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APPLICATION OF VARIETIES OF TECHNOGENIC RAW MATERIALS IN CEMENT TECHNOLOGY

The possibility of manufacturing a mineral binder using large-tonnage waste from other industries has been studied. The object of the research are mixtures for the manufacture of cement clinker based on systems of chalk – clay – scope of paper production and chalk – clay – husks of rice processing. At the same time, urgent tasks of developing the raw material base for cement production and resource conservation were solved. The development of new initial mixtures was carried out taking into account the peculiarities of the chemical and mineralogical composition of varieties of technogenic raw materials. According to the chemical composition, rice alkali is characterized by a content of 15.6 wt. % SiO_2 with a large quantitative ratio of SiO_2:Al_2O_3=65.2 and a small amount of alkaline earth and alkaline oxides. Scop differs from alkali in a large amount of CaO (25.8 wt. %), a lower content of SiO_2 at a quantitative ratio of SiO_2:Al_2O_3=1.3. In this case, there are quantitative ratios of oxides CaO:SiO_2=2.5, CaO:Al_2O_3=3.3, CaO:SiO_2:Al_2O_3=3.3:1.4:1, which determine the probable phase transformations during firing. The main rock-forming mineral in rice husks is amorphous silica; Scope is marked by the presence of crystalline phases of calcite, quartz, and kaolinite. The analysis of the possible content of the studied wastes and the determination of the compositions of the raw mixtures were carried out using the computer program «Clinker». Analysis of computer calculations and experiments indicates the possibility of reducing by 11–16 wt. % consumption of natural raw materials in the composition of mixtures for the manufacture of clinker in comparison with the known production composition. According to X-ray phase analysis, the features of the development of crystalline phases during the firing of mixtures using varieties of technogenic raw materials at a maximum temperature of 1400 °C were established. Based on the data of technological testing, the differences in indicators of binding properties were determined – the setting time of cement when used in the composition of raw mixtures of rice husk and paper scope.

Keywords: *large-tonnage waste, mineral binder, rice husk, paper scope, raw mix, crystalline phases.*

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1. Introduction

The integrated use of raw materials meets the challenges of resource saving and chemical technology [1–3]. A large number of studies of silicate raw materials of natural and technogenic origin have been carried out. At the same time, the most significant practical result was the use of large-tonnage wastes from metallurgy and thermal power engineering – blast-furnace slag, ash and ash, as substitutes for part of the clinker in cement production technology [4–6].

In view of the high mass content of the initial mixtures for the manufacture of cement clinker, it seems appropriate to increase the amount of industrial waste in their composition as a technogenic raw material. However, at present, a small amount (1.5–5.0 wt. %) of iron-containing industrial waste is introduced into the composition of raw mixtures as fluxing additives. In this regard, regarding the increase in the volume of disposal of large-tonnage waste and the expansion of the raw material base of cement production, attention is drawn to:

– rice husk [7–9];
– scope [10, 11].

It is indicated that in the manufacture of 1 kg of white rice, 0.28 kg of rice husks are formed as a by-product of production during the grinding process. As a result, with the annual rice production in the world of 750 million tons, more than 150 million tons of waste is generated. At the same time, rice alkali can become a source of amorphous silicon dioxide as an activator of physicochemical processes of structure formation of silicate systems [12, 13].

Scope is formed during the production of paper and cardboard and is a mixture of cellulose fibers, organic dispersed and inorganic substances. Features of the composition and a certain heat-generating ability of the scope determined the directions of well-known research and development on its utilization in the energy and agro-industrial complexes for the manufacture of building materials [14–16]. At the same time, in relation to building materials, it is proposed to use the scope as filler in the manufacture of heat and sound insulating plates and as a raw material component for the manufacture of expanded clay and agloporite – expanded granular ceramic materials.

However, the actual volumes of disposal of large-tonnage waste, including rice husk and scope, do not correspond

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to the quantitative level of generation and accumulation. Further solution of such problems of resource saving and chemical technology of silicates requires determining the regularities of the influence of the concentration of raw materials on the structure formation and properties of products. In the direction of solving such problems in the production of cement, this work has been completed.

The results of the analysis of known data lead to the conclusion that a significant increase in the volume of industrial waste disposal in cement technology requires scientifically based solutions for the development of new initial mixtures, taking into account the characteristics of the chemical and mineralogical composition of varieties of technogenic raw materials.

So, mixtures for the manufacture of cement clinker based on chalk-clay-technogenic raw materials have become *the object of research.*

The aim of research is to analyze the possibilities and large-tonnage waste from the production of paper and rice in the raw mix for the production of cement clinker.

2. Research methodology

Raw mixtures were prepared by dosing the components by weight, mixing and homogenizing in a ball mill, firing and grinding the final product in accordance with modern cement technology.

Samples of raw mixtures were burned in the oven for 15 hours at a maximum temperature of 1400 °C, holding at a maximum of 1.5 hours. All samples of the comparison mixtures were fired simultaneously to exclude the possibility of a difference in the degree of heat treatment.

Methods for the physicochemical analysis of silicate raw materials and testing the properties of the binder material that were used in this work included:

– analysis of the chemical composition using standardized procedures;
– X-ray diffraction analysis (powder preparations) using a DRON-4-0 diffractometer. When deciphering the phase composition, the database of the International Committee for Powder Diffraction Standards (ICPDS) was used;
– determination of indicators of cement properties in accordance with applicable standards.

To determine the rational compositions of the initial mixture, the following types of raw materials were used:

– chalk of the Zdolbuniv deposit of the Rivne region (Ukraine);
– clay from the Kryvyn deposit in the Khmelnytskyi region (Ukraine);
– red mud – alumina production wastes – Zaporizhzhia Aluminum Plant JSC (Ukraine);
– husks – rice processing wastes of Rice Ukraine LLC, Kherson region (Ukraine);
– scope – paper production wastes of PJSC «Kyiv Cardboard and Paper Combine» (Ukraine).

Samples of raw materials differ significantly in genesis and composition.

According to the chemical composition (Table 1), chalk is characterized by a predominant content of CaO (55.0 wt. %), Kryvyn clay – by a high content of SiO_2 at a quantitative ratio of SiO_2:Al_2O_3=4:1. Rice alkali is marked by a high content of SiO_2 (15.6 wt. %) with a high quantitative ratio of SiO_2:Al_2O_3=65.2 and a small amount of alkaline earth and alkaline oxides.

The scope sample differs from alkali in a large amount of CaO (25.8 wt. %), a lower content of SiO_2 at a quantitative ratio of SiO_2:Al_2O_3=1.3. In this case, there are quantitative ratios of oxides CaO:SiO_2=2.5, CaO:Al_2O_3=3.3, CaO:SiO_2:Al_2O_3=3.3:1.4:1, which determine the probable phase formation during firing.

Red mud has the highest content of iron and titanium oxides.

3. Research results and discussion

According to the mineralogical composition, chalk is characterized by:

– the predominant content of calcite;
– Kryvyn clay belongs to the group of polymineral;
– the main rock-forming mineral of rice husk is amorphous silica;
– the scope is marked by the presence of crystalline phases, mainly calcite, quartz, kaolinite (Fig. 1, 2).

Based on the above data, using the CLINKER computer program [17], the composition of the studied raw mixtures for the manufacture of cement clinker based on the traditional chalk-clay system with varieties of technogenic raw materials as the 3rd component was determined (Table 2).

At the same time, it is obvious that the composition of mixtures using scope and rice husks (S20, 2L) in comparison with the known iron-containing additive (Vk) is characterized by a decrease in the share of natural raw materials (82–87 versus 98 wt. %) and a corresponding increase in the share of waste (13–18 vs. 2 wt. %).

Table 1

Chemical composition of raw materials

Raw material	The content of oxides, wt. %									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	Na_2O	K_2O	l.o.i.
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
Red mud	7.10	16.60	50.00	5.28	6.34	0.18	0.11	2.10	–	11.70
Husk	15.64	0.24	0.12	–	0.61	0.45	0.18	0.48	0.28	82.00
Scope	10.23	7.80	0.56	0.27	25.77	1.27	0.20	0.33	0.17	50.41

Note: l.o.i. – loss on ignition

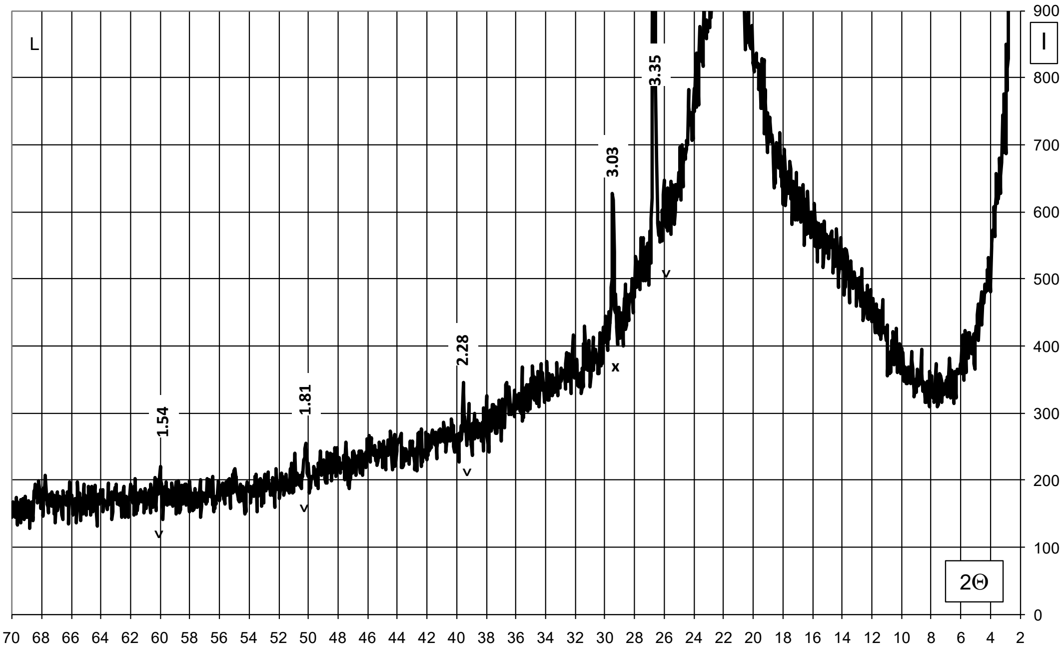

Fig. 1. Diffractogram of rice husk sample: v – quartz; x – calcite

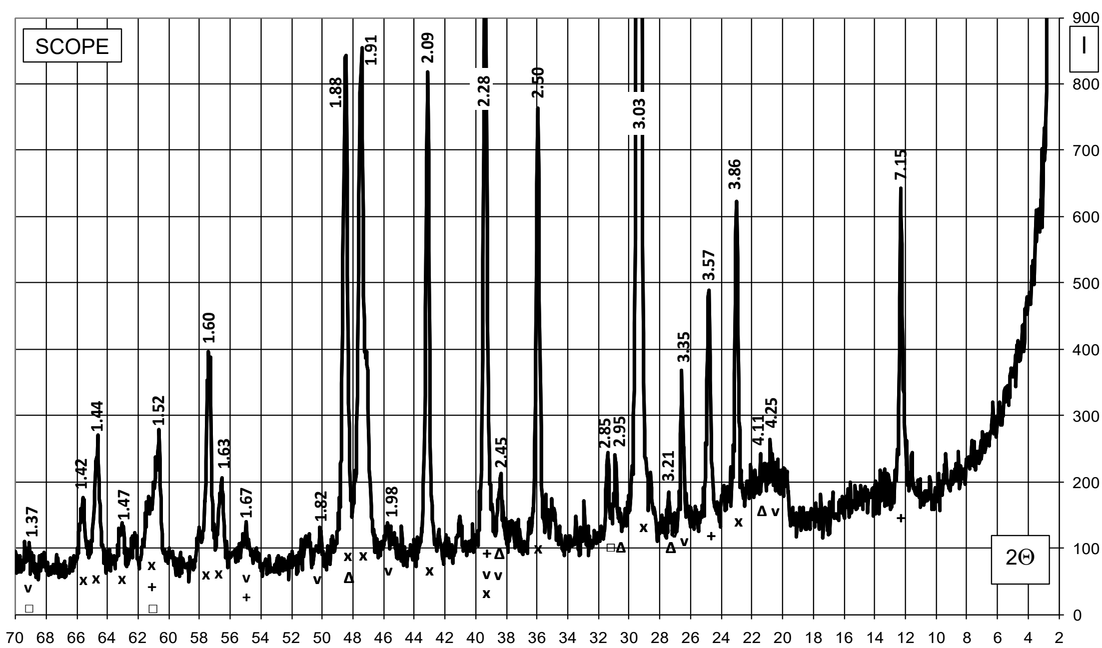

Fig. 2. Diffraction pattern of the scope sample: + – kaolinite; x – calcite; v – quartz; Δ – feldspar

Table 2

Composition of raw mixes

Probe code	Component content, wt. %				
	Chalk	Kryvyn clay	Red mud	Scope	Rice husk
Vk	77.2	21.1	1.7	–	–
S20	68.7	18.6	–	12.7	–
2L	66.00	16.0	–	–	18.0

Analysis of the chemical composition of the studied raw mixtures indicates the presence of differences associated with the quantitative ratio of the components and varieties of technogenic raw materials (Table 3). Thus, according to the quantitative ratio of oxides SiO_2:Al_2O_3, which in the chemical technology of silicates characterizes the possible degree of sintering during firing, the following series is determined: 2L(4.8)>Vk(3.6)>20S(3.2). That is, the 20S mixture is relatively more refractory and probably requires a slightly higher firing temperature. Differences in the quantitative ratio of oxides of calcium, silicon, aluminum and iron determine the likelihood of formation during firing of the main clinker phases. Thus, the CaO:SiO_2 ratio is 3.1 for Vk and 20S mixtures against 2.8 for a 2L mixture, which in the latter case indicates a high probability of the formation of calcium silicate phases. According to the CaO:Al_2O_3 ratio, the following series takes place: 2L(13.1)>Vk(11.0)>20S(9.8). That is, the 20S mixture is characterized by a relatively higher probability of formation of crystalline phases of aluminates and calcium aluminosilicates during firing.

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Table 3

Chemical composition of raw mixes

Probe code	Component content, wt. %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	l.o.i
Vk	14.14	3.93	2.21	43.32	0.64	0.10	35.66
20S	13.66	4.23	1.24	41.84	0.73	0.15	38.15
2L	13.47	2.82	1.04	37.04	0.59	0.11	44.93

Note: l.o.i. – loss on ignition

Regarding the content of iron oxides, the smallest amount (1.04 wt. %) is the mixture 2L, the largest (2.21 wt. %) is the production mixture Vk.

The data of X-ray phase analysis correlate with the indicated differences in the chemical composition (Fig. 3–5). First of all, this concerns the 2L mixture, which is characterized by a lower content of calcite (0.249 and 0.209 nm), kaolinite (0.715 nm) and hydromica (0.990 nm).

The obtained calculated and experimental data testify to the difference in the compositions and structure of cement clinker made from the studied mixtures during the differentiation of varieties of technogenic raw materials.

So, in terms of chemical composition, with approximately the same CaO content (67.3–67.7 wt. %), the 2L clinker sample is distinguished by a smaller amount of aluminum oxides and a large quantitative ratio of SiO_2:Al_2O_3 – 4.8 versus 3.2–3.6 (Table 4).

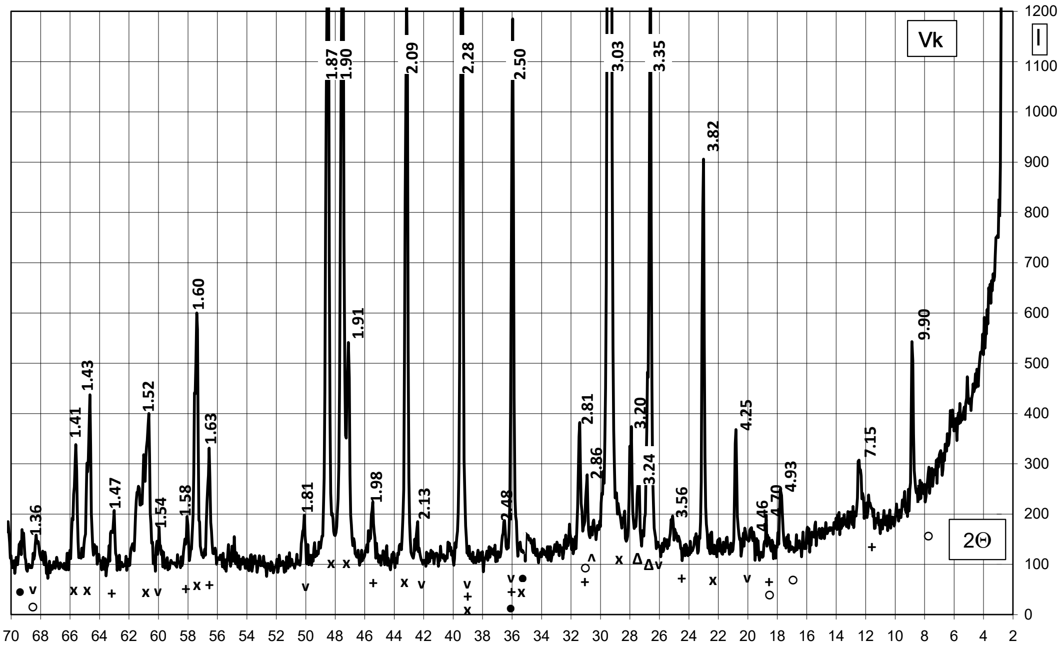

Fig. 3. Diffraction pattern of the raw mixture Vk: x – calcite; v – quartz; Δ – feldspar; + – kaolinite; o – hydromica; ^ – dolomite; ● – goethite

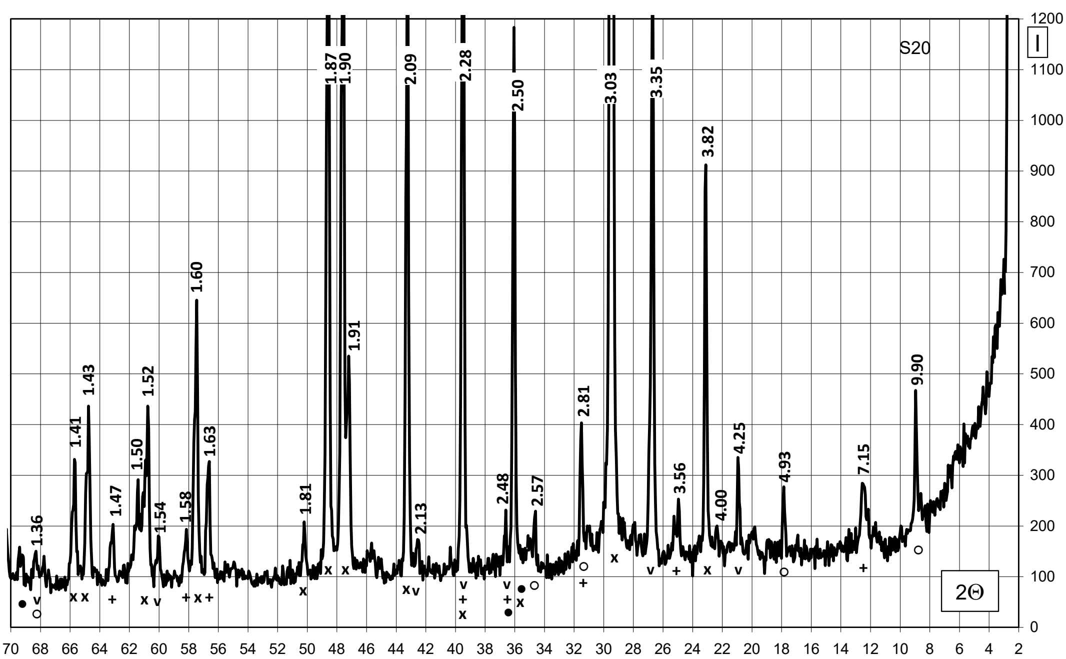

Fig. 4. Diffraction pattern of the raw mixture 20S: x – calcite; v – quartz; + – kaolinite; o – hydromica; ● – goethite

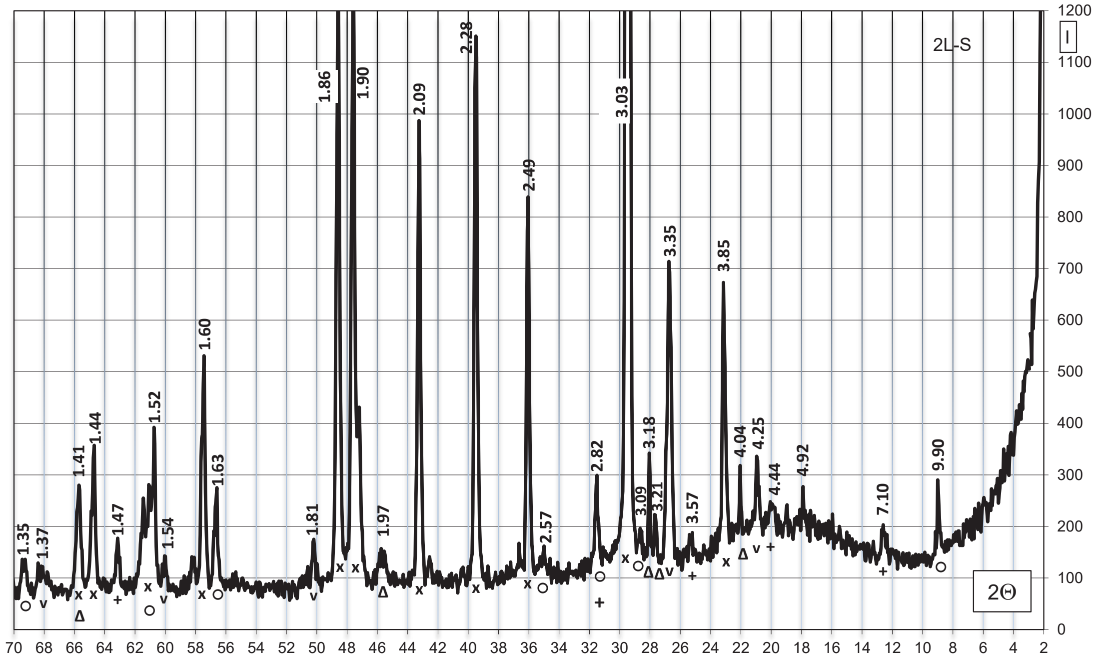

Fig. 5. Diffraction pattern of raw mix 2L: x – calcite; v – quartz; + – kaolinite; o – hydromica; Δ – feldspar

According to the results of X-ray phase analysis after firing the studied raw mixtures at a maximum temperature of 1400 °C, cement clinker samples with a similar qualitative phase composition have differences in the degree of development of individual components (Fig. 6–8):

– relative to the crystalline phases of calcium silicates, with an approximately equal level of formation of C_3S and C_2S, sample 20S is distinguished by a large amount of wollastonite CS (0.297 nm);
– relative to the crystalline phases of calcium aluminosilicates, samples 20S and 2L are distinguished by an increase in the formation of gellenite C_2AS (0.286 nm);
– relative to the crystalline phases of calcium aluminates, the 20S sample is characterized by a large formation of C3A (0.270 and 0.156 nm) and CA (0.405, 0.300 and 0.209 nm);
– sample 2L is marked by a lower content of iron-containing crystalline C_4AF (0.262 and 0.733 nm) and glass phase (according to the diffuse halo area).

Table 4

The chemical composition of clinker

Probe code	Component content, wt. %					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Vk	21.98	6.11	3.43	67.33	0.99	0.16
20S	22.09	6.83	2.01	67.65	1.18	0.24
2L	24.46	5.12	1.89	67.26	1.07	0.20

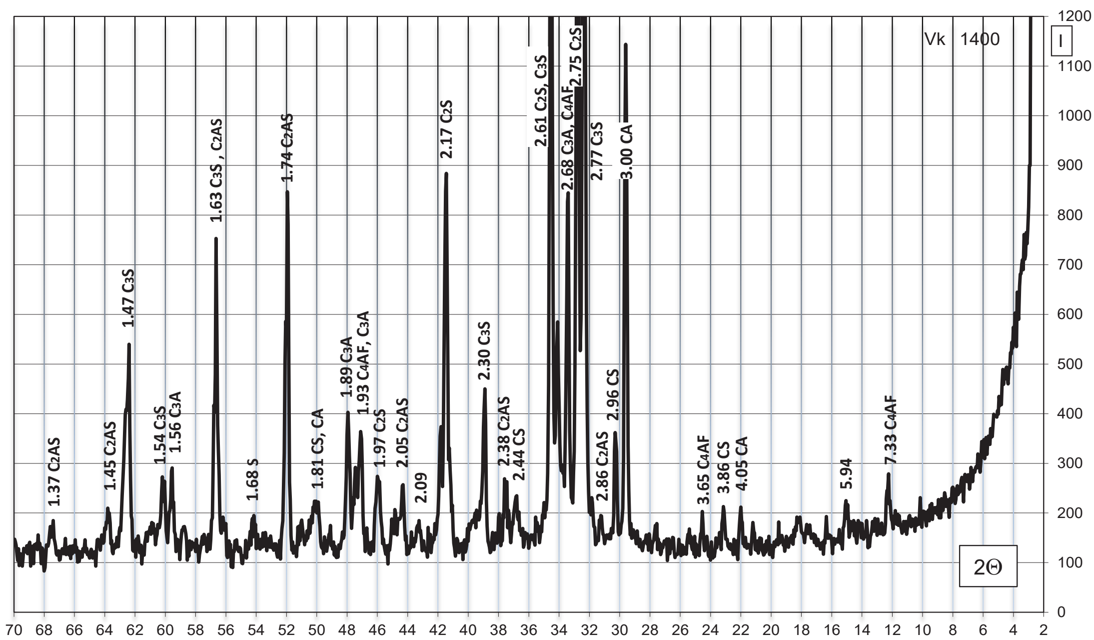

Fig. 6. X-ray diffraction pattern of a sample of clinker Vk after firing at 1400 °C

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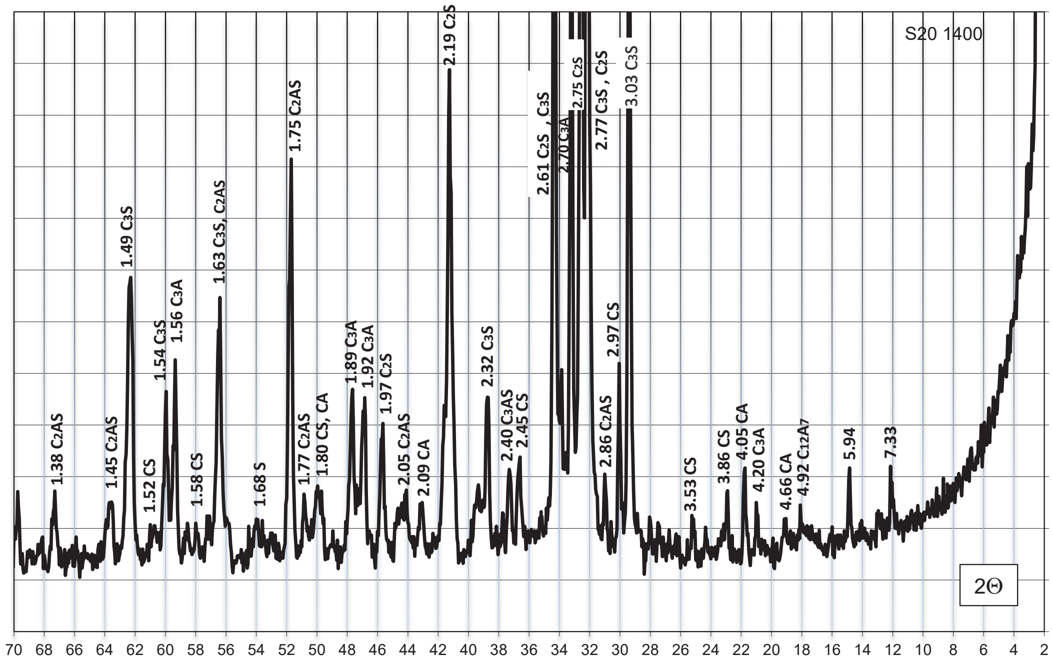

Fig. 7. X-ray diffraction pattern of clinker sample 20S after firing at 1400 °C

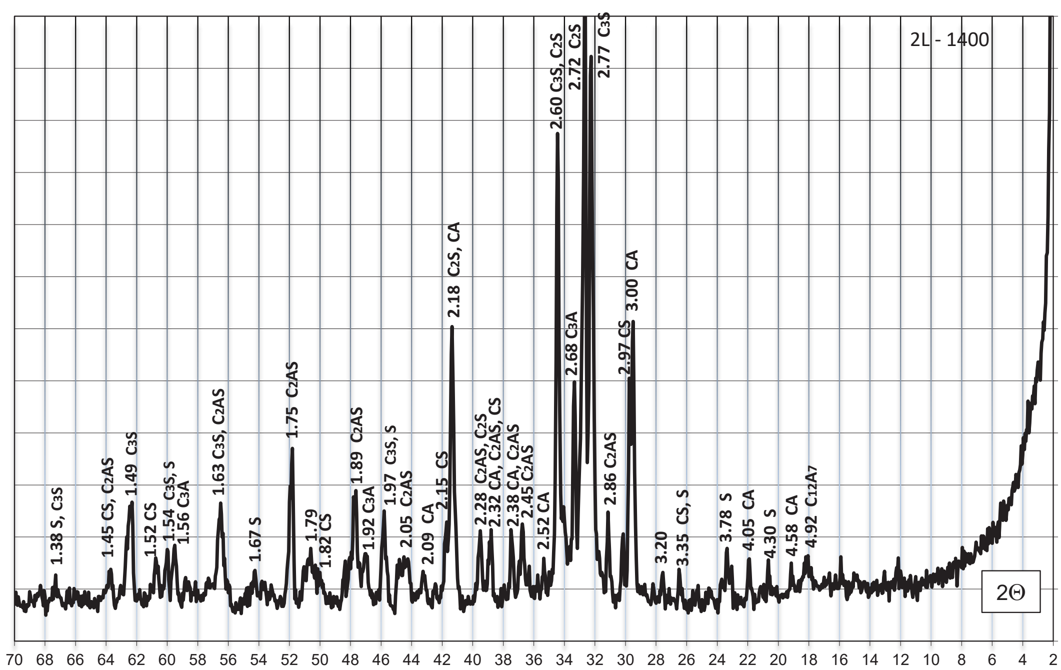

Fig. 8. X-ray diffraction pattern of clinker sample 2L after firing at 1400 °C

According to the results of technological testing after firing at a maximum temperature of 1400 °C according to the classification of DSTU B V.27-91-99, the binder mineral samples of the obtained material belong to the group of medium strength (30–50 MPa), with certain differences in setting speed (Table 5).

So, samples Vk and 2L belong to the group of fast-wearing (onset time from 15 to 45 minutes), the typical representatives of which are considered to be anhydrite and aluminous cement. At the same time, with the same setting start time, sample 2L differs from Vk in the intensification of the process and a corresponding decrease in the end setting time.

Sample S20 belongs to the group of normal pressure (starting time from 45 to 120 minutes), the characteristic representatives of which are Portland cement, pozzolanic cement and Portland slag cement.

Table 5

Binder properties

		Vk	S20	2L
Grinding fineness, sieve residue 008, wt. %		14	15	15
Setting time, min	start	30	65	30
	finish	115	125	50
Compressive strength after 28 days, MPa		39.0	39.4	38.6

This work touches upon the issues of utilization of only two types of waste as man-made raw materials for the production of cement clinker. However, the expediency of developing this line of research into other types of waste is obvious. It is clear that the practical implementation of these developments requires a comprehensive solution of scientific, technical and logistical issues related to the transportation of technogenic raw materials.

4. Conclusions

In the course of the study, the features of the chemical and mineralogical composition of paper and rice production wastes were established. At the same time, emphasis is placed on the quantitative ratio of the oxides CaO, SiO_2, Al_2O_3, which indicate probable phase transformations during firing. Based on the analysis of computer calculations and experiments, the possibility of reducing by 11–16 wt. % of the cost of natural raw materials compared to a known production warehouse. X-ray diffraction analysis established the features of the development of crystalline phases during the firing of mixtures with varieties of waste at a maximum temperature of 1400 °C. Differences in indicators of binding properties of cement were determined when using rice husks and paper scopes. The use of large-tonnage industrial waste in the mass-intensive production of cement contributes to a comprehensive solution of the issues of silicate technology and resource saving.

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