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Materials Science

Development of Technology for Producing Highly Refractory Materials Using Local Raw Materials and Industrial Waste

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(Presented by Academy Member Ramaz Katsarava)

This paper studies the development of technology for producing highly refractory materials using local raw materials, chrol sand and industrial waste. The obtained materials were studied using electronic and optic-microscope, X-ray, refractory and thermal analyses. Physical and technical characteristics of the material have been investigated. After the decomposition of dolomite at 900°C, above 1000°C the process of mineral formation begins. Finally, annealing takes place at 1450°C and the samples acquire operational properties. The last temperature delay was 1 and 4 hours. At different values of the saturation coefficient (KH), the content of free unwanted CaO in the material changes. At different values of the saturation coefficient KH, the content of free unwanted CaO in the material changes. The intensive baking process takes place at 1450-1500°C with a delay of 4 hours. It is within this temperature range that complete bonding of calcium oxide with silicate and formation of tricalcium silicate ends, as well as crystallization of periclase. In the process of roasting dolomite-chrol sand (Georgia) magnesitic shards, as a result of chemical interaction, new phases: periclase and alite are formed. At a mixture ratio of 4:1, complete bonding of calcium oxide with silicon dioxide of fine sand is taking place, forming tricalcium silicate, and high-quality well-baked clinker is obtained by firing at 1450-1500°C. A high-quality well-baked clinker without free calcium oxide is obtained, which is confirmed by physico-technical properties and structural analysis. *© 2024 Bull. Georg. Natl. Acad. Sci.*

dolomite, chrol sand, high-refractory clinker, composite, alite, belite, periclase

Our goal is to use the ore available in Georgia, namely Skuri dolomite, to produce refractory bricks with the addition of sand from chrol and magnesite brick slags, production of highly refractory clinker on their basis and the subsequent development of brick production technology to replace magnesite refractories of metallurgical thermal units and outbuildings in the sintering zone of rotary cement kilns [1-5].

The chemical composition of dolomite and sand from the Skuri deposit is given in Table 1. The main oxides of dolomite are CaO and MgO. To obtain

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clinker, the ratio of the mixture of dolomite and fine sand was calculated based on the chemical composition [6,7].

Table 1. Ingredients of raw materials

Name of raw material	Kazmi I, gram	Kazmi II, gram
Dolomite	60	60
Quartz sand	20	15
Magnesite lichen	20	25

Typically, the composition of clinker is determined using the saturation coefficient, silicate and clay modules.

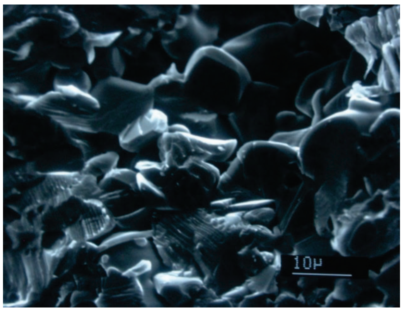
The production of any type of fire-resistant product is associated with quite a large number of difficulties. After all, such products have to be used at fairly high temperatures and in aggressive environments. Their physical and technical properties must correspond to the operating conditions. This, in turn, requires a fairly strict approach to admission conditions. Adding magnesite brick to such a mixture will lead to an increase in the amount of the desired periclase mineral – MgO, which ensures a composite with even better performance properties. To obtain highly refractory clinker according to both compositions we selected (Table 1), the mixtures were prepared as an aqueous suspension in a porcelain ball mill. The suspension was dried in a thermostat at 110°C and moistened by adding 10% water, forming samples in a semi-dry manner. The samples were molded under hydraulic pressure with dimensions of 20 mm in diameter and 20 mm height, with molding pressure of 80 MPa. We left the samples in the air for 24 hours and then baked them in an oven at a temperature of 1400°C. The firing process is a very important stage, during which samples undergo various physical and chemical transformations.

First, mechanically bound water is lost, then a chemical reaction of dolomite decomposition occurs at 700-900°C, and above 1000°C the process of mineral formation begins. Finally, sintering occurs and the samples acquire all the properties that will be characteristic of them. Accordingly, we chose the sample frying mode. At different values of KN, the content of free CaO changes, which determines the properties of the resulting clinker. Therefore, for the design of clinker and the mode of its production, it is necessary that it contains a minimum amount of free calcium oxide.

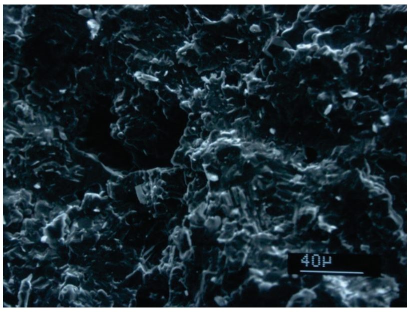
For this purpose, the following was studied: dolomite – chrol sand – slags of magnesite, processes of mixing and formation of minerals depending on temperature. The rate of temperature increase to 1000°C was 10°C/min, 1000-1400°C to 6°C/min. The last temperature delay was 1 and 4 hours. The physical and technical characteristics of clinker were assessed by determining porosity, density and compressive strength, and the process of material lubrication and mineral formation by methods of differential thermal, X-ray diffraction and micro-X-ray spectral analysis. The physical and technical characteristics of clinker are presented in Table 2.

Table 2. Physical and technical characteristics of clinker

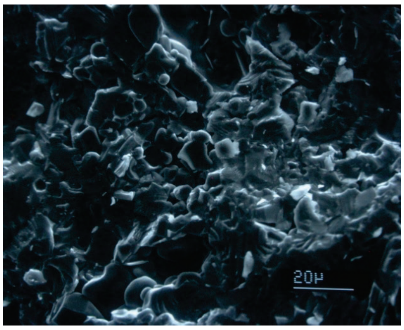
The ratio of components, mass. %		Roasting temperature, °C	Delay, last temp., hour	Physical and technical characteristics			
Dolomite	Quartz sand magnesite lichen			compressive strength σ . mpa	water absorption w, %	open porosity ∏, %	density, p, g/cm³
4	1	1350	1 4	318 296	2.10 1.98	5.80 5.10	2.52 2.74
		1400	1 4	355 377	1.30 0.99	3.63 2.50	3.45 3.62
		1450	1 4	400 480	0.77 0.70	2.08 1.85	3.64 3.69
		1500	1 4	492 517	0.70 0.62	1.85 1.82	3.76 3.78



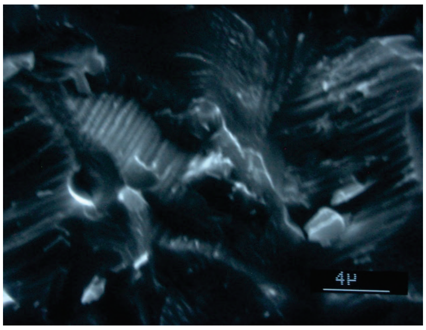
a) X1000



b) X2000

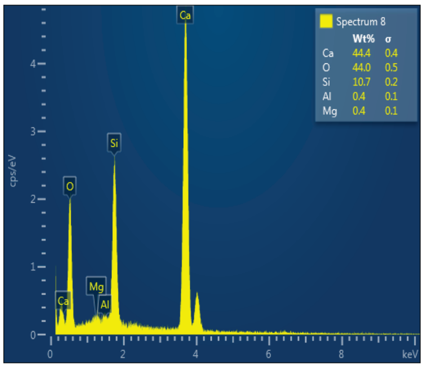


c) X3000

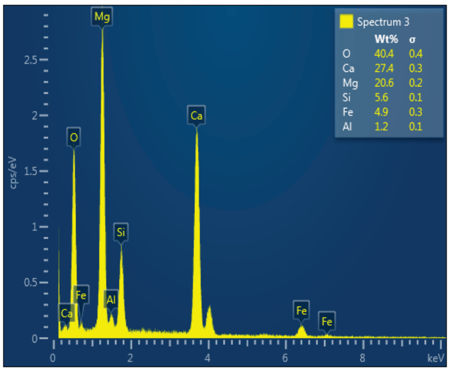


d) X350

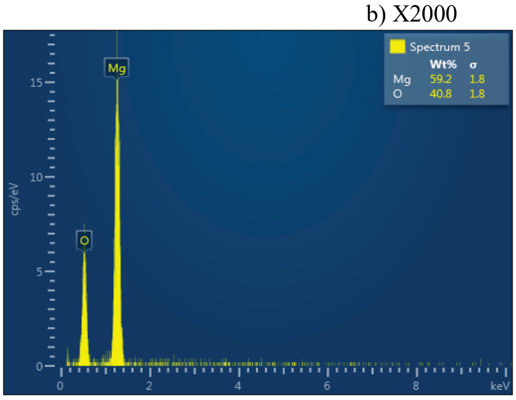
Fig. 1. Electron microscopic images of clinker fired at 1450°C at different magnifications.



a) X1000



b) X2000



c) X3000, d) X3500

Fig. 2. X-ray microspectral analysis of clinker fired at 1450°C.

To ensure acceptable product properties, it is advantageous to bind free CaO into tricalcium silicate C_3S (allite), which is stable to >2000°C. The harder dicalcium silicate, whose melting point is 2100°C, undergoes an allotropic transformation, accompanied by a change in volume. Thus, the transformation β<γ at 670°C occurs with a change in volume by 10%, which leads to the decomposition of clinker into powder.

Thus, when firing dolomite-chrol sand-magnesite slags, as a result of chemical interaction, new phases are formed: periclase and alite (Fig. 1). The composition of newly formed minerals and their content is determined by the ratio of the mixture taken and the firing temperature.

With a mixture ratio of 4:1, complete binding of calcium oxide with silicon dioxide of fine sand occurs with the formation of tricalcium silicate, and firing at 1450-1500°C leads to the production of high-quality, well-burnt clinker with the desired phase composition.

Micro-X-ray spectral analysis is show in Fig. 2. in different sections. We present diagrams showing the content of elements in relatively short sections, which gives a clear idea of the content of the constituent elements of the phase in this section. For example: spectra 4 and 5 show the percentage of Mg and O in periclase-containing elements. The amount of carbon here is 2.6%, which confirms our opinion expressed above. Spectrum 8 shows the percentage of elements containing alite, confirming the presence of alite in this region.

Conclusion

- Georgian dolomites (Abano, Skuri, Mukhuri) and deposits, as well as chrol sand and magnesite slags, including their resources, chemical and mineralogical composition were studied.
- Research is carried out using chemical, thermographic, X-ray diffraction and micro-X-ray spectral analysis methods.
- Local dolomites have been studied. For a saturation coefficient value KH = 0.95, the ratio of dolomite and chrol sand is 4:1. The composition of the theoretically desired newly formed minerals is calculated. The addition of magnesite slags increases the amount of MgO in clinker.
- The processes of calcination and mineral formation during firing of samples obtained from a mixture of dolomite and chrol sand in a 4:1 ratio, as well as with the addition of magnesite slags, depending on the firing temperature, were studied.
- Using X-ray diffraction analysis, the chemical processes occurring during firing of samples obtained in a 4:1 ratio at temperatures of 900-1450°C were studied.
- It has been established that when a mixture of dolomite, chrol sand and magnesite slags are fired, new phases are formed as a result of chemical interaction: periclase, alite, the content of which is determined by the ratio of the mixture taken and the firing temperature.
- The chemical and mineralogical composition of clinker obtained on the basis of dolomite, chrol sand and magnesite slags has been studied. The result is high-quality, well-burnt clinker with a given phase composition, which is confirmed by the results of physical and technical properties and electron microscopic analysis.

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მასალათმცოდნეობა

მაღალცეცხლგამძლე მასალების მიღების ტექნოლოგიის დამუშავება ადგილობრივი ნედლეულის და წარმოების ნარჩენების გამოყენებით

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** საქართველოს ტექნიკური უნივერსიტეტი, ბიონანოკერამიკისა და ნანოკომპოზიტების ტექნოლოგიის ინსტიტუტი, თბილისი, საქართველო*

(წარმოდგენილია აკადემიის წევრის რ. ქაცარავას მიერ)

სამუშაოს მიზანს წარმოადგენს მაღალცეცხლგამძლე მასალების მიღების ტექნოლოგიის დამუშავება ადგილობრივი ნედლეულის, ქროლის ქვიშისა და წარმოების ნარჩენების გამოყენებით. მიღებული მასალები შესწავლილ იქნა ელექტრონული და ოპტიკური მიკროსკოპული, რენტგენის, ცეცხლგამძლე და თერმული ანალიზის მეთოდებით. შესწავლილია მასალის ფიზიკურ-ტექნიკური მახასიათებლები. დოლომიტის 900°C ტემპერატურაზე დაშლის შემდეგ 1000°C ზევით იწყება მინერალების წარმოქმნის პროცესი. საბოლოოდ, წრთობა ხდება 1450°C ტემპერატურაზე და ნიმუშები იძენს ოპერატიულ თვისებებს. ბოლო ტემპერატურის დაყოვნება იყო 1 და 4 საათი. გაჯერების კოეფიციენტის სხვადასხვა მნიშვნელობებში [KH], იცვლება მასალაში თავისუფალი არასასურველი CaO-ს შემცველობა. ინტენსიური შეცხობის პროცესი 1450-1500°C ტემპერატურაზე 4 საათის დაყოვნებით მიმდინარეობს. სწორედ ამ ტემპერატურულ დიაპაზონში ხდება კალციუმის ოქსიდის სრული შეერთება კალციუმის სილიკატთან და წარმოიქმნება სამკალციუმიანი სილიკატი, ასევე ხდება პერიკლაზას კრისტალიზაცია. შეიძლება დავასკვნათ, რომ მაგნეზიტის ნამსხვრევების გამოწვის პროცესში დოლომიტი-ქროლის ქვიშა (საქართველო) ქიმიური ურთიერთქმედების შედეგად წარმოიქმნება ახალი ფაზები: პერიკლაზა და ალიტი. 4:1 ნარევის თანაფარდობით ხდება კალციუმის ოქსიდის სრული შეერთება წმინდა ქვიშის სილიციუმის დიოქსიდთან, წარმოიქმნება სამკალციუმიანი სილიკატი და მიიღება მაღალი ხარისხის კარგად შემცხვარი კლინკერი 1450-1500°C ტემპერატურაზე გამოწვით, კალციუმის ოქსიდის გარეშე, რაც დასტურდება ფიზიკურ-ტექნიკური თვისებებით და სტრუქტურული ანალიზით.

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