Studying the composition and properties of white eco-cement

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Abstract: *The possibility to produce white Eco-cement with the use of a dry method under low-temperature firing of a raw material mixture based on the CaO – SiO2 – Al_2O_3 – MgO system is shown. Computer calculations were performed and an analysis of the dependence of the characteristics of cement clinker on the quantitative ratio of raw components was carried out. A new composition of the raw material mixture with a decrease of 19 wt. % amount of the carbonate component and, accordingly, CO_2 emissions during combustion was determined. The peculiarities of phase transformations in the material during firing with a maximum temperature of 1100 ^oC when microtalcum was introduced into the initial mixture with the formation of pericloze, ockermanite and merwinite as a factor in the structure and properties of cement clinker were noted.*
Keywords*: ECO-CEMENT,RAW MATERIAL MIXTURE, MICROTALC, FIRING, PHASE COMPOSITION, PROPERTIES.*

1. Introduction

The production of the most common mineral binder, Portland cement, is characterized by significant energy costs by high-temperature firing (1400-1500 °C) of clinker as well as by its grinding with additives to a highly dispersed state [1-3]. At the same time, the physical and chemical transformations of rock-forming minerals into carbonate components, which make up the majority (75-80 wt. %) of the composition of the raw material mixtures, cause significant emissions of CO_2 into the atmosphere [4].

It is noted that cement clinker kilns account for about 5% of total CO_2 emissions into the atmosphere. The problem lies in cement's chemistry, which is a sort of double-whammy of CO_2 production. To turn Portland cement's key ingredient, calcium carbonate—found in limestone or chalk—into a finished product called alite, the minerals must be broken down in kilns heated to more than 1400 ℃. The heating process uses tremendous amounts of energy, which is typically generated using gas or coal, the most carbon-intensive fossil fuel. Then, the ensuing chemical process releases a second wallop of CO_2 as a byproduct of turning calcium carbonate into calcium oxide. In total, producing 1 ton of cement releases 770 kilograms of CO_2 into the atmosphere.

When solving the specified problems of resource conservation and environmental safety of cement production, considerable attention is given to the Eco-cement technology using raw material mixtures with a lower content of carbonate components [5-8] and the use of industrial waste [9,10].

The production of white Eco-cement is complicated by special requirements regarding the chemical composition of raw materials with the minimization of the content of colored oxides [11-13]. The solution of this scientific and technical problem requires the development of new compositions of raw material mixtures, the analysis of the features of phase formation and the properties of white hydraulic mineral binder under the conditions of low-temperature firing, which became the goal of the presented work.

2. Results and discussion

The selection of research objects in this work was carried out in accordance with the main goal – to obtain a white mineral binding material during low-temperature firing with a decrease in the content of the carbonate component in the initial mixture. In accordance with the above, raw materials must have:

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

Materials of natural and industrial origin were used for the production of the raw material mixture:

- chalk of the Zdolbuniv deposit of the Rivne region;
- aluminum hydroxide – a product of processing bauxite into alumina;
- pyloquartz - a product of enrichment and fractionation of quartz sand;
- microtalc – a product of enrichment and fractionation of talc powder.

According to the chemical composition, among the studied raw materials, the sample of Zdolbuniv chalk is characterized by a high content of CaO, the sample of aluminum hydroxide - the largest amount of aluminum oxide, the sample of pyloquartz - the largest amount 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).

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

Table 1: *Chemical composition of raw materials*

Samples	Content of oxides, wt. %									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	Na_2O	K_2O	LOI
chalk	0,77	0,25	0,13	-	55,0	0,25	0,08	-	-	43,49
hydrate of aluminium oxide	-	65,0	-	-	-	-	-	-	-	35,0
pyloquartz	99,16	0,16	0,06	-	-	-	-	-	-	0,12
microtalc	61,32	0,26	0,10	-	5,39	27,40	-	-	-	5,53

The samples were fired for 15 hours at a maximum temperature of 1100 °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.

Methods of physical - chemical analysis of silicate raw materials and testing of properties of astringent substances which were used in this work included:

- chemical composition analysis using standardized 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);

- determination of the whiteness of materials using a leukometer Carl Zeiss JENA.

The analysis of mineralogical composition of raw material showed:

- the basic rock-forming mineral of chalk is calcite (97,6 mass.%) with the admixtures of dolomite, quartz and kaolinite;
- hydrate of aluminium oxide is characterized by the presence of hydrargillite (gibbsite), diaspore, boehmite with the insignificant admixture of ilmenite;
- the main rock-forming mineral of pyloquartz is β-quartz;
- the main rock-forming mineral of microtalc is talc with quartz impurities.

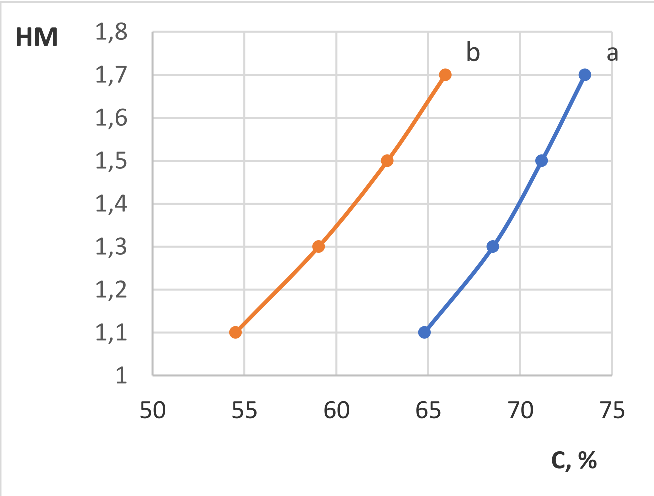
It is obvious that by the calcination of the specified raw materials during the destruction of lattices of the main rock-forming minerals, chalk and aluminum hydroxide will become a source of CaO and Al_2O_3 oxides, pyloquartz - a source of SiO_2, and microtalc - SiO_2 and MgO oxides in the process of phase formation of cement clinker [14-16].

Results and Discussion

The composition of the initial 3-component raw material mixtures basedon the chalk-aluminum hydroxide- pyloquartz and chalk-aluminum hydroxide-microtalc systems was determined according to known recommendations regarding low-temperature firing cement technology in the range of values of the hydraulic modulus HM=1.1–1.7 using a specially created program for computer calculations [17].

It was established that in the specified HM interval, the quantitative ratio of the system components changes significantly, 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.

It was determined that at the minimum aluminum hydroxide concentration for the studied systems of 10 wt. % in the range of values of HM=1.1-1.7, the possible content of the carbonate component is 68.3-73.5 wt. % when using pyloquartz and 54.5-62.8 wt. % when using a microtad (Fig. 1). At the same time, there is a directly proportional relationship between the concentration of the carbonate component and the values of the hydraulic modulus of the binder.



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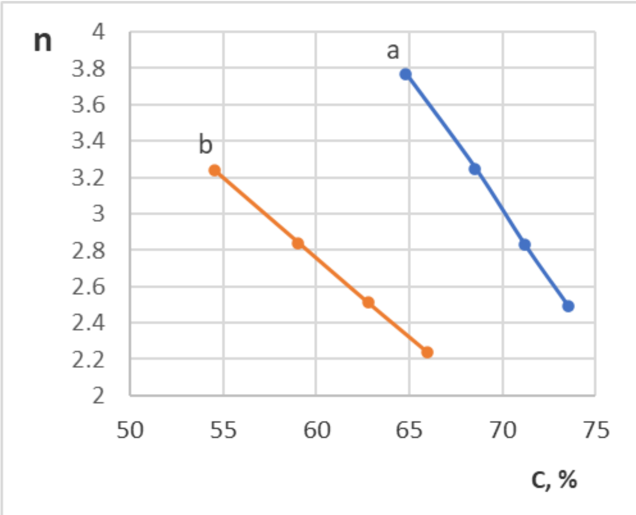

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Fig. 1 *Dependence of the hydraulic (1) and silica (2) moduli on the concentration of the carbonate component when using pyloquartz (a) and microtalc (b)*

As for the cement modulus n of the binder, there is an inversely proportional dependence of its values on the concentration of the carbonate component: in the ranges of 2.5-3.8 for systems with pyloquartz and 2.2-3.2 for systems with microtalc.

The raw material mixtures chosen for the production of mineral binding material with the same amount of aluminum hydroxide differ significantly in the content of the carbonate component - chalk (Table 2).

Table 2: *Composition of raw mixtures*

Code of mixture	Quantity of components, mass %			
	chalk	hydrate of aluminium oxide	pyloquartz	microtalc
K9	73,5	10,0	16,5	-
K12	54,5	10,0	-	35,5

According to the chemical composition, the investigated 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 a potential for phase formation during firing (Table 3).

Table 3: *Chemical composition of raw mixtures*

Sample code	Content of oxides, wt. %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI.
K9	16,99	6,71	0,11	40,45	0,18	0,06	35,50
K12	22,18	6,73	0,11	31,91	9,86	0,04	29,17

Thus sample K12 differs from K9 by:

- a smaller amount of calcium oxides, a much higher content of magnesium oxide with a quantitative ratio of CaO : MgO = 3.2;
- quantitative ratios of CaO : SiO_2 = 1.4 versus 2.4 and CaO : $A_{l2}O_3$ = 4.7 versus 6.0.

The analysis of the chemical composition of cement clinker from experimental mixtures (Table 4) indicates that at low values of the saturation coefficient SF= 0.35-0.64, the formation of crystalline phases C_2S and C_3A is most likely when the amount of iron-containing compounds is minimized.

Table 4: *Chemical composition of clinker*

Sample code	Content of oxides, wt. %					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
K9	26,34	10,40	0,17	62,72	0,28	0,09
K12	31,31	9,51	0,15	45,03	13,92	0,06

The results of the X-ray phase analysis obtained in this work indicate on certain peculiarities in the physical and chemical transformations during firing of the studied mixtures with a maximum temperature of 1100 ºC (Fig. 2, 3).

Thus, after firing to the maximum temperature of 1100 ºC with approximately the same development of the C_2S and CA crystalline phases, sample K12 differs from sample K9 by:

- a significantly smaller amount of free CaO (1.69; 2.38 Å) and quartz (3.835; 4.25 Å);
- formation of periclase (2.10; 1.48 Å), ockermanite $2CaO•MgO•2SiO_2$ (2.87 Å) and merwinite $3CaO•MgO•2SiO_2$ (2.66 Å);
- greater development of C_2AS hellenite (2.86 Å);
- a smaller groove of the crystalline phases of wollastonite CS (2.97; 3.48 Å) and mayenite $C_{12}A_7$ (4.90 Å).

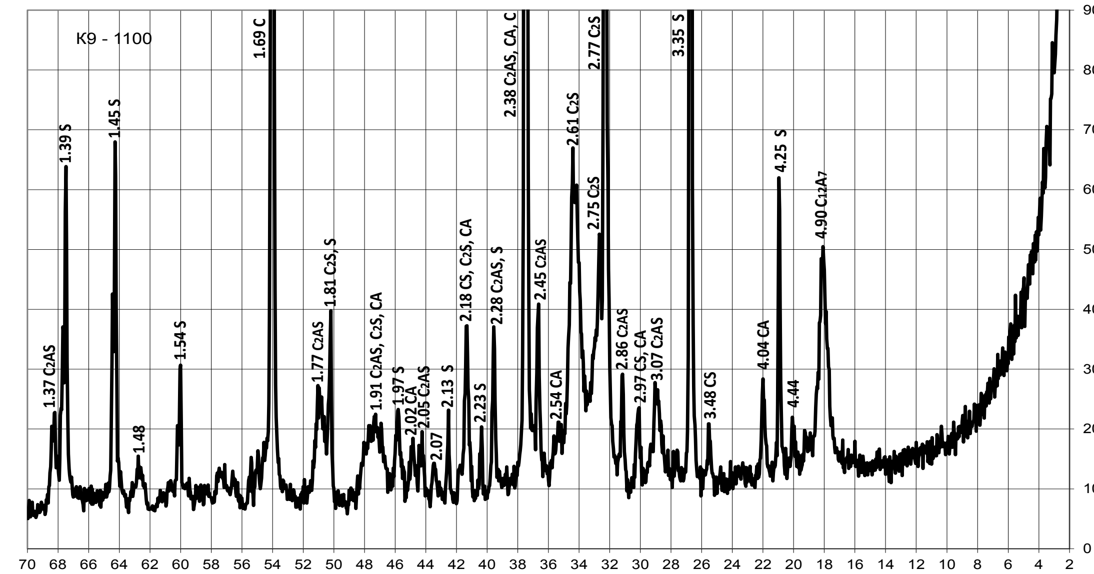

Fig. 2 *X-ray diffraction of sample K9 (1100 ºC).*

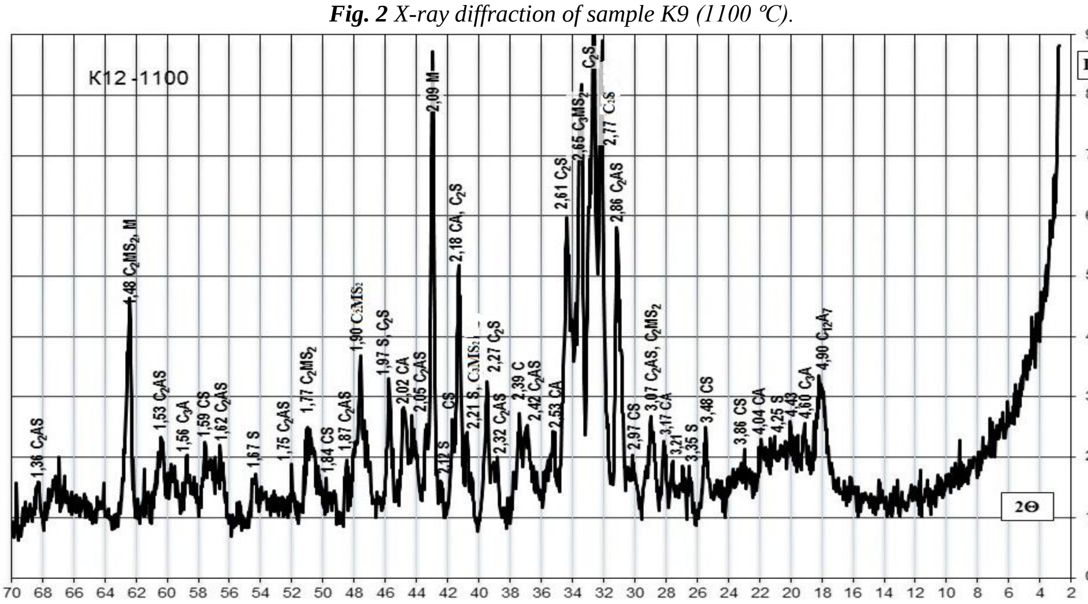

Fig. 3 *X-ray diffraction of sample K12 (1100 ºC).*

The results of the testing of the studied samples of the binder indicate differences in the influence of the composition on the property indicators (Table 5). Thus, according to the classification of DSTU B V.27-91-99 [18], when fired at a maximum temperature of 1100 ºC, the binder from the K9 mixture belongs to the group of ultra-fast hardeners (starting time no later than 15 min.), which is considered typical for expanding and tensioning cement. The sample K12 belongs to a fast-hardening one (time of onset from 15 to 45 min.), which is considered typical for anhydrite and alumina cement. At the same time, the sample K12 differs from K9 in the general slowing down of the hardening process.

Table 5: *Properties of mineral astringent material*

Characteristics	Sample code	
	K9	K12
Finess of grinding, sieve residue no. 008, mass. %	7	7
Initial setting time, min	10	30
Final setting time, min	25	60
Compressive strength, MPa	32	34,5
Whiteness, %	88	90

According to the specified standard, the samples of the binder produced belong to the group of medium strength (from 30 to 50 MPa per compression). 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 standard for white Portland cement [19,20].

Conclusions

1. The development and practical use of mineral binders of the Eco-cement type with a reduction in the content of the carbonate component of the raw material mixture contributes to the comprehensive solution of the issues of ecology, resource conservation and chemical technology for the production of silicate materials.

2. The possibility of producing white Eco-cement by a dry method at a maximum firing temperature of 1100 °C based on the chalk-aluminum hydroxide-microtalc system with a decrease in the content of the carbonate component and, accordingly, CO_2 emissions into the atmosphere by 19-20% compared to known compositions, was determined:

3. The peculiarities of phase formation during low-temperature firing of white Eco-cement clinker, manifested in the formation of crystalline phases of periclase and calcium-magnesium silicates - ockermanite $2CaO•MgO•2SiO_2$ and mervinite $3CaO•MgO•2SiO_2$, were established.

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