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WHITE MINERAL BINDER BASED ON CaO - SiO_2 - Al_2O_3 SYSTEM WITH VARIETIES OF SILICA COMPONENT

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ABSTRACT

The features of application of varieties of silica components in a raw mixture based on CaO - SiO_2 - Al_2O_3 system for production of white binding material of Roman cement type at the low temperature baking are shown. Intensification of phase transformations in the material at 1100°C baking with addition into the initial mixture of fine disperse amorphous silica with increased reactive capability is marked.

Keywords: Roman cement, raw mixture, silica component, baking, phase composition, properties.

INTRODUCTION

Production of the most widespread mineral binder - Portland cement, including white one, is characterized by considerable power consumption at the high temperature baking (1400 - 1500°C) of clinker and its grinding with additions until getting highly disperse state [1 - 4]. The modern requirements of resource saving increase the relevance of production of hydraulic mineral binders of low temperature baking (900 - 1200°C) of Natural cement [5 - 7] or Roman cement [8, 9] types, that can become in a series of works a substitute for more power consuming and expensive Portland cement. In this connection it becomes relevant to use white Roman cement, which is not produced, but by technological features should joint the solution of energy-saving problems and production of new binding material with high decorative properties.

Technology of making of mineral binder for Roman cement type is mainly based on the application of one variety of raw material, namely mergel [6, 10, 11], distribution of which is limited [12]. Limitedness of raw materials resources, relatively low indexes of properties, first of strength, provoked rapid reduction of output volumes and application of Roman cement. However, binder of white Roman cement type has a perspective of application in modern building under condition of increase of indexes of properties, in particular decorative ones, at lower power consumption in comparison with Portland cement.

Solution of this scientific and technical problem requires application of carbonate, alumina and silica raw materials with minimum content of colouring oxides, development of new compositions of initial raw mixtures, analysis of peculiarities of phase formation and properties of white hydraulic mineral binder obtained under conditions of low temperature baking. This is the aim of this study.

EXPERIMENTAL

The study was carried out according to the main aim of the work, i.e. obtaining of an white mineral binding material at the low temperature baking. It means that the raw material must have:

• an increased reactive capability providing intensification of physical and chemical reactions in the silicate system at baking with reduction of the maximal temperature;

• the minimum content of colouring oxides for rising the whiteness of finished product.

The natural and artificial materials were used for production of initial raw mixture:

- chalk of Zdolbuniv deposit, Rivne area, Ukraine;

- aluminium oxide hydrate – product of processing of bauxits, Mykolaiv area, Ukraine;

- pyloquartz - product of dispegration and suturation of quartz sand, Novoseliv deposit, Kharkiv area, Ukraine;

- aerosil - pyrogenic silica, Kyiv, Ukraine.

The chemical composition of a sample of chalk is characterized with high content of CaO, aluminium oxide hydrate sample has the largest amount of aluminium oxide, the samples of dispersible quartz sand (pyloquartz) and aerosil demonstrate the highest content of silica (Table 1).

The raw mixtures have been prepared by dispensing the components by mass, mixing and homogenizing in a ball mill, baking and milling of the final product in accordance with the modern dry technology of mineral binders.

Samples of raw mixtures have been bubbled in a furnace for 15 h at maximum temperature 1100°C with a hold at a maximum for 1.5 h. All samples of the mixtures that have been compared were blasted together to exclude the possibility of a difference in the degree of heat treatment. The properties of the binding material (setting time, compressive strength) were determined according to standard procedures.

The methods for physical-chemical analysis of silicate raw materials and testing of properties of binder substances used in this work included:

- chemical composition analysis using standard procedures;

- X-ray diffraction analysis (powder - like preparations) using a diffractometer DRON-3M (radiation CuKα 1-2, voltage 40 kV, current 20 mA, speed 2 degrees/min).

The analysis of the mineralogical composition of the investigated raw material using DRON - 3M diffractometer showed that:

- the main rock-forming mineral of Zdolbuniv chalk is calcite (97,6 wt. %) with additives of dolomite, quartz and kaolinite, 0.5 and 0.6 wt. %, respectively;

- aluminium oxide hydrate is characterized with the presence of hydrargillite (gibbsite), diaspore, boehmite with the insignificant admixture of ilmenite;

- the main rock-forming mineral of pyloquartz is crystalline β- quartz, and that of aerosils is an amorphous silica with additives of crystalline γ- quartz (Figs. 1 and 2).

Obviously, that reactive capability of oxides of calcium and aluminium increases in physical and chemical processes at baking of mixtures, caused by their formation at breakdown of calcite and hydrate of aluminium oxide lattices [13], and in relation to silica oxide by gine dispersion of pyloquartz and activity of amorphous silica from aerosil.

RESULTS AND DISCUSSION

The composition of initial 3-component raw material mixtures based on chalk - hydrate of aluminium oxide - pyloquartz and chalk - hydrate of aluminium oxide - aerosil systems was determined according to well-known recommendations in relation to technology of Roman cement in 1,1 - 1,7 values interval of hydraulic module $HM = \dfrac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3}$ using new software for computer calculations [14].

Table 1. Chemical composition of raw materials.

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
chalk	0,77	0,25	0,13	55,0	0,25	0,08	43,49
aluminium oxide hydrate	-	65,0	-	-	-	-	35,0
dispersible quartz sand	99,66	0,16	0,06	-	-	-	0,12
aerosil	99,80	0,05	0,01	-	-	-	0,03

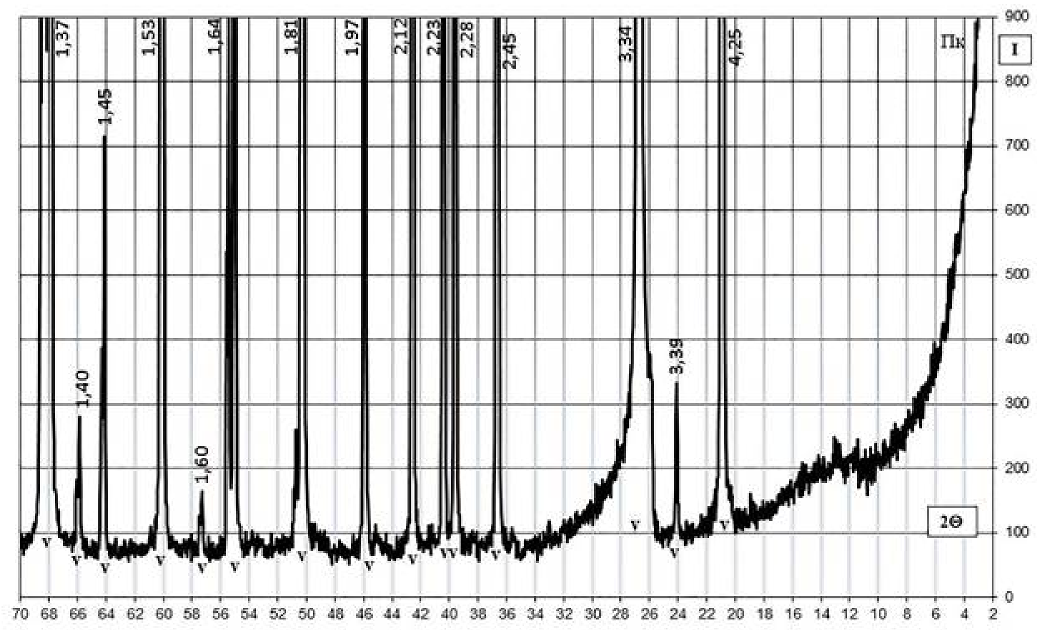

Fig. 1. X-ray diffraction pattern of dispersible quartz sand (pyloquartz): v – β-quartz.

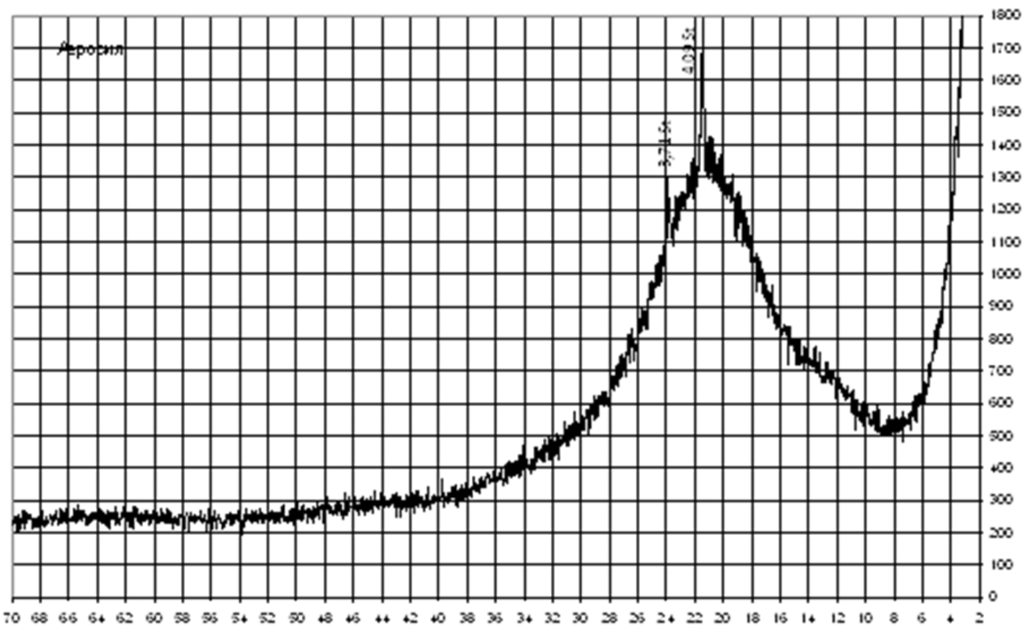

Fig. 2. X-ray diffraction pattern of aerosil: St – γ-quartz.

It is determined that in the indicated HM interval it is possible to observe substantial changes in quantitative relationship of the system components, at that together with the dependence of concentration of alumina-silica components on hydraulic module there is a substantial change of silica module values.

It is found that the minimum for the investigated systems concentration of hydrate of aluminium oxide, namely 10 mass. % , in HM=1,1 - 1,7 interval values provokes identical changes of possible content of pyloquartz or aerosil from 25,2 to 16,5 wt. % (Fig. 3). There is an inversely proportional dependence between the concentration of silica components and values of binder hydraulic module.

In relation to the silica module n of binders, it is a direct proportion of its values in 2,5 - 3,8 interval from the concentration of researched silica components .

The binders based of investigated systems are

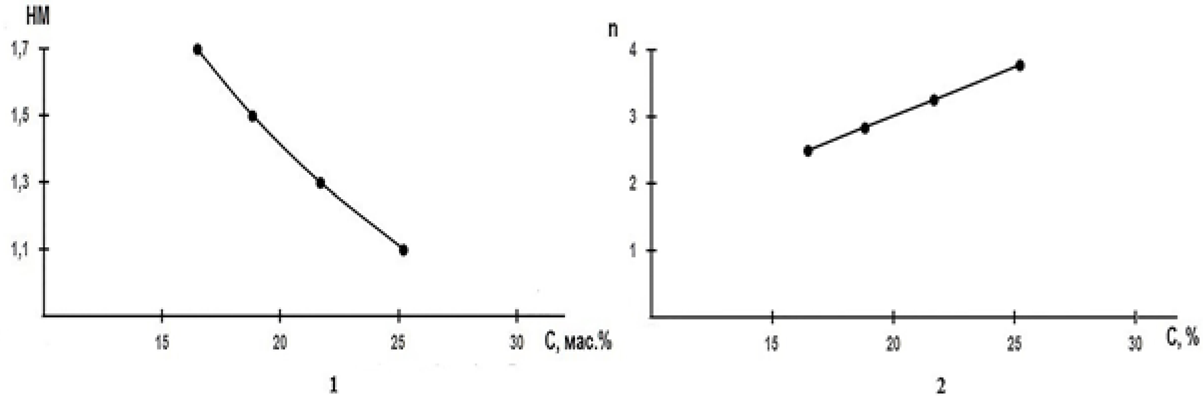

Fig. 3. Dependence of hydraulic HM (1) and silica n (2) modules on concentration of dispersible quartz sand and aerosil content (C) in the systems based of chalk and aluminium hydrate

characterized with the changes of chemical composition according to quantitative correlation of components. Thus, the binders demonstrate the increase of amount of SiO_2 from 26,3 to 37,5 wt. % and reduction of amount of CaO from 62,7 to the 52,2 wt.% and Al_2O_3 from 10,4 to 9,8 % when using pyloquartz or aerosil with increase of concentrations at approximately even content of MgO at the level of 0,24 - 0,28 and Fe_2O_3 at the level of 0,11 - 0,17 wt. %. At that, quantitative relationships of oxides that determine formation of phase composition of material at baking change: SiO_2 : Al_2O_3 from 2,5 to 3,8, CaO : SiO_2 from 2,4 to 1,4, CaO : Al_2O_3 from 6,0 to 6,3. Minimization of content of colouring oxides (Fe_2O_3 at the level of 0,11 - 0,17 wt. %) is very important for the aim of this work.

Mineral binders, selected for further research, are characterized with similar quantitative relationship of components of initial raw material mixture, however differ in silica component varieties (Table 2).

The results of X-ray phase analysis obtained in this work indicate some differences in physical and chemical transformations at baking of the investigated mixtures that correlates with the indicated composition and depends on a kind of silica component (Fig. 4, 5).

Obviously, that after baking at the maximal temperature of 1100ºC the samples from K4 with aerosils mixtures is characterized by substantial differences in phase composition in comparison with sample K9 with pyloquartz:

- as for crystalline phases of calcium silicates it is intensification of formation of wollastonite $CaO{\cdot}SiO_2$ (2,97 Å) and $2CaO{\cdot}SiO_2$ (2,61 Å);
- as for crystalline phases of calcium alumina silicates it is intensification of formation of gehlenite $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$ (2,86 Å);
- as for crystalline phases of calcium aluminates it is intensification of formation of $CaO{\cdot}Al_2O_3$ (2,52 Å) at insignificant differences for mayenite $12CaO{\cdot}7Al_2O_3$ (4,90 Å);
- considerable reduction to content of CaO (2,38 Å).

The results of testing of binder samples from the investigated mixtures show the differences of influence of silica components on the indexes of material properties (Table 3).

Thus, in accordance with the classification of DSTU B B.27-91-99 [15], after baking at the maximal temperature of 1100 ºC the studied samples were referred to different groups by a setting rate.

Table 2. Compositions of raw mixtures of researched binders.

Code of mixture	Quantity of components, wt. %			
	chalk	aluminium hydrate ooxide	dispersible quartz sand (pyloquartz)	aerosil
K4	73,5	10,0	-	16,5
K9	73,5	10,0	16,5	-

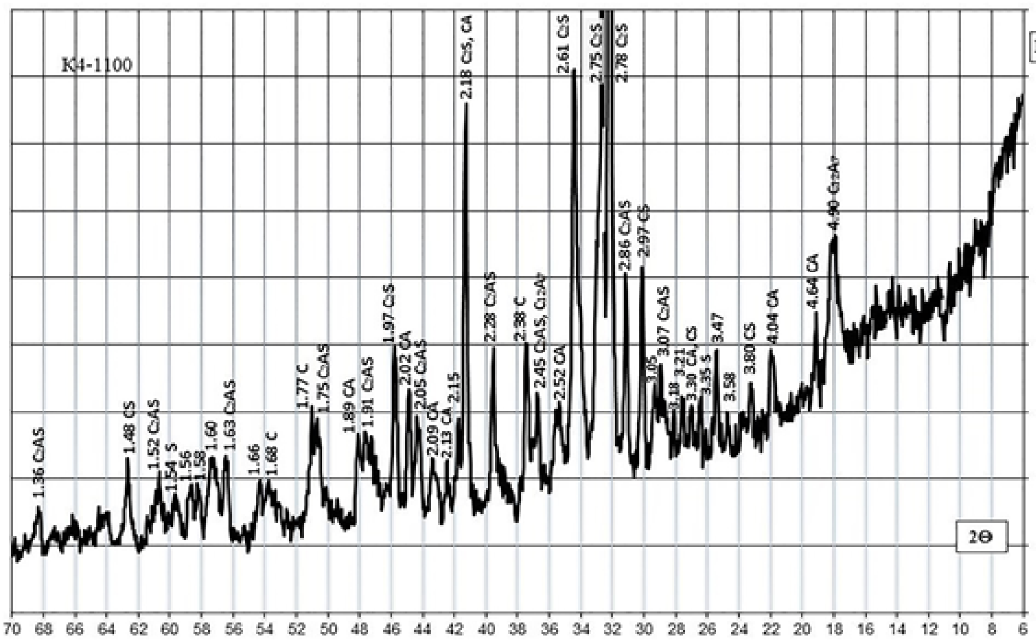

Fig. 4. X-ray diffraction pattern of sample K4 (1100ºC).

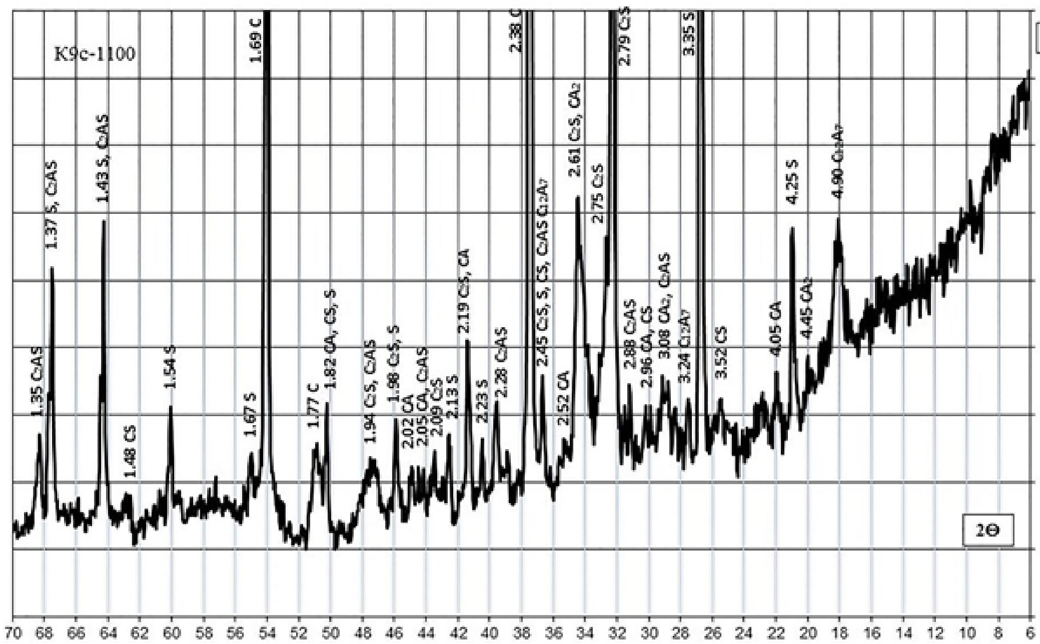

Fig. 5. X-ray diffraction pattern of sample K9 (1100ºC).

Binder from K4 mixtures with aerosils by setting rate refer to a group of quick setting ones (start period is from 15 to 45 min), that is considered typical for anhydrite and alumina cement and K9 with pyloquartz comes to the ultra-quick-setting (start period is up to 15 min), that is considered characteristic for expanding and self-stressing cement. Thus, the sample K4 differs from K9 by general decrease of setting process.

The samples of binder belong on the indicated standard to low strength group (from 10 to 30 MPa at compression), however substantially exceed the regulated indexes of Roman cement and on the indexes of whiteness reach the requirements of standard for white Portland cement [16].

CONCLUSIONS

1. Development and practical use of mineral binder of low temperature baking promotes complex solution

Table 3. Properties of mineral binding material.

Indices	Code of sample	
	K4	K9
Finess of grinding, sieve residue no. 008, mass. %	7	8
Initial setting time, min	35	10
Final setting time, min	395	25
Compressive strength, MPa	24	22
Whiteness, %	82	80

of problems of resource saving and chemical technology of silicate building materials manufacturing.

2. Determined compositions of raw mixture based on chalk with application of alumo-siliceous complexes of aluminium hydroxide, namely dispersible quartz sand and aluminium hydroxide – aerosil allow getting at the maximal baking temperature of 1100°C the mineral binder, that exceeds Roman cement on the indexes of compressive strength (22 - 24 against 10 - 15 MPa) and whiteness (80 against 55 %).

3. Application of silica component with high content of amorphous silica dioxide with increased reactive capability in the raw material mixture provides intensification of phase transformation into material at baking at 1100ºC with increase of formation of silicates (CS, C_2S type) and calcium aluminosilicate (as C_2AS).

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