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Composite Cements with Mineral Additives of Intrusive and Metamorphic Rocks of Central Aldan (Yakutia)

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Abstract. The creation of new compositions with mineral additives requires fundamental research of the chemical activity of mineral additives. As an active mineral additive used waste production of chromdiopside and phlogopite –dunite and diopside Aldan region (Yakutia). The use of overburden reduces the cost of production of building materials and improves the environmental situation in the region. The obtained dependence of the strength developed in cements, their composition, preparation of the raw mix, modes of curing and keeping maturing. For the first time, using a set of technological approaches including pre-annealing, mechanical activation and autoclave synthesis, a high-strength composite cement with additives of magnesium silicates exceeding the strength of Portland cement by 56.8% was obtained. In our previous experiments, the introduction of up to 40% diopside in Portland cement did not increase the strength of the cement stone due to the chemical inertness of the additive. Magnesium chloride - MgCl2 was used for mixing in order to activate hydration. It is shown that the high rate of formation of the solid phase during the closure with magnesium chloride leads to the development of stresses and strains leading to a decrease in strength in the later stages of hardening. The optimal technological approach is water mixing and autoclave synthesis. Possible consumers can be cement plants, enterprises for the production of building materials, representatives of medium and small businesses, as well as enterprises of the mining industry interested in the disposal of waste production.

1. Introduction

Modification of cement with various mineral additives is one of the ways of improving cement mechanochemical properties. As a progressive trend technogenic and natural raw materials containing magnesium silicates are used in manufacturing building materials [1-6].

The natural magnesium rocks diopside and dunite can be applied as active mineral additives. Activity of mineral additives, i.e. capability to bind calcium hydroxide at usual temperatures is caused by magnesium oxides content in diopside and dunite, considered to be in chemically active form [7-10]. Finely ground diopside and dunite possess binding properties and when mixing with Portland cement, the properties of composite material are defined by properties of Portland cement and magnesium additive as well as results of their interaction.

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2. Materials and research methods

In Aldan area (Yakutia) there is large quantity of mining wastes, including magnesium silicate rocks presented by raw materials wastes such as chromdiopside and phlogopite. The wastes are presented by intrusive rocks dunites and metamorphic rocks diopsides.

Intrusive alkaline - ultrabasic massif of Inagli, is located in upper courses of the river of Inagli - the right inflow of the Aldan river. The central part of chromdiopside massif (semiprecious jewelry stone) is combined with dunite deposits which are revealed in the circus-shaped hollow formed by the river Inagli. [11].

Dunites are represented as massive middle- or fine-grained rocks of dark grey colour with a greenish tint. The chemical composition of the studied dunite (Test № 250-M): SiO_2 -.36,24%, TiO_2 – 0,02%, Al_2O_3 – 1,42%, $Fe_2O_3$5,31%, $Cr_2\ O_3$ – 0,34%, MnO – 0,13%, MgO – 55,7%, CaO – 0,59%, Na_2O – 0,08%, K_2O – 0,3%,

The increased magnesium and alumina composition is caused by intensive serpentine content at hydrothermal and hydrothermal-contact modifications of ultrabasic rocks.

The X-ray phase analysis has been executed on the x-ray diffractometer Shimadzu XKC 7000c by use of radiation Si - anode, thermoanalysis (TT/DCK/STA have been carried out by means of the analyzer for synchronous thermal analysis NETSCH TT-DCK STA 449 Jupiter.

The petrographic and X-ray phase analysis revealed that as a result of hydrothermal processes serpentine group minerals are formed comprising 40-50 % from the rock mass called serpentines made up of antigory ($Mg_3\,[Si_2O_5]\,(OH)_4$, lizardite ($Mg_3\,[Si_2O_5]\,(OH)_4$ and clinochrysotile $Mg_3A1_2O_5\,(OH)_4$ ($3MgO$-$2SiO_2$-$2H_2O$). The ratio of the basic rock forming minerals in dunite test is the following: olivine - 60-70 %, serpentine groups minerals - from 30 to 40%, chromdiopside till 3. The roentgenogram of dunite is shown on figure 1.

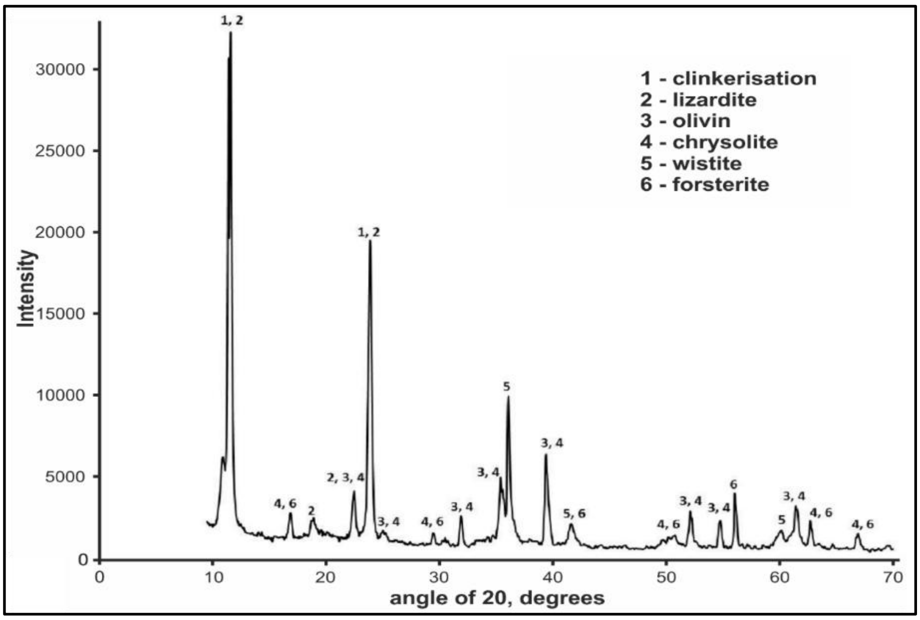


Figure 1. Dunite roentgenogram of Inagly area.

The similar outcome is revealed due to significant losses at toasting 10,88 mass. % and the low silicate module 1,34 corresponding to forsterite - 1,34.

The thermograms outcomes confirm the results of X-ray phase analysis on the content of serpentine groups minerals. So, on the thermogram endothermic effects corresponding to removal of free water at 81,4 °C are observed; at temperatures 134,1, 177,2 and 360,3 °C step-be-step dehydration of clinochrysotile and lizardite is noted; at temperature 684,4 °C there is removal of constitutional, chemically complexed water to an excess approximately in 630 °C. The exothermic effect from maxima to 822,6 °C corresponds to crystallization of a new phase – forsterite out of dehydrated serpentine minerals.

In the Central - Aldan all phlogopite deposits coincide with diopside rocks strata consisting of Fedorovsky suite[12]. One of industrially mined-out phlogopite deposits Bezymyanny is located in 30 km to the south of the city of Tommot. Monomineral diopside slates of dark grey, usually greenish - grey colour are overburden rocks. The chemical composition of the studied diopside (Test № 107-M) : SiO_2 – 45,3%, Al_2O_3 – 9,8%, Fe_2O_3 - 3,7%, MgO – 15,0%, CaO – 18,1%, Na_2O – 0,7%, ppp – 2,1%.

Diopside slates unlike dunites possess higher content of SiO_2 (44,71-52,36 %), Al_2O_3 (2,8-11,22 %) and lower MgO (10,90-15,6). For specification of mineralogical structure radiographic researches on the sample 107 TH (figure 2) have been conducted.

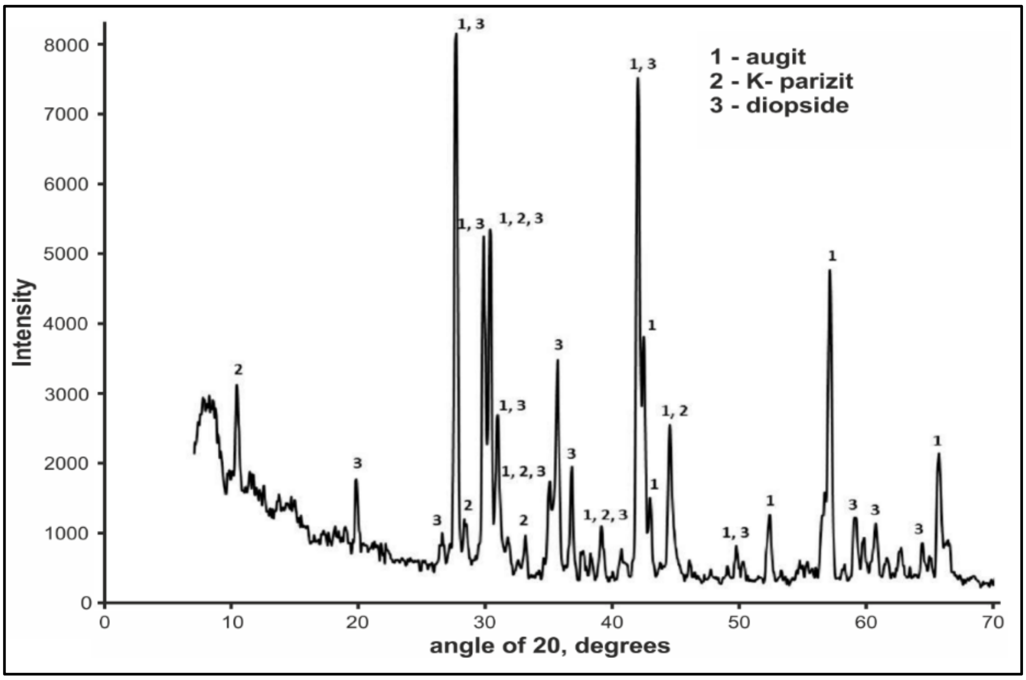


Figure 2. The diopside roentgenogram of Bezymyanny deposit.

The studied diopside crystal slate consists of diopside $CaMg[Si_2,O_6]$ (monocline pyroxenes group), plagioclase (Na $[AlSi_3O_8]$, olivine (Mg, Fe) $_2$ $[SiO_4]$, forsterite, etc.

3. Results and their discussion

For investigation of composite cement with the active mineral additive –dunite and diopside the following initial materials were used:

1. Portland cement PC – 500 of Verhne-Bestyakhsky plant: %: SiO_2-20,4; $A1_20_3$-4,1; MgO-4,06; Sao - 58,06; Fe_20_3 - 2,76; SO_3 - 8,1, other components - 1,96
2. The active mineral additiveы dunite (Test № 250-M) and diopside (Test № 107-M)

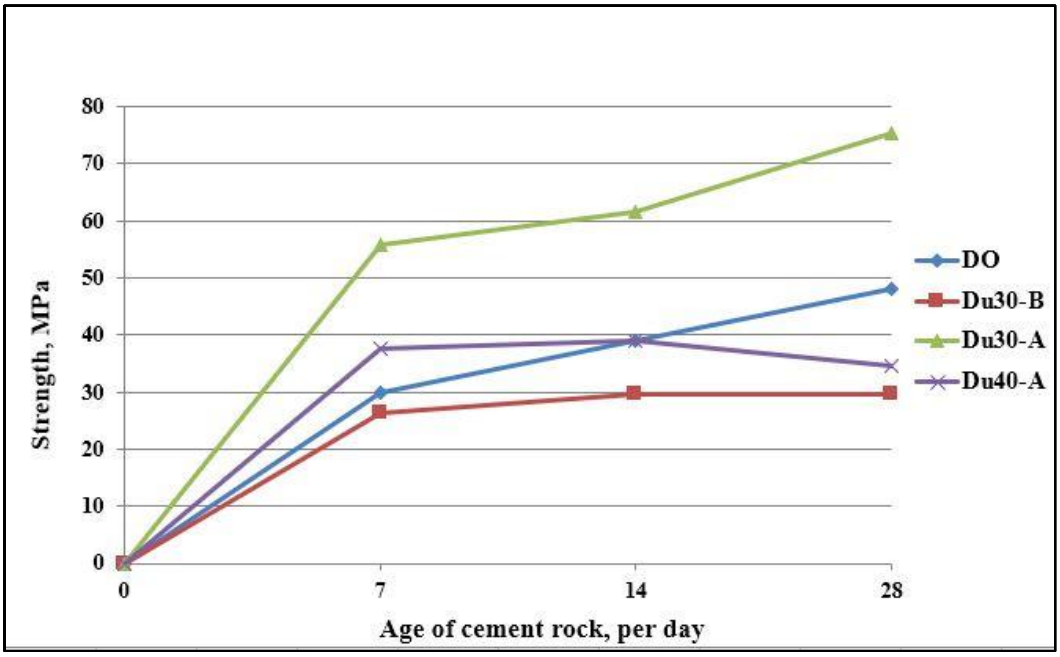
The rocks used as mineral additives – dunite and diopside are shattered on the laboratory jawbreaker to fraction of 5 mm and grinded on the spherical mill to fraction of 2-3 mkm.

For the further work dunite and diopside additive was attained by the purpose of providing cement specific surface with the additive at level 5000 - 6000 cm^2/g.

For researching the abovementioned relations the mixtures containing dunite from 30 to 50 %, and separately with diopside -40 % have been prepared. The cement with dunite and diopside additive shut by water and magnesium chloride ($MgCl_2$) on concentration 1,7 moll. The rest samples of cement shut by water were hardened in air – wet conditions.

Cube-shaped cement samples of size 2x2x2cm were investigated out of the solution of normal density. The basic part of cement was hardened on the air, as experiment a part of samples has undergone autoclave synthesis.

The samples with dunite additive of air hardening after exposing in air-wet conditions were tested for compression. On each series 6 samples were tested by means of test cars UTS-20K (Germany) and by a universal test car Zwick/RoellZ600 (figure 3).



Du – dunite.

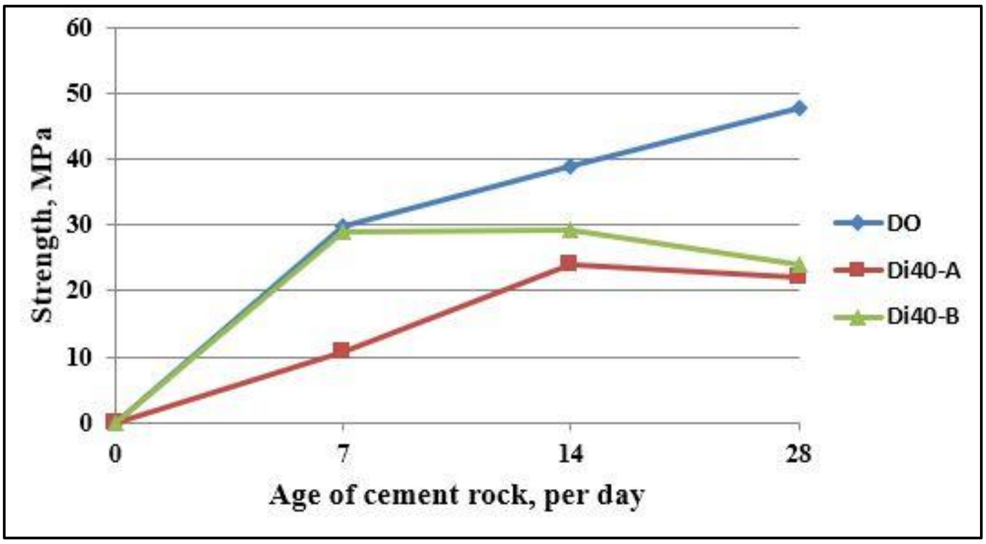
Figure 3. Compression strength of cement rock with dunite additive.

On figure 3 shoun: 1 - DO - Portland cement; 2. Du30-B - PC with 30% dunite- aerial hardening conditions; 3. Du30-A - PC with 30% dunite- autocluve hardening conditions; 4. Du40-A - PC with 40% dunite- autocluve hardening conditions;

As the table and figure have testified, the samples with dunite additive of 30% shut by water with air-wet hardening obtain lower strength properties as compared to the initial cement PC 500 on 38 %. It shows lower hydraulic activity of dunite additive in the specified conditions.

The compression strength of samples with 40 and 50 % dunite additive shut by chloride of magnesium with concentration 1,7 moll on autoclave steaming have lower strength than at control samples. At samples Du40-A the initial strength is higher than at controls, but the final strength is lower on 28 %. The strength decreases with percentage increase of the additive up to 50 %.

In the experiences conducted earlier the inlusion to 40 % diopside in Portland cement did not cause cement durability due to chemical inertness of the additive [13-14]. In order to activate the hydration for shutting magnesium chloride - $MgCl_2$ (figure 4) is used.



Di - Diopside.

Figure 4. Compression strength cement rock with diopside additive.

On figure 4 shoun: 1. DO - Portland cement; 2. Di40-B - PC with 40% diopside - aerial hardening conditions; 3. Di40-A - PC with 40% diopside - autocluve hardening conditions.

The experiments have shown that at air hardening the samples shut by magnesium chloride due to the mixture coagulation obtain the lower durability. The higher temperature of the clinker at such shutting testifies to high speed of the solid phase formation. The coagulation is characteristic as a rule for colloid systems. As a result, probably, there is a process of chemical shrinkage (counteractions). The counteraction, as it is known, is accompanied by pressure and deformations in hardening system [15-16].

According to the researches of last years the hydration process of binders includes not only their purely chemical interaction with water or electrolyte solutions with formation hydrate forms, but also concomitant physical, physical-chemical and colloid-chemical processes and the phenomena including dissolution, hydrolysis, crystallization, polymerization and polycondensation. Subject to conditions they provide grasping and hardening of binders and formation of a spatial capillary-porous structure of certain durability and firmness [17].

It is known that fine grinding contributes to the intensification of physical - chemical reactions and is considered to be the defining process in mechanoactivation of substances as when exposed mechanical forces the physical and chemical properties of materials [18-19] undergo a change. For improving the quality of binders a combined two – step method of mechanoactivation (rough and fine grinding). At rough grinding the impact crushing machines (a jawbreaker) are considered to be the most effective, while at fine grinding stage the shock vibrating activation (pivotal, string mills and a disintegrator) is noted. It not only reduces power consumption at grinding, but also prevents the occurrence of ultrafine fractions. As a result of the experiments conducted, dunite grinding is noted to be optimum to specific surface of 6000 cm/g.

4. Conclusion

1. The petrographic and physical methods of the researches have become a justifier for working out optimum modes for the preliminary preparation of mineral additives.
2. It is shown that the joint grinding of the mineral additive and Portland cement allows to evenly distribute the dispersed additive powder in the cement test, thus providing the volumetric uniformity in a cement stone.
3. Dunite grinding to specific surface of 6000 cm/g is found to be optimal.

4. For the first time by means of a complex of technological approaches including preliminary annealing, mechanoactivation and autoclave synthesis the high-strength composite cement with additives of magnesium silicates is obtained exceeding the Portland cement durability on 56,8 %.
5. Application of magnesium chloride as a shutter has caused a reaction with rapid formation of a solid phase that at later hardening stages results in the development of pressure and deformations reducing the cement durability.

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