

Resistance of the Hardened Cement with Calcined Clays

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Abstract: The article discusses the effect of calcined clays on the properties of Portland cement. An optimal method for calcining clays is proposed, which makes it possible to reduce the proportion of Portland cement clinker in cement to 60% and increase the strength characteristics from 55 MPa to 79 MPa. The study of the composition and structure of clays made it possible to select the optimal heat treatment parameters, at which the calcination products are characterized by the highest pozzolanic activity. It is shown that the use of alkali-activated calcined clays significantly increases the strength and durability of hardened cement binders compared to the composition without additives. In addition, calcined clays increase the frost resistance of cement in a 5% NaCl solution. The obtained experimental data are confirmed by thermodynamic calculations and the results of scanning electron microscopy.

Keywords: portland cement, metakaolin, geopolymers, frost resistance, clays activation.

1. INTRODUCTION

Portland cement with mineral additives is widely used around the world. The clinker factor in Europe ranges from 0.7 to 0.75 [1]. Moreover, the special Limestone Calcined Clay Cement (LC3) technology, where calcined clays and limestone are used as mineral additives, allows to achieve a clinker factor index equal to 0.5 [2]. However, the soft European climate, where this technology has found application, doesn't assume alternating temperatures in cold seasons, when the temperature fluctuates from -20°C to + 5°C in one season. These conditions are more typical for the territories with a temperate continental climate, such as the countries of northern Europe, the Western part of Russia, and the Urals. Moreover, the zones along the sea and ocean coasts are particularly vulnerable. It is known, that the seawater, which contained chlorides and sulfates salts, could settle on the surface of concrete structures and have an adverse effect in combination with frosts. In this way, the preference in construction in such conditions is given to additive-free cement composition.

Within the framework of this article, a group of researchers faced the task of finding out how much mineral additives could be used in cement in such conditions, as well as answering a number of questions. What kind of mineral additives could preferably use to increase the strength and frost resistance of the composite? In which way do mineral micro-fillers affect the properties of

types of cement?

1.1. The study's Background

The internal defects can be localized in cement mineral additives, thus reducing the stress concentration in the composite. The pore system and the hydration process are transformed, etc. [3, 4]. Most finely ground dispersed fillers are used to improve the strength and deformity properties of composite materials. Thus, due to the rational use of mineral additives to cement, in addition to reducing the clinker factor, it is possible to effectively increase resistance in aggressive environments of hardened cement [5, 6].

Generally, the contact zones of aggregate and cement gel, osmotic pressure, and ice crystallization pressure are mainly analyzed when considering the frost resistance of cement concretes, [7-12]. However, authors consider the frost resistance of the binder component itself (cement) as one of the reasons affecting the frost resistance of concrete on a par with the above.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and Methods

The tests were carried out with Portland cement CEM I 52, 5N GOST 31108-2020 produced by «HeidelbergCement RUS». Calcined clays were used as active mineral additives. Thermal activation was carried out in two ways: in the presence of alkalis (1M NaOH solution), further AC, and without firing intensifiers (further TAC).

The calcination temperature of the clays was changed from 650°C to 800°C, while the heat treatment time was 60 minutes for each of the selected temperatures.

The clay deposit has a significant impact on the content of the main clay oxides (silicon and aluminum oxides) in the composition of aluminosilicate. Therefore, clays produced by «Gornozavodskcement» (Russia) in the Western Urals (Clay 1) and «HeidelbergCement RUS» (Clay 2), were selected for the study and shown in Table 1.

The change in the chemical and mineralogical composition of clays before and after heat treatment was determined using X-ray phase analysis and infrared spectroscopy (IS). It was found that natural Clay 1 contains kaolinite as the main clay mineral, in addition, chlorite and muscovite phases are present. Natural Clay 2 – illite, kaolinite, and hydrosilicates. Clays belong to layered silicates with a 2:1 structure.

To increase the mobility of the mixture, regulate water demand, and impart special properties to cement stone, chemical additives produced by the BASF Chemical concern were added together with the mixing water: MasterGlenium ACE plasticizer in an amount of 0.7% (further SP) and Glenium Air 125 air-entraining additive in an amount of 0.5% (further AE).

Determination of the normal consistency, setting time dough, and strength was carried out according to standard methods [13]. Changes in the phase composition depending on the hardening conditions were recorded using the methods of XRD, differential thermal analysis (DTA), and pycnometric method, as well as by studying the specific surface of cement stone hydrates by electron scanning microscopy performed at the Center for Collective Use of the D.I. Mendeleev RCTU.

Pozzolan activity was measured by the method of absorption of lime from lime solution by an active mineral additive [14].

3. RESULTS AND DISCUSSION

3.1. Influence of Calcination Modes on Clay Activity

It is known that natural clays cannot be used as a mineral additive, since, on the one hand, they are inert aggregates, and on the other hand, they lead to a sharp decrease in the construction and

technical properties of cement. However, it has been established that under certain conditions of calcination, it is possible to achieve their high pozzolanic activity [15-16].

Natural clays have a diverse chemical and mineralogical composition depending on their deposit. Therefore, clays from different deposits, characterized by different chemical and mineralogical compositions, were selected as initial samples. Therefore, to determine the optimal temperature of calcination, natural clays were investigated using DTA. As a result of the analysis, the optimal modes were established: for Clay 1 – 700°C for 1 hour, and Clay 2 – 750°C for 1 hour.

To confirm the data obtained, the pozzolanic activities for all compositions were determined at the next stage (Table 2). It was found that the pozzolanic activity of clays directly depends on the temperature and time of calcination, which confirms the results of DTA. So, for Clay 1 (T= 700 °C, τ= 60 min), the activity is 450 mg/g of the additive, and for Clay 2 (T= 750°C, τ= 60 min) – 415 mg/g of the additive.

It is known that the calcination process can be intensified by introducing various additives [17-21]. So, alkaline activation of clays with a solution of NaOH (1 M) was carried out before calcination. Natural clays were thoroughly mixed with the solution, after which they were dried at T= 100- 120°C to remove excess moisture, after which they were fired. Using X-ray phase analysis and infrared spectroscopy, it was found that to achieve the maximum activity, it is necessary to reduce the temperature of calcination by 100-150. This fact positively affects the process of obtaining Portland cement with thermally activated clays [22-23].

A decrease in the calcination temperature of clays and an increase in their activity is associated with the process of changing the structure of clays. The introduction of inorganic compounds into the interlayer space is carried out. As a result of pillarization, hydrolysis of metal ions occurs with the formation of polynuclear hydroxo complexes. It should be noted, that the distance between the aluminosilicate layers increases in an aqueous solution of alkali. The modified material was dried and calcined at set temperatures (from 650°C to 800°C). The heat treatment was accompanied by the dehydration and dehydroxylation of the embedded polyhydroxocations. As a result – the metal oxide



clusters in the interlayer space of clays are formed. Which are firmly connected with the aluminosilicate layers of clay by oxygen bridges. These bridges prevent the convergence of layers, forming a stable two-dimensional microporous structure in which the interlayer distance is significantly increased compared to the natural material. Thus, the activity of Clay 1 in the presence of alkali (T= 550°C, τ= 60 min) is 590 mg/g of the additive, and for Clay 2 (T= 600°C, τ= 60 min) – 550 mg/g of the additive. The activity increased by ~1.3 times compared to the activity of heat-treated clays without intensifiers. Figure 1 clearly shows that the alkaline solution significantly increases the intensity of Si-O and Al-O vibrations, which also confirms the activity data.

3.2. Effect of Thermally Activated Clays on Hardened Cement's Strength

It is known that cement has a complex mineralogical composition, which provides the

necessary indicators of strength, water resistance, and corrosion resistance [24].

The main cement minerals are alite (C₃S), belite (C₂S), tricalcium aluminate (C₃A), aluminoferrite (C₄AF), gypsum (CaSO₄*2H₂O), free calcium (CaO), and magnesium (MgO) oxides. As a result of the interaction of these minerals with water, hydro silicates (HS), hydro aluminates (HA), hydro ferrites, and calcium hydro sulfoaluminates are formed. This process leads to cement hardening [4, 13]. Special attention should be paid to free calcium and magnesium oxides, as they can increase the volume of hydrate formations later, which can significantly disrupt the structure of hardened cement. To regulate the content of Ca(OH)₂ and Mg(OH)₂ in hardened cement, active mineral additives– metakaolin can be used [13, 24]. In addition to metakaolin, other, similar active mineral additives can be used. For example, calcined clays can bind Ca(OH)₂ and Mg(OH)₂ to form HS and HA as well as metakaolin.

Table 1. Chemical composition of clays

Clays	Content, %								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	R ₂ O	P ₂ O ₅	TiO ₂
Clay 1	43.64	26.66	7.18	12.75	1.81	4.65	2.57	-	0.74
Clay 2	65.76	24.11	5.44	2.29	1.68	0.56	0.16	-	-

Table 2. Pozzolan activity of clays heat-treated under different conditions

Clays	T, °C (τ = 60 min)	The quantity of CaO absorbed by 1 g of supplements, mg	τ, min (T= const, °C)	The quantity of CaO absorbed by 1 g of supplements, mg
Clay 1	650	320	700	30
	700	450		60
	750	385		90
	800	360		120
Clay 2	650	320	750	30
	700	350		60
	750	415		90
	800	370		120

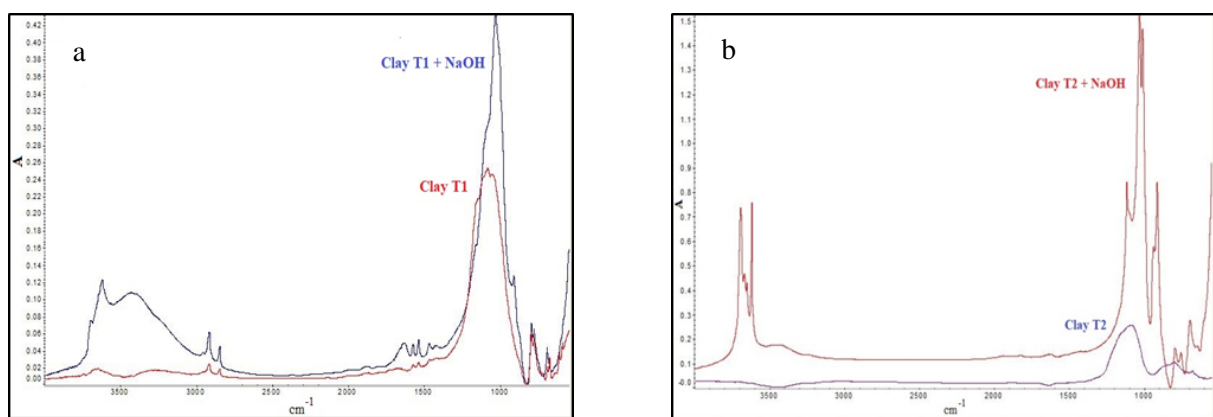


Fig. 1. IR-spectrogram of thermally activated clays: a – Clay 1, b – Clay 2

The amorphized aluminosilicate of the composition – $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ formed as a result of calcination. This phase actively interacts with calcium hydroxide $\text{Ca}(\text{OH})_2$, which is a product of cement hydration. As a result, HS, HA of various compositions, as well as $\text{Al}(\text{OH})_3$ are formed (Fig. 2). It was confirmed by thermodynamic calculations.

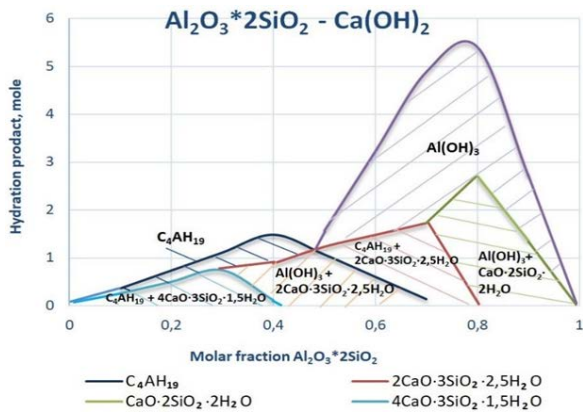


Fig. 2. The interaction of calcium hydroxide with thermally activated clay in two-component system $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{Ca}(\text{OH})_2$

Following these calculations, it is possible to observe high basic HA ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 19\text{H}_2\text{O}$) and highly basic HA ($4\text{CaO} \cdot 3\text{SiO}_2 \cdot 1,5\text{H}_2\text{O}$) in $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{Ca}(\text{OH})_2$ system at first (in the zone of the minimum molar fraction of metakaolin) in the presence of excess water. Then the basicity of the HS decreases ($\text{CaO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 2,5\text{H}_2\text{O}$). Moreover, the $\text{Al}(\text{OH})_3$ forms instead of HA. So, it positively affects the strength of hardened cement and leads to the further formation of HA of various compositions. To confirm the theoretical data obtained, the strength of hardened cement with calcined and

alkali-activated clays was studied. In the first stage, Portland cement clinker was mixed with calcined clays (the content of heat-treated clay from 0% to 20% by weight of cement). The optimal content of the active mineral additive in the cement composition was 15% (Fig. 3). With a further increase in the content of the additive, the strength decreases, but at the same time remains higher than the index of the additive-free cement (bending strength – 30.1 MPa, compressive strength – 54.2 MPa). It should be concluded, that Portland cement clinker replacing (at least by 15%) does not decrease, but continues to grow the strength of hardened cement for 28 days intensively. For cement with heat-treated Clay 1, bending strength is 39.4 MPa, and compression strength is 65.1 MPa, for Clay 2 – 36.8 MPa and 67.2 MPa, respectively (Fig. 3).

Due to the higher activity of alkali-activated clays, they can be used to replace not 15% of Portland cement clinker, but 25% - without loss of strength (Fig. 4).

The strength of compositions with alkali-activated Clay 1 is 46.2 MPa when bending and 76.2 MPa when compressing for 28 days of hardening, with Clay 2 – 44.2 MPa when bending and 79.3 MPa when compressing.

Thus, all heat-treated clays increase the strength of cement. Let's compare the best compositions with ordinary Portland cement (OPC) (Fig. 5). The composition with alkali-activated Clay 2 (AC2) is characterized by maximum strength-bending strength of 44.2 MPa, the compression strength of 79.3 MPa. Similar results for cement with alkali-activated Clay 1 (AC1). At the same time, heat-treated Clay 1 (HC1) and Clay 2 (HC2) are also suitable as active mineral additives in cement, but their effectiveness is lower.

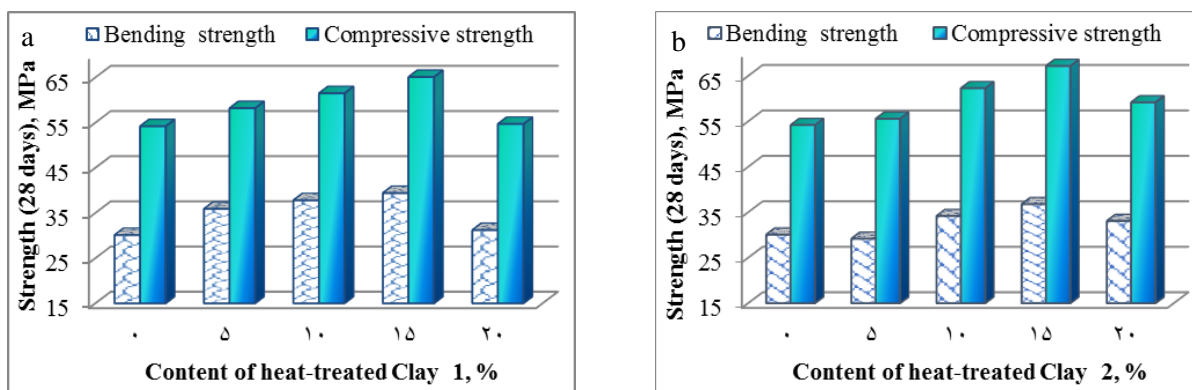


Fig. 3. The strengths of hardened cement with calcined clays : a – Clay 1, b – Clay 2



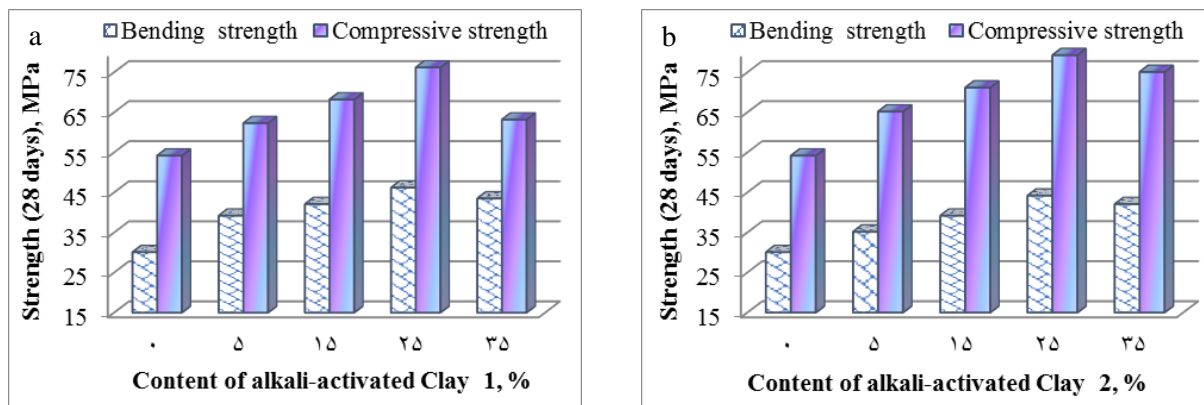


Fig. 4. The strengths of hardened cement with alkali-activated clays: a – AC1, b – AC2

In the case of alkali-activated clays, the Portland cement clinker can be replaced by at least 25%. Calcined clays, like most active mineral additives, lead to an increase in the water demand for cement dough and mortar. Therefore, it is reasonable to use plasticizing and other modifying additives together.

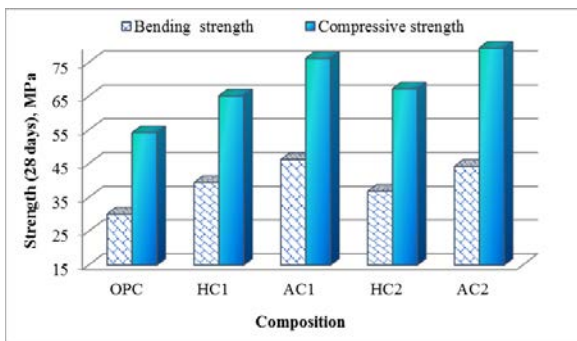
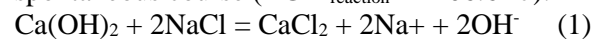


Fig. 5. The strengths of hardened cement with calcined (only) and alkali-activated calcined clays

3.3. The Effect of Alkali-Activated Clay on the Frost Resistance of Portland Cement

It is known that when testing cement concretes for frost resistance by the accelerated method, the 5% NaCl aqueous solution is used to saturate and thaw samples [25]. In real conditions, the sources of chlorides are deicing salts and seawater. It is considered, that in the medium of sodium chloride, the destruction of samples occurs several times faster, as a result of which there isn't necessary to carry out 100, 200, 300, or more cycles of alternating freezing and thawing. Solutions of easily soluble salts (in particular chloride salts), when they get into the pore solution of cement stone, can shift the equilibrium and increase the solubility of the initial hydrate phases. The most sensitive is the phase of

portlandite $\text{Ca}(\text{OH})_2$. The compound has a low solubility in water under normal conditions (only 0.189 g/100 g of H_2O at 20 °C). However, according to the thermodynamic calculations carried out according to reference data [26-28], it can be verified that the isobaric-isothermal potential of the portlandite and sodium chloride interaction (under equilibrium conditions at 20°C) is much less than zero, which indicates its spontaneous course ($\Delta G_{\text{reaction}}^{298} = -206.6 \text{ kJ}$):



The interaction of portlandite with chlorides in an aqueous solution leads to an exchange reaction of Calcium chloride formation. CaCl_2 has an increased solubility (74 g/100 g H_2O at 20°C). As a result, the Ca^{2+} and (again) Cl^- ions transit into a pore solution. This adversely affects the integrity of the structure and may lead to further transformation and destruction of the hydrate system. Fig. 6 presents the dynamics of the strength and real density behavior according to frost resistance determining the hardened cement OPC and cement with alkali-activated clay (AC1) both in the presence of additives SP and AE.

The pycnometric method of real density determining is real sense to all recrystallizations in the structure of a material. A rapid drop in the strength characteristics of additive-free cement occurs after 10 cycles of freezing and thawing, however, further, the structure appears to be transformed and compacted due to the recrystallization of phases, which is why it is possible to observe the dynamics of strength increasing until the end of the experiment. This drop correlates with density date changes. The structure of hardened cement with alkali-activated clay looks more stable, the strength drop occurs evenly, but stepwise.

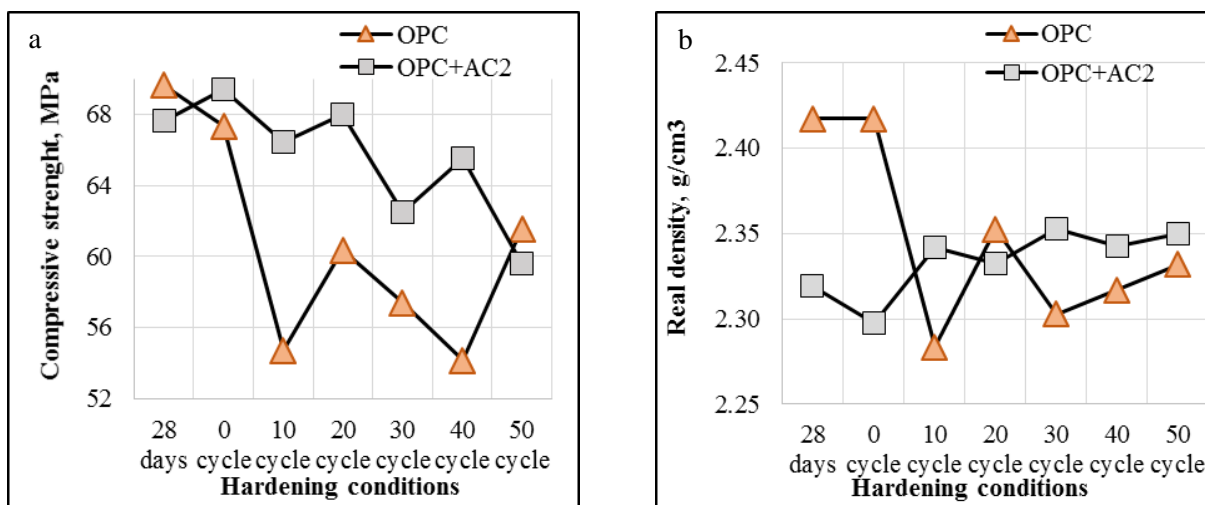


Fig. 6. Compressive strength (a) and real density (b) of hardening cement with alkali activated clay (AC2) and without clay (OPC)

The high specific surface area of clays, which entailed an increase in water demand even in the presence of chemical additives, decreased the density of hardened cement. However, in contrast with the additive-free composition, by 10 cycles the density rapidly increases from 2.2978 g/cm³ to 2.3474 g/cm³. Further, the structure is also compacted, but with less intensity. As a result of the above, it can be concluded that the structure of hardened cement with the addition of clay is more stable and, at least, is not inferior in physicommechanical parameters to the additive-free composition. In particular, this is possible due to the portlandite content reducing in the composition of AC1 since the OPC composition had the most rapid drop in strength at the beginning of the experiment to determine frost resistance (10 cycles). Just during the active course of the exchange reaction between the Ca(OH)₂ and transition the Ca²⁺ and Cl⁻ ions into a pore solution. For a detailed analysis of the cement stone structure during this most sensitive period for samples, the method of scanning electron microscopy was used. The data obtained are presented in Fig. 7. The photos obtained according to electron microscopic present that in the case of the OPC composition, not only portlandite but also the adjacent HS were destroyed after 10 cycles of freezing and thawing. Figure 7-b clearly shows the “pitted” surface hydration products of alite. This fact affects the types of cement strength characteristics. The structure of the OPC+AC1 composition is represented by a hydrosilicate gel of variable

composition, which served as a kind of protective layer for the hydrate phases of hardened cement (Fig. 7-c). It can be seen that this layer is very dense (Fig. 7-d) and, even under the influence of an aggressive solution and the pressure of ice crystallization, preserved the structure's integrity. The hydro silicates interact with a solution of sodium chloride (Fig. 7-d2). There are corroded surfaces resembling the peeling of the protective layer. The distraction doesn't occur here. There are many pores of 10-15 microns in size, which affects the ability to withstand the emerging internal stresses during freezing of physically bound water and/or recrystallizations. Thus, it can be concluded that the use of alkali-activated clays as an additive to cement does not worsen in any way, but in some way even improves the frost resistance of hardened cement.

4. CONCLUSIONS

It was found that clays are characterized by their unique chemical and mineralogical composition. This must be taken into account when selecting the temperature of the calcination regime. The activity of heat-treated clays directly depends on the selected temperature and calcination time. The NaOH solution reduces the temperature of the calcination of clays by 100-150°C, while there is an increase in pozzolan activity (from 415 to 590 mg/g of the additive). Moreover, alkali-activated clays can significantly increase the strength of cement (by 1.5 times) and reduce the clinker component by at least 25%. This is due to the intercalation reaction of clay as a result of

calcination with alkali. Additionally, the aluminosilicates react with $\text{Ca}(\text{OH})_2$ with HS and HA of different composition formations. By physical and mechanical characteristics controlling methods, as well as by the SEM method, it was found that types of cement with

alkali-activated clays can successfully resist freezing and thawing, including in the presence of an aqueous solution of chloride salts. The layer of hydrosilicate gel formation in the hardened cement has a great tendency to interact with ions of the pore fluid and prevent the destruction process.

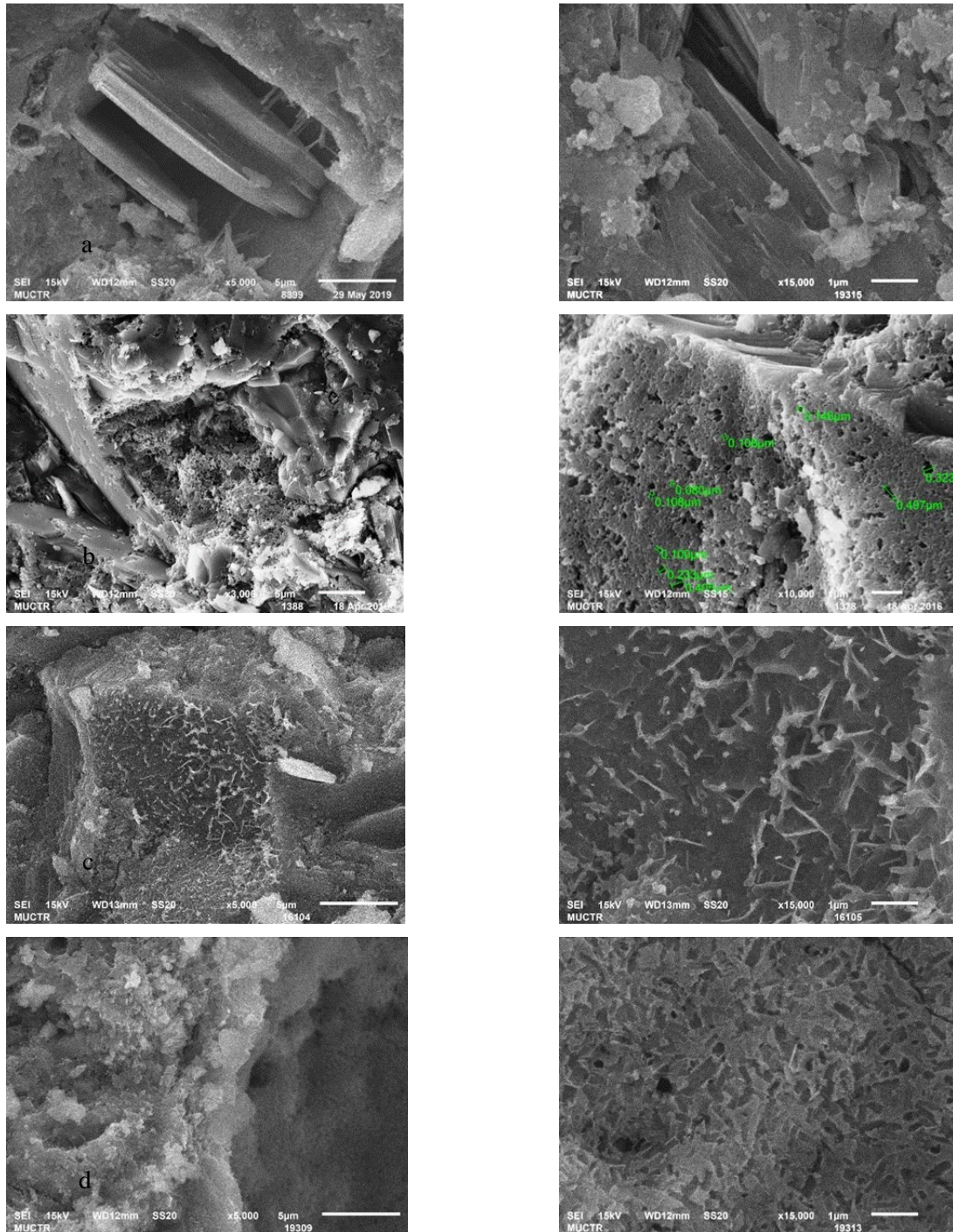


Fig. 7. Structure of the hardened cements before (a, c) and after (b, d) frost resistance tests (10 freezing and thawing cycles). Compositions: a, b – OPC; c, d – OPC+AC1. Zoom: a1 - $\times 5000$; a2 - $\times 15000$; b1 - $\times 3000$; b2 - $\times 10000$; c1 - $\times 5000$; c2 - $\times 15000$; d1 - $\times 5000$; d2 - $\times 15000$

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