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OPTIMIZATION OF SPINEL-CONTAINING ALUMINA CEMENTS BASED ON THE $CaO-Al_2O_3-CoO-NiO$ SYSTEM COMPOSITION

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This paper presents the optimization of alumina cement formulations and an experimental investigation of the physical, mechanical, and technical properties of high performance, heat resistant cements derived from the $CaO-Al_2O_3-CoO-NiO$ system. Compositions were optimized using a simplex lattice experimental design and visualized with composition–property simplex diagrams. The studies were carried out based on the tetrahedron compounds $CoAl_2O_4-NiAl_2O_4-CaAl_4O_7-CaAl_2O_4$ to simultaneously enhance the heat resistance and strength of the developed combinations. All three-component cross-sections in the defined tetrahedron of the $CaO-Al_2O_3-CoO-NiO$ system were evaluated and optimal formulations were identified within the following ranges (wt.%): $CoAl_2O_4$ 5–30; $NiAl_2O_4$ 5–30; $CaAl_4O_7$ 20–40; and $CaAl_2O_4$ 20–50. Physicomechanical testing determined the most promising composition to be (wt.%): $CaAl_2O_4$ 50; $CoAl_2O_4$ 20; and $NiAl_2O_4$ 30. This cement exhibits a high strength at the age of 28 days of curing (62 MPa) and fire resistance up to 1720^0C. The refractory spinel containing alumina cement was synthesized using industrial chemical wastes as raw materials. The results demonstrate that these resource saving refractory cements meet all relevant standards and offer competitive performance. Employing recycled raw materials enables the development of novel refractory binders and contributes to improved environmental conditions in Ukraine's industrial regions.

Keywords: optimization, multicomponent system, experimental design, synthesis; resource-efficient technology, refractoriness, strength.

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Introduction

In recent years, industries using high-temperature equipment have seen a significant rise in the production and use of refractory cements, particularly those incorporating waste byproducts. This trend has led to considerable savings in raw materials, energy, and labor. In this context, the development of efficient refractory materials based on alumina cements – derived from chemical industry waste and formulated with a predefined set of operational and special characteristics – appears promising. Therefore, the research into utilizing chemical industry waste, such as wastewater treatment residues and spent catalyst carriers, which contain components similar to those of traditional raw materials for producing alumina cement, is of great interest. The use of secondary raw materials will create new high-temperature binding materials that can withstand aggressive environments and elevated temperatures by forming hydraulically active and spinel compounds during synthesis. This approach also promises to significantly improve the environmental situation in industrial regions of Ukraine.

From this perspective, optimizing the

formulations and studying the physical-mechanical properties of composition in the $CaO-Al_2O_3-CoO-NiO$ system is highly relevant, as its compounds can serve as key constituents in heat-resistant cements produced using various combinations of industrial waste as raw materials.

The objective of this work is to experimentally optimize the compositions and explore the physical-mechanical and technical properties of high-performance heat-resistant cements based on compositions within the $CaO-Al_2O_3-CoO-NiO$ system.

To achieve this goal, theoretical studies on the subsolidus structure of the $CaO-Al_2O_3-CoO-NiO$ system have been carried out. The geometric-topological characteristics of its phases were defined, allowing for the development of binders with a set of specific characteristics based on the compounds of this system [1,2].

It has been noted that during hydration of such cements, calcium aluminates are the main hydraulically active compounds. Formation of hydroaluminates of varying degrees of activity during hardening imparts high strength to the cement matrix and enhances its resistance to aggressive sulfate environments, while the presence of cobalt aluminate contributes to higher operating temperatures and high electrochemical stability. At the same time, presence of nickel spinel contributes to exceptional hardness and structural stability, as well as enhanced resistance to mechanical wear. Furthermore, both spinels can impart unique properties such as magnetic and electrical conductivity, finding applications in energy storage and conversion technologies. Presence of pure oxides in the cement compositions is undesirable, as they may transform during service, making the consideration of tetrahedra containing these phases technically unfeasible. Among the tetrahedra containing technologically significant phases, the largest volume is associated with $CaAl_{12}O_{19}-CoAl_2O_4-NiAl_2O_4-CaAl_4O_7$ and $CoAl_2O_4-NiAl_2O_4-CaAl_4O_7-CaAl_2O_4$, which has led to the development of specialized binders based on the compounds of these selected tetrahedra. The theoretical justification for choosing these sections was based on the calculation of melting temperatures and eutectic compositions [3,4].

Since the first section includes three hydraulically inert compounds, composition optimization was conducted based on the $CoAl_2O_4-NiAl_2O_4-CaAl_4O_7-CaAl_2O_4$ tetrahedron to simultaneously enhance heat resistance and strength. Therefore, studying this region of the four-component $CaO-Al_2O_3-CoO-NiO$ system is of interest from the standpoint of predicting cement properties and optimizing their compositions.

Experimental

To synthesize samples with the desired phase composition, raw mixtures were successively ground, mixed, and fired. The grinding and mixing of raw materials were carried out in a laboratory ball mill using the «wet method» (slurry water content of 50 wt.%). The fineness of grinding was monitored by sieve analysis (complete pass through sieve No. 006). Prior to firing, the raw mixtures were formed by double-sided pressing under a specific pressure of 60–80 MPa. The samples were fired in a furnace with silicon-carbide heating elements at the specified synthesis temperatures with isothermal holding. Temperature measurements during calcination were made using a platinum-platinum-rhodium thermocouple. The completeness of synthesis of compounds was monitored by X-ray phase analysis and chemical analysis, ensuring no free oxides of calcium, cobalt, and nickel were present [6].

Physical-mechanical tests of the cements were conducted according to Strelkov's small sample method [6], and optimal cement compositions were tested in accordance with the following state standards: DSTU EN 196-1:2019 Methods of testing cement. Part 1: Determination of strength[1], DSTU B EN 196-3:2015 Methods of cement testing. Part 3: Determination of setting time and soundness[2], and DSTU B EN 196-6:2015 Methods of testing cement. Part 6: Determination of fineness[3]. The refractory properties of the developed materials were determined according to the ISO 528:1983[4].

Optimization of compositions was carried out using the simplex-lattice method of experimental design, with the Office Excel software package. Simplex diagrams of «composition vs. property» were constructed using the Triangle V.1.0 software package [5].

[1] DSTU EN 196-1:2019 (EN 196-1:2016, IDT). Methods of testing cement. Part 1: Determination of strength. (2020.01.01). 34 p.

[2] DSTU B EN 196-3:2015 (EN 196-3:2005+A1:2008, IDT).Methods of cement testing. Part 3: Determination of setting time and soundness. (2016.07.01). 18 p.

[3] DSTU B EN 196-6:2015 (EN 196-6:2010, IDT). Methods of testing cement. Part 6: Determination of fineness. (2016.07.01). 24 p.

[4] ISO 528:1983. Refractory products. Determination of pyrometric cone equivalent (refractoriness). (1983.12.01). 7 p.

Results and discussions

To achieve high-strength, heat-resistant cement, stepwise optimization was performed in each of the three-component sections of the chosen pseudosection $CoAl_2O_4$–$NiAl_2O_4$–$CaAl_4O_7$–$CaAl_2O_4$. To prepare materials with the desired operational characteristics, selection of the optimal phase ratio in the final product and its properties was made using lattices for a third-order incomplete polynomial. Based on experimental data, regression equations of the «composition vs. property» dependences were obtained, and their adequacy was tested using Student's test and additional control experiments.

Based on the results of the calculations and mathematical processing of the experiments, «composition vs. property» diagrams have been constructed.

The experimental design matrices are presented in Tables 1–4. Here, the following notations are used: $Y_{\sigma\ compression}$ is the compressive strength at 28 days (MPa); and Y_m is the calculated melting temperature determined by the visual-pyrometric method from eutectic diagrams (^{0}C).

In the $CaAl_2O_4$–$CoAl_2O_4$–$NiAl_2O_4$ section, data were obtained on the strength of water-hardened samples and the estimated melting temperature derived using the visual-polythermal method based on eutectic diagrams (Table 1).

The regression equations for the «composition vs. property» dependences are as follows:

$$Y_{\sigma\ compression}=60x_1+72x_1x_2+48x_1x_3+666x_1x_2x_3,$$

$$Y_m=1875x_1+2253x_2+2293x_3-340x_1x_2-284x_1x_3-796x_2x_3-1446x_1x_2x_3,$$

where x_1, x_2, x_3 are the relative contents of $CaAl_2O_4$, $CoAl_2O_4$, and $NiAl_2O_4$, phases respectively.

The «composition vs. property» diagrams and projections of iso-strength lines for compressive strength and melting temperature of the compositions in the $CaAl_2O_4$–$CoAl_2O_4$–$NiAl_2O_4$ system are shown in Fig. 1.

From the analysis of the presented diagrams, it is established that over 50% of the compositions, after hardening, have a mechanical strength exceeding 50 MPa. The area of high strength characteristics is shifted towards $CaAl_2O_4$ as the only hydraulically active phase.

The isothermal lines corresponding to melting temperature are shifted toward the spinel phases, as they represent the most refractory compounds. Therefore, the region of optimal compositions in the $CaAl_2O_4$–$CoAl_2O_4$–$NiAl_2O_4$ section is located near the center of the diagram and is bounded by the following phase contents (wt.%): $CaAl_2O_4$ 20–60; $CoAl_2O_4$ 10–50; and $NiAl_2O_4$ 10–50. Within this range, compressive strength values of 40–60 MPa and melting temperatures of 1900–1950^{0}C are achieved.

In the $CaAl_2O_4$–$CaAl_4O_7$–$NiAl_2O_4$ section, data were obtained on the strength of water-hardened samples and the estimated melting temperature derived using the visual-polythermal method based on eutectic diagrams (Table 2).

The regression equations for the «composition vs. property» dependences are as follows:

$$Y_{\sigma\ compression}=49x_1+45x_2-8x_1x_2+110x_1x_3+62x_2x_3+201\cdot x_1x_2x_3,$$

$$Y_m=1602x_1+1762x_2+2020x_3-20x_1x_2-1024x_1x_3-768x_2x_3+396x_1x_2x_3,$$

where x_1, x_2, x_3 are the relative contents of $CaAl_2O_4$, $CaAl_4O_7$, and $NiAl_2O_4$ phases, respectively.

The «composition vs. property» diagrams and projections of iso-strength lines for compressive strength and melting temperature of the compositions

Table 1

Experimental design matrix for composition optimization in the $CaAl_2O_4$–$CoAl_2O_4$–$NiAl_2O_4$ section

Polynomial coefficients	Notations and physical meaning of factors				
	Phases			Experimental data	
	$CaAl_2O_4$	$CoAl_4O_4$	$NiAl_2O_4$	$Y_{\sigma\ compression}$	Y_m
η_1	1	0	0	60	1875
η_2	0	1	0	0	2253
η_3	0	0	1	0	2293
η_{12}	0.5	0.5	0	48	1979
η_{13}	0.5	0	0.5	42	2013
η_{23}	0	0.5	0.5	0	2074
η_{123}	0.33	0.33	0,33	58	1929
control point	0.2	0.3	0.5	40	1985

in the $CaAl_2O_4$–$CaAl_4O_7$–$NiAl_2O_4$ system are shown in Fig. 2.

Analysis of the diagrams shows that over 70% of compositions exhibit compressive strengths exceeding 40 MPa after hardening. The high-strength region is located near the $CaAl_2O_4$–$CaAl_4O_7$ segment, which forms the basis of high-alumina cement.

Regarding melting temperatures, the isothermal lines are shifted toward the spinel phase. In general, 70% of compositions in this section demonstrate refractory properties.

The region of optimal compositions in the $CaAl_2O_4$–$CaAl_4O_7$–$NiAl_2O_4$ section is confined to the following phase contents (wt.%): $CaAl_2O_4$ 10–50; $CaAl_4O_7$ 30–50; and $NiAl_2O_4$ 10–50. These compositions yield compressive strengths of 40–50 MPa and melting temperatures of 1600–1650^{0}C.

In the $CaAl_2O_4$–$CaAl_4O_7$–$CoAl_2O_4$ section, data were obtained on the strength of water-hardened samples and the estimated melting temperature derived using the visual-polythermal method based on eutectic diagrams (Table 3).

The regression equations for the «composition vs. property» relationships are as follows:

$$Y_{\sigma\ compression}=60x_1+32x_2+8x_1x_2-16x_1x_3+8x_2x_3+414x_1x_2x_3,$$

$$Y_m=1870x_1+2020x_2+2230x_3+140x_1x_2+100x_1x_3+200x_2x_3-6720x_1x_2x_3,$$

where x_1, x_2, x_3 are the relative contents of $CaAl_2O_4$, $CaAl_4O_7$, and $CoAl_2O_4$ phases, respectively.

The «composition vs. property» diagrams and projections of iso-strength lines for compressive strength and melting temperature of the compositions in the $CaAl_2O_4$–$CaAl_4O_7$–$CoAl_2O_4$ system are shown

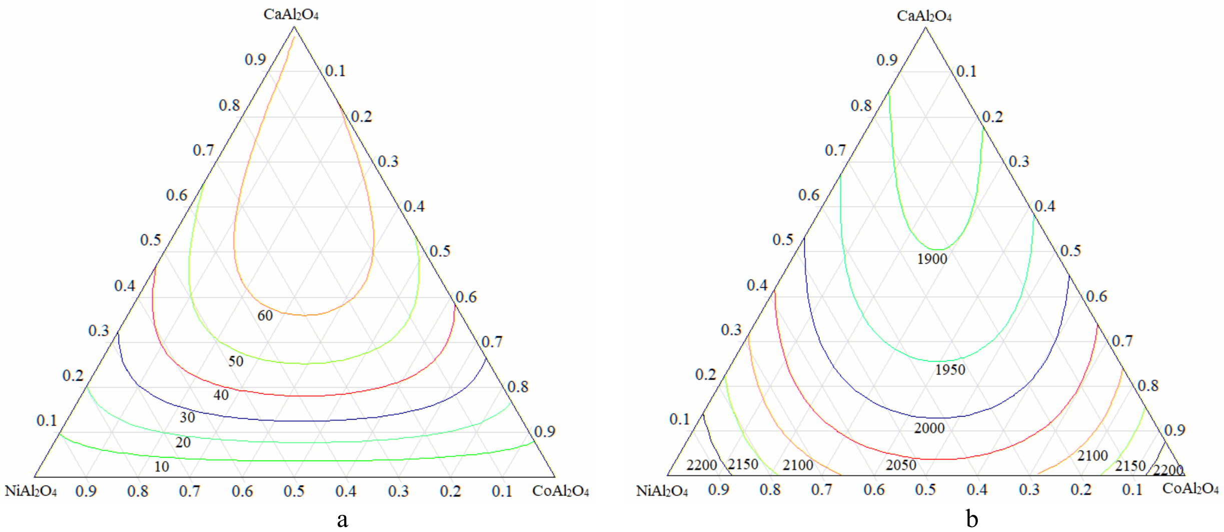


Fig. 1. Composition vs. property diagrams in the $CaAl_2O_4$–$CoAl_2O_4$–$NiAl_2O_4$ section:
a – compressive strength (MPa) vs. composition; b – melting temperature (^{0}C) vs. composition

Table 2

Experimental design matrix for composition optimization in the $CaAl_2O_4$–$CaAl_4O_7$–$NiAl_2O_4$ section

Polynomial coefficients	Notations and physical meaning of factors				
	Phases			Experimental data	
	$CaAl_2O_4$	$CaAl_4O_7$	$NiAl_2O_4$	$Y_{\sigma\ compression}$	Y_m
η_1	1	0	0	49	1602
η_2	0	1	0	45	1762
η_3	0	0	1	0	2020
η_{12}	0.5	0.5	0	45	1677
η_{13}	0.5	0	0.5	52	1555
η_{23}	0	0.5	0.5	38	1699
η_{123}	0.33	0.33	0.33	57	1608
control point	0.2	0.3	0.5	49	1650

in Fig. 3.

Although this section is analogous to the previous one (comprising two hydraulically active phases and one spinel phase), the diagrams differ slightly. The «composition vs. compressive strength» diagram confirms that over 70% of compositions achieve compressive strengths above 40 MPa, with the high-strength region located in the $CaAl_2O_4$–$CaAl_4O_7$ section (the basis of alumina cement). However, the isothermal lines of melting temperature indicate refractory properties across all compositions in this section.

The optimal composition range in the $CaAl_2O_4$–$CaAl_4O_7$–$CoAl_2O_4$ section is defined by the following phase contents (wt.%): $CaAl_2O_4$ 10–60; $CaAl_4O_7$ 10–50; and $CoAl_2O_4$ 20–50. These compositions yield compressive strengths of 40–50 MPa and melting temperatures of 1700–2000°C.

In the $CaAl_2O_4$–$CaAl_4O_7$–$CoAl_2O_4$ section, data were obtained on the strength of water-hardened samples and the estimated melting temperature derived using the visual-polythermal method based on eutectic diagrams (Table 4).

The regression equations for the «composition vs. property» relationships are as follows:

$$Y_{\sigma\ compression}=32x_1+8x_1x_2+88x_1x_3+207x_1x_2x_3,$$

$$Y_m=1762x_1+2230x_2+2020x_3+316x_1x_2-768x_1x_3-400x_2x_3+3960x_1x_2x_3,$$

where x_1, x_2, x_3 are the relative contents of $CaAl_4O_7$, $CoAl_2O_4$, and $NiAl_2O_4$ phases, respectively.

The «composition vs. property» diagrams and projections of iso-strength lines for compressive strength and melting temperature of the compositions

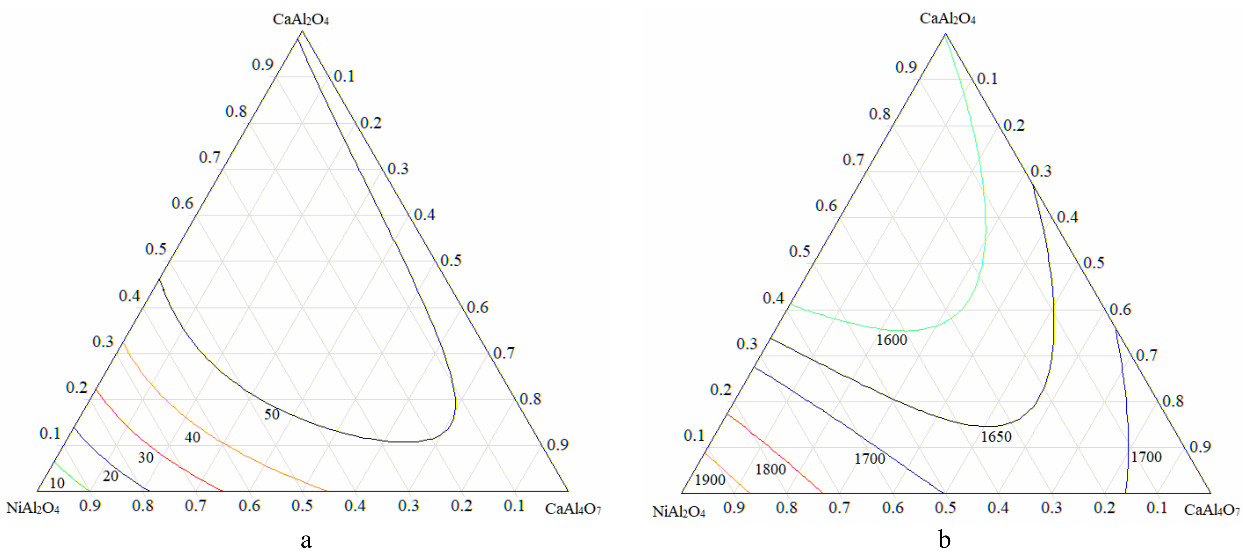


Fig. 2. Composition vs. property diagram in the $CaAl_2O_4$–$CaAl_4O_7$–$NiAl_2O_4$ section:
a – compressive strength (MPa) vs. composition; b – melting temperature (°C) vs. composition

Table 3

Experimental design matrix for composition optimization in the $CaAl_2O_4$–$CaAl_4O_7$–$CoAl_2O_4$ section

Polynomial coefficients	Notations and physical meaning of factors				
	Phases			Experimental data	
	$CaAl_2O_4$	$CaAl_4O_7$	$CoAl_2O_4$	$Y_{\sigma\ compression}$	Y_m
η_1	1	0	0	49	1602
η_2	0	1	0	45	1762
η_3	0	0	1	0	2230
η_{12}	0.5	0.5	0	48	1620
η_{13}	0.5	0	0.5	36	2075
η_{23}	0	0.5	0.5	30	2175
η_{123}	0.33	0.33	0.33	51	1840
control point	0.2	0.4	0.4	45	1940

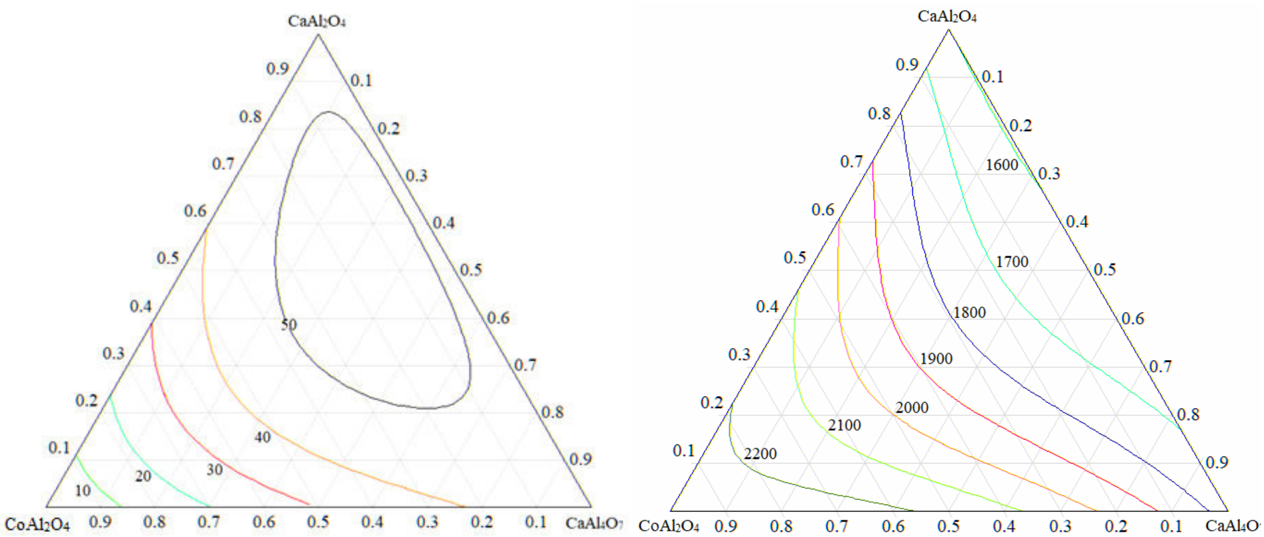
in the $CaAl_4O_7$–$CoAl_2O_4$–$NiAl_2O_4$ system are shown in Fig. 4.

From the analysis of the presented diagrams, it was established that due to the relatively low strength of the sole hydraulically active phase $CaAl_4O_7$, the overall mechanical strength of compositions within the $CaAl_4O_7$–$CoAl_2O_4$–$NiAl_2O_4$ section does not exceed 40 MPa. However, the general melting temperature of the compositions in this cross-section exceeds 1700°C. Therefore, these compositions can be classified as highly refractory, as this property exceeds 2000°C for more than 50% of the investigated formulations. The region of optimal compositions within the $CaAl_4O_7$–$CoAl_2O_4$–$NiAl_2O_4$ section is located near the $CaAl_4O_7$–$NiAl_2O_4$ boundary and is limited by the following phase content (wt.%): $CaAl_4O_7$ 50–70%; $CoAl_2O_4$ 0–10%; and $NiAl_2O_4$ 20–50. In this region, compressive strength values of up to 40 MPa are achieved, with melting temperatures in the range of 1700–1800°C.

Based on the computational results, to develop refractory cements within the $CoAl_2O_4$–$NiAl_2O_4$–$CaAl_4O_7$ section of the CaO–Al_2O_3–CoO–NiO system, the optimal compositions were selected to contain (wt.%): $CoAl_2O_4$ 5–30; $NiAl_2O_4$ 5–30; $CaAl_4O_7$ 20–40; and $CaAl_2O_4$ 20–50.

To verify the adequacy of the obtained regression models, compressive strength and melting temperatures were determined for control points within the various compositional sections (Tables 1–4). As shown by the presented data, the calculated regression equations are adequate, since the predicted mechanical strength and melting temperatures show satisfactory agreement with experimental results.

For the synthesis of refractory spinel-containing cements, raw material mixtures were prepared, and



a b

Fig. 3. Composition vs. property diagram in the $CaAl_2O_4$–$CaAl_4O_7$–$CoAl_2O_4$ section:
a – compressive strength (MPa) vs. composition; b – melting temperature (°C) vs. composition

Table 4

Experimental design matrix for composition optimization in the $CaAl_4O_7$–$CoAl_2O_4$–$NiAl_2O_4$ section

Polynomial coefficients	Notations and physical meaning of factors				
	Phases			Experimental data	
	$CaAl_4O_7$	$CoAl_2O_4$	$NiAl_2O_4$	$Y_{\sigma\ compression}$	Y_m
η_1	1	0	0	32	1762
η_2	0	1	0	0	2230
η_3	0	0	1	0	2020
η_{12}	0.5	0.5	0	18	2175
η_{13}	0.5	0	0.5	38	1699
η_{23}	0	0.5	0.5	0	2025
η_{123}	0.33	0.33	0.33	29	2056
control point	0.4	0.3	0.3	33	2020

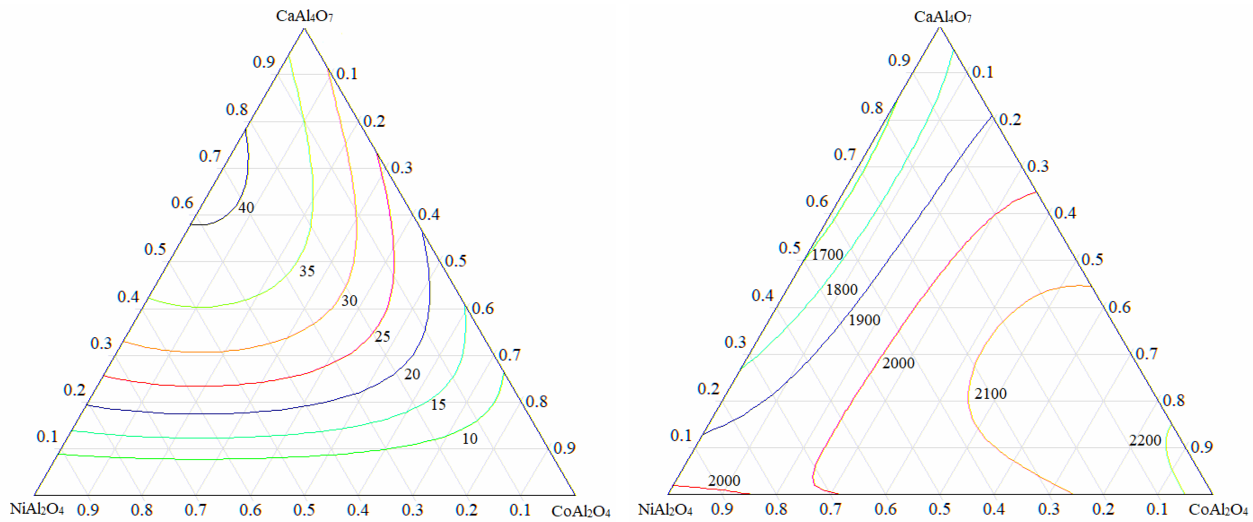
their chemical and phase compositions are presented in Table 5.

The raw material mixtures were ground and fired following the previously described methodology. The firing temperature of the cements ranged between 1400–1450^{0}C depending on their phase composition, with an isothermal hold at peak temperature maintained for 3 hours.

Testing of the compositions was carried out using small specimens [5], which were cured for 24 hours under moist conditions and subsequently stored in water. Refractoriness was determined according to the method described in ref. [6]. The results of the physical-mechanical property tests of the synthesized cements are presented in Table 6.

Based on the results of physical-mechanical testing, the developed alumina cements were classified as hydraulic binders with a standard consistency in the range of 0.25–0.33. They are characterized as rapid-hardening (compressive strength at 1 day of curing ranges from 28 to 43 MPa), and high-strength (compressive strength at 28 days ranges from 38 to 63 MPa) hydraulic materials. Moreover, more than 50% of the compositions exhibit refractoriness above 1580^{0}C.

Following the conducted studies, the optimal



a b

Fig. 4. Composition vs. property diagram in the $CaAl_4O_7$–$CoAl_2O_4$–$NiAl_2O_4$ section:
a – compressive strength (MPa) vs. composition; b – melting temperature (^{0}C) vs. composition

Table 5

Chemical and phase composition of the developed cements

No.	Chemical composition, wt.%				Phase composition, wt.%			
	CaO	Al_2O_3	CoO	NiO	$CaAl_2O_4$	$CaAl_4O_7$	$CoAl_2O_4$	$NiAl_2O_4$
1	14.19	60.41	12.71	12.69	40	–	30	30
2	21.29	61.8	8.47	8.46	60	–	20	20
3	17.74	61.10	8.47	12.69	50	–	20	30
4	24.98	70.79	–	4.23	40	50	–	10
5	26.37	69.40	–	4.23	50	40	–	10
6	22.82	68.72	–	8.46	40	40	–	20
7	22.82	68.71	8.47	–	40	40	20	–
8	26.37	69.39	4.24	–	50	40	10	–
9	25.61	65.92	8.47	–	60	20	20	–
10	8.63	65.99	16.91	–	–	40	20	40
11	15.09	72.21	4.24	8.46	–	70	10	20
12	12.94	70.13	4.24	12.69	–	60	10	30
13	17.11	65.96	8.47	8.46	30	30	20	20
14	13.57	65.27	10.59	10.57	20	30	25	25
15	14.96	63.88	10.59	10.57	30	20	25	25

composition was determined to contain 50 wt.% $CaAl_2O_4$, 20 wt.% $CoAl_2O_4$, and 30 wt.% $NiAl_2O_4$. This cement demonstrated high compressive strength of 62 MPa at 28 days of curing and refractoriness of 1720^{0}C.

The produced spinel-containing refractory alumina cement with enhanced physical-mechanical properties was synthesized using industrial waste as raw materials, namely: sludge from the decarbonization of river water in external water supply systems ($CaCO_3$ as a main component); spent catalysts from hydroprocessing of hydrocarbon feedstocks (Co(Ni)Mo(W)S on a γ-Al_2O_3 support as main components); and steam-air reforming of methane (NiO on a γ-Al_2O_3 support as a main component).

The main physical-mechanical properties of the developed spinel-containing alumina cement and its comparison with the properties of the commercial Gorkal-50 alumina cement are shown in Table 7.

The obtained results indicate that the cements developed based on calcium, cobalt, and nickel aluminates belong to the class of hydraulic binders with low normal consistency, are rapid-hardening, fast-setting, and exhibit high refractoriness. These materials can be recommended for the production of refractory concretes, gunning masses (shotcretes), and mortars intended for application in high-temperature units across various industrial sectors.

Conclusions

Based on the experimental research, the

Table 6

Physical-mechanical properties of the developed cements

No.	Standard consistency	Setting time, h, min		Compressive strength, MPa, at age (days)			Refractoriness, ^{0}C
		initial	final	1	7	28	
1	0.28	1–05	5–30	42	48	61	1730
2	0.29	1–10	5–00	43	49	63	1680
3	0.29	0–55	5–50	42	48	62	1720
4	0.31	1–10	2–10	32	48	51	1490
5	0.30	0–45	1–45	32	47	51	1480
6	0.31	0–55	1–50	33	47	52	1460
7	0.26	1–10	5–30	32	49	52	1580
8	0.25	1–10	5–40	32	47	51	1500
9	0.26	1–20	5–40	32	48	51	1550
10	0.31	2–40	6–10	28	30	35	1730
11	0.33	2–20	6–00	28	32	39	1540
12	0.32	2–30	6–05	29	32	38	1530
13	0.26	1–00	2–00	31	39	45	1830
14	0.25	1–30	2–10	30	36	41	1710
15	0.26	0–50	1–50	33	37	46	1700

Table 7

Comparative characteristics of the developed cements

Property	Requirements according to the state standard DSTU B V.2.7-258:2011	Gorkal-50	Developed cement
Compressive strength, MPa, not less than, at the age of: – 1 day – 3 days	 22.5 40.0	 – 45	 42 48
Fineness (residue on sieve No. 008 according to the state standard DSTU EN 196-6), %, not more than		10	complete pass
Setting time, min – initial, not earlier than – final, not later than	 45 10	 90 8	 55 6
Refractoriness, ^{0}C, not less than	1580	1700	1720

physical-mechanical and technical properties of refractory spinel-containing cements have been determined and their compositions optimized. These cements, developed within the $CaO-Al_2O_3-CoO-NiO$ system, exhibit high-performance characteristics. The main physical-mechanical properties of the developed cement are: normal consistency in the range of 0.25–0.33; compressive strength at 1 day of curing from 28 to 43 MPa; and compressive strength at 28 days from 38 to 63 MPa. A key technical attribute of the majority of the developed compositions is their refractoriness, which exceeds 1580^0C.

The results confirm that the refractory spinel-containing cements, produced via a resource-efficient technology, comply with applicable standards and regulatory documentation. Comparative analysis of performance characteristics demonstrates that the developed cement can serve as a viable alternative to conventional alumina cement in the manufacture of high-strength refractory concretes and mortars, particularly for use in high-temperature industrial units across a range of sectors.

REFERENCES

1. *Do* pytannia pro spivisnuvannia nikelevoi i kobaltovoi shpineli / Khrystych O.V., Korohodska A. M., Shabanova H. M., Lohvinkov S.M. // Visnyk Natsionalnoho Tekhnichnoho Universytetu «KhPI». – 2024. – Vol.1. – No. 11. – P.57-62.

2. *Physicochemical* principles of creating alumina cements based on nickel and cobalt spinel / Khrystych O.V., Shabanova G.N., Korogodska A.N., Logvinkov S.M., Mykhailova E.A. // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2024. – No. 5. – P.85-90.

3. *Kharakterystyka* subsolidusnoi budovy systemy $CaO-Al_2O_3-CoO-NiO$ / Khrystych O.V., Korohodska A.M., Shabanova H.M., Lohvinkov S.M., Vorozhbiian R.M. // Visnyk Natsionalnoho Tekhnichnoho Universytetu «KhPI». – 2024. – Vol.2. – No. 12. – P.40-44.

4. *Otsinka* temperatur ta skladiv evtektyk poli komponentnykh pereriziv systemy $CoO-NiO-Al_2O_3$ / Khrystych O.V., Korohodska A.M., Shabanova H.M., Lohvinkov S.M., Volobuiev M.M. // Vcheni Zapysky Tavriiskyi Natsionalnyi Universytet im. V.I. Vernadskoho, Seriya Tekhnichni Nauky. – 2024. – Vol.35. – No. 74, 3. – P.33-137.

5. *Kumar Sh., Barai S.V.* Concrete fracture models and applications. – Berlin: Springer-Verlag, 2011. – 262 p.

6. *Shabanova H.M. Korohodska A.M., Khrystych O.V.* Viazhuchi materialy: praktykum. – Kharkiv: NTU «KhPI», 2014. – 220 p.

7. *Powder* diffraction file. Inorganic phases. Alphabetical index (chemical & mineral names). Pennsylvania (USA): JCPDS, 1985. – 1856 p.

8. *Kazimirov V.P., Rusanov E.* Renthenohrafiia krystalichnykh materialiv. – Kyiv: VPTs «Kyivskyi Universytet», 2016. – 287 p.

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ОПТИМІЗАЦІЯ СКЛАДІВ ШПІНЕЛЬВМІСНИХ ГЛИНОЗЕМИСТИХ ЦЕМЕНТІВ НА ОСНОВІ КОМПОЗИЦІЇ СИСТЕМИ $CaO-Al_2O_3-CoO-NiO$

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У статті наведено результати оптимізації складів глиноземистого цементу та експериментальних досліджень фізико-механічних і технічних властивостей жаростійких цементів з високими експлуатаційними характеристиками на основі композицій системи $CaO-Al_2O_3-CoO-NiO$. Оптимізацію складів здійснювали за допомогою симплекс-гратчастого методу планування експерименту з побудовою симплекс-діаграм «склад–властивість». Дослідження здійснювались на основі сполук тетраедру $CoAl_2O_4-NiAl_2O_4-CaAl_4O_7-CaAl_2O_4$ для одночасного підвищення жаростійкості та міцності розроблених комбінацій. Розглянуто всі трикомпонентні перерізи у визначеному тетраедру і системи $CaO-Al_2O_3-CoO-NiO$ та за результатами розрахунків обрано оптимальні склади композицій із наступним вмістом, мас.%: $CoAl_2O_4$ 5–30; $NiAl_2O_4$ 5–30; $CaAl_4O_7$ 20–40; $CaAl_2O_4$ 20–50. За результатами проведених фізико-механічних випробувань раціональним обрано наступний склад, мас.%: $CaAl_2O_4$ 50, $CoAl_2O_4$ 20, $NiAl_2O_4$ 30. Цей цемент характеризується високою міцністю у віці 28 діб тверднення (62 МПа) і вогнетривкістю 1720^0С. Виготовлений вогнетривкий шпінельвмісний глиноземистий цемент з підвищеними фізико-механічними властивостями був синтезований на основі відходів хімічних виробництв як сировинних матеріалів. Визначено, що розроблені за ресурсозберігаючою технологією вогнетривкі глиноземні цементи є конкурентоспроможними та відповідають вимогам нормативної документації. Застосування вторинної сировини дасть змогу створювати нові тугоплавкі в'яжучі матеріали та значно поліпшити екологічну ситуацію у промислових регіонах України.

Ключові слова: оптимізація, багатокомпонентна система, планування експерименту, синтез, ресурсозберігаюча технологія, вогнетривкість, міцність.

OPTIMIZATION OF SPINEL-CONTAINING ALUMINA CEMENTS BASED ON THE $CaO-Al_2O_3-CoO-NiO$ SYSTEM COMPOSITION

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This paper presents the optimization of alumina cement formulations and an experimental investigation of the physical, mechanical, and technical properties of high performance, heat resistant cements derived from the $CaO-Al_2O_3-CoO-NiO$ system. Compositions were optimized using a simplex lattice experimental design and visualized with composition–property simplex diagrams. The studies were carried out based on the tetrahedron compounds $CoAl_2O_4-NiAl_2O_4-CaAl_4O_7-CaAl_2O_4$ to simultaneously enhance the heat resistance and strength of the developed combinations. All three-component cross-sections in the defined tetrahedron of the $CaO-Al_2O_3-CoO-NiO$ system were evaluated and optimal formulations were identified within the following ranges (wt.%): $CoAl_2O_4$ 5–30; $NiAl_2O_4$ 5–30; $CaAl_4O_7$ 20–40; and $CaAl_2O_4$ 20–50. Physicomechanical testing determined the most promising composition to be (wt.%): $CaAl_2O_4$ 50; $CoAl_2O_4$ 20; and $NiAl_2O_4$ 30. This cement exhibits a high strength at the age of 28 days of curing (62 MPa) and fire resistance up to 1720^0C. The refractory spinel containing alumina cement was synthesized using industrial chemical wastes as raw materials. The results demonstrate that these resource saving refractory cements meet all relevant standards and offer competitive performance. Employing recycled raw materials enables the development of novel refractory binders and contributes to improved environmental conditions in Ukraine's industrial regions.

Keywords: optimization; multicomponent system; experimental design; synthesis; resource-efficient technology; refractoriness; strength.

REFERENCES

1. Khrystych OV, Korohodska AM, Shabanova HM, Lohvinkov SM. Do pytannia pro spivisnuvannia nikelevoi i kobaltovoi shpineli [On the question of coexistence of nickel and cobalt spinel]. *Visnyk Natsionalnoho Tekhnichnoho Universytetu «KhPI»*. 2024; 1(11): 57-62. (*in Ukrainian*). doi: 10.20998/2079-0821.2024.01.07.

2. Khrystych OV, Shabanova GN, Korogodska AN, Logvinkov SM, Mykhailova EA. Physicochemical principles of creating alumina cements based on nickel and cobalt spinel. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2024; (5): 85-90. doi: 10.32434/0321-4095-2024-156-5-85-90.

3. Khrystych OV, Korohodska AM, Shabanova HM, Lohvinkov SM, Vorozhbiian RM. Kharakterystyka subsolidusnoi budovy systemy $CaO-Al_2O_3-CoO-NiO$ [Characterization of the subsolidus structure of the $CaO-Al_2O_3-CoO-NiO$ system]. *Visnyk Natsionalnoho Tekhnichnoho Universytetu «KhPI»*. 2024; 2(12): 40-44. (*in Ukrainian*). doi: 10.20998/2079-0821.2024.02.07.

4. Khrystych OV, Korohodska AM, Shabanova HM, Lohvinkov SM, Volobuiev MM. Otsinka temperatur ta skladiv evtektyk poli komponentnykh pereriziv systemy $CoO-NiO-Al_2O_3$ [Estimation of temperatures and compositions of eutectics of multicomponent cross-sections of the $CoO-NiO-Al_2O_3$ system]. *Vcheni Zzapysky Tavriiskyi Natsionalnyi Universytet imeni VI Vernadskoho Seriya Tekhnichni Nauky*. 2024; 35(74): 133-137. (*in Ukrainian*). doi: 10.32782/2663-5941/2024.3.2/19.

5. Kumar S, Barai SV. *Concrete fracture models and applications*. Berlin: Springer-Verlag; 2011. 262 p.

6. Shabanova HM, Korohodska AM, Khrystych OV. *Viazhuchi materialy: praktykum* [Binding materials: handbook]. Kharkiv: NTU «KhPI»; 2014. 220 p. (*in Ukrainian*).

7. *Powder diffraction file. Inorganic phases. Alphabetical index (chemical & mineral names)*. Pennsylvania (USA): JCPDS; 1985. 1856 p.

8. Kazimirov VP, Rusanov E. *Renthenohrafiya krystalichnykh materialiv* [X-ray diffraction of crystalline materials]. Kyiv: VPTs «Kyivskyi Universytet»; 2016. 287 p. (*in Ukrainian*).