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Short Communication

Mineralogical Composition of Clay and Properties of Cement

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Abstract

The influence of the mineralogical composition of the raw material mixture on the phase formation and properties of low-temperature fired cement (≤ 1200 °C) was studied. Computer calculations of the composition of raw mixtures were carried out and the dependence of the possible concentration of clay component varieties on the given characteristics of cement was shown. The peculiarities of phase formation during firing and the properties of the binding material were revealed.

Introduction

The chemical and mineralogical composition of raw materials and raw material mixtures is an important factor in the structure formation and determination of the properties of silicate materials. This corresponds to the position of modern materials science about the relationship composition → structure → properties. Cement production is traditionally based on the use of natural carbonate and clay raw materials for the production of clinker. The mixture of these components should ensure the presence of a certain amount of calcium, silicon, aluminum and iron oxides, the combination of which, when fired at a maximum temperature of 1400 °C, forms clinker crystalline phases C_2S, C_3S, C_3A, C_4AF, which determine the properties of cement. The high energy intensity of Portland cement determines its market value with a corresponding increase in the cost of materials and structures using such a binder. This increases the expediency of manufacturing a binding material similar to natural or Roman cement. The production technology of such mineral binders requires significantly lower energy consumption, but even with limited quality, it can find practical use [1-9] while simultaneously solving the issues of production efficiency and resource saving.

Constant attention is paid to the analysis of the composition and properties of cement raw materials. However, the known research and development concern primarily varieties of carbonate raw materials, which is connected with its predominant content in the composition of the starting mixtures. At the same time, solving the problems of optimizing the composition of raw materials for cement production requires a deepening of scientific ideas about the influence of the chemical and mineralogical composition of the clay component on the phase formation and properties of the material, in the direction of which the presented work was carried out.

Results and Discussion

The objects of the study were raw material mixtures for the production of mineral binding material based on binary systems of limestone - a clay component of different chemical and mineralogical composition. At the same time, two polymineral clays were used - spondylova clay and kryvinska clay and unenriched kaolin KSSK (Table 1). On the basis of computer calculations using the program "RomanCem" [10], it was established that in the specified HM interval, the necessary quantitative ratios of the components of binary limestone-clay systems depend significantly on the type of the latter, while there is an inverse relationship between the content of the clay component and the number of the hydraulic module proportional dependence (Figure 1). When using KSSK kaolin, its required content is 22.4-32.0wt.%, kryvinska clay - 24.3-34.7wt.%, spondylova clay - 31.4-44.8wt.%. The use of spondyljva clay significantly reduces the required amount of carbonate raw material - limestone.

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
limestone	3,13	0,06	1,05	-	52,82	0,52	0,10	-	-	42,32
spondylova	53,62	8,87	3,26	0,10	14,60	2,00	1,26	0,29	2,36	13,72
kryvynska	60,96	15,66	5,57	0,79	3,33	2,04	0,16	0,30	2,70	8,48
KSSK	69,48	19,27	0,32	0,33	0,31	0,65	0,17	0,60	3,54	5,25

The differences in the chemical and mineralogical composition of the binary mixtures correspond to the indicated changes in the types and quantitative ratio of the components. As for the mineralogical composition (Table 2), mixtures with spondyl clay compared to Krivina clay with the same calcite content differ by a lower content of kaolinite, montmorillonite, feldspar, iron hydroxides and rutile with a higher amount of hydromica and quartz. Mixtures with KSSK kaolin differ from mixtures with the specified clays by a significantly higher content of kaolinite and feldspar, the absence of montmorillonite inclusions, small admixtures of hydromica, iron hydroxides, and rutile. Based on the calculations and analysis, the following compositions of binary mixtures based on limestone with various types of clay component were selected for further research (Table 3). The analysis of the studied mixtures based on limestone with varieties of clay component showed differences in their phase composition after firing (Figures 2-4).

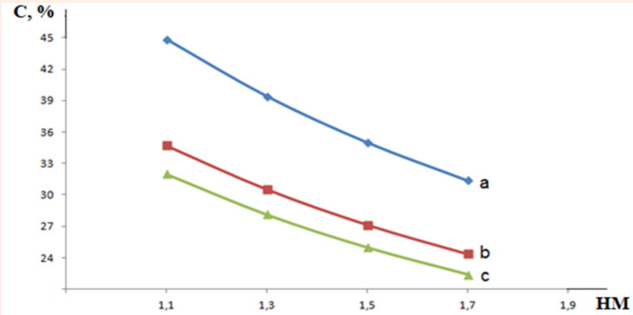

Figure 1: Dependence of the content of spondylova clay (a), kryvinska clay (b), KSSK kaolin (c) in binary system based on limestone on the hydraulic module HM.

Table 2: Mineralogical composition of binary mixtures with varieties.

Clay component	Mineral Content, %							
	Calcite	Kaolinite	Hydro-Mica	Montmorillonite	Quartz	Feldspar	Iron hydroxide	Rutile
spondylova clay	62,3-71,4	0,9-1,3	5,5-7,9	6,3-9,0	13,2-15,2	0,8-1,1	1,9-2,2	0,03-0,04
kryvynska clay	62,3-71,2	2,4-3,4	2,7-3,8	7,4-10,4	9,1-11,5	2,6-3,7	2,4-2,9	0,17-0,24
kaolin KSSK	63,3-72,1	8,5-12,1	0,4-0,5	-	11,0-14,3	4,5-6,4	0,9-1,0	0,07-0,08

Table 3: Composition of raw mixtures.

Code of Mixture	Quantity of Components, Mass %			
	Limestone	Spondylova Clay	Kryvynska Clay	KSSK Kaolin
9-1	55,0	45	-	-
8-1	65,5	-	34,5	-
7-1	68,0	-	-	32,0

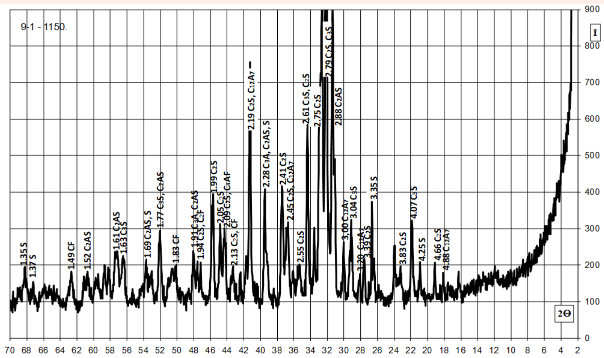

Figure 2: X-ray diffraction of sample 9-1 (1150 °C).

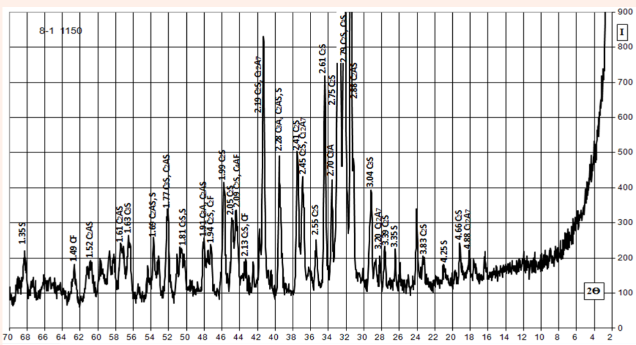

Figure 3: X-ray diffraction of sample 8-1 (1150 °C).

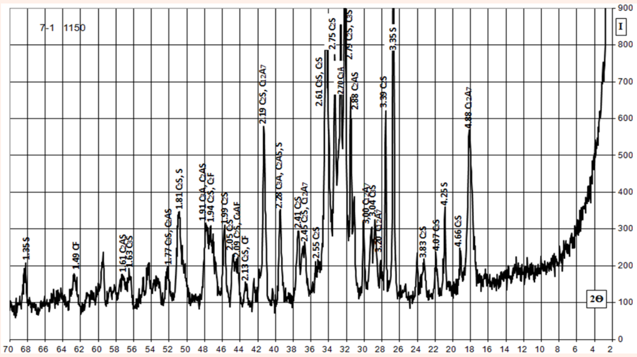

Figure 4: X-ray diffraction of sample 7-1 (1150 °C).

According to the results of X-ray phase analysis, differences in structural transformations during firing of the studied mixtures were revealed. Thus, the ratio of the intensities of the characteristic reflexes indicates that after firing at 1150 °C, the material of mixture 9-1 with spondyl clay and 8-1 with krivin clay is distinguished by a significantly greater development of the C_2AS crystalline phase of helenite. The material of sample 7-1 with KSSK kaolin, with a relatively lower C_2AS development compared to the specified samples with clays, is characterized by a higher content of C_3A, $C_{12}A_7$ and quartz phases. Regarding the formation of calcium silicates, with a significant overall excess of the C_2S phase over C_3S, the material of samples 8-1 and 7-1 is characterized by a relatively higher content of C_2S than in sample 9-1. Testing of the technological properties of the solution using the obtained binding material showed that, according to the classification of DSTU B V.27-91-99 [11], the samples belong to the group with reduced strength (10-30 MPa), which is typical for natural or Roman cement , and according to the speed of hardening - to normal hardening (Initial setting from 45 min. to 2 h.), which is typical for Portland cement (Table 4).

Table 4: Properties of mineral astringent material.

Characteristics	Sample Code		
	9-1	8-1	7-1
Finess of grinding, sieve residue no. 008, mass. %	7	7	7
Consistency, %	33	31	30
Initial setting time, min	70	50	45
Final setting time, min	130	90	85
Compressive strength, MPa			
2 days	3,9	4,3	2,8
7 days	14,8	15,7	12,6
28 days	26,7	29,2	22,4

Conclusion

a. The chemical and mineralogical composition of clay raw materials as one of the main components of the starting mixtures for the production of mineral binders is an important factor influencing the physical and chemical processes during their heat treatment and the final properties of the material.

b. It has been established that the use of varieties of polymineral clays and kaolin in limestone-based systems allows obtaining at a maximum firing temperature of 1150 °C normal-hardening binding materials with a strength of 22-29 MPa compared to slow-hardening cement-type materials with a strength of 10-20 MPa. At the same time, it is possible to vary the hardening terms when changing the type of clay component.

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