

# DEVELOPMENT OF BINDERS BASED ON THE CaO–Fe<sub>2</sub>O<sub>3</sub> SYSTEM

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*The object of research is the processes of structure formation and modeling of the properties of a specialized binder. The development of new binding materials based on production waste with high early strength indicators could make it possible to speed up construction period and is one of the urgent tasks at present. This study focused on the creation of binders based on the CaO–Fe<sub>2</sub>O<sub>3</sub> system. The developed binder of the CaO–Fe<sub>2</sub>O<sub>3</sub> system has the following composition: limestone – 26 %; red slime – 74 %, which has a dense fine-porous structure and high early strength indicators – 22.5 MPa with a density of 1960 kg/m<sup>3</sup>. There is also an increase in the average density of samples annealed at a temperature of 1200 °C for 60 minutes, ground and mixed with water, in comparison with samples fired at 1100 °C for 60 minutes, by 500 kg/m<sup>3</sup>, due to new formations. The prospect of using modified composite binders with special functional properties has been substantiated. The use of production waste based on the CaO–Fe<sub>2</sub>O<sub>3</sub> system could make it possible to obtain materials with high physical and mechanical properties, which makes them promising for application in various areas of the construction industry. The development of such binders will help reduce the environmental impact of the construction industry, owing to the use of affordable and effective components. This approach will not only contribute to the improvement of the quality of building materials but also help reduce the ecological burden on the environment by using alternative resources and industrial waste. The developed binder could be used for the development of solutions for 3d printing, as well as repair of concrete coatings*

*Keywords: composite binder, specialized binder, alternative resources, 3d printing, aluminat cements*

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## 1. Introduction

The rapid development of the world economy and the influence of scientific and technological progress lead to the constantly growing production capacities in the industrial sector. The increase in the volume of production requires the use of an increasingly large raw material base and leads to the deterioration of the state of non-renewable natural resources due to the rapid depletion of reserves and damage to the environment. Associated industrial products and waste are an integral part of the production process, and their disposal is complicated due to their diverse nature. Placing red mud over large areas in sludge storage facilities and natural depressions is a significant hazard. Thus, the global accumulation of red mud reaches about 2.7 Gt. However, each year its amount increases by 120 Mt, which leads to a number of problems related to the ongoing costs of its safe storage or processing.

In addition, in the process of manufacturing alumina, a by-product is formed – red mud, which accumulates in large quantities and is an environmental problem. However, it does contain beneficial chemical elements such as iron and aluminum oxides. These elements can help reduce the use of natural resources, such as limestone, because waste replaces part of the necessary raw materials.

Research on this topic is relevant as it will make it possible to use valuable components of the CaO–Fe<sub>2</sub>O<sub>3</sub> sys-

tem (limestone and red mud) to create new types of binders. This, in turn, will make it possible not only to reduce the amount of waste but also to develop mortars and concretes of special purpose with high technical and operational indicators. That is why the development of a binder with special properties based on production waste is relevant and requires a solution.

Scientific research on this topic is important as it is aimed at the formation of a fast-hardening binder that has similar technological and physical-mechanical properties to cements with special properties, which makes it possible to replace their use. The results of such studies are needed in practice because construction terms could be accelerated due to the high strength indicators of the developed binder in the first day of hardening. Also, the cost of construction would be reduced by replacing special types of cement with a cost of 600–720 USD/ton.

## 2. Literature review and problem statement

Typically, red mud is dust and clay particles that are prone to aggregation, so the actual dispersed composition may vary. In the process of treating most types of bauxite according to the Bayer method, they are crushed to a size of 0.063 mm. Coarse fractions of dispersed sludge (1000–50 μm) are represented mainly by quartz and iron-rich phases.

The 100–250  $\mu\text{m}$  fraction consists of quartz, hematite, and calcite; in the 50–100  $\mu\text{m}$  fraction, hematite and aluminohematite predominate; fraction 10–50  $\mu\text{m}$  – hematite, aluminohematite, aluminogelite, the content of hydrogarnets increases [1, 2]. An unsolved issue in work [2] is the use of red mud as the main raw material in the development of a binder obtained at a low firing temperature. The reason for this may be the objective difficulties associated with the consumable part during firing, which makes relevant studies impractical. An option to overcome these difficulties can be the use of plauns contained in in red mud. This is exactly the approach reported in works [1, 2]; however, a significant decrease in firing temperature was not achieved.

All this gives reason to assert that it is expedient to conduct a study on the development of a binder with a low firing temperature.

The object of research in [1] was raw material mixtures for the production of binding material based on the silicate system of chalk – clay – red mud. The following were used: chalk, clay, and red slime – waste from the alumina production at PJSC “Zaporizhsky Aluminum Plant” (Ukraine).

According to the chemical composition, among the studied raw materials, the sample of Zdolbniv chalk is characterized by a high content of CaO. The Kryvin clay sample has the largest amount of aluminum oxide with a ratio of  $\text{SiO}_2:\text{Al}_2\text{O}_3=4:1$ . The red mud sample has the highest content of  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , the sum of alkaline earth and alkaline oxides of the  $\text{RO}+\text{R}_2\text{O}$  type=8.62 wt.%. Analysis of the mineralogical composition of the studied raw materials was carried out using a DRON-3M diffractometer.

The main rock-forming mineral of the Zdolbniv chalk is calcite (97.6 wt.%) with admixtures of dolomite (1.2 wt.%), quartz and kaolinite – 0.5 and 0.6 wt.%, respectively:

- Krivinsky clays belong to the group of polymineralic ones with a high content of montmorillonite (30 wt. %), quartz, and feldspars;

- the red mud sample is characterized by the presence of goethite  $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ , hematite  $\text{Fe}_2\text{O}_3$ , hydrargillite  $\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ , rutile  $\text{TiO}_2$ , and ilmenite  $\text{FeTiO}_3$  [2].

The research the results of which are presented in works [1, 2] was carried out with a combination of modern physicochemical methods of analysis with standardized testing of the properties of raw materials and binders. However, there is an issue that needs to be resolved – increasing the percentage of red mud in the composition in order to improve the operational characteristics of the developed binder. The reason for this is the cost of preparing raw materials and the complexity of operations. This problem can be solved by using red mud with a content of particles smaller than 5  $\mu\text{m}$  more than 50 %. This approach is used in work [3]. However, it is advisable to conduct a study on the development of a two-component binder with high technical characteristics.

The authors of papers [3, 4] used granulated blast furnace slag, sodium silicate (CH) with a coefficient of  $R=3.4$ , red mud dried and crushed to 10  $\mu\text{m}$ , washed sand, and raw sand with a particle size of 0–4  $\mu\text{m}$ . The  $R$  ratio was changed by adding anhydrous sodium hydroxide, >98 % purity granules. As a result, the mortar samples demonstrated high technical characteristics, despite the low content of blast furnace slag – 36 MPa for the 70:30 % ratio of red mud/granulated blast furnace slag [3, 4]. The disadvantage of work [3] is the high labor intensity and cost of technological operations. The research needs to be refined, in particular in the direction of studying the process of structure formation. Works [3, 4]

report the results demonstrating the high efficiency of using the specified materials and methods. However, the issues of labor intensity and cost of technological operations remain unsolved. This may be due to the complexity of the material preparation process and the high cost of reagents. A possible solution to these problems is the optimization of the technological process or the search for alternative, less expensive materials and methods. This approach was implemented in work [5], in which new methods of processing materials are proposed, which reduce labor intensity and cost. However, these methods also have their limitations and require additional research. Therefore, it is advisable to carry out further research aimed at optimizing processes and finding new materials, which could reduce costs and increase the efficiency of construction mortars.

Work [5] reports the results of research into the use of ferronickel and fayalite slags with ground concrete waste for the production of inorganic polymers. The uniaxial compressive strength of the manufactured samples with a ratio of 25 % of ground concrete waste: 25 % of fayalite slags: 50 % of ferronickel slags, curing at 60 °C for 24 hours and aging for 7 days, obtained high strength (47 MPa). But the issues related to the lack of early strength, slow setting, and hardening remained unresolved. The reasons for the existence of these problems may be related to the characteristics of the materials used, the fundamental impossibility of achieving rapid hardening under such conditions, or the expendable part in the process optimization plan, which makes relevant research impractical. An option to solve this problem is to optimize the composition of the mixture or change the hardening conditions. This is the approach used in work [6]; however, the study revealed other problems related to the durability of the material. All this gives reason to assert that it is expedient to conduct a study on investigating methods for improving early strength and accelerating the hardening process of inorganic polymers based on ferronickel and fayalite slags.

Work [6] describes the study on the use of industrial waste as a substitute for cement in pervious concrete. Fly ash was used as a replacement. The compressive strength of permeable concrete with fly ash is in the permissible range of 4–35 MPa. Some studies cited in the paper report an initial strength reduction of up to 65 %, but the author states that strength increases with curing time. This can be explained by the presence of silica in fly ash. The disadvantage is the initial decrease in strength. But there are issues that need to be resolved, related to the initial decrease in strength. The reasons for this are related to the hydration processes in cement systems that contain fly ash, or the expendable part in terms of additional additives, which makes relevant studies impractical. An option to overcome the relevant difficulties may be the use of special additives to accelerate hardening or optimization of the composition of the mixture. This is the approach used in work [3], but it does not take into account all possible chemical interactions of additives with other components of the mixture. All this gives reason to assert that it is appropriate to conduct a study to further investigate mechanisms of the influence of fly ash on the strength of pervious concrete and the development of methods to overcome the initial decrease in strength.

Works [7, 8] refer to the study of the assessment of the ecotoxicity of steel slag and concrete mixtures with a partial replacement of steel slag with 13 % of the weight of Portland cement and 30 % of the weight of the partial replacement.

The researchers conducted leaching tests in accordance with the standards EN 12457-2 and UNI EN 15863. Leaching was carried out on four samples of steel slag and four samples of concrete mixtures with partial replacement of steel slag. The filtrates were characterized using a plant-based approach to assess their environmental impact. As a result, it turned out that none of the samples caused phytotoxic effects, all samples supported seed germination and did not affect cell division. However, issues related to the long-term stability and behavior of such materials under real operating conditions remained unresolved [9, 10]. The reason for this may be objective difficulties associated with the limited duration of research and laboratory conditions, which cannot always fully imitate actual conditions. It is also possible that it is fundamentally impossible to take into account all options for the influence of external factors, such as climatic conditions and mechanical loads. An option to overcome the relevant difficulties may be to conduct long-term field studies and build models that will allow for a more accurate prediction of the behavior of materials under real conditions. All this gives reason to assert that it is expedient to conduct a study on the long-term stability and behavior of concrete mixtures with partial replacement of steel slag under actual operating conditions [11, 12].

The research carried out in [13] considers the evaluation of efficiency of the technological process of production of construction products with metallurgical slag fillers. In the course of the study, different fractions of metallurgical slag and formulations of concrete mixtures were used, which included 10–25 % of metallurgical powder. Samples were produced and subjected to strength tests. The results showed that the addition of metallurgical slag increases the strength up to 23 %, after which the strength stabilizes. Automation of the slag loading process increased productivity by 23 % and reduced costs by 11 %, making the technology promising for the production of building materials.

Gypsum slag cement, containing 75–85 % slag, 10–15 % dihydrate gypsum or anhydrite, up to 2 % calcium oxide or 5 % Portland cement clinker, became the most widely used from the sulfate-slag group. Activators are thoroughly mixed with slag or their joint grinding (sulfate-slag, lime-slag binders), or watering with aqueous solutions (slag-alkaline binders) [1, 2].

Currently, there are many technologies that make it possible to effectively perform work on the installation and repair of concrete coatings, the selection of which is made taking into account specific objects. However, the majority of horizontal coatings, and especially the coatings of special logistics centers, have increased technological and operational requirements. Floors laid using standard technologies using heavy concrete, characterized by high compressive strength, have always had the same problem – low resistance to tearing and the formation of shrinkage cracks during hardening. And during further operation, such disadvantages as low frost resistance, low impact resistance, tendency to abrasion, high degree of penetration of water and chemicals are revealed. Under these conditions, fiber-reinforced concrete [13, 14], in particular fiber-reinforced concrete from high-modulus polymer materials, is a competitive material, as shown by the results of many studies. Disperse reinforcement technology allows reducing labor costs, increasing chemical inertness and adhesion to the old base [13, 14]. It can also be used in the development of binding red mud, which helps reduce the firing temperature and improve the main technological and physical-mechanical properties (Fig. 5, 6).

Existing techniques for preparing dispersed-reinforced concrete mixture at the construction site require the mandatory use of expensive dry concrete mixtures and special mixers with low productivity. The lack of clear and tested in practice recommendations for the technology of preparation and laying of dispersed reinforced concrete, without the use of dry mixtures and special mixers, significantly limits their use in the arrangement of floors. In this regard, the technology of preparation and laying of dispersed reinforced concrete mixture during the installation of coatings needs improvement and verification under the conditions of construction site.

Studies [9, 10] discuss the possibility of carbothermic red mud recovery for iron extraction and sodium removal. The researchers determined the effects of recovery time, temperature, and basicity on melting and dealkalization processes. Temperatures from 1350 to 1450 °C and different basicity values were used in the experiments. To evaluate the efficiency of the process, the microstructure of the pellets was analyzed using scanning electron microscopy and X-ray diffraction. The results showed that under optimal conditions (temperature 1450 °C, basicity 1.5, recovery time 12 minutes), the level of metallization and sodium removal reached 96.63 % and 90.62 %, respectively. This indicates the possibility of effective use of carbothermal recovery for red mud treatment. The reasons for this may be related to the instability of phase transitions at high temperatures, the fundamental impossibility of achieving stable strength indicators without additional components, as well as the high cost of conducting experiments. An option for solving the relevant problems may be the use of additional additives that stabilize phase transitions, or modification of the technological process. This is the approach used in work [1]; however, further research is needed to optimize the process and reduce costs. Therefore, the development of binding material using secondary raw materials is an urgent problem that needs to be solved.

Analyzing the production of individual parts and products in different areas [9, 10], it can be concluded that the development of a binder with a stable ettringite phase is promising, which could make it possible to control the expansion of cement stone, which is associated with its formation.

Solving the problems of providing the population with housing and restoring social facilities is possible through the development and use of new binders and technologies. One of these is 3D printing technology, by creating concrete, solutions, and composite materials that would meet regulatory requirements in construction.

This allows us to state that it is appropriate to conduct a study on the development of a binding material from production waste based on the CaO-Fe<sub>2</sub>O<sub>3</sub> system.

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### 3. The aim and objectives of the study

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The purpose of our research is the development of binders based on the CaO-Fe<sub>2</sub>O<sub>3</sub> system. This could make it possible to reduce the amount of industrial waste while simultaneously increasing the quality of the binder with high technical and operational characteristics.

To achieve the goal, the following tasks were set:

- to build and investigate the regression equation “composition – compressive strength”;
- to develop a technological scheme for the production of binder;

– to investigate the structure and basic physical and mechanical properties of the developed binder based on the CaO-Fe<sub>2</sub>O<sub>3</sub> system.

#### 4. The study materials and methods

The object of our study is the process of structure formation and control over secondary raw material firing factors in order to obtain the necessary structure and properties of binders.

The main hypothesis of the research assumes the possibility of developing a binder with special properties by using iron-containing production waste, which could make it possible to regulate the firing process and obtain a binder with specified properties.

A set of modern methods of X-ray diffractometry, raster electron microscopy, low-temperature dilatometry, etc. was used during the experiments. When determining the main physical-mechanical and construction-technical properties of composites based on alumina cement and mortars based on them, current regulatory documents and methods were used: DSTU B.V. 2.7-187:2009, DSTU EN 196-1:2019 (EN 196-1:2016, IDT). When optimizing compositions based on alumina cement, experimental and statistical methods of experiment planning were used.

Red mud was used for the development of binders based on waste from the Mykolaiv Alumina Plant (Ukraine). The chemical and granulometric compositions of the raw components are given in Tables 1, 2 and Fig. 1.

Table 1

Chemical composition of raw components

No. of entry	Type of raw materials	Chemical composition, wt. %												
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	CaSO <sub>4</sub>	CO <sub>2</sub>	Losses during ignition
1	Red mud from Mykolaiv Alumina Plant	6.26	14.75	50.46	5.32	–	–	6.5	–	–	2.86	–	–	12.1
2	Limestone	–	–	–	–	–	–	56	–	–	–	–	44	2.0

Table 2

Content of fractions (% by weight) of red mud from the Mykolaiv Alumina Plant

Type of raw materials	Grain size, μm	Fraction content, % wt.				
		10	15	25	25	25
Red mud from Mykolaiv Alumina Plant		0.470	1.120	2.838	7.747	15.50

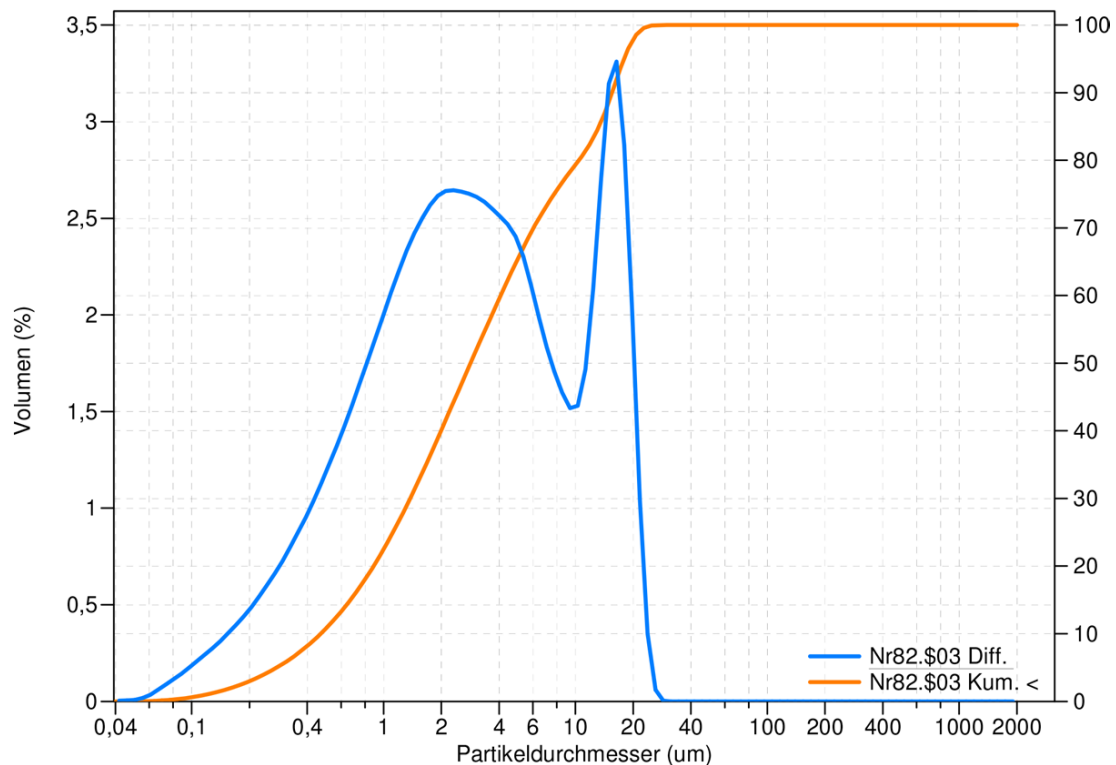


Fig. 1. Granulometric composition of red mud from the Mykolaiv Alumina Plant

The mineral composition of the red mud from the Mykolaiv Alumina Plant (Fig. 2) is represented by hematite ( $d/n=0.268; 0.25; 0.219; 0.183; 0.168; 0.148; 0.145$ ); hydro argillite (gibbsite) ( $d/n=0.4821; 0.433; 0.242; 0.214; 0.204; 0.179; 0.168; 0.145$ );  $\beta$ -quartz ( $d/n=0.322; 0.152; 0.138$ ); calcium carbonate ( $d/n=0.227; 0.209; 0.175$ ); (Fig. 2).

Table 3 gives the chemical composition of electro corundum, which is included in the composition of binders made using red mud, and the percentage content of the main chemical elements and oxides, such as aluminum oxide ( $Al_2O_3$ ).

**Table 3**  
Chemical composition of electro corundum

Grain number	Chemical composition, %	
	$Al_2O_3$	
Faction-160	93.2	
Faction-160	93.3	
Faction-160	93.0	
Faction-160	93.2	
Faction-160	93.3	

Hydrated lime ( $CaCO_3$ ) manufactured by MINTORG LLC, Kamianets-Podilskyi, Khmelnytska oblast, Ukraine, was also used for the development of the binder (Table 4).

**Table 4**

Main characteristics of hydrated lime ( $CaCO_3$ )

Material		Purpose	Indicators		
name	standard document				
Hydrated lime	DSTU B V 2.7-90-99	binders	The residue on the sieve is 0.2 mm, the moisture content is not more than 0.8 %		
Calcium lime of grades			1	2	3
Active CaO+MgO, not less: without additives			90	80	70
with additives			65	55	-
Active MgO, no more:			5	5	5
CO <sub>2</sub> , no more: no additives			3	5	7
with additives			4	6	-
Unquenchable grains, not more than:			7	11	-

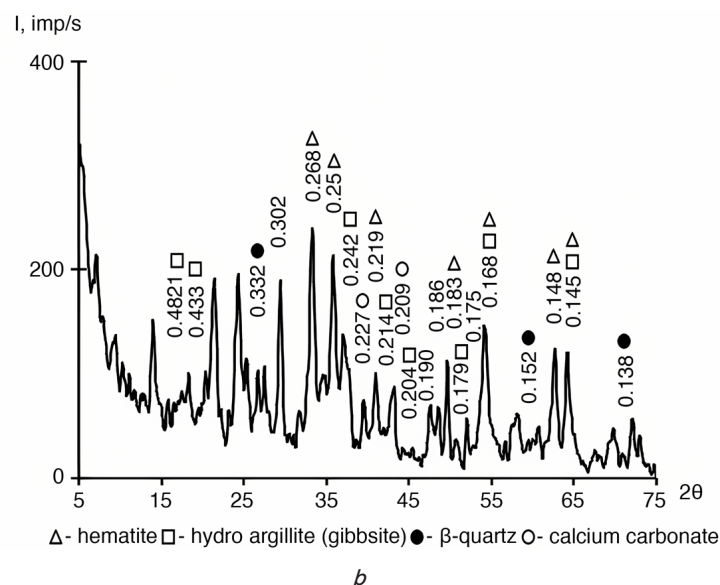
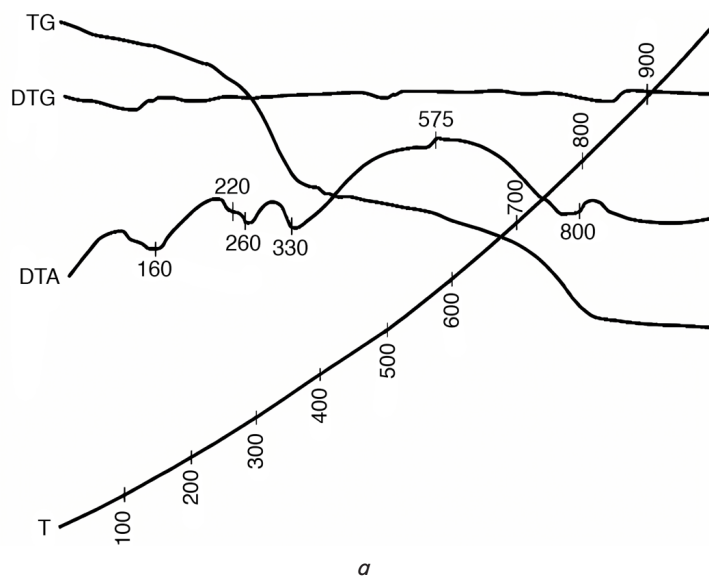


Fig. 2. Curves of analyzes of red mud from the Mykolaiv Alumina Plant: *a* – differential-thermal; *b* – mineral

The results of analyzes and the characteristics of materials indicate the possibility of effective use of iron-containing waste to create new types of binders with specified properties, which can have a significant impact on the economy and environmental friendliness of building materials.

**5. Results of research on the development of binders based on the CaO–Fe<sub>2</sub>O<sub>3</sub> system**

**5.1. Construction and study of the “composition – compressive strength” regression equation**

The optimal composition was determined using the simplex lattice design of the experiment. Influence coefficients were calculated, regression equations were obtained, and “composition-compressive strength limit” diagrams were constructed (Fig. 3, 4). The planning matrix included the following variables: electro corundum (X<sub>1</sub>), red slime (X<sub>2</sub>), and dihydrate gypsum (G) (X<sub>3</sub>). The change in the state charts was based on the data of the input components given in Table 5. The output variable was the limit of compressive strength (Table 5, Fig. 3, 4).

The mathematical model obtained in the process of planning and conducting the experiment takes the following form:

$$R = 53.21 X_1 + 49.82 X_2 + 44.75 X_3 + 17.42 X_1 X_2 + 4.92 X_1 X_3 + 35.86 X_2 X_3 \tag{1}$$

According to the calculated mathematical model, diagrams “composition – compressive strength” were constructed (Fig. 3, 4).

To verify the adequacy of the resulting model, six parallel studies were conducted at the verification point located in the center of the simplex. Adequacy at these points was checked using Student’s test (*t* test). The obtained data on the dependences of the input components were processed using Statistica SPSS V 7.0 and StatGraphics V 2.1 software; they are shown in Fig. 3, 4.

As the content of red mud and gypsum increases, the strength indicators decrease. Based on the general appearance of the response surface in Fig. 3, 4, *a*, the dark red isoline has a value of 56 MPa with coordinates (X<sub>1</sub>=0.333–0.4; X<sub>2</sub>=0.3–0.5; X<sub>3</sub>=0–0.75). Recalculation of these values in natural form (Table 5) gives the following optimal composition: X<sub>1</sub>=55–56.3 %; X<sub>2</sub>=17.1–17.6 %; X<sub>3</sub>=25.9–28.2 %.

Table 5

Planning Matrix

Point of plan	Component content at encoded scale			Natural content of components, % by weight			Ultimate compressive strength (R), MPa
	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	Electro corundum	Red mud	Dihydrate gypsum	
1	1	0	0	58	16.1	25.9	53.15
2	0	1	0	55	19.1	25.9	49.76
3	0	0	1	55	16.1	28.9	44.69
4	0.5	0.5	0	56.5	17.6	25.9	56.1
5	0.5	0	0.5	56.5	16.1	27.4	50.44
6	0	0.5	0.5	55	17.6	27.4	56.48
7	0.333	0.333	0.333	56	17.1	26.9	55.20

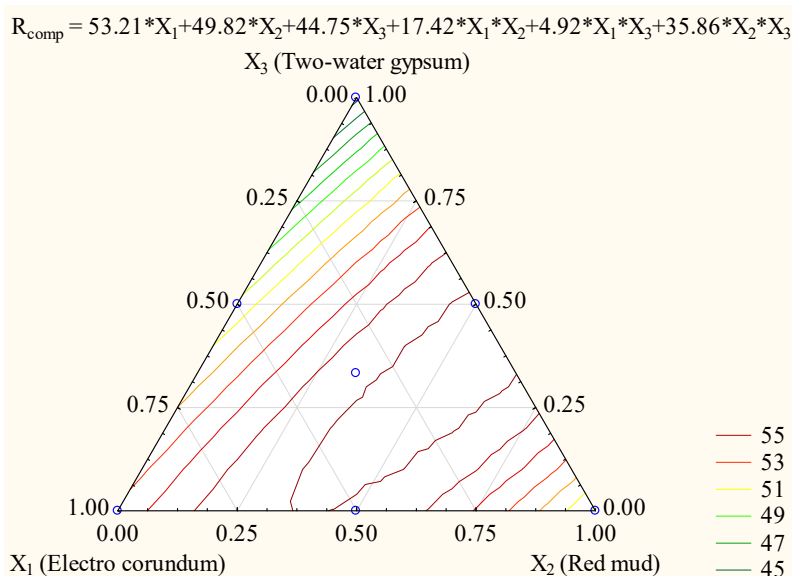
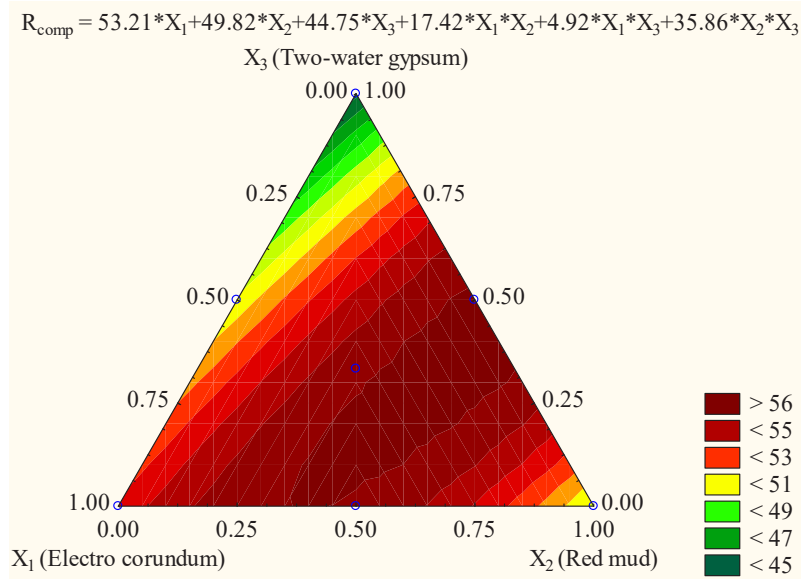
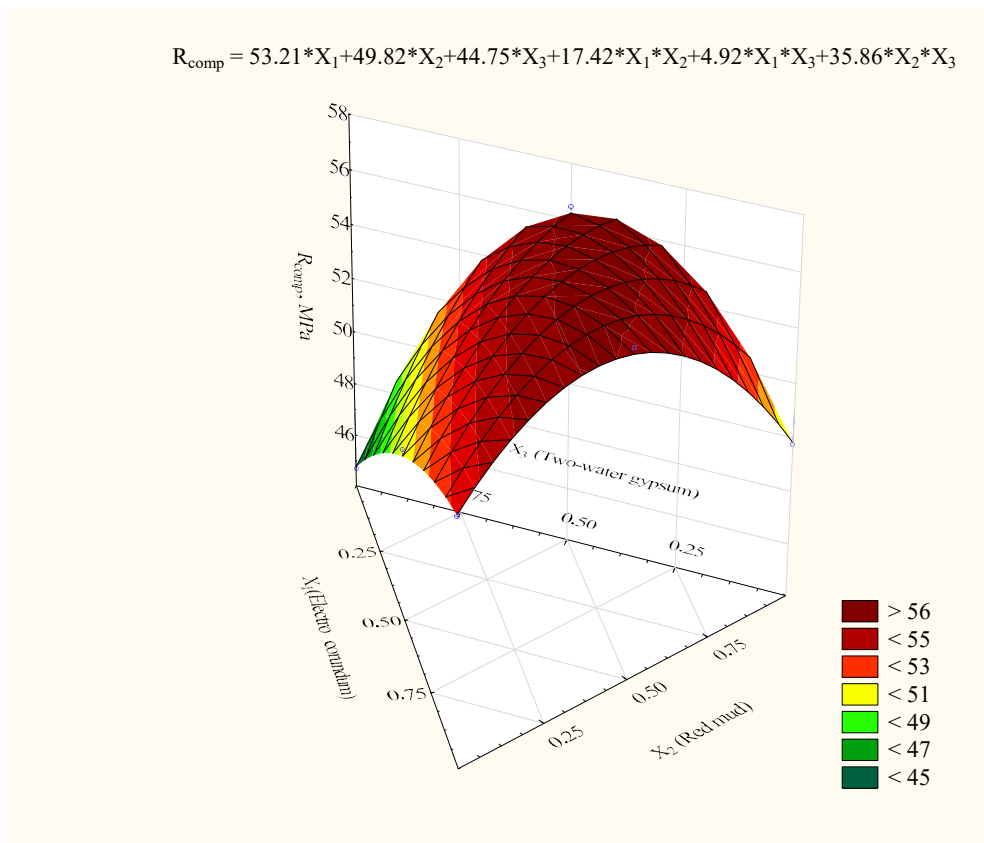


Fig. 3. Composition-compressive strength diagram for a binder containing electro corundum, red mud, and gypsum



a



b

Fig. 4. Diagrams of the composition influence: electro corundum, red mud, and dihydrate gypsum on the compressive strength limit: a – two-dimensional projection; b – three-dimensional projection

**5. 2. Development of a technological scheme for the production of binder**

Table 6 gives data on the grain composition of the components used for the development of binders based on red slime from the Mykolaiv Alumina Plant. Tables 3, 4

give data on the content of particles of different sizes in percentage ratio.

According to the results of the calculated raw material mixture, the binder was manufactured according to the technological scheme (Fig. 5).

Table 6

Grain composition

Name of grain composition indicators – particle content in accordance with DSTU	Technical requirements DSTU 9246-1:2023 for Mineral powder-I, not less than, %	Actual values	Extended uncertainty*, $\delta$	Complies with the requirements of the Regulations**
– smaller than 0.071 mm	80	83.71	0.20440	+
– smaller than 0.315 mm	90	94.65		
– smaller than 1.25 mm	100	100		

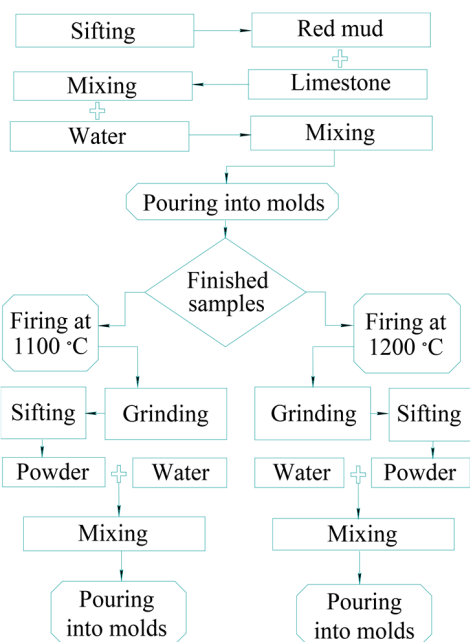


Fig. 5. Technological scheme of binder production

From the beginning, 592 g of red mud is sifted through a sieve with an opening size of 0.04 mm. This makes it possible to remove large particles and achieve homogeneity of the material. The first step is important to enable even mixing and reaction of the slurry with other components.

371 g of limestone was added to the sifted sludge. Limestone acts as an activator, promoting hydration and the formation of strong bonds in the final product. After the addition of limestone, the mixture was thoroughly mixed to achieve a uniform distribution of the components. The total mass of the obtained mixture was 963 g.

After determining the water-solid ratio (W/S), which is 0.33, 317 ml of water was added. Water is necessary to start the hydration processes and transform the dry mixture into a paste-like mass. It is important to follow the ratio precisely in order to obtain the desired physical properties of the final product.

All components were thoroughly mixed until a homogeneous paste-like mass was obtained. A plastic consistency was achieved during mixing. Due to the presence of iron oxide, the mixture acquires a red tint.

The resulting paste was poured into molds, successively tamping the mixture in each mold. This process is necessary to remove air bubbles and avoid the formation of voids, which can affect the strength and uniformity of the final product.

The molds were left for the necessary period for hardening, so that the material gained sufficient strength. During

this time, chemical reactions took place that provided the necessary mechanical properties of the binder material.

5.3. Studying the structure and basic physical-mechanical properties of the developed binder based on the CaO–Fe<sub>2</sub>O<sub>3</sub> system

The firing process was carried out at a temperature of 1100 °C (Fig. 6).

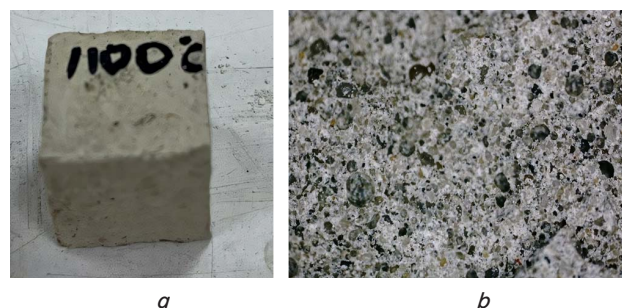


Fig. 6. The sample fired at a temperature of 1100 °C: a – photograph; b – photomicrograph

The samples after firing had a strength of 8.3 MPa. Next, the samples should be ground and sieved.

The obtained powder is mixed with the addition of water, forming a homogeneous mass:  $m_{tot}$  – 90 g,  $m_{H_2O}$  – 48 ml, W/S – 0.54.

The mixture is again poured into molds for further processing.

At the next stage, the samples were fired at a temperature of 1200 °C (Fig. 7).



Fig. 7. The sample fired at a temperature of 1200 °C: a – photograph; b – photomicrograph

The strength of unground samples immediately after firing was 50.3 MPa.

After grinding the fired samples, the powder was mixed with water, forming a homogeneous mass:  $m_{tot}$  – 132 g,  $m_{H_2O}$  – 55 ml, W/S – 0.41.



During the process of burning limestone, thermal decomposition of calcium carbonate ( $\text{CaCO}_3$ ) into calcium oxide ( $\text{CaO}$ ) and carbon dioxide ( $\text{CO}_2$ ) occurred. The reaction formula takes the following form:



As a result of this process, limestone loses part of its mass due to the release of carbon dioxide. Consequently, the residual material, which consisted mainly of calcium oxide, has a lower mass compared to the original limestone.

To ensure the correct chemical composition of the finished product after firing, these mass losses must be taken into account. This is achieved by adding more limestone at the initial stage. Thus, after the release of  $\text{CO}_2$  and mass loss, the residual  $\text{CaO}$  will be in the required amount to achieve the desired product composition:

1.  $X_{\text{CaO}} (\%) = 207.92 / 800 * 100 = 26\%$  – limestone.

2.  $X_{\text{Fe}_2\text{O}_3} (\%) = 592.36 / 800 * 100 = 74\%$  – red mud from the Mykolaiv Alumina Plant.

Charts of the dependence of compressive strength limits on the ratio of components are shown in Fig. 8.

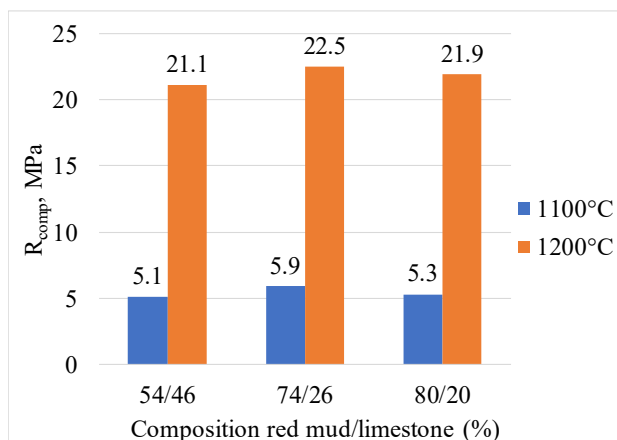


Fig. 8. Charts of dependence of compressive strength limits on the ratio of components and firing temperature

Due to the different firing temperatures, the following differences between the samples were observed. The first variant, fired at 1100 °C, turned out to be larger in size but when grinding, there was a noticeable difference in the strength of the samples. Option two, fired at 1200°C, was stronger, indicating a higher temperature advantage to achieve better mechanical properties of the final product.

For comparison, samples with different percentages of red mud and limestone were taken. Red mud is a byproduct of aluminum production that contains iron oxides and other minerals. Limestone is a sedimentary rock consisting mainly of calcite (calcium carbonate). The use of these materials in different proportions makes it possible to study their influence on the compressive strength of samples.

## 6. Discussion of results of the development of binders based on the $\text{CaO}-\text{Fe}_2\text{O}_3$ system

New techniques for obtaining compositions for the production of binders are quite effective in economic and technical terms. In contrast to [11], in which the developed

composite binder has a problem – the instability of the ettringite phase. The solution to this problem becomes possible owing to the development of a binder that does not contain factors of instability of the ettringite phase –  $\text{Ca}(\text{OH})_2$  and highly basic hydro aluminates (Tables 1, 3, 4, Fig. 1, 2). This is possible owing to the selection and calculation of the ratio of components, which in the process of hydration will have a sufficient amount of low basic hydro aluminates and  $\text{Al}(\text{OH})_3$  gel (Tables 1, 3, 4, Fig. 1, 2).

Solving the problem of stability of the ettringite component is possible using modern technologies and techniques for obtaining a binder – modifying calcium sulfoaluminates with red mud (Fig. 6). This will make it possible to purposefully regulate the rate of hydration and coordinate the process of structure formation in time and increase the stability of the ettringite phase (the main component of cement stone) (Fig. 6–8).

The developed binders using red mud confirm the effectiveness of the proposed technology (Table 5, Fig. 5, 8).

In contrast to study [10], in which the main attention was focused on the analysis of mechanical properties and microstructure, the result of the study of the structure of the developed binder based on the  $\text{CaO}-\text{Fe}_2\text{O}_3$  system makes it possible to obtain a fine-gap structure (Fig. 6, 7) with stable properties and saving energy resource. This becomes possible owing to the use of red mud with a particle size of less than  $5\ \mu\text{m}$  (up to 50 %) (Table 2), which lowers the firing temperature by 200–300 °C due to the presence of alkalis in its composition (Table 1).

Thus, the developed binder, with improved technological, physical-mechanical, and operational properties, can be used to repair concrete coatings (Fig. 7, 8).

The limitation of the study is that the results are adequate when using red mud up to 80 %. Taking them into account, they will meet practical or theoretical expectations.

The disadvantages of the study are the reduction of the amount of waste – red mud.

The development of this research consists in the development of iron-containing ettringite as a substitute for natural raw materials.

## 7. Conclusions

1. Based on the derived regression equation and determining, based on its analysis, optimal ratios, the following compositions of the input components were established: electro corundum – 55–56.3 %; red slime – 17.1–17.6 %; dihydrate gypsum – 25.9–28.2 %. These ratios provide a value of the output variable of 56 MPa.

Compositions have been also determined to ensure the appropriate quality of the finished product after firing: 26 % – limestone, red mud – 74 %.

2. The proposed technological scheme has a number of features. With its help, it is possible to solve unsolved problems of labor intensity and cost of technological operations by optimizing the technological process or searching for alternative, less expensive materials. The main one is red mud, which is already in a ready-to-use state. In this way, the issue of the complexity of the material preparation process and the high cost of reagents is solved. The use of this technological scheme could make it possible to reduce the cost of raw materials since 74 % of waste – red mud is used in the composition of the mixture, to reduce the firing temperature

by 200 °C due to the reduction of the starting temperature of sintering, and to obtain a given structure of high-strength binders based on it.

3. Raw samples with a loose structure, fired at a temperature of 1100 °C, have a compressive strength of 5.9 MPa, with a crack structure, fired at a temperature of 1200 °C – 22.5 MPa. Changing the percentage of red mud and limestone can affect the mechanical properties of the material. For example, increasing the content of red mud can lead to a decrease in strength due to the high content of iron oxides, which can create internal defects. On the other hand, the addition of limestone can increase strength due to calcium carbonate, which promotes better adhesion of particles in the material.

sonal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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#### Data availability

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All data are available, either in numerical or graphical form, in the main text of the manuscript.

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#### Conflicts of interest

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The authors declare that they have no conflicts of interest in relation to the current study, including financial, per-

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#### Use of artificial intelligence

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The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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