UDC 691.542

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ON THE USE OF TECHNOGENIC RAW MATERIALS IN CHEMICAL CEMENT TECHNOLOGY

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The article addresses the integrated solution of ecological, resource-saving, and mineral binder technology issues. The possibility of producing cement clinker using large-tonnage waste from the agro-industrial sector and non-ferrous metallurgy as technogenic raw materials was studied. With the help of the «Clinker» computer program, the composition and content of these wastes in the raw material mixture were calculated and analyzed based on specified clinker characteristics. New raw material compositions within the «chalk–rice husk–red mud» system were developed, incorporating 54–59 wt.% of the mentioned wastes. It was experimentally confirmed that medium-strength cement can be produced from such mixtures, and the setting properties can be adjusted from normal to rapid-hardening by varying the ratio of rice husk to red mud. Additionally, the relationship between cement properties and clinker composition, particularly the formation of crystalline phases of aluminates, aluminosilicates, and calcium silicates, was demonstrated.

Keywords: cement, resource saving, raw material mixture, crystalline phases, properties.

DOI: 10.32434/0321-4095-2025-161-4-49-57

Introduction

The technology of mineral binding materials involves the use of large volumes of natural carbonate and clay raw materials, whose resources are finite and non-renewable. Modern requirements for resource conservation and environmental protection are met by reducing the use of natural raw materials through their replacement with man-made materials – wastes from various industries [1,2].

A practical solution to such problems requires identifying patterns of how raw materials of different origins and compositions influence structure formation and the properties of the resulting products, which are the subject of ongoing research and development.

In cement production, the use of waste from other industries is well known and regulated by current standards, primarily as partial substitutes for clinker in finely ground form. Granulated blast furnace slag and fly ash from thermal power plants are used in the largest quantities [3,4]. A small amount (1.5–5.0 wt.%) of iron-containing industrial waste is introduced into raw material mixtures for clinker production as fluxing additives, which has limited significance for the overall volume of their utilization. Therefore, increasing the content of man-made components in high-volume starting mixtures for cement clinker production can contribute to a comprehensive solution to resource conservation challenges and expand the raw material base for industrial production.

At the same time, large-tonnage wastes from the agricultural industry, such as rice husk [5], and from non-ferrous metallurgy, such as red mud [6], are attracting attention as potential man-made raw materials. It has been reported that the production of 1 kg of white rice generates approximately 0.28 kg of rice husk as a by-product of the milling process. As a result, with an annual global rice production of 750 million tons, over 150 million tons of rice husk waste is generated. Moreover, rice husk can serve as a source of amorphous silicon dioxide, which acts as an activator of the physical and chemical processes involved in the structure formation of silicate systems [7].

Red mud, a by-product formed during alumina production from bauxite via the Bayer process in non-ferrous metallurgy, occupies a significant place among large-tonnage industrial wastes [8]. The production of 1 ton of alumina typically results in the generation of 1–1.5 tons of red mud. With the current global alumina production exceeding 133 million tons per year, approximately 175 million tons of red mud are produced annually.

Well-known research and development efforts have been dedicated to exploring effective ways to utilize red mud, including its application in the manufacturing of construction and composite materials [9]. At the same time, noteworthy are studies on the use of red mud in Portland cement technology as an iron-containing corrective additive in raw mixtures for clinker production [10].

The presented analysis highlights the potential for the integrated use of various types of waste as man-made raw materials in the resource-intensive production of mineral binding materials. This has become the focus of our research and represents an urgent challenge in both the chemical technology of silicates and environmental protection.

The analysis of existing data leads to the conclusion that the utilization of industrial waste as man-made raw materials in cement technology needs to be significantly increased. Achieving this requires scientific and technical solutions focused on developing new compositions of raw material mixtures.

Experimental, results and discussion

Objects and methods of research

The object of the study was raw material mixtures for cement clinker production based on the chalk–rice husk–red mud system.

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

The samples of raw mixtures were fired in a furnace for 15 hours at a maximum temperature of 1400^{0}C, with a holding time of 1.5 hours at peak temperature. All comparative samples were fired simultaneously to eliminate any differences in the degree of heat treatment.

The physicochemical analysis methods for silicate raw materials and the testing of binder properties used in this study included [11,12]:

– analysis of chemical composition using standardized procedures;

– X-ray diffraction analysis (of powdered samples) performed on DRON-4-0 and Philips X'Pert PRO – MRD diffractometers, connected to a computer via an interface;

– determination of cement properties in accordance with current standards.

The quantitative analysis of the studied materials in the composition of the raw material mixtures, based on specified cement clinker characteristics, was performed using the developed computer program «Clinker» [13].

The principle of solving the problem rapidly using a computer and specialized software can be summarized as follows:

1. A table containing the chemical composition of an unlimited number of potential raw components is entered.

2. The values of the saturation coefficient (SF) for two-component mixtures, and both the SF and the silica modulus (n) for three-component mixtures, are specified.

3. Based on the selected calculation formulae, all combinations of two or three components that meet the specified clinker characteristics are identified.

Thus, when working with a sufficiently large set of potential raw materials, it becomes possible to promptly determine the rational component ratios for the initial raw material mixture.

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

– chalk from the Zdolbuniv deposit in the Rivne region;

– rice husk – a processing by-product from Ltd. «Rice of Ukraine» in the Kherson region;

– red mud – alumina production waste from PJSC Mykolaiv Alumina Plant and PJSC Zaporizhzhia Aluminum Plant.

The raw material samples differ significantly in their origin and composition.

According to its chemical composition, the chalk sample is characterized by a predominant CaO content (55.0 wt.%), while the rice husk sample contains a higher amount of SiO_2 (15.6 wt.%) with a high SiO_2:Al_2O_3 ratio of 65.2 and a low content of alkaline earth and alkali oxides (Table 1).

Red mud samples are characterized by a high content of iron oxides and exhibit compositional differences related to the type of bauxite used as the raw material, as well as to the technological parameters of its processing. The MGZ sample contains slightly higher amounts of SiO_2, TiO_2, and Na_2O compared to the ZALK sample, but a slightly lower amount of CaO.

According to the mineralogical composition

(Figs. 1 and 2), chalk is characterized by a predominant content of calcite, while the main mineral component of rice husk is amorphous silica. The mineralogical composition of the studied red mud samples is characterized by the presence of goethite ($Fe_2O_3{\cdot}H_2O$), hematite (Fe_2O_3), hydrargillite ($Al_2O_3{\cdot}3H_2O$), rutile (TiO_2), and ilmenite ($FeTiO_3$), with some variations in their quantitative ratios.

Determination and analysis of the composition of raw mixtures

The determination and analysis of the possible quantitative ratios of the studied raw materials in the composition of the starting masses for cement production were carried out using the computer program «Clinker». According to the results of the computer calculations (Table 2), the possible content of rice husk and red mud is 55.7–60.1 wt.% and 45.7–47.2 wt.%, respectively. However, the silica and alumina module values do not meet the recommended ranges of n=1.9–3.0 and p=0.90–2.0 for cement clinker [14].

When using three-component mixtures, the possible total content of rice husk and red mud, within the ranges of SF=0.80–0.95 and n=1.9–3.5, is from 54 to 59 wt.% (Fig. 3). At the same time, the quantitative ratio of rice husk to red mud varies from 8.3 to 17.5.

Based on the results of computer calculations and the above analysis of the dependence of the possible use of man-made raw materials on the characteristics of cement, raw material mixtures D10 and D12 were selected for further research. These mixtures are characterized by a reduced use of natural raw materials, with a total industrial waste content of 56.1–56.4 wt.% (Table 3).

The chemical compositions of the raw mixtures and the resulting clinker correspond to the specified quantitative ratios of components (Table 4). According to their chemical composition, the initial mixtures are characterized by SiO_2:Al_2O_3 ratios ranging from 8.6 to 11.4, CaO:SiO_2 ratios from 2.7 to 2.8, and CaO:Al_2O_3 ratios from 24.3 to 31.1, with iron oxide content ranging from 1.8% to 25%. The clinker produced from these mixtures, all having the same saturation coefficient (SF=0.90), differs in silica modulus n from 2.5 to 3.5 and shows a reduced alumina modulus p ranging from 0.4 to 0.5.

Table 1

Chemical composition of the raw materials

Sample	Content of oxides, wt.%									
	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
rice husk	15.64	0.24	0.12	–	0.61	0.45	0.18	0.48	0.28	82.00
red mud ZALK	7.10	16.60	50.00	5.28	6.34	0.18	0.11	2.10	–	11.70
MGZ	9.80	16.50	47.80	5.80	4.10	0.24	0.10	4.20	–	11.00

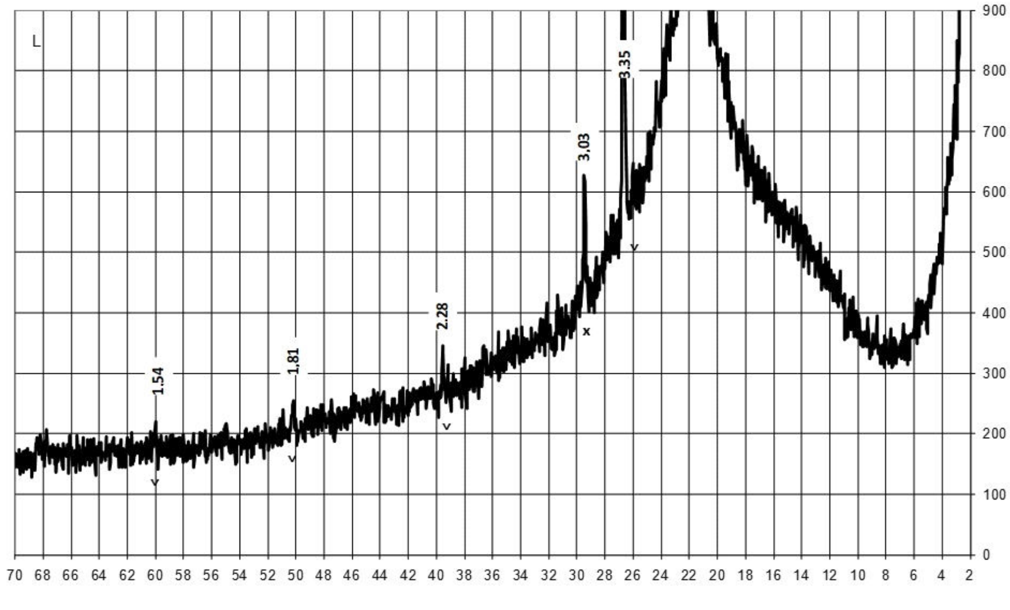

Fig. 1. X-ray diffraction pattern of rice husk: v – β-quartz; x – calcite

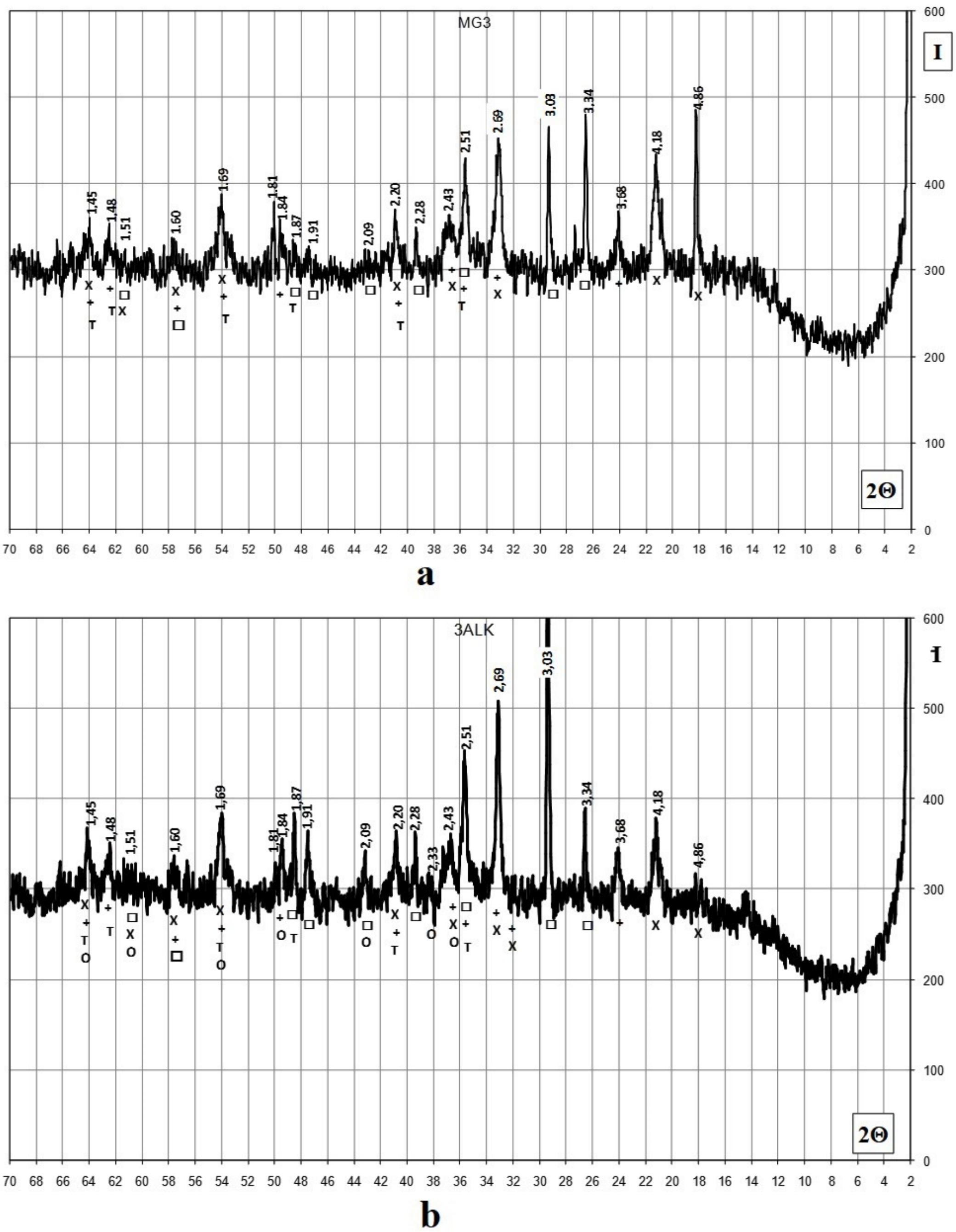

Fig. 2. X-ray diffraction patterns of red mud: MGZ (a) and ZALK (b): x – goethite; + – hematite; т – rutile; o – hydrargillite

Table 2

Composition of binary raw material mixtures and characteristics of the resulting clinker

Composition	Composition of the mixture, %			Characteristics of clinker		
	chalk	rice husk	red mud	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–red mud	52.8–54.3	–	45.7–47.2	0.80–0.95	0.12	0.34

Table 3

Composition of raw mixtures

Designation of mixture	Quantity of components, wt.%		
	chalk	rice husk	red mud
D10	43.9	51.7	4.4
D12	43.6	53.3	3.1

The mineralogical composition corresponds to the specified phase and chemical compositions of the studied mixtures (Fig. 4).

Phase composition and properties of cement

X-ray phase analysis revealed specific features of phase formation in the cement clinker obtained from the investigated raw material mixtures during firing (Figs. 5 and 6).

It was established that at the maximum firing temperature of 1400°C, samples D10 and D12 differ in the qualitative composition of calcium aluminates and aluminosilicates:

– sample D10 is characterized by the formation of crystalline phases of calcium aluminosilicate helenite (C_2AS) at 2.85 and 2.40 Å, and single calcium aluminate (CA) at 4.05 and 2.52 Å;

– sample D12 is characterized by the formation of $C_{12}A_7$ at 4.90 Å and C_3A at 2.70 and 1.56 Å.

Regarding the crystalline phases of calcium silicates, sample D12 differs from D10 by the formation of CS wollastonite (2.97 Å) and a slightly higher amount of C_3S (3.02, 2.61, 1.75 Å) compared to C_2S.

Both samples contain C_2F ferrites and C_4AF calcium aluminoferrites.

According to the results of technological tests (Table 6), after firing at a maximum temperature of 1400°C, the obtained binding material, according to the classification of the Ukrainian state standard DSTU B V.27-91-99, belongs to the medium-strength group (30–50 MPa). Regarding the hardening rate, sample D10 belongs to the normal hardening group (onset time from 45 minutes to 2 hours), typical representatives of which include Portland cement, pozzolanic cement, and slag Portland cement. Sample D12 belongs to the fast hardening group (onset time from 15 to 45 minutes), with specific representatives being anhydrite and alumina cements.

The obtained research results represent a step toward a comprehensive solution to resource conservation and the utilization of large-volume industrial waste in mass cement production. Unlike existing approaches where individual wastes are

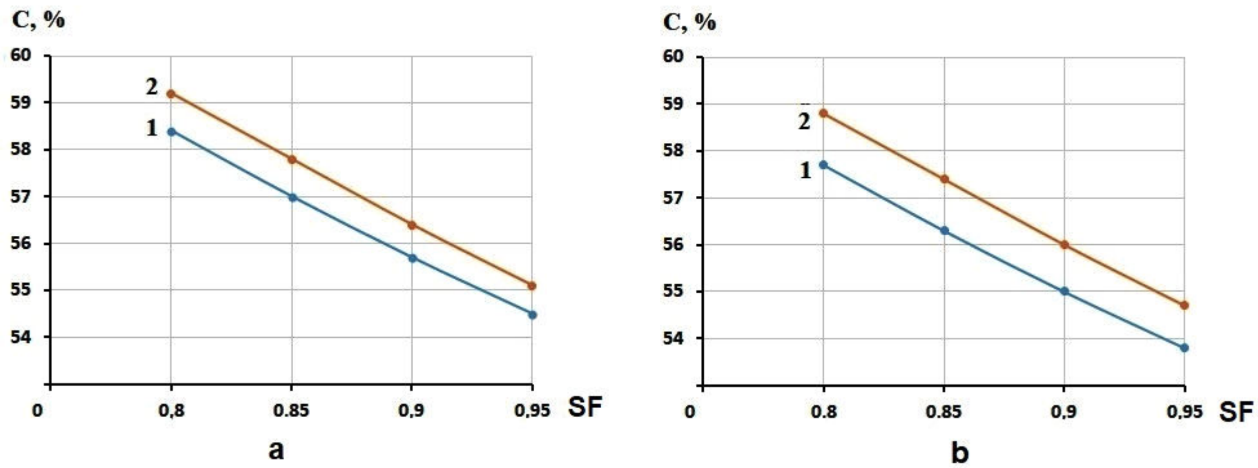

Fig. 3. Dependence of the content of man-made raw materials (C) in the mixture based on the chalk–rice husk–red mud system of ZALK (a) and MGZ (b) on the clinker saturation coefficient (SF) at silica modulus n=1.9 (1) and n=3.5 (2)

Table 4

Chemical composition of raw mixtures and clinker

Designation of sample	Content of oxides, wt.%						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
D10	8.83	1.02	2.50	24.80	0.35	0.13	62.37
	23.47	2.71	6.64	65.90	0.93	0.35	–
D12	8.99	0.79	1.78	24.53	0.36	0.13	63.42
	24.58	2.16	4.86	67.06	0.98	0.36	–

introduced in amounts of 1–5 wt.%, new raw material mixture compositions with a predominant content of man-made raw materials are proposed. However, the practical implementation of these developments requires addressing several applied issues, including the standardization of requirements for waste composition as man-made raw materials in cement chemical technology, logistics, and more. Further in-depth research on the peculiarities of physicochemical processes, considering variations in mixture preparation methods and firing regimes, is advisable.

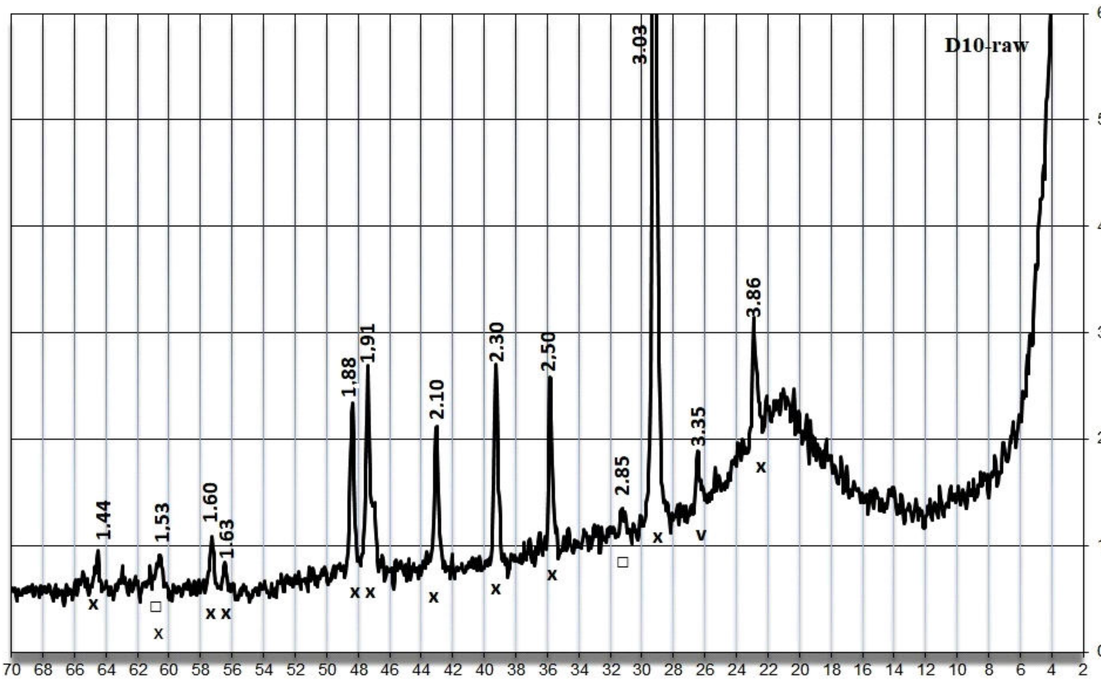

Fig. 4. X-ray diffraction pattern of raw material mixture D10: v – β-quartz; × – calcite; □ – dolomite; + – hematite

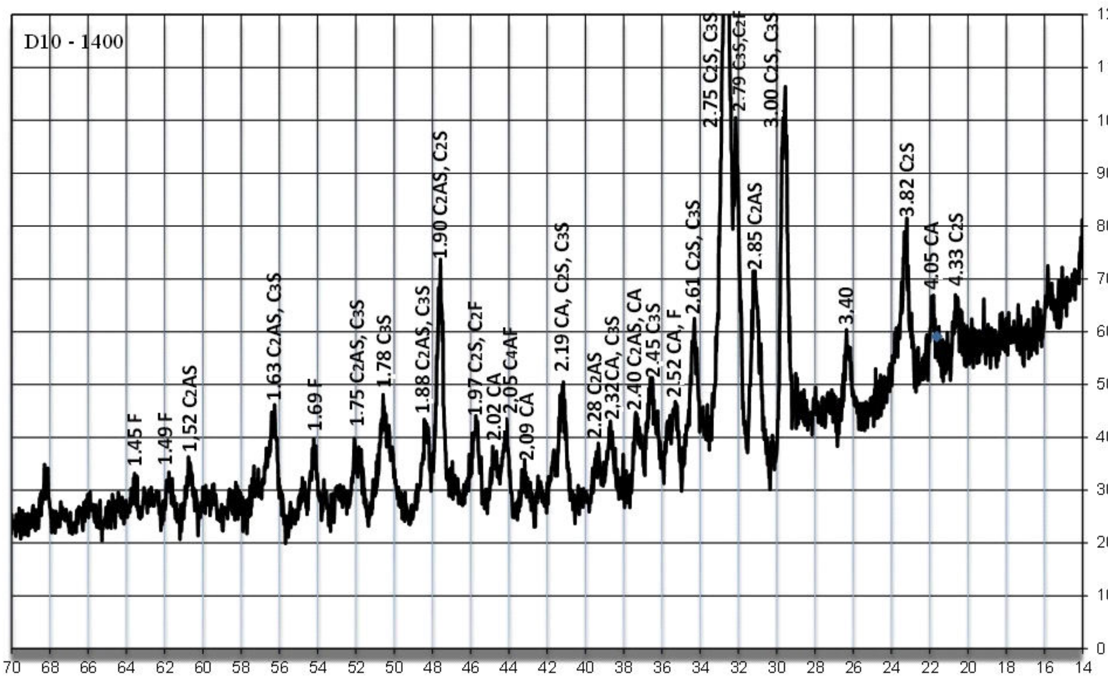

Fig. 5. X-ray diffraction pattern of sample D10 (1400^0C)

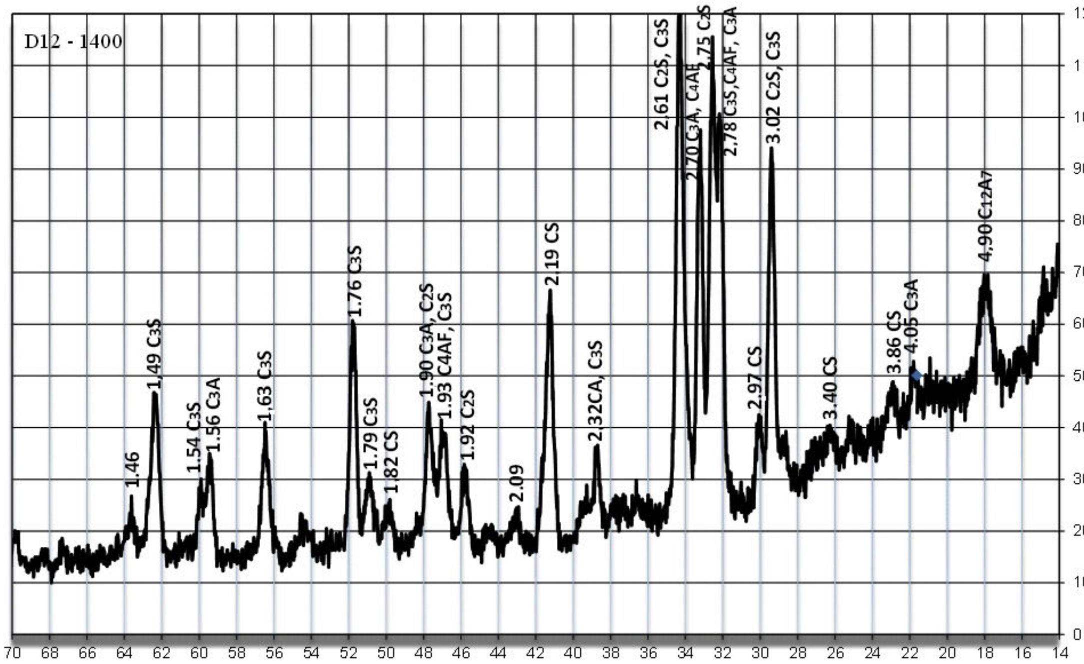

Fig. 6. X-ray diffraction pattern of sample D12 (1400^{0}C)

Table 6

Properties of the mineral binding material

Characteristic	Value	
	D10 sample	D12 sample
fineness of grinding, sieve residue No. 008, wt.%	13	14
consistency, %	35	35
initial setting time, min	80	20
final setting time, min	135	35
compressive strength, MPa:		
- 2 days	5.7	5.1
- 7 days	23.8	21.3
- 28 days	42.3	40.6

Conclusions

1. The use of large-volume industrial waste in mass cement clinker production is a promising area in environmental chemical engineering.

2. Analysis of computer calculations indicates the possibility of introducing 54–59 wt.% of agricultural and non-ferrous metallurgy waste into raw mixtures for cement clinker production based on the «chalk–rice husk–red mud» system.

3. The possibility of producing medium-strength cement with normal and fast hardening from mixtures containing 56 wt.% man-made raw materials, by varying the «rice husk:red mud» ratio from 11.8 to 16.2, has been experimentally confirmed.

4. X-ray phase analysis established the features of clinker composition related to the formation of crystalline phases of aluminates, aluminosilicates, and calcium silicates, which determine the properties of the obtained cement.

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Received 07.02.2025

ЩОДО ВИКОРИСТАННЯ ТЕХНОГЕННОЇ СИРОВИНИ В ХІМІЧНІЙ ТЕХНОЛОГІЇ ЦЕМЕНТУ

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У статті розглядається комплексне вирішення питань екології, ресурсозбереження та технології мінеральних в'яжучих матеріалів. Досліджено можливість одержання цементного клінкеру з використанням великотоннажних відходів агропромислового комплексу та кольорової металургії як техногенної сировини. За допомогою комп'ютерної програми «Clinker» виконано розрахунок і аналіз складу та вмісту цих відходів у сировинній суміші на основі заданих характеристик клінкеру. Розроблено нові склади сировинних сумішей у системі «крейда–рисова лузга–червоний шлам» із сумарним вмістом зазначених відходів 54–59 мас.%. Експериментально підтверджено можливість одержання цементу середньої міцності з таких сумішей, а також регулювання властивостей тверднення від нормального до швидкого шляхом зміни співвідношення рисова лузга:червоний шлам. Крім того, продемонстровано зв'язок між властивостями цементу та особливостями складу клінкеру, зокрема щодо формування кристалічних фаз алюмінатів, алюмосилікатів і кальцієвих силікатів.

Ключові слова: цемент; ресурсозбереження; сировинна суміш; кристалічні фази; властивості.

ON THE USE OF TECHNOGENIC RAW MATERIALS IN CHEMICAL CEMENT TECHNOLOGY

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