CORPUS PUBLISHERS

Journal of Mineral and Material Science (JMMS)

ISSN: 2833-3616

Volume 5 Issue 5, 2024

Article Information

Received date : November 12, 2024

Published date: November 29, 2024

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DOI: 10.54026/JMMS/1097

Key Words

White Cement; Raw Material Mixture; Dust Quartz; Microtalc; Firing; Temperature; Phase Composition; Properties

Research Article

Aspects of White Cement Production

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Abstract

The results of research aimed at the development of chemical technology for the production of white cement under the conditions of resource conservation and energy saving according to the program of sustainable development are given. Based on computer calculations using the created program "RomanCem", the quantitative ratios of carbonate, aluminum and silica-containing components of the raw material mixtures for the production of white low-temperature firing cement (≤ 1200 °C) and Eco-cement were determined As a result of the study of 3-component systems based on chalk with aluminum hydroxide, dust quartz and microtalc, new compositions of starting mixtures were developed with a decrease in the content of carbonates and, accordingly, emissions of CO_2 into the atmosphere, with a minimization of the content of colored oxides and a corresponding increase in the whiteness of cement. Peculiarities of the phase formation of the investigated mixtures during firing in the range of maximum temperatures of 1100-1200 °C and including the synthesis of ockermanite $2CaO•MgO•2SiO_2$ when using microtalc were revealed.

Introduction

The production of the most common mineral binder, Portland cement, is characterized by significant energy costs during high-temperature firing (≥ 1400 °C) of clinker and its grinding with additives to a highly dispersed state [1-3]. At the same time, there are significant emissions of CO_2 into the atmosphere due to transformations of rock-forming minerals of carbonate components, which make up the majority (75-80 wt. %) of the composition of the original raw material mixtures. To a large extent, this applies to the white cement production technology (Figure 1), where high energy intensity is associated with the use of the wet method and the maximum clinker firing temperature ≥ 1500 °C [4-6]. At the same time, special requirements are added regarding the chemical composition of raw materials with the minimization of the content of colored oxides.

Figure 1: White cement in modern architecture.

The development of binder production technology is based on the scientific principles of the physical chemistry of silicates, the physical and chemical mechanics of dispersed structures, and modern materials science, which considers the relationships in the composition-structure-properties system.

Structure formation in the process of cement production

According to the provisions of physico-chemical mechanics, the technological process of production of silicate materials is essentially a process of formation and successive transformations of their structure. At the same time, three main types of structure are distinguished: coagulation, condensation and crystallization. Therefore, in order to effectively regulate the properties and improve the quality of silicate materials, including cement, the processes of structure formation and production technologies should be comprehensively considered. In the modern production of cement, wet, combined and dry methods are used, which, with certain differences in the process parameters of the technology and the structure formation of dispersed systems, must ensure equally high specified product properties.

The properties of cement are closely related to the raw materials, production parameters, clinker composition, degree of its dispersion and additives during grinding. Common to all methods of cement production is the formation of a dispersed system of raw materials at the stage of grinding, grinding, mixing and homogenization of raw materials. Regardless of the chemical nature, physical properties and purpose, dispersed systems with the participation of solid phases are divided into three main groups [7]. With wet and combined methods, as a result of grinding, mixing, homogenization of a mixture of raw materials with water, cement slurry is produced – an aqueous dispersion system belonging to the 2nd group: two-phase systems of the type solid dispersed phase – liquid dispersion medium. With the dry method, as a result of grinding, mixing, drying of the mixture of starting materials, a dispersed system is formed, which belongs to the 3rd group: three-phase systems of the solid dispersed phase type – water-liquid and air-gas dispersion medium.

The coagulation structure of silicate systems is formed by the interaction of particles of the dispersed phase and water. Such a structure can be characterized by structural-mechanical and technological properties. The main indicators of structural and mechanical properties should include the conditional modulus of deformation E_e, which reflects the degree of molecular interaction forces of particles, viscosity and the limit direction of shear, and the main technological indicators – humidity and fluidity. It was found that the values of structural-mechanical constants and bond energy Eε depend on the crystal structure of the rock-forming minerals of the raw material. As for carbonate raw materials – chalk and limestone, their main rock-forming mineral is calcite, while differences in the structure of water systems are primarily determined by the types and amount of certain impurities.

Rock-forming minerals of clay components are represented by three types of spatial arrangement of atoms in the crystal structure (1:1, 2:1, layer-band), but are capable of sorption, ion exchange, and the formation of stable coagulation structures in a wide range of indicators of the specified properties. This is due to the fact that minerals of different structural types have heterogeneous external anionic networks, and minerals of the same type have different degrees of structural order, which affects the amount and distribution of charge on the surface and the interaction energy of adjacent layers. The charge on the surface of clay minerals is not identical in magnitude and sign in different places of the crystals and especially changes in their end parts – on the so-called "broken" bonds. Molecules and ions of the dispersion medium interact mainly with oxygen atoms of the surface of the layers with the formation of weak hydrogen bonds.

Dispersed structures are especially manifested in systems consisting of highly dispersed and anisodiametric particles, which due to interaction form a coagulation structure with elastic-brittle properties. When in dispersed systems the particles are separated by a layer of dispersion medium, which plays the role of a hydrodynamic lubricant, the coagulation structures acquire plastic-viscous properties. An increase in the thickness of water shells has a plasticizing effect. A characteristic of highly concentrated dispersed systems is the combination of two general features: a highly developed interphase surface and a large concentration of the dispersed phase in the liquid dispersion medium. As a result of such a combination in concentrated systems, thermodynamically stable spatial structures arise, formed by the adhesion of particles of the dispersed phase between themselves. The main properties in highly concentrated systems are mainly determined by the ratio between the potential energy of interaction (cohesion) of particles and the kinetic energy provided by external mechanical influences.

The cement technology uses raw material mixtures that differ in the concentration of particles of the dispersed phase. The coagulation structures of such mixtures have common basic features, but they differ significantly in terms of structural-mechanical and technological properties. Coagulation structure of raw mixtures is determined by surface properties and hydrophilicity, chemical and mineralogical composition, dispersion and concentration of dispersed phase particles. The latter increases significantly in mixtures when transitioning from wet to combined and dry production methods. Peculiarities of the formation of the coagulation structure of cement slurry in the technological process are determined by stages: the interaction of the surface of the particles of the components of the dispersed phase with the aqueous dispersion medium, the change of the chemical – mineralogical and granulometric compositions during the joint grinding of carbonate and clay components and mineral additives, partial destruction and change of rheological characteristics under external pressure during transportation, increase in the concentration of the dispersed phase during partial (combined method) or intensive (wet method) dehydration in a rotary kiln.

The process of formation of coagulation-condensation and condensation structures in modern Portland cement technology takes place at the stages of production of the raw mixture with combined and dry production methods. With the wet method of production, the stage of condensation structure formation is minimized in time and actually gives way to the processes of phase transformations and the formation of the clinker crystallization structure during firing.

Features of white cement production technology

The properties of cement are related to the composition, structure and dispersion, which are primarily determined by Portland cement clinker as the main part of the final product, the types and amount of additives and the degree of dispersion during grinding. Portland cement clinker is made from raw mixtures that, after firing, form a material consisting of crystalline and amorphous phases. It is noted that depending on the composition of the raw material mixture and the production technology, the crystalline phase of the clinker contains calcium silicates, calcium aluminosilicates, calcium aluminates, calcium aluminoferrites, calcium ferrites, and the amorphous phase is represented by aluminosilicate glass containing oxides of calcium, magnesium, iron, etc.

According to the current DSTU B V.2.7-257:2011 [8], white Portland cement clinker consists mainly of calcium silicates and aluminates, is obtained by firing a raw material mixture with a low iron content before sintering, and has a whiteness of at least 70% on an absolute scale after grinding. At the same time, the whiteness is characterized by the light reflection coefficient of the surface of the sample [9]. It is noted that the technology of white cement is significantly different from the technology of ordinary cements: special raw materials with a low content of iron oxides and other coloring substances are required, special arrangement of mills to minimize pollution (iron scale) in the grinding process, a special mode of firing and cooling [5,10-12].

The raw material base for the production of white cement: For the production of white Portland cement, the purest varieties of carbonate and sandy-clay raw materials are used - limestones, clays and sands with a minimum content of coloring oxides of iron, titanium, manganese, chromium. Pure limestone or chalk is used as a carbonate component, and kaolin, its enrichment waste and other materials are used as a clay component. To increase the silicate module, white iron-free fine-grained quartz sand or other pure rocks containing a large amount of silica are added to the raw material mixture. The content of iron oxide should not exceed (wt.%): in the carbonate component - 0.1, in clay and siliceous raw materials - 1.0, and TiO_2 - 0.8. If the amount of Fe_2O_3 in the clay component is significantly below the specified limit, then the content of Fe_2O_3 in the lime component can be increased. Both components should contain only traces of manganese and chromium oxides.

It is not recommended to use kaolins with inclusions of large grains of sand, which settle in mixers and containers, causing inconvenience both during transportation and during the preparation of a raw material mixture of a given chemical composition. The possibility of replacing such kaolins with refractory clay from the Latnensky and Chasov-Yar deposits, which was used at the Shchuriv cement plant, was studied. Along with additives that affect the course of the clinker formation process, other alloying additives that improve the properties of the clinker (strength, whiteness) can be introduced into the cement raw mixture during the production of white portland cement. The effect of a number of additives (containing TiO_2, V_2O_5, Mn_2O_3, NiO oxides) and their combination on the whiteness and mechanical strength of cement clinker was studied. In addition to clinker, the composition of white cement includes gypsum, which also gives the material whiteness, as well as diatomite and inert additives.

General features of white cement technology: In the production of white cement, in addition to the use of appropriate raw materials, it is necessary to observe special conditions to protect them from contamination in the technological process. To prevent

iron from entering the cement, raw materials and clinker are ground in a mill, in which the lining and grinding bodies are made of particularly wear-resistant metallic (xpo-nickel steel) and non-metallic (uralite, high-alumina porcelain) materials. Furnaces for firing clinker are lined with special refractory bricks. only fuel that does not emit soot and ash is used.

Due to the absence or low content of iron oxides in the raw material mixture, the firing of white cement becomes difficult and is carried out at elevated temperatures. In this regard, for the intensification of the sintering process, it is advisable to introduce minepalyzative substances into the raw material mixture: fluorspars, sodium silicon fluoride, and others. When leaving the furnace, clinker with a small iron content retains a greenish color to some extent. To increase the whiteness of clinker with a low iron content, it is subjected to a special treatment - bleaching, the essence of which is the reduction of Fe_2O_3 to Fe_3O_4. This contributes to the elimination of green color and increases the whiteness of cement.

Clinker is fired in a weakly reducing environment, quickly cooled and additionally bleached, for example, by immersing hot clinker in a special pool of water. Special devices can also be used - bleachers. In the process of cement production, it is repeatedly subjected to additional bleaching, which is wet, water and gas. With the wet method of cement production, bleaching by the chlorination method is used, in which calcium, sodium or ammonium chloride salts are introduced into the raw material mixture. As a result of the chemical reaction of the interaction of iron oxides with raw materials, iron trichloride is formed, which is released during firing. The water method consists in bleaching already fired clinker in a special liquid environment. In gas bleaching, burnt clinker is cooled and cleaned in converted gas, after which it also undergoes water treatment.

To increase whiteness, clinker is bleached by rapid cooling with water from 1250-1350 to 500-600 °C. After cooling, it is instantly separated from the water and it dries due to its own heat. The bleaching effect is also performed by bleaching clinker in a special apparatus - a bleacher, in which the clinker is exposed to a short-term action (within a few minutes) of a reducing oxygen-free gas environment at a temperature of 800 - 1000 °C, followed by cooling (without access to oxygen) to approximately 200 °C. When grinding bleached dried or cooled cement clinker, diatomite and gypsum are added to it. The specific surface of white cement is greater than that of Portland cement of other types. In the production process, contamination is also excluded at the stage of transshipment and packing of cement.

Firing of white cement clinker: Formation of the crystallization structure of silicate dispersion systems is carried out during their high-temperature heat treatment - firing. With the use of thermodynamic analysis, data were obtained on the course of phase transformations in oxide systems, for individual rock-forming minerals and clay systems. An important conclusion is the increased reactivity of oxides that are formed directly in the firing process during the destruction of lattices of rock-forming minerals [13-15].

White Portland cement clinker is fired in rotary kilns, which structurally differ little from kilns used for the production of ordinary cement. If the clinker begins to be whitened immediately after firing by rapid cooling in water, then in the final part of the rotary kiln there are no conventional devices for cooling the clinker (recuperators or other coolers). This is explained by the fact that in this case the clinker must be unloaded from the furnace at high temperatures and quickly cooled in water. The sintering zone of the rotary kiln is lined with talc or magnesite refractory bricks. The use of chromo magnesite bricks is unacceptable, as the possibility of the content of coloring oxides in the clinker during firing increases.

For clinker firing, ashless fuel is used - fuel oil or natural gas. The firing temperature of low-iron white Portland cement clinker is high and reaches 1500-1550 °C. At the same time, there are certain differences in the physico-chemical processes that take place during the heat treatment of the raw material mixture to obtain clinker. According to current standards [8,16], white Portland cement clinker consists mainly of calcium silicates and aluminates.

The question of the development of white cement technology

The innovative development of white cement technology should be connected with the transition from the energy-consuming wet to the energy-saving dry method of production characteristic of the modern cement industry [17-19]. The production of white cement by the dry method, under the condition of minimizing the maximum firing temperature, requires the development of new starting raw material mixtures, the chemical and mineralogical composition of which will ensure the specified properties [20-23]. At the same time, a high degree of dispersion and, accordingly, the free energy of the particles of the selected components can become a factor in increasing the reactivity during the firing of the starting mixtures [24,25].

Modern requirements of resource conservation and ecology increase the relevance of cement production while reducing the maximum firing temperature and the content of the carbonate component. An example of solving such problems with regard to the firing temperature (≤ 1200 °C) is the technology of natural cement [26-28] or Roman cement [29-31], and with regard to the content of the carbonate component – work in the direction of obtaining Eco-cement [32,33]. For a long time, the technology for the production of a mineral binding type of natural or Roman cement is based mainly on the use of one type of raw material - marl, the distribution of which is limited. It is obvious that under the condition of expansion of the raw material base, provision of standardized property indicators, in particular strength and whiteness, with lower energy consumption compared to Portland cement, the white Eco-cement type binder has the prospect of becoming a substitute for more energy-intensive and expensive Portland cement in a number of construction works.

Solving the problems of the innovative development of the chemical technology of white cement is related to the search for suitable varieties of alumino- and silica-containing raw materials, the determination of the rational ratio of the components of the mixture, the analysis of the features of phase formation and the properties of the material, which became the goal and subject of research in this work.

Experimental Part

Research objects and methods

The object of the study was silicate systems for the dry production of white portland cement at the maximum clinker firing temperature of 1400 °C and white cement at low temperature (≤ 1200 °C) firing. In accordance with the specified goal, when choosing raw materials, it was assumed that they should have:

a. increased reactivity, ensuring the intensification of physical and chemical reactions in the silicate system during firing with a decrease in the maximum temperature;
b. minimum content of color oxides to increase the degree of whiteness of the final product.

For the production of the raw material mixture, the following was used:

a. chalk of Zdolbuniv deposit, Rivne region;
b. aluminum hydroxide of «Mykolaiv Alumina Plant»;
c. dust quartz of «Novoselivsky GZK», Kharkiv region;
d. aerosil 200 – synthesized silicon dioxide;
e. microtalc – a product of enrichment and fractionation of natural talc.

The methods of physical and chemical analysis of silicate raw materials and testing the properties of binders included:

a. determination of chemical composition according to current standards;
b. X-ray phase analysis of powder preparations using DRON 4-07 and DRON-3M diffractometers (CuKα 1-2 radiation, voltage 40 kV, current 20 mA, speed 2 degrees/min.);
c. determination of whiteness using a Carl Zeiss leukometer;
d. computer calculations of the composition of raw mixtures using the programs "RomanCem";
e. testing of binding properties and physical and mechanical characteristics.

The raw materials were prepared according to the modern dry method of cement production by dosing the components by weight, mixing and homogenizing in a ball mill, firing and grinding the final product. The samples were fired for 15 hours at a maximum temperature of 1100-1400 °C with a holding time of 1.5 hours. All samples of the mixtures compared were fired simultaneously and together to exclude differences in the degree of heat treatment. The properties of the binding material were determined according to standardized methods.

Characteristics of the source materials: According to the chemical composition, among the studied raw materials, the sample of zdolbunivska chalk is characterized by a high content of CaO, the sample of aluminum hydroxide - the largest amount of aluminum oxide, the samples of dust quartz - the largest content of silica, the sample of microtalc - a high content of magnesium oxide with a quantitative ratio of SiO_2:CaO:MgO = 11:1:5 (Table 1).

Table 1: Chemical composition of raw materials.

Samples	Content of Oxides, wt. %						
	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
aluminum hydroxide	-	65,0	-	-	-	-	35,0
dust quartz	99,66	0,16	0,06	-	-	-	0,12
microtalc	61,32	0,26	0,10	5,39	27,40	-	5,53

Analysis of the mineralogical composition of the studied raw materials showed (Figures 2-6):

a. the main rock-forming mineral of the chalk is calcite (97.6 wt.%) with admixtures of dolomite (1.2 wt.%), quartz and kaolinite - respectively 0.5 and 0.6 wt.%;
b. aluminum hydroxide is characterized by the presence of hydrargillite (gibbsite), diaspore, boehmite with a minor admixture of ilmenite;
c. the main rock-forming mineral of dust quartz is crystalline β-quartz;
d. the main rock-forming mineral of microtalc is talc with quartz impurities.

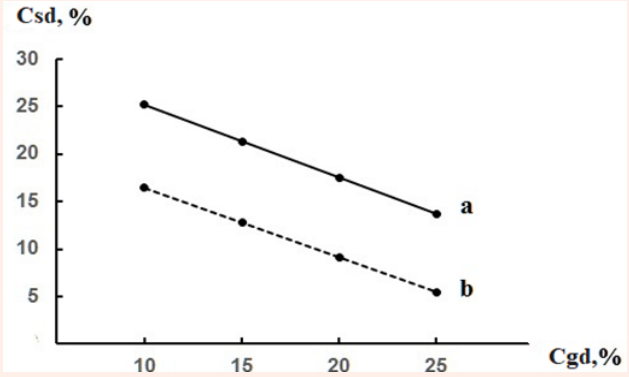

Figure 2: Dependence of the content of dust quartz (Csd) and aluminum hydroxide (Cgd) in the chalk based system at SF=1.10 (a) and SF=1.70 (b).

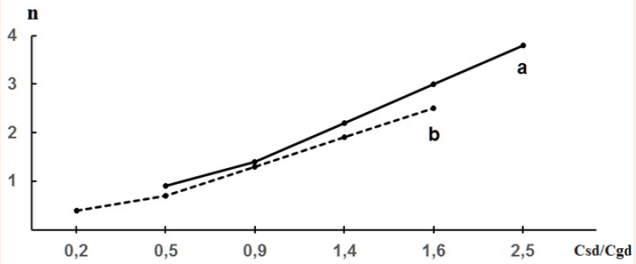

Figure 3: Dependence of binder silica modulus (n) on the quantitative ratio of dust quartz and aluminum hydroxide (Csd/Cgd) at SF=1.10 (a) and SF=1.70 (b).

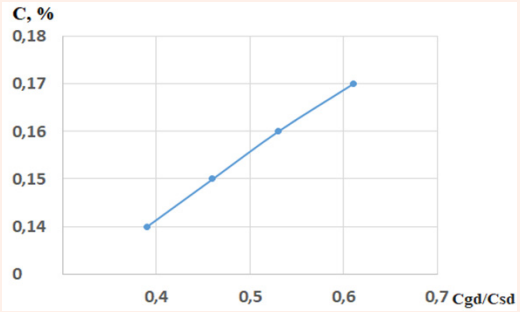

Figure 4: Dependence of colored oxides content (C) on the quantitative ratio of aluminum hydroxide and dust quartz (Cgd/Csd) in chalk based system.

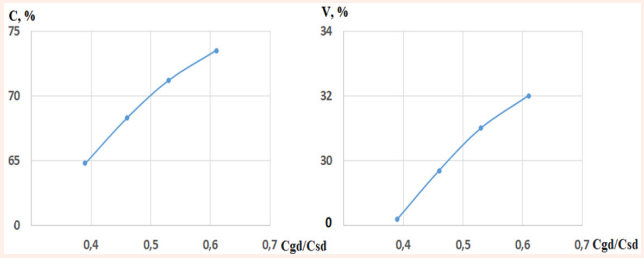

Figure 5: Dependence of chalk content C (1) and CO_2 emissions V (2) on the quantitative ratio of aluminum hydroxide and dust quartz (Cgd/Csd).

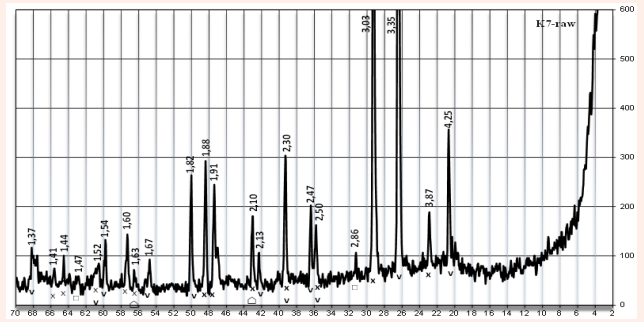

Figure 6: X-ray diffraction of raw material mixture K7: x calcite, □ dolomite, v quartz, ☖ diaspore.

In the studied silicate system, the increased reactivity in the physicochemical processes of phase formation of cement clinker [14-16] during the firing of mixtures in the case of calcium and aluminum oxides is caused by their formation during the destruction of calcite lattices and aluminum hydroxide, SiO_2 and MgO oxides during the destruction of talc lattices. In addition, with respect to silicon dioxide, the increased reactivity is determined by the fine dispersion of dust quartz (Table 2), the largest share of which (69.91 wt.%) consists of particles of fractions 0.05-0.01 mm, and the developed specific surface is 2720 cm^2/g.

Table 2: Granulometric composition of dust quartz.

Sample	Content (wt.%) of Particle Fractions, mm				
	1,00-0,05	0,05-0,01	0,01-0,005	0,005-0,001	< 0,001
dust quartz	2,54	69,91	12,05	10,40	5,10

Silicate systems for production of white eco-cement

In order to determine the possibility of obtaining white cement by a dry method under the condition of firing at a maximum temperature of ≤ 1200 °C, silicate systems based on chalk as a carbonate raw material with a minimum content of colored oxides with varieties of finely dispersed aluminum and silicon-containing materials were investigated. The analysis of the quantitative ratio of the studied materials in the composition of the raw material mixtures at the specified values of the cement characteristics was carried out using the created computer program "RomanCem".

The principle of prompt solution of the problem based on the software is reduced to the following:

a. Tabular data with a number of chemical compositions of probable raw components are entered.
b. The value of the hydraulic module HM is set.
c. According to the accepted calculation formula, all combinations of two or three components that provide the specified values of HM are determined. Thus, with any sufficiently large raw material base, it is possible to quickly determine the rational ratio of components in the original raw material mixture.

Analysis of the system chalk – aluminum hydroxide – dust quartz: The composition of the initial 3-component raw mixtures based on the system of chalk – aluminum hydroxide – dust quartz was determined according to the known recommendations for low-temperature firing cement technology in the range of values of the hydraulic modulus HM = 1.1–1.7 using the created program "RomanCem" for computer calculations.

On the basis of computer calculations, it was established that the possible composition and characteristics of the investigated silicate system significantly change in the indicated range of HM values. At the same time, the significant role of the quantitative ratio of aluminum-silica-containing components is determined. Along with the dependence of the concentration of alumino-silica-containing components on the hydraulic modulus, a significant change in the values of the silica modulus is observed (Figure 2, [33]). It was determined that in the range of concentrations of aluminum hydroxide from 10 to 25 wt. % required content of dust quartz changes from 25 to 14 wt. % at a given HM = 1.1 and from 16.5 to 5.5 at HM = 1.7.

According to the quantitative ratio of the components of the mixture, binders based on the studied silicate system are characterized by changes in chemical composition. Thus, at HM = 1.1, binders with increasing concentrations of aluminum hydroxide from 10 to 25 wt. % with an approximately equal content of CaO at the level of 52% and Fe_2O_3 at the level of 0.14% are characterized by a decrease in the amount of SiO_2 from 37.5 to 22%, an increase in the amount of Al_2O_3 from 9.8 to 25.4%. According to this, the silica modulus n decreases from 3.8 to 0.5. At HM = 1.7, binders with increasing concentrations of aluminum hydroxide from 10 to 25 wt. % with an approximately equal content of CaO at the level of 63% and Fe_2O_3 at the level of 0.15-0.17% are characterized by a decrease in the amount of SiO_2 from 26.3 to 9.8%, an increase in the amount of Al_2O_3 from 10.4 to 26.9%. According to this, the silica modulus n decreases from 2.5 to 0.4. From the point of view of the purpose of this study, it is important that in the specified ranges of HM and Cas/Csd values, the compositions of raw mixtures are characterized by a low level of the content of colored iron oxides C = 0.14-0.17% (Figure 4).

With regard to ecological issues, the possibility of reducing the content of the amount of the carbonate component - chalk in the starting mixtures with a corresponding reduction in CO_2 emissions into the atmosphere (Figure 5) is of interest. Mineral binders chosen on the basis of the analysis of the composition of raw materials and computer calculations for further research are characterized by differences in the quantitative ratio of the components of the original mixture and the numbers of hydraulic and silica modules (Table 3). It is obvious that the K7 mixture with Cas/Csd = 0.4 differs from K9 with Cas/Csd = 0.6 in chemical composition: the content and quantitative ratio of oxides: SiO_2 : Al_2O_3 - 3.8 versus 2.5, CaO : SiO_2 - 1.4 vs. 2.4, CaO : Al_2O_3 = 5.3 vs. 6.0 with a low content of iron oxides - 0.10-0.11% (Table 4).

Table 3: Composition of the raw material mixtures.

Code of Mixture	Content of Components, wt.%		
	Chalk	Aluminum Hydroxide	Dust Quartz
K7	65,0	10,0	25,0
K9	73,5	10,0	16,5

Table 4: Chemical composition of the raw material mixtures.

Code of Mixture	Content of Oxides, wt. %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
K7	25,62	6,70	0,10	35,66	0,16	0,05	32,95
K9	16,99	6,71	0,11	40,45	0,18	0,06	35,50

The content of carbonates - calcite and dolomite in the mineralogical composition of the mixtures determines the reduction of possible emissions of CO_2 into the atmosphere during the firing of clinker from the K7 mixture to the level of 28.3 against 32.0% for K9. The composition of the rock-forming minerals calcite – quartz – aluminum hydroxides corresponds to the given data on the material and chemical composition of the mixtures (Figure 6). The obtained results of the X-ray phase analysis indicate certain differences in the physicochemical transformations during firing of the studied mixtures, which are correlated with the specified chemical and mineralogical composition and depend on the content and ratio of the components and the maximum firing temperature.

Thus, after firing at a maximum temperature of 1100 °C (Figures 7 & 8) with the same qualitative phase composition, sample K7 differs from K9 by a greater amount of quartz, calcium silicates of the CS and C_2S types, calcium aluminate of the CA type, and hellenite C_2AS. After firing to the maximum temperature of 1200 °C (Figures 9 & 10) with approximately the same qualitative phase composition, sample K7 differs from sample K9:

i. more crystalline quartz (3.34; 4.25 Å);
ii. in relation to calcium aluminosilicates - by greater development of C_2AS hellenite (2.86 Å);
iii. in relation to calcium aluminates - by a greater development of CA (2.51; 4.05 Å) with a significantly smaller amount of mayenite $C_{12}A_7$ (4.92 Å);
iv. in relation to calcium silicates - by greater development of C_2S (2.75; 2.77 Å).

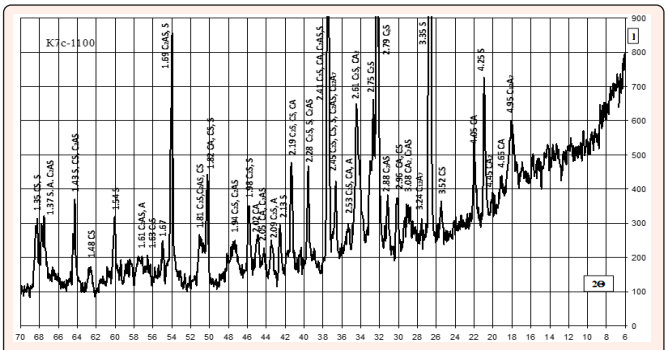

Figure 7: X-ray diffraction of sample K7 (1100 °C).

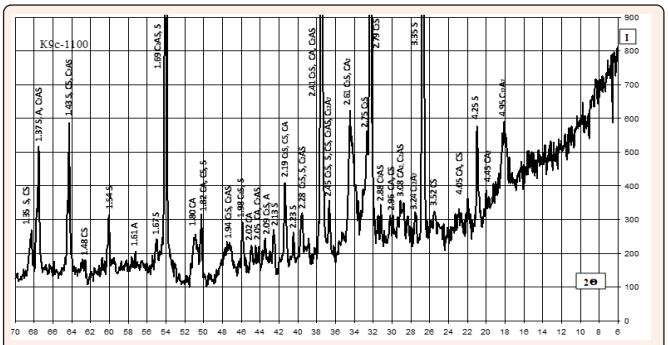

Figure 8: X-ray diffraction of sample K9 (1100 °C).

The results of testing samples of the binder from the studied mixtures indicate differences in the influence of the composition and degree of firing of the starting mixtures on the indicators of the properties of the binder material (Table 5).

Table 5: Properties of the binding material.

Characteristics		Sample Code and Indicators at Firing Temperature, °C			
		1100		1200	
		K9	K7	K9	K7
Finess of grinding, sieve residue 008, mass. %		8	7	8	8
Consistency, %		55	50	55	50
Setting time, min	Initial setting time	10	15	30	30
	Final setting time	25	90	60	75
Compressive strength, MPa		22,0	21,0	27,5	25,3
Whiteness, %		80	80	86	85

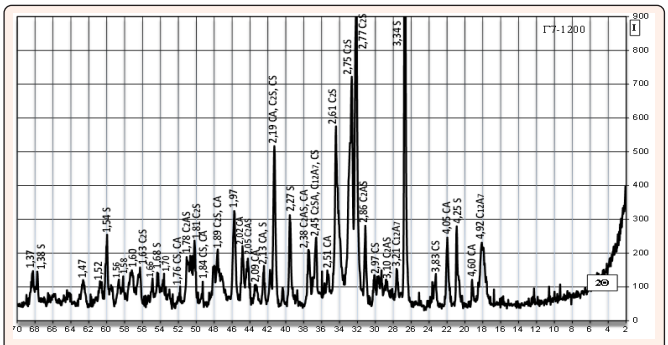

Figure 9: X-ray diffraction of sample K7 (1200 °C).

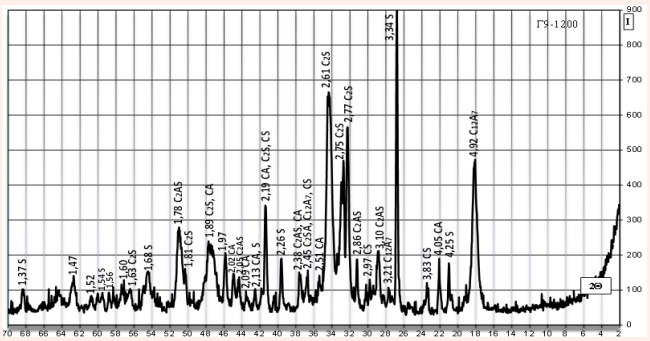

Figure 10: X-ray diffraction of sample K9 (1200 °C).

Thus, according to the classification of DSTU B V.27-91-99, according to the speed of hardening, the binder from K7 and K9 mixtures when fired at a maximum temperature of 1100 °C belongs to the group of ultra-fast hardening (starting time no later than 15 min.), which is considered typical for expanding and tensioning cement. When the maximum firing temperature is increased to 1200 °C, the time of onset of hardening of the samples doubles - as a result, they move to the group of fast hardening (time of onset from 15 to 45 min.), which is considered characteristic of anhydrite and alumina cement. At the same time, sample K7 differs from K9 in the slowing down of the hardening process, which is associated with a higher ratio of the quantitative content of quartz and aluminum hydroxide Spk/Sgd - 2.5 versus 1.6. According to the specified standard, the binder samples belong to the group of reduced strength (from 10 to 30 MPa per compression), but they significantly exceed the regulated indicators of natural or Roman cement, and in terms of whiteness, they meet the requirements of the white Portland cement standard [34,35].

Analysis of chalk-aluminum hydroxide-microtalc system: The composition of the initial 3-component raw material mixtures based on chalk-aluminum hydroxide-microtalc systems was determined according to the known recommendations for Roman cement technology in the range of 1.1 - 1.7 hydraulic modulus HM using the created computer program "RomanCem". It was found that in the specified HM interval, the quantitative ratio of the system components changes significantly (Figure 11), while along with the dependence of the concentration of the components on the hydraulic modulus, a significant change in the values of the silica modulus is observed.

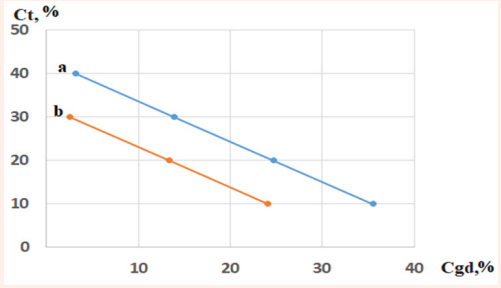

Figure 11: Dependence of the amount of microtalc Ct on aluminum hydroxide content Cgd in the chalk based mixture at HM = 1.1 (a) and HM = 1.7 (b).

At the minimum concentration of aluminum hydroxide for the studied systems of 10 wt. % in the range of values of HM = 1.1-1.7, the possible content of microtalc varies equally - from 35.5 to 24.1 wt. % (Figure 12). At the same time, there is an inversely proportional relationship between the concentration of microtalc and the values of the hydraulic modulus of the binder. As for the silica modulus n of the binder, there is a directly proportional dependence of its values in the range of 2.2-3.2 on the concentration of microtalc (Figure 13).

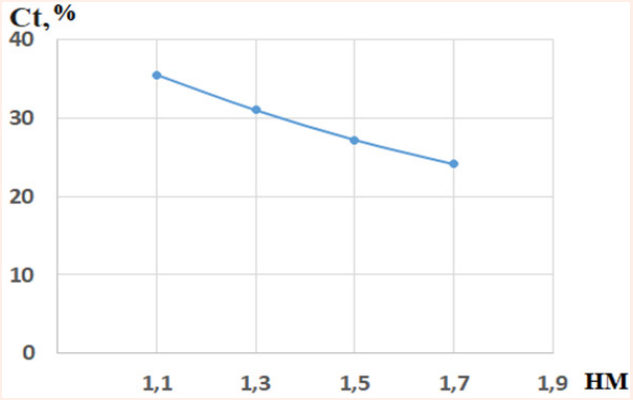

Figure 12: Dependence of the amount of microtalc Ct on the hydraulic module HM at aluminum hydroxide content Cgd = 10 wt. %.

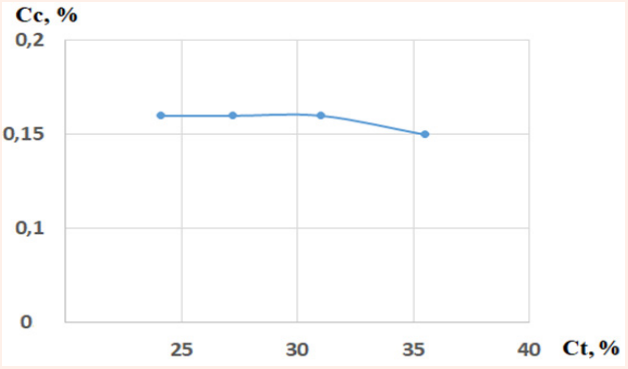

Figure 13: Dependence of silica module (n) on the amount of microtalc Ct at the aluminum hydroxide content Cgd = 10 wt. %.

From the point of view of the purpose of this work, it is important to minimize the amount of colored oxides after firing the mixtures at the level of Cc = 0.15-0.16 (Figure 14). The raw material mixtures chosen for the production of mineral binding material are characterized by a significantly lower content of the carbonate component in comparison with known compositions (Table 6). At the same time, with the same content of aluminum hydroxide, the mixtures differ in the quantitative ratio of chalk and microtalc.

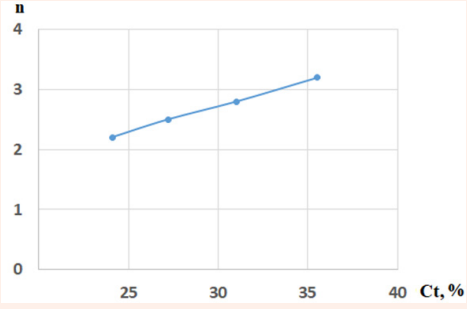

Figure 14: Dependence of colored oxides content (Cc) on the amount of microtalc Ct at the content of aluminum hydroxide Cgd = 10 wt. %.

Table 6: Composition of the raw material mixtures.

Code of Mixture	Content of Components, wt.%		
	Chalk	Aluminum Hydroxide	Microtalc
K14	66,0	10,0	24,0
K12	54,5	10,0	35,5

According to the chemical composition, the studied raw material mixtures are characterized by the same amount of aluminum and iron oxides, but they differ significantly in the content and quantitative ratios of other oxides, which determine the potential for phase formation during firing (Table 7).

Sample K12 differs from K14:

i. a lower content of calcium oxides and a quantitative ratio of CaO: MgO = 3.2 versus 5.6;

ii. quantitative ratios of CaO : SiO_2 = 1.4 versus 2.5 and CaO : Al_2O_3 = 4.7 versus 5.6;

Table 7: Chemical composition of the raw material mixtures.

Sample Code	Content of Oxides, wt. %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
K14	15,27	6,72	0,11	37,59	6,76	0,05	33,50
K12	22,18	6,73	0,11	31,91	9,86	0,04	29,17

The mineralogical composition of the K12 mixture differs from K14 by the lower content of calcite $CaCO_3$, which is 57.0 vs. 67.1 wt. %. At the same time, possible CO_2 emissions during clinker firing are correspondingly smaller - 25.1 versus 29.5%. The composition of the rock-forming minerals calcite – talc – aluminum hydroxide corresponds to the given data on the material and chemical composition of the mixtures (Figure 15).

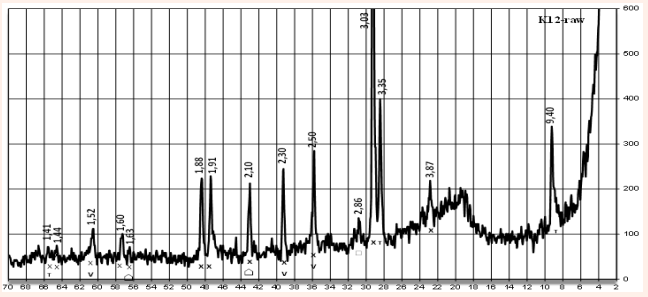

Figure 15: X-ray diffraction of raw material mixture K12: x calcite, □ dolomite, т talc, ☖ diaspore.

The results of the X-ray phase analysis obtained in this work indicate certain peculiarities in the physical and chemical transformations during firing of the studied mixtures in the range of maximum temperatures of 1100-1200 °C (Figures 16-19). These features of phase formation are correlated with the specified chemical composition and are primarily manifested in the formation of periclase and calcium-magnesium silicates - ockermanite $2CaO•MgO•2SiO_2$ and merwinite $3CaO•MgO•2SiO_2$. At the same time, with almost the same qualitative phase composition, the studied clinker samples differ in the degree of development of individual phases.

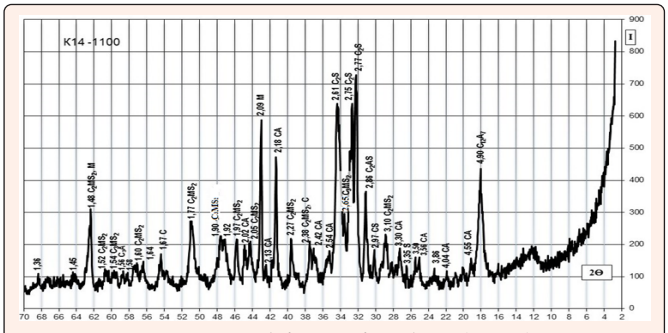

Figure 16: X-ray diffraction of sample K14 (1100 °C).

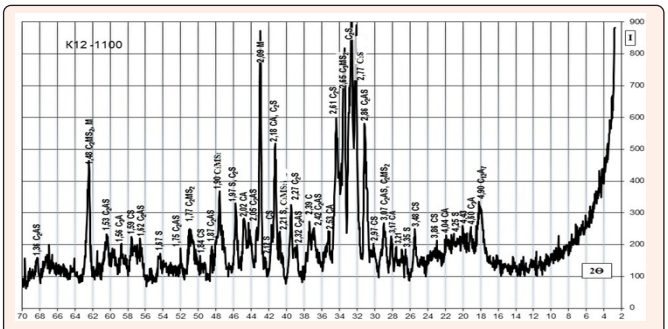

Figure 17: X-ray diffraction of sample K12 (1100 °C).

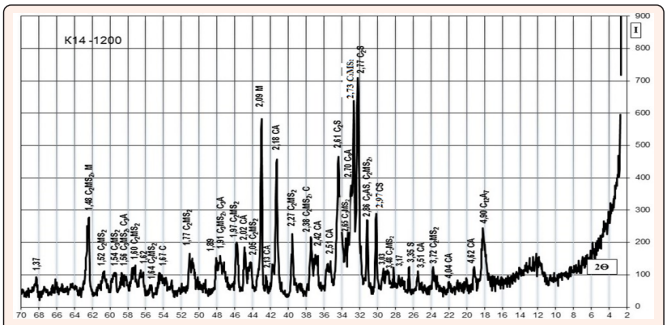

Figure 18: X-ray diffraction of sample K14 (1200 °C).

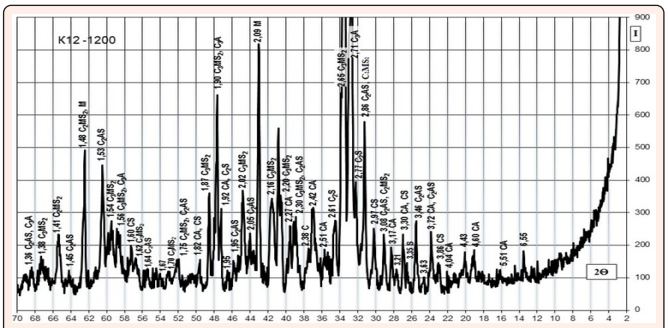

Figure 19: X-ray diffraction of sample K12 (1200 °C).

Thus, after firing to a maximum temperature of 1100 °C with approximately the same development of the crystalline phases of CS and C_2S calcium silicates, sample K12 with a higher content of microtalc differs from sample K14:

in relation to the crystalline phases of calcium aluminosilicates - by the intensification of the formation of C_2AS helenite (2.86 Å);

i. in relation to the crystalline phases of calcium aluminates – by the intensification of the formation of CA (2.52 Å) with a decrease in the amount of mayenite $C_{12}A_7$ (4.90 Å);

ii. intensification of periclase formations (2.10; 1.48 Å), ockermanite $2CaO•MgO•2SiO_2$ (2.87 Å) and mervinite $3CaO•MgO•2SiO_2$ (2.66 Å).

After firing to the maximum temperature of 1200 °C, sample K12 differs from sample K14:

i. less development of the crystalline phases of calcium silicates CS (2.97 Å) and C_2S (2.77; 2.61 Å);

ii. in relation to the crystalline phases of calcium aluminosilicates - by the intensification of the formation of C_2AS helenite (2.86 Å);

iii. in relation to the crystalline phases of calcium aluminates – by intensification of the formation of CA (2.52 Å) while minimizing the amount of mayenite $C_{12}A_7$ (4.90 Å);

iv. intensification of periclase formations (2.10; 1.48 Å), ockermanite $2CaO•MgO•2SiO_2$ (2.87 Å) and mervinite $3CaO•MgO•2SiO_2$ (2.66 Å).

The results of the testing of the studied samples of the binder testify to the differences in the influence of the composition and degree of firing on the property indicators (Table 8).

Table 8: Properties of the binding material.

Characteristics		Sample Code and Indicators at Firing Temperature, °C			
		1100		1200	
		K14	K12	K14	K12
Finess of grinding, sieve residue 008, mass. %		7	8	8	7
Consistency, %		62	57	57	50
Setting time, min	Initial setting time	10	30	60	85
	Final setting time	50	60	110	125
Compressive strength, MPa					
2 days		3,8	4,0	4,9	5,1
7 days		17,0	17,9	20,8	21,7
28 days		33,0	34,5	39,5	41,0
Whiteness, %		88	90	90	92

Thus, according to the classification of DSTU B V.27-91-99, when fired at a maximum temperature of 1100 °C, the binder from the K14 mixture belongs to the group of ultra-fast hardeners (starting time no later than 15 min.), which is considered typical for expanding and tension cement. Sample K12 belongs to fast-hardening (time of onset from 15 to 45 min.), which is considered typical for anhydrite and alumina cement. When fired at the maximum temperature of 1200 °C, according to the rate of hardening, both samples of the binder belong to the group of normal hardening (start time from 45 min. to 2 hours), which is considered typical for Portland cement and slag Portland cement. At the same time, sample K12 differs from K14 in the general slowing down of the hardening process.

According to the specified standard, the binder samples belong to the group of medium strength (from 30 to 50 MPa per compression). At the same time, a significant increase in strength with an increase in the maximum firing temperature is evident. From the point of view of the purpose of this work, it is important to achieve high whiteness indicators in accordance with the requirements of the white Portland cement standard.

Conclusion

a. The innovative development of the chemical technology of white cement with the reduction of the maximum firing temperature and, accordingly, the specific fuel consumption contributes to solving the issues of resource conservation and increasing the efficiency of producing decorative mineral binders and products made from them. At the same time, the decrease in the content of the carbonate component in the composition of the raw material mixtures causes a corresponding reduction in CO_2 emissions into the atmosphere.

b. During the study of silicate system chalk-aluminum hydroxide-dust quartz for the production of white cement of low-temperature firing (≤ 1200 °C) it was established that in the range of the quantitative ratio of aluminum- and silica-containing components Cgd / Csd from 0.4 to 0. 6, the silica modulus of the binder changes in an inversely proportional dependence within n = 3.8-2.5 at a low content of colored iron oxides at the level of C = 0.11-0.17%.

c. The specified compositions of the raw material mixture based on chalk with the use of alum - silica-containing complexes of aluminum hydroxide - dust quartz make it possible to obtain a mineral binder in a dry way at a maximum firing temperature of 1100-1200 °C, which exceeds natural or Roman cement in terms of strength (21 -27 vs. 10-15 MPa) and whiteness (80-85 vs. 55-60%).

d. The determined compositions of the raw material mixture based on the system of chalk - aluminum hydroxide - microtalc allow to obtain a mineral binder of increased whiteness (88-92%) by the dry method at the maximum firing temperature of 1100-1200 °C, which meets the requirements in terms of hardening speed and compressive strength to portland cement.

e. The necessary physico-mechanical and decorative properties of cement during low-temperature firing of clinker from the developed mixtures are achieved by forming a system of crystalline phases of calcium silicates CS, C_2S, aluminosilicate C_2AS, and alumina calcium CA and magnesium-containing - periclase, ockermanite and merwinite. At the same time, the increased whiteness of the manufactured material is associated with the absence of iron-containing phases, primarily C4AF, and the formation of ockermanite $2CaO•MgO•2SiO_2$ and mervinite $3CaO•MgO•2SiO_2$ allows minimizing the amount of free magnesium oxide, which is limited by current standards due to negative impact on the properties of cement stone.

f. The decrease in the content of the carbonate component in the developed compositions of raw materials, along with the reduction of the maximum firing temperature, allows the resulting mineral binders to be classified as Eco-cements.

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