Comprehensive Neutralization of Fuel Energy Waste in the Production of Calcining Efficient Building Materials

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Abstract: The development of technologies for producing ceramic building materials based on energy waste fuels is associated with the study and identification of their valuable properties, which ensure the possibility of producing wares with high performance characteristics. The physicochemical and technological properties of ash and slag and high-calcium waste from the Novocherkassk Regional Power Station have been studied and their influence during high-temperature treatment on the basic properties of ceramic bricks - porosity, density, strength, depending on the chemical and mineralogical composition of the clay raw material has been established. The use of the mathematical planning method using a Scheffe lattice plan of incomplete 3rd order made it possible to determine the areas of structures formation with different properties depending on the content of waste and clay raw materials and to establish the area of tailored compositions, which can significantly reduce the number of experiments performed. Studies of the phase composition have shown that the strength properties of ceramics are ensured by the formation of new crystalline phases

1 INTRODUCTION

The fuel and energy complex generates a huge amount of waste, the disposal of which is the most important task of environmental safety. Depending on the production methods, the resulting waste is characterized by different chemical, granulometric composition and permanence of properties.

However, a thorough study of fuel energy waste using a set of modern physical and chemical methods makes it possible to identify valuable properties and obtain various materials based on them, most often for construction purposes (Abdrakhimova, 2019; Fedorova, Shaforost, 2015).

For the production of building materials, solid energy waste is of interest, the most significant of which is ash and slag waste (ASW), accounting for about 99%, currently used in an amount of no more than 4%, and the rest occupies large areas of enterprise territories. As a result of burning coal in the furnaces of steam boilers, sintered and even fused pieces of ash are formed, ranging in size from 0.2 to 20...30 mm.

The teams of Russian and foreign scientific schools have been engaged in the disposal of ash and slag for a long time. Most often, technologies for neutralizing ash and slag are associated with the production of foam glass-crystalline materials based on them (Grushko, 2020; Yatsenko, 2014).

2 SOLID WASTE FROM FUEL ENERGY AND ITS CHARACTERISTICS

One of the promising directions is the use of ash and slag waste as an alkali-containing mineralizer (Table 1) for the production of burnt clay masonry materials (Yatsenko, Palamarchuk, 2002; Yatsenko, 2005).

Another fuel energy waste is high-calcium waste (HCW), which is formed as a result of chemical water treatment during cooling of boiler furnaces at power

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plants. They are a serious problem in the operating cycle of these industries, due to the large tonnage, the need to equip large-area settling tanks, and environmental pollution (Yatsenko, Ratkova, 2005).

The studies of HCW have shown a slight fluctuation in their chemical and mineralogical composition, associated with the constant regional composition of the water used for cooling. Thus, the phase composition of the HCW of the Novocherkassk State Regional Power Station is represented by calcite and a metastable reactive phase of aragonite.

The integrated use of electrical energy waste in the production of effective solid ceramic bricks, characterized by a porosity of more than 30%, while implementing previously established patterns of their use, is of scientific interest. Thus, the HCW, containing about 90% of calcium carbonate (Table 1), at roasting temperatures above 950 °C decomposes with the formation of CaO and CO_2, facilitating the porosity of the ceramic material, and interacts with other components of the mass with the formation of new crystalline phases (Yatsenko, Yatsenko, Zakarlyuka, 2017). The porosity of the ceramic will depend on the content of waste introduced into it, and the strength will depend on the phase composition. In the formation of the phase composition, alkali-containing additives play an important role, which help reduce the decarbonization temperature of calcium-containing materials.

3 STUDY OF THE ROLE OF VKO AND ZSHO IN THE PRODUCTION OF FIRED BUILDING MATERIALS

In this work, to produce ceramic durable and porous bricks based on solid fuel energy waste, ash and slag waste from the Novocherkassk Regional Power Station was used as such an additive.

To regulate the technological and physical-technical properties of the material, local clays of the Rostov region of the Vladimirovskoye and Kamennobrodskoye deposits have been introduced, the chemical composition of which is given in Table 1.

Table 1: Chemical composition of natural raw and industry-related materials.

Material	Content, % in mass.									Sum
	SiO_2	Al_2O_3 + TiO_2	FeO+ Fe_2O_3	CaO	MgO	K_20	Na_2O	SO_3	nnn	
Novocherkassk Regional Power Station HCW	5.10	2.60	1.70	45.10	4.60	0.30		-	40.30	99.70
Novocherkassk Regional Power Station ASW	54.56	20.19	11.92	3.72	1.64	3.35	0.98	0.08	3.44	99.88
Kamennobrodskoye Clay	61.25	12.01	5.19	6.48	1.25	2.89		-	10.38	99.45
Vladimirovskoye Clay	57.48	22.86	2.29	0.83	1.39	3.48		-	9.30	97.63

To establish the maximum possible content of HCW to ensure high porosity, the main components of the mass were varied as follows, % in mass: clay - 20, HCW - 40...50, ASW - 30...40. Roasting was carried out at a temperature of 950°C. The research results are presented in Table 2.

Table 2: Properties of ceramics depending on the content of energy waste.

Compo-	Materials content, % in mass.	Property indicators			
					Strength,

sition No.	Kamen-nobrods koye Clay	Vladimiro vskoye Clay	HCW	ASW	Water absorption, %	Pore content, %	Density g/cm3	MPa
1	20.0	-	50.0	30.0	58.0	63.0	1.00	7.4
2	20.0	-	45.0	35.0	52.0	57.0	1.05	7.5
3	20.0	-	40.0	40.0	27.0	36.0	1.18	9.6
4	-	20.0	50.0	30.0	33.1	41.0	1.20	9.3
5	-	20.0	45.0	35.0	32.0	40.0	1.20	9.4
6	-	20.0	40.0	40.0	30.0	39.0	1.20	9.4

4 RESULTS OF STUDIES OF THE PHASE COMPOSITION AND PROPERTIES OF CERAMICS DEPENDING ON THE METHOD OF POROSITY USING THE MATHEMATICAL PLANNING METHOD AND THEIR DISCUSSION

The research results show the greatest porosity when introducing HCW in an amount of 50%. At the same time, the presence of its own carbonate in Kamennobrodskoye clay increases porosity to 63%. Having the same HCW content, the samples based on Vladimirovskoye clay have a porosity of only 41%. As the ASW content increases, the strength properties increase. The optimal composition based on Vladimirovskoye clay contains 45% high-calcium and 35% ash and slag waste and is characterized by the following properties: porosity - 39%, density - 1200 kg/m3, compressive strength - 9.4 MPa.

To increase porosity, the additional porosity was used at the preparation stage for the mass based on Vladimirovskoye clay (composition 61) through the use of reactions associated with the release of gaseous products between carbonates and acids:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2\uparrow + 2H_2O$$

Sulfuric acid (2%) was introduced into the plastic mass in an amount of 10%. The molding of samples from a porous mass with a moisture content of 30% was carried out in metal molds. The dried samples were roasted at the temperatures of 950 and 1000°C at exposure at maximum temperature for 2 hours. The research results presented in Figure 1 show that when containing 6_1 (40% HCW, 40% ASW and 20% Vladimirovskoye clay) when using chemical porosization at the stage of mass preparation and decarbonization, the HCW at roasting temperatures of 950 and 1000 °C more porous structure of the material (porosity 45 and 55%) compared to composition No. 6, with a density of 1.2 and 1.0 is formed

g/cm3, strength 4.0 and 5.5 MPa.

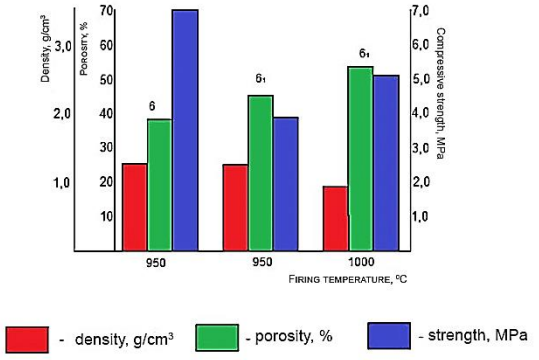

Figure 1: Properties of samples of composition 6 and 6_1 depending on the roasting temperature and porosization methods

The obtained properties are ensured by the formation of a porous structure and phase composition due to physicochemical processes occurring in clay-carbonate systems at a roasting temperature of 1000 °C.

To establish the influence of the content of industry-related energy waste using the thermal porosity method, we used a mathematical method of experiment planning using an incomplete 3rd order Scheffe lattice design, the matrix of which is given in Table. 3.

Table 3: Experiment design matrix.

Composition no.	Component content, wt. %			∑, %
	HCW	SRPS slag	Vladimirovskoye Clay	

X1	80.0	-	20.0	100.0
X2	-	-	100.0	100.0
X3	-	80.0	20.0	100.0

The experimental data obtained with the help of mathematical planning are given in table. 4.

Table 4:The studies results according to the Scheffe plan.

Experience no.	Furnace-charge composition, unit fractions			Response functions			
	X1	X2	X3	Water absorption,% (U1)	Porosity, % (U2)	Density, g/cm3 (U3)	Strength, MPa (U4)
1	1	0	0	61.0	69.0	0.76	0
2	0	1	0	8.9	17.49	1.89	12.76
3	0	0	1	9.1	18.35	1.87	28.27
4	0.5	0.5	0	31.3	41.51	1.26	11.72
5	0	0.5	0.5	8.4	16.99	1.90	15.62
6	0.5	0	0.5	39.3	50.15	1.23	2.25
7	0.333	0.333	0.333	28.4	40.73	1.37	11.85
8*	0.6	0.2	0.2	48.2	54.58	1.08	2.04

* Experience 8 corresponds to the control point.

According to the formulae corresponding to the Scheffe plan, the incomplete third order polynomials of general form are calculated:

$$y = \sum b_i x_i + \sum b_{ik} x_{ik} + \sum b_{ikl} x_i x_k x_l$$

Where: ; ; $b_i = y$ $b_{ik} = 4y_{ik} - 2y_i - 2y_k$

$$b_{ikl} = 27y_{ikl} - 12(y_{ik} + y_{kl} + y_{il}) + 3(y_i + y_k + y_l).$$

The incomplete third order polynomial for strength (a), porosity (b), density (c) has the form:

У1 = 41.55· X1 + 0 · X2 – 34.48· X3 – 42.98 · X1 · X2 – 65.12 · X2 · X3 + 4.78· X1 · X3 – 205.82 · X1 · X2 · X3. (A)

У2 = 16.01 · X1 + 50.06 · X2 + 21.56 · X3 – 10.46 · X1 · X2 + 29.24 · X2 · X3+ + 1.82 · X1 · X3 + 151.5 · X1 · X2 · X3 (b)

У3 = 1.875 · X1 + 1.268 · X2 + 1.849 · X3 – 0.622 · X1 · X2 - 0.566 · X2 · · X3+ 0.232· X1 · X3 – 2.856 · X1 · X2 · X3 (c)

The results obtained on the basis of equations (a, b, c), presented in the diagrams (Fig. 2), make it possible to establish the range of post-roasting properties depending on the content of industry-related energy waste.

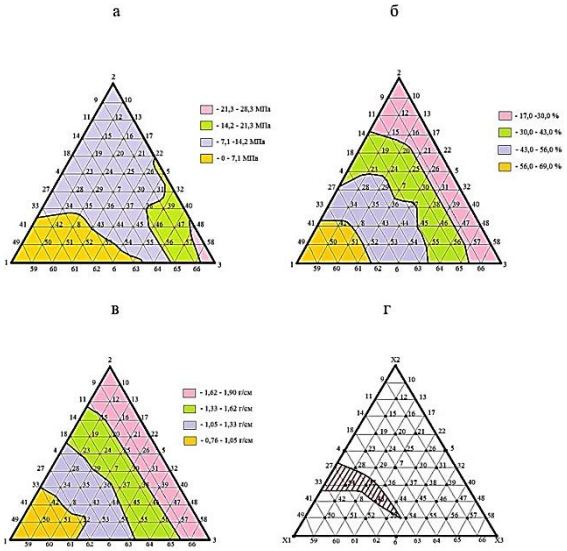

Figure 2: Diagram of strength (a), porosity (b), density (c) depending on the content of technogenic waste, area of optimal properties (d).

The results of the studies made it possible to establish the area of the compositions with optimal properties (Fig. 2, d), which is highlighted by shading. This area includes compositions (27, 33, 34, 35, 43) with a porosity of more than 40%, which classifies such ceramics as low-density, with a density of less than 1.2 g/cm3 (effective ceramic brick) and a strength of more than 7.5 MPa. The calculated properties of the compositions of the optimal region are given in Table 5.

Table 5: Properties of optimal area compositions.

Composition no.	Furnace-charge composition, unit fractions			Response functions			
	X1	X2	X3	Water absorption,% (U1)	Porosity, % (U2)	Density, g/cm3 (U3)	Strength, MPa (U4)
27	0.6	0.4	0	36,656	46,730	1.149	10,230
33	0.7	0.3	0	42,304	52,089	1,044	8,313
34	0.6	0.3	0.1	39,504	52,942	1.106	8,643
35	0.5	0.3	0.2	36,030	51,895	1,188	9,396
43	0.5	0.2	0.3	37,630	53,623	1.182	7,502

To study the phase composition of a ceramic material with optimal properties, we chose the composition 43, containing clay - 36.0%, HCW - 40.0%, ASW - 24.0%. Based on this composition, the experimental studies were carried out (Table 6), the results of which indicate their reproducibility and comparability with the calculated ones.

Table 6: Calculated and experimental data on the properties of ceramic samples.

Composition no.	Water absorption,%	Porosity, %	Density, g/cm3	Strength, MPa
43(calculated)	37.6	53.6	1.183	7.5
43(experiment)	37.5	49.5	1.217	9.5

It should be noted that the resulting diagrams make it possible to establish the composition of ceramic masses based on technogenic waste from the Novocherkassk Regional Power Station, with a different set of properties, including high-strength properties and meeting the requirements for producing ordinary ceramic bricks.

X-ray phase studies (Figure 3) showed that in a ceramic sample of composition 43 the following crystalline phases are incredible: β-quartz (0.426, 0.337, 0.245, 0.181, 0.145nm), a solid solution of the melilito-helenite row (0.371, 0.324, 0.285 nm), hedenbergitis $CaO \cdot FeO \cdot 2SIO_2$ (0.300; ; 0.238 nm), which ensures the strength properties of the ceramic material.

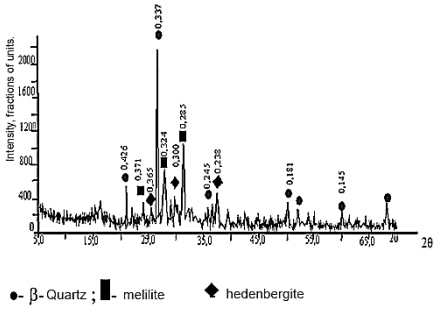

Figure 3: Phase composition of a sample of composition 43.

5 CONCLUSIONS

Thus, when forming the structure of ceramics based on technogenic raw materials from the Novocherkassk Regional Power Station, the phase composition of the shard depends on the physicochemical processes occurring during low-temperature sintering. In such masses, the melilite phase is formed predominantly due to the interaction of metakaolinite directly with $CaCO_3$ and hedenbergite, provided that it contains a sufficient amount of CaO, SiO_2 and alkaline components.

The use of the method of mathematical experimental planning makes it possible to obtain reproducible results when conducting a minimum number of studies and, in industrial production conditions, to respond quickly to changes in the physicochemical and technological properties of raw materials and production factors.

The integrated use of fuel energy waste in the production of ceramic roasting materials helps to improve their performance properties, ensures the recycling of technogenic raw materials and improves the environmental situation.

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