Usage of Rice Husk for the Production of Low-Temperature Cement: Physico-Chemical and Technological Aspects

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The aim of the work was to deepen scientific understanding of the physicochemical aspects of phase formation of silicate systems of the CaO-SiO_2-Al_2O_3 type when using rice husk as a silica-containing component of technogenic origin.

The research methods included a complex of chemical, X-ray phase analyses, computer calculations and technological testing of materials. Based on the analysis of the results of calculations regarding compliance with the required values of the cement modulus characteristics, possible quantitative ratios of the carbonate component and rice husk were determined.

As a result of technological testing, the compositions of the initial binary mixture based on marl with a content of up to 28 wt. % rice husk were determined, which ensures the production of a mineral binder - an analogue of Roman cement with an increase in strength indicators by 1.5 times.

According to the data of X-ray phase analysis, the peculiarities of physicochemical transformations during the firing of the compositions were established, which are associated with the increased reactivity of amorphous rice husk silica to phase formation with a change in the quantitative ratio of crystalline phases of calcium silicates, the development of C_2AS and A_3S_2 phases distributed in the glass phase.

A conclusion was made about the possibility and feasibility of using rice husk to produce cement fired by low temperature for a comprehensive solution to the issues of chemical technology and resource saving.

Introduction

The chemistry of silicon and its most common compounds - silicates [1,2] is the basis of the creation and development of technology for production of materials for various purposes, including binders [3,4].

Cement [5], whose properties are determined by chemical and phase compositions [6], which mainly depend on the choice of raw materials and the degree of heat treatment - firing, occupies an important place among binders. At the same time, Portland cement production technology is characterized by significant energy consumption associated with clinker firing at a maximum temperature of over 1400 °C and fine grinding of the final product.

From this arises the relevance of research and development in the direction of obtaining a binding material similar to the natural or Roman cement, the production of which involves a lower firing temperature (≤ 1200 ºC) and, accordingly, requires significantly lower energy consumption.

For a long time, the technology for production of mineral binders of the natural or Roman cement type [7-9] is mainly based on the use of one type of raw material - marl as a natural source of CaO, SiO_2, Al_2O_3 oxides, which are necessary for the formation of a given phase composition of the mineral binder during firing. However, the distribution of marl deposits is limited, which makes it necessary to create new raw material compositions for production of mineral binding low-temperature firing with the complex use of various types of raw materials of natural and man-made origin.

At the same time, rice husk attracts attention as a potential man-made raw material [10,11]. 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 rice in the world 750 million tons, more than 150 million tons of waste are being produced every year. At the same time, rice husk, along with organic substances, contains mineral substances, among which silica stands out due to its morphology, the amorphous form of which determines the increased reactivity in the processes of physical and chemical transformations of silicate systems.

Based on the peculiarities of the chemical composition, science-intensive developments have been developed to obtain pure silicon dioxide from rice husk [12-14] as an important component of radio electronics.

From the point of view of the purpose of these studies, the results of developments on the use of rice processing waste in the technologies of mineral binding materials and concrete are important [15-17]. The possibility of improving the technological properties of the concrete mixture and the final product is indicated.

The purpose of this study was to create a mineral binding material of low-temperature firing (≤ 1200 °C) using rice husk as a source of amorphous silica of increased reactivity.

Experimental part

Research methods and objects

The object of the study was raw material mixtures for production of mineral binder based on compositions of natural carbonate rocks with rice husk.

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.

Samples of raw material mixtures were fired in a kiln for 15 hours at a maximum temperature of 1200 °C, holding at a maximum of 1.5 hours, with the temperature rise rate being 150 °C per hour and the cooling rate being 215 °C per hour. 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 methods.

- X-ray diffraction analysis (powdered drugs) using diffractometers DRON–4–0, connected through an interface to the computer.

- determination of cement properties in accordance with current standards. Strength testing was performed on beams measuring 160•40•40 mm with repetition of each series of samples, the relative error of compressive strength values was 7.7% with a confidence probability of 0.95.

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

- chalk of the Zdolbuniv deposit, Rivne region;

- limestone of the Dubovetsky deposit, Ivano-Frankivsk region;

- marls of the Mezhyhirsko-Dubovetsky deposit, Ivano-Frankivsk region and the Bakhchisaray deposit, AR Crimea;

- husk - rice processing waste of company "Rice of Ukraine", Kherson region.

Samples of raw materials differ significantly in their genesis and composition. Carbonate rocks are natural raw materials of sedimentary roots, rice husks are man-made raw materials.

Analysis of the chemical and mineralogical composition of raw materials

According to the chemical composition (**Table 1**), among carbonate rocks, chalk and limestone are close, but limestone differs from chalk by a lower quantitative ratio of CaO : SiO2 (16.9 vs. 71.4) and a slightly higher content of Fe_2O_3 (1.05 vs. 0.13 mass . %). Marls differ from chalk and limestone by a lower content of calcium oxide, a higher content of silicon and aluminum oxides, and a slightly higher content of iron oxides. At the same time, Dubovetsky marl (D) differs from Bakhchysarai marl (B) by a lower content of calcium oxide (42.1 vs. 47.2 wt. %), a higher content of silicon and aluminum oxides with quantitative ratios of SiO_2 : Al_2O_3 - 2.9 vs. 2.7, CaO : SiO_2 - 2.5 vs. 5.7, CaO : Al_2O_3 - 7.4 vs. 15.2.

The chemical composition of rice husk is characterized by a high proportion of losses during roasting, which is associated with organic substances, and a significantly higher SiO2 content compared to other oxides.

Table 1. Chemical composition of raw materials

Samples	Content of oxides, wt. %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
chalk	0.77	0.25	0.13	55.0	0.25	0.08	-	-	43.49
limestone	3.13	0.06	1.05	52.82	0.52	0.10	-	-	42.32
marl D	16.70	5.67	1.71	42.13	`0.68	0.17	-	-	33.21
marl B	8.32	3.11	1.31	47.22	1.02	0.65	-	-	39.37
rice husk	15.64	0.24	0.12	0.61	0.45	0.18	0.48	0.28	82.00

According to its mineralogical composition, marl is characterized by the content of calcite, quartz, and kaolinite; rice husk contains amorphous silica and organic substances (**Figure 1, 2**).

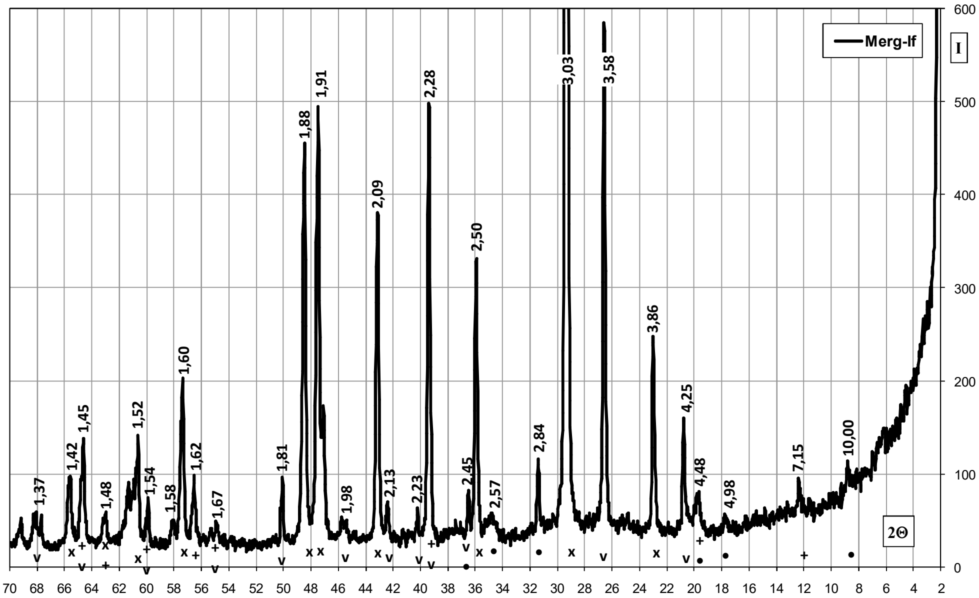

Figure 1. X-ray diffraction of marl: v quartz, + kaolinite, x calcite, ● hydromica

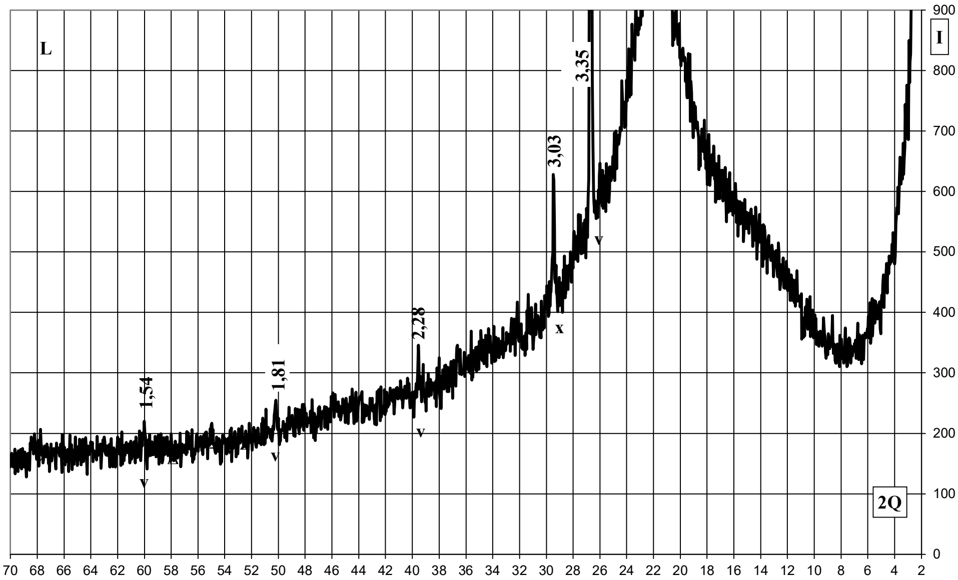

Figure 2. X-ray diffraction of rice husk: **v** quartz; **x** calcite

The given chemical and mineralogical composition of raw material samples indicates the nature and content of their losses during heat treatment (LOI). Obviously, in the case of marl (33.2 wt. %), this is due to the destruction of calcite lattices: $CaCO_3 \rightarrow CaO + CO_2\uparrow$, kaolinite and hydromica with H_2O removal. In the case of rice husk, mass loss (82.0%) is complex in nature and consists of CO_2 and hydrogen emissions due to organic components - cellulose $(C_6H_{10}O_5)n$ and lignin $(C_{31}H_{34}O_{11})n$.

Analysis of compositions of carbonate raw material - rice husk

The analysis of the possible content of rice husk in binary mixtures for production of mineral binders was carried out based on chemical composition data and calculations using the created computer program "Roman Cement" [18].

The results of computer calculations showed that the possible content of rice husk in the binary raw material mixtures significantly depends on the type of carbonate component (**Figure 3**).

Thus, when using binary mixtures with chalk or limestone in the interval of recommended values of the hydraulic modulus HM=1.1-1.7, the possible content of rice husk is from 63 to 76 wt. %, when using Bakhchisarai marl - from 49 to 66 wt. %, when using Dubovets marl - from 4 to 48 wt. %.

In accordance with the specified differences in qualitative composition and quantitative ratios of components, the chemical compositions of mineral binders from binary mixtures differ (**Table 2**).

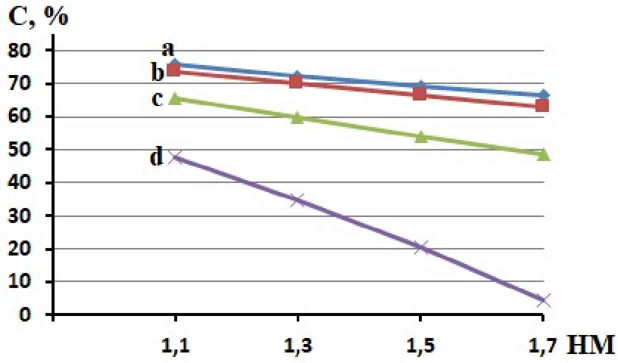

Figure 3. Dependence of the content of rice husk (C) in a mixture based on chalk (a), limestone (b), marl B (c), marl D (d) on the hydraulic module HM

The specified differences in chemical composition determine the value of silica and alumina modules of the binder material, and their dependence on the type of carbonate component and the possible content of rice husk (**Figure 4**).

It is obvious that in the range of values of the hydraulic modulus HM=1.1-1.7, binders obtained from binary mixtures using chalk or limestone are characterized by higher values of the silica modulus n=17.44-31.8 than when using marls, where n=2.5-7.6. At the same time, binders based on the chalk-husk system exceed the limestone-husk system with n=17.4-21.8 in terms of silica modulus values of n=29.8-33.8. The Bakhchisarai marl-scale binder system with n=4.9-7.6 exceeds the Dubovetskyi marl-scale system with n=2.5-4.0 in terms of silica modulus.

Table 2. Chemical composition of binder from binary mixtures

Compositions	Content of oxides, wt. %					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
chalk - rice husk	35.19-45.29	0.79-0.89	0.39-0.45	51.28-61.89	1.25-1.49	0.49-0.60
limestone-rice husk	34.36-44.54	0.52-0.72	1.32-1.46	51.17-61.74	1.46-1.68	0.46-0.57
marl B - rice husk	29.89-40.81	3.74-4.27	1.61-1.81	50.78-61.12	1.85-2.01	1.05-1.06
marl D – rice husk	25.68-37.54	7.09-8.38	2.19-2.55	51.54-62.19	1.03-1.32	0.17-0.32

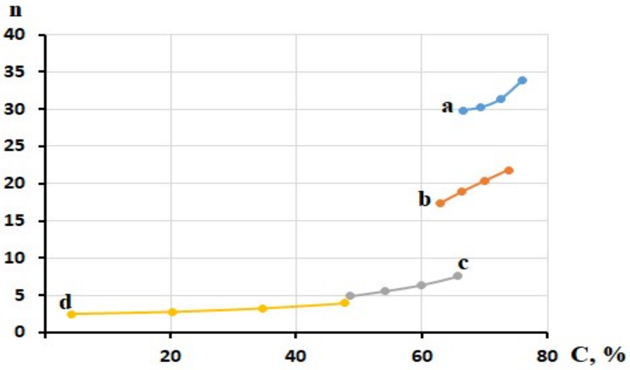

Figure 4. Dependence of the silica modulus (n) on the content of rice husk (C) in mixture based on chalk (a), limestone (b), marl B (c), marl D (d)

Thus, among the researched systems of varieties of carbonate raw materials with rice husk in the case of the Dubovets marl-husk system with the content of the latter C=4.3-27.7 wt. % it is possible to obtain mineral binders characterized by silica modulus n=2.4-3.0, which corresponds to the recommended parameters for cement.

According to the results of the analysis of computer calculations, raw material mixtures based on the composition of Dubovets marl and rice husk were selected for further research (**Table 3**).

Table 3. Composition of raw mixtures

Code of mixture	Quantity of components, mass %	
	marl	rice husk
1m+	100	-
G19	95.7	4.3
G18	72.3	27.7

It is obvious that in terms of chemical composition, mixture G18 with a higher content of rice husk differs from both others in the content and quantitative ratio of oxides: SiO_2 : Al_2O_3 - 3.9 vs. 2.9-3.0, CaO : SiO_2 - 1.9 vs. 2.4 -2.5 with approximately equal CaO : Al_2O_3 = 7.3-7.4 (and a lower content of iron oxides - 1.3 against 1.6-1.7% of **Table 4**).

Table 4. Chemical composition of raw mixtures

Code of mixture	Content of oxides, wt. %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
1m+	16.70	5.67	1.71	42.13	0.68	0.17	33.21
G19	16.66	5.44	1.65	40.35	0.67	0.11	35.12
G18	16.44	4.17	1.27	30.62	0.61	0.12	46.77

The composition of rock-forming minerals corresponds to the given data on the material and chemical composition of mixtures based on marl-rice husk compositions (**Figure 5, 6**).

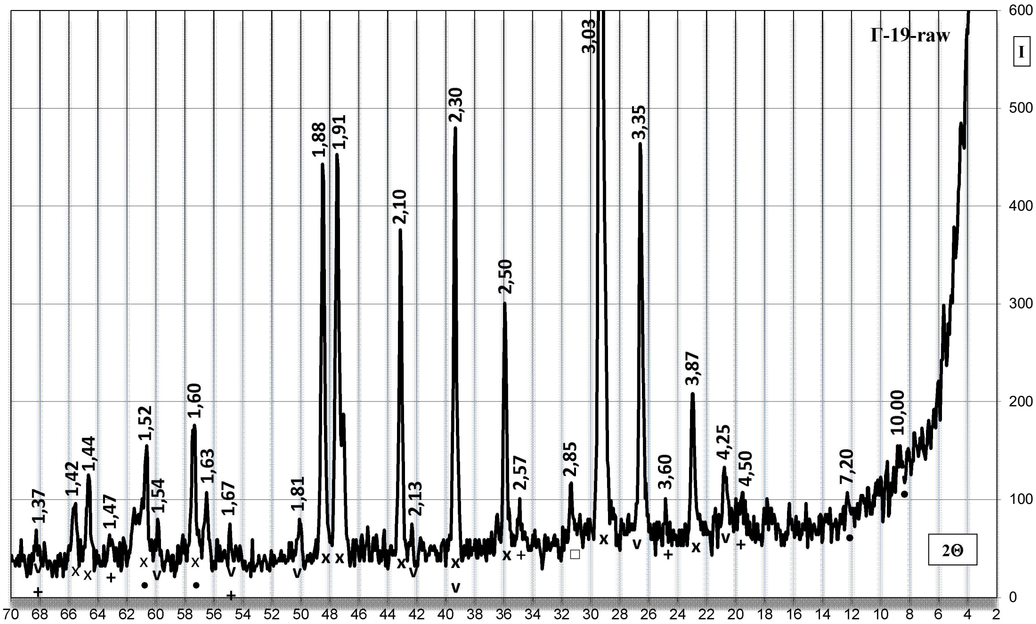

Figure 5. X-ray diffraction of raw mixture G19: v quartz; x calcite, + kaolinite ● hydromica

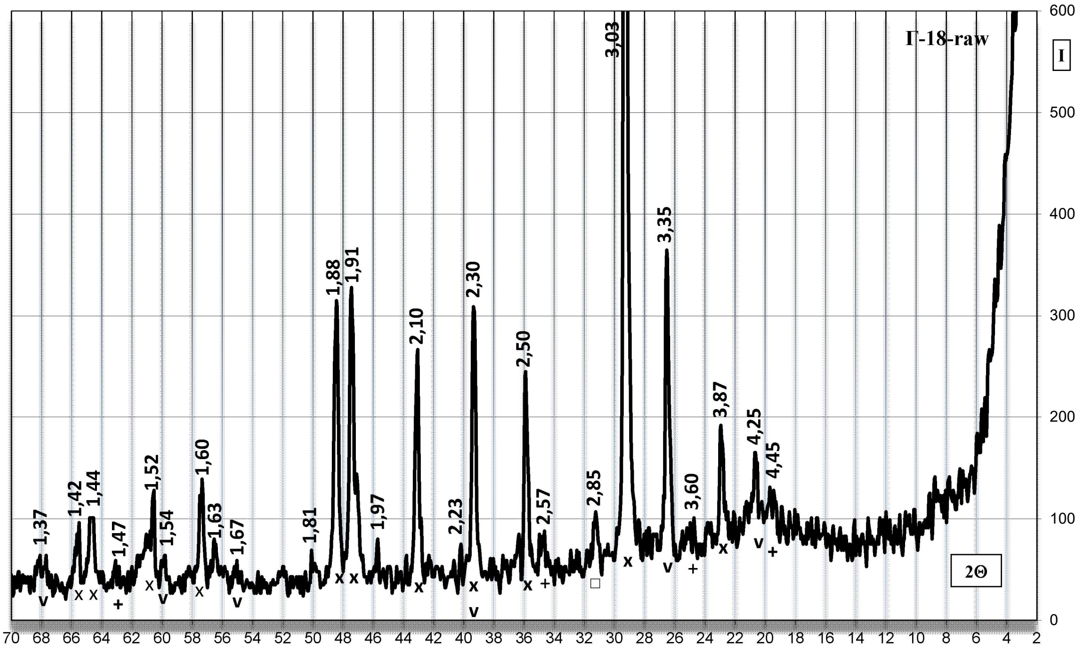

Figure 6. X-ray diffraction of raw mixture G18: v quartz; x calcite, + kaolinite, ● hydromica

At the same time, with an increase in the content of man-made raw materials and the quantitative ratio of husk: marl from 1: 22 in the G19 mixture to 1: 2.6 in the G18 mixture, a diffuse halo appears in the interval 2Θ = 19-22, which is associated with amorphous silica in the composition of rice husks.

Phase composition and properties of the binder material

The results of X-ray phase analysis show the features of phase transformations during firing of the investigated raw material mixtures (**Figure 7-9**).

After firing at the maximum temperature of 1200 ºC, the complete destruction of the crystal lattices of the indicated rock-forming minerals of the raw components, the formation of new crystalline phases and glass phases takes place. The latter is significantly affected by the use of rice husk.

Thus, after firing at 1200 °C, the material from the mixtures based on the marl-rice husk system differs from the sample 1m+ based on marl:

• by the development of the amorphous glassy phase - by the area of the diffuse halo in the interval 2Ɵ = 10-24;

• the development of the crystalline phase of «A_3S_2» (mullite - 5.47, 3.638 Å);

• in relation to the crystalline phases of calcium silicates - by the decrease in the development of «C_2S» (bilinite 2.79, 2.75, 2.61 Å);

• in relation to the crystalline phases of calcium aluminosilicates - by the intensification of the development of «C_2AS» (bilinite - 2.84, 1.75 Å);

• in relation to crystalline phases of calcium aluminates – by intensification of «CA» formation (monocalcium aluminate - 2.52 Å); with less development of «$C_{12}A_7$» (mayenite - 4.90 Å).

The specified differences from sample 1m+ increase with an increase in the content of man-made raw materials and the quantitative ratio of rice husk: marl from 1: 22 in the G19 mixture to 1: 2.6 in the G18 mixture.

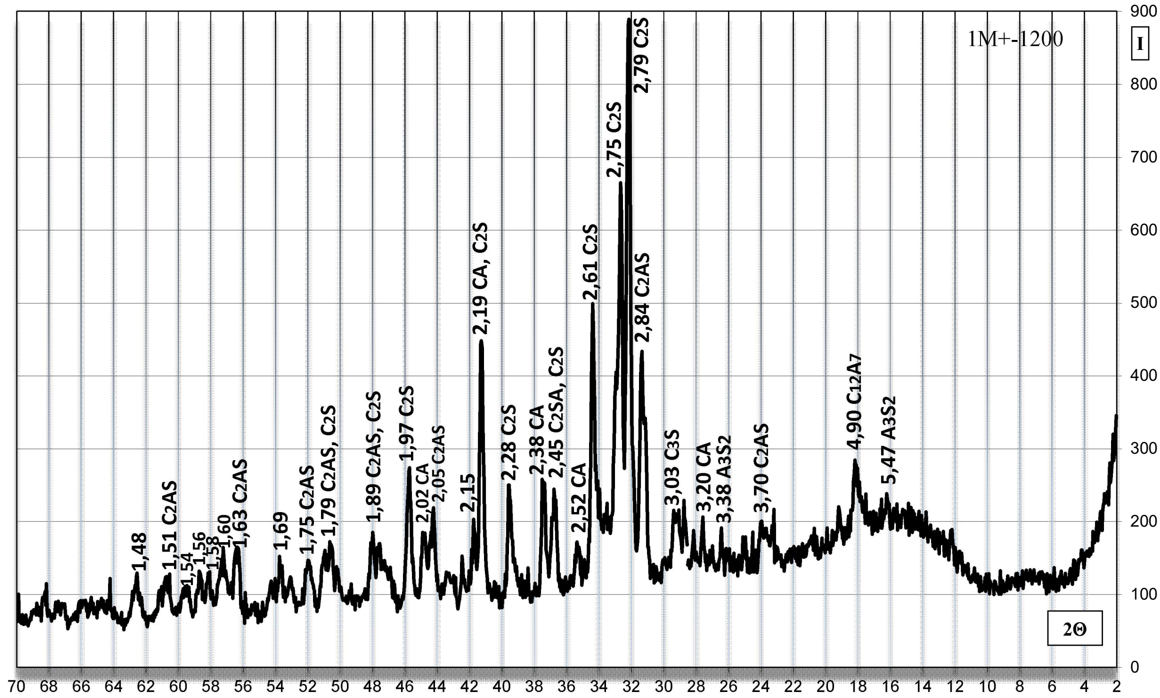

Figure 7. X-ray diffraction of sample 1m+ (1200 °C)

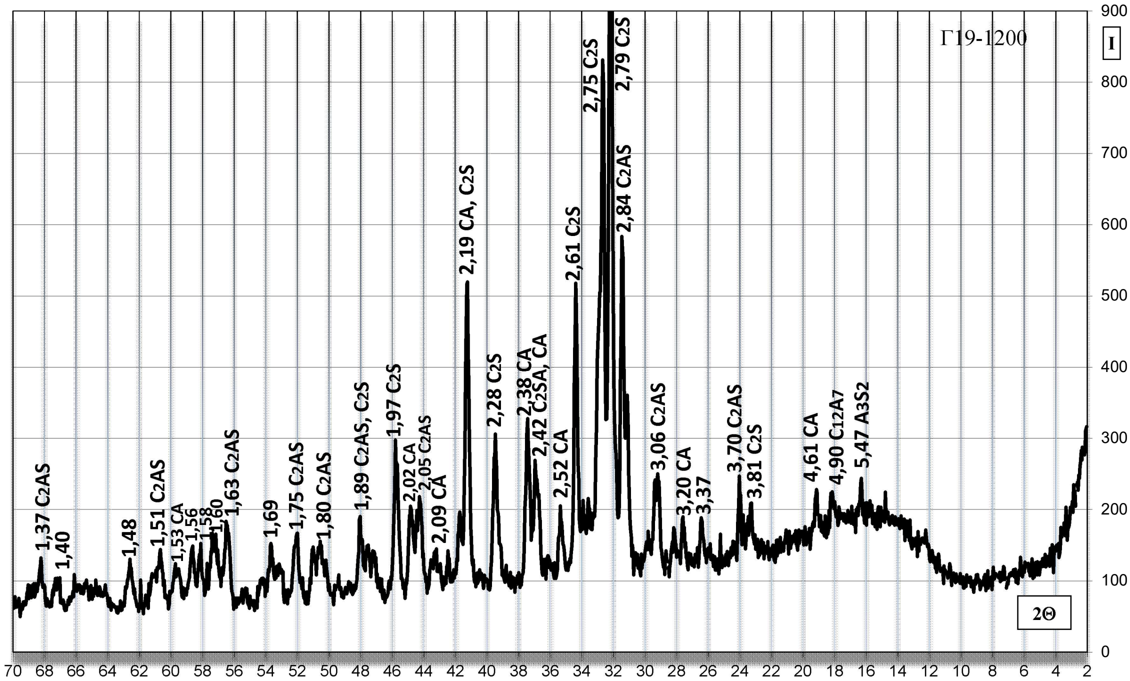

Figure 8. X-ray diffraction of sample G19 (1200 °C)

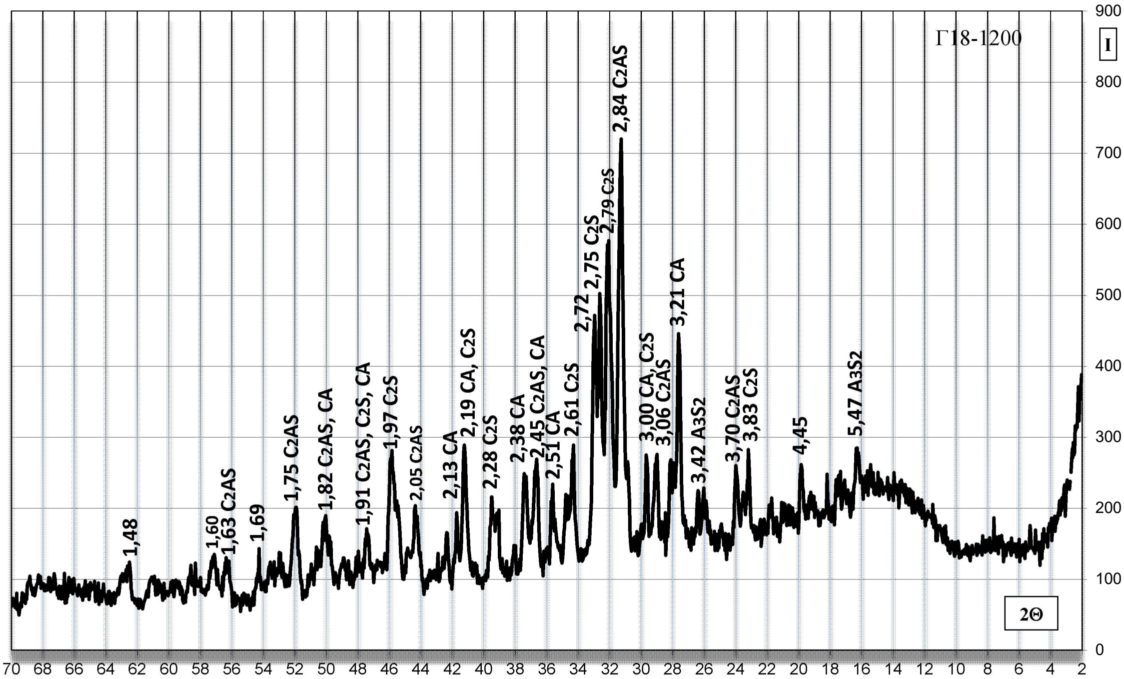

Figure 9. X-ray diffraction of sample G18 (1200 °C)

According to the results of technological tests (**Table 5**), after firing at a maximum temperature of 1200 °C according to the classification of DSTU B V.27-91-99 "Binding Minerals", the obtained material belongs to the group of reduced strength (10-30 MPa), which characteristic of romance cement. At the same time, when rice husk is used, an increase in strength is achieved - by 1.5 times for sample G18 versus 1m+.

According to the speed of hardening, samples 1M+ and Г19 belong to the group of fast hardening (time of onset from 15 to 45 min.), characteristic representatives of which are considered anhydrite and alumina cement. Sample G18 belongs to the group of normal hardening (starting time from 45 min. to 2 h), typical representatives of which are Portland cement, pozzolanic cement, and slag Portlandcement.

The obtained research results correspond to the provision of modern materials science on the relationship between the composition, structure and properties of materials, while the specific features of the chemical and mineralogical composition of rice husk, which contains amorphous silica of increased reactivity, is a factor of phase formation during the calcination of silicate raw mixtures. In turn, the effectiveness of using rice husk depends on the type of carbonate rocks and is most evident in the composition with marl. This, in turn, is connected with the differences in the chemical and mineralogical composition of marl.

Table 5. Properties of binding material

Characteristics	Sample code		
	1m+	G19	G18
Finess of grinding, sieve residue no. 008, mass. %	7	7	7
Consistency, %	35	35	40
Initial setting time, min	25	20	60
Final setting time, min	40	35	210
Compressive strength, MPa			
2 days	2,0	2,4	3.6
7 days	9,5	10.5	14.3
28 days	18.7	20.2	27.4

At the same time, compared to the above-mentioned well-known studies, the results obtained in this work are novel and differ in:

• from works [12-14] – the purpose and direction of the research, namely the use of multi-tonnage rice processing waste in mass cement production versus the production of individual batches of pure silicon dioxide;

• from works [15-17] – practical use of rice husk in chemical cement technology, taking into account calorific value during firing versus the use of rice husk ash with the loss of calorific value factor and with significantly smaller volumes of formation.

Conclusions

1. In accordance with the provisions of modern materials science on the relationship between composition, structure and properties, the peculiarities of the chemical and mineralogical composition of varieties of carbonate raw materials and rice husk as a factor of structure formation and characteristics of the mineral binder have been established._At the same time, the importance of the influence of amorphous silica of rice husk on physicochemical transformations during firing of raw compositions is noted.

2. Based on the results of composition analysis and computer calculations, the relationship between the quantitative ratio of rice husk and types of carbonate components with the modular characteristics of cement was established. At the same time, the feasibility of using binary raw mixtures based on marl with a content of 4.3 - 27.7 wt.% of rice husk was determined, which indicates the possibility of increasing the volumes of utilization of these wastes in mass-intensive cement production.

3. Peculiarities of physicochemical transformations during firing of mixtures at 1200 °C associated with increased reactivity of amorphous silica of rice husk were established: changes in the quantitative ratio of crystalline phases of calcium silicates, development of

phases of calcium aluminosilicates C_2AC and mullite A_3S_2 distributed in the glass phase.

4. Based on the results of technological testing, it is shown that obtaining a mineral binder - an analog of Roman cement with increase of strength in 1.5 times is possible.

5. The prospects and technical and economic efficiency of the industrial use of research results are determined by expanding the range and raw material base of cement production while reducing the consumption of natural materials, utilization of agro-industrial waste, reducing the maximum firing temperature and specific fuel consumption.

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