

INFLUENCE OF POZZOLANA ADDITIVE ON PORTLAND CEMENT IN CHLORIDE AND SULFATE ENVIRONMENT AT LOW TEMPERATURE

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This study investigated the influence of natural pozzolana (opoka) additive on the hydration of Portland cement and the effects of chloride and sulfate ions on the formed hydrates under 4°C temperature. In the samples 5, 15 and 25 % (by weight) of the Portland cement was replaced with pozzolana additive – opoka. The specimens were cured in water at 20°C for 28 days. Then all samples were soaked in saturated NaCl solution at 4°C for 3 months. Later they were immersed into 5 % Na₂SO₄ solution and held there for 3 month at 4°C. All specimens were examined by thermal, X-ray diffraction and FT-IR analysis after every immersion in different solutions. It was estimated that under normal conditions opoka promotes the formation of calcium silicate hydrates and initiate the formation of monocarboaluminate. Monocarboaluminate affected by a saturated NaCl solution, becomes unstable and takes part in reactions producing Friedel's salt at 4°C temperature. It was obtained, that opoka takes place in the pozzolanic reaction even at low temperature in a saturated NaCl solution. However, ettringite remained stable under the examined conditions and Thaumassite is mostly depends on decomposition of ettringite in 5 % Na₂SO₄ at 4°C temperature.

INTRODUCTION

Portland cement concrete structures with access to the sea (quays, jetties, etc.) are influenced by chloride. Studies of detrimental effects of chloride are actual in countries with cold climates because they are using mixtures of sand and either salt or a saturated salt solution as road deicing materials. Such an environment exposes the concrete to high concentrations of chloride which can have a significant impact on the durability of concrete structures (gutters, sidewalks, road shoulders, highway bridges, etc.). NaCl, NaCl-based deicers are the most deleterious to concrete. Sodium chloride (NaCl) remains the principal road deicer in use despite its well-known corrosive effects on metals.

The exposition level of chloride depends to concentration of the solution and type of ions in it [1]. The increasing of these ions accelerates the speed of sulfate attack and the amount of initiated ettringite [2]. S. O. Ekolu and co-writers [1] presents two likely mechanisms – in presents of low chloride ions concentration, SO₄²⁻ are adsorbed by C–S–H and genesis ettringite and monosulfate, where Cl⁻ ions reacts with monosulfate and releases SO₄²⁻. These sulfate ions in present of SO₄²⁻ from C–S–H forms secondary ettringite [3]. In high concentration of chloride ions, SO₄²⁻ are adsorbed

by C–S–H and forms ettringite and monosulfate, but Cl⁻ ions not only reacts with monosulfate but also with ettringite and develops Friedel's salt and gypsum. In this scenario the models do not expand [4]. It is believed that in presents of CO₃²⁻ ions and thaumasite formation Friedel's salt is unstable [5, 6].

The corrosion of armature in Portland cement concrete structures are caused by chloride ions in solution which reaches it by pores. Cl⁻ ions can be initiated in Portland cement hydration products or exist like free ions, which fill the pores. Because of that the resistance of chloride corrosion depends to the ability to bind chloride ions [7].

There are several factors that influence chloride binding. It is very important how the chloride ions included in Portland cement concrete paste. There are two categories: inner chloride ions that are mixed in as solutions with grinded Portland cement; exterior chloride ions that interact with already hardened concrete. Exterior chloride ions are common field of studies, because the inner Cl⁻ ions quantity in Portland cement is limited.

When Portland cement products are used in humid full of sulfate ions environment in low temperature the main factor of their destruction is the formation of thaumasite. Thaumassite is rear, natural existent mineral, which can also by synthesized in laboratory [8]. Thaumassite

is a complex hydrate with formula $\text{Ca}_3\text{Si}(\text{CO}_3)(\text{SO}_4)(\text{OH})_6 \cdot 12(\text{H}_2\text{O})$ [9]. In this few years the scientists came to the idea that thaumasite forms in Portland cement concrete and destroys C–S–H bonds in Portland cement also it forms temperature in lower than 15°C [9]. The destruction of Portland cement concrete by the formation of thaumasite is called low temperature sulfate corrosion. However, the durability of Portland cement concrete is not defined by the existence of thaumasite, but by the conditions of its formation [10]. Scientists consider that natural pozzolana additive diminish the amount of calcium hydroxide in cement paste. This factor helps to magnify endurance for sulfate and other harmful solutions. Portland cement with pozzolana pH values are lower than typical Portland cement, it consequence that cement with pozzolana are more resistance to sulfate attack [11, 12]. However, amorphous SiO_2 from pozzolana solubility is very delicate when pH values rises from 12 to 14. The higher pH values, the rapid reaction of amorphous SiO_2 . Also pozzolana reactions are more sensitive to temperature than regular Portland cement. Natural pozzolana additives react slower under 15°C temperature, however over 27°C temperature reactions accelerates [13]. This temperature sensitivity usually limits quantity of additives in Portland cement concrete structures which are exposed in cool environment, moreover it increases the ability to use these pozzolana additives in worm surroundings. Lithuania contains abundant limestone and natural pozzolana, which consists of amorphous SiO_2 and finely dispersed CaCO_3 . The aim of this work was to investigate the influence of natural pozzolana opoka on the hydration process of Portland cement and the effect of Cl^- ions and sulfate attack on the hydrates formed.

EXPERIMENTAL

Samples (20 × 20 × 20 mm) were formed of pure ordinary Portland cement CEM I 42.5 and Portland cement with 5, 15, 25 % (by weight) replaced by pozzolana – opoka. The ratio of water to cement was 0.33. At first day after formation, the samples were kept in molds at 20 ± 1°C and 100 % humidity. After 24 hours of specimen formation, they were transferred to water and stored there for 27 days at 20 ± 1°C. After that, samples were transferred to a saturated NaCl solution and stored there for 3 months at 4 ± 1°C. After that the samples were immersed to 5 % Na_2SO_4 solution for another 3 months at 4 ± 1°C temperature. Hydration of samples was stopped using acetone.

The composition of raw materials is given in Tables 1 and 2 (the hydraulic activity of pozzolana is 220 mg of CaO/g).

The X-ray diffraction (XRD) data were collected with a DRON-6 powder X-ray diffractometer with Bragg-Brentans geometry using Ni-filtered CuK_α radia-

tion, operating at an anode voltage U_a of 30 kV and an emission current of 20 mA. The step-scan covered the angular range 5 - 60° (2θ) in steps of 2θ = 0.02°. Measurement accuracy 2θ = 0.01°.

Table 1. Oxide composition of raw materials.

Oxide composition (mass %)						
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
54.1	2.7	1.3	23.2	0.62	0.24	0.87
Loss on ignition 16.97 %						

Table 2. Mineral composition of pozzolana (opoka).

Component	wt. %
Amorphous $\text{SiO}_2 \cdot n\text{H}_2\text{O}$	22.2
Ancerite $\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$	1.3
Calcite CaCO_3	36.1
Cristobalite SiO_2	19.2
Muscovite $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F}, \text{OH})_2$	4.1
Plagioclase $\text{NaAlSi}_3\text{O}_8$	1.1
Quartz SiO_2	12.0
Tridymite SiO_2	4.0

Simultaneous thermal analysis (differential scanning calorimetry [DSC] and thermogravimetry [TG]) was completed on a Netzsch STA 409 PC Luxx simultaneous thermal analysis instrument with ceramic sample handlers and crucibles of Pt-Rh. At a heating rate of 15°C/min, the temperature ranged from 30°C to 1000°C under a nitrogen atmosphere. Measurement accuracy ± 3°C.

Infrared (IR) spectra have been measured using a PerkinElmer Fourier transform-IR (FT-IR) system Spectrum X spectrometer. Samples were prepared in vacuum compressor by mixing 1 mg of the sample in 200 mg of KBr and compressing tablets. The spectral analysis was performed in the range 4000 - 400 cm^{-1} with a spectral resolution of 1 cm^{-1} . Measurement accuracy ± 0.01 cm^{-1} .

RESULTS AND DISCUSSION

The effect of opoka on the hydration of Portland cement under normal conditions

XRD analysis of all samples hydrated in water for 28 days (Figure 1) indicated high-intensity peaks characteristic to portlandite (d -spacing: 0.492; 0.263 nm), calcite (d -spacing: 0.303; 0.228; 0.191; 0.187 nm), unhydrated C_3S (d -spacing: 0.304; 0.297; 0.278; 0.219; 0.193 nm), unhydrated C_2S (d -spacing: 0.278; 0.274; 0.261; 0.219 nm), ettringite (d -spacing: 0.971; 0.561; 0.387; 0.256 nm) and monocarboaluminate (AFm – monosulfate) (d -spacing: 0.758; 0.379 nm). In samples

with 15 and 25 % opoka additive was also indicated high-intensity peaks characteristic to quartz (*d*-spacing: 0.335; 0.426; 0.182 nm), which is one of the main forming material of opoka. Principal difference of X-ray diffraction analysis data for all samples is the intensity of peaks for characteristic compounds. By increasing the amount of pozzolana used in samples, the X-rays showed that the intensity of peaks for calcite and quartz is linear increases, but for portlandite and tricalcium silicate decreases.

DSC-TG analysis shows three main endothermic peaks in the ranges of 90 - 150°C, 430 - 450°C and 670 - 730 °C. The first temperature range can be attributed to dehydration of most Portland cement hydrates (such as calcium silicate hydrates, calcium aluminum hydrates, and ettringite) [14], however maxima peaks at the different temperatures can be attributed even to the different AFt or AFm phases: the first peak at ~ 100°C

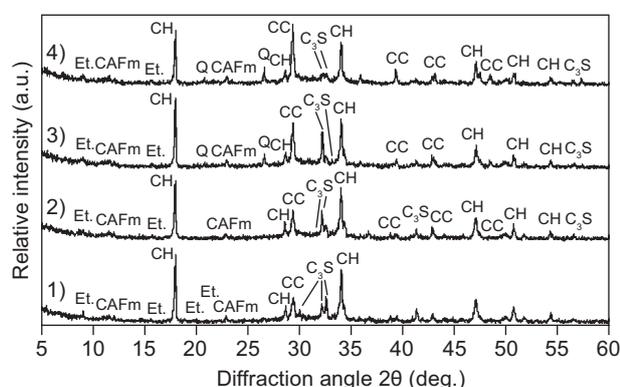


Figure 1. X-ray patterns of Portland cement samples cured for 28 days under normal conditions, where part of it were changed by opoka: 1) 0 wt. %; 2) 5 wt. %; 3) 15 wt. %; 4) 25 wt. %; indexes: CC – CaCO₃, CAFm – Ca₄Al₂O₆CO₃·11H₂O, CH – Ca(OH)₂; Q – SiO₂; C₃S – 3CaO·SiO₂; C₂S – 2CaO·SiO₂; E – (CaO)₃(Al₂O₃)(CaSO₄)₃·32H₂O.

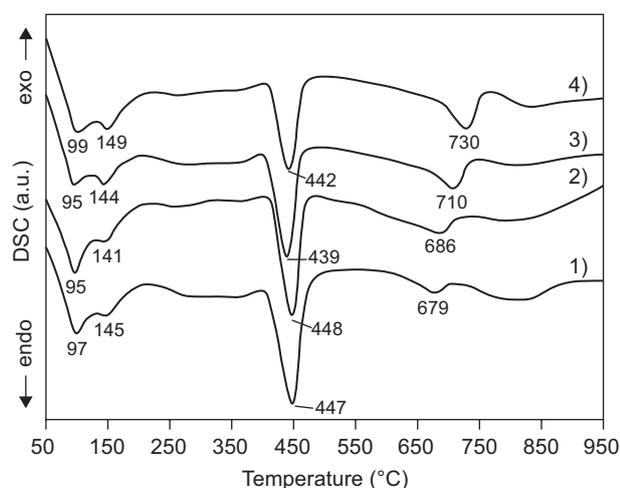


Figure 2. DSC patterns of Portland cement samples cured for 28 days under normal conditions, where part of it were changed by opoka: 1) 0 wt. %; 2) 5 wt. %; 3) 15 wt. %; 4) 25 wt. %.

appears as the result of Ettringite or CSH dehydration [14, 15], while at the 145°C – can be attributed to C-AFm dehydration and 670 - 730°C to calcite and monocarboaluminate [16]. At 430 - 450°C temperature range dehydrates portlandite. The mass loss established using TG analysis is listed in Table 3.

Table 3. TG analysis results of samples cured under normal conditions.

Amount of pozzolana additive – opoka (%)	Mass loss (%) temperature range (°C)		
	90-150	430-450	670-730
0	7.61	4.18	1.48
5	7.72	3.78	2.67
15	9.28	3.73	3.24
25	9.85	3.68	5.34

Differential scanning calorimetric DSC and thermogravimetric TG analysis shows, that in specimens with higher pozzolana additive content, endothermic peak characteristic to portlandite (temperature range ~ 430 - 450°C) intensity and mass loss are fractionally decreased from 4.18 till 3.68 %. While mass loss typical to decomposition of calcite and monocarboaluminate is increasing consistently when increasing the amount of opoka additive, because calcium carbonate is one part of composition in opoka, the same tendency is seen in changes of mass loss at 90 - 150°C and the peak intensity at around 145°C what is the evidence of formation of monocarboaluminate. It shows that natural pozzolana additive promotes the formation of portlandite and C-AFm.

To have in mind that the Portland cement is with pozzolana additive, the quantity of portlandite and calcium silicate hydrates should be decreasing, because less Portland cement is reacting (XRD results shows less

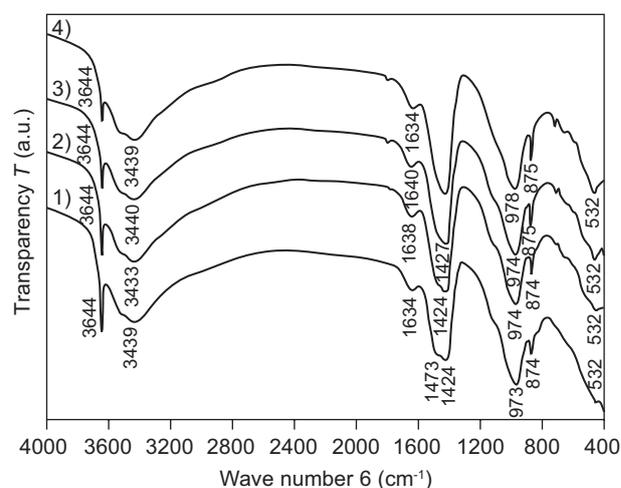


Figure 3. FT-IR patterns of Portland cement samples cured for 28 days under normal conditions, where part of it were changed by opoka: 1) 0 wt. %; 2) 5 wt. %; 3) 15 wt. %; 4) 25 wt. %.

After samples were soaked in the saturated NaCl solution and kept there for 3 months, thermal effects characteristic of Friedel's salt (thermal effect around 312°C) were identified in the DSC data (Figure 5) in all samples (the Friedel's salt if present yields an endothermal effect till 350°C at which dehydroxylation occurs [20]). At this temperature DSC intensity and mass loss of Portland cement with higher content of opoka slightly increase (Table 4). DSC-TG analysis confirmed that opoka promotes the formation of Friedel's salt at low temperature.

Table 4. TG analysis results of samples cured for 28 days in water and 3 months in a saturated NaCl solution.

Amount of pozzolana additive – opoka (%)	Mass loss (%) temperature range (°C)	
	~ 312	430-450
0	3.8	4.05
5	4.0	3.70
15	4.1	3.27
25	4.2	2.73

The mass loss of the pure Portland cement samples during the endothermic effect characteristic of portlandite (at approximately 430°C) after curing in NaCl solution for 3 months (4.05 wt. %) (Table 4) remained the same as after 1 month (28 days) of hydration in water (4.18 wt. %), whereas the mass loss of the samples with 25 % of opoka increased from 3.68 wt. % after 1 month in water to 2.73 wt. % after 3 months in the saturated NaCl solution. This trend can be seen in all samples with opoka. Thus, it can be concluded that pozzolanic reaction takes place in all samples with opoka even in the saturated NaCl solution at low temperature. However, DSC endothermic peak due to dehydration of Ettringite

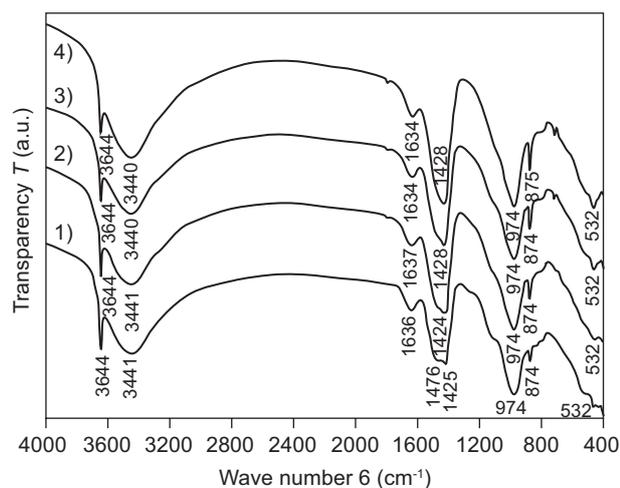


Figure 6. FT-IR patterns of Portland cement samples cured for 28 days under normal conditions and 3 months in a saturated NaCl solution at low temperature, where part of it were changed by opoka: 1) 0 wt. %; 2) 5 wt. %; 3) 15 wt. %; 4) 25 wt. %.

was observed in all samples, what confirms the stability of Ettringite in examined condition.

The IR spectrum curves (Figure 6) of all samples shows the intensity difference of absorption band characteristic of portlandite (3644 cm⁻¹): slightly weaker in the samples with higher content of opoka.

Absorption bands at about 3640 cm⁻¹, 3480 cm⁻¹ (ν_{OH}), 1621 cm⁻¹ (δ_{H_2O}), 785 cm⁻¹, 620 cm⁻¹, and 532 cm⁻¹ (vibration of M–O or M–O–H bands) are characteristic of Friedel's salt [21]. All absorption bands except the one at 532 cm⁻¹ were overlapped by other cement minerals, so only this peak shows the formation of Friedel's salt after 3 months of curing in the saturated NaCl solution. Moreover, with increase of opoka content intensity of this peak increases too. It confirms the higher content of Friedel's salt in the samples with opoka and that opoka promotes the formation of this phase.

The effect of opoka on the hydration of Portland cement in a saturated NaCl solution after 3 months and 5 % Na₂SO₄ solution after 3 months in low temperature

XRD analysis of all samples hydrated 3 months at 4 °C temperature in 5 % Na₂SO₄ solution showed the formation of Thaumascite (*d*-spacing: 0.959; 0.551; 0.341 nm), while the intensity of diffraction patterns characteristic to Friedel's salt haven't changed (Figure 7). It means that Friedel's salt remains stable under the examined conditions. It should be noted, that Ettringite was identified in all samples too. Diffraction peaks intensity due to Portlandite remains the same trend as it was after samples treatment in NaCl solution – with increase of opoka content the intensity decreases.

DSC analysis of all samples shows decrease of endothermic peak characteristic to Ettringite (~95°C) to compare with samples treated in NaCl solution (Figure 8).

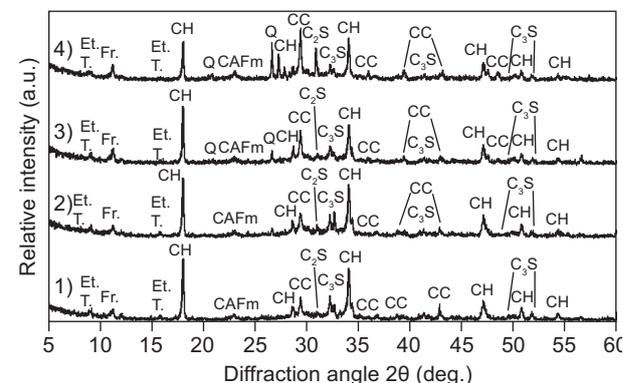


Figure 7. XRD patterns of Portland cement samples cured for 28 days under normal conditions, 3 months in a saturated NaCl and 3 months in 5 % Na₂SO₄ solution at 4°C temperature, where part of it were changed by opoka: 1) 0 wt. %; 2) 5 wt. %; 3) 15 wt. %; 4) 25 wt. %; indexes: T – Ca₃Si(OH)₆(CO₃)(SO₄)·12H₂O.

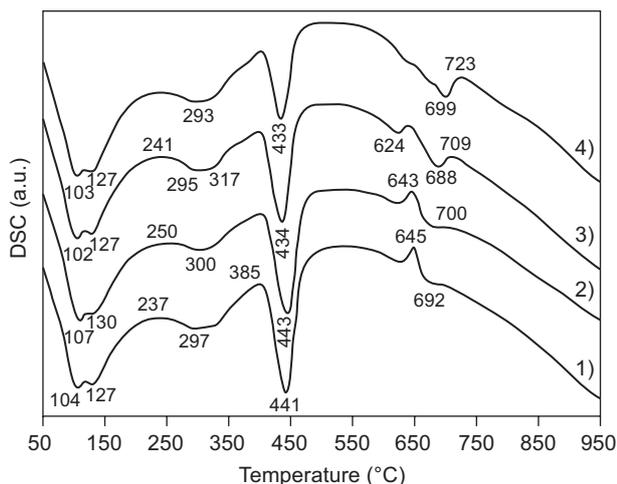


Figure 8. DSC patterns of Portland cement samples cured for 28 days under normal conditions, 3 months in a saturated NaCl and 3 months in 5 % Na₂SO₄ solution at 4 °C temperature, where part of it were changed by opoka: 1) 0 wt. %; 2) 5 wt. %; 3) 15 wt. %; 4) 25 wt. %.

Table 5. TG analysis results of samples cured for 28 days in water, 3 months in a saturated NaCl and 3 months in 5 % Na₂SO₄ solution at 4 °C temperature.

Amount of pozzolana additive – opoka (%)	Mass loss (%) temperature range (°C)	
	430-450	670-730
0	3.85	1.98
5	3.53	2.23
15	3.86	4.86
25	2.71	5.89

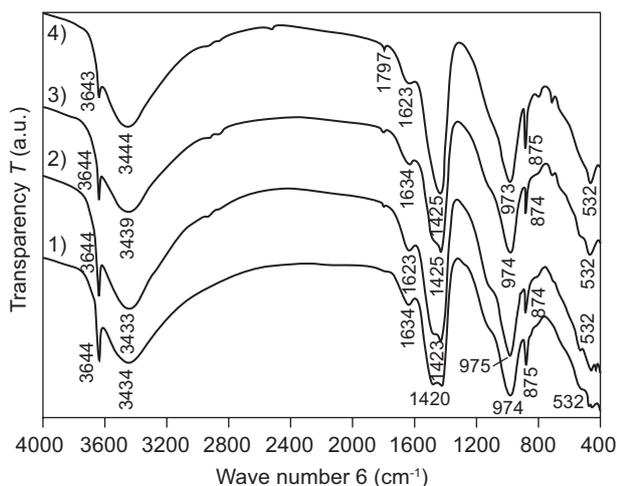


Figure 9. FT-IR patterns of Portland cement samples cured for 28 days under normal conditions, 3 months in a saturated NaCl and 3 months in 5 % Na₂SO₄ solution at 4 °C temperature, where part of it were changed by opoka: 1) 0 wt. %; 2) 5 wt. %; 3) 15 wt. %; 4) 25 wt. %.

However thermal effect due to Friedel’s salt dehydration at about 310°C temperature remain the same as an evidence of Friedel’s salt stability under sulphate environment at low temperature. It should be noted, that DSC pattern intensity due to Ettringite slightly decreases with increase of opoka, while change of portlandite is negligible - it means less stability of Ettringite under low temperature. From obtained data it can be concluded that formation of Thaumassite is mostly depends on decomposition of Ettringite to compare with all identified aluminate phases.

FT-IR analysis confirmed the formation of Thaumassite in all samples, because absorption bands at 750 and 501 cm⁻¹ were identified [8] (absorption maxima at 1100 and 673 cm⁻¹ are overlapped by absorption characteristic to other cement minerals). The absorption band at 1118 cm⁻¹ confirmed the existence of Ettringite.

CONCLUSIONS

1. It was estimated that under normal conditions opoka promotes the formation of calcium silicate hydrates and initiate the formation of monocarboaluminate.
2. Monocarboaluminate affected by a saturated NaCl solution, becomes unstable and takes part in reactions producing Friedel’s salt at 4°C temperature. Opoka pro-motes the formation of monocarboaluminate, and that is because it promotes and formation of Friedel’s salt in examined conditions.
3. It was obtained, that opoka takes place in the pozzolanic reaction even at law temperature in a saturated NaCl solution. However, ettringite remained stable under the examined conditions.
4. Experiment result showed, that thaumasite is mostly depends on decomposition of ettringite in 5 % Na₂SO₄ at 4°C temperature, while Friedel’s salt remained stable.

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