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USE OF ILMENITE ORE ENRICHMENT WASTES IN THE PRODUCTION OF PORTLAND CEMENT CLINKER

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We presented the results of the research on the influence of d-elements of ilmenite ore beneficiation wastes of the Vilnohirsk Mining and Metallurgical Plant on the structure and properties of Portland cement clinker minerals, firing properties and their hydraulic activity. It was established that the use of the enrichment wastes as an aluminosilicate component of the raw material mixture for clinker firing contributes to the reduction of the consumption of blast furnace granulated slag, simultaneously increasing the consumption of limestone. The presence of compounds of d-elements contained in the wastes of enrichment of ilmenite ore in the proposed raw material mixture for obtaining Portland cement clinker increases the saturation coefficient up to 99% and improves the processes of decarbonization and sintering during clinker firing. The physical-mechanical characteristics of the developed cements, in particular the compressive strength limit indicators, are not inferior to those produced according to the classical formulation. Cements obtained on the basis of clinkers, according to their properties, correspond to type II cements (state standard DSTU B.V. 2.7-46:2010). Partial replacement of the clay component in the raw material mixture by ilmenite ore enrichment wastes allows significantly expanding the raw material base for the production of Portland cement clinker and effectively influencing the technological process of firing.

Keywords: industrial secondary products, Portland cement clinker, firing, hydraulic activity, efficient use.

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Introduction

Regulation of the physical and chemical processes of structure formation and improvement of the properties of binders can be carried out through scientifically based modification with various substances that contain compounds of s-, p-, and d-elements, which are typical of natural materials, as well as of mineral dispersed systems of man-made origin (secondary products of industry). The trends observed both in the world and in domestic practice determine the expansion of the raw material base due to the use of secondary products of industry, which allows reducing the energy intensity of technological processes and the consumption of products and improving the environmental condition [1–3]. Such materials include multi-ton waste from the Vilnohirsk Mining and Metallurgical Plant, a part of the JSC «United Mining and Chemical Company», which is one of the largest producers of titanium raw materials worldwide. The use of such wastes in raw material mixtures for preparation of Portland cement clinker is relevant and has scientific and practical significance.

Industrial secondary products contain compounds of s-, p-, and d-elements. The specified compounds are based on the elements of periodic table and combined into the following blocks: s-elements (Na, K, Ca and Mg); p-elements (Al and Si); and d-elements (Fe, Mn, Ti, Co and Cr). Among the compounds of s-elements, the most interesting are CaO, MgO, Na_2O and K_2O. According to the sequence of energy levels, they can be divided into

3s (Na and Mg) and 4s (K and Ca), respectively. Their ionization energies are as follows: Na 498 eV, Mg 736 eV, K 418 eV, and Ca 590 eV. Their electronegativity are as follows: Na 0.93, K 0.82, Ca 1.00, and Mg 1.33 [4]. The cations in order of decreasing ability to replace each other are located in the following way: Mg, Ca, K, Na.

CaO and MgO oxides are included in the group of carbonate and sulfate rocks of the earth's crust, which are used to obtain binders; elements K and Na form compounds that affect the hydration processes of mineral binders [5–7].

Al_2O_3 and SiO_2 are important compounds of p-elements; they are the main components of Portland cement clinker. Compounds of d-elements are also interesting. These ones include compounds of iron, manganese, titanium, zirconium, hafnium, etc. Thus, d-element (Fe) and p-element (Al) in the clinker melt, due to amphotericity and depending on the conditions, exist in the form of complexes with quaternary $[MeO_4]^{5-}$ or hexadecimal $[MeO_6]^{6-}$ coordination. They show acidic properties in quaternary coordination, and basic properties in hexadecimal coordination [8].

Compounds of d-elements are reducing agents. Cr_2O_3, Mg_2O_3, TiO_2, and Fe_2O_3 are mineralizers and accelerate solid phase reactions. They contribute to the formation of a regulated structure of fired materials.

The indicated compounds of s-, p-, and d-elements are contained in various production wastes, including wastes from the beneficiation of ilmenite ore at the Vilnohirsk Mining and Metallurgical Plant.

Experimental, results and discussion

In this work, we studied the effect of d-elements of ilmenite ore beneficiation wastes from the Vilnohirsk Mining and Metallurgical Plant on the structure and properties of Portland cement clinker minerals, firing properties and their hydraulic activity.

Ilmenite ore beneficiation wastes are a highly dispersed light brown powder. X-ray phase and complex thermal analyzes showed the presence of such minerals as montmorillonite, kaolinite, quartz, feldspars, iron-containing minerals, titanium-containing minerals, and carbonates. The chemical composition is represented by such oxides as SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, etc.

One of the minerals in Portland cement clinker is dicalcium silicate (C_2S), which determines the most important properties of Portland cement. With moderate cooling, β-C_2S turns into γ-C_2S, which leads to a decrease in hydraulic activity, and the preservation of β-, α'-, α-modification of C_2S can be carried out at the expense of various stabilization additives or special technologies.

The introduction into the composition of the raw material mixture of mineral dispersion systems of technogenic origin, which have d-elements (Fe^{2+}, Mn^{2+}) that are isomorphically replacing Ca^{2+}, allows stabilizing high-temperature modifications of $2CaO{\cdot}SiO_2$.

Impurities that create isomorphic solid solutions of embodiment cause a significant increase in the entropy of $2CaO{\cdot}SiO_2$. This is explained by the fact that V^{5+}, Cr^{6+}, and Mn^{6+} ions are significantly different from Ca^{2+} and Si^{4+} ions and cannot replace them equally in the C_2S structure. They have low solubility and stabilize the metastable β-$2CaO{\cdot}SiO_2$ modification. In the investigations, the effect of d-elements on the content of $3CaO{\cdot}SiO_2$, aluminosilicate and aluminoferrite phases was considered.

Materials whose chemical composition is

Table 1

Chemical composition of materials used

Material	Chemical composition, wt.%						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	WFP
limestone	4.00	1.32	0.95	52.08	2.05	–	39.15
blast furnace granulated slag	39.37	6.92	0.50	47.68	5.92	0.21	–
staurolite concentrate	32.03	49.18	15.39	1.49	1.19	0.73	–
stove dust	9.82	0.58	59.05	8.63	1.09	1.42	19.41

Table 2

Estimated chemical and mineralogical composition of clinker, wt.%

No. of clinker	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	C_3S	C_2S	C_3A	C_4AF
1	21.88	4.81	3.01	65.35	4.81	0.15	63.19	15.05	7.65	9.14
2	21.92	4.82	3.01	65.48	4.47	0.13	63.32	15.08	7.66	9.16

Table 3

Actual chemical and mineralogical composition of clinker, wt.%

No. of clinker	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	C_3S	C_2S	C_3A	C_4AF
1	21.72	4.56	3.44	64.12	3.50	0.10	62.38	14.86	6.25	10.46
2	21.30	4.68	3.56	64.00	3.68	0.10	61.51	14.65	6.36	10.82

Table 4

Physical and mechanical properties of cements

No. of cement	R_{008}, wt.%	S_{sp}, m^2/kg	Normal density, %	Terms of longing, h–min		Compressive strength limit, aged, days		
				beginning	end	2 MPa	7 MPa	28 MPa
without additive	10.4	382	28.5	2–40	5–20	24.4	46.7	75.8
with additive	11.2	376	29.0	3–00	5–40	26.2	45.9	74.2

presented in Table 1 were used as components of raw mixtures.

The composition of raw mixtures was calculated according to the saturation coefficient (KH=0.92), silicate (n=2.8) and aluminate (p=1.6) modules. The actual chemical and calculated compositions of the synthesized clinkers are given in Tables 2 and 3.

The components of the raw material mixture pre-ground to a residue on sieve No. 008 equal to 10−12 wt.% were mixed and subjected to additional combined grinding. Tablets with a diameter of 30 mm and a height of 10 mm were formed from the obtained raw material mixtures (pressing pressure of 30 MPa). Firing was carried out in a furnace with silicon carbide heaters at the temperature of 1723 K with an isothermal holding time of 40 min. Cooling of combustion products is rapid in the air. The content of free calcium oxide in the obtained clinkers, which was determined by the ethyl glycerate method, was 0.46 and 0.24 wt.% for clinker No. 1 and No. 2, respectively, which indicates the almost complete completion of mineralization processes.

Synthesized clinkers were crushed together with gypsum stone in the amount of 2.0 wt.% in terms of SO_3. The dispersion of the obtained cements was determined in accordance with the state standard GOST 310.2. The normal density and time of hardening of cements are in accordance with the state standard GOST 310.3, and the compressive strength is based on cube samples of size $(1.41\times1.41\times1.41)\cdot10^{-2}$ m. The obtained results are presented in Table 4.

As follows from the above research results, when using beneficiation wastes as an aluminosilicate component of the raw material mixture for clinker firing, the consumption of blast furnace granulated slag is reduced with a simultaneous increase in the consumption of limestone. According to the main construction and technical indicators, cement obtained using enrichment wastes is not inferior to cement using staurolite concentrate [9,10].

Partial replacement of the clay component in the raw material mixture with ilmenite ore beneficiation wastes also makes it possible to significantly expand the raw material base for the production of Portland cement clinker and effectively influence the technological process of firing.

Cements obtained on the basis of clinkers, made using wastes from the enrichment of ilmenite ore of the Vilnohirsk Mining and Metallurgical Plant, which contain compounds of d-elements, according to their properties, correspond to type II cements (state standard DSTU B.V. 2.7-46:2010).

Conclusions

It is substantiated that the physicochemical properties of compounds of s-, p-, d-elements of the second group of the periodic system of elements allow purposefully using the mineral dispersion systems of man-made origin in the production of cement clinker. The analysis of the results showed that the presence in the proposed raw material mixture for obtaining Portland cement clinker of compounds of d-elements contained in the wastes of ilmenite ore enrichment increases the saturation coefficient up to 99% and improves the processes of decarbonization and sintering during clinker firing.

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ВИКОРИСТАННЯ ВІДХОДІВ ЗБАГАЧЕННЯ ІЛЬМЕНІТОВОЇ РУДИ ПРИ ОДЕРЖАННІ ПОРТЛАНДЦЕМЕНТНОГО КЛІНКЕРУ

Сторчай Н.С., Савін Ю.С.

Наведено результати дослідження впливу d-елементів відходів збагачення ільменітової руди Вільногірського гірничого металургійного комбінату на структуру та властивості мінералів портландцементного клінкеру, випалювальні властивості та їх гідравлічну активність. Встановлено, що при застосуванні відходів збагачення як алюмосилікатного компоненту сировинної суміші для випалу клінкера знижуються витрати доменного гранульованого шлаку з одночасним підвищенням витрат вапняку. Наявність в запропонованій сировинній суміші для одержання портландцементного клінкеру сполук d-елементів, що містяться у відходах збагачення ільменітової руди, підвищує коефіцієнт насичення до 99%, покращує процеси декарбонізації та спікання при випалі клінкеру. Фізико-механічні характеристики розроблених цементів, зокрема показники межі міцності на стиск, не поступаються таким, що виготовлені за класичною рецептурою. Цементи, одержані на основі клінкерів, за своїми властивостями відповідають типу цементів II, ДСТУ Б.В. 2.7-46:2010. Часткова заміна в сировинній суміші глиняного компонента відходами збагачення ільменітової руди дозволяє значною мірою розширити сировинну базу для одержання клінкеру портландцементу, ефективно впливати на технологічний процес випалу.

Ключові слова: вторинні продукти промисловості, портландцементний клінкер, випал, гідравлічна активність, ефективне використання.

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