Journal of Multidisciplinary Engineering Science and Technology (JMEST)
ISSN: 2458-9403
Vol. 8 Issue 8, August - 2021

Cement Clinker From New Mixture Raw Material

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***Abstract*— The possibility of cement clinker manufacturing by the integrated use of natural raw materials of volcanic origin and heat energy wastes has been studied. The analysis of the dependence of the composition of the raw mixture based on the system chalk - perlite - fly ash on the specified characteristics of cement using the developed computer program "Clinker" has been carried out. The composition of the initial mixture for the manufacturing of cement clinker was determined with a quantitative ratio of perlite : fly ash = 1.5. The features of the formation of the phase composition and properties of the binder during the firing of the raw mixture in the range of maximum temperatures 1200 - 1400 0C are shown.**

Keywords— cement, mixture raw material, composition, firing, phases crystalline, properties.

I. INTRODUCTION (

The expansion and increase in efficiency of production of silicate materials is associated with the integrated use of raw materials of natural and technogenic origin [1-4]. The practical solution of such problems requires the corresponding development of the scientific and technical foundations of chemical technology of silicates - the determination of patterns regarding the influence of concentration of raw materials on structure formation and properties of the materials. In the direction of solving the problem of expanding the raw material base for the production of mineral binders, this work has been done.

Rocks of volcanic origin are one of the sources of natural silicate raw materials [5-8].

Among the rocks of volcanic origin, perlite occupies a significant place in terms of distribution and reserves. Based on the peculiarities of the structure and attitude to heat treatment, the main direction of using this material was the manufacture of expanded perlite, which is used in construction and agriculture [9].

At the same time, increasing the efficiency of the existing open-pit mines requires expanding the areas of practical application of perlite. One of these promising areas can be the mass-intensive production of ceramics [10-12]and cements [13].

Waste from other industries is used in the production of cement and concrete [8; 14]. Thus, waste heat - fly ash is used as a mineral additive in the composition of composite cements and concretes [15-17]. However, the amount of practical use of multi-tonnage waste of thermal power is much lower than the volume of their accumulation. Based on this increase in the use of fly ash as man-made raw materials in resource-intensive cement production remains an urgent task of comprehensively addressing the issues of chemical technology of silicates and environmental protection.

Formulation of the problem. The results of the analysis of known data lead to the conclusion about the relevance and feasibility of scientific and technical solutions for the development of new compositions of mixtures with the integrated use of natural and man-made raw materials for the manufacture of cement clinker.

II. EXPERIMENTAL PART

The object of the study were raw material mixtures for the manufacturing of cement clinker based on the chalk - perlite - fly ash system.

The raw material 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 technology of cement industry.

Samples of raw material mixtures have been burned in an oven during 15 hours on maximum temperature 1200-1400 °C keeping a hold at a maximum of 1.5 hours. All samples of the mixtures that have been compared were burned together to exclude the possibility of a difference in the degree of heat treatment.

Methods of physical - chemical analysis of silicate raw materials and of 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 DRON-3M diffractometer (CuKα 1-2 radiation, voltage 40 kV, current 20 mA, speed 2 degrees / min);

- determination of indicators of cement properties in accordance with current standards.

To determine the rational composition of the initial mixture varieties of raw materials were used:

- chalk of Zdolbuniv deposit of Rivne region;

- perlite of the Beregovo deposit of the Transcarpathia region;

- fly ash of Burshtyn Thermal Power Station in Ivano-Frankivsk region.

Samples of raw materials differ significantly in genesis and composition.

Chalk and perlite are natural raw materials of sedimentary and volcanic origin, respectively, fly ash is a man-made raw material - waste of heat energy.

The chemical composition of the chalk sample is characterized by a predominant CaO content (55.0 wt.%), perlite sample - a high content of SiO2 (72.1 wt.%) by the quantitative ratio of SiO2:Al2O3 = 5.6 and a significant amount of alkaline oxides Na2O + K2O = 8.1 wt. % (Tab. 1). The sample of fly ash has higher content of Fe2O3 22.2 wt. %) and Al2O3 with a quantitative ratio of SiO2:Al2O3 = 2.6.

TABLE I. CHEMICAL COMPOSITION OF RAW MATERIALS

Samples	chalk	perlite	fly ash
SiO_2	0.77	72.08	46.12
Al_2O_3	0.25	12.92	18.00
Fe_2O_3	0.13	1.50	22.17
TiO_2	-	0.90	1.78
CaO	55.0	0.88	4.03
MgO	0.25	0.63	1.46
SO_3	0.08	-	0.21
Na_2O	-	3.76	-
K_2O	-	4.33	2.10
LOI	43.49	3.0	1.49

The mineralogical composition of the chalk is characterized by a predominant content of calcite; perlite – by a developed glass phase with crystalline inclusions of quartz and feldspar; fly ash is marked by the presence of glass phase and crystalline phases, mainly - quartz, mullite (Fig. 1; 2).

Calculations and analysis of the composition of raw materials for the manufacturing of cement clinker have been performed using the computer program "Clinker" [18] according to known recommendations for numerical values of the saturation coefficient of SF, silica n and alumina p modules.

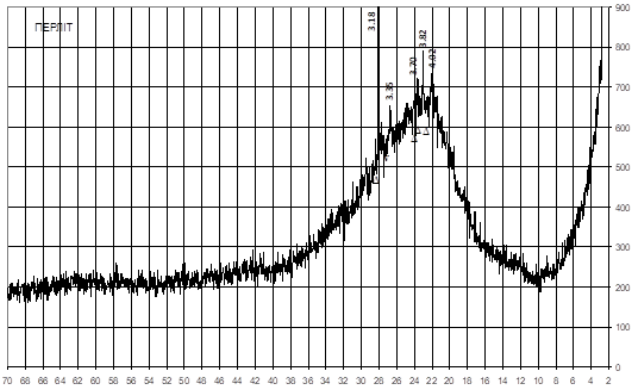

Fig. 1. X-ray diffraction of Transcarpathian perlite:v- β-quartz, Δ - feldspar

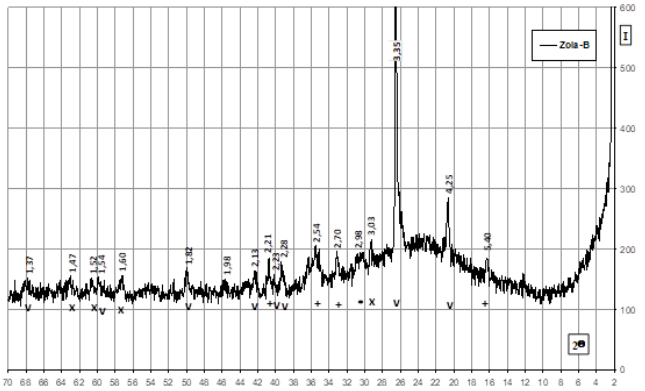

Fig. 2. X-ray diffraction of fly ash: v- β-quartz, + - mullite, x – calcite

The analysis of the obtained results has shown that in the recommended range of SF the possible concentration of perlite in the composition of the raw material mixtures significantly depends on the varieties and the quantitative ratio of other components.

According to the results of computer calculations in binary mixtures based on limestone at the recommended number of saturation coefficient SF = 0.90, the possible content of perlite is about 17 wt. %, and fly ash - about 22 wt. %, however, the numbers of silica modulus do not correspond to n = 1.9 - 3.0, recommended for Portland cement clinker (Table 2).

TABLE 2. COMPOSITION OF BINARY MIXTURES AND CHARACTERISTICS OF CLINKER

System		chalk - perlite	chalk - fly ash
Composition of initial mixture, wt. %	chalk	80.88	78.25
	perlite	19.12	-
	fly ash	-	21.75
Clinker characteristics	SF	0.90	0.90
	n	4.70	1.29
	p	6.79	0.71

When using 3-component mixtures based on the system of chalk - perlite – fly ash in the range of values of SF = 0.80-0.95 and n = 2.0 - 3.5, the possible content of perlite is from 9.2 to 17.9 wt.%, fly ash - from 3.3 to 13.4 wt.% (Fig. 3). In the range of

concentrations of perlite Cp = 9.5-14.8 wt.% clinker at SF = 0.90 corresponds to the recommended values of the numbers of silica (n = 2.0-3.0) and alumina (p = 1.2-2.0) modules (Fig. 4).

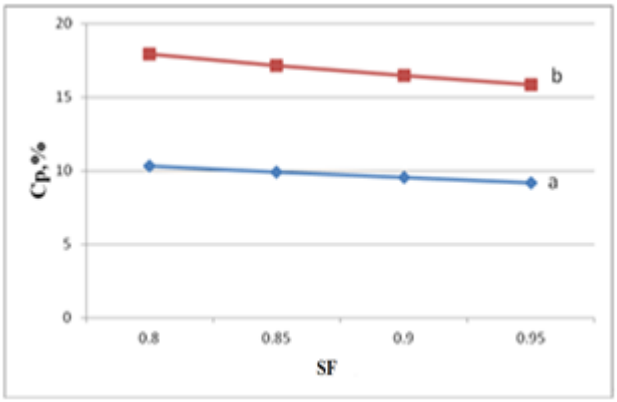

Fig. 3. The dependence of perlite content (Cp) in the mixture on basis of chalk – fly ash system from saturation factor SF of clinker at silica modulesn=2.0 (a) and n=3.5 (b)

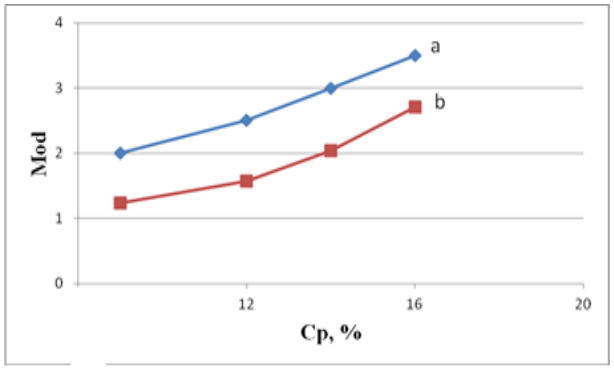

Fig. 4. The dependence of silica (a) and alumina (b) modules at SF = 0.90 from perlite content (Cp) in the mixture on basis of chalk – fly ash system

The raw material mixture 09-2 was chosen for the study, which is characterized by the quantitative ratio perlite: fly ash = 1.5 (Tab. 3), and the chemical composition - the ratios SiO2:Al2O3 = 4.1, CaO:SiO2 = 3, CaO:Al2O3 = 12.2 with an iron oxide content of 2.3% (Tab. 4).

TABLE 3. COMPOSITION OF RAW MIXTURES

Code of mixture	Quantity of components, mass. %		
	chalk	perlite	fly ash
09-2	79.0	12.6	8.4

TABLE 4. CHEMICAL COMPOSITION OF RAW MIXTURES

	Code of mixture	
	09-2	
Oxides content, %	**SiO_2**	14.76
	Al_2O_3	3.61
	Fe_2O_3	2.30
	CaO	43.93
	MgO	0.42
	SO_3	0.08
	LOI	34.90

The specified quantitative ratio of components and chemical composition correspond to the following design characteristics of cement clinker (Tab. 5).

TABLE 5. DESIGN CHARACTERISTICS OF CLINKER

Code of sample		09-2
Crystalline phases content, %	**C_3S**	57.64
	C_2S	18.64
	C_3A	8.72
	C_4AF	10.73
Clinker characteristics	**SF**	0.90
	n	2.50
	p	1.57

X-ray phase analysis of sample 09-2 allowed us to investigate the process of clinker phase formation in the range of maximum firing temperatures 1200 - 1400 0C (Figs. 5; 6).

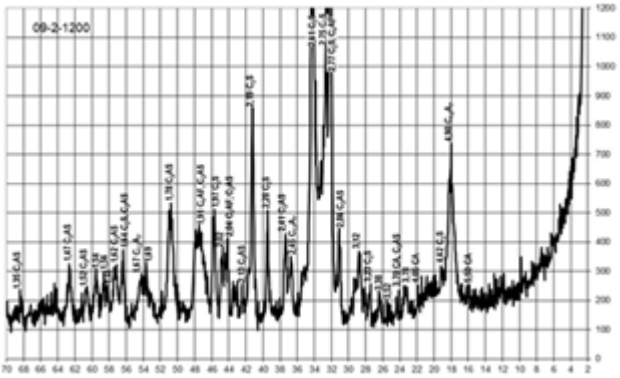

Fig. 5. X-ray diffraction of sample 09-2 (1200 ºC)

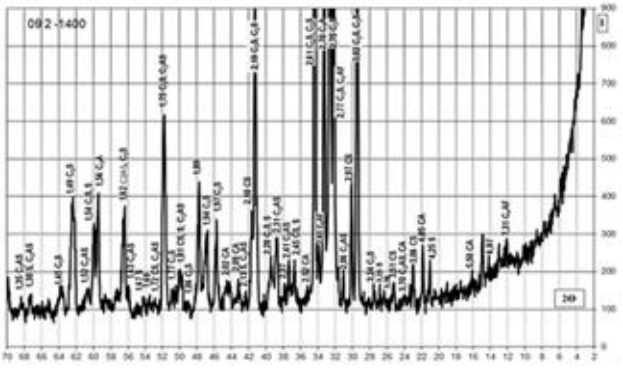

Fig. 6. X-ray diffraction of sample 09-2 (1400 ºC)

It is established that with increasing the maximum firing temperature from 1200 to 1400 0C the material differs:

• for crystalline phases of calcium silicates - formation of C_3S (1.45; 1.49; 1.86; 2.19; 3.02 Å) and wollastonite CS (2.97 Å);

• relative to the crystalline phases of calcium aluminosilicates - much less formation of C_2AS gelenite (2.86; 2.41; 2.13 Å);

• with respect to the crystalline phases of calcium aluminates - significant formation of C_3A (2.70 Å); when minimizing the amount of mayonite $C_{12}A_7$ (4.90 Å);

• with respect to iron-containing crystalline phases - by intensification of C_4AF formation (2.63Å).

According to the classification of DSTU B V.27-91-99 on the rate of hardening after firing at a maximum temperature of 1200 ºC sample 09-2 belongs to the group of ultra-fast-setting (initial time up to 15 min.). The characteristic representatives of which are expansion and stress cement (tab. 6).

TABLE 6. PROPERTIES OF MINERAL ASTRINGENT MATERIAL

Properties	Maximum firing temperature, ºC	
	1200	1400
Finess of grinding, sieve residue no. 008, mass. %	10	10
Initial setting time, min	5	90
Final setting time, min	35	150
Compressive strength (28 days), MPa	27.4	39.2

After firing to a maximum temperature of 1400 ºC sample 09-2 belong to the group of normalizing (starting time from 45 minutes to 2 hours), the typical representatives of which are Portland cement and slag Portland cement.

III. CONCLUSIONS

1. Expansion of the raw material base for production of cement with the use of perlite and waste of heat energy contributes to comprehensive solution of the problems of resource saving and chemical technology of silicates.

2. The possible content of Transcarpathian perlite in composition of raw materials for the manufacturing of cement clinker on basis of chalk – perlite – fly ash system is 9.5 - 16.5 wt.%.

3. According to X-ray phase analysis and technological testing, the possibility of the degree of development of glass phase and crystalline phases, the quantitative ratio of clinker minerals and binder properties of material from maximum firing temperature of clinker has been determined.

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