

Influence of dunite mineral additive on strength of cement

**A A Vasilyeva¹, L V Moskvitina¹, S G Moskvitin¹, M P Lebedev¹ and
G D Fedorova²**

¹V.P. Larionov Institute of Physical-Technical Problems of the North of the Siberian Branch of the Russian Academy of Sciences, 1 Oktyabrskaja str, Yakutsk, 677980, Russia

²M.K. Ammosov North-Eastern Federal University, 58 Belinsky str, Yakutsk, 677027, Russia

E-mail: kiir@mail.ru

Abstract. The work studies the applicability of dunite rocks from Inagli massif (South Yakutia) for the production of mixed (composite) cement. The paper reviews the implementation of dunite for manufacturing materials and products. The chemical and mineral compositions of Inagli massif dunite rocks are presented, which relegate the rocks to magnesia-silicate rocks of low-quality in terms of its application as refractory feedstock due to appreciable serpentinization of dunite. The work presents the results of dunite study in terms of its applicability as an additive to Portland cement. The authors have established that dunite does not feature hydraulicity and can be used as a filling additive to Portland cement in the amount of up to 40%. It was unveiled that the mixed grinding of Portland cement and dunite sand with specific surface area of 5500 cm²/g yields the cement that complies with GOST 31108-2016 for CEM II and CEM V normal-cured cements with strength grades of 32.5 and 42.5. The work demonstrates the benefits of the studies of dunite as a filling additive for producing both Portland cement with mineral component and composite (mixed) cement.

1. Introduction

The elaboration of mixed cements using various mineral additives is an urgent problem in construction materials science, since it reduces the consumption of Portland cement clinker, which production consumes a lot of energy and releases significant amount of CO₂. The usage of mixed cements both reduces the cost of construction materials and ensures the environmental safety of the process. One of the main approaches to the enhancement of mixed cements is the optimization of the composition by various mineral additives.

In this connection, magnesia silicates that are widely used in production of refractory and ceramic materials, mineral wool and as an additive to heavy concrete [1–3] are of increased interest due to their structural peculiarities and chemical composition. Among strong points of dunites in production of articles and materials, along with increased material thermal resistance, are the stability of chemical composition, high dielectric properties and health safety (e.g. no silicosis danger, since dunite does not contain free silicon oxide). Dunite can be used as an additive to obtain composite cementing agent [4–5]. According to the researchers, mechanochemical activation of dunite in a mixture of Portland cement clinker and gypsum produces mixed calcium-magnesium silicates, which allows substituting 30–40% of Portland cement clinker without a decrease of the cement activity. The increased compressive and



bending strength of dunite-based cement mixture is explained by the occurrence of magnesium hydrosilicates with fibrous structure [5]. These results were obtained by the scientists of Baikal Institute of Nature Management of SB RAS under the supervision of L.I. Khudokova, who were the first to introduce the term *dunite cement* (RF Patent No. 2288899 as of April 14, 2005). There is no other information on this topic both in national and international sources.

Taking into consideration that the authors of the aforementioned works have concluded the increased hydration activity of dunite cements, the present work is aimed at studying the applicability of Inagli massif dunite rocks (South Yakutia) as a mineral additive to Portland cement.

The goal is to be achieved by:

- fine grinding of the rock under study into mineral additive and its study as an additive to the cement, and
- studying the effect of mixed grinding of Portland cement with dunite sand on the strength of the cement.

2. Materials and methods

2.1. Dunite rock

The Inagli alkali-ultrabasic massif is located in the northern boundary area of the Aldan Shield, at the head of Inagli River, which is the right tributary of Aldan River, somewhat 30 km to the west of Aldan city. The central part of the massif with the area of 16 km² is composed of forsterite dunites on a narrow (from 5 to 25 meters) discontinuous margin of pyroxene-olivine rocks, which composition corresponds to peridotites and micaceous pyroxenites. Dunites are medium-to-small grain rocks of dark-grey color with steely shade. The composition of dunites of Inagli massif was mineralogically studied by L.V. Rasin in [6].

Table 1. Mineralogical composition of Inagli massif dunites [6].

Minerals	Weakly serpentized dunite (vol%)	Serpentized dunite (vol%)	Dunite shatter (vol%)	from zone	Fresh dunite from massif (vol%)	from core
Olivine	73.5	60.5	61.5		85.5	
Serpentine	21.5	33.0	30.0		12.0	
Mica	2.5	3.5	3.0		0.5	
Chrome-diopside	1.5	0.7	3.0		-	
Magnetite	0.5	0.3	0.5		0.3	
Chromospinelide	0.5	1.0	0.5		1.7	
Calcite	-	1.0	1.5		-	
Total	100	100	100		100	

The rock sample under study is characterized by greenish light-brown color of porphyric structure with inclusions of dark grains. The sample was labeled as D1.

The chemical composition of the dunite sample was determined by energy-dispersive analysis using JCM-6000 electron microscope (JEOL, USA). The results are presented in table 2; the X-ray spectrum is depicted in figure 1.

Table 2. Chemical composition of dunite.

Name	Content of oxides (wt%)								Ratio	
Inagli massif dunite (Yakutia)	MgO	SiO ₂	CaO	Al ₂ O ₃	MnO	Fe ₂ O ₃	Δm _{LOI}		MgO/SiO ₂	MgO/Fe ₂ O ₃
	45.61	34.59	1.06	0.41	0.39	8.07	10.88		1.34	5.65

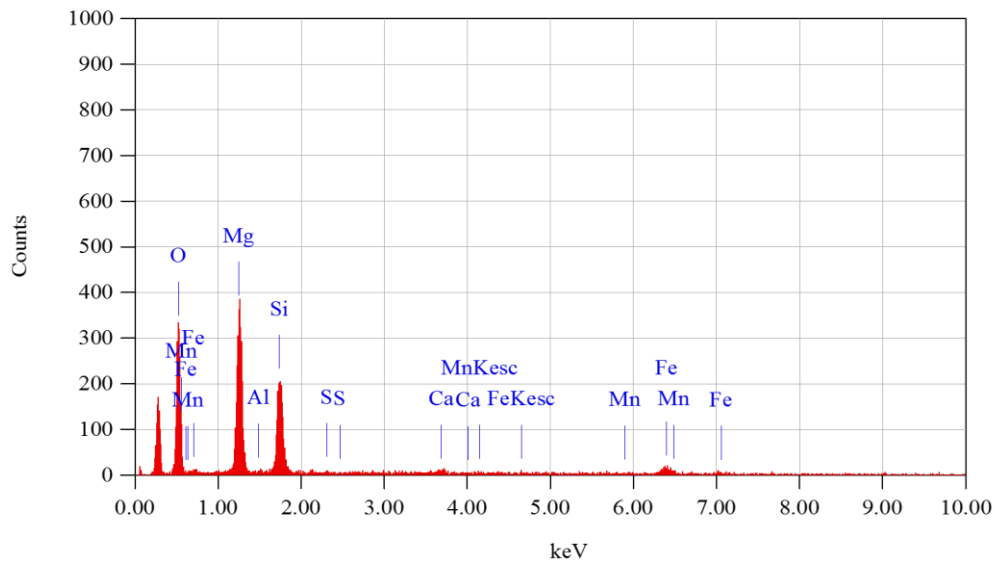


Figure 1. X-ray spectrum of Inagli massif dunite elements.

The mineral composition of the samples was determined by:

- XRD analysis using XRD-7000 X-ray diffractometer (Shimadzu, Japan) with Cu anode (the scan step was 0.05 °/min, time of intensity measurement in scan points was 0.5 s, tube voltage was 40 kV, current was 30 mA), and
- thermal analysis (TGA, TGA-DTA and TGA-DSC) using STA 449 F3 Jupiter® simultaneous thermal analyzer (NETZSCH, Germany) at a temperature of up to 1000 °C in air.

The X-ray pattern is presented in figure 2; the thermogram is depicted in figure 3.

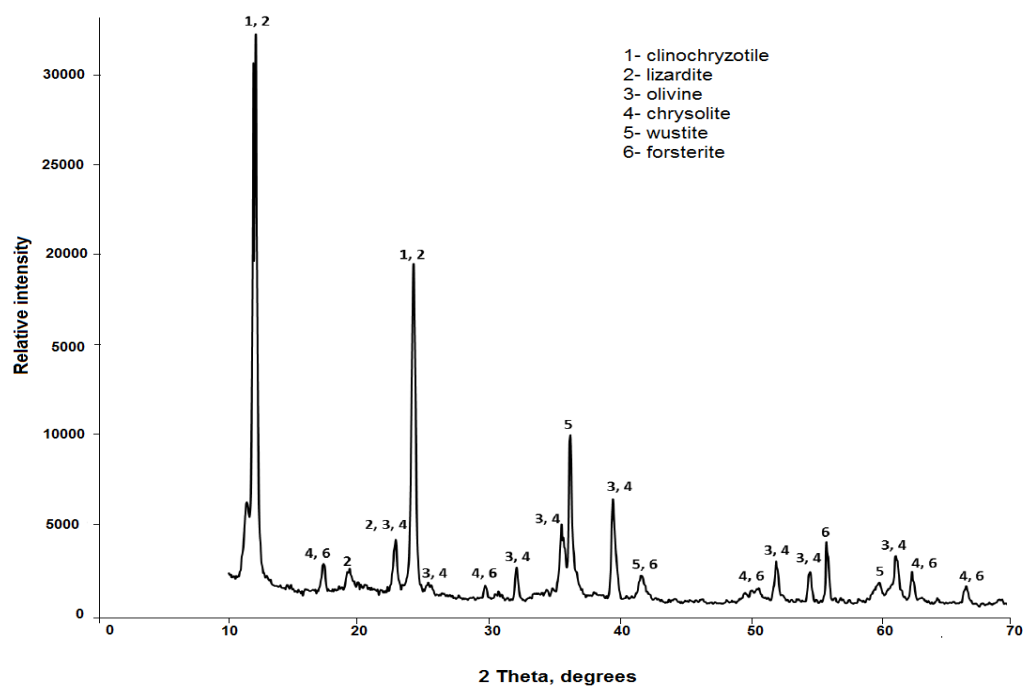


Figure 2. X-ray pattern of dunite of Inagli massif.

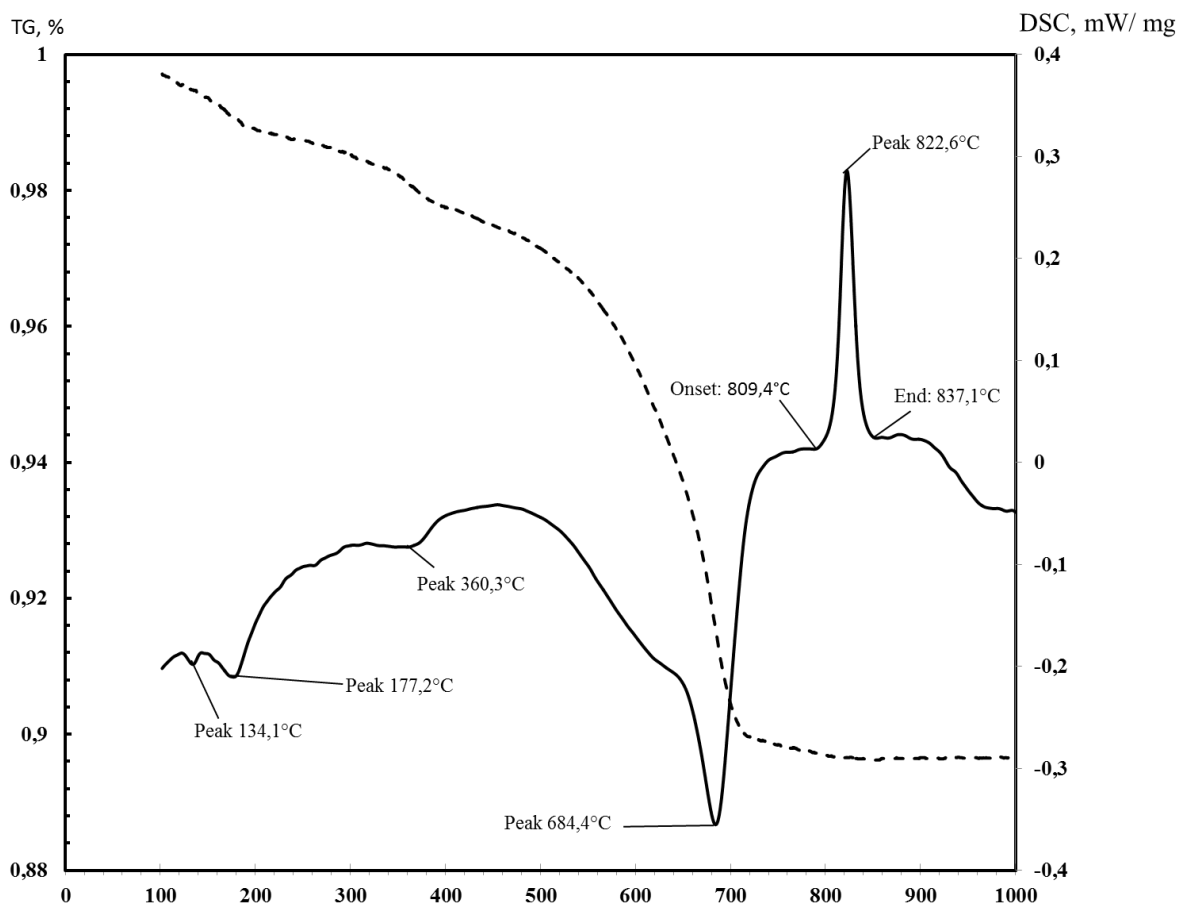


Figure 3. Thermogram of Inagli massif dunite.

The analysis of the X-ray patterns of Inagli massif dunite elucidates the main rock-forming minerals to be olivine $(\text{Mg,Fe})_2\text{SiO}_4$, chrysotile $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ and wustite FeO . The presence of such serpentinite minerals as clinochrysotile $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ and lizardite $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ testifies a prominent alteration and serpentinization of the dunite rock. This is confirmed by the large value of loss on ignition of 10.88 wt% and low silicate ratio of 1.34, which corresponds to forsterite-1.34. The thermogram vindicates the XRD analysis results on the presence of serpentinite minerals. For instance, the thermogram features endothermic effects that at 81.4 °C correspond to the removal of free water; at 134.1 °C, 177.2 °C and 360.3 °C, step-wise dehydration of clinochrysotile and lizardite; at 684.4 °C, with the inflection at somewhat 630 °C, the removal of constitutional, i.e. chemically bound, water. The exothermic effect with the maximum at 822.6 °C corresponds to the crystallization of a new phase—forsterite—from dehydrated serpentinite minerals. The elevated magnesium content of the studied samples can be due to intense serpentinization of rocks under hydrothermal and hydrothermal-contact alteration of ultrabasic rocks. As a result of such alteration, the serpentine minerals are formed that are collectively referred to as serpentines, antigorite $(\text{Mg}_3[\text{Si}_2\text{O}_5](\text{OH})_4)$, lizardite $(\text{Mg}_3[\text{Si}_2\text{O}_5](\text{OH})_4)$, chrysotile $(\text{Mg}_3[\text{Si}_2\text{O}_5](\text{OH})_4)$, that contain magnesium. The results confirm the correspondence of the sample chemical composition to ultrabasic rocks, dunites, from the central core of Inagli massif.

2.2. Portland cement

The experiments used PC400-D0 Portland cement (Yakutskcement, Russia) that complies with GOST 10178-85. The mineral composition is 58.70% C_3S , 16.38% C_2S , 6.44% C_3A , 14.35% C_4AF ; specific surface area is 3140 cm^2/g .

2.3. Preparation of dunite additive and its characteristics

Dunite additive was produced as follows:

- crushing of rock in a laboratory jaw crusher;
- screening of material through a 5-mm sieve;
- milling in a laboratory drum mill during 1, 2 and 3 hours.

The true density of grains of the rock under study was determined by pycnometer method. The specific surface area and mean particle size of finely milled additive was determined on PSKh-2 device (Russia) by the air permeability method.

The characteristics of the prepared additives are given in table 3.

Table 3. Characteristics of finely milled mineral (dunite) additive.

Item no.	Additive label	Rock true density (g/cm ³)	Milling time (hours)	Specific surface area (cm ² /kg)	Mean particle size (μm)
1	D ₁	2.69	1	3750	5.0
2	D ₂		2	5510	3.9
3	D ₃		3	7280	3.03

Further works involved additive D₃ to ensure the specific surface area of the cement with the additive of 4000–4500 cm²/g.

2.4. Preparation of mixed cement and testing methods

To evaluate the impact of the mineral additive (dunite) content on cement properties, two samples of cements were prepared with different content of the mineral additive (20% and 40%) in the cementing agent by mechanical mixing of the initial Portland cement with mineral additive D₃. The samples were mixed in a laboratory vibration mixer. The reference samples were prepared from Portland cement without any additive.

The cements under study were also prepared by mixed grinding of Portland cement PC 400-D0 and dunite sand in Aktivator 2S ball mill (Aktivator, Russia).

The cement properties were determined as per GOST 310 except for the samples that were intended for strength testing. These samples after extraction from the mold were placed into a chamber of standard curing ($t_{\text{air}} = 20 \pm 2$ °C, $W_{\text{rel}} = 95 \pm 5\%$).

To determine the compression strength, the samples with the dimensions of 2x2x2 cm were mold from cement paste of normal density that were wet-cured at the temperature of 20 ± 2 °C.

The kinetics of cement paste curing was studied on the samples from cement paste with water-to-cement ratio of 0.4 and dimensions of 2x2x2 cm that were cured in the chamber of standard curing and tested after 3, 7, 14 and 28 days of curing.

3. Results and discussion

The physical and mechanical properties of the cements are presented in table 4.

Table 4. Physical and mechanical properties of cements.

Cement characteristics	Testing method	Requirements as per GOST 10178-85	Real values		
			PC 400-D0	80%PC + 20% D ₃	60%PC + 40% D ₃
1 Specific surface area (cm ² /g) (mean grain diameter (μm))	GOST 310.2-76*		3140 (6.15)	3840 (5.20)	4100 (5.00)
2 Cement paste thickness (%)	GOST 310.3-76*	-	26.75	26.50	27.00
3 Curing time: beginning, h-min	GOST 310.3-76*	not earlier than 0-45	2-50	3-05	2-50
ending, h-min		not later than 10-00	3-30	3-40	3-50
4 Uniformity of cement volume change	GOST 310.3-76*		-	-	-
5 Compression strength (MPa) 7 days	GOST 310.4-81*	-	29.9*	13.2*	9.4*
28 days		at least 39.2	37.4*	33.2*	21.1*
6 Bending strength (MPa) 7 days	GOST 310.4-81*		4.6*	4.0*	3.2*
28 days			6.7*	5.9*	4.6*
7 Cement grade		400			

*Samples were cured in the chamber of standard curing

The specific surface area of initial Portland cement and cements under study with 20% and 40% of mineral additive amounted to 3140, 3840 and 4100 cm²/g, correspondingly. The cements with mineral additive have elevated specific surface area as compared to initial Portland cement. In spite of this effect, the water demand of cements with mineral additives remains virtually unchanged. The normal thickness of the cement paste lies within $\pm 0.25\%$.

The introduction of the mineral additive in the amount of up to 40% of the cement mass also has no significant effect on the time of cement curing. In terms of curing time, the curing beginning time of the cements (not earlier than 75 min) complies with the requirements of GOST 10178-85 *Portland cement and Portland Blastfurnace cement. Product specifications* and GOST 31108-2003 *Standard cements. Product specifications*.

The activity of initial Portland cement amounted to 37.4 MPa, which is lower than required by GOST 10178-85 (39.2 MPa) by 4.6%. This can be explained by the curing of the samples in the chamber of standard curing instead of wet-curing. The activity of the Portland cements with the content of mineral additives of 20% and 40% of the cement mass amounted to 33.2 and 21.1 MPa, respectively, which is less than that of initial Portland cement; i.e. the growth of the specific surface area has no effect on the strength. This indicates the inertness of the dunite additive.

Figure 4 demonstrates the growth of the strength of cement samples from cement paste with normal thickness having the dimensions of 2x2x2 cm that were wet-cured.

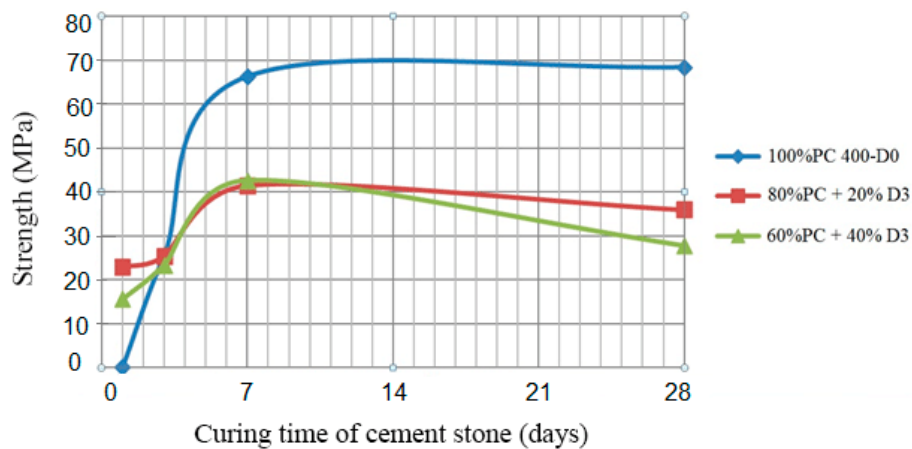


Figure 4. Strengthening of samples from cement paste of normal thickness.

Obviously, the strength of specimens with the mineral additives is nearly two times lower than that of specimens from initial cement PC 400-D0; this also indicates that the mineral additive with the specific surface area of $7280 \text{ cm}^2/\text{g}$ is an inert additive (filler). The experiment has established as well that the cements with mineral additive fairly intensely strengthen during first 7 days, while further they weaken. Probably, this is connected with the change to the uniformity of the volume during curing in the presence of magnesium oxide. This effect is to be studied further.

To elucidate the causes of the determined strength characteristics, we decided to study the structure of the cement stones. The specimens were selected from among the 7-day samples after testing. The images taken by 3700 scanning electron microscope (JEOL, USA) are presented in figure 5. The comparison of the images of cement stones at 500x magnification (a, d, h) demonstrates that the cements with mineral additives feature appreciable cracking in the cement stone as compared to initial cement. In addition, the opening of the cracks increases with raising content of the additive. This complies with the received strength characteristics. The images with 5000x and 10,000x magnification show the grains of the mineral additive and the contact zone between the additive and cement stone. The cracks discovered in the contact zone have possibly occurred during the tests and reflect weak strength of the contact zone. The determined strength properties of the cements denote that the mineral additive from the rock under investigation is an inert additive even after its mechanical activation by milling down to the specific surface area of $7280 \text{ cm}^2/\text{g}$. The received result does not agree with that in [5], which demonstrated the increased binding of dunite with Portland cement clinker into mixed hydrosilicates. Probably, during mixed grinding of clinker, mineral additive and gypsum, hard dunite rock acts as a grinding agent and increases the specific surface area of the clinker fraction of the cement, which leads to the activation of the cement mixture. This can probably increase the strength in the case of simultaneous milling with dunite sand.

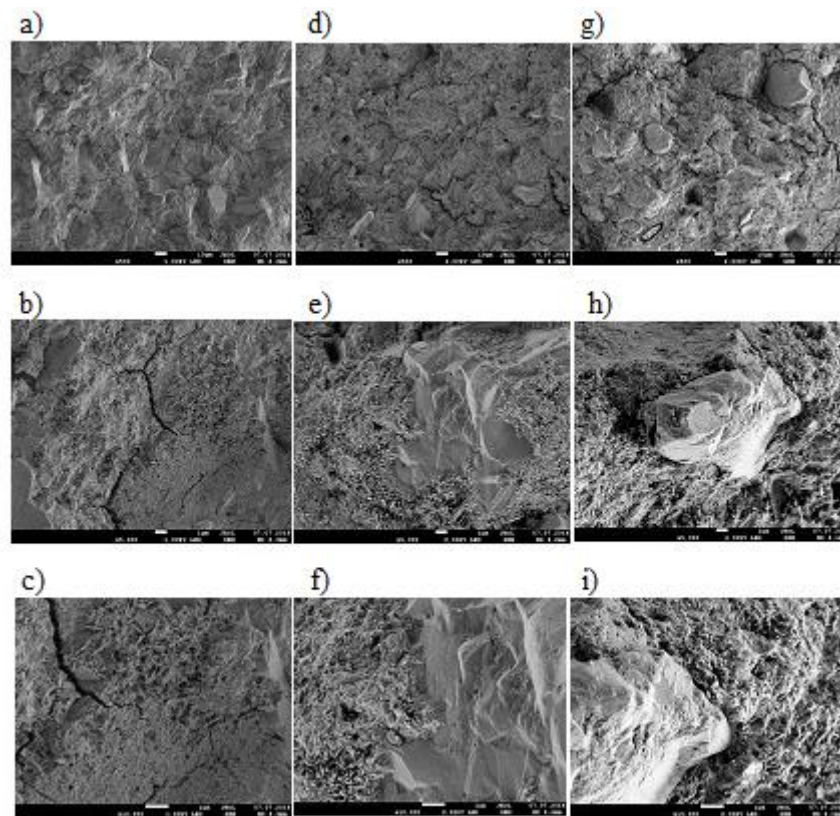


Figure 5. SEM images of cement stones structure at 500x (a, d, g), 5000x (b, e, h) and 10,000x (c, f, i) magnification: 100%PC 400-D0 (a, b, c), 80%PC 400-D0 + 20%D3 (d, e, f) and 60%PC 400-D0 + 40%D3 (g, h, i).

The characteristics of cements under study prepared by different methods are presented in Table 5; the results of density and strength testing of cement stones for different curing time are in table 6.

Table 5. Specific surface area and mean particle diameter of cements.

Cement label	Cement composition	Method of cement preparation with additive	Specific surface area (cm ² /kg)	Mean particle size (μm)
D0	100%PC00-D	-	3140	6.2
D20	80%PC + 20% D ₃	Mechanical mixing	3840	5.2
D40	60%PC+40% D ₃	Mechanical mixing	4100	5.0
Dds20	80%PC + 20% DS	Mixed grinding	5570	3.5
Dds40	60%PC + 40% DS	Mixed grinding	5540	3.7

Evidently from table 6, the cements prepared by mixed grinding of cement and dunite sand demonstrated higher strength (41.7 and 35.1 MPa, respectively for 80%PC + 20% DS and 60%PC + 40% DS specimens) as compared to cements of corresponding composition prepared by mechanical mixing of cement with mineral additive. The received results also demonstrate that dunite rock is inert. Nevertheless, preliminary testing has shown that the mixed grinding of cement with dunite sand has better efficiency against finely milled mineral additive for cement.

Table 6. Density and compression strength of cement stone with water-to-cement ratio of 0.4.

Cement label	Cement composition	Density (kg/m ³) /compression strength of cement stones in MPa (% of R ₂₈) after curing time (days)			
		3	7	14	28
D0	PC 400-D0	1990/26.0	2010/32.2	2082/43.0	2018/51.0
D20	80%PC + 20% D ₃	1930/18.2	1860/18.4	1854/18.2	1910/23.4
D40	60%PC+40% D ₃	1870/13.6	1910/12.9	1909/22.4	187320.9
Dds20	80%PC + 20% DS	2040/28.7	1910/36.6	1937/41.6	1923/41.7
Dds40	60%PC + 40% DS	1870/17.6	1890/24.8	1870/34.3	1948/35.1

Apparently, the increased strength vs. the introduction of milled mineral additive is conditioned by high specific surface area of the cement.

4. Conclusion

The studied mineral additive from dunite rock in terms of chemical composition belongs to ultrabasic rocks—dunites of Inagli massif central core; in terms of chemical and mineral composition it belongs to magnesia-silicate rocks of low quality regarding its application as refractory feedstock due to appreciable serpentinization of dunite.

The study has established that the investigated dunite rock does not feature hydraulicity and belongs to inert mineral additives.

The work elucidated that the mixed grinding of Portland cement and dunite sand down to specific surface area of 5500 cm²/g allows producing cement that complies with GOST 31108-2016 for normal-cured CEM II and CEM V cements with strength grades of 32.5 and 42.5.

The work has demonstrated the benefits of the studies of dunite as a filling additive for producing both Portland cement with mineral component and composite (mixed) cement.

References

- [1] Khoroshavin L B, Kosolapova E P 1968 Refractory concretes from dunite *Collected papers of the Eastern Refractories Institute* **7** 127-133
- [2] Belogurova O A, Grishin N N and Mamontov V P 2001 Evaluation of dunites of Pados-tundra deposit as refractory raw material *Building and technical materials from natural and technogenic raw materials of the Kola Peninsula* (Apatity: Publishing House of the Kola Science Centre of the Russian Academy of Sciences) pp 45-53
- [3] Bondarenko A V, Balamygin D I 2008 Modern refractory materials based on dunite of Solov'yevogorskoe deposit *Refractories and technical ceramics* **3** 5-9
- [4] Khudyakova L I, Konstantinova K K and Narkhinova B A 2002 Acquisition of heat-resistant composite binder materials *Building Materials* **11** 44-45
- [5] Khudyakova L I, Voiloshnikov O V, Kotova I I et al. 2010 Waste of mining enterprises as raw materials for production of building materials *Vestnik of the Far East Branch of the Russian Academy of Sciences* **1** 81-84
- [6] Razin L V, Khvostova V P and Novikov V A 1965 Metals of platinum group in rock-forming and accessory minerals of ultrabasic rocks *Geochemistry* **2** 159-174