PRODUCTION OF PORTLAND CEMENT CLINKER IN RAW MIXTURES BASED ON MINING AND METALLURGICAL PRODUCTION WASTES

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ABSTRACT

The chemical-analytical and physico-chemical properties of flotation waste generated during the enrichment of lead-zinc ores of the Almalyk MMC, steelmaking slags of Uzmetkombinat JSC, formed after the extraction of residual ferrous compounds and limestones of the Shavazsay deposit for the purpose of polishing Portland cement clinker on their basis, have been studied. As a result of experiments, a real possibility was established of obtaining Portland cement clinker of optimal mineralogical composition based on the studied waste, used as the main component in raw mixtures, under optimal firing temperature conditions.

Keywords: Portland cement, utilization waste, industrial waste, crystal structure, X-ray phase analysis, mineralogical composition, phase.

INTRODUCTION

Currently, comprehensive scientific research and practical work on the processing of technogenic waste accumulated in the dumps of mining [1, 2], metallurgical [3, 4], thermal power [5], chemical [6 - 8] and several other industries is being intensively carried out around the world. Comprehensive scientific research devoted to the development of technologies for the production of Portland cement using natural mineral raw materials and secondary resources, the study of the composition, structure and properties of building materials using natural resources and industrial waste as an alternative in order to reduce the sintering temperature of raw material mixtures, improve their physical and mechanical properties and technological properties are carried out in leading scientific institutions and higher educational institutions of the world.

It is known that in the building materials industry, a significant part of its volume is made up of cementitious materials, particularly Portland cement, the production of which requires a large number of raw materials and energy costs. In the production of Portland cement, energy costs (electricity, fuel) reach 60 % of the total costs spent to obtain the final product [9]. Therefore, the use of alternative and non-traditional raw fuel components always remains a pressing issue.

It should be noted that the main technological and physical-mechanical characteristics of Portland cement are largely determined by the properties of the initial components of the raw material compositions.

Expanding the raw material base of the construction industry, developing building materials based on non-traditional materials and waste from metallurgical production [10, 11], instead of natural ones, today remains an urgent and pressing task posed to researchers working in this area.

Comprehensive studies of technogenic materials from various industries to produce cement clinker show that the use of blast furnace and copper smelting slags promotes the formation of clinker minerals at lower temperatures, which significantly reduces the consumption of electricity and natural raw materials for clinker firing and helps improve the ecological state of the environment [12].

In this regard, to save natural raw materials and find alternative sources for their replacement, recycling waste from various industries by involving silicate materials in the production, we have conducted research on the use of flotation waste from the enrichment of lead-zinc ores (FWLZ), as well as processed steelmaking slag JSC "Uzmetkombinat" in the production of Portland cement clinker.

EXPERIMENTAL

Materials

To carry out the research, we used flotation waste generated during the enrichment of lead-zinc ores, steelmaking slags of Uzmetkombinat JSC, formed after the extraction of residual ferrous compounds and limestones of the Shavazsay deposit (Table 1).

Methods

To identify the phase composition of the components used and the obtained samples, X-ray phase analysis was used on a LABX XRD-6100 SHIMADZU diffractometer using CuKα radiation (β-filter-Ni, wavelength 1.5418 Å, current mode and tube voltage 30 mA, 30 kW). The constant rotation speed of the detector was 4 º/min with a step of 0.02º (ω/2θ – coupling), the scanning angle varied from 4 to 80°. In the calculations and in the identification of the phases, the international directories of X-ray powder patterns ICDD PDF-2 2007 were used.

RESULTS AND DISCUSSION

As can be seen in Table 1 from the material composition of the components in terms of the content of oxides necessary for the formation of the mineralogical composition of Portland cement clinker, all the given components meet the requirements of generally accepted standards.

Flotation waste from the enrichment of lead-containing ores (FWLZ) of the Almalyk Mining and Metallurgical Plant is formed during the flotation enrichment of rocks containing lead and zinc compounds. It is known that more than 90 % of the waste rock from the total mass of ore, after flotation processing, is pumped into dumps. The main chemical compounds that make up the FWLZ are silica 44.98 - 47.58 %, alumina 9.22 - 9.88 %, iron oxide 4.66 - 6.82 %, calcite 14.56 - 16.32 % etc. (Table 1).

In terms of its material composition, FWLZ is close to the composition of loess clays used in the production of Portland cement. Determination of the fractional composition using the sieve analysis method showed that it mainly consists of grains of quartz, calcite, and clay minerals with particle sizes of 0.1 - 0.01 mm.

On the X-ray diffraction patterns of samples of the Shavazsay limestone sample (Fig. 1), mainly diffraction maxima are observed, related to the calcite mineral d = 0.383, 0.303; 0.284, 0.248, 0.227, 0.208, 0.190, 0.187, 0.162, 0.160, 0.152, 0.151, 0.144, 0.142 nm, as well as lines with low intensity, are attributed to β-quartz impurities.

The X-ray pattern (Fig. 2) of FWLZ records the

Table 1. Chemical composition of samples.

Samples	№	Mass content of oxides, %							LOI,	Total,
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O	%	%
FWLZ	1	47.58	9.22	4.66	15.88	7.81	3.22	2.54	7.89	98.80
	2	46.23	9.88	5.44	14.56	6.39	2.12	2.23	9.52	96.37
	3	44.98	9.75	6.82	16.32	6.88	2.41	2.14	9.78	99.08
Slag "Uzmetkombinat"	1	27.81	7.25	20.29	31.16	8.10	1.26	1.13	1.50	98.50
	2	26.74	7.09	21.02	31.87	7.95	0.97	1.07	0.61	97.32
	3	27.18	7.11	20.35	30.96	8.12	1.05	1.03	1.12	96.92
Shavazsay limestone	1	1.53	0.63	0.10	54.3	0.31	0.14	0.15	42.50	99.66
	2	1.72	0.53	0.11	54.42	0.43	0.11	0.13	41.02	98.47
	3	1.42	0.60	0.09	53.98	0.35	0.12	0.10	42.38	99.04

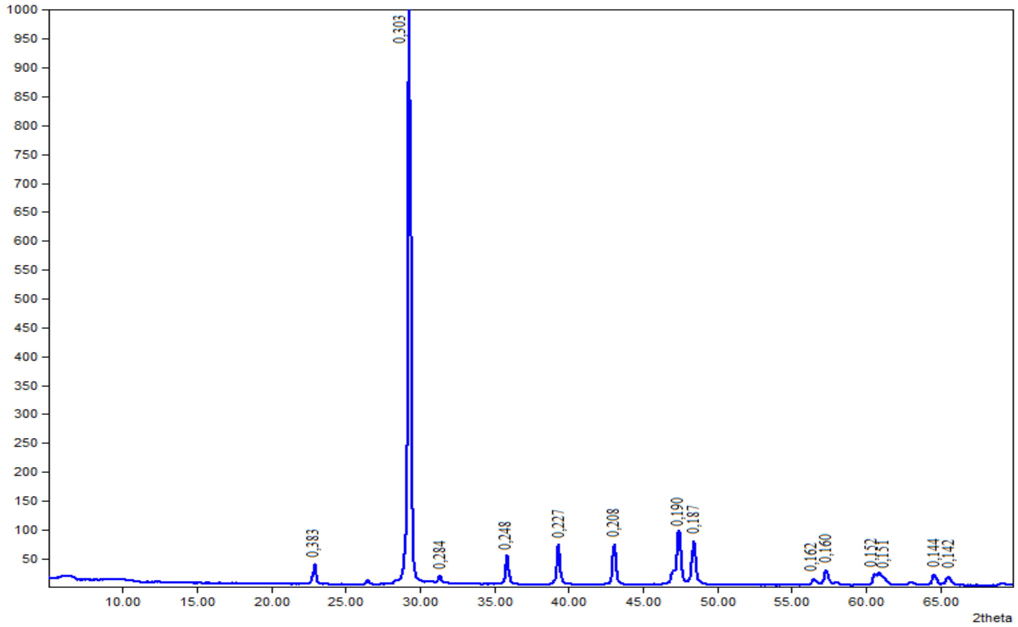

Fig. 1. X-ray diffraction pattern of Shavazsay limestone.

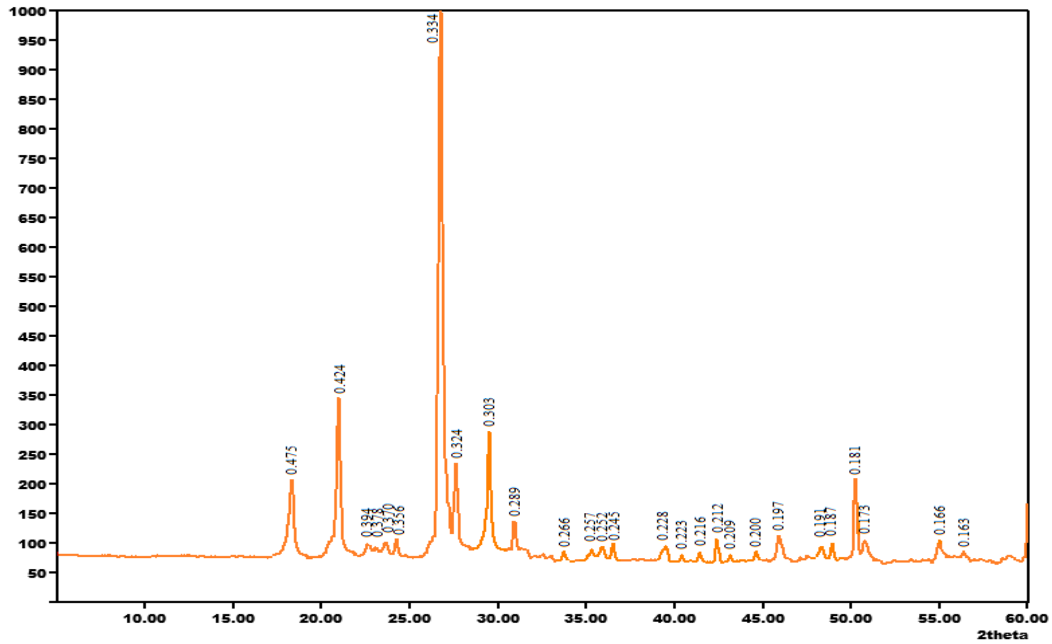

Fig. 2. X-ray diffraction pattern of FWLZ.

maximum interplanar distances inherent in quartz d = 0.424; 0.334; 0.245; 0.228; 0.223; 0.181; 0.166 nm, maxima inherent in calcium carbonate d = 0.303; 0.197; 0.187; 0.163 nm, as well as clay minerals hydromica and feldspars with d = 0.475; 0.394; 0.324; 0.257; 0.252; 0.191 nm.

Iron-containing slag is formed during metal smelting in converter furnaces of Uzmetkombinat JSC and accumulates in dumps. Currently, the company is engaged in extracting residual amounts of iron from dump slag. We used slag after extraction of iron with a residual content of iron oxide (Fe_2O_3) of up to 20 - 21 % (Table 1). The results of X-ray phase analysis of slag (Fig. 3) of Uzmetkombinat JSC showed the presence of diffraction reflections corresponding to minerals, gehlenite (d = 0.423, 0.302, 0.284, 0.272, 0.212, 0.203, 0.197, 0.181, 0.137 nm); hematite (d = 0.268, 0.222, 0.187 nm) and quartz (d = 0.334, 0.245, 0.227, 0.197 nm).

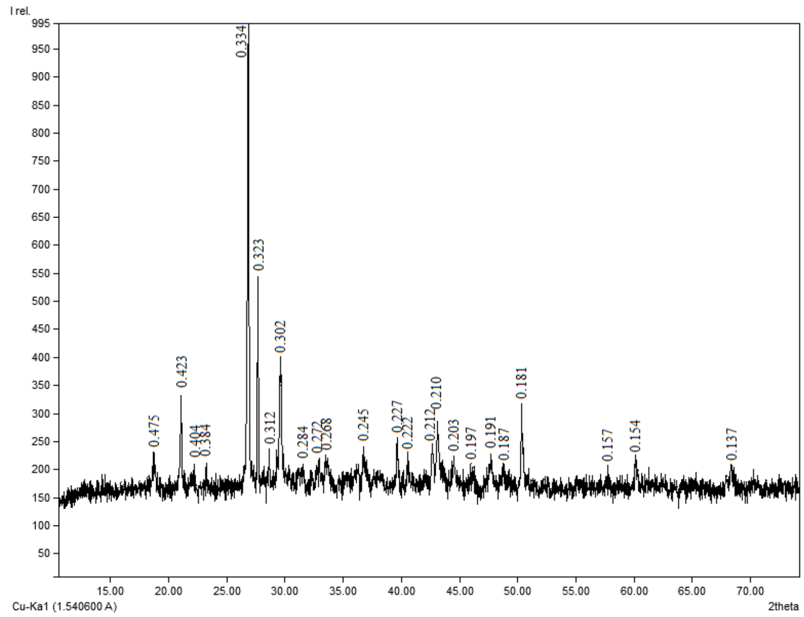

Fig. 3. X-ray diffraction pattern of slag “Uzmetkombinat”.

As a result of several experimental studies of compositions consisting of $CaCO_3$ FWLZ - slag “Uzmetkombinat”, reliable information was obtained on phase transformations, reactions of silicate, aluminate and ferrite components in the solid state at various ratios and temperatures. Using the results obtained, the raw material compositions for the production of Portland cement clinker were calculated.

To calculate the raw material composition of cement clinker, we set different values of the silicate modulus, which for many cement plants is accepted from 1.8 to 2.5. The value of the saturation coefficient (SC), which determines 1the saturation of silica with calcium oxide, is also used for the calculation [13, 14]. When compiling the Portland cement raw mix, we adopted SC = 0.85 in composition No. 1 and SC = 0.91 in composition No. 2, and the silicate modulus is the same in both compositions n = 2.1.

To obtain clinker, the prepared raw mix compositions were ground to the required fineness, sifting through sieve No. 008. Upon reaching the required fineness, the mixtures were moistened with water to moisture content at which molding of cylindrical samples on a metal mold with a diameter of 3 mm and a height of 10 mm was possible. The molded samples were dried at room temperature of 25 - 30°C for 24 h and fired in a furnace at a temperature of 1350 - 1450°C.

The chemical and mineralogical characteristics of laboratory experimental clinkers were studied by X-ray diffraction and chemical analytical methods. A study of the assimilation of CaO in burnt clinker showed that the complete assimilation of CaO in prepared raw mixtures occurs in the temperature range of 1380 - 1400°C when held for 30 min. Based on the obtained results, the mineralogical composition of the obtained clinkers was calculated using the generally accepted method. The calculations showed that the content in mass % of the main minerals of Portland cement clinker: tricalcium silicate C3S is 62.01 and 63.21, dicalcium silicate C2S 16.27 and 16.36, tricalcium aluminate C3A 3.48 and 3.51, and tetracalcium aluminoferrite C4AF 16.2 and 16.81. The results showed that the actual mineralogical composition of the obtained clinkers differs slightly from the calculated composition.

X-ray phase analysis (Fig. 4.) of the studied samples showed that in the synthesized clinkers there are lines corresponding to well-crystallized alite minerals d = 0.303; 0.276; 0.265; 0.259; 0.218 nm, belite d = 0.280; 0.265 nm, as well as tricalcium aluminate C_3A with d = 0.191; 0.174; 0.142 nm.

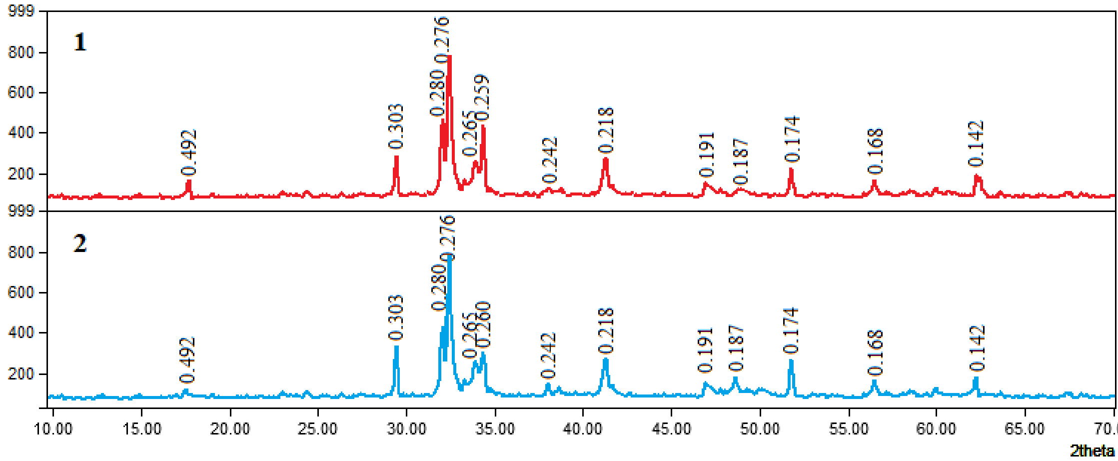

Fig. 4. X-ray diffraction patterns of clinkers based on flotation waste at n = 2.1: 1) FWLZ with SC = 0.85; 2) FWLZ with SC = 0.91.

Fig. 5. Microphotography of synthesized clinker.

Petrographic analysis revealed that (Fig. 5) the amount of alite phase content is greater in raw mixtures with CS = 0.91, and the predominance of the belite phase is observed in clinker with CS = 0.85. Clinker with CS = 0.91 based on FWLZ shows that the alite phases are in a state of complete crystallization. The content of the main clinker minerals C_3S, C_2S, C_3A and C_4AF are within acceptable regulatory limits. The sizes of alite range from 5 to 40 μm, belite from 5 to 30 μm. The minerals have a regular shape, the intermediate phase has needle-shaped and prismatic inclusions.

CONCLUSIONS

Thus, a real possibility has been established of obtaining clinkers of optimal mineralogical and crystalline composition based on the studied waste from the enrichment of lead-containing ores from mining and metallurgical production and metallurgical slag as the main component in raw mixtures, under optimal firing conditions and temperatures.

Authors' contributions: *K.U.: Calculation of raw mixes for obtaining clinker, discussion of the results of physical and chemical studies; Z. K.: Discussion of the results of physical and chemical studies; S.N.: Preparation of raw mixtures for obtaining clinker, X-ray phase and microscopic examination of the obtained samples; F.K.: Firing of prepared raw materials and study of the mineralogical composition of clinker; J.N.: Grinding and preparation of calculated raw material compositions, molding of samples for firing.*

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