Autoclave Synthesis of Composite Cements on Magnesium Silicates

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Abstract. The use of various mineral additives in the production of cements and concretes is one of the urgent tasks of building materials science, as it reduces the consumption of Portland cement clinker, the production of which is accompanied by a large consumption of electricity and the release of CO2 during its production. The use of mixed cements reduces not only the cost of building materials, but also solves the environmental safety of the environment. The work is devoted to the development of composite cements using mineral additives - dunite of one of the widespread magnesia rocks in Central Aldan (Yakutia). Dunit composes inaigl Massif and is located in the industrially developed area of Central Aldan. Petrographic and thermographic studies became the basis for the preliminary preparation of the charge. Pre-annealing, fine joint grinding and additional mechanical activation of the charge are applied. Selected resource-saving, optimal mode of autoclave synthesis of composite binder. It is shown that the autoclave synthesis was able to obtain a high-strength cement stone twice the strength of the cement stone from Portland cement PC 500. It is found that increasing the mechanical strength of the products curing at autoclave composite binders the synthesis achieved by the introduction of a system of micro - silicates of magnesium (serpentinization of dunite). At the same time, finely ground and pre-annealed magnesium silicates perform the role of a micro-filler in the system, contributing to an increase in the density of the formed stone, and the active component involved in the formation of a strong crystallization structure.

1. Introduction
The use of various mineral additives in the production of cements and concretes is one of the urgent tasks of building materials science, as it reduces the consumption of Portland cement clinker, the production of which is accompanied by a large consumption of electricity and the release of CO2 during its production. The use of mixed cements reduces not only the cost of building materials, but also solves the environmental safety of the environment. In addition, the solution of utilization of man-made waste represented by overburden rocks of mining and processing plants.

Trends in the development of modern world civilization can confidently predict the growth of negative changes in the environment as a result of man-made impact. Today, science and technology are faced with the task of creating new resource-saving technologies that can not only slow down these negative changes in the natural environment, but also create conditions for its self-recovery. The most promising areas of this work are the creation and dissemination of "green" (environmentally friendly) technologies in the most resource-intensive sectors of human activity, including construction.
cement-based concrete is the most common building material. Such value of concrete in modern construction is caused by its advantages in comparison with other materials – widespread raw material base, simplicity of technology and rather high technical and construction characteristics. The demand for cement concrete is projected to increase in the future. However, in the long term, the mass use of concrete can have negative consequences due to the exhaustion of the raw material base and environmental factors of cement production. Among the factors hindering the production of cement, include high costs of mineral and fuel raw materials per ton of cement produced – 1.6 tons of carbonate and aluminosilicate rocks and 0.4 tons of fuel equivalent, carbon dioxide emissions, which are comparable to the volume of clinker production, as well as the release of gases NO, SO2, etc., emissions of dust into the atmosphere. The increase in the content of carbon dioxide and dust in the atmosphere leads to the development of the greenhouse effect, and sulfur dioxide – to acid rain [1-4]. Currently, the countries of the European Union, North America, Canada and other industrialized countries are actively working on the introduction of the concept of sustainable development in the construction industry [5]. This concept is based on the idea of meeting the needs of people in environmental types of building materials without harming the environment. Within the framework of ensuring the concept of life-sustaining development, not only requirements are imposed on concrete, taking into account the properties during operation, but also requirements for environmental safety of raw materials and finished concrete, rational energy and resource saving in the production of cement [6-7].

In this regard, natural magnesia silicates are of interest, which are now widely used in the production of refractory and ceramic materials due to structural features and chemical composition [8-10].

In the sixties of the last century by autoclave synthesis various building products were obtained on the basis of natural minerals, rocks and the passing products (tails) containing hydroxides of magnesium. In autoclave processing the increase of durability processes was defined. So, the durability of pressed samples from burnt serpentine after autoclave processing is 10-12 times higher than the durability of the same samples under normal hardening conditions [11-13].

Autoclave synthesis concretes are the materials obtained in autoclave processing in the environment of water vapour of high pressure (0,8-1.3 MPa) and the corresponding temperature (173-194°C) of Portland cement and active mineral additive. The autoclave synthesis concretes as compared to standard cement non-autoclave concretes contain chemically active components as fillers which are taking part in the process of structure-forming and hardening of the material.

For the last years the autoclave synthesis is being widely used for manufacturing cellular concrete and foam concrete. Composite concretes of autoclave synthesis in our country and abroad practically have not been produced and investigated.

The studies conducted in the middle of the last century have shown that the durability of samples by the pressing method (at 40 MPa) from alkaline-ultramafic, ultramafic and basic rocks containing dunites, olivines and pyroxene of Monchegorsky and Kvodorsky massifs ranged as follows: 3,7-7,0 MPa; 5,3-7,2 MPa; 6,1-8,3 MPa in storing on air in 28 days. After autoclave processing the durability of samples has essentially increased, and reached 22,5 MPa. The autoclave synthesis has proven its efficiency to be applied in obtaining a wide range of multipurpose concretes from different sources of raw materials with tensile strength from 0,8-20 MPa to 100 MPa and more in the case of certain technological principles (raw materials selection, preparation of mixes, introduction in a mix of various additives, selection of a formation method etc.) [14-17].

2. Materials and research methods
Serpentine dunites being used as the active mineral additive the alkaline – ultramafic intrusive Inagli massif located in Aldan area [18]. According to petrographic and X-ray phase studies (diffractometer Shimadzu XKC 7000) the modified serpentine dunites contain minerals of serpentine groups – clinochrysotile, lizardite, serpentine, along with olivine and forsterite. The ratio of the basic rock-
forming minerals in dunite test is the following: olivine - 60-70 %, minerals of serpentine group - from 30 to 40 %, chrome diopside - to 3.

The thermoanalysis (TG/DSK/DTA) was conducted by means of the thermoanalyzer for synchronous thermal analysis NETSCH TT-DCK STA 449 Jupiter.

The given thermograms confirm the results of X-ray phase analysis on identifying significant amount of serpentine minerals (Picture 1). So, the thermogram revealed endothermic effects corresponding 81,4 °C with removal of free water; at temperatures 134,1, 177,2 and 360,3 °C there is step dehydration of clinochrysotile and lizardite; at temperature 684,4 °C to an excess approximately in 630 °C there is removal of constitutional, chemically mixed water. The exothermic effect from maxima in 822,6 °C corresponds to crystallization of a new phase as forsterite from dehydrated serpentine minerals.

![Figure 1. The dunite thermogram of Inagli massiv.](image)

### 3. Results and discussion

The materials studied have shown that dunite rocks with high serpentine degree can be applied as the active mineral additive in the mixed cements on a basis of Portland cement clinker with the condition of using mechanichemical processing of dunite rocks.

The mechanical activation of the modified dunite causes the mechanichemical destruction of serpentine minerals with partial removal of crystallized water that will make chemically active system in relation to minerals of cement clinker as well as in hardening. Such minerals as olivine, forsterite, chrysolite at active machining are exposed to considerable amorphosis that will result in possible interaction with minerals of cement clinker and subsequently with water while forming not only calcium hydrosilicates in the system, but also magnesium hydroxyl in hydration products and hardening [19].

Following initial materials were applied in our researches for use of magnesium raw materials:

Portland cement of the Verkhne-Bestyahsky cement factory in %: SiO₂ -20,4; Al₂O₃ -4,1; MgO - 4,06; CaO- 58,06; Fe₂O₃ - 2,76; SO₃ - 8,1, other components – 1,96 (table. 2.3)
Active mineral additive dunite with the following composition of basic oxides, mass %: SiO$_2$ - 36.24; Al$_2$O$_3$ - 1.42; MgO - 55.7; CaO - 0.6; Fe$_2$O$_3$ - 5.31; others – 0.6 (Test № 250-M) (table.1)

**Table 1.** Mineralogical composition of Portland cement clinker 500. JC CS «Yakutcement» [19].

| C$_3$S | C$_2$S | C$_3$A | C$_4$AF | Silicate module | Alumina module | Saturation coefficient |
|-------|-------|-------|--------|----------------|----------------|-----------------------|
| 58.70 | 16.38 | 6.44  | 14.35  | 2.97           | 1.49           | 0.88                  |

The dunite sample was crushed on a drum-type mill within 2 hours, as a result the average diameter of the crushed grains amounted 2 microns, and the specific surface of powder was 8403 cm$^2$.

The cement samples shut by water, by a standard technique of GOST 10180-2012 presented as cubes in the size 2x2x2 cm were tested [20]. A part of the samples was hardened in air-damp conditions, the rest of samples were subjected to autoclave synthesis.

The mode of autoclave hardening is characterized by following parameters:
1. Temperature rise up to 120°C - 1 hour
2. Pressure rise in an autoclave 1.0-1.5 atm. - 1 hour
3. Hardening in an autoclave at 120°C and pressure 1.5 atm. - 6 hours
4. Cooling of samples in an autoclave - 12 hours.

At concrete hardening in an autoclave at higher temperatures and steam pressure 9-10 the atmospheric pressure arising at temperature 97-100°C in regular intervals "presses out" a product acting as a form to a certain extent. However, with this pressure basically destructive processes have already come to the end; the structure defects formed at an initial stage of steaming appear irreversible and consequently the superfluous pressure in the further temperature rise above 100°C hardly influences on formation of concrete structure. Results of the compression test are presented in table 2 and figure 2.

**Table 2.** Compression strength of cement rocks with dunite additive.

| Cement marking | Cement composition | Sealer | Hardening conditions | Durability of cement rock samples on compression in MPa, Age, per day |
|----------------|--------------------|--------|----------------------|--------------------------------------------------------------------|
| DO             | PC 500-D0          | H$_2$O | Aerial               | 7  | 14  | 28  |
| Du30-B         | 70%PC + 30% Du$_3$ | H$_2$O | Aerial               | 29.90 | 39.10 | 48.00 |
| Du30-A         | 70%PC + 30% Du$_3$ | H$_2$O | Autoclave            | 26.38 | 29.57 | 29.71 |

Du- duonite
DO – Portland cement(PC)
Du30-B - PC with 30% duonite- aerial hardening conditions
Du30-A - with 30% duonite- autoclave hardening conditions
According to table 2 and figure 2, the samples with 30% dunite additive, shut by water with air-damp hardening, have demonstrated the lower properties than initial cement PC 500-D0 on 38%. It is due to the hydraulic activity of dunite additive in the specified conditions. Probably, it is connected with soundness in the hardening process with magnesium oxide. The samples of 30% dunite additive, shut by water with autoclave steaming in all hardening processes have shown higher compressive strength as compared with the control samples. After 28 daily hardening the strength of samples with 30% dunite additive on autoclave hardening was 56.8%, higher than the controls.

It is established that the higher mechanical strength of hardening composition binders on autoclave synthesis is attained due to micro-additives such as magnesium silicates (serpentine dunite). In this process finely milled and preliminary annealed magnesium silicates are considered as micro-additives, conductive to the higher density of a formed rock as well as the active component in formation of a firm crystallized structure.

4. Conclusion
1. The comparative analysis of aerial and autoclave hardening has shown that the strength improvement on cement compression shut by water with autoclave hardening is on 60.5% higher as compared with cement aerial hardening PC 500.
2. The strength of cement with 30% dunite additive of autoclave hardening is higher than Portland cement PC 500 on 56.8%.
3. The mechanical activation of modified dunites causes mechanochemical destruction of serpentine minerals with partial removal of crystallized waters that makes the system chemically active both in relation to minerals of cement clinker, and at further hardening.
4. It is established that the higher mechanical durability of hardening composition binders on autoclave synthesis is attained at the expense of magnesium silicates (serpentine dunites). In this process finely milled and preliminary annealed magnesium silicates are considered as micro-additives, conductive to the higher density of a formed rock as well as the active component in formation of a firm crystallized structure.
5. By means of composite cement on autoclave synthesis it is possible to obtain various small-pieces materials: tiles and paving slabs, borders, window sills and ceramics, table-tops, tombstones.
References
[1] Mehta P K 2016 Greening of the Concrete Industry for Sustainable Development // ACI Concrete International vol 24(7) pp 23-28
[2] Lian H, Wu Z 2015 Sustainable development of concrete and high performance cementitious material Concrete 6 pp 8-12
[3] Davidovits J 2015 Geopolymer Chemistry and Applications 4th edition. Saint-Quentin (France) p 644
[4] Eroshkina N A, Korovkin M O 2017 Investigation of properties of geopolymer binder based on magmatic rocks and concrete on their basis XiX. Internationale Baustofftagung. Bauhaus - Universität Weimar Band 1 pp 1175-1180
[5] Richard P, and Cheryrezy M 2016 “Composition of Reactive Powder Concrete” Cement and Concrete Research vol 25 7 pp 1500–1511
[6] Eroshkina N A, Korovkin M O, Korovchenko I V 2015 Resource-Saving efficiency of technology of geopolymer binders on the basis of magmatic rocks Modern scientific researches and innovations 3 URL: http://web.snauka.ru/issues/2015/03/50975
[7] Kalashnikov V I, Gulyaeva E V, Valiev D M, Volodin V M, Khvastunov A V 2011 High-Performance powder-activated concretes of various functional purposes using superplasticizers Building materials 11 (M.) pp 44-47
[8] Bozhenov P I, Prokofiev V V 1972 Use of tailings of Kovdorsky magnetite ores in manufacturing building materials Coll. of conf. papers Kolsky department AS USSR. pp 32-36
[9] Bozhenov P I, Salnikova V S, Prokofiev V V 1970 Use of magnesium - containing waste in manufacture of building materials Bulletin VDNH 3 pp 74-76
[10] Bozhenov P I, Salnikova V S 1955 About binding properties of some natural minerals XIII scientific and technical conference LICI (L.LICI) pp 185-187
[11] Khoroshavin L B, Kosolapova E P 1968 Refractory concretes from dunit/SB. trudov Eastern Institute of refractories Issue 7 (Sverdlovsk) pp 127-133
[12] Belogurova O A, Grishin N N, Mamontov V P 2013 Evaluation of dunites of Pados-tundra Deposit as refractory raw materials Construction and technical materials from natural and man-made raw materials of the Kola Peninsula (Apatity) pp 45-53
[13] Bondarenko A V, Balamygin D I 2008 Modern refractory materials based on dunite of Solovyovogorsky Deposit Refractories and technical ceramics 3 pp 5-9
[14] Miruk O A 2005 Formation of the Hydrate of magnesia mixed binder Izv. higher educational. Construction (M) 10 pp 43-46
[15] Khudyakova L I, Konstantinov, K K, Narihanova B A 2002 Obtaining heat-resistant composite binding materials Building materials (M.) 11 pp 44-45
[16] Khudyakova L I, Voyloshnikov O V, Kotov I I, and etc. 2010 Waste of mining enterprises as raw materials for producing construction materials Herald of Feb RAS 1 pp 81-84
[17] Khudyakova L I, Voyloshnikov O V, Kotova I Yu 2015 Effect of mechanical activation on the formation and properties of composite cementitious materials Building materials 3 (M.) pp 37-41
[18] Glagolev A A, Korchagin A M, Harchenkov A G 1974 Arbarastah and Inagli alkaline – ultrabasic massifs.(M., Science) p 176
[19] Vasilyeva A A, Moskvitin S G, Moskvitina L V, Fedorova G D 2018 Experience of obtaining mixed cements in various ways on the basis of Portland cement with dunite mineral additive VIII Eurasian Symposium on strength of materials and machines for cold climate regions: vol 1 (Yakutsk Tsumori Press) pp 433-440
[20] GOST 10180-2012 2018 Concrete. Methods for strength determination using reference specimens (M. Standardinform)

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