THE INFLUENCE OF BINDERS AND ADDITIVES ON THE COMPOSITE OF THE CaO-MgO-SiO_2 SYSTEM FOR LINING THE SINTERING ZONE OF HIGH-TEMPERATURE FURNACES

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Abstract: *The goal of the research was to obtain competitive refractory products, the use of which would be budgetary. To achieve this goal, we used mixtures prepared with the addition of sand and brick dust to dolomite. We planned to obtain highly refractory clinker from them.*

A comparative study of dolomites, sands, and magnesite brick slags was conducted to determine their suitability for producing highly refractory clinker. The research was conducted using chemical, thermal, X-ray structural, petrographic, and micro-X-ray spectral analysis methods. A composite of dolomite-sand-magnesite brick slags using a carbon additive and a binder was investigated for its impact on the physical and technical properties of the composite.

This shows that the main components of the composite are minerals in the form of MgO-periclase and tricalcium silicate-alite. Electron microscopic images of the DN-8 composite show a well-burnt surface of the sample, on which the formed crystals of the main phases contained in the clinker stand out. Namely, periclase and alite, although very small inclusions of belite are also observed. In addition, a plasticizer of complex action is introduced into the charge, on the basis of which it is established that on the basis of dolomite-sand-magnesite brick slags clinker, it is possible to obtain a highly fire-resistant carbon-containing composite with high physical and technical indicators.

Keywords: *Dolomite-sand-magnesite brick slags composite, binder, additive, differential thermal analysis, electron microscopy, technological flow chart.*

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Introduction

In many foreign countries, instead of magnesite refractory materials, dolomite refractories are used [1-4]. Highly refractory dolomite-sand-magnesite brick slags, clinker, and a composite based on it are obtained using the technology developed in [5-6].

The quality of such refractory materials is determined by the simultaneous action of several factors. One of the important things is to obtain an ideal structure, which must be maintained throughout the entire service life of the refractory. It also plays an important role in the formation and processing. An ideal grain surface can be achieved by using certain additives and binders that improve working conditions: high plasticity, mass-forming ability, abrasion resistance, and resistance to deformation thermal processing.

The studies were conducted using differential thermal and electron microscopic analysis methods. As a binder, we can consider an optimal pressing pressure of 100 MPa, the addition of 15% graphite nanopowder and 20% solution of magnesium sulfate and water, with the use of which a satisfactory result was obtained. A phase analysis of samples of optimal composition (sample 1) (Table 1) was carried out using X-ray diffraction and electron microscopy methods.

The influence of changing the amount of additive and molding pressure on these properties was also studied. The composition also includes a complex action plasticizer.

Experimental part

We weighed the components and prepared the mixture as an aqueous suspension in a porcelain ball mill. Then we dried the suspension in a thermostat. We diluted the mixture by adding 10% water and formed samples - cylinders, with dimensions H-25 mm and D-20 mm - which were fired in a silica furnace at 1450 °C. The process of calcination of materials and mineral formation was evaluated by determining porosity, density, and compressive strength, as well as by differential thermal, X-ray structural, petrographic, and electron microscopy methods. The physical and technical characteristics of clinker are presented in Table 1.

Table 1. Physical and mechanical parameters of samples

Supplemental sample number	ratio dolomite--sand -Fig	composition %		forming pressure	Type and amount of binders, %		Roasting temperature T^0C	water absorption, w, %	Porosity, П, %	Apparent density, g/cm^3	Strength limit in compression, MPa
		clinker	Graphite		water	$MgSO_4$					
D.n.-1	4/1	90	10	80	10	-	1450	6,28	14.50	2.93	180.70
D.n.-2	4/1	90	10	100	10	-	1450	5,72	13.80	3.05	192.60
D.n.-3	4/1	85	15	80	10	-	1450	5,35	13.00	3.00	198.30
D.n.-4	4/1	85	15	100	10	-	1450	5,20	13.00	3.26	209.70
D.n.-5	4/1	90	10	80	-	10	1450	6.12	14.10	3.26	187.30
D.n.-6	4/1	90	10	100	-	10	1450	5.00	12.90	2.98	200.8
D.n.-7	4/1	85	15	80	-	10	1450	4.40	12.40	3.09	206.50
D.n.-8	4/1	85	15	100	-	10	1450	4.31	12.10	3.53	181.20

The differential thermal analysis method was performed on a Kurnakov apparatus. It shows the weight loss of a substance and the phase transformation temperature of the substance.

X-ray structural analysis shows the crystalline phases of the studied material. The analysis was performed on the DRON-3 apparatus.

The electron microscopy images of the resulting composite show the surface of the hardened sample, on which the main constituent phases are observed. The analysis was performed on a JEOL YSM 65 OLW instrument..

Water absorption, porosity, and density were determined according to GOST 2409-91 using a vacuum apparatus. Density is an important characteristic for characterizing the quality of a composite material. The density of materials is characterized by water absorption and open and apparent porosity. The determination of the tensile strength is carried out on a tensile machine and is calculated by the formula $\boldsymbol{\sigma}=P/\boldsymbol{S}$, where P is the destructive force of the sample and $\boldsymbol{S}$ is the cross-sectional area. Refractory property shows the property of a material to withstand high temperatures without melting. It is determined using standard cones in a Kryptol furnace. The refractoriness of a sample is determined by the number of cones melted with it and is expressed in °C. Thermal resistance characterizes the ability of a material to withstand rapid temperature changes and is based on determining the number of heat transfers that the product can withstand after heating to 1300 °C and cooling in running water, as determined by GOST-7875-91. The samples were heated in a furnace with silicon carbide heaters.

Results and discussion

Dolomite, sand, and magnesite brick slags were studied, and their comparative studies were carried out. As a result of the study of dolomite and sand, it was established that they can be used to produce highly refractory clinker. During the firing of dolomite-sand-magnesite bricks and slags, the processes of sintering and mineral formation were studied depending on the firing temperature using differential thermal, X-ray structural, petrographic, and electron microscopy methods. Samples fired at 1200 and 1300 °C contain a certain amount of crystalline periclase and calcium silicates, including C_2S ($2CaOSiO_2$ Dicalcium silicate). Since C_2S interacts with free CaO, the peaks of which disappear, alite is formed. Accordingly, the intensity of its characteristic peaks increases.

Fig. 1 and 2 show the microstructures of clinkers 1 and 2, respectively. Clinker 1 is a 3:1 ratio of internal content kazm, three parts by weight dolomite, one part by weight chrysolite sand, and one part by weight magnesite aggregate. Clinker 2 is a clinker made from a 4:1 mixture of four parts by weight dolomite, 1 part by weight quartz sand, and 1 part by weight magnesite brick slag. We conducted a comparative study of clinker obtained from two different ratios of kazma, where we obtained a better indicator at the ratio of 4:1. Accordingly, we conducted the following studies at this ratio [7-14].

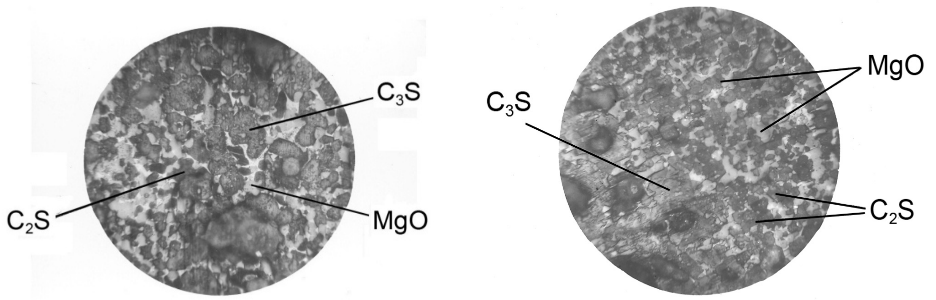


Fig.1. Microstructure of clinker 1 fired at 1450 °C. The figure shows alite (C_3S), periclase, and belite (C_2S)

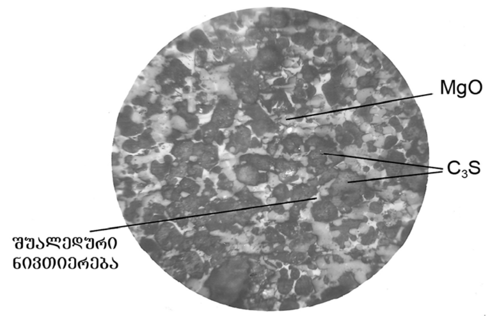


Fig.2. Microstructure of clinker 2 fired at 1450 °C

Fired clinker 2 consists of MgO and C_3S ($3CaOSiO_2$-tricalcium silicate) crystals. Fig. 6 clearly shows that clinker fired at 1450 °C with a saturation coefficient of 2 KH=0.95 mainly consists of MgO and C_3S crystals. The complete identification of the crystalline phase is shown in the electron microscopy images. The main phases visible in the case of clinker 1 are periclase, alite and belite. In the image of clinker 2, no belite crystals are visible.

Various binders used in the production of refractory materials are known from the literature. The following binders were selected for the experiment: 25% magnesium sulfate solution, aqueous solution of technical lignosulfonates, methylcellulose, and polyvinyl alcohol. The best results were obtained using solutions of magnesium sulfate and methylcellulose (Tables 1, 2).

The impact of clinker pressing pressure and the amount of graphite nanopowder and binder on the properties of the composite was studied. The results are given in Table 1.

Obtaining a composite with a wear-resistant structure is largely associated with the correct choice of carbon-containing additive. By using a carbon additive (graphite nanopowder) and a binder (20% magnesium sulfate solution) on the clinker, its properties are improved and a high-quality fire-resistant composite is formed. The optimal pressing pressure is 100 MPa, 15% graphite nanopowder is added, and the binder can be a solution of magnesium sulfate or water.

The properties of the composite obtained by adding graphite nanopowder, plasticizer and antioxidant (silicon), and binder (methylcellulose) to the clinker are presented in Table 2.

Table 2. Physical and technical characteristics of samples.

Supplemental sample number	Composition of the mixture, its %					Physical and technical indicators				
	clinker	Graphite	Silicon	Methyl cellulose	plasticizer	Strength limit in compression, σ, MPa	open porosity, П%	Apparent density, p g/cm3	Fire resistance, ^{0}C	Thermal stability (13000C-water), heat exchange
D.n.-9	100	-	_	8	0,8	312,70	13,20	3,05	>1770	7
D.n-10	88,5	10	1,5	10	-	67,00	14,20	2,45	>1770	7
D.n-11	82,7	15	2,3	10	-	101,40	13,80	2,99	>1770	7
D.n-12	82,5	15	2,5	10	0,8	345,00	10,10	3,25	>1770	7

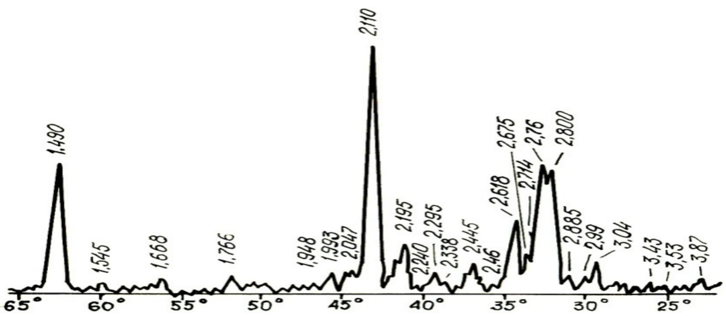
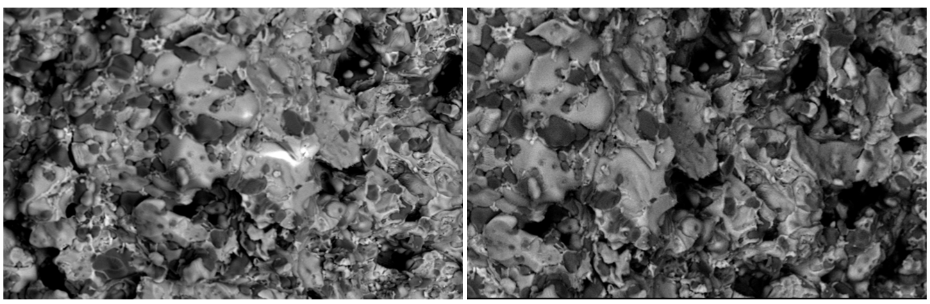


Fig. 3. X-ray image of dolomite-sand-magnesite brick composite D.n-8

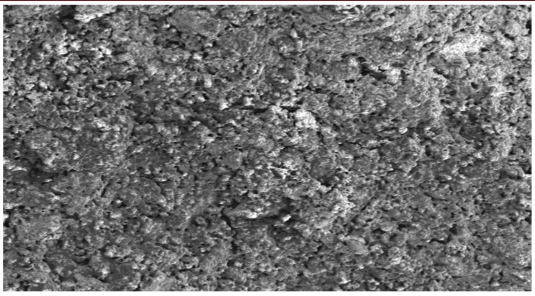
Finally, the optimal composition: clinker-binder-graphite-silicon-plasticizer. From the X-ray diffraction pattern of the composite in Fig. 3, it can be seen that it contains the same minerals as the dolomite-sand-magnesite brick slags clinker (MgO, C_3S).

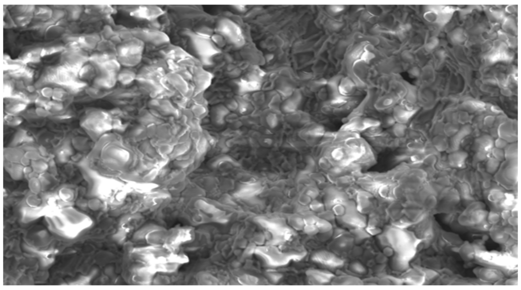
Electron microscopic images of the D.n.-8 composite sample (Fig. 4 and 5) show crystals of the main phases: periclase and alite, with a small amount of belite inclusions. Intermediate compounds: C_3A ($3CaO \bullet Al_2O_3$), C_2F ($2CaO \bullet Fe_2O_3$) and C_4AF ($4CaO \bullet Al_2O \bullet Fe_2O_3$) are distributed unevenly in the composite.



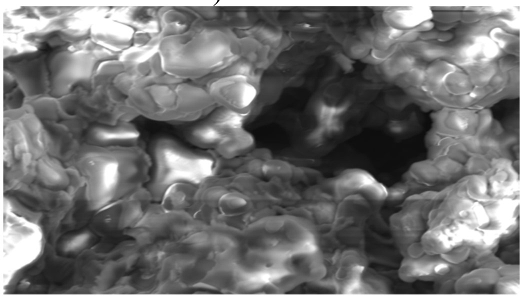
a) X950 b) X1000

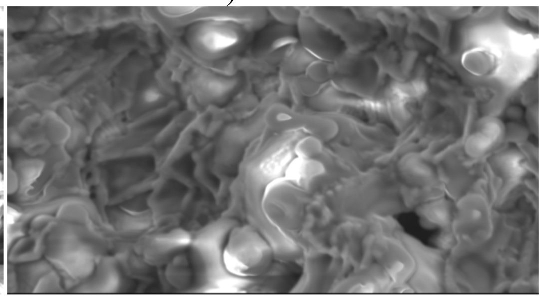
Fig. 4. Electron microscopic images of dolomite-serpentinite composite D.n.-8 at different magnifications (a) X950 and (b) X1000



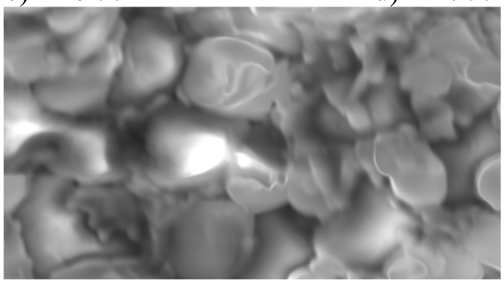


a) X 130 b) X 1000





c) X1900 d) X2700



e) X5000

Fig. 5. Electron microscopic images of dolomite-sand-magnesite brick slags composite D.n.-8 at different magnifications (a) X 130; (b) X 1000; (c) X1900; (d) X2700; (e) X5000

Fig.s 4 and 5 show the presence of two-color minerals, which is confirmed by X-ray structural analysis data.

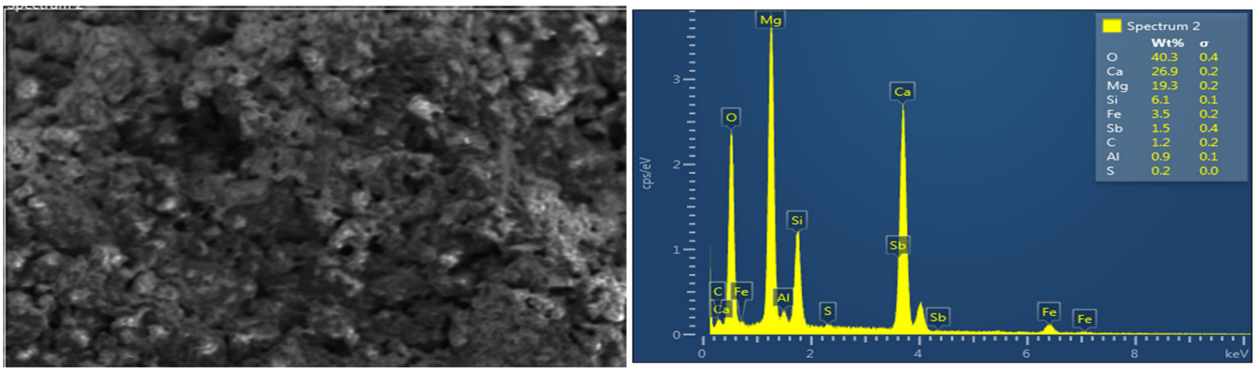


Fig. 6. Micro-X-ray spectral analysis of dolomite-sand-magnesite composite brick D.n.-8

Fig. 6 shows the micro-X-ray spectroscopic analysis of the composite D.n-8 in the spectrum section 2, the diagram of the constituent elements, and their percentage content. It can be seen that the elements containing periclase and alite from the main composite minerals are oxygen, calcium, magnesium, and silicon. Their percentage content is 40.3, 26.9, 19.3, and 6.1%, respectively.

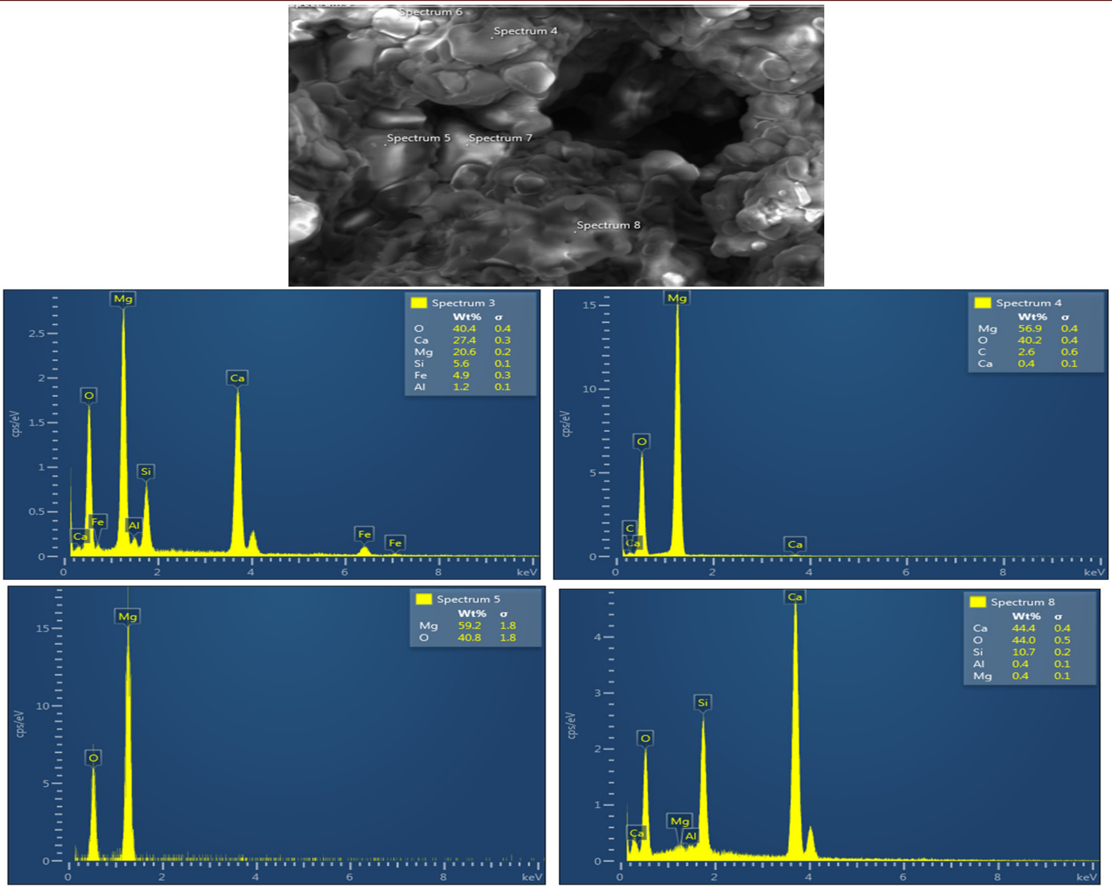


Fig. 7. Micro-X-ray spectral analysis of dolomite-sand-magnesite brick slags composite D.n.-8

The diagrams show the content of elements in relatively short sections of the spectrum 4, 5 and 8. This gives a clear idea of the content of the constituent elements of the phase present in this area. For example: spectra 4 and 5 show the percentage of elements Mg and O. Spectrum 8 shows the percentage of elements containing alite.

Conclusion

1. The chemical and mineralogical composition of dolomite-sand-magnesite brick slags, as well as the physical and technical properties of the obtained samples, were studied. It has been determined that the best physical and technical indicator is obtained with a dolomite-sand-magnesite brick ratio of 4:1. The optimal firing temperature is 1450 °C and the final temperature delay is 4 hours.
2. With a mixture ratio of 4:1, the CaO obtained from the decomposition of dolomite completely combines with the SiO_2 of the sand to form C_3S and the mixture is fired at 1400-1450 °C.
3. Based on the research conducted the impact of the binder on the properties of the composite was studied. Methylcellulose was chosen as the binder. Graphite nanopowder is used as an additive, and methylcellulose solution is used as a binder, resulting in a carbon-containing composite with high-performance properties. In addition, a complex-action plasticizer is introduced into the charge and it has been established that, based on the resulting clinker, it is possible to obtain a highly refractory carbon-containing composite to replace expensive magnesite refractories in the lubrication zone of a cement kiln and for lining a metallurgical furnace. We compared the results of the experiment with bank standards.

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