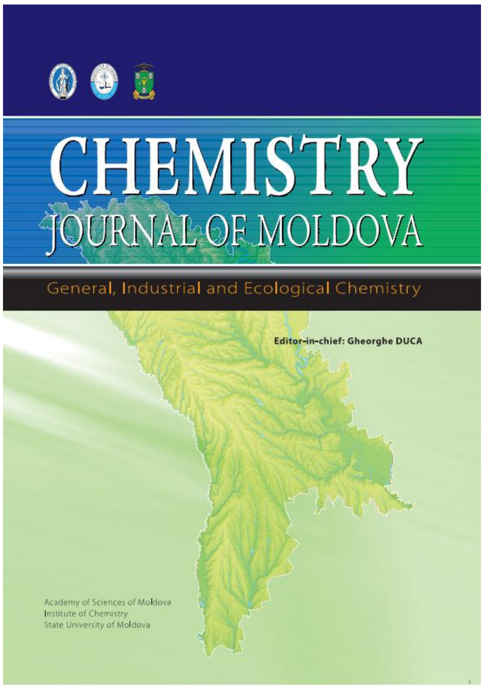

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Abstract. The features of the cement clinker containing rice husk are investigated. The dependence of the raw mixture composition on the set product burning characteristics has been analysed using the software "CLINKER". The mixture compositions have been identified on the basis of the chalk–clay–rice husk system, with the introduction of man-made stock of 6.0–18.0 mass %. The features of the phase composition and the binder properties, by varying the rice husk content, mixture ratio and burning temperature were studied.

Keywords: cement, clinker, rice husk, crystalline phase, property.

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Introduction

Increased volumes of manageable large-tonnage wastes from metallurgy, chemical industry and agrarian production call for complex solving of tasks related to the silicate production development for environment and resource preservation [1-3]. Solving of these tasks requires a corresponding development of scientific and technical principles of silicate chemical technologies, with the identification of regularities regarding the impact of different raw materials concentrations on the structure and properties of silicate materials [4,5].

Stock base expanding in the silicate materials production is studied by numerous researchers. Moreover, the use of wastes from other industries as the technological raw material into the processes is emphasized [6-8]. The largest practical achievement in this field of research was the use of nonferrous-metals industry wastes, namely blast furnace granulated slag and of thermal power sector wastes, namely fly ash from thermal power stations as the components of slag Portland cement and composite cements [9,10]. From among other large-tonnage wastes, the rice husk attracts attention [11,12]. It is stated that manufacturing of 1 kg of white rice gives 0.28 kg of rice husk as the by-product in the milling process. As a result, over 150 million tons of wastes are generated, considering an annual global rice production capacity of 750 million tons.

Large volumes of generated and accumulated rice production wastes may be regarded as hazardous to the environment; this emphasizes the urgency of development of new methods for waste disposal considering their physical and chemical properties and impact on characteristics of probable product types. In this connection, the application of rice husk in silicate productions is of particular interest. In addition, the rice husk can be a source of amorphous silica, as an activator of physical and chemical processes of silicate system structure formation [13-15]. This is proved experimentally by published scientific reports regarding the impact of rice husk additives on brick [16,17], porcelain [18] and concrete [19,20] properties. The results of most of these studies lead to the conclusion that the use of rice husk in manufacturing of silicate materials is directed towards its addition to raw compositions in the frames of the existing technology. However, most of the studies on the use of waste from rice production in the technology of astringent materials are associated with the preliminary thermal treatment of rice husk, the study of the properties of rice husk ash and the influence of its addition on the properties of cement and concrete [21-24]. These works do not address the issue of increasing the volume of utilization of rice husk as a significant component of raw mixtures for the manufacturing of cement clinker, and this underlines the actuality of our researches in this field.

The aim of the research presented in this work was to investigate the effect of rice husk on phase formation of the raw material mixture during burning and on the properties of cement clinker. The features of the phase composition and the binder properties were studied by varying the rice husk content, mixture ratio and burning temperature.

Experimental

Materials

Chalk (chalk, MD-2 type, Zdolbuniv deposit, Rivne area, Ukraine), clay (clay, polymineral type, Kryvyn deposit, Rivne area, Ukraine) and rice husk (wastes from the production of rice, LTD. "Rice of Ukraine", Kherson area, Ukraine) were used as raw materials.

The raw 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 mineral binders.

Samples of raw mixtures have been bubbled in an oven for 15 hours in the range of maximum temperatures of 1200°C and 1400°C keeping a hold at a maximum of 1.5 hours. All samples of the mixtures that have been compared were blasted together to exclude the possibility of a difference in the degree of heat treatment. The properties of the binding material (setting time, compressive strength) were determined according to standardized procedures [25,26].

Methods

Methods of physical - chemical analysis of silicate raw materials and testing of properties of astringent substances which were used in this work included:

- *chemical composition analysis* using standardized procedures [27,28];
- *X-ray diffraction analysis* (powder - like preparations) using a diffractometer DRON-3M (radiation CuKα 1-2, voltage 40 kV, current 20 mA, speed 2 degrees/min).

The raw mixtures based on the chalk–clay–rice husk systems were used in the present study to make Portland cement clinker. The chemical compositions of the output stock samples (Table 1) differ in terms of quantitative content of oxides and form the following rows, mass % for:

- SiO_2: chalk < rice husk < clay;
- Al_2O_3: clay > chalk and rice husk;
- CaO: chalk > clay > rice husk;
- Fe_2O_3: clay > chalk and rice husk.

The main rock-forming mineral of the rice husk is the amorphous silica (Figure 1) that is confirmed by the X-ray phase analysis [30].

Table 1

Chemical composition of raw materials (mass %).

Samples	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*TiO_2*	*CaO*	*MgO*	*SO_3*	*Na_2O*	*K_2O*	*LOI***
Chalk	0.77	0.25	0.13	-	55.0	0.25	0.08	-	-	43.49
Clay	60.96	15.66	5.57	0.79	3.33	2.04	0.16	0.30	2.70	8.48
Rice husk*	15.64	0.24	0.12	-	0.61	0.45	0.18	0.48	0.28	82

* *Correlated with known data [29];*
** *LOI is the loss on ignition.*

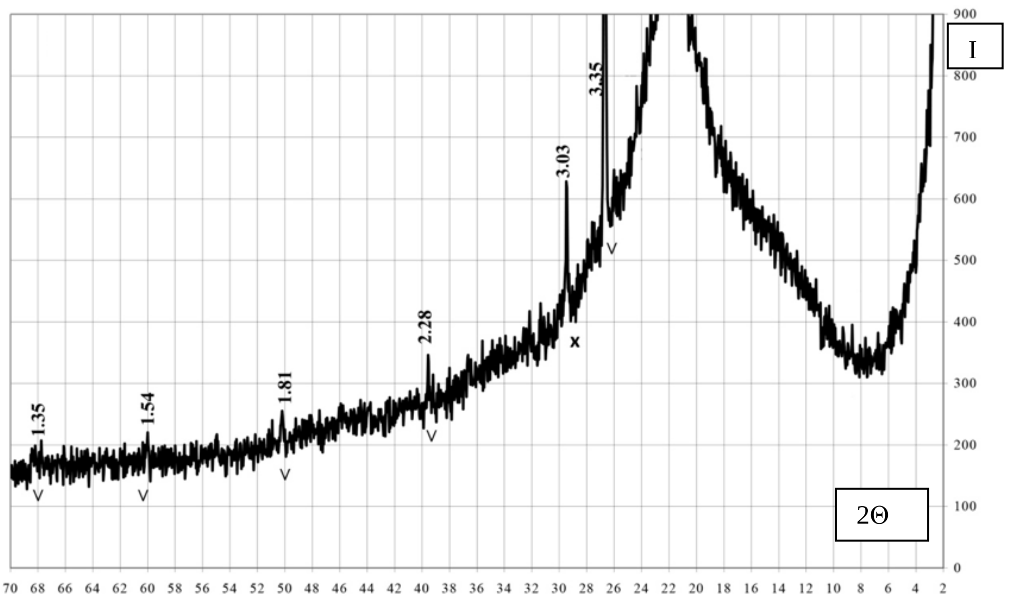

Figure 1. X-ray diffraction of rice husk: v - quartz, x – calcite [30].

It is evident that in the studied silicate system, the use of clay and rice husk for manufacturing of cement clinker will serve as the source of SiO_2, which is required to create the main clinker minerals in the process of burning. However, because of different crystallisation levels, the crystal β-quartz was introduced into the system with the clay, and amorphous silica was introduced with the rice husk.

The *calculations and the analysis of raw mixtures* to obtain Portland cement clinker have been performed with the software application "CLINKER" according to the recommendations for numerical values of the saturation factor (*SF*), and silica *n* and alumina *p* modules [31]. The basic steps of using the software are as follows:

1. A table listing chemical compositions of possible raw components is entered;
2. Values of *SF* and *n*, *p* modules are set;
3. Using the accepted calculation formulas, all combinations of two, three or four components that guarantee the required performance of the clinker are identified. To this end, if a rather large raw material base is available, rational proportions of components in the output raw mixture can be promptly identified.

Results and discussion

Analysis of raw mixtures containing rice husk for clinker production

The analysis of the obtained results showed that the concentration of the rice processing wastes as part of raw mixtures within the recommended intervals *SF* depends considerably on types and quantitative ratio of other components; moreover, an inverse proportional dependence exists between the content of wastes and saturation factor value (*SF*). The possible content of rice husk may vary within 5.6 to 18.4 mass % and it increases with the reduced *SF* value and clay quantity in the three-component mixture on the chalk–clay–rice husk (Figure 2).

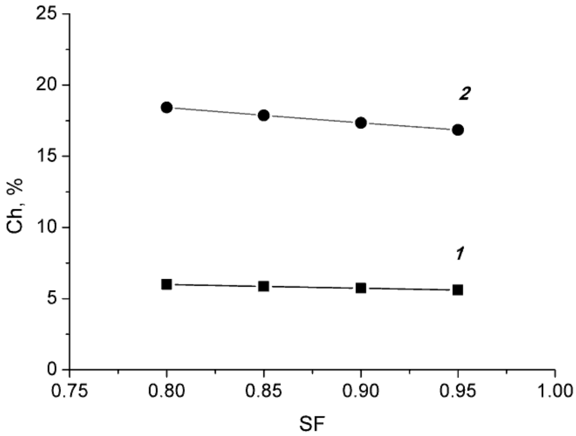

Figure 2. Correlation between the rice husk content (*Ch*) in the mixture chalk–clay–rice husk and the saturation factor (*SF*) of clinker in the silica module: *(1) n*= 3.0; *(2) n*= 3.5.

Based on computer calculations, 3-component raw mixtures were taken for further study and for manufacturing the Portland cement clinker on the basis of the chalk–clay–rice husk system (Table 2).

The studied mixtures differ in the rice husk content and different quantitative ratio of other components. Thus, sample 2S differs from sample 1S with the less (1.9 against 2.8) quantitative ratio of carbonate-containing component (chalk) to the sum of alumino- and silica-containing (clay and rice husk) components, and less quantitative ratio of clay to rice husk (0.9 to 3.4). The analysis of the chemical composition of the studied mixtures proves that when the rice husk content increases, sample 2S differs from sample 1S with the less content of CaO (47.0 versus 41.2 mass %) at a considerable reduction in the quantitative ratio $CaO:SiO_2$ (2.75 *versus* 2.80) and definite increase of $CaO:Al_2O_3$ (13.1 *versus* 11.6), and reduction in the content of Fe_2O_3 and MgO (Table 3).

Table 2

Composition of raw materials mixtures (mass %).

Code of mixture	*Chalk*	*Clay*	*Rice husk*
1S	73.5	20.5	6.0
2S	66.0	16.0	18.0

Table 3

Chemical composition of raw mixtures (mass %).

Code of mixture	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*CaO*	*MgO*	*SO_3*	*LOI*
1S	14.62	3.56	1.31	41.15	0.65	0.11	38.60
2S	13.47	2.82	1.04	37.04	0.59	0.11	44.93

Phase composition and clinker properties in the case of using rice husk

Three-component mixtures with different quantitative ratio of the components, different values of the clinker performance and phase composition were studied. In case of the mixtures on the basis of the chalk–clay–rice husk, sample 2S with the rice husk content of 18 mass % and its quantitative ratio to the clay of 1.1:1 must differ from sample 1S with 6 mass % and its quantitative ratio to the clay of 1:3.4 in an inconsiderable increase in C_3S and C_2S and some decrease in the quantity of C_3A and C_4AF (Table 4).

According to the X-ray phase analysis, some features of phase transformation have been defined during burning of the studied mixtures at the maximal temperatures of 1200 and 1400 °C (Figure 3-6).

Table 4

Description of the clinker.

Code of mixture	*Parameters of clinker*			*Crystalline phases, %*			
	SF	*n*	*p*	C_3S	C_2S	C_3A	C_4AF
1S	0.85	3.0	2.72	49.76	30.71	11.77	6.45
2S	0.85	3.5	2.71	51.12	31.55	10.36	5.74

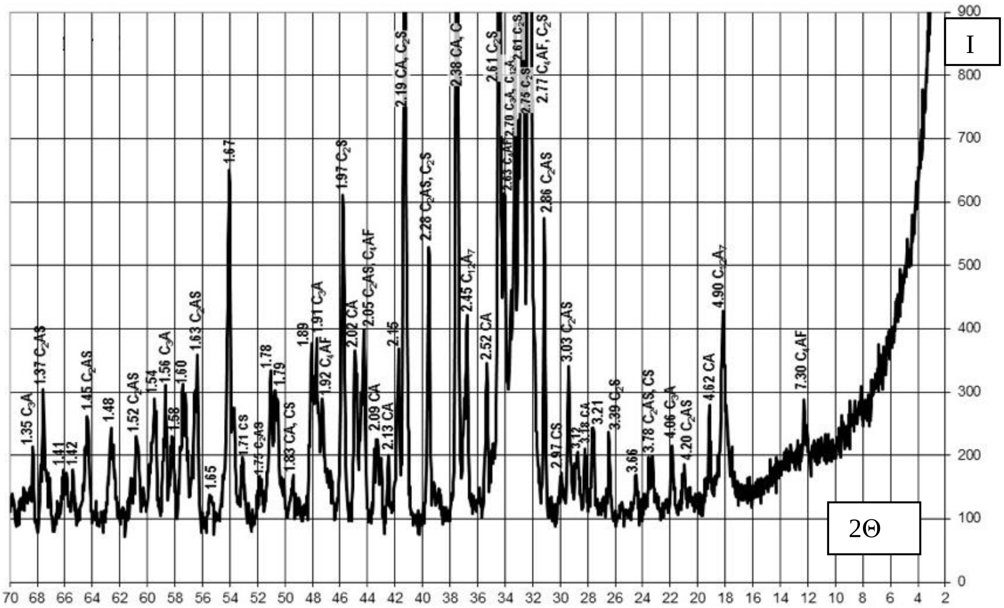

Figure 3. X-ray diffraction of clinker sample 1S (1200 ºC).

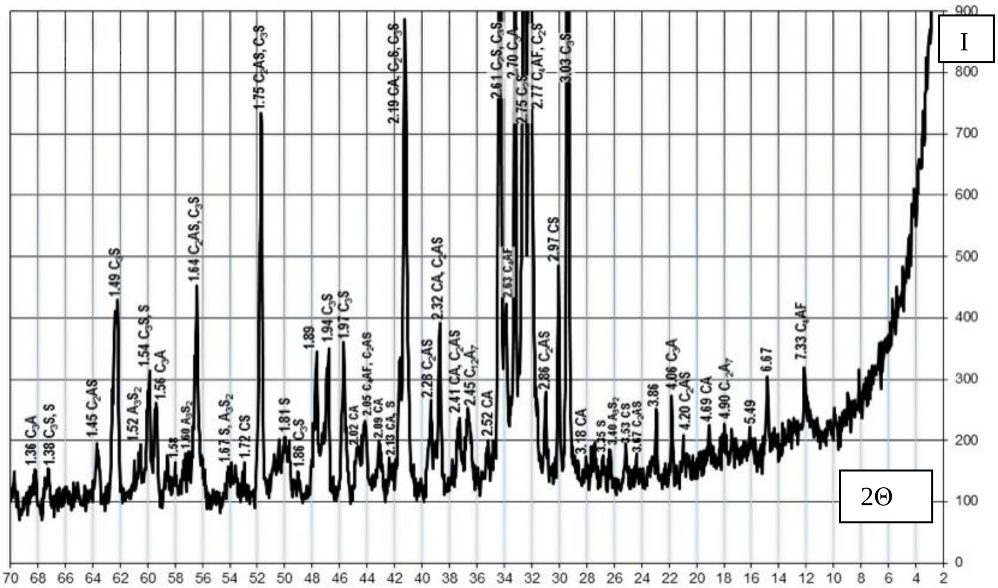

Figure 4. X-ray diffraction of clinker sample 1S (1400 ºC).

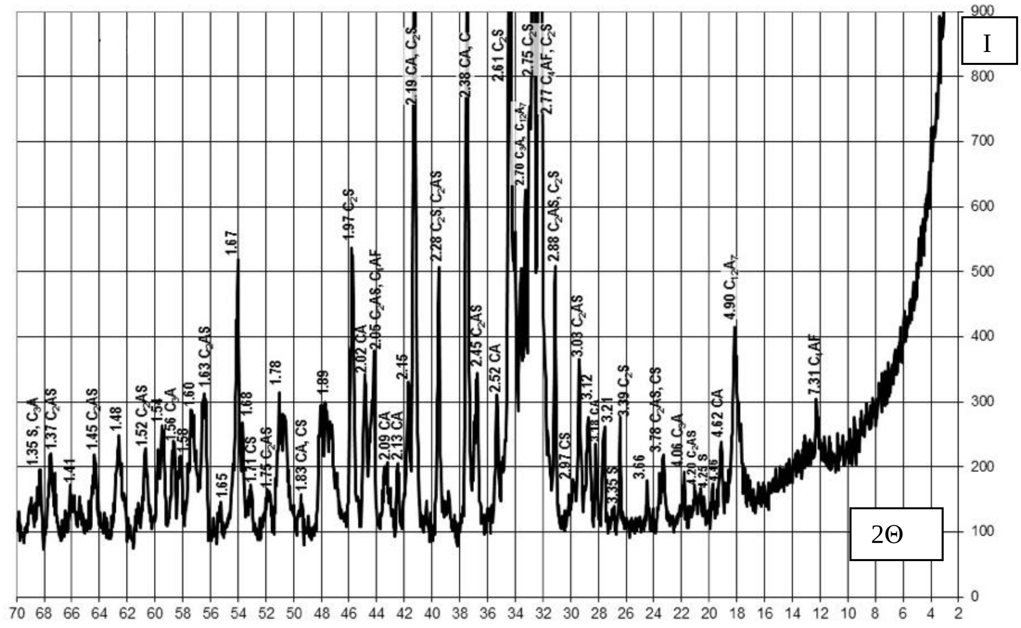

Figure 5. X-ray diffraction of clinker sample 2S (1200 ºC).

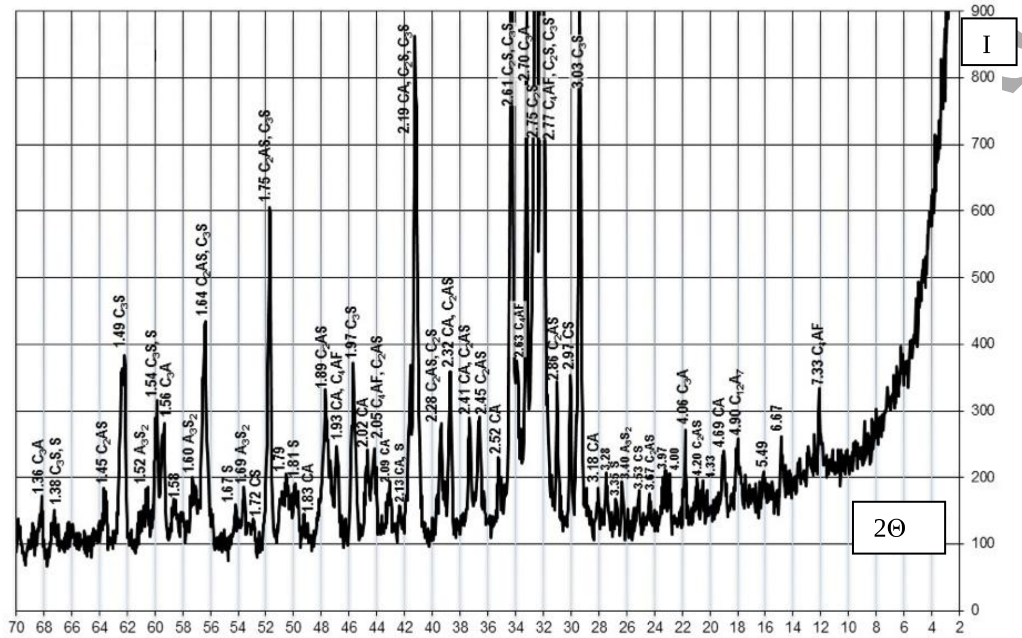

Figure 6. X-ray diffraction of clinker sample 2S (1400 ºC).

It is evident that when the burning temperature increases from 1200 to 1400 °C, the samples with the composition of mixtures 1S and 2S show the same trends of the phase composition changing:

- as to the crystalline phases of calcium silicates – generation of C_3S (1.86, 3.03 Å), intensive production of wollastonite CS (2.97 Å), with minor differences in C_2S;
- as to the crystalline phases of calcium aluminosilicates - decreased content of gehlenite C_2AS (2.86 Å);
- as to the crystalline phases of calcium aluminates - intensive production of C_3A (2.70 Å); with decreased content of CA (2.52 Å) and mayenite $C_{12}A_7$ (4.90 Å);
- decreased content of CaO (2.38 Å) and C_4AF (2.63 Å).

However, in case of the same qualitative phase composition, sample 2S produced from the mixture with the 18 mass % of rice husk differs from sample 1S with the 6 mass % of rice husk by a smaller content in $CaO \cdot SiO_2$, $3CaO \cdot SiO_2$, $CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and a larger content of $CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$ and $2CaO \cdot Al_2O_3 \cdot SiO_2$. The obtained results of sample testing show the difference in composition of the output raw mixtures and maximal value of the burning temperature (Table 5).

In accordance with the classification of DSTU B B.27-91-99, after burning at the maximal temperature of 1200°C and 1400°C, at a setting rate, the studied cement samples on the basis of the chalk – clay – rice husk were referred to different groups.

With a relatively less content of the rice husk after burning at a temperature of 1200 ºC, sample 1S was referred to the group of quick setting ones (the term of beginning is 15 to 45 min). This is considered to be typical for anhydrite and aluminous cements. After increasing the burning temperature to 1400 ºC, it was referred to normally setting ones (the term of beginning is 45 min to 2 h). This is considered to be typical for Portland cement and slag Portland cement.

When increasing the rice husk content to its quantitative ratio 1:1 to clay, sample 2S was referred to the group quickest setting ones (the term of beginning is up to 15 min) after burning at a temperature of 1200 ºC. This is considered to be typical for expanding and self-stressing cement. After increasing the burning temperature to 1400 ºC, it was referred to the group of quick setting ones.

In the course of the research undertaken, the rational composition of raw mixtures was determined on the basis of the system chalk – clay – rice husk for the manufacturing of cement clinker with baking on a maximum temperature of 1400 ºC. In this case, the possibility of adjusting the binding properties of the material from the fast to normal setting is shown due to appropriate changes in the phase composition.

Among the positive aspects of this study should be denoted the directed use of rice husk as a component of the initial mixture, which becomes a source of amorphous silica with increased reactivity in the process of burning, and influences the phase formation and properties of cement clinker.

The main weakness of this study is the use of chalk as raw composition material. Obviously, the expansion of the number of basic carbonate components, first of all limestones and marls, will open up additional opportunities to achieve the goal and to increase efficiency of the study.

Table 5

Properties of clinker samples.

Quality index	*Code of sample and burning temperature*			
	1200ºC		*1400ºC*	
	1S	*2S*	*1S*	*2S*
Finesse of grinding, sieve residue no. 008, mass. %	7	8	7	8
Initial setting time, min	20	10	65	20
Final setting time, min	25	20	110	35
Compressive strength, MPa	33.4	31.7	40.2	38.6

Conclusions

The increase in the volumes of practically used large-tonnage of industrial wastes, including the rice husk resulted from the rice production in the agro-industrial sector, facilitates the solution of the complex issues related to ecology, resources preservation and technology of the manufacturing of silicate building materials.

The expediency of rice husk utilization in the binder technology is defined by the presence of amorphous silica in the chemical composition with an increased reactivity in the process of formation of silicate system structure during burning.

To produce the cement clinker, it is possible to introduce 6–18 mass % of rice husk into raw mixtures obtained based on the chalk–clay–rice husk system, when the quantitative ratio of rice husk to clay ranges between 1:3.4 and 1.1:1.

Due to the X-ray analysis and technological tests, the possibilities of adjustment of the quantitative ratio between clinker minerals and binders when varying the rice husk content in the output mixture by the maximum burning temperature were determined.

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