SCIENTIFIC AND EXPERIMENTAL SUBSTANTIATION FOR THE PRODUCTION OF FIREPROOF AND HEAT-RESISTANT MATERIALS FROM MAGNESIA-SILICATE ROCKS

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Abstract: *This article touches upon the technologies for fireproof and heat-resistant concrete production based on local raw materials: magnesia-silicate rock from the Sevan deposit, which can be used in thermal units to replace small-piece masonry bricks and figured elements. Raw materials were studied, the magnesia modulus was determined, chemical, radiographic, thermographic, and dilatometric analyses were carried out. To reduce volumetric shrinkage and porosity and convert clinoenstatite into forsterite, the rock was pre-baked in the presence of* MgO. *The proposed technology is low-power and urgent, especially in the energy crisis. Based on the mentioned rocks, multifunctional, cost-effective, fireproof, and heat-resistant forsterite materials have been developed, compressive strength ranges from 40 ... 60 MPa, the melting point of 1600°C, and heat resistance* **-** *5 thermal cycles.*

Keywords: *fireproof and heat-resistant concrete, ultrabasic magnesia-silicate rock, clinoenstatite, forsterite, forsterite concrete, phosphate binder, low-power technology.*

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Received: 17.11.2022
Revised: 06.12.2022
Accepted: 19.12.2022

Introduction

In world practice, the construction of thermal units has traditionally been implemented with expensive fireproof and heat-resistant small-size brickwork and figured elements obtained from various raw materials through various technological, high-temperature processing and functionally graded coatings [1], which is labor-intensive and requires high-quality and high-value handiwork. The latter is because ensuring the effective implementation of technological processes in these units leads to the need to build structures with complex contours. Alternatively, the world's experience shows that due to the varying degree thermal deformability of brick [2] and masonry under high temperatures, the structures made from them typically require regular repairs and fail quickly, which leads to the interruptions, downtimes of thermal units and, in general, technological production processes performed in them, as well as to high material and labor costs. Using fireproof concrete in the construction of thermal units in various spheres of application will create an opportunity to exclude similar problems [3-8].

Compared to traditional fireproof bricks, fireproof concrete does not require expensive preliminary high-temperature treatments [9,10,12]. In the planned regimes, the conversion reactions that ensure fire resistance occur during the initial heating of the already-built units. The production of fireproof concrete and the corresponding structures based on it make up about 3-5% of the total volume of fireproof material production. This indicator is high in many industrialized countries, such as the USA, England, France, Germany, Austria, Japan, etc. [11]. The first reason for the relatively low level of fireproof concrete consumption is the lack of high-quality fillers, binders, and various additives. The second is that in the technology of fireproof concrete, besides the stringent requirements for the chemical and mineral composition of the raw materials, there are other strict requirements, such as ultra-purity of fillers and additives (complete exclusion of admixtures), precise grain sizes, high precision dosing, competent selection of binders, their efficient and strict combination with additives, etc. In various countries, the solution to these issues is provided by organizing the production of fireproof dry mixes for concrete.

Special fireproof cement (alumina, super-alumina), liquid glass, phosphate materials, Portland cement mixed with special additives, etc. are used as binders in these mixtures.

Materials and Methods

RA has abundant raw material reserves, including aluminosilicate and magnesium silicate rocks, which are used in the production of fireproof and heat-resistant materials. There are more than a dozen mines of the latter. These rocks contain dunites, serpentinites, peridotites, talc, etc. These mines are on the northwestern shore of Lake Sevan and provide valuable raw materials for high-temperature material production. Dunite rocks from the Shorzha mine were used in this research.

The following chemical binders are used in fireproof and heat resistant concretes: H_3PO_4 solution with a density of 1.6 g/cm^3, magnesium and sodium acid phosphates - $Mg(H_2PO_4)_2$, NaH_2PO_4.

Main part

The primary demand for fireproof materials in Armenia was met by the use of fireproof bricks supplied by Russia and Ukraine.

Through investigations conducted in RA beginning in 1986, fireproof concrete compositions were produced, and their qualities were researched. Achievements recorded during research are presented in many scientific papers [6-7,14,16-17,19-21]. For concrete and granular fireproof materials, the ultrabasic rocks of the Sevan basin were used as essential raw materials. This research was carried out in accordance with the existing standard methods. However, due to some objective and subjective reasons, the research in that direction was stopped, but the problem remained relevant. The availability of raw materials and the high cost of imported raw materials fueled the continuation of these projects. Analyzing the existing data, one might confirm that the deposits of the Sevan region, where sufficient reserves are available, are complex combinations of different rocks, including peridotites, pyroxenes, dunites, and serpentinites, which are mainly composed of magnesium orthosilicate ($2MgO \cdot SiO_2$- forsterite) and metasilicate ($MgO \cdot SiO_2$- clinoenstatite or enstatite) and are distinguished by the complexity of the mineral composition.

The mineral composition of superbasic rocks includes: olivines composed of orthosilicate ($2MgO \cdot SiO_2$) and fayalite ($2FeO \cdot SiO_2$), pyroxenes composed of enstatite or clinoenstatite, hypersthene ($MgO \cdot FeO \cdot 2SiO_2$), diopside ($CaO \cdot MgO \cdot 2SiO_2$), spinel minerals composed of chromite ($FeO \cdot CrO_3$), magnetite ($FeO \cdot Fe_2O_3$), magnesium hydrosilicates, the product of autometamorphism of olivine and pyroxene. The main minerals of this group are: anthophyllite ($Mg(OH)_2Si_8O_{22}$), talc ($Mg_3(OH)_2Si_{14}O_{18}$), serpentine ($Mg_3(OH)_4Si_2O_5$). When serpentine is heated to 600-650°C, it decomposes and removes water, increasing the porosity to 25-30%. Forsterite and amorphous silica soil are formed via decomposition.

$$2(3MgO \cdot 2SiO_2 \cdot 2H_2O) = 3(2MgO \cdot SiO_2) + SiO_2 + 4H_2O.$$

Free silica reacts with forsterite to form clinoenstatite when the temperature is raised to 1200-1400°C.

$$2MgO \cdot SiO_2 + SiO_2 = 2(MgO \cdot SiO_2).$$

The material's porosity decreases, and at 1400°C it stabilizes, reaching about 14–18%. This reaction is accompanied by significant material shrinkage (21.1%) [14, 15]. Due to the significant amount of serpentinite in dunite and the volumetric changes caused by it, it is advisable to calcine the rock beforehand, including MgO as an additive, to reduce the volumetric shrinkage, reduce the porosity, and convert the clinoenstatite to forsterite.

$$Mg_3(OH)_4Si_2O_5 + MgO = 2Mg_2SiO_4 + 2H_2O.$$

For the forsterite formation from pure serpentinite, it is theoretically vital to introduce a 12.6% additive [13, 16, 17]. Meanwhile, because the reaction between clinoenstatite and magnesium oxide occurs in the solid phase and does not proceed to the end, magnesium oxide is added more than the calculated amount (about 20–25%).

However, the low concentrations of iron oxide in the rock must be replaced with magnesium ferrite, a compound with a relatively high melting temperature, which reduces the fire resistance slightly and causes the following reaction:

$$Fe_2O_3 + MgO = MgFe_2O_4.$$

If we characterize the magnesium silicate rocks according to the forsterite modulus $M_f = \frac{MgO}{SiO_2}$, we find that compared to the technological composition of forsterite, they represent different values as raw materials (for forsterite $M_\Phi = 1.335$), with a melting temperature of 1890°C. The characteristic properties of some natural minerals are presented in Table 1.

Table 1. Some natural minerals and their properties

Mineral name	Formula	Composition, %				Real density, g/sm^3	Molecular mass	Melting temperature, $°C$
		MgO	SiO_2	FeO	H_2O			
Forsterite	$2MgO \cdot SiO_2$	57.9	42.7	-	-	3.21	140.7	1890
Fayalite	$FeO \cdot SiO_2$	-	29.5	70.5	-	4.07	203.7	1065
Enstatite	$MgO \cdot SiO_2$	40.2	59.8	-	-	3.16	100.38	1557
Serpentite	$3MgO \cdot 2SiO_2 \cdot 2H_2O$	43.7	43.3	-	13.0	2.55	277.1	1515
Talc	$3MgO \cdot 4SiO_2 \cdot 2H_2O$	31.9	64.4	-	4.7	2.75	379.2	1450
Olivine	$2(MgFe)O \cdot SiO_2$	Variable				3.32	-	1300
Periclase	MgO	100	-	-		-	40	2800
Quartz	SiO_2	-	100	-		2.68	60	1710

Following a preliminary analysis of the rocks' properties, research was implemented on producing refractory and heat-resistant materials from magnesium silicate rocks, and evaluating the rocks as fillers used in their compositions [6, 7, 15, 18, 20].

Results and Discussion

For the production of refractory and heat-resistant forsterite materials, several magnesium silicate rocks were used in our research, which are rich in magnesite and magnesite-dunites. Some rocks, such as serpentinite, particularly serpentinized dunite, and peridotite, do not possess the properties of fireproof forsterite raw materials due to an insufficient quantity of magnesium oxide (37% - 42%).

The chemical compositions and radiographs of two dunite rock samples from the Shorzha deposit in the Sevan basin are presented below (Table 2, Fig.1). X-ray analysis was carried out with an X-ray diffractometer - DRON 2, with Kα = 1.5418Å, voltage 25kV, power 20mA. X-rays were taken at an angle of 200 in the range of 6...60°.

Table 2. Chemical compositions of dunite rocks

Sample №	Content of components by mass, %									MФ
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Loss on ign.	
1.	36.74	0.27	0.93	8.87	0.33	37.52	trace	trace	15.04	1.02
2.	31.24	0.21	0.69	7.30	0.22	41.27	trace	trace	19.10	1.32

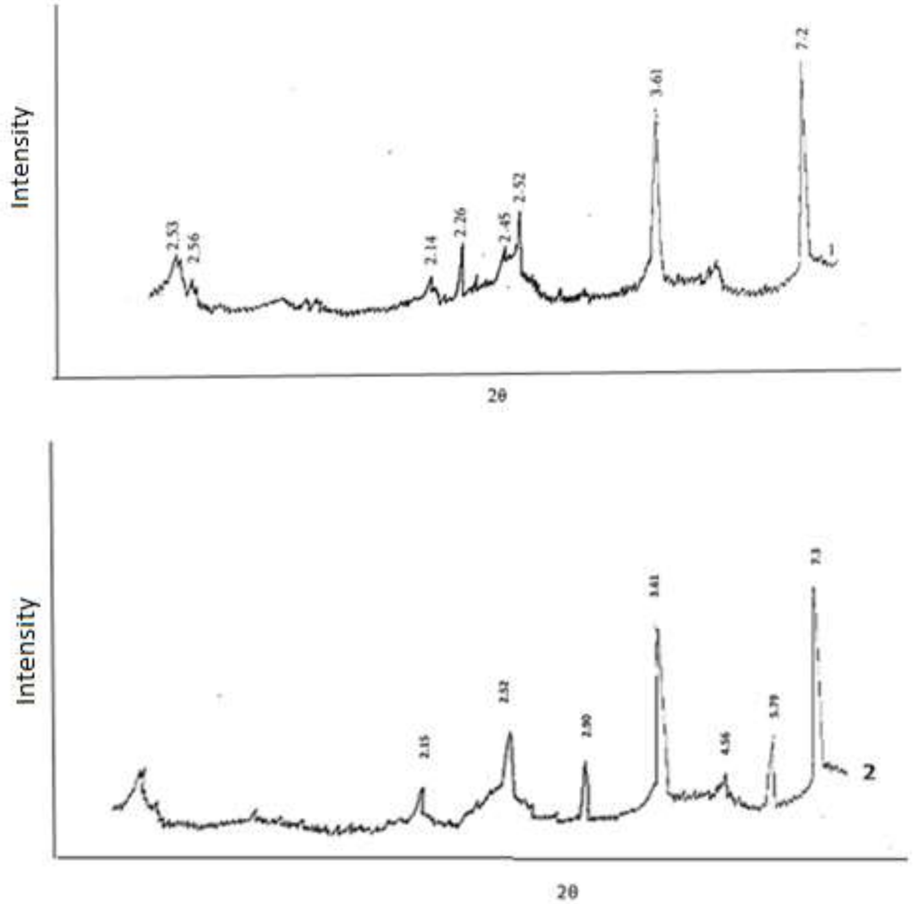

Fig. 1. *Dunite X-rays, 1- sample №1, 2- sample №2*

Considering the above-mentioned circumstance, during the preparation of the raw mix, magnesite powder from the magnesium-containing rocks of the same deposit is added to the main raw material to form forsterite [21]. For calcined forsterite refractory materials, only preliminary calcination of natural magnesium silicate rocks is required to prevent a significant degree of porosity and shrinkage during operation. This is in contrast to the two-stage procedure for obtaining refractory materials.

By using Sevan magnesium silicate rocks, the development of low-energy technologies can decrease the specific energy capacity of high-temperature materials [24]. Taking into account the fact that the basis for the forsterite refractory material preparation is the formation of the maximum quantity of magnesium orthosilicate, the optimization of the crystallization and synthesis conditions becomes vital for investigating the process's kinetics and phase changes. The phase changes were investigated under heat treatment by derivatographic, X-ray phase, petrographic, and dilatometric analysis.

X-ray analysis (Fig. 1) primarily identifies antigoritic serpentinite (7.20, 3.61, 2.52*Å)* and olivine (2.52, 2.45, 2.26 *Å*) in sample No1. The orientational content of the phases under the microscope is, respectively, 80 and 20%.

Antigorite (7.20, 3.61, 2.52Å), olivine (2.52, 2.45, 2.26Å) and hydromagnesite (5.79, 2.90, 2.15Å) were identified by X-ray analysis in sample No 2, where the content is ~ 8.5%. To explain the physicochemical processes occurring in the rock, the thermograph of serpentinized dunite of Sevan deposit is presented (Fig. 2).

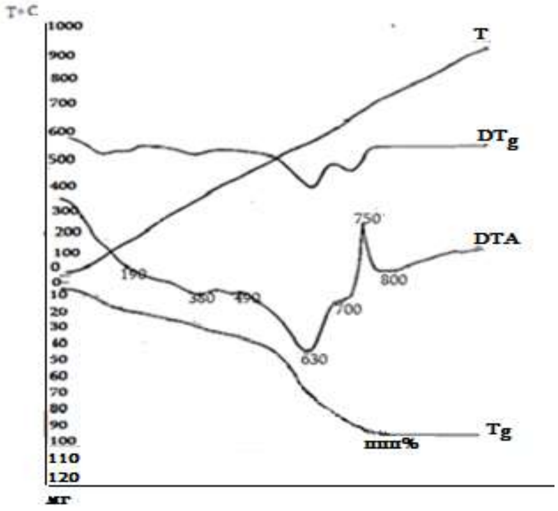

Fig. 2. *Thermograph of serpentinized dunite of Shorzha deposit*

The analysis was carried out on a 1500 FMOM derivatograph (Hungary), using calcined alumina as a standard.

Several mass loss endoeffects on the thermograph were observed during the derivatographic examination of the samples up to 750°C. When heated to a temperature of 190°C, the water in the macropores was removed from the rock samples.

The water in the large pores is free water, and its evaporation is not accompanied by volume reduction, i.e., rock shrinkage. The endoeffect at 380°C is most likely caused by brucite $Mg(OH)_2$ decomposition in small quantities.

When the temperature is raised to 700°C, first the water that is loosely bound in the capillaries and adsorbed on the surface of the crystals is removed, followed by the water that is removed from the layers of the rock crystal structure. The removal of this type of weakly bound water occurs intensively, leading to significant shrinkage.

However, mass loss occurs at a greater rate than volumetric shrinkage, resulting in a decrease in the rock's average density and a significant increase in strength due to the elimination of the "softening effect."

Decomposition of the antigorite crystal lattice occurs in the temperature range of 490...750°C, with a minimum of the endo effect at 630°C. Further phase changes in the dunite composition are evidenced by the exoeffect, with a maximum of 750°C. It is reasonable to assume that new minerals are crystallized from dehydrated and amorphized antigorite ($Mg_3(OH)_4Si_2O_5$), which is identified by X-ray analysis as olivine and pyroxene, forsterite (2.50, 2.44, 1.732, 1.472 Å), and enstatite (3:15, 2:87, 1:489 Å).

However, to reduce the shrinkage, produce high-quality sinters, and convert the metasilicate component to forsterite, an experiment was conducted to introduce magnesium oxide into the composition. X-ray analysis of dunite pre-calcined at 1450°C and (dunite $+MgO$) mixture after heat treatment at 600...1550°C was carried out.

The results of the analysis showed that in the presence of magnesium oxide, the number of crystalline phases increases to some extent. Free MgO reflexes are observed in the temperature range of 600...1350°C.

Traces of the latter and enstatite are observed even at the temperature of 1450°C and only at 1550°C the forsterite monocrystalline phase is synthesized.

The synthesis of a regular monocrystalline phase, forsterite, in (dunite + MgO) mixtures processed at 1450°C with a delay of at least one hour is possible, according to physicochemical research.

The implementation of the forsterite synthesis reaction also depends on kinetic factors, the main ones being the activation energy and the rate of the given process [16]. In the case of pyrosilicate reactions at high temperatures, the effect of activation barriers becomes insignificant, and the probability of the reaction proceeding under the given conditions is directly dependent on the reaction rate constant. The research analysis results for the production of dunite-phosphate concretes with low-energy technology allow to select the kinetic parameters of concrete having melting temperatures above and below the refractory limit (1580°C) (which was determined in the muffle furnaces of Naber, with a temperature range of 1350...1400°C, carborundum - 1450...1500°C and kryptol - 1700...1800°C).

The optimal indicators of the data (Table 3, A) can be used to obtain refractory and heat-resistant concretes: refractory (with refractory above 1580°C) and heat-resistant (with refractory below 1580°C) [22, 23]. Dunite-phosphate concrete samples with dense structures were subjected to X-ray analysis, which identified two primary crystalline phases, where forsterite $2MgO \cdot SiO_2$ was predominant.

Table 3. Optimal range of composition indicators with H_3PO_4 (A), $Mg(H_2PO_4)_2$ (B), NaH_2PO_4 (C)

N	Content of ingredients, %		Drying temperature, °C	Melting temperature,°C	Compressive strength, *MPa*	Linear shrinkage, %
	Dunite cement	Phosphate binder				
A	50…70	8.9…9.0	250…300	1580…1870	60…70	0.85…2.25
	50…60	8.5…10.0	250…300	1580…1770	70…90	0.85…3.5
	50	8.5…10.0	200…300	1480…1580	65…110	2.5…3.5
B	40…50	15.4…21.0	110…250	1580…1870	30…42	0.85…2.25
	50	21.0…23.0	110	<1580	33…34	1.0
C	50	9.0…11.0	110…250	>1750	15…25	0.8…1.0

Conclusion

Considering into account the fact that there is no production of flammable and fire-resistant materials in RA, and these materials are in high demand, the task is set to develop high-temperature material components and production technology with local raw materials. To solve this problem, high-temperature dunite-phosphate dense concretes with a melting temperature of 1600°C, a compressive strength of 40...60 MPa, a porosity of 15. . .20% and a heat resistance of more than 5 temperature changes were developed on the basis of Shorzha magnesium silicate rocks.

The expediency of using Sevan magnesium silicate rocks as a filler in fireproof concrete was also confirmed, after preliminary calcining these rocks at a temperature of 800°C, because without the latter it is impossible to ensure proper quality due to the occurrence of significant shrinkage during calcination. High-temperature refractory and fire-resistant concrete can be obtained with great economic profitability in various sectors of the economy.

Acknowledgements

The work was carried out with the basic funding of scientific and technical activities from the RA state budget within the framework of the program "Maintenance and Development of the Research Laboratory of Construction and Urban Economy".

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