Mineral Binding Material using Red Mud

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Submitted: September 15, 2023; **Published:** October 04, 2023

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Abstract

The possibility of producing a mineral binder material for low-temperature firing (≤ 1200°C) with the integrated use of natural raw materials and alumina production waste - red mud has been studied. An analysis was carried out of the dependence of the binary and ternary compositions of the initial raw material mixtures on the specified characteristics of the binder material using the developed computer program "Roman Cem". The compositions of mixtures for the manufacture of mineral binder material using 2.4-29.1 wt. % of red mud as technogenic raw material was determined. The features of the formation of the phase composition and properties of the binder during firing of raw material mixtures with a maximum temperature of 1100oC are shown.

Keywords: Material; Mineral binder; Red mud; Raw material mixture; Composition; Firing; Phases crystalline; Properties

Introduction

The technology of mineral binding materials is associated with the use of large volumes of carbonate and clay natural raw materials, the resources of which are exhaustive and non-renewable [1-3]. The modern requirements of resource saving [4-8] correspond to the reduction of the use of natural raw materials with the replacement of them by man-made materials - waste from various industries [7-11].

In the production of cement, the use of waste from other industries is known and regulated by current standards [12,13], mainly as substitutes for part of the clinker when it is finely ground. At the same time, granulated blast furnace slag and TPP fly ash are used in the largest quantities [14,15]. A small amount (1.5 - 5.0 wt.%) of iron-containing industrial waste is introduced as fluxing additives to the composition of the raw material mixtures for the production of clinker, which slightly affects the volume of their utilization. It is obvious that the increase in the content of man-made components in the composition of mass-intensive starting mixtures for the production of clinker will contribute to the comprehensive solution of the problems of resource saving and provision of the raw material base of industrial production.

The practical solution of such problems requires determining the patterns of influence of raw materials of different genesis and composition on the structure formation and properties of

products, in the direction of which research and development are carried out. At the same time, multi-ton wastes of ferrous and non-ferrous metallurgy attract attention as a possible man-made raw material.

Wastes of non-ferrous metallurgy [16] are slags, sludges, ore beneficiation wastes. Thus, a by-product of the processing of bauxite into alumina according to Bayer's method is red mud [17-19]. According to the specified industrial method, during the treatment of bauxite with caustic soda, approximately 35-40% of the original ore goes to waste, forming an alkaline red mud with a concentration of the solid phase of 15-40%. As a result, 0.8-1.5 t of red mud is formed during the production of 1 ton of alumina. Data are available that with the annual world production of 101 million tons of alumina, 120 million tons of red mud are being produced, including about 1 million tons in Ukraine during the operation of Mykolayiv Alumina Plant and Zaporizhzhya Aluminum Combine.

Red mud is characterized by an increased content of iron oxides, ferrites and calcium alumina ferrites, aluminates, aluminosilicates and sodium ferrites [20]. Large volumes of accumulation of red mud create an ecological hazard, which emphasizes the relevance of the development of its disposal, if to take into account physical and chemical properties and the impact on the characteristics of silicate systems and the properties of the final product [21-23]. From the point of view of the volumes of

formation and composition, the use of red mud as a man-made raw material in the mass production of mineral binding materials is promising [24-26]. At the same time, the choice of the most acceptable technical solutions for a significant increase in the amount of man-made raw materials should be based on the development and implementation of new compositions based on relevant research of silicate systems, the results of which are presented in this work.

Experimental Part

The object of the study was raw material mixtures for the production of low-temperature fired cement with the complex use of natural and man-made raw materials. 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 mixtures were fired in a furnace for 15 hours at a maximum temperature of 1050-1400°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:

a)	analysis of chemical composition using standardized procedures.

b)	X-ray diffraction analysis (powdered drugs) using diffractometers DRON-4-0 and Philips X'Pert PRO - MRD, connected through an interface to a computer.

c)	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:

a)	chalk of Zdolbuniv deposit in Rivne region and limestone of Dubovetsky deposit in Ivano-Frankivsky region

b)	marl of Dubovetsky deposit in Ivano-Frankivsky region (marl D) and marl of Bakhchisaraysky deposit in Crimea region (marl B)

c)	pyloquatz of PJSC "Novoselitsky mining and beneficiation plant" of Kharkiv region

d)	perlite from the Berehiv deposit of Zakarpattia region

e)	red mud - alumina production waste of PJSC Mykolaiv Alumina Plant (MGZ) and PJSC Zaporizhzhya Aluminum Plant (ZALK).

Samples of raw materials differ significantly in their genesis and composition. According to the chemical composition, among the studied raw materials, samples of Zdolbniv chalk and Dubovets limestone, known for their use in cement production, are characterized by a high content of CaO (Table 1).

Table 1: Chemical composition of raw materials.

Samples	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
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
clay	60,96	15,66	5,57	0,79	3,33	2,04	0,16	0,30	2,70	8,48
pyloquartz	99,66	0,16	0,06	-	-	-	-	-	-	0,12
perlite	72,08	12,92	1,50	0,90	0,88	0,63	-	3,76	4,33	3,0
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

Marl samples differ from chalk and limestone in a significantly higher content of silicon and aluminum oxides, and in their content and quantitative ratio of SiO_2: Al_2O_3. The sawdust sample is characterized by a predominant silica content, the pearlite sample by a significant amount of silica with a ratio of SiO_2: Al_2O_3 = 6 : 1 and alkaline oxides of the type R_2O = 8.09 wt. %. Red mud samples are characterized by a high content of iron oxides and have differences related to the composition of the raw bauxite raw material and technological parameters of its processing. Thus, the

MGZ sample is characterized by a slightly higher content of SiO_2, TiO_2 and Na_2O than that of ZALK with a slightly lower amount of CaO.

The main rock-forming mineral of chalk and limestone is calcite with admixtures of dolomite, quartz and kaolinite. Marl samples are a natural mixture of carbonate and clay rocks and, accordingly, the rock-forming minerals calcite, kaolinite, and quartz. Sawdust consists mainly of crystalline quartz, the pearlite

sample is characterized by a developed glass phase with crystalline inclusions of quartz and mullite. The mineralogical composition of 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 $FeTiO_3$ (Figure 1). In order to identify the possibility of increasing the amount of red mud utilization in the technology of binding materials, an analysis of the composition of raw materials for the production of material of the natural or Roman cement type was carried out. The composition of the raw material mixtures was determined in accordance with known recommendations for Roman cement technology in the range of specified values of the hydraulic modulus HM=1.1 - 1.7 using computer calculations using «RomanCem» program [27].
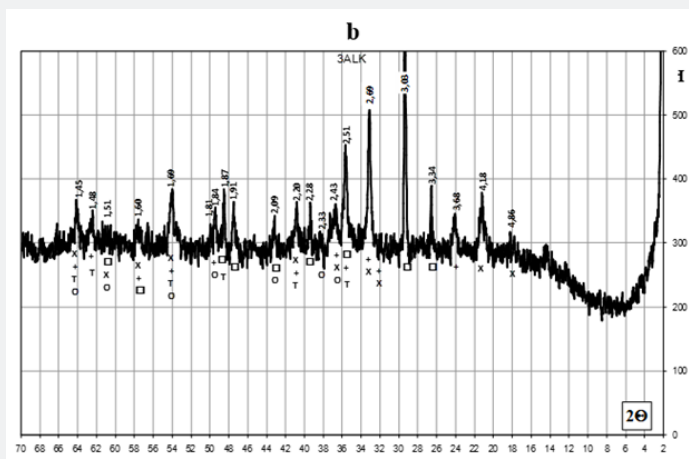

Figure 1: X-ray diffraction of red mud MGZ (a) and ZALK (b): x - goethite, + hematite, т - rutile, o – hydr- argillite.

The analysis of the obtained results showed that in the specified HM interval, the possible concentration of both studied samples of red mud in the composition of binary raw mixtures significantly depends on the types of carbonate components (Figure 2), while there is an inversely proportional relationship between the content of the mud and the number of the hydraulic module.
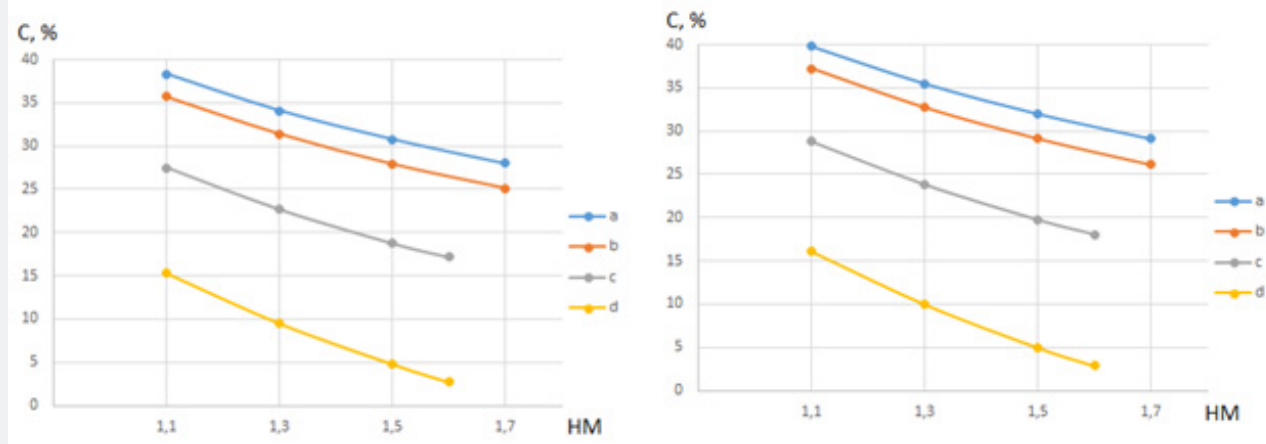

Figure 2: Dependence of the content of red mud MGZ (1) and ZALK (2) in mixture based on chalk (a), limestone (b), marl B (c), marl D (d) on the hydraulic module HM.

a) In a mixture based on chalk or limestone, the possible content of red mud is quite close: 28.0-38.3 wt. % for the MGZ sample and 29.1-39.8 wt. % for the ZALK sample.

b) In a mixture based on Bakhchisarai marl B, the possible content of red mud is 17.2-27.5 wt. % for the MGZ sample and 18.0-28.8 wt. % for the ZALK sample.

c) In a mixture based on Dubovets marl D, the possible content of red mud is 2.7-15.3 wt. % for the MGZ sample and 2.9-16.1 wt. % for the ZALK sample.

However, with a sufficiently high possible content of waste in binary mixtures, the binders of them do not meet the recommended for cement level of silica modulus n=1.9-3.0 and alumina modulus p= 0.9-2.0 (Table 2). The practical value can be a binary mixture containing, wt. %: 97.0 Dubovets marl and 3.0 red mud. According to the analysis, such a mixture should provide a binder with the closest to the recommended modulus values.

Table 2: Characteristics of the binder based on binary mixtures.

Carbonate Components	Red mud MGZ		Red mud ZALK	
	silica modulus n	alumina modulus p	silica modulus n	alumina modulus p
chalk	0,17-0,18	0,35	0,13-0,16	0,22-0,34
limestone	0,22-0,27	0,33-0,34	0,18-0,22	0,32
marl B	0,39-0,54	0,47-0,56	0,34-0,49	0,44-0,53
marl D	0,92-1,81	0,79-1,93	0,85-1,78	0,75-1,87

Table 3: Composition of raw mixtures.

Code of Mixture	Quantity of Components, mass %		
	chalk	clay	red mud
Chg	63,0	10,0	27,0
Chg1	63,0	30,0	7,00
Chg4	73,0	10,0	17,0
Chg3	72,5	25,0	2,5

Table 4: Chemical composition of raw mixtures.

Sample Code	Content of Oxides, wt. %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
Chg	9,06	7,04	16,50	35,86	0,42	0,10	31,20
Chg1	20,09	6,43	6,04	35,83	0,82	0,10	30,70
Chg4	8,31	5,13	10,68	41,01	0,43	0,10	34,49
Chg3	16,58	4,68	2,84	41,00	0,71	0,10	34,09

Chalk - Clay - Red Mud Systems

On the basis of computer calculations, it was established that in a three-component mixture based on the system of chalk - Krivinsky clay - red mud, the possible content of the latter is from 2.4 to 18.4 wt. % at HM=1,7 and from 2.4 to 29.1 wt. % at HM=1.1 and increases with a decrease in the hydraulic modulus and the amount of clay (Figure 3). The studied mixtures based on the Krivinsky chalk-clay-red mud system are characterized by differences in the quantitative ratio of components and chemical composition (Tables 3 & 4).

At the hydraulic modulus of HM=1.1, mixtures of Chg with a maximum of red mud with the same content of CaO from Chg1 clearly differ in the amount of SiO_2 (9.1 vs. 20.1 wt.%), the ratio of SiO_2: Al_2O_3 (1.3 vs. 3.1) and Fe_2O_3 content (16.5 vs. 6.0 wt.%). At the hydraulic modulus HM=1.7, mixtures of Chg4 with a maximum of red mud at the same content of CaO with Chg3 clearly differ in the amount of SiO_2 (8.3 vs. 16.6.1 wt.%), the ratio of SiO_2: Al_2O_3 (1.6 vs. 3 .5) and Fe_2O_3 content (10.7 vs. 2.8 wt.%). After firing the investigated mixtures, the obtained binders differ in chemical composition (Table 5). The obtained results of testing samples of the studied materials after firing at a maximum temperature of 1100°C indicate certain differences in their binding properties.

According to the classification of DSTU B V.27-91-99 [28], according to the speed of hardening, the samples of the binder based on the chalk-clay-red mud system belong to the group of fast-hardening (starting time from 15 to 45 min.), characteristic representatives of which are considered to be anhydrite and alumina cement and slag-alkaline binders (Table 6). However, it is obvious that an increase in the content of red mud in the initial mixture leads to a certain increase in the end time and in general the hardening process. Thus, with a hydraulic module of HM=1.7, with an increase in the content of red sludge from 2.5 to 17 wt. % with the same hardening start time, the end of the process is extended from 145 to 235 min.
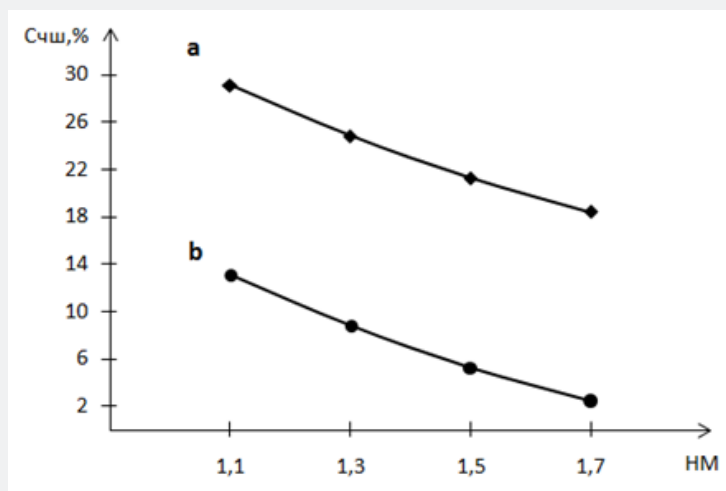
Figure 3: Dependence of the red mud concentration (C) on the hydraulic modulus (HM) at clay content of 10 (a) and 25 wt. % (b).

According to the speed of hardening of a sample of a solution with a binder based on the system of chalk – clay-red mud, they belong to the group of fast hardening (starting time from 15 to 45 min.), characteristic representatives of which are considered anhydrite and alumina cement and slag-alkaline binders. At the same time, it is obvious that an increase in the content of red mud in the initial mixture leads to a decrease in the time of the beginning and end of hardening of the solution, that is, to a general intensification of this process. Thus, with a hydraulic module of HM=1.7, with an increase in the content of red mud from 2.5 to 17 wt. % the beginning of hardening of the material decreases from 30 to 25 min., the end - from 235 to 180 min.

Table 5: Chemical composition of binders.

Sample Code	Content of Oxides, wt. %				
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO
Chg	52,01	13,14	10,21	23,93	0,61
Chg1	51,69	28,99	9,27	8,72	1,19
Chg4	62,47	12,66	7,82	16,27	0,66
Chg3	62,20	25,16	7,10	4,31	1,08

Table 6: Properties of binding materials.

Characteristics		Sample Code		
Chg		Chg4	Chg3	
Finess of grinding, sieve residue no. 008, mass. %		7	8	8
Bulk density, g/cm³		1,43	1,46	1,53
Consistency, %		57,0	64,0	75,0
Setting time, min.	initial	20	15	15
	final	190	235	145
Compressive strength, Mpa 28 days		22	23	21
Color		light red	light red	pale red

The results of the X-ray phase analysis obtained in this work indicate certain differences in the physical and chemical transformations during firing of the studied mixtures, which correlate with the specified chemical composition and depend on the content of red mud in them and the ratio of components (Figures 4 & 5). Thus, after firing to the maximum temperature of 1100°C, a sample of Chg from a mixture containing 27 wt. % of red mud with its quantitative ratio to clay of 2.7: 1, differs from Chg3

by significantly greater development of iron-containing crystalline phases C2F, CF, C4AF. Sample Chg3 from a mixture containing 2.5 wt. % of red mud with its quantitative ratio to clay of 1:10 is characterized by the development of crystalline phases of quartz, silicates (C2S), aluminosilicates (C2AS) and aluminates (CA, C3A) of calcium.
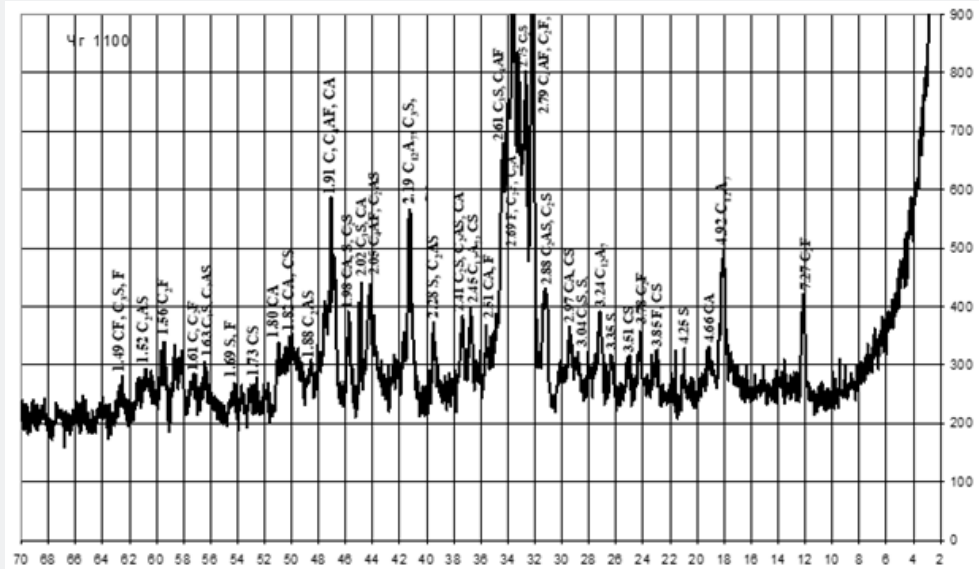

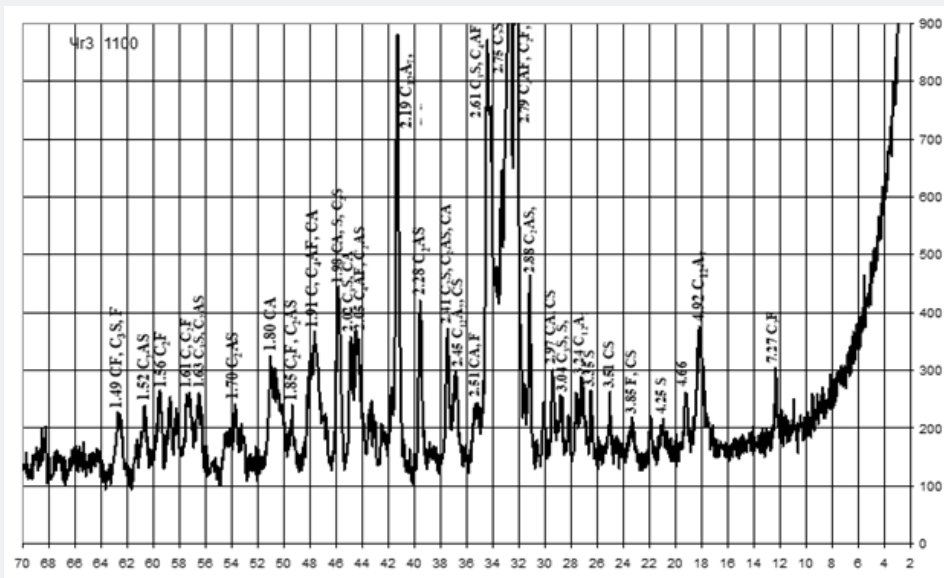**Figure 4:** X-ray diffraction of sample Chg (1100oC).

Figure 5: X-ray diffraction of sample Chg3 (1100oC).

Chalk - Perlite - Red Mud Systems

On the basis of computer calculations, it was established that in a three-component mixture based on the chalk - perlite - red mud system, the possible content of the latter ranges from 2.8 to 28.2 wt. % and increases with a decrease in the hydraulic modulus and amount of perlite (Figure 6). The studied mixtures are characterized by differences in the quantitative ratio of components and chemical composition (Tables 7 & 8). At the same time, mixtures Ch, Ch1, in comparison with those typical for cement production, are characterized by a significantly lower content of carbonate raw materials.
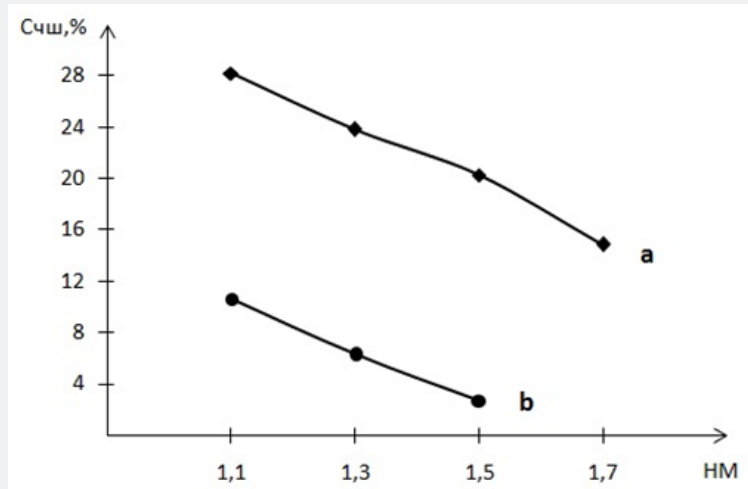
Figure 6: The dependence of red mud concentration (C) on the hydraulic modulus (HM) at a perlite content of 10 (a) and 25 wt. % (b).

Table 7: Composition of raw mixtures.

Code of Mixture	Quantity of Components, Mass %		
	chalk	perlite	red mud
Ch	62,0	10,0	28,0
Ch1	65,0	30,0	5,0
Ch4	69,5	10,0	20,5
Ch3	72,0	25,0	3,0

Table 8: Chemical composition of raw mixtures.

Sample Code	Content of Oxides, wt. %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
Ch	10,57	6,66	15,56	36,07	0,28	0,05	30,81
Ch1	24,63	5,31	3,21	36,48	0,37	0,05	29,95
Ch4	10,03	5,25	11,29	39,86	0,28	0,06	33,23
Ch3	20,57	4,23	1,99	40,20	0,36	0,06	32,59

According to the chemical composition, with a hydraulic modulus of HM=1.1, mixtures Ch and Ch1, with slight differences in the CaO content, differ significantly in the amount of SiO_2 (10.6 vs. 24.6 wt.%) and Fe_2O_3 content (15.6 vs. 3.2 wt. %). Accordingly, the quantitative ratios of oxides SiO_2: Al_2O_3 (1.6 vs. 4.6), which affects the refractoriness of the mixture, and CaO : SiO_2 (3.4 vs. 1.5), CaO : Al_2O_3 (5.4 vs. 6.9), CaO:Fe_2O_3 (2.3 versus 11.4) differ, which determine the probability of formation of new compounds during firing. At HM=1.5, the mixtures Ch4, Ch3 differs from Ch, Ch1 in a slightly higher content of CaO, a slightly lower content of silicon, aluminum and iron oxides. At the same time, mixtures Ch4 and Ch3 differ in quantitative ratios of oxides SiO_2:Al_2O_3 (1.9 vs. 4.9), CaO : SiO_2 (4.0 vs. 2.0), CaO:Al_2O_3 (6.5 vs. 9.5), CaO :Fe_2O_3 (3.5 vs. 20.2). After firing the studied mixtures, the obtained binders differ in chemical composition and silica modulus (Table 9). With

the value of the silica modulus in the range of 0.48-3.31 and the alumina modulus in the range of 0.43-2.13, samples Ch1 and Ch3 are noted to be the largest.
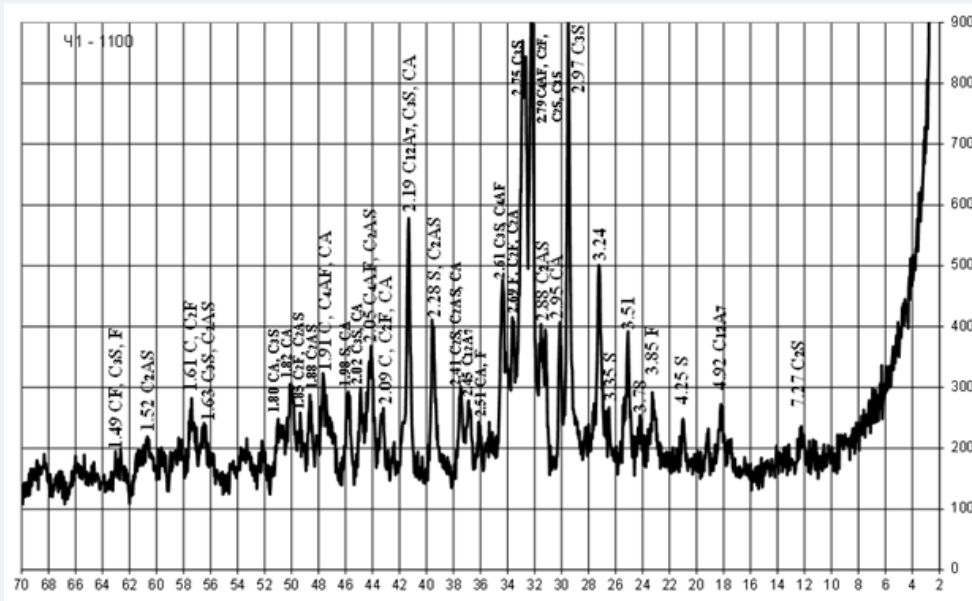
According to the classification of DSTU B V.27-91-99, according to the speed of hardening, samples of binders based on the chalk-perlite-red system belong to the group of normal hardening (starting time from 45 min. to 2 h), typical representatives of which are Portland cement and slag portland cement (Table 10). However, it is obvious that an increase in the content of red mud in the initial mixture leads to a decrease in the time of the start and end of hardening, that is, to a general intensification of this process. Thus, with the same hydraulic module HM=1.1, when the content of red increases from 5 to 28 wt. % the beginning of hardening of the material decreases from 70 to 45 min., the end - from 200 to 105 min.

Table 9: Chemical composition of binders.

Sample Code	Content of Oxides, wt. %				
	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO
Ch	52,13	15,28	9,62	22,49	0,41
Ch1	52,08	35,16	7,58	4,58	0,53
Ch4	59,70	15,02	7,86	16,91	0,42
Ch3	59,64	30,51	6,28	2,97	0,53

Table 10: Properties of binding materials

Characteristics		Sample Code			
Ch		Ch1	Ch4	Ch3	
Finess of grinding, sieve residue no. 008, mass. %		7	8	8	7
Bulk density, g/cm^3		1,52	1,61	1,55	1,60
Consistency, %		46,5	35,5	61,5	45,5
Setting time, min	initial	45	70	65	80
	final	105	200	185	255
Compressive strength, Mpa 28 days		22	23	21	22
Color		light red	pale red	light red	pale red

Figure 7: X-ray diffraction of sample Ch1 (1100oC).

Samples of a solution with a binder based on the chalk-perlite-red mud system, according to the speed of hardening, belong to the group of fast-hardening (starting time from 15 to 45 minutes), characteristic representatives of which are considered anhydrite and alumina cement and slag-alkaline binders. samples of the solution in comparison with the samples of the binder are marked by the intensification of the hardening process with a decrease in the time of beginning and end. The results of the X-ray phase analysis obtained in this work indicate certain differences in the physical and chemical transformations during firing of the investigated mixtures, which depend on the content of red mud in them and the ratio of components (Figures 7 & 8).
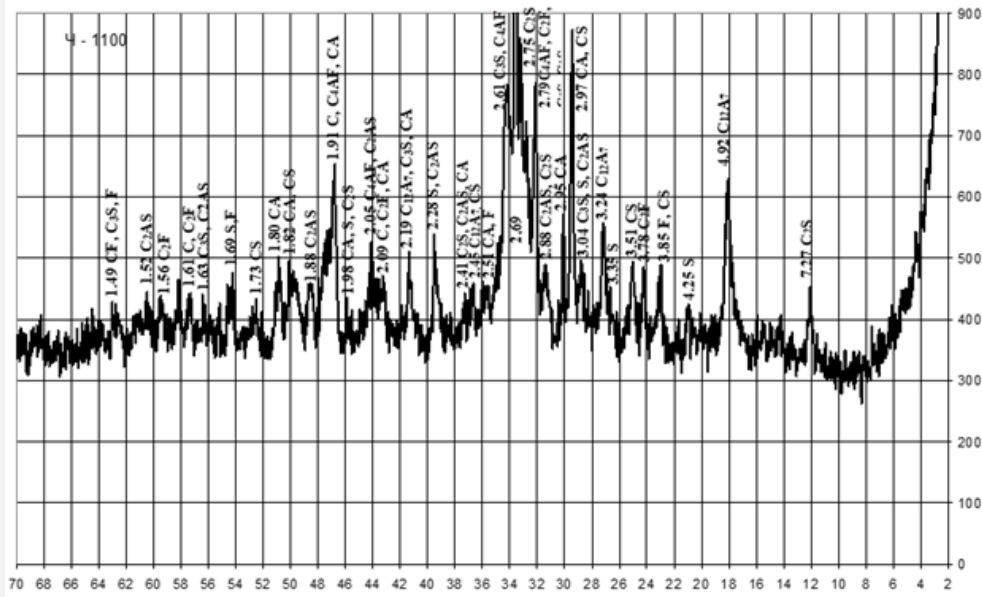
Figure 8: X-ray diffraction of sample Ch (1100oC).

So, the raw material mixture Ch1 containing 5 wt. % of red mud with a quantitative ratio of 1:6 to perlite is characterized by the presence of a glass phase associated with pearlite, the main rock-forming mineral - calcite, quartz and iron oxides. Raw material mixture Ch, containing 28 wt. % of red mud with its quantitative ratio to perlite of 2.8: 1, is characterized by the presence of a glass phase associated with perlite, the main rock-forming mineral - calcite, quartz and iron oxides. After firing at the maximum temperature of 1100°C, the crystal lattices of the main rock-forming minerals of the original raw material mixtures are destroyed and new crystalline phases are formed. At the same time,

sample Ch with a relative maximum of red mud is characterized by significantly greater development of iron-containing crystalline phases CF, C2F, C4AF.

Chalk - Pyloquartz - Red Mud Systems

On the basis of computer calculations, it was established that in a three-component mixture based on the system of chalk - pyloquartz - red mud, the possible content of the latter is from 3.5 to 27.7 wt. % and increases with a decrease in the hydraulic modulus and amount of pyloquartz (Figure 9).
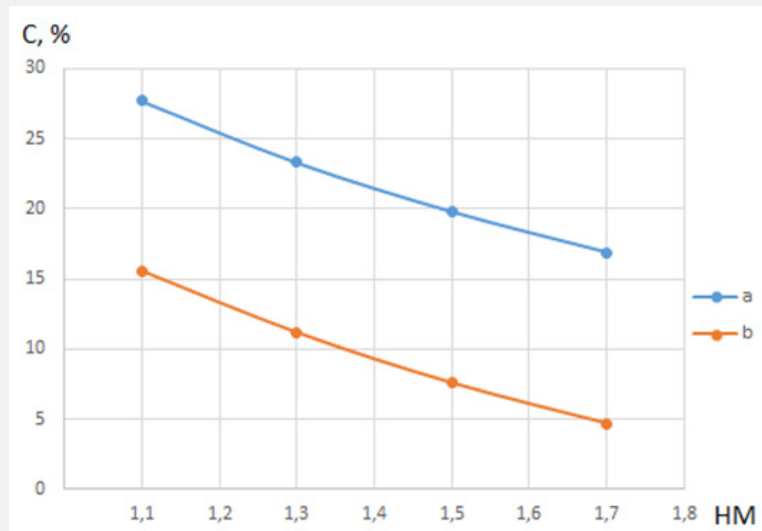

Figure 9: Dependence of red mud concentration (C) on the hydraulic module (NM) with content of pyloquartz at 10% (a) and 20.

The studied mixtures based on the chalk-pyloquartz system are characterized by differences in the quantitative ratio of components and chemical composition (Tables 11 &12). At the same time, mixtures Ch10 and Ch11, in comparison with those typical for cement production, are characterized by a significantly lower content of carbonate raw materials. According to the chemical composition, with the same hydraulic modulus HM = 1.1, mixtures Ch10 and Ch11, with slight differences in the CaO content, differ significantly in the amount of SiO_2 (12.6 vs. 21.6 wt.%) and Fe_2O_3 content (15.1 vs. 8.6 wt.%). Accordingly, the quantitative ratio of oxides SiO_2: Al_2O_3 (2.4 vs. 7.2), which affects the refractoriness of the mixture, and CaO : SiO_2 (2.9 vs. 1.7), CaO:Al_2O_3 (7.0 vs. 12.2) differ , CaO:Fe_2O_3 (2.4 versus 4.3), which determine the probability of formation of new compounds during firing.

Table 11: Composition of raw mixtures

Code of Mixture	Quantity of Components, Mass %		
	chalk	pyloquartz	red mud
Ch10	62,5	10,0	27,5
Ch11	64,5	20,0	15,5
Ch12	70,0	10,0	20,0

.

Table 12: Chemical composition of raw mixtures.

Sample Code	Content of Oxides, wt. %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
Ch10	12,59	5,18	15,14	36,20	0,22	0,05	30,62
Ch11	21,64	3,00	8,56	36,53	0,19	0,05	30,30
Ch12	12,04	3,77	10,86	40,00	0,22	0,06	33,05

Mixture Ch12 at HM=1.5 differs from Ch10, Ch11 by a slightly higher content of CaO and is characterized by quantitative ratios of oxides SiO_2:Al_2O_3=3.2, CaO : SiO_2 = 3.3, CaO : Al_2O_3 = 10.6, CaO:Fe_2O_3 = 3.7. After firing the investigated mixtures, the obtained binders differ in chemical composition and silica modulus (Table 13). With a silica modulus value in the range of 0.62-1.87, sample Ch11 is the largest, and the alumina modulus of the samples is at the level of 0.34-0.35. According to the classification of DSTU B V.27-91-99, after firing at the maximum temperature of 1100°C, the studied samples of the binder based on the chalk - pyloquartz system belong to different groups according to the hardening speed (Table 14). With a relatively lower content of red mud and the largest content of pyloquartz with their quantitative ratio of 1.5: 2, sample Ch11 belongs to the ultra-fast hardening group (starting time no later than 15 minutes), which is considered typical for expanding and tensioning cements.

.**Table 13:** Chemical composition of binders.

Sample Code	Content of Oxides, wt. %				
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO
Ch10	52,18	18,15	7,46	21,82	0,32
Ch11	52,21	30,93	4,29	12,23	0,27
Ch12	59,74	17,98	5,63	16,23	0,33

Table 14: Properties of binding materials.

Finess of Grinding, Sieve Residue no. 008, Mass. %		7	7	8
Bulk density, g/cm³		1,55	1,63	1,57
Consistency, %		37,5	38,0	44,5
Setting time, min.	initial	20	10	75
	final	50	60	130
Compressive strength, Mpa 28 days		18	20	19
Color		light red	pale red	light red

With the relatively highest content of red mud and its quantitative ratio with pyloquartz 2.8:1, sample Ch10 belongs to the group of fast hardening (starting time from 15 to 45 min.), which is considered typical for anhydrite and alumina cements. With a quantitative ratio of red mud to pyloquartz of 2:1, sample Ch12 belongs to the normal-hardening group (onset period from 45 min. to 2 h), characteristic representatives of which are Portland cement and Portland slag cement. The obtained results of the X-ray phase analysis indicate certain differences in the physical and chemical transformations during firing of the studied mixtures, which depend on the content of red sludge in them and the ratio of components (Figures 10-12).
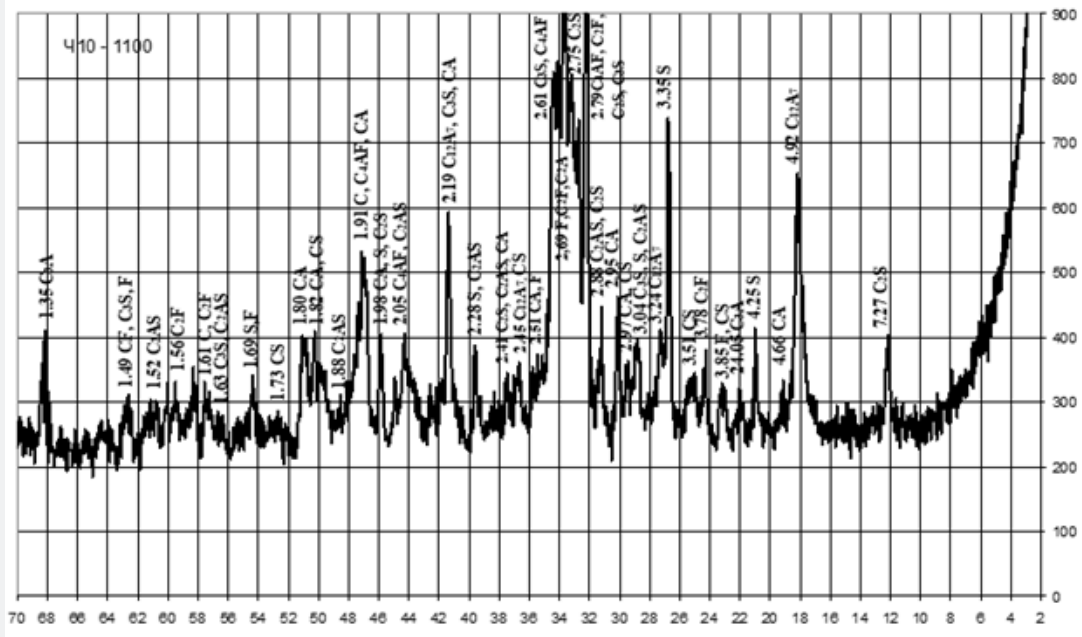

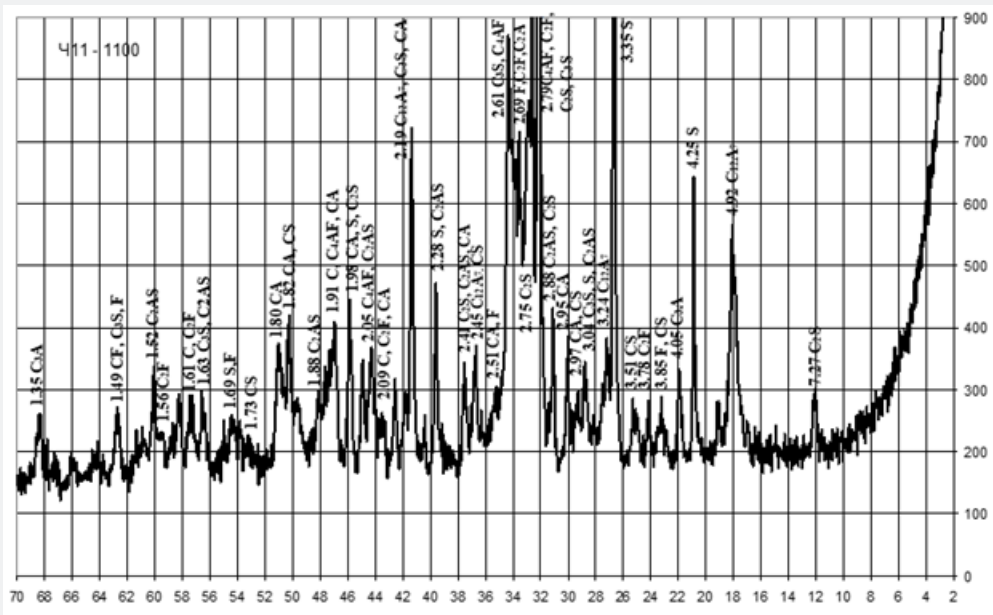**Figure 10:** X-ray diffraction of sample Ch10 (1100oC).

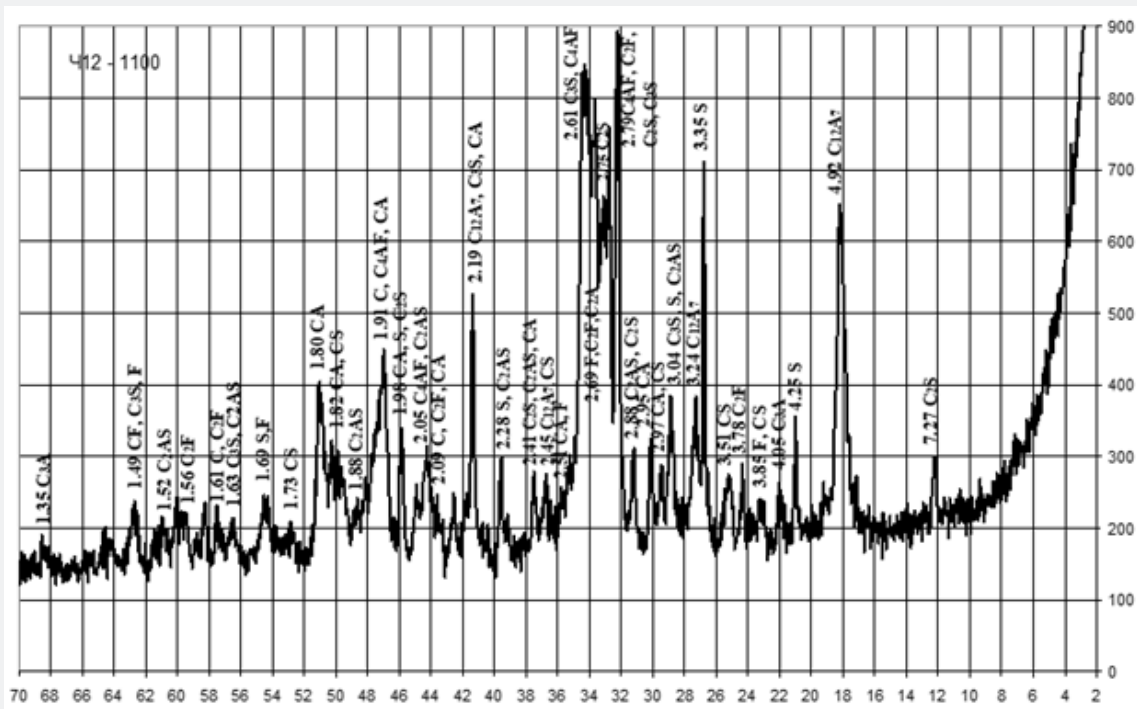**Figure 11:** X-ray diffraction of sample Ch11 (1100oC).

Figure 12: X-ray diffraction of sample Ch12 (1100oC).

Thus, after firing to the maximum temperature of 1100°C, sample Ch10 from a mixture containing 27.5 wt. % of red mud with its quantitative ratio to pyloquartz 2.8 : 1, differs from Ch11 from a mixture containing 15.5 wt. % of red slime with its quantitative ratio to pyloquartz 1.5 : 2, significantly greater development of iron-containing crystalline phases C4AF, C2F. Sample Ch11 is characterized by greater development of quartz, aluminosilicates (C2AS), aluminates (CA) and calcium silicates (C2S). The possibility of introducing 27.0 - 28.0 wt. % to the composition of raw mixtures based on chalk-polymineral clay, chalk-perlite, chalk-quartz systems for the production of mineral binder when fired at a maximum temperature of 1100°C (Table 15).

Table 15: Compositions of raw mixtures with the maximum content of red mud.

Sample Code	Quantity of Components, Mass %				
	chalk	clay	pyloquartz	perlite	red mud
Chg	63,0	10,0	-	-	27,0
Ch10	62,5	-	10,0	-	27,5
Ch	62,0	-	-	10	28,0

Discussion

These studies correspond to the principle of modern materials science about the relationship "composition-structure-properties". With the use of computer calculations, it was possible to determine the quantitative limits of utilization of one of the multi-use industrial wastes - red sludge for the production of an energy-saving type of low-temperature fired cement. At the same time, the features of the use of red mud are considered when varying the composition of mixtures with natural raw materials of different genesis.

It is obvious that the obtained results do not solve the entire set of problems for the utilization of red mud as a man-made raw material in the production of cement, but it is a significant positive step in this direction. Probably, certain weaknesses of the submitted work include the limitation of red mud samples with waste from Ukrainian enterprises, which is related to the practical capabilities of the authors in modern conditions.

Conclusion

a)   The use of red mud as a component of the raw material mixture for the production of mineral binding materials is one of the directions for the utilization of multi-tonnage non-ferrous metallurgy waste.

b)   In the production of low-temperature fired cement (≤1200°C) with a hydraulic modulus of HM=1.1-1.7, the possible content of waste in a three-component mixture is:

i.   2.4-29.1 wt. % in the "chalk - clay - red mud" system with provision, at the indicated minimum, the values of siliceous n=2.21-2.35 and alumina p=1.65-1.84 modules

ii.   4.9-28.2 wt. % in the "chalk – perlite – red mud" system with provision, at 4.9-5.7 wt. %, values of siliceous n=2.23-2.89 and alumina p=1.16-1.66 modules

iii.   3.5-27.7wt. % in the "chalk - pyloquartz - red mud" system with provision at 4.9- 15.6 wt. % values of silica n=1.90-2.89 and alumina p=0.35-1.66 modules.

c)   The manufactured materials belong to the group of fast-hardening materials but differ in the intensity of the process: hardeners based on the "chalk-clay-red mud" system are characterized by a longer time to the end of hardening, and those based on the "chalk-perlite-red mud" system - by a longer time to the beginning of hardening. They belong to the groups of mineral binders with reduced strength (10-30 MPa) but will meet or exceed the compressive strength indicators regulated for natural and Roman cement.

d)   The marked color of the obtained cement, which increases with an increase in the content of red mud, improves the decorative properties of the material in accordance with the requirements of architecture.

e)   The possibility of reduction to 62-65 wt. % of the content of the carbonate component in the original raw material mixtures is important for solving the issues of resource saving and ecology.

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