Modified roman cement

Shelikhov Nikolay and Sagdiyev Ruslan

Kazan State University of Architecture and Engineering, Kazan, Russian Federation
E-mail: ruslan-kgasu@yandex.ru

Abstract. The purpose of this research is to equip the roman cement with properties exceeding the properties of the known analogies.

Roman cement's compositions modified by chemical and mineral additives have been developed and proposed. The mode of calcinations of carbonate and clay raw material with high MgO has been optimized. As a result, the durability of roman cement from 15 to 22 MPa has been received. Mineral additives like slag, zeolite breed and clay dust were chosen and used that rose the durability up to 35 MPa relatively. A combination of complex additives have been proposed.

To optimize the mode of calcinations and to define a combination of complex additives the method of mathematical planning was used. The dependence of binder's strength from the temperature, durability of calcinations, saturation rate, type and consistence of modified additives has been acquired.

Modified roman cement has the advantages if compared with known analogies and has the following features: strength 35MPa, normal consistency 30%, setting time is not earlier than 35 minutes, the end is not late than 420 minutes, softening rate is 0.98.

Modified roman cement can be successfully used to produce dry building mixtures (mortar's strength 5,10, 15 MPA), low strength mortars (strength 5,7.5 MPa) and concret (strength 10, 15, 20, 25 MPa) and other building materials.

Structure of carbonate raw material and clay for the production of roman cement is recommended.

Keywords: dolomites, roman cement, chemical and mineral additive, calcinations.

1 Introduction

Use of lime, lime mortar and Roman cements was the common practice in past times [1]. In the present day, the need to obtain alternative binding materials is caused by solution of the following problem: reduction of CO₂ emissions, production of binding materials for restoration and production of hydraulic binding agent, which is not worse than Portland cement. CO₂ emissions, as a rule, can be reduced by dilution of the main binding material, for example, lime, natural products or by-products of different production industries [2]. Various puzzolanes (primarily ashes) are used as the additives depending on what problem of CO₂ emissions and waste disposal is resolved. The binding materials obtained by such a way have high strength up to 6 MPa and restricted base of raw materials [3, 4]. Repair and rebuild of an estate require the binding materials with structure and parameters suitable for the restored buildings [5, 6]. The main objective of the restoration works is increasing of life cycle of the initial hydraulic limes and Roman cements by application of chemical and mineral additives. Increase of corrosion stability [7], reduction of shrinkage [8], porosity control [9] do not cause significant increase of the strength due to what the scope of application of these binding materials can be enlarged. The activities intended to study effect of the external factors during solidification [10] are
in process, the content of binding materials is determined using the neural networks [11], these methods allow improving the characteristics of the binding materials only in a minor way [12]. All above-mentioned problems can be resolved due to the development of the binding materials with characteristics, which are not worse than Portland cement made based on the hydraulic limes and Roman cements. CO₂ emissions can be reduced by lowering roasting temperature, due to carbonization processes [13] and lack of C₃S₂ in the binding materials [14, 15]. Preservation of architectural heritage will be ensured owing to the associativity with historical grounds [16]. Study of the methods used to optimize the performance characteristics of the binding materials is focused on considering improvement of roasting and use of additives. Increase of strength of the lime-based binding materials till 18 MPa was achieved due to use of ash and fluid-bed roasting, mentioned in the paper [17]. In the paper [18], the authors propose to manufacture the hydraulic binding materials made based on magnesial carbonate-argillaceous raw materials with strength up to 22 MPa. The organic additives demonstrated good results; they increased strength of the mortars by 44% [19, 20]. Due to complex use of the various methods we can make the hydraulic binding materials with the highest performance characteristics, suitable for application for restoration works with reduced CO₂ emissions and such binding materials can partially substitute Portland cement.

2 Materials and methods

2.1 Raw Materials

Dolomite, from Matyushensky field in Tatarstan and clay, from Koshyakovskiy field (Table 1 and Table 2) were chosen to produce roman cement as a result of the analyses of the deposits and the structure of the local material.

To modify roman cement some organic and active mineral additives were chosen. For rapid hardening calcium formiate was chosen. To provide plasticizing effect superplasticizer of “Melflux” policarboxylates group was chosen. Three superplasticizers, namely, Melment F10, C-3 and Pantarhit PC 160 PLV were used to achieve comparative characteristics.

Six types of natural and by products with specific surface area of 250-700 m²/kg were used as active mineral additives. Among them there are natural raw material such as zeolite containing rocks (ZCR), diatomite; by products such as microsilica, metacaolinit, metallurgical slug, ceramic dust.

2.2 Calculation of the structure of the raw mix

Calculation of the raw mix structure is carried out by the method developed to calculate the structure of cement.

Taking into consideration that the raw material in producing the roman cement is not calcinated till clinkering and solid-phase reactions between silica and calcium oxide bring to the formation of low-basic silicate (mostly 2CaO SiO₂), coefficient of saturation is Eq. 1:

\[ KS = \frac{CaO - (1.65Al₂O₃ + 0.35Fe₂O₃ + 0.7SO₃)}{1.86SiO₂} \]  

(1)
For two component raw material blend the relation between materials was calculated basing on the chemical structure of these materials using the formula Eq. 2:

$$X = \frac{1,86 \cdot S_2 \cdot KS + 1,65 \cdot A_1 + 0,35 \cdot F_2 - C_2}{C_1 - 1,86 \cdot S_1 \cdot KH - 1,65 \cdot A_1 - 0,35 \cdot F_1},$$

(2)

where, \(X\) – quantity of mass portion of carbonate raw material to one mass portion of clay; \(\text{CaO} - C; \ \text{SiO}_2 - S; \ \text{Al}_2\text{O}_3 - A; \ \text{Fe}_2\text{O}_3 - F\).

3 Results and Discussion

3.1 The influence of the temperature and the duration of calcinations on the quality of the binder. Method of planning the experiment

Determination of calcinations optimal parameters to produce roman cement was carried out with the following mixtures (Table 3).

The structures are designed on CS (coefficient of saturation) and represent a torment with a specific surface \(S_s = 250 \text{ m}^2/\text{kg}\).

On optimizing the parameters of calcinations the method of mathematical planning of experiment was used.

\(X_1\) – coefficient of saturation, CS; \(X_2\) – temperature of calcinations, \(^\circ\text{C}\); \(X_3\) – duration of calcinations, hour are used as the variable coefficients.

Table 3. Structures to obtain low-calsinating hydraulic binders.

| №  | Structure | CS   | Proportion, dolomite:clay | Quantity, % carbonate raw material (dolomite) | Quantity, % clay | Hydraulic module |
|----|-----------|------|---------------------------|---------------------------------------------|------------------|-----------------|
| 1  | 0,70      | 2,5  | 71,6                      | 28,4                                        |                  | 1,30            |
| 2  | 0,80      | 2,8  | 73,9                      | 26,1                                        |                  | 1,42            |
| 3  | 0,90      | 3,1  | 75,9                      | 24,1                                        |                  | 1,54            |
| 4  | 1,0       | 3,6  | 78,2                      | 21,8                                        |                  | 1,70            |
| 5  | 1,3       | 4,6  | 82,2                      | 17,8                                        |                  | 2,03            |
| 6  | 1,5       | 5,8  | 85,3                      | 14,7                                        |                  | 2,38            |
| 7  | 1,7       | 6,4  | 86,6                      | 13,4                                        |                  | 2,55            |

Figure 1. Relation of the strength of romancement to the temperature and coefficient of saturation. Duration of calcinations is 240 min.

The limit of strength when binders’ compression is 28 day, MPa is taken as the parameter of optimization \(Y\) (response function).
As the result of the experiment and mathematical processing the equations of regression for roman cement Eq. (3) were obtained. The equations are shown as the polynomial of the second degree:

\[
Y = -504.47B_0 + 409.46B_1X_1 + 0.742B_2X_2 + 0.178B_3X_3 + 0.018B_1B_2X_1X_2 + 0.01B_1B_3X_1X_3 - 240.98B_1^2X_1^2 - 0.0004B_2^2X_2^2 - 0.0003B_3^2X_3^2.
\]  

(3)

In figure 1 one of the main graphic pictures of the experiments and calculations results is shown as two-parameter relation of binders’ strength to the temperature of calcinations and the structure of the mixture characterized by a coefficient of saturation, CS.

The relation of the strength of roman cement is shown as a convex surface with a biaxial inflection in the field of temperatures 850-950°C and CS = 0.8; the point of a maximum of strength with value 22 MPa has coordinates with temperature 900°C, CS = 0.82.

3.2 Modification of roman cement

As a result of the research the roman cement with the following characteristics was obtained, Table 4. The binder received was used in further research.

Table 4. Technical characteristics of roman cement.

| №  | Parameters          | Size of parameters |
|----|---------------------|--------------------|
| 1  | Strength, MPa       | 20                 |
| 2  | Dispersity, %       | 15                 |
| 3  | Standart consistency, % | 49-54             |
| 4  | Initial setting time, min. | 45               |
| 5  | Final setting time, min. | 419             |
| 6  | Storage age, day.   | 45                 |
| 7  | Soundness           | satisfactory       |
| 8  | Coefficient of water-resistance | 0,9            |

3.3 The influence of hardening accelerator on the speed of hardening of roman cement

The acceleration of binders’ hardening with application of calcium formiate is mainly a result of calcium formiate changing the solubility of silicate part of roman cement and forms double and basic salts with a product of its hydration Ca(OH)_2. The decrease in concentration of alkali promotes the hydration of new portions hydraulically active minerals and the process repeats.

![Figure 2. Influence of the hardening accelerator, calcium formiate, on the speed of strength growth for roman cement: 1 (■) – without additive; 2 (▲) – 1% additive; 3 (♦) – 3% additive; 4 (●) – 5% additive.](image)

Figure 2. Influence of the hardening accelerator, calcium formiate, on the speed of strength growth for roman cement: 1 (■) – without additive; 2 (▲) – 1% additive; 3 (♦) – 3% additive; 4 (●) – 5% additive.
By character of strength growth curve (figure 2) greatest strength growth rates are observed in initial period. During the first 3 day 43 % from standard strength of roman cement is achieved and for optimum process of setting and hardening 3 % calcium formiate for 100 % roman cement is necessary.

3.4 The influence of plasticizer on the strength of roman cement

The efficiency of superplasticizers depends on the structure, availability and the kind of functionally active groups, their arrangement in molecules, length and shape of circuits, molecular mass.

The influence of plastificizers on strengthening characteristics of roman cement is shown in a histogram in figure 3. The greatest effect is obtained for plasticizer Melflux 2641 (strength 25 MPa, increase of strength 25 %).

3.5 The influence of mineral additives on roman cement

The influence of 6 types of the mineral components (Zeolite, slag, ceramic dust, microsilica, metacaolinite and diatomite) on properties of roman cement is determined. All mineral components in certain quantitative limits promote increase of strength. The maximum strength is shown by the binder with ceolit additive of 15-16 %, value of strength − 29,36 MPa, that makes the strength of romancement increase up to 50%. The efficiency of zeolite is explained by the increase of a degree of hydration of minerals, and also the increase of volume of hydraulic new formations, at the expense of chemical interaction of aluminium silica phases of zeolite with Ca(OH)$_2$.

High strength parameters are also achieved by adding of 10% microsilica. The strength of romancement thus is 29,6 MPa.

3.6 Selection of the structure of the complex additive

The optimum structure of complex additive to obtain the modified roman cement is determined as a result of the research where hardening accelerator is calcium formiate; plasticizer is Melflux; mineral additive is zeolite;

Complex additives content test was carried out on the binder shown in Table 4. In research the method of mathematical planning was used.

The following parameters are taken as variable factors: 
  X1 − amount of additive to plasticizer, %;  
  X2 − amount of additive to hardening accelerator, %;  
  X3 − amount of mineral additive, %.

Ultimate comprehensive strength of binders at the age of 28 days, MPa is taken as optimizing parameter Y (response function)

The test and mathematical analysis of the results made it possible to derive the regression equation for romacement Eq. (4). The equations are presented as a second degree polynomial:

\[
Y = -26.578 B_0 + 32.017B_1X_1 + 7.777 B_2X_2 + 4.145 B_3X_3 - 0.119 B_12X_1^2 + 0.238B_13X_1X_3 - 0.155 B_23X_2X_3 - 12.133 B_1X_1 - 0.716 B_{22}X_2^2 - 0.115 B_{33}X_3^2 .
\]  

(4)

Figure 4 presents elements of response surface (strength) of romacement.
The highest strength of roman cement up to 35.4 MPa was reached on introducing 13% celot, 1.17% plasticizer and 5% hardening accelerator. Since in regression equation Eq. (4) all significant factors are positive thus other combinations of additives that raise the strength are possible.

Figure 4. Dependence of strength of romancement on the degree of filling and amount of plasticizer. Hardening accelerator is 5%.

Figure 5 presents thermograms with two types of cement stones during the hydration of roman cement: figure 5a – without additives, fig. 5b – modified by complex additive of optimal composition. Thermogram shows endothermic effects and mass loss curve. Endothermic effect at t 412.5°C corresponds to decomposition of hydrosilicates of $2\text{CaO SiO}_2 \cdot \text{H}_2\text{O}$ types at $t = 453^\circ\text{C}$ to decomposition of $\text{Mg(OH)}_2$, at $t = 735 – 750^\circ\text{C}$ corresponds to decomposition of hydrosilicates of $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

Figure 5. Thermograms of roman cement: a) without additives, b) with modified complex additive of optimal composition.
A conclusion is made after thermograms has been compared that modified roman cement is hydrated, in larger amount that is proven by large quantity of endothermic effects for all phases (by 14% on phase $2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ and by 31% on phase $2\text{CaO}\cdot3\text{SiO}_2\cdot2\text{H}_2\text{O}$). It proves that complex additive intensifies the processes of hydration and hardening of hydraulically active roman cement. A mass loss curve shows the increased amount of hydraulic new formations on strengthening of modified roman cement.

4 Conclusions
Results of scientific work are:
1. Main regularities of influence of raw material calcination parameters on the properties of roman cement;
2. Regularities of the influence of hardening accelerator - calcium formiate on the properties of roman cement. It contributes on:
   - increasing of strength up to 16%;
   - reducing the water requirement from 50 to 39;
   - accelerating the hardening in the initial period;
3. Regularities of the influence of organic (plasticizers) and mineral additives on the properties of roman cement.
   The influence of four types of plasticizers was investigated. Plasticizers help to reduce water demand, increase water resistance and durability up to 25%. The most effective plasticizer for roman cement is Pantarhit RS 160 PLV.
   The influence of six types of mineral additives on the properties of roman cement was determined. All mineral additives in certain quantitative limits increase the strength. The roman cement containing the mineral additive of zeolite in dosages of 15-16% shows the maximum strength.

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