline phases was detected in the period of 28 days. Natural dolomitic marl was treated at the same conditions in order to compare the crystalline phases formed in naturally and artificially made binders. The results of XRD analysis show that crystalline phases of synthesized composition after firing are equal to crystalline phases in dolomitic marl fired at the same temperature. The main crystalline phases are quartz (SiO₂), calcium oxide (CaO), dicalcium silicate (2CaO•SiO₂), tricalcium aluminate (3CaO•Al₂O₃), gehlenite (2CaO•Al₂O₃•SiO₂) and magnesium oxide (MgO). Chemical and mineralogical composition that is close to historical material is one of the main requirements for restoration materials as they provide compatibility.

Keywords: *clay, compatibility, crystalline phases, dolomite, low-temperature binder.*

1. Introduction

One of historically widely used low-temperature binders has been romancement – i.e. natural cement, produced from clay containing carbonatic rocks. During 19th/20th century it was the main hydraulic binder applied for the construction of buildings. (Varas et al. 2005)

Historical romancement was a natural hydraulic binder produced by firing marl (mineral composed from 60–75 % calcite or dolomite and 25–40 % clay) below its' sintering temperature (800–1200°C) and grinding. This type of binder firstly was patented by James Parker in 1796. Romancement distinguished itself from other hydraulic binders by short setting time (usually 7–20 min), warm brown color and good durability. (Kozlowski et al. 2004)

In Latvia, in contrast to other parts of Europe, dolomitic romancement was used. However since the middle of 20th century its production has been stopped. (Grosvalds et al. 1997) At the same time, there is a great necessity for compatible materials for restoration purposes. Thus the aim of given research was to synthesize a hydraulic binder with chemical and mineralogical composition close to historical dolomitic romancement.

2. Methods

2.1. Raw materials

In order to obtain a mixture with chemical composition identical to historical dolomitic romancement from Quaternary period clay and dolomite full chemical analysis of raw materials was carried out. In addition, local dolomitic marl (Dzūkste deposit, Latvia) – raw material of natural dolomitic romancement – was also analyzed. The results of chemical analysis are shown in Table 1.

Content of carbonates (CaCO₃ + CaCO₃•MgCO₃) in clay reaches 23 %. It is calculated according to loss of ignition (LOI) at 1000 °C, which corresponds to CO₂ that is released from carbonates. XRD diffraction analysis (Fig. 1) approves that clay from deposit Spartaks is typical carbonate clay. Dominant clay mineral is illite. Kaolinite, microcline, plagioclase and quartz are also detected.

Dolomite from deposit Kranciems contains 88 % carbonates (mostly dolomite) and 12 % impurities as quartz and clay minerals (Fig. 2). CaO/MgO ratio is 1.56. The CaO/MgO mass ratio of pure dolomite is 1,39. (Kurss et al. 1997)

Table 1. Chemical composition of raw materials for low temperature fast-setting cement, mass %

| Component | Sample | Dolomitic marl (Dzukste deposit) | Quaternary period clay (Spartaks deposit) | Dolomite (Kranciems deposit) | Error ± absolute % |
|--------------------------------|--------|----------------------------------|---|------------------------------|--------------------|
| Loss of ignition at 400°C | | 0.64 | 1.70 | 0.60 | 0.3 |
| Loss of ignition at 1000°C | | 37.87 | 11.62 | 38.87 | 0.3 |
| SiO ₂ | | 13.26 | 49.52 | 8.47 | 0.5 |
| CaO | | 25.87 | 9.04 | 27.88 | 0.5 |
| MgO | | 16.15 | 3.48 | 17.83 | 0.5 |
| Al ₂ O ₃ | | 4.77 | 14.84 | 4.92 | 0.5 |
| Fe ₂ O ₃ | | 0.85 | 5.07 | 0.58 | 0.1 |
| Na ₂ O | | 0.03 | 0.50 | 0.11 | 0.01 |
| K ₂ O | | 0.10 | 3.39 | 0.21 | 0.01 |
| CaO/MgO | | 1.60 | – | 1.56 | – |

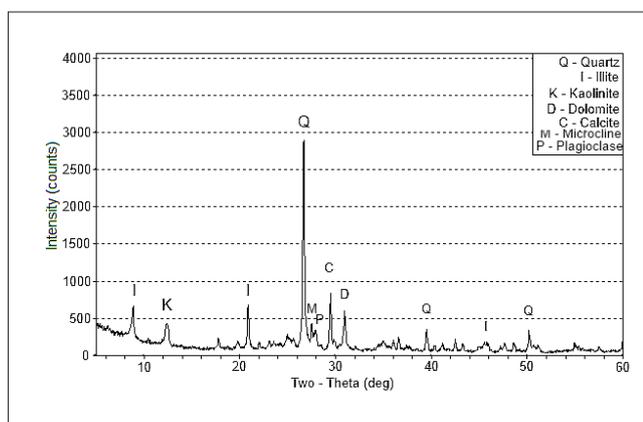


Fig. 1. XRD of clay from Spartaks deposit, Latvia

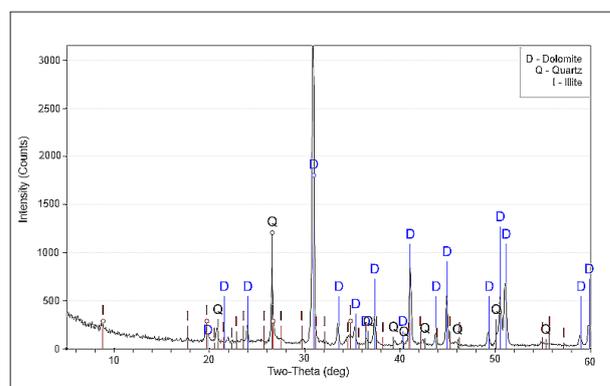


Fig. 3. XRD of dolomitic marl from Dzukste deposit, Latvia

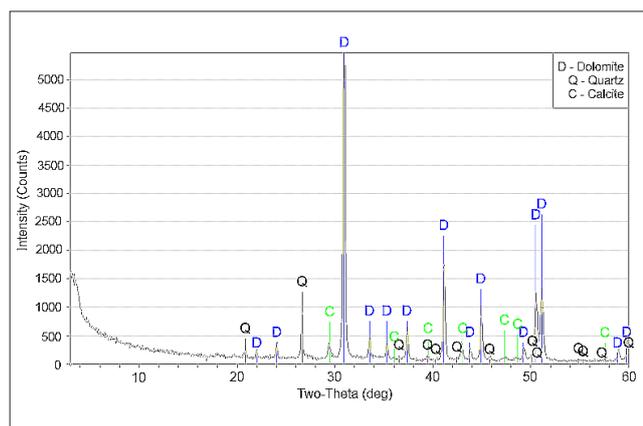


Fig. 2. XRD of dolomite from Kranciems deposit, Latvia

Chemical analysis (table 1) shows that carbonate ($\text{CaCO}_3 + \text{CaCO}_3 \cdot \text{MgCO}_3$) content in dolomitic marl from deposit Dzukste is 80 % and the rest 20 % are clay minerals and quartz. It is approved by XRD analysis (Fig. 3): dolomite, illite and quartz are the only crystalline phases detected in marl before firing.

2.2. Experimental procedure

In order to synthesize artificial dolomitic fast-setting cement, local raw materials – Quaternary period clay (Spartaks deposit, Latvia) and dolomite (Kranciems deposit, Latvia) in mass ratio 24:76 were used. The choice of mass ratio is based to chemical composition of dolomitic marl from which historically dolomitic romancement was produced. Both the chemical and crystalline composition of the raw materials were analyzed.

Specimens were prepared by weighing the requisite amounts of raw materials – clay and dolomite – and homogenizing the mixture in dry state. Plate samples were shaped under the pressure of 20 MPa (by adding 10 % water), dried and fired in the temperature range of 650–1050 °C in 50 °C steps with the holding time at each temperature for 2 hours. After firing water was added to samples for hydraulic hardening. Natural dolomitic marl was parallelly treated at the same conditions.

Development of phases in obtained material depending on production temperature has been investigated immediately after firing and after hydraulic hardening for 3, 7 and 28 days. Chemical and crystalline composition has been compared in fired natural dolomitic marl and synthesized mixture.

2.3. Analytical techniques

In order to detect chemical and mineralogical composition both of raw materials as well as the synthesized compositions, the following methods were used: 1) full chemical analysis (carried out according to EN 196-2 and A Laboratory Manual for Architectural Conservators (Teutonico, J. M., 1988)); 2) XRD (Rigaku Ultima + with $\text{CuK}\alpha$. Radiation at scanning interval $0-60^\circ$ (2θ) and speed $2^\circ/\text{min}$); 3) DTA/TG (SETARAM SETSYS Evolution – 1750).

3. Results

DTA analysis of synthesized composition (Fig. 4) shows two endothermic effects in temperature interval $124-227^\circ\text{C}$ which corresponds to release of adsorbed and chemically bounded water from clay minerals. Two sharp endothermic effects at temperatures 777°C and 853°C represents dissociation of dolomite and calcite respectively. (Svinka *et al.* 2011) Total mass loss reaches 32.6 %.

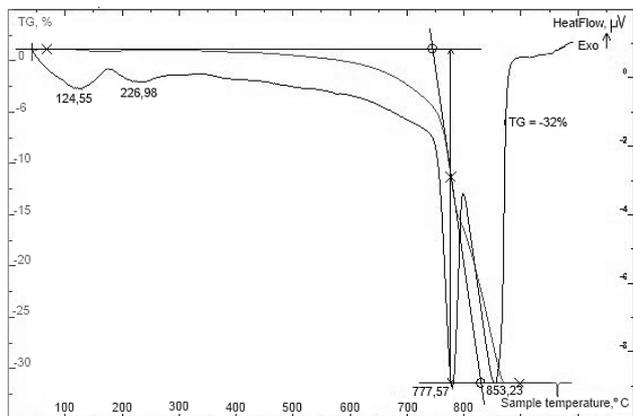


Fig. 4. DTA and TG of synthesized mixture before firing

The results of XRD analysis show that crystalline phases of synthesized composition after firing are equal to crystalline phases in dolomitic marl fired at the same temperature (Fig. 5). The main crystalline phases are quartz (SiO_2), calcium oxide (CaO), dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$), tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) and magnesium oxide (MgO). Some portlandite ($\text{Ca}(\text{OH})_2$) is detected because of rapid reaction between CaO and water in moist environment.

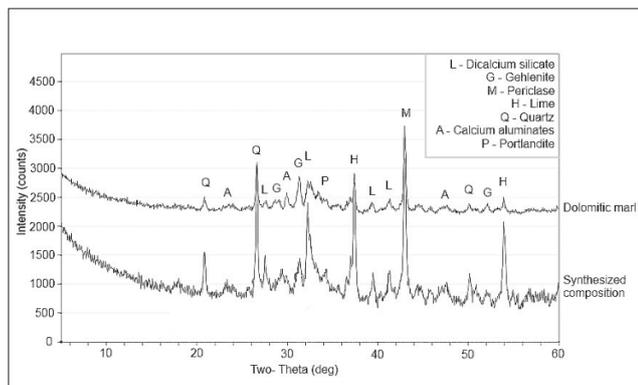


Fig. 5. XRD of natural dolomitic marl and synthesized composition after firing at 900°C temperature

Difference is notable in free CaO content – there is more of it in synthesized composition than in marl after firing.

The relative changes of the amount of crystalline phases were observed by measurement of the characteristic peaks of each phase at equal conditions. Formation of two main cement minerals depending on firing temperature is shown in Fig. 6 and Fig. 7. The tendency is similar for both – synthesized composition and natural dolomitic marl. Crystallization of dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$) and tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) begins at 800°C temperature and increases at higher temperatures. Dicalcium silicate crystallization reaches maximum at 950°C .

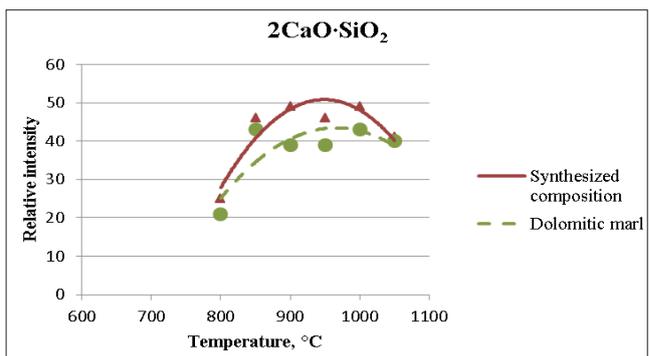


Fig. 6. The changes of amount of dicalcium silicate crystalline phase depending on the firing temperature

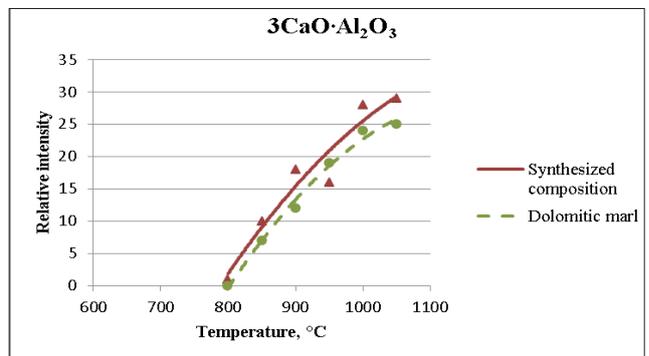


Fig. 7. The changes of amount of tricalcium aluminate crystalline phase depending on the firing temperature

Crystalline phases after hydration are the same in both – fired marl and synthesized material. They are following: calcite (CaCO_3), quartz (SiO_2), periclase (MgO), portlandite ($\text{Ca}(\text{OH})_2$), gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$), brucite ($\text{Mg}(\text{OH})_2$), dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$) and calcium aluminate hydrates (mostly $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$) (Fig. 8).

When water is added to the mixture, rapid formation of calcium aluminate hydrates occurs. Hydration is completed in few hours. The calcium aluminate hydrates mainly are detected to be $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$. In the specimens fired above 800°C after 28 days of hydration XRD analysis shows that more $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ is formed in samples fired at higher temperatures (beginning with 900°C). Rapid formation of this phase provides quick setting.

Hydration of dicalcium silicate is slow. Even after 28 days of hydraulic hardening there still is significant amount of unhydrated mineral in the specimens.

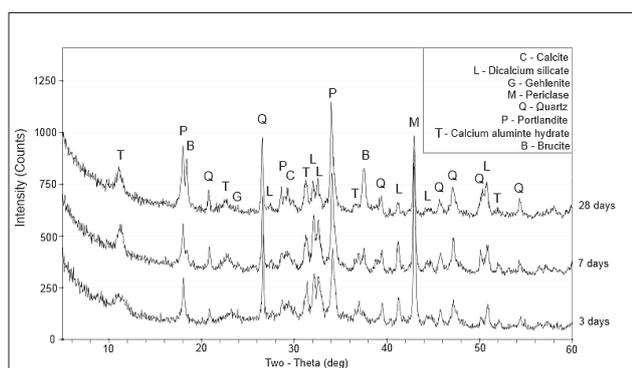


Fig. 8. XRD of synthesized mixture after firing at 900°C temperature and hydraulic hardening for 3, 7 and 28 days

The chemical as well as mineralogical composition of synthesized binder closely conforms with marl's composition (table 2).

Table 2. Comparison of chemical composition of synthesized binder and dolomitic marl, mass %

| Sample Component | Synthesized composition | Dolomitic marl (deposit Dzukste) | Error ± absolute % |
|--------------------------------|-------------------------|----------------------------------|--------------------|
| SiO ₂ | 28.07 | 21.56 | 0.3 |
| CaO | 40.15 | 42.07 | 0.5 |
| MgO | 24.80 | 26.26 | 0.5 |
| Al ₂ O ₃ | 5.06 | 7.76 | 0.5 |
| Fe ₂ O ₃ | 1.04 | 1.38 | 0.1 |
| Na ₂ O | 0.04 | 0.05 | 0.01 |
| K ₂ O | 0.32 | 0.16 | 0.05 |

4. Discussion

The formation of cement minerals is possible just after the dissociation of dolomite, when free CaO is released. Accordingly to data obtained by DTA analysis, it occurs at 777°C temperature. This is approved by XRD analysis, which detects 2CaO·SiO₂ and 3CaO·Al₂O₃ crystalline phases present already at temperatures above 800°C.

Hydraulic hardening could not be achieved without formation of cement minerals. Tricalcium aluminate provides quick setting (characteristic to romancement), but dicalcium silicate – gradual growth of strength which is important for longevity of mortar. The results of XRD analysis approve that these minerals have been formed in synthesized compositions after firing at temperatures higher than 800°C.

It is complicated to detect cement minerals' hydration products by XRD analysis, because calcium aluminate hydrates form fine crystals or stay at amorphous state, but all dicalcium silicate hydration products are gel-like with indefinite structure. (Hughes et al. 2009)

The main difference between synthesized binder and burned natural dolomitic marl is in the content of free lime –

it is higher in synthesized composition and could be caused by lower compactness of grains during firing process.

Temperatures above 900°C are inappropriate in order to obtain hydraulic binder from dolomite and clay, due to the formation of inactive MgO (periclase) which hydrates slowly and may cause damage after application of it in mortar. In addition, crystallization of gehlenite (mineral without hydraulic activity) occurs starting with 850°C temperature and higher. This phase also is undesirable if a binder with high hydraulicity is required.

5. Conclusions

Crystalline phases of artificially synthesized composition (24% clay and 76% dolomite) after firing are equal to crystalline phases in dolomitic marl fired at the same temperatures. They are quartz (SiO₂), calcium oxide (CaO), dicalcium silicate (2CaO·SiO₂), tricalcium aluminate (3CaO·Al₂O₃), gehlenite (2CaO·Al₂O₃·SiO₂) and magnesium oxide (MgO).

Chemical and mineralogical composition of mixture closely conforms with natural marl's composition. Difference is notable in free CaO content – there is more of it in synthesized composition than in marl after firing.

Crystallization of dicalcium silicate (2CaO·SiO₂) and tricalcium aluminate (3CaO·Al₂O₃) in both – synthesized composition and natural dolomitic marl – begins at 800°C temperature and increases at higher temperatures. Dicalcium silicate crystallization reaches maximum at 950°C.

Crystalline phases after hydration are calcite (CaCO₃), quartz (SiO₂), periclase (MgO), portlandite (Ca(OH)₂), gehlenite (2CaO·Al₂O₃·SiO₂), brucite (Mg(OH)₂), dicalcium silicate (2CaO·SiO₂) and calcium aluminate hydrates (mostly 4CaO·Al₂O₃·13H₂O).

The calcium aluminate hydrates mainly are detected to be 4CaO·Al₂O₃·13H₂O. In the specimens fired above 800°C after 28 days of hydration XRD analysis shows that more 4CaO·Al₂O₃·13H₂O is formed in samples fired at higher temperatures (beginning with 900°C).

The hydration of dicalcium silicate occurs relatively slow. After 28 days considerable amount of this mineral has remained.

Temperature of 800–850°C has been chosen as optimal for production of hydraulic binder from mixture of clay and dolomite similar to natural dolomitic romancement.

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References

- Grosvalds I., Lagzdina S., Sedmalis U. 1997. Dolomitic romancement – low temperature hydraulic binder. In: *Abstracts of 10th International Congress on the Chemistry of Cement, Gothenburg, Sweden, 1997, Vol. 2, 52–55.*
- Hughes D. C., Jaglin, D., Kozłowski R., Mucha D. 2009. Roman cements – Belite cements calcined at low temperature. *Cement. Concr. Res.*, 39 (2), 77–89.
<http://dx.doi.org/10.1016/j.cemconres.2008.11.010>

- Kozłowski R., Adamski G., Mucha D. 2004. Roman cements – key materials in effectively restoring the built heritage of the 19th century/early 20th century. In: *Scientific Journal of Riga Technical University, Material Science and Applied Chemistry, Riga, Latvia, 2004, Vol. 8, 102–109.*
- Kurss V., Stinkule A. 1997. Latvijas derīgie izrakteņi [Mineral resources of Latvia]. Riga, LU, 122.
- LVS EN 196-2:2005. *Test methods of cement.*
- Svinka V., Bidermanis L., Svinka R., Lindina L., Cimmers A., Timma I. 2011. Termoķīmiskas reakcijas mālu minerālos šūnu keramikas iegūšanai [Thermochemical Reactions of Clay Minerals for Production of Honeycomb Ceramics]. In: *Scientific Journal of Riga Technical University, Material Science and Applied Chemistry, Riga, Latvia, 2011. Vol. 24, 56–60.*
- Teutonico J.M. 1988. *A Laboratory Manual for Architectural Conservators.* ICCROM, Rome, 35–52.
- Varas M., Alvarezdebuergo, M., Fort, R. 2005. Natural cement as the precursor of Portland cement: Methodology for its identification. *Cement. Concr. Res.*, 35 (11), 2055–2065. <http://dx.doi.org/10.1016/j.cemconres.2004.10.045>

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