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Issues of waste disposal in cement technology

ABSTRACT

The possibility of cement production with increasing volumes of disposal of multi-tonnage waste from other industries has been studied. With the use of the "Clinker" computer program, new compositions of raw material mixtures based on the system of chalk - rice husk - TPP waste ash with a content of 42-51 wt.% of the specified waste were determined. The features of physicochemical transformations and the formation of the phase composition of cement clinker during the firing of a mixture based on man-made raw materials with a maximum temperature of 1400 °C and the properties of a mineral binding material are shown.

Keywords: cement, rice husk, fly ash, raw material mixture, composition, firing, crystalline phases, properties.

1. INTRODUCTION

Resource saving and environmental protection are important factors of stable development [1,2]. At the same time, considerable attention is paid to the issue of effective disposal of industrial, agricultural and household waste as alternative sources of energy and raw materials [3,4].

To a large extent, the complex use of raw materials of natural and man-made origin corresponds to the tasks of resource saving and chemical technology for the production of silicate building materials [5-7].

A significant amount of research and development in this direction is known. Thus, in the production of cement and concrete. In concrete production, the use of cactus processing waste is gaining attention, which leads to a significant increase in the strength and durability of products and structures [8-10].

In cement production, blast furnace slag is used in significant quantities as a substitute for part of the clinker during grinding [11-14]. A small amount (1.5-5.0 wt. %) of iron-containing industrial waste is introduced into the composition of raw mixtures - for the production of clinker as fluxing additives.

Taking into account the high mass density of mixtures for the production of cement clinker, it seems appropriate to increase the amount of industrial waste used in them as man-made raw materials under the conditions of compliance in composition.

At the same time, rice husk [15-18], slag and ashes of thermal power plants [19-23] attract attention among multi-tonnage waste. It is indicated that during the production of 1 kg of white rice, 0.28 kg of rice husk is formed as a by-product of production in the milling process. As a result, with the annual production of 750 million tons of rice in the world, more than 150 million tons of waste is generated. At the same time, rice husk can become a source of amorphous silicon dioxide as an activator of physicochemical processes of structure formation of silicate systems.

Fly ash is obtained at thermal power plants that use pulverized coal. It is a significant part of heat energy waste, the total volumes of which are generated and accumulated in billions of tons.

It is recognized that the physical properties of these wastes depend on a number of factors, including the type of coal, combustion conditions or combustion temperature. Acid ash consists mainly of reactive SiO₂ with a mass content of at least 25% and Al₂O₃, while the content of calcium oxide does not exceed 10%.

There are well-known studies and developments on the use of fly ash as a component for the production of composite cement, heavy, light and porous concrete and building mortars, as well as as a finely ground additive for heat-resistant concrete [24,25].

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However, the actual volumes of rice husk and fly ash utilization do not correspond to the quantitative level of formation and accumulation of these wastes. Based on this, increasing the volume of their use as man-made raw materials in the resource-intensive production of mineral binding materials is an urgent task of comprehensively solving the issues of chemical technology of silicates and environmental protection.

The practical solution of such problems requires the appropriate development of the scientific and technical foundations of chemical technology and materials science - the determination of regularities regarding the influence of the concentration of raw material types on the structure formation of silicate systems and product properties. In the direction of solving such problems regarding the production of cement, the presented work was carried out.

Setting the problem. The results of the analysis of known data lead to the conclusion that a significant increase in the utilization of industrial waste as man-made raw materials in cement technology requires scientific and technical solutions for the development of new compositions of starting mixtures for the production of clinker, taking into account the relevant features of phase formation during firing.

2. EXPERIMENTAL PART

2.1. Materials and methods

The object of the study was raw material mixtures for the production of cement clinker based on the system of chalk - rice husk - fly ash.

The raw mixtures were prepared by dosing the components by weight, mixing and homogenizing in a ball mill, firing and grinding the final product according to modern cement technology.

Table 1. Chemical composition of raw materials

Samples	Content of oxides, wt. %									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	LOI
chalk	0,77	0,25	0,13	-	55,0	0,25	0,08	-	-	43,49
rice husk	15,64	0,24	0,12	-	0,61	0,45	0,18	0,48	0,28	82
fly ash	46,12	18,00	22,17	1,78	4,03	1,46	0,21	-	2,10	1,49

The fly ash sample contains a significant amount of iron, silica and aluminum oxides with a quantitative ratio of SiO₂ : Al₂O₃ = 2.6. At the same time, the quantitative ratios of oxides CaO : SiO₂ : Al₂O₃ : Fe₂O₃ = 1.0 : 11.4 : 4.5 : 5.5.

According to its mineralogical composition, chalk is characterized by a predominant content of calcite; rice husk contains amorphous silica and organic substances; fly ash is characterized by the

Samples of raw mixtures were fired in a furnace for 15 hours at a maximum temperature of 1400 °C, keeping at a maximum of 1.5 hours. All samples of the mixtures that were compared were fired at the same time to exclude the possibility of a difference in the degree of heat treatment.

The methods of physical-chemical analysis of silicate raw materials and testing of binder properties used in this work included:

- analysis of chemical composition using standardized procedures;
- X-ray diffraction analysis (powdered drugs) using diffractometers DRON-4-0, connected through an interface to a computer;
- determination of cement properties in accordance with current standards.

Various types of raw materials were used to determine the rational composition of the initial mixture:

- chalk of the Zdolbuniv deposit, Rivne region;
- rice husk - processing waste of Ltd "Rice of Ukraine", Kherson region;
- fly ash - waste from the production of Burshtyn TPP, Ivano-Frankivsk region.

Samples of raw materials differ significantly in their genesis and composition. Chalk is a natural raw material of sedimentary origin, rice husk and fly ash are man-made raw materials.

According to the chemical composition, the chalk sample is characterized by a predominant content of CaO (55.0 wt. %), the rice husk sample is characterized by a higher content of SiO₂ (15.6 wt. %) with a large quantitative ratio of SiO₂ : Al₂O₃ = 65.2 and a small amount of alkaline earth and alkaline oxides (Table 1).

development of a glass phase and the presence of crystalline phases of quartz, calcite, and mullite (Fig. 1, 2).

The given chemical and mineralogical composition of raw material samples indicates the nature and content of their losses during heat treatment (roasting). Evidently, in the case of chalk (43.49 wt. %) this is connected with the destruction of the calcite lattice: CaCO₃ → CaO + CO₂↑, in the

case of fly ash (1.49 wt. %) – with the oxidation of residual carbon and the removal of CO₂↑ In the case of rice husk, mass loss (82.0%) is complex in

nature and consists of CO₂ and hydrogen emissions due to organic components - cellulose (C₆H₁₀O₅)_n and lignin (C₃₁H₃₄O₁₁)_n.

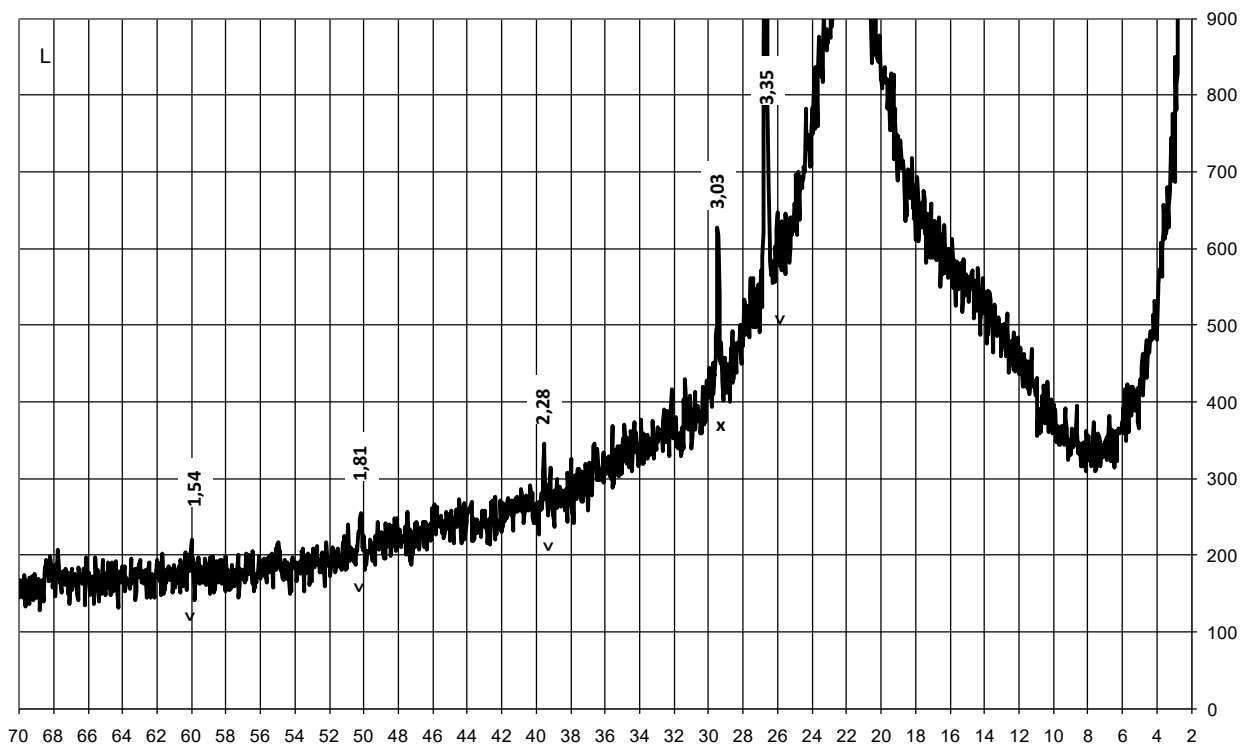


Figure 1. X-ray diffraction of rice husk: v - quartz; x - calcite

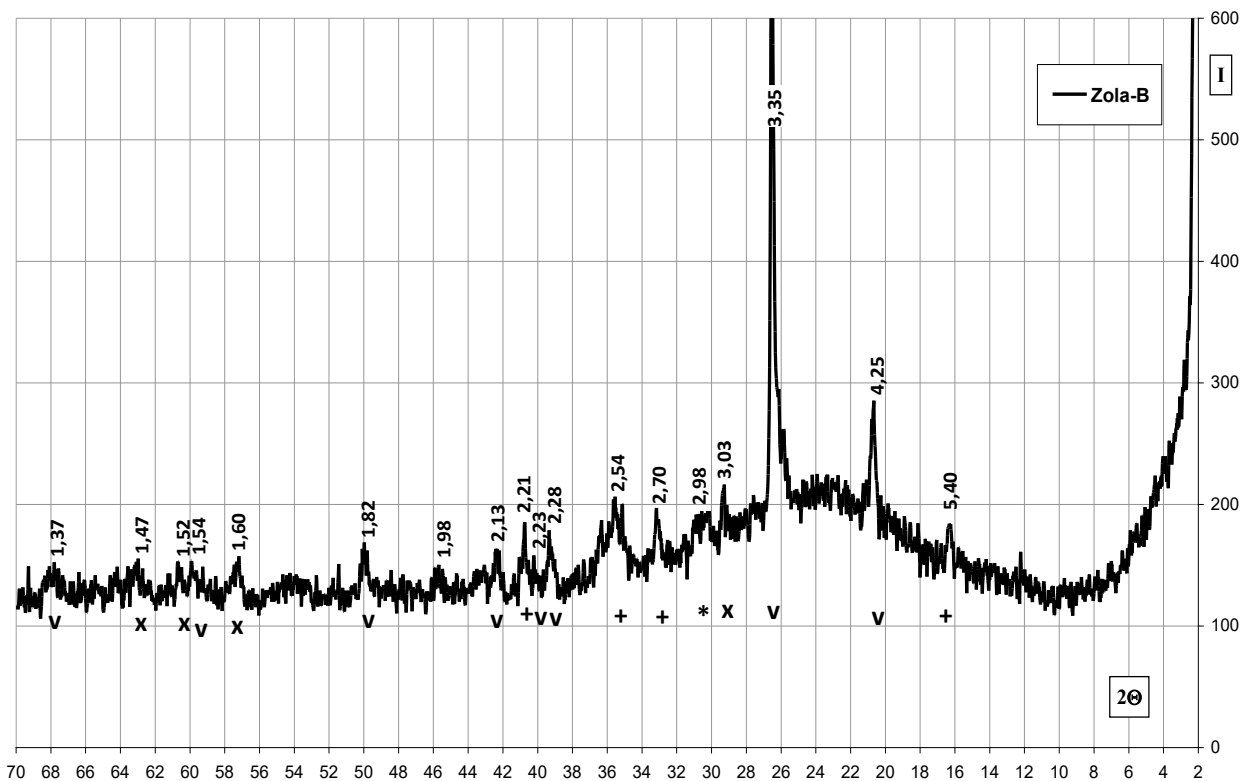


Figure 2. X-ray diffraction of fly ash: v- quartz, +- mullite, x- calcite

2.2. Determination of the composition of raw mixtures

Calculations and analysis of the composition of raw mixtures for the production of cement clinker were carried out using the created computer program "CLINKER" [26]. This made it possible to quickly determine the rational ratio of the components in the original raw material mixture based on the given values of the saturation

coefficient of SF, silica n and alumina p modules. According to the results of computer calculations, the possible content of rice husk is 55.7-60.1 wt. %, and fly ash - 23.9-26.6 wt.%, however, the numbers of silica and alumina modules do not correspond to the recommended $n = 1.9 - 3.0$ and $p = 0.90 - 2.0$ for cement clinker (Table 2).

Table 2. Composition of binary mixtures and characteristics of clinker

Systems	Composition of the mixture, %			Characteristics of clinker		
	chalk	rice husk	fly ash	SF	n	p
chalk-rice husk	39,9-44,3	55,7-60,1	-	0,80-0,95	24,6-27,2	1,89-1,95
chalk-fly ash	73,4-76,1	-	23,9-26,6	0,80-0,95	1,17	0,83

When using 3-component mixtures, the possible total content of rice husk and fly ash in the interval of SF=1.9-3.5 is from 39 to 52 wt. % when varying the quantitative ratio of rice husk: fly ash from 2.1 to 7.3 (Fig. 3).

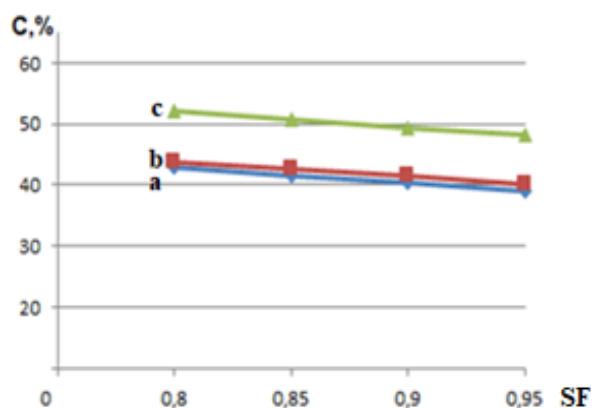


Figure 3. Dependence of the content of man-made raw materials (C) in the mixture based on the system of chalk – rice husk – fly ash on the saturation coefficient of SF clinker at silica modulus $n=1.9$ (a), $n=2.0$ (b) and $n=3.5$ (c)

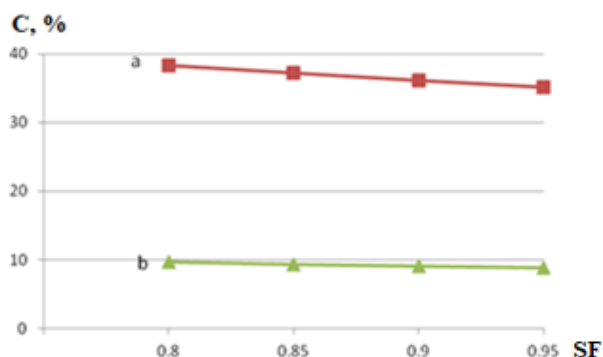


Figure 4. Dependence of the content of husk (a) and fly ash (b) in a chalk-based mixture on the saturation coefficient of SF of clinker at silica modulus $n=2.5$

At the same time, in the interval of values of the saturation coefficient SF=0.80-0.95 with $n=2.5$, the possible content of rice husk is 35.2-38.3 wt. %, and fly ash is 8.8-9.4 wt. % (Fig. 4).

Based on the analysis of the results of computer calculations, raw material mixtures 10L, 11L were selected for further research, which at SF=0.85 in the interval of values $n=2.5-3.5$ and $p=0.85-0.90$ are characterized by a general with a technogenic raw material content of 42.5-50.5 wt.% with a quantitative ratio of rice husk: fly ash from 2.4 to 7.3 (Table 3).

Table 3. Composition of raw mixtures

Code of mixture	Quantity of components, mass %				
	chalk	clay	red mud	fly ash	rice husk
Bk	77,2	21,1	1,7	-	-
10L	57,5	-	-	12,5	30,0
11L	49,5	-	-	6,0	44,5

At the same time, for comparison, the raw material mixture Bk was used, the composition of which is known for its use in the current production of cement.

According to the chemical composition (Table 4), the studied mixtures 10L, 11L differ from Bk:

- with a lower content of silicon and aluminum oxides - higher quantitative ratios of $SiO_2:Al_2O_3$, which are 4.4-7.4 against 3.6. This indicates their relatively higher melting point and the possibility of intensifying the clinker firing process;
- with a lower content of calcium and magnesium oxides - by quantitative ratios of $CaO:SiO_2$ (2.7-2.8 vs. 3.1) and $CaO:Al_2O_3$ (12.4-19.6 vs. 11.0), which indicates probable differences in phase formation during.

Table 4. Chemical composition of raw mixtures

Code of mixture	Content of oxides, wt. %						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	LOI
Bk	14,14	3,93	2,21	43,32	0,64	0,10	35,66
10L	11,32	2,60	3,05	32,32	0,47	0,13	50,11
11L	10,42	1,41	1,56	27,68	0,42	0,13	58,38

2.3. Phase formation and properties of cement

The mineralogical composition of the investigated mixtures is characterized by the presence of calcite and dolomite and is distinguished by the presence of an amorphous

phase in samples 10L, 11L (Figs. 5, 6). At the same time, the development of the amorphous phase (by the area of the diffuse halo) is significantly greater in the 11L mixture, which correlates with the material composition.

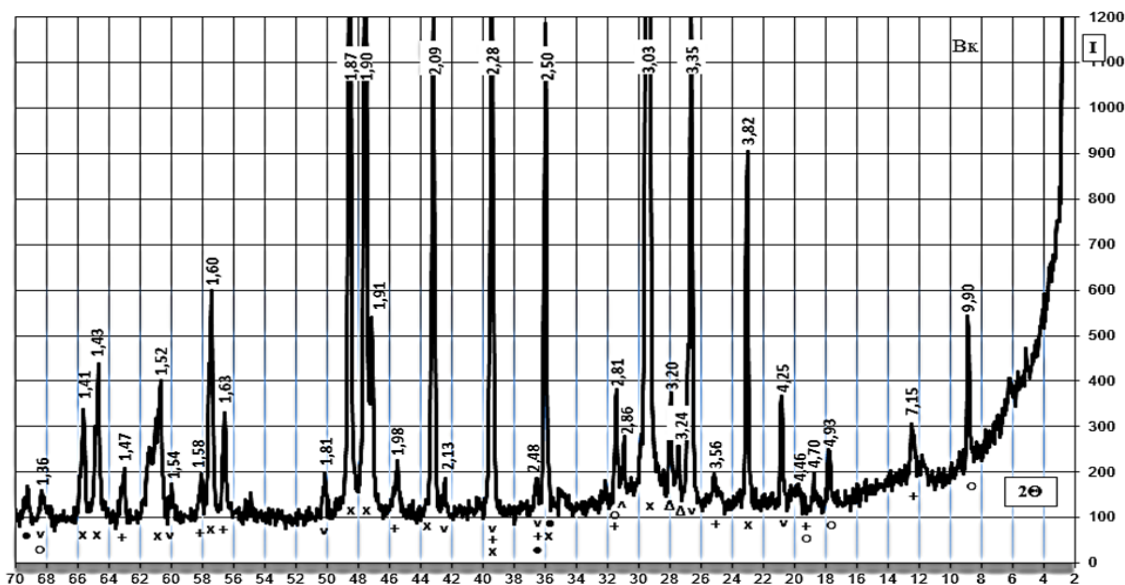
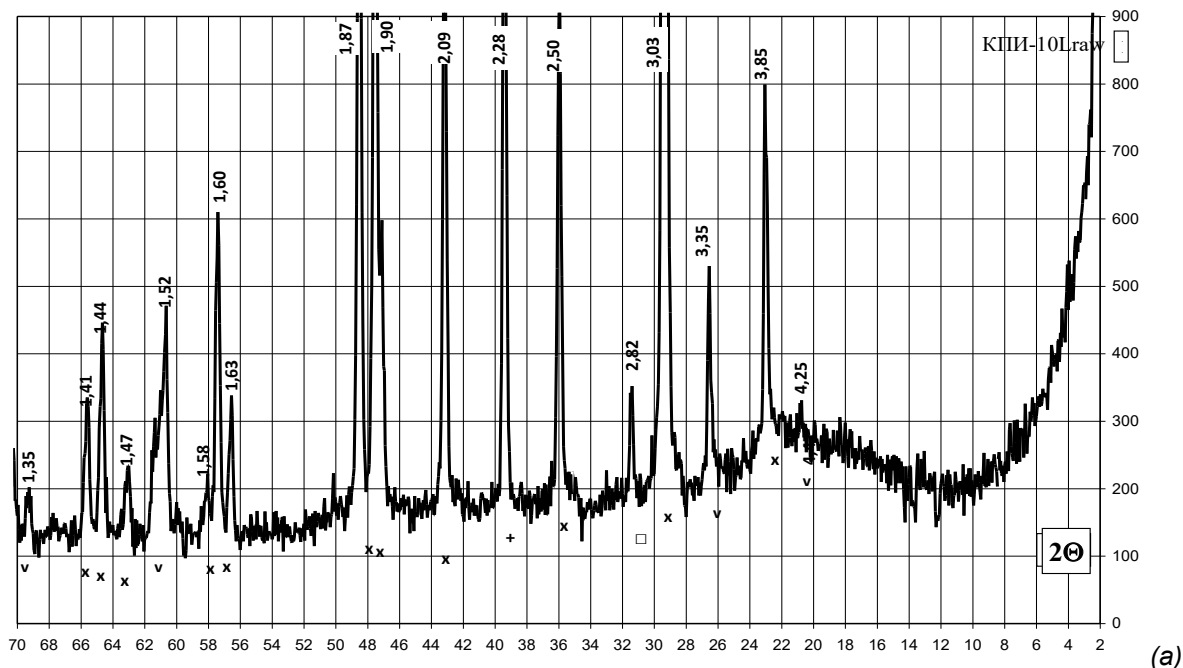


Figure 5. X-ray diffraction of raw mixtures Bk: x calcite; v quartz; Δ feldspar; + kaolinite; o hydromica; ^ dolomite; • goethite



(a)

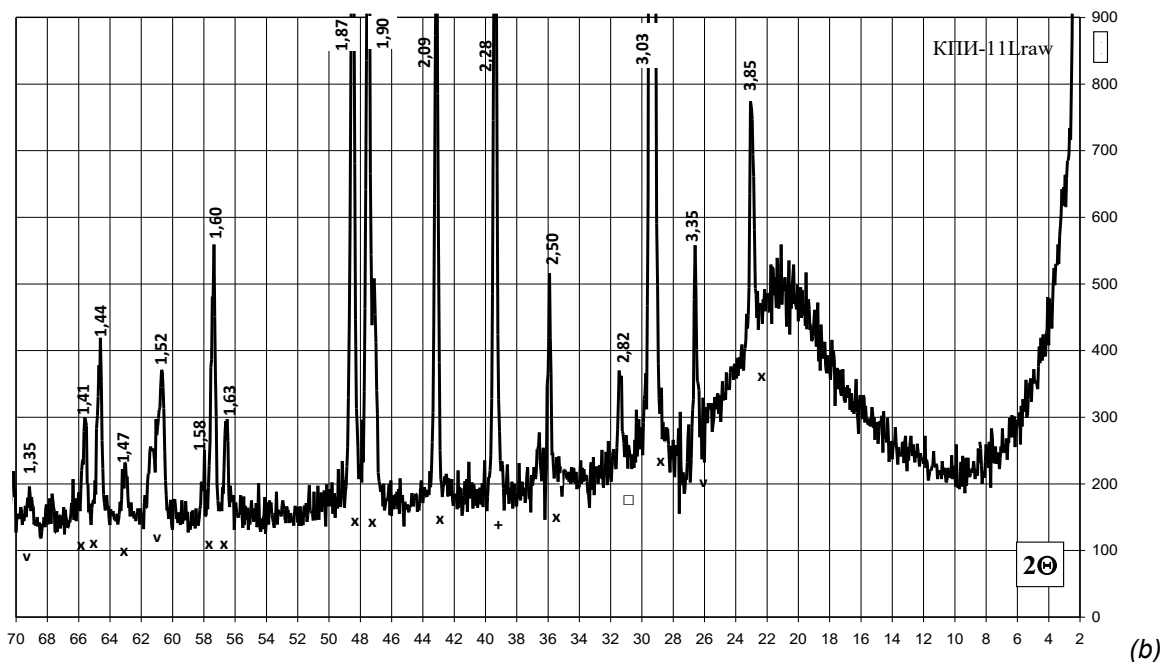
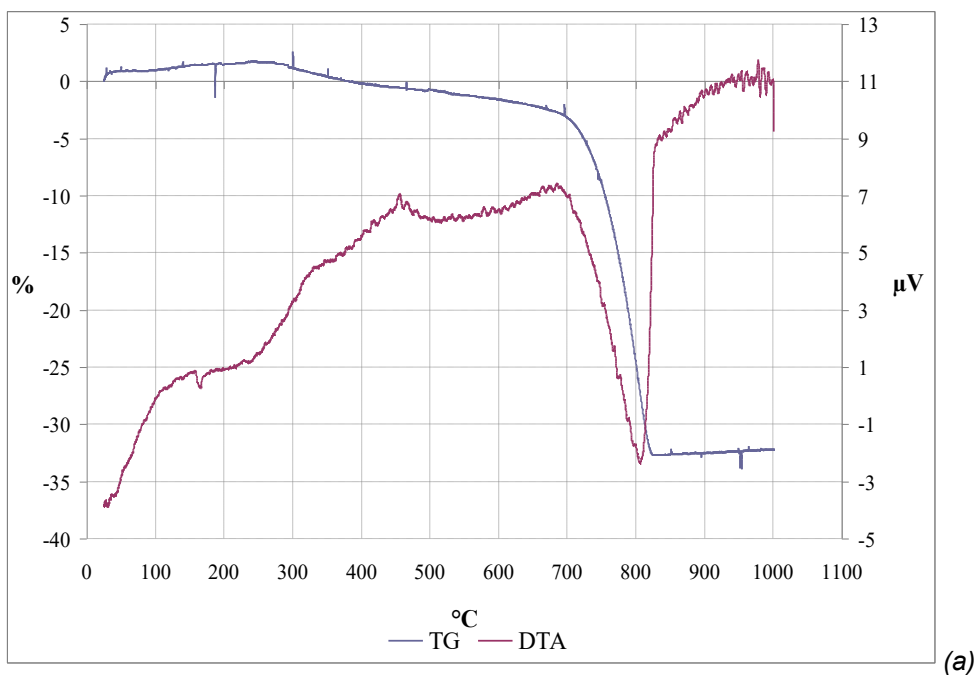


Figure 6. X-ray diffraction of raw mixtures 10L (a) i 11L (b) : x calcite, □ dolomite

The results of thermal and X-ray phase analysis made it possible to reveal the peculiarities of physicochemical transformations and phase formation during firing of the studied mixtures to obtain cement clinker.

It was established (Fig. 7) that when the temperature rises to 1000 °C in the mixtures, the destruction of rock-forming substances takes place. In the mixture of Bк, this process has a known character in the form of endothermic effects associated with the destruction of crystal lattices of

minerals of the clay component and calcite, and in the mixture with man-made raw materials, the destruction of the organic component (cellulose, lignin) is characteristic with a significant loss of mass with a maximum in the interval 300-500 °C. At the same time, the significantly lower intensity and area of the endoeffect in the range of 800-900 °C, associated with the destruction of the calcite lattice, corresponds to a smaller amount of carbonate raw materials in the material composition.



(a)

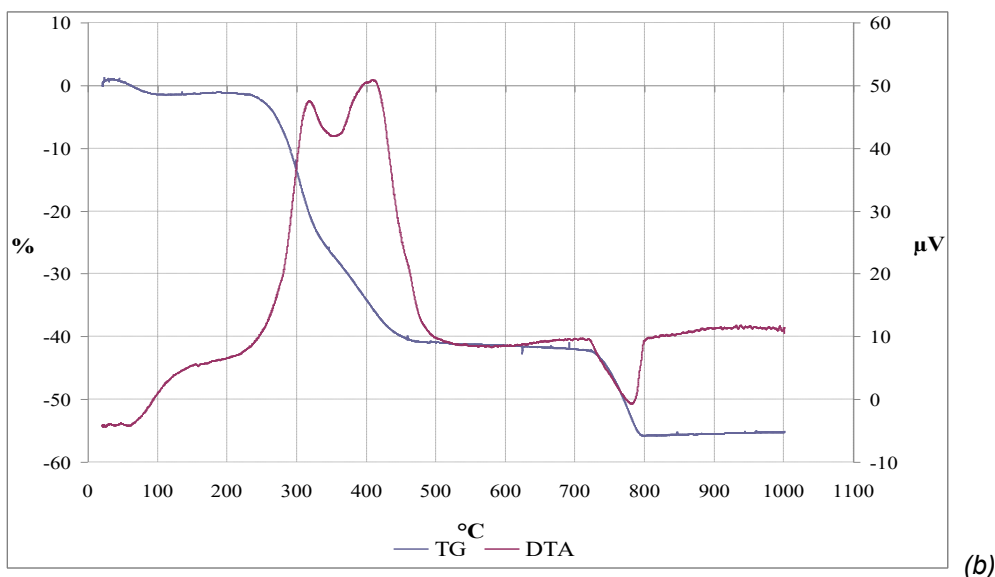


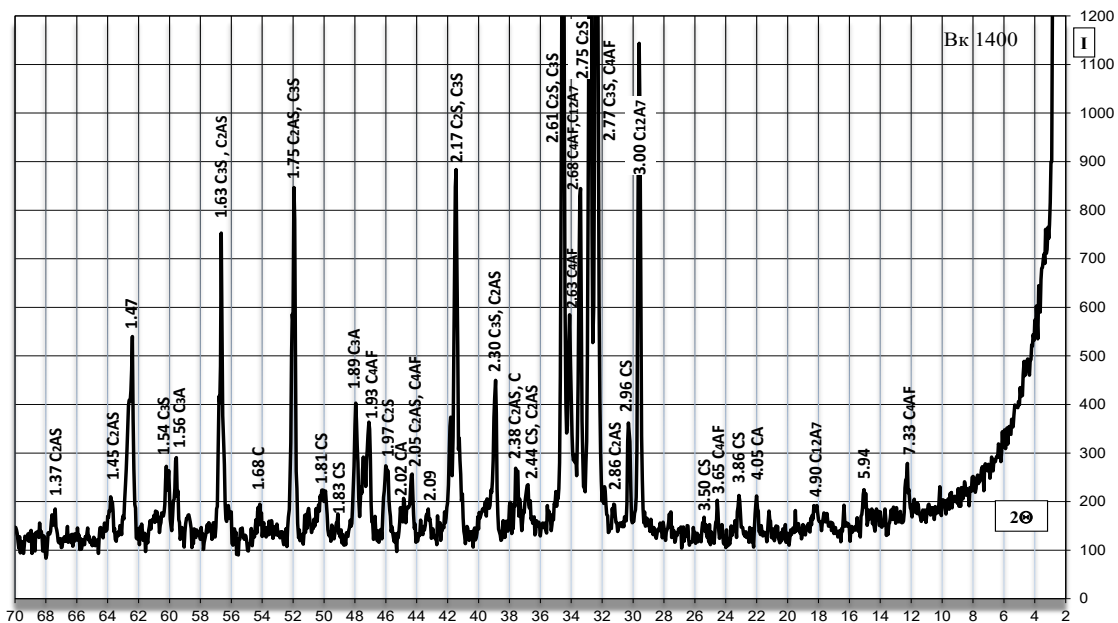
Figure 7. Termicalanalysis of mixtures Bk (a) and 11L (b)

According to the calculated characteristics of the chemical composition (Table 5), clinker from mixtures 10L, 11L should differ from Bk by greater formation of dicalcium silicate with a decrease in the quantitative ratio of C₃S:C₂S to 1.6 versus 3.6, with a significantly lower probability of C₃A formation. At the same time, it is determined that

with an increase in the quantitative ratio of rice husk : fly ash in the mixture, the probability of the formation of crystalline phases of calcium silicates during firing increases, and the probability of the formation of calcium aluminate and iron-containing phases decreases.

Table 5. Calculation characteristics of clinker

Sample code	Characteristics of clinker			Content of crystalline phases, %			
	SF	n	p	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Bk	0,91	2,30	1,78	58,2	16,33	14,29	10,43
10L	0,85	2,00	0,85	47,42	29,27	3,44	18,57
11L	0,85	3,51	0,90	52,33	32,30	2,60	11,40



Figur 8. X-ray diffraction of sample Bk (1400 °C)

research, new compositions of raw mixtures for the production of clinker with a content of 42-51 wt. % composition of man-made raw materials. This is significantly different from the initial mixtures known in the industry, where individual wastes are introduced in the amount of 1-5 wt. At the same time, the practical implementation of the completed developments requires the solution of a number of applied issues: standardization of requirements for the composition of waste as man-made raw materials for the chemical technology of cement, optics, etc. It is advisable to further deepen research on the peculiarities of physico-chemical processes when varying the compositions of types of man-made raw materials and methods of preparing mixtures for obtaining cement clinker.

4. CONCLUSIONS

1. The use of multi-tonnage waste from agro-industry - rice husk and thermal power industry - fly ash as man-made raw material is promising for the production of clinker in the mass production of cement.

2. Analysis of computer calculations and experiments indicate the possibility of introducing 39-52 wt. % of the specified waste with a quantitative ratio of husk: ash from 2.1 to 7.3.

3. The possibility of manufacturing clinker of normal-hardening cement brand 400 from starting mixtures with a content of 42.5-50.5 wt. % of man-made raw materials at the maximum firing temperature of 1400 °C was experimentally confirmed.

4. According to the data of thermal and X-ray phase analysis, the peculiarities of physico-chemical transformations during firing of the studied mixtures were established, which are associated with the increased reactivity of amorphous silica of rice husk and the influence of the glass phase of fly ash on the phase formation of clinker with a change in the quantitative ratio of crystalline phases of calcium silicates, the development of aluminate phases calcium type CA, C₁₂A₇ and aluminosilicates type C₂AS.

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IZVOD

PITANJA ODLAGANJA OTPADA U TEHNOLOGIJI CEMENTA

Proučavana je mogućnost proizvodnje cementa sa povećanjem obima odlaganja više tonažnog otpada iz drugih industrija. Korišćenjem računarskog programa „Klinker“ utvrđeni su novi sastavi sirovinskih mešavina na bazi sistema kreda – pirinčana ljuska – otpadni pepeo TE sa sadržajem 42-51 tež.% navedenog otpada. Osobine fizičko-hemijskih transformacija i formiranja faznog sastava cementnog klinkera pri pečenju smeše na bazi veštačkih sirovina sa maksimalnom temperaturom od 1400 °C prikazana su svojstva mineralnogv ezivnog materijala.

Ključnereči: cement, pirinčana ljuska, leteći pepeo, mešavina sirovina, sastav, pečenje, kristalne faze, svojstva.

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