Roman KOTIV[1], Tetiana KROPYVNYTSKA[1], Myroslav SANYTSKY[1,2]
[1] Lviv Polytechnic National University
[2] Czestochowa University of Technology

DECORATIVE MULTICOMPONENT CEMENTS FOR FINISHING MORTARS

The paper is devoted to the research of decorative multicomponent cements and Roman cement for finishing mortars that are characterized by improved quality parameters. The use of fine mineral additives allows to obtain multicomponent low energy consumption cements. The chemical composition of multicomponent cement is similar to Roman cement. XRD and SEM carried out on cement paste allow the identification of the AF_m and AF_t type phases as hydration products responsible of the flash setting typical to multicomponent cement. The results of physical and mechanical properties of multicomponent cement and Roman cement are shown. The use of decorative multicomponent cement is an alternative solution, suitable for restoration, finish works and to decorate facades.

Keywords: **Roman cement, decorative multicomponent cement, finishing mortar**

INTRODUCTION

One of the major problems of the old buildings reconstruction is restoration of decorative architectural facades. A well-known binder material for the restoration and conservation of monuments and finishing of buildings is Roman cement. Project ROCARE continued development of historical material - Roman cement for the restoration and finishing of building facades to save European architectural heritage. Plasters based on Roman cement possess good atmosphere resistance, sufficient compressive strength and adhesion to the base [1, 2].

The main clinker phases of Roman cement are calcium silicate β-C_2S and calcium aluminates CA and $C_{12}A_7$ that provide ability to hydraulic hardening. In addition to the chemical composition of raw materials, the properties of Roman cement are significantly affected by various impurities and size of quartz inclusions, which leads to increased water demand, rapid hardening and shrinkage. Lack of proper raw material considerably complicates the production of Roman cement and increases its cost [3].

Finishing mortars based on white and color Portland cement are used to provide decorative properties of facade surface. White Portland cement is characterized by a high content of CaO, which leads to the formation of clinker minerals C_3S and C_2S. Calcium hydroxide formed during hydration of C_3S can lead to efflorescence. Replacement part of white Portland cement clinker to fine mineral additives allows to select and adjust the chemical composition of multicomponent cement that meets the chemical composition of Roman cement. Chemical basis of active mineral additives consists in binding of calcium hydroxide, which is part of the binder or formed during the hardening cement. Binding occurs in the interaction of $Ca(OH)_2$ with active forms of SiO_2 and Al_2O_3, contained in the mineral additive with the formation of calcium hydrosilicates C-S-H (I) and calcium hydroaluminate [4].

Management of buildings in corrosive environment of urban development requires an integrated scientific approach to the problems of research, production and use of new materials during their restoration and finishing works. One of the major trends in the global cement industry is the development of multicomponent cements based on alite Portland cement clinker. The use of multicomponent cements enables not only to save fuel and energy (30÷40%) in the production of cement, but also to increase output of concrete and mortar based on this binder [5, 6].

Development of multicomponent low energy consumption cements of new generation - analogue of Roman cement that by their chemical composition, physical and mechanical properties and color are close to Roman cement, characterized by necessary strength and durability are actual for use in plasters for restoration, finishing and decorating works [7].

1. MATERIALS AND METHODS

To carry out comparative studies Roman cement manufactured in the Institute of Ceramics and Building Materials (Poland) and white Portland cement CEM I 52.5 N "CIMSA" (Turkey) were used. As mineral additives of bright colors metakaolin (SiO_2 and Al_2O_3 respectively 53.4 and 43.8 mass.%), silica (SiO_2 – 96.0 mass.%), zeolite (SiO_2 and Al_2O_3 respectively 68.8 and 11.9 mass.%) and carbonate micro filler containing 95.0 mass.% of $CaCO_3$ were used. As superplasticizer complex admixture of sulfonaphthalene formaldehyde type were used.

Physico-mechanical tests of cements and concretes were carried out according to usual procedures. The evaluation of the properties of plasticized cementitious systems was carried out through a flowing and compressive strength tests. The physico-chemical analysis (methods of XRD, SEM, porometry, differential calorimetry) were used for investigation of cementitious systems hydration processes. The particle size distribution of fine ground SCMs was determined by laser granulometer Mastersizer 2000.

2. RESULTS AND DISCUSSION

Chemical compositions of cements of different types are presented in Figure 1. The main components of cements are oxides such as CaO, SiO_2, Al_2O_3 and Fe_2O_3. As seen in Figure 1 for white Portland cement content of CaO is 70.5 mass.%. For Roman cement and belite cement regular decrease of total content of CaO component respectively to 52.9 and 53.0 mass.% are observed, which prevents efflo-efflorescence in plaster. At the same time the content of SiO_2 and Al_2O_3 in Roman cement increases 1.68 and 2.1 times compared to the white Portland cement CEM I and is respectively 31.0 and 8.4 mass.%. As an analogue of Roman cement decorative multicomponent cement was developed (mass.%: CaO - 41.3; SiO_2 - 28.9; Al_2O_3 - 8.2; Fe_2O_3 - 2.75).

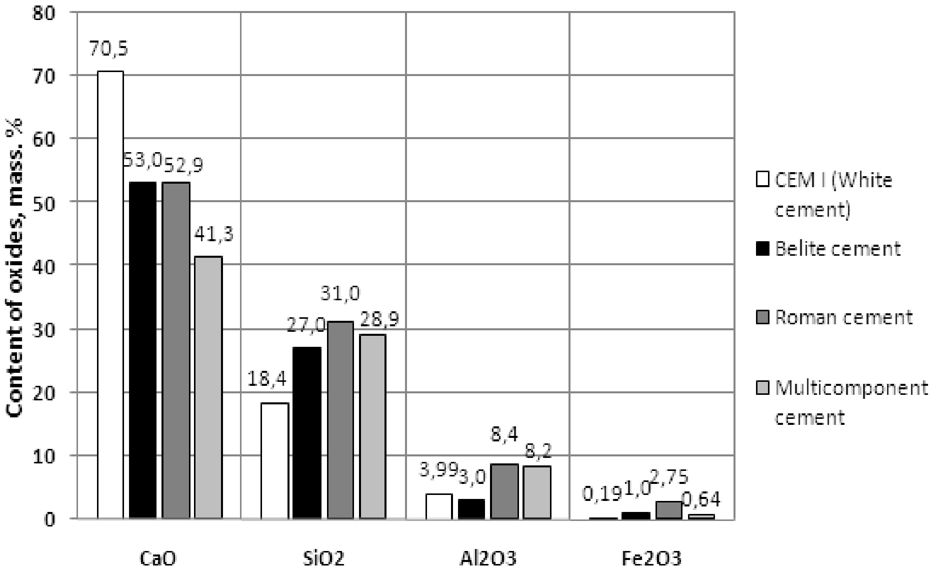


Fig. 1. Content of main oxides in different type of cements

Decorative multicomponent cement obtained by mixing of white Portland cement CEM I 52.5 N, metakaolin, silica and limestone in different proportions. According to the particle size distribution of (Fig. 2a, b) Roman cement (SSA = 800 m^2/kg) and multicomponent cement (SSA = 840 m^2/kg) fraction Ø1; Ø10; Ø20 and Ø60 µm are respectively 14.5, 47.3, 59.4, 86.0 and 8.0, 36.8, 52.2, 76.9%, and the grain size D50 and D90 corresponds to 11.83, 69.61 and 18.86, 111 µm. For spherical particles by reducing the diameter from 10 to 0.6 µm the coefficient of surface activity for Roman cement and multicomponent cement increases respectively from 1.0 to 10.0 μm^{-1} and from 1.2 to 5.0 μm^{-1} (Fig. 2c, d).

As can be seen in Table 1, Roman cement is characterized by increased water demand (40%) and accelerated setting time (initial - 8 min, final - 13 minutes). Adding 5 mass.% of gypsum dihydrate to Roman cement reduces water demand by 17.5%, initial setting time increases and compressive strength at 3, 7 and 28 days of hardening increases in 4.5, 4.8 and 2.7 times. For multicomponent cement with water demand 34% initial setting time is 3 hours 40 minutes. At the same time compressive strength at 3, 7 and 28 days increases respectively 3.4, 6.1 and 2.8 times compared to Roman cement.

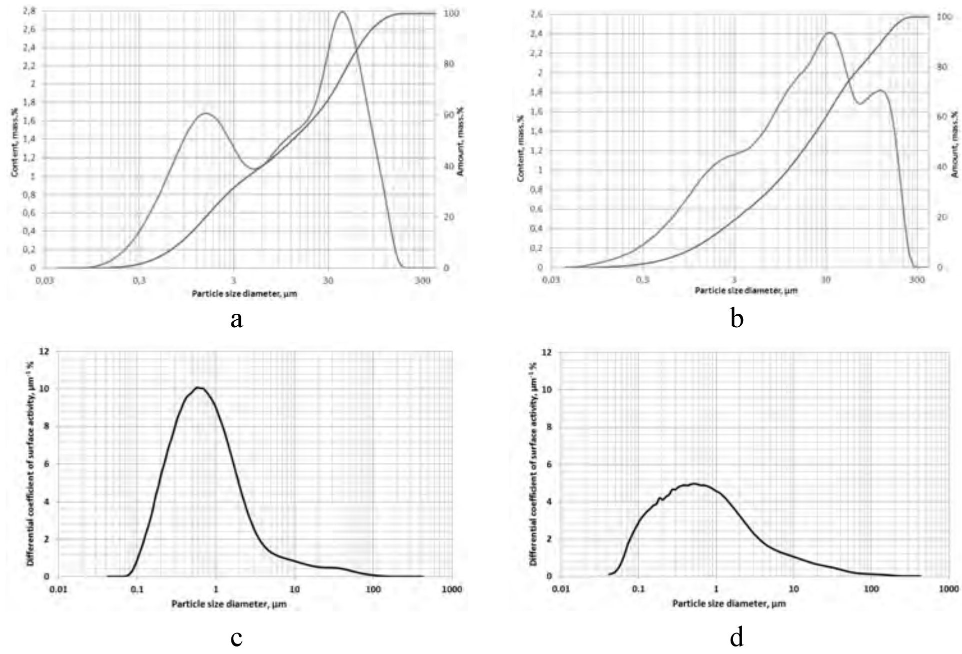


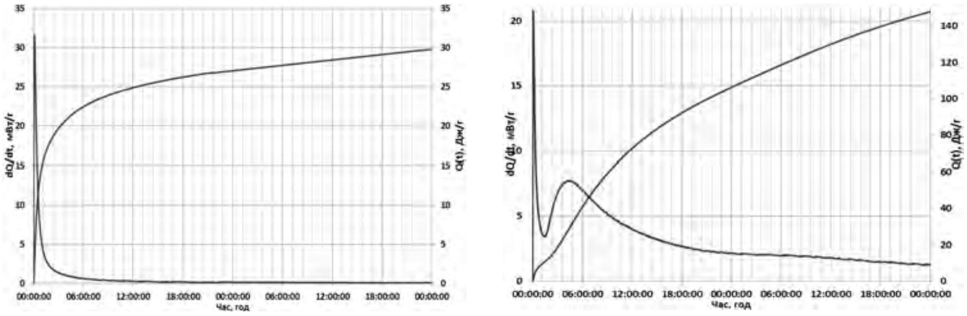
Fig. 2. Particle size distribution (a, b) and differential coefficient of surface activity (c, d) of Roman cement and multicomponent cement

Table 1. **Physical and mechanical properties of Roman cement and multicomponent cement paste**

Binder	Water demand [%]	Setting time [h-mm]		Compressive strength, at the age, days [MPa]			
		initial	final	1	3	7	28
Roman cement	40.0	0-8	0-13	4.9	6.1	7.6	20.8
Roman cement with gypsum	33.0	0-16	0-19	10.8	27.5	37.0	55.6
Multicomponent cement	34.0	3-40	4-50	19.6	20.8	46.8	58.3

By differential calorimetry analysis thermokinetic characteristics of Roman cement and multicomponent cement were investigated. As shown in Figure 3, Roman cement is characterized by a short induction period (τ = 12 min) and low heat of hydration (29.8 J/g). For multicomponent cement duration of the induction period is increased to 1 h 20 min, and the heat of hydration is 148.9 J/g. A higher value of heat emission associated with the presence of minerals C_3S and C_3A in the composition of multicomponent cement.

According to XRD analysis not hydrated Roman cement is characterized by intense lines of belite phase (d/n = 0.302; 0.275; 0.218 nm), also present lines of calcite (d/n = 0.303; 0.277; 0.208; 1.912 nm) and quartz (d/n = 0.424, 0.334 nm).



a b

Fig. 3. The heat of hydration of Roman cement (a) and multicomponent cement (b)

Hydration of Roman cement takes place in two stages. The first - a hydration of aluminate phase with the formation of calcium hydroaluminate C_2AH_8, that allows it to rapidly set and to gain strength in the initial stage of hardening. Second - when belite phase activates with the formation of calcium hydrosilicate C_2SH_2, which provides gain of strength in later periods of hardening. For Roman cement, hydrated for 28 days, lines of $C_3A{\cdot}CaCO_3{\cdot}12H_2O$ (d/n = 0.761 nm) and hydrocalumite $Ca_4Al_2(OH)_{14}{\cdot}6H_2O$ (d/n = 0.820; 0.288 nm) are fixed. Compared to the C-A-S reactant, very little C_2S reacts before 28 days. The hydration of C_2S is well advanced after 90 days and leads to the precipitation of calciumhydroxide CH co-precipitating with microcrystalline calcium silicate hydrates C-S-H.

Figure 4 shows the XRD patterns of the multicomponent cement paste after 28 days of hardening. The crystalline phases of not hydrated clinker minerals, calcite (d/n = 0.303; 0.249 nm), quartz and phases of crystalline hydrates namely: ettringite (d/n = 0.973; 0.561 nm) and little amount of calcium hydroxide (d/n = 0.490; 0.263 nm) are fixed.

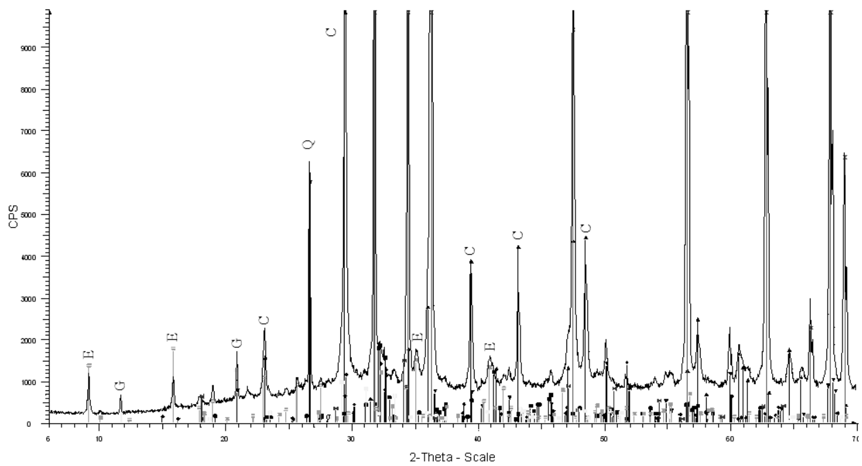


Fig. 4. XRD pattern of multicomponent cement after 28 days of hardening

By the SEM method it is established that Roman cement paste, hydrated for 28 days, is characterized by porous structure with a large number of capillary pores. On the surface of the pores is observed the formation of small crystals of calcium hydroaluminates (C-A-H), and ettringite is formed. After hardening for 1 year of Roman cement with the addition of gypsum cracks are observed, due to the formation of a large number of secondary ettringite crystals.

The SEM method proves that structure of multicomponent cement paste is condensed by colmatation of open pores by portlandite and AF_m phases (Fig. 5). Hardening of such cements should be considered in terms of the complex interaction of all its components - namely, clinker, carbonate filler, active mineral additives and gypsum. According to the data of electron microscopy (Fig. 5) cement paste based on multicomponent cement is characterized by a dense structure of hydrated solid phase that is formed by crystalline splices of hexagonal crystals of portlandite, AF_m- phases and calcite, which reinforce mass of gel phase of C-S-H and act as compensators of cement paste shrinkage.

According to EDX, the relative content of elements in interpore space in the sample of cement paste meets ettringite (Fig. 5). At enough high concentration of calcium ions in the liquid phase of cement paste in interpore space occurs crystallization of ettringite by topochemical method in the form of small needle-shaped crystals that promote the synthesis of the strength of the cement matrix due to its compaction [10]. Chemical affinity and similarity of the crystal lattice parameters of microfiller and cement hydration products allow to get a new low energy consumption cement materials with multifunctional properties.

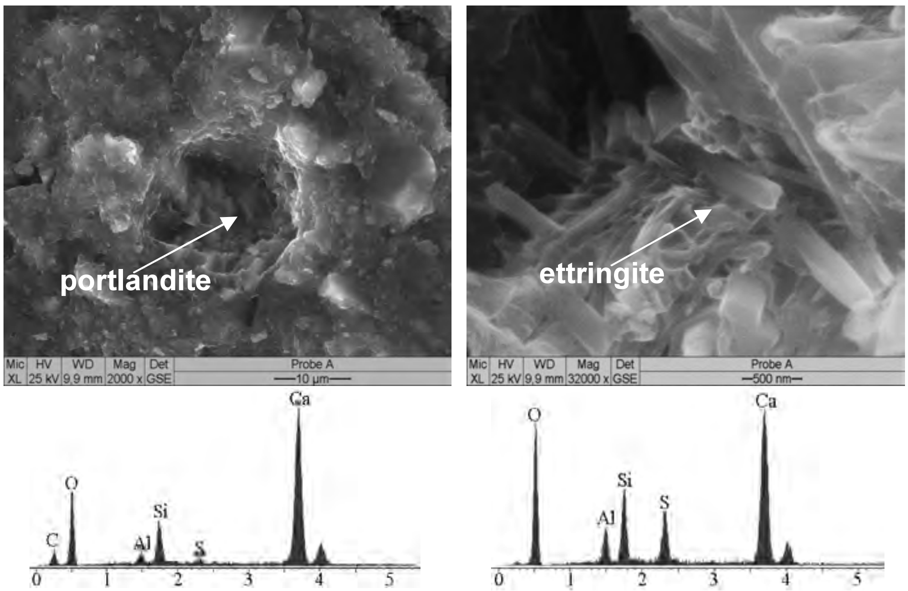


Fig. 5. The SEM images and the EDX spectrum of multicomponent cement

As can be seen in Table 2, multicomponent cement is characterized by lower water demand and increased strength at an early and project age compared to Roman cement. Thus, at W/C = 0.36 after 2 and 28 days of hardening strength increases 4.9 and 1.4 times.

Table 2. **Physical and mechanical properties of Roman cement and multicomponent cement (Cement : Sand = 1:3)**

Indicators		Roman cement	Multicomponent cement
Water-cement ratio W/C		0.55	0.36
Flowability, PK [mm]		130	110
SSA [m^2/kg]		800	840
A_{008} [mass.%]		1.0	3.5
Compressive strength [MPa], at the age	2 days	2.1	10.3
	7 days	21.8	23.0
	28 days	21.8	30.1
	90 days	33.0	33.8
	365 days	37.1	38.2

Designed decorative multicomponent cement is used in construction in the manufacture of bright colors building mortars for plastering surfaces of buildings and structures in order to provide a complete decorative facing, restoration of decorative architectural facades and restoration works.

CONCLUSION

Analysis of the material composition of cements allows in certain margin to design average chemical composition of decorative multicomponent cement as analogue of Roman cement. Synergistic combination of bright colors fine mineral additives, fillers and polyfunctional admixtures in multicomponent cement contributes to the intensification of the structure formation processes and increase durability. Regulation of properties of decorative multicomponent cements by selecting and optimizing the components (mineral additives and chemical modifiers) are the main direction to get and improve quality and technological characteristics of finishing mortars.

REFERENCES

[1] Szeląg G., Sanytsky M., Kropyvnytska T., Kotiv R., Roman cement - binder for finishing works in building, Building Materials and Products 2012, 1, 7-12.

[2] Hughes D.C., Jaglin D., Kozłowski R., Mucha D., Roman cements - Belite cements calcined at low temperature, Cement and Concrete Research 2009, 39, 77-89.

[3] Gosselin C., Scrivener K.L., Feldman S.B., Microstructure of Roman cements used for architectural restoration, 2nd Conference on Historic Mortars 2010, 993-1004.

[4] Runova R., Dvorkin L., Dvorkin O., Nosovsky J., Binder materials: Tutorial - K., Osnova, 2012, 448.

[5] Sanytsky M., Sobol Ch., Markiv T., Modified composite cements, Edition of Lviv Polytechnic National University 2010.

[6] Giergiczny Z., Małolepszy J., Szwabowski J., Sliwinski J. Cementy z dodatkami mineralnymi w technologii betonów nowej generacji / Gorazdze cement, Opole 2002.

[7] Sanytsky M., Kropyvnytska T., Kotiv R., High-performance masonry and finishing mortars with complex air entraining admixtures, IBAUSIL, 17 Internationale Baustofftagung, - Weimar (Germany) 2009, Band 1, P.0543-0548 (P.1.02).

DEKORACYJNY CEMENT WIELOSKŁADNIKOWY DO ZAPRAW TYNKARSKICH

Artykuł przedstawia rozwój i badania dekoracyjnych wieloskładnikowych cementów oraz cementu romańskiego do zapraw tynkarskich, które cechują lepsze parametry jakościowe. Stosowanie drobnoziarnistych dodatków mineralnych pozwala na uzyskanie wieloskładnikowych cementów zawierających niższą ilość klinkieru. Skład chemiczny cementów wieloskładnikowych jest podobny do składu cementu romańskiego. Identyfikację faz AF_m i AF_t przy hydratacji wieloskładnikowych cementów prowadzono metodami XRD i SEM. Podano wyniki fizycznych i mechanicznych właściwości cementów wieloskładnikowych oraz cementu romańskiego. Zastosowanie dekoracyjnego cementu wieloskładnikowego jest alternatywą i nadaje się do renowacji, prac wykończeniowych oraz do dekoracji elewacji budynków.

Słowa kluczowe: **cement romański, dekoracyjny cement wieloskładnikowy, zaprawa tynkarska**