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Lightweight concrete based on siliceous compositions of natural origin

Легкий бетон на основе кремнистых композиций природного происхождения

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Ключевые слова: бетон; магнезиальное вяжущее; щелочно-силикатная реакция

Abstract. The focus in the release of construction materials is determined by waste recycling, saving energy costs and environmental management by means of reducing dump areas. The production of magnesia binders from dolomite waste meets all these requirements. There was made an effort to create a new material based on magnesia binder and lightweight silicate aggregate made from tripolith of Vladimir region deposit. In the course of the work, samples were synthesized and tested for strength and thermal conductivity, and also an optimal granulometric composition of the aggregate was defined. This research shows that the material is strong, cheap, alkali-silicate corrosion resisting and very promising in compare with classic Portland cement concretes.

Аннотация. Приоритет в выпуске строительных материалов определяется использованием отходов промышленности, снижением энергоемкости и решением экологических проблем за счет сокращения площадей занятых отвалами. Всем этим требованиям отвечает производство магнезиальных вяжущих из отходов доломитового производства. Была предпринята попытка создать новый материал на основе магнезиального вяжущего и легкого силикатного заполнителя, изготовленном из трепела Владимирского месторождения. В ходе работы были синтезированы образцы, которые были испытаны на прочность и теплопроводность, а также подобран оптимальный гранулометрический состав заполнителя. Исследование показывает, что материал является прочным, дешевым, стойким к щелочно-силикатной коррозии и очень перспективным по сравнению с классическими бетонами на основе портландцемента.

1. Introduction

Nowadays, the problem of high cost of housing is quite relevant for people of almost all countries in the world. At the same time, there are a lot of dolomite waste dumps in many countries including Russia. That is why magnesia concrete made from dolomite production waste was chosen as an object of this research. The works of P.P. Budnikov, M.I. Kuzmenkov, TN. Chernykh[1], A.E. Ivanov and many others[2, 3] are devoted to the issues of magnesia binders. The purpose of this work is to try to create cheap high-quality construction material from dolomite waste and reduce volumes of dolomite waste dumps.

The production of magnesia cements does not hold a prominent place in the national construction sector, which is completely unjustified by any arguments, because magnesia cements have exceptional distinct properties in strength, abrasion, and bactericidal power. Besides, their production history and applications are centuries old.

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Unlike magnesia concretes, cement ones as well as Portland cement mortars are known to have a delayed hardening, nonhomogeneous composition and conglomerate structure. Therefore, traditional concretes do not meet modern standards for abrasion and crack resistance. Being formed in the process of hydration, crystalline and colloidal newgrowths dry up and thicken over time, which is followed by the cement shrinkage[4–6].

Calcium hydroxide belongs to one of the silicate mineral products (alite and belite) which interact with water. It means that as a result of hardening, an alkaline medium always appears in a cement stone. This phenomenon also has its pros and cons. As it is known, there is no iron corrosion in an alkaline medium. Therefore, concretes based on Portland cement (and its varieties) protect steel reinforcement from corrosion. This is one of the key factors for high durability of reinforced concrete.

When using magnesia binders in mortars, there forms a dense, non-porous material, having high abrasion, petrol, oil and water resistance[1, 7, 8].

Unlike other binders, magnesia binders have a very high adhesion not only to mineral, but also to organic substances. Due to a high density of the material, low alkalinity and the presence of bischofite in the magnesia cement composition, the organic fillers do not rot in them. This fact makes it possible to make a hypothesis concerning bactericidal power and mold and fungus resistance of materials based on magnesia binders.

The use of magnesium salts as grouting fluid changes the hardening mechanism [9]. High concentration of magnesium salts promotes the formation of complex salts of various composition: MgCl2 · 5MgO · 17H2O (Sorel, 1867), MgCl2 · 5MgO · 8H2O (Bender, 1871), MgCl2 · 3MgO · 10H2O (Robinsson and Wagman, 1909), MgCl2 · 3MgO · 7H2O (Larman, 1911). Due to the formation of such compounds, magnesium hydroxide is removed from the solution, and new portions of magnesium oxide undergo a hydration reaction [10].

Table 1 presents the comparative analysis of Portland- and magnesia cements.

Table 1. Comparative analysis of Portland- and magnesia cements

Characteristics	**Type of cement**	
	Magnesia cement	Portland cement
Total composition	$3MgO \cdot MgCl_2 \cdot 11H_2O$	$12CaO \cdot 6SiO_2 \cdot 7H_2O$
Structural formula	$[Mg_4^{2+}(OH)_6^{-}(H_2O)_6]^{2+}Cl_2^{-} \cdot 2H_2O$	$Ca[Si_6O_{17}](OH)_{14}$ (hillebrandite)
Crystal structure	Roughly anisodesmic, formed by doubled chains of octahedra Mg (OH, H2O) 6, connected by chlorine ions and water molecules	Quasi-coordinated, poorly anisodesmic, band, represented by alternation of xonotlitic and portlandite elements: $Ca[Si_6O_{17}](OH)_2 \cdot 6Ca(OH)_2$
Macrostructure	Felted structure	Massive structure
Density ρ, g / m^3	1.86	2.69
Fragility HV (GPa)/ K_{1c}	0.5	3.8
Thermal conductivity λ, W / (m · K)	0.5–1.6	1.3–1.8
Compressive strength, σ_p, MPa	50–120	3.5–80

Unlike Portland cement, magnesia cement does not create an alkaline medium i.e. the solubility of magnesium hydroxide is insignificant, and its basic properties are not strong. So magnesia concrete eliminates alkali-silicate reaction in concrete, which can destroy the body of the concrete and promotes the formation of cracks, especially with a large-sized aggregate [11,12,13,14,15,16]. Organic aggregates are not destroyed in a neutral medium. In addition, magnesia cement prevents the development of microorganisms that can destroy the aggregate. The application of magnesium chloride solutions, which are considered to be good fire-resistant impregnations, makes these materials fire-proof[10].

The advantages of magnesian concretes are:

- Higher adhesion to different substrates (up to 3 MPa);

- High shrink resistance. Consequently, magnesia concrete does not crack. This fact gives an advantage when arranging the surface cast: it becomes possible to create coatings on large areas without functional joints;
- Abrasive resistance and lack of dust. High-strength magnesia concretes do not raise dust throughout their entire thickness;
- Compressive strength is higher than 50 MPa. Following 3 months' operation, the magnesia concrete strength increases up to 80–120 MPa. This characteristic makes it possible to use magnesia concretes in workshops with high dynamic loads;
- Fast strength generation within a short time. At the age of 1 day the strength of concretes and mortars reaches 30–50 %, and at the age of 7 days 60–90 % of the maximum possible strength. High speed of hardening and strength generation makes it possible to use the structures a few hours after the casting;
- Oil and petrol resistance due to a dense structure with closed pores;
- Anti-electrostatic properties. The fact that magnesia concretes do not accumulate static electricity makes this material essential in premises with a large number of electrical devices (computers, motors, transformers, etc.).

Consequently, magnesia concrete is of better quality compared to the traditional Portland cement according to such characteristics as strength, abrasive resistance, good adhesion, high hardening speed, lack of shrinkage, and many other properties.

On top of that, magnesia binders are inert to different silica-containing materials. This property makes it possible to produce concretes based on a magnesia binder with a silica-containing aggregate, whereas Portland cement reacts with the aggregate silicates. This leads to an alkali-silicate interaction that destroys concrete body [10].

For the first time ever the main characteristics of alkaline-silicate reactions were described by Stanton. Hydroxide ions in a pore solution react with certain types of silica placed in an aggregate. This leads to internal stresses that can cause fracture or crack propagation [17]. Fracture can occur within a few days or only many years later. On the surface of non-prestressed concrete they normally form a small crack network and sometimes large cavity pockets. In prestressed concrete cracks tend to propagate parallel to the reinforcement. On the thin sections there can be seen cracks that can propagate through the aggregate. Silica gel is allocated from concrete and resides in cracks in the form of shells around the aggregate particles or elsewhere in the paste. High content of alkali metal oxides in cement, reactive component in the aggregate and access to water are necessary conditions for alkaline-silicate reactions in Portland cement concrete. K + and Na + ions are present in the cement in the form of sulfates and in silicate and aluminate phases. On reaction with compounds containing these ions, their anions enter the products with low solubility, for example ettringite, C-S-H or AFm-phase, and simultaneously an equivalent amount of OH-. K + and Na + ions play a negative role at this stage, because their hydroxides are soluble, which allows OH- to pass into the pore space [18].

The authors of the given article have made an effort to synthesize lightweight concrete on the basis of both traditional foam glass and lightweight aggregate made of silicon-containing natural materials, such as tripolith and diatomite.

These rocks have been called siliceous due to their high silica content, SiO2 content in them varies from 50 up to 90 %. The second necessarily present oxide is Al2O3. They represent light fine-porous powders, composed of the smallest opal fragments of diatomic algae and crystobalite as well as clay minerals[19].

Table 2 represents tripolith composition of the Vladimir region.

Table 2. Chemical composition of tripolith in the Vladimir region

Chemical compounds	SiO2, %	Al2O3, %	Fe2O3, %	CaO, %	MgO, %	SO3, %
Quantity	73 - 89	3.8 – 15.6	0.3 – 5.3	0.5 – 2.5	0.4 – 1.9	0 -1.6

This material possesses the following physical properties:

- Porosity 50-70, (%)
- Hardness 1-3, (Mohs scale)
- Thermal conductivity 0.17-0.23, (W / (m · ° C)).

In construction and construction industry siliceous rocks are used in the form of manufactured objects (blocks, stones), crushed products (crushed stone), ground products (hydraulic additives, fillers), in the form of raw materials for the production of sintered (agloporite, sintered aggregate, lightweight bricks, wall and heat-insulating materials), foamed (expanded-clay and siliceous gravel and sand) and molten materials (glass, glaze, glass float, etc.).

In 1960s of the 20th century, on the basis of sintering processes there were launched studies on siliceous rocks with the aim to use siliceous rocks as raw materials for concrete aggregates. In the result of these studies it was established that in siliceous rocks, in the process of the aggregate production by calcination, sintering takes place more often than foaming. The obtained aggregate was used as a heat insulating material due to its microporosity. Numerous diverse studies on physical, technical and technological properties of sedimentary siliceous rocks made it possible to obtain an aggregate based on a gaize called "thermolite".

In central regions of the European Russia (including the Vladimir region) there are numerous deposits of tripolith and gaize with a productive layer from 16 up to 27 meters.

2. Methods

In the course of the given study there was synthesized a lightweight aggregate (figuratively called "diapen") based on the tripolith and diatomite of the Zheldobinsk deposit.

The production technology of "diapen" includes the following stages:

- excavated tripolith is crushed to powder
- alkaline component is added to the obtained powder
- the obtained powder is moistened and mixed to a ductile mass
- raw granules are being formed
- granules are pelletized and sintered in a rotating kiln

The obtained granules were tested for strength, thermal conductivity, water absorption. The results are presented in Table 3.

Table 3. Diapen physical and technical properties

Density, kg / m^3	Strength, MPa	Thermal conductivity, W/(m·°K)	Water absorption,% $_{vol}$	Fire resistance
200-500	4-7	0.05-0.08	5-7	Non-flammable

The prime cost of tripolith excavation is not high, that’s why "diapen" is almost twice cheaper than its closest competitor i.e. expanded clay and 5 times cheaper than a foam glass.

To determine the optimum grain particle size with the maximum use of the lightweight aggregate, and to achieve the maximum thermal conductivity coefficient while maintaining sufficient structural strength there was used Andreassen-Andersen formula

$$P(D) = \frac{D^q - D_{min}^q}{D_{max}^q - D_{min}^q}$$

where P(D) is the total share of the solid matter with the particles smaller than D, D is the particle size (micron), D_{max} and D_{min} are respectively the largest and smallest particle sizes (micron) in the mix, q is the distribution modulus.

Table 4 shows the grain particle size of the aggregate when selecting the optimal casting density for concrete.

Table 4. Grain particle size of the fine aggregate to achieve maximum casting density

Grain size, mm	Grain particle size of "diapen", %$_{vol}$						
	C-1	C-2	C-3	C-4	C-5	C-6	C-7
5 – 2.5	65	65	65	65	65	70	70
2.5 – 1.5	5	10	10	15	20	5	10
1.5 – 1.0	10	5	10	10	5	5	10
1.0 – 0.5	20	20	15	10	10	20	10

After carrying out the tests, it was found that the composition C-1 has the optimal grain size ratio.

In this work there were synthesized lightweight concretes based on the investigated types of binders and aggregates. Compositions for lightweight concretes based on the magnesia binder and diapen are presented in Table 5.

Table 5. Compositions for lightweight concrete

Concrete grade	Components, $\%_{mass}$			
	Semi-sintered dolomite waste	Diapen	Bishofite	Water
M-1	50	15	30	Rest
M-2	55	10	30	Rest
M-3	55	5	35	Rest
M-4	65	5	25	Rest

3. Results and Discussion

The obtained compositions were tested for mechanical and thermophysical properties. The results are given in Table 6.

Table 6. Mechanical and thermophysical properties of light concretes

Concrete grade	Characteristics		
	Strength, MPa	Thermal conductivity, W/(m·°K)	Density, kg / m^3
M-1	28	0.25	540
M-2	30	0.30	600
M-3	30	0.33	610
M-4	25	0.34	600

As it can be seen from Table 6, the composition M-1 has the optimum operational characteristics.

Tests on alkali-silicate interaction indicate that magnesia concretes do not undergo corrosion when using a silicate-containing aggregate. The results are shown in Figure 1.

Figure 1. Samples after the accelerated test on alkali-silicate interaction

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Figure 2 illustrates samples of lightweight concretes based on the magnesia cement and light silicate aggregates.

Figure 2. Sample section of lightweight concrete based on the magnesia binder

The mineralogical and chemical composition of the synthesized concretes was determined by X-ray diffraction analysis on the diffractometer "D8 Advance" Bruker AXS (Germany) with the following shooting conditions: copper X-ray tube (CuKα-radiation), with a nickel filter. The voltage on the X-ray tube was 40 kW, current strength 40 mA, exposure 0.6 hours, sample diameter 10 mm.; the rotational speed of the goniometer was 4 degrees/min.; response time 1.0 sec; rate of pulses 1·104 imp. / sec.

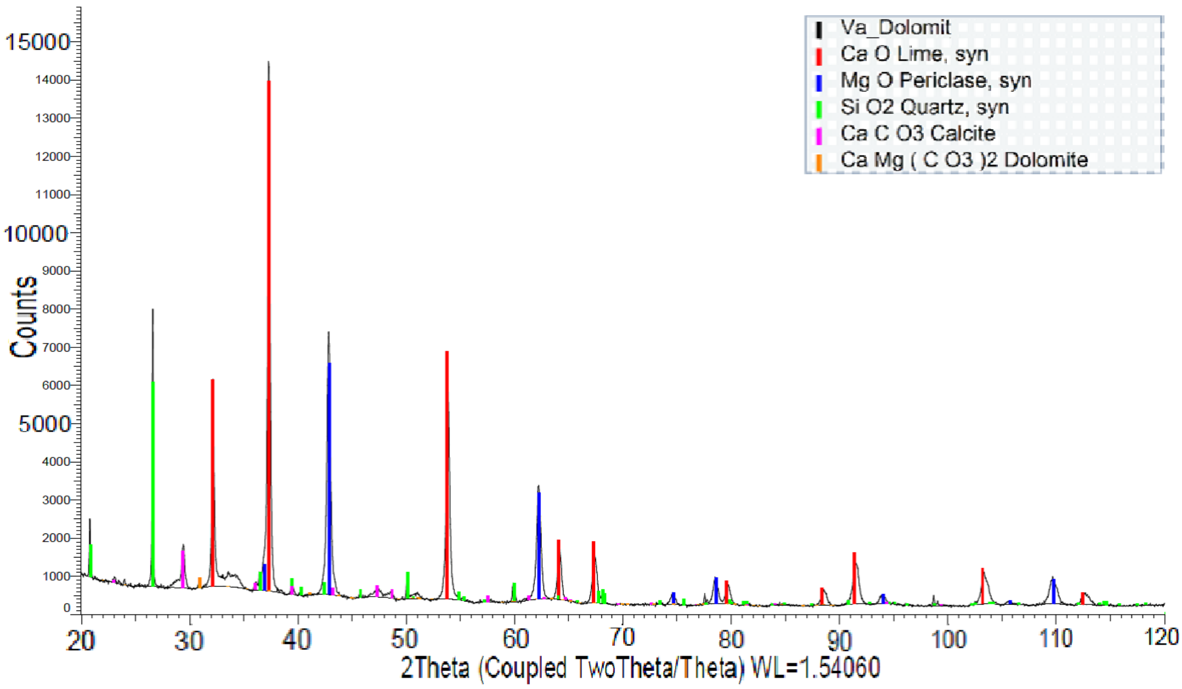

Figure 3 X-ray diffraction pattern and a pie chart of magnesia concrete phase composition

X-ray study of concrete magnesium matrix showed that the sample is periclase (magnesium oxide) MgO with a cubic structure, space group Fm-3 and a lattice size of 4.21 A.

Figure 4 illustrates the microstructure of magnesia concrete, obtained by the scanning electron microscopy.

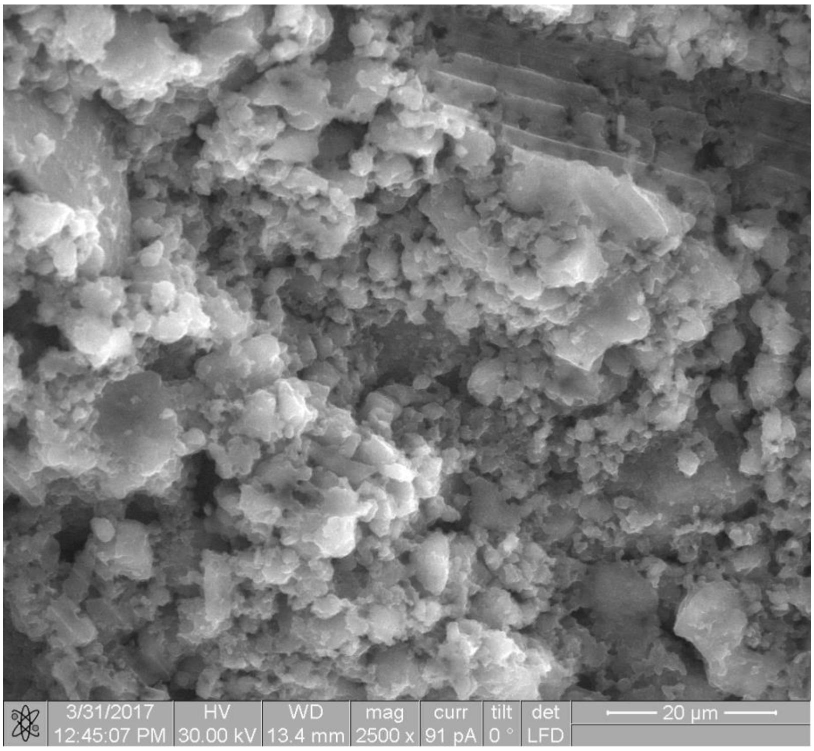

Figure 4 Micrograph of the magnesia composition with "diapen" aggregate

The results obtained during the work indicate that lightweight magnesia concrete synthesized on the basis of dolomite waste has high strength, high water resistance, high adhesion and good thermal insulation performance. The results are in full agreement with the results achieved by leading specialists in this field: M.I. Kuzmenkova, T.N. Chernykh and others.

The research allows to obtain lightweight concrete for solving the problems of "green building", which is now gaining popularity in all countries of the world [20].

4. Conclusions

1. There were developed energy-efficient construction compositions based on the integrated use of dolomite waste and domestic siliceous rocks.
2. There was calculated and selected the composition for lightweight concrete with the highest casting density in accordance with Andreassen-Andersen formula.
3. There were presented comparative characteristics for various types of concrete and made conclusions concerning reasonability of Sorel cement production from dolomite waste.
4. The studies on microstructure and phase analysis of magnesia lightweight concrete showed that the main crystalline phase is periclase.
5. There were developed basic technological parameters for obtaining a lightweight aggregate "diapen" from domestic tripolith and diatomite.
6. There was given practical and theoretical proof for the technology of the new lightweight concrete, eliminating alkali-silicate interaction.

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