

INFLUENCE OF POZZOLANA ON THE HYDRATION OF C₄AF RICH CEMENT IN CHLORIDE ENVIRONMENT

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This study investigated the influence of natural pozzolana - opoka additive on the hydration of C₄AF rich cement and the effects of chloride ions on the hydrates formed. In the samples, 25 % (by weight) of the sintered C₄AF rich cement and OPC was replaced with pozzolana. The mixtures were hardened for 28 days in water; soaked in a saturated NaCl solution for 3 months at 20°C. It was estimated that under normal conditions, pozzolana additive accelerates the hydration of calcium silicates and initiates the formation of CO₃²⁻-AFm in the Brownmillerite rich cement. However, the hydration of Brownmillerite cement with opoka additive is still slower to compare with hydration of Portland cement. Also, opoka decreases total porosity and threshold pore diameter of Brownmillerite cement paste after two days of hydration. After 28 days of hydration threshold pore diameter became smaller even to compare with threshold pore diameter of Portland cement. Opoka additive promotes the formation of Friedel's salt in Brownmillerite samples treated in saturated NaCl solution, because CO₃²⁻-AFm affected by saturated NaCl solution become unstable and takes part in reactions producing Friedel's salt.

INTRODUCTION

Although the calcium silicate and calcium aluminate phases are good candidates for metal retention in real cement, the role of the ferric-calcium aluminate phase (C₄AF) should not be neglected. The ferric-calcium aluminate content in Portland cement is 2 - 7 wt. %, and the Fe₂O₃ content is in the 1 - 3.5 wt. % range [1]. However, the AFm and AFt phases as a product of C₄AF hydration have received little attention. Many studies have shown that the minerals formed during the hydration of C₄AF are essentially similar to those formed from tricalcium aluminate (C₃A) under comparable conditions [2, 3]. Both types of phase contain Al³⁺ and Fe³⁺ and tend to undergo further changes to form hydrogarnet phases. There is pure knowledge about pozzolana influence on C₄AF hydration, especially in the cement stone. C₄AF mineral pastes appear to be much more expansive than C₃A pastes in the presence of CaCl₂. In presence of gypsum the rate of generation of expansive stress is lower for C₄AF systems than for C₃A systems. Increased reactivity of gypsum and formation of AFt phases during hydration of C₄AF in presence of chloride contributes to large expansive forces in the system. Monochloroaluminate also contributes to expansion [4].

In countries with cold climates, mixtures of sand and either salt or a saturated salt solution are used as road deicing materials. These materials can have a significant impact on the durability of concrete structures

(road shoulders, gutters, sidewalks, etc.). Traditional and relatively new materials are used as deicers: sodium chloride, magnesium chloride, calcium chloride, calcium magnesium acetate, potassium acetate, potassium formate, sodium acetate, and others. The detrimental effects of deicers on Portland cement concrete take three main forms:

- 1) physical deterioration, such as "salt scaling";
- 2) aggravation of aggregate-cement reactions by the deicers;
- 3) chemical reactions between deicers and cement paste.

The bound chloride would be released subjected to many factors harmful to the durability problem, such as acidification, carbonation, chemical erosion and stray current, as the bound usually are not firm [5].

Chloride ions influences cement stone durability, an effect that has been found to be related to the reaction between the aluminous compounds and Cl⁻ ions [6, 7]. It is estimated that the primary compound that is formed is Friedel's salt [8, 9]. Friedel's salt is a chloride-containing calcium aluminate hydrate found to exist as a stable hydration product in cement. It has the composition 3CaO·Al₂O₃·CaCl₂·10H₂O. There is interest in Friedel's salt because of its role as a diffusion barrier against chloride ions, which causes corrosion of steel that is embedded in concrete [10, 11]. Such an environment exposes the concrete to high concentrations of chloride.

When NaCl is used as a deicing material, the attendant formation of Friedel's salt plays an important role in the related cement chemistry.

In order to reduce the corrosion reactions of cement stone, pozzolana additives can be used [12-15]. Diverse and controversial opinions can be found in the literature on the addition of pozzolana containing limestone. Scientists consider the addition of pozzolana to neat cement pastes and mortars reduces the diffusion coefficient of chloride ions [16]. Lithuania contains abundant natural pozzolana called opoka, which consists of amorphous SiO₂ and finely dispersed CaCO₃.

The aim of this work was to investigate the influence of natural pozzolana (opoka) on the hydration process of C₄AF rich cement and the effect of Cl⁻ ions on the hydrates formed.

EXPERIMENTAL

Samples (20×20×20 mm) were formed of pure Brown-millerite cement (BC), Ordinary Portland cement (OPC) and Brownmillerite cement (BC) with 25 % (by weight) replaced by pozzolana - opoka. The ratio of water to cement was 0.3. During the first day, the samples were kept in molds at 20 ± 1°C and 100 % humidity. After 24 hours of formation, the samples were transferred to water and stored there for 27 days later soaked in a saturated NaCl solution for 3 months at 20°C. Hydration of samples was stopped using acetone.

C₄AF rich system (further "Brownmillerite cement" - BC) was obtained as a result of synthesis from pure oxide mixture: SiO₂ (burnt for 1 h at 1000 °C), CaO (burnt for 1 h at 1000°C), Al₂O₃, Fe₂O₃. Mixture was mixed in plastic container for 1 h (30 rev./min). Then each 45 g of mixture were moistened with 4.5 g of water (10 %) and formed a tablet by pressing (30 MPa) in the cylinder (diameter - 40 mm). Regime of heat treatment in furnace was: 3 h heated to 1000°C and kept for 1 h, then reached 1450°C in 2 h and kept for 1 h more, in 30 min. cooled to 1200°C and in 10 min. to ~40°C. Obtained clinker was ground in disc mill to 290 m²/kg by Blain. Oxide and mineral composition of BC are given in Table 1 and Table 2.

Table 1. Oxide composition of BC.

Component (wt. %)			
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO
22.2	4.51	6.7	66.59

Table 2. Mineral composition of BC.

Component (wt. %)			
C ₃ S	β-C ₂ S	C ₄ AF	C ₃ A
46.3	34.1	16.6	1.0

The composition of pozzolana - opoka is given in Tables 3 and 4. The pozzolan activity was assessed using the modified Chapelle method [17]. This test consisted of placing the 1.000 g of mineral admixture and 1.000 g of calcium oxide in a water volume of 250 ml. The solutions were kept for 16 h in an oven at 90°C. At the end of the period, the CaO content was determined for titration with hydrochloric acid (HCl) solution and using phenolphthalein as indicator. The results were expressed by fixed CaO, which is equal to the difference between 1 000 g and the mass of CaO obtained from titration. (hydraulic activity of pozzolana is 220 mg of CaO/g).

Table 3. Oxide composition of opoka.

Component (wt. %)						
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
54.1	2.7	1.3	23.2	0.62	0.24	0.87

Loss on ignition 16.97 %

Table 4. Mineral composition of opoka.

Component (wt. %)			
Amorphous SiO ₂ ·nH ₂ O	Ancerite Ca(Fe,Mg,Mn)(CO ₃) ₂	Calcite CaCO ₃	Cristobalite SiO ₂
22.2	1.3	36.1	19.2
Muscovite KAl ₂ (AlSi ₃ O ₁₀)(F,OH) ₂	Plagioclase NaAlSi ₃ O ₈	Quartz SiO ₂	Tridymite SiO ₂
4.1	1.1	12.0	4.0

The composition of Ordinary Portland cement (OPC) clinker is given in Table 5 and Table 6. OPC was obtained by mixing of OPC clinker and 4.5 % gypsum (320 m²/kg).

Table 5. Oxide composition of Portland cement clinker.

Component (wt. %)						
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
20.1	5.32	3.75	62.80	4.54	0.14	0.93

Table 6. Mineral composition of OPC clinker.

Component (wt. %)			
C ₃ S	β-C ₂ S	C ₄ AF	C ₃ A
67.1	5.9	12.7	5.5

The X-ray diffraction (XRD) data were collected with a DRON-6 powder X-ray diffractometer with Bragg-Brentan geometry using Ni-filtered CuK_α radiation, operating at a voltage of 30 kV and an emission current of 24 mA. The step-scan covered the angular range 5 - 60° (2θ) in steps of 2θ = 0,02°.

Oxide composition was obtained by S4 Explorer (XRF), CuK_{α} radiation, operating at a voltage of 20 kV and an emission current of 5 mA.

Simultaneous thermal analysis (differential scanning calorimetry [DSC] and thermogravimetry [TG]) was carried out on a Netzsch 409 PC Luxx simultaneous thermal analysis instrument with ceramic sample hand-lers and crucibles of Pt-Rh. At a heating rate of $15^{\circ}C/min$, the temperature ranged from $30^{\circ}C$ to $1000^{\circ}C$ under a nitrogen atmosphere.

Infrared (IR) spectra have been measured using a PerkinElmer Fourier transform-IR (FT-IR) system Spectrum X spectrometer. Samples were prepared by mixing

1 mg of the sample in 200 mg of KBr. The spectral analysis was performed in the range $4000 - 400\text{ cm}^{-1}$ with a spectral resolution of 1 cm^{-1} .

Measurements of pore size distribution, etc., were proceeded using mercury intrusion porosimetry (Auto Pore III. 9400 (Micromeritics), weight of sample $0.5 \pm 0.2\text{ g}$, holder 0617 – (10) 5 bulb, 1.131 Stem., max. pressure 60 000 psi (414 MPa), comply with $0.003\text{ }\mu\text{m}$ diameter).

A conduction calorimeter (Thermometric TAM AIR III) was used for the determination of the rate of hydration heat liberation (isothermal $20 \pm 0.1^{\circ}C$).

RESULTS AND DISCUSSION

The influence of opoka on the hydration of Brownmillerite cement under normal condition

To study the interaction of opoka and hydrating Brownmillerite cement (BC), the opoka blended BC pastes and a reference cements of pure BC and OPC pastes were monitored by XRD during hydration (Figure 1). During the hydration of cement several reactions take place simultaneously or successively. The occurrence of one reaction can affect the kinetics and reaction products of a second reaction and so on, leading to a complex interplay of reactions.

XRD analysis of all samples hydrated in water (Figure 1) indicated patterns characteristic of unhydrated tricalcium silicate (d -spacing = 0.304; 0.297; 0.278; 0.219; 0.193 nm), dicalcium silicate (d -spacing = 0.278; 0.274; 0.261; 0.219 nm) and Portlandite (d -spacing = 0.492; 0.263 nm). Moreover, the peaks characteristic

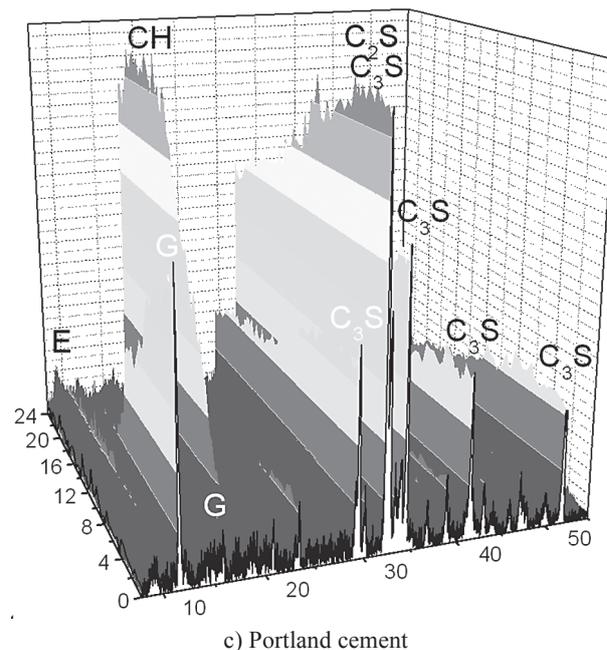
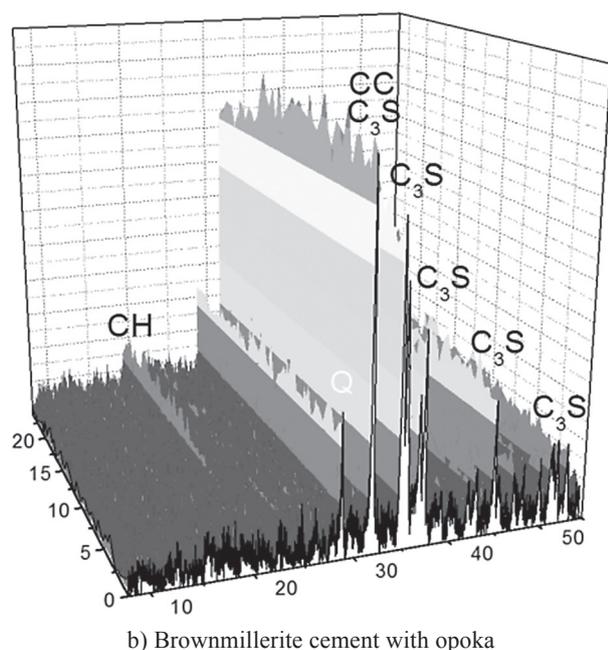
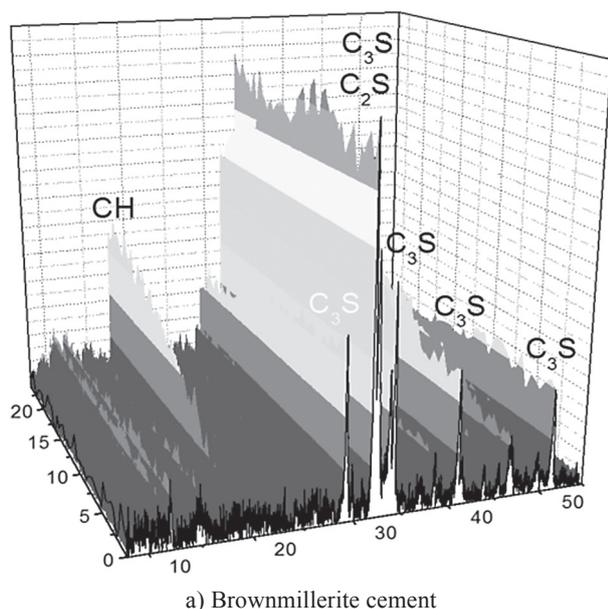


Figure 1. X-ray patterns of samples cured for 24 hours under normal conditions (indexes: CC - $CaCO_3$, CAFm - $Ca_4Al_2O_6CO_3 \cdot 11H_2O$, CH - $Ca(OH)_2$; Q - SiO_2 ; C_3S - $3CaO \cdot SiO_2$; E - $(CaO)_3(Al_2O_3)(CaSO_4) \cdot 32H_2O$).

of quartz (d -spacing = 0.335; 0.426; 0.182 nm) and calcite (d -spacing = 0.303; 0.228; 0.191; 0.187 nm) were identified in the samples with opoka. Intensity of patterns attributed to gypsum (d -spacing = 0.428; 0.287; 0.268 nm) decreases with increasing the duration of hydration of Portland cement samples (Figure 1c): after 11 hours and 20 min. it is left only weak traces of this compound, while first evidences of Ettringite (d -spacing = 0.971; 0.561; 0.387; 0.256 nm) appears after 3 h. and 50 min.

It is important to note, that first diffraction patterns of Portlandite were identified after 2 h. 30 min. in the BC samples (Figure 1a), in the BC samples with opoka (Figure 1b) - only after 5 h., while in the Portland cement (Figure 1c) - after 1 h 50 min. of hydration. It can be seen that, hydration of Brownmillerite is slower than of Portland cement. Opoka changes the process of BC early hydration, because Portlandite was identified later - reasonable explanation would be the interaction between amorphous SiO_2 from opoka and formed Portlandite.

Isothermal calorimeter (TAM AIR III) was used to assess the evolution of the heat of hydration of the cement pastes (Figure 2).

The rate of heat development curves for BC and opoka blended BC cements in comparison with pure PC cement are shown in (Figure 2).

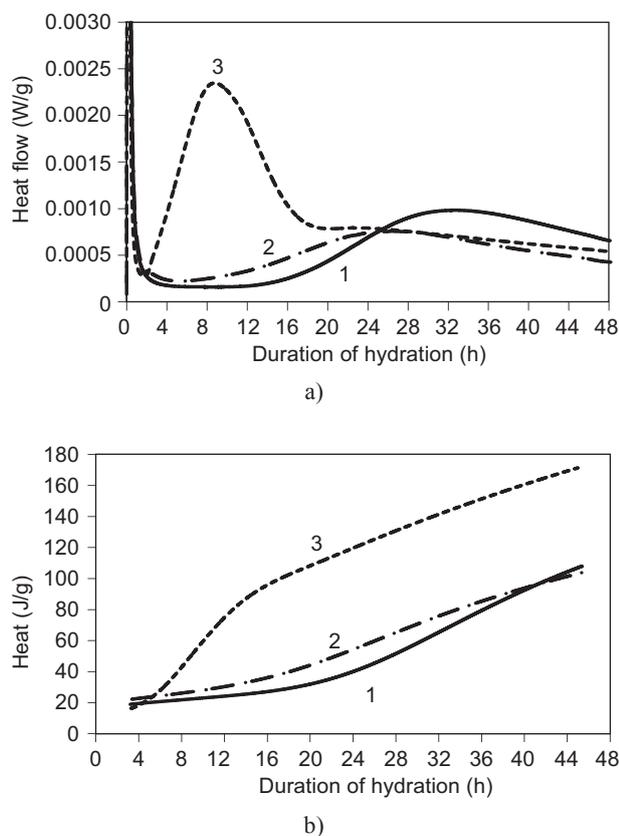


Figure 2. Heat flow (a) and heat (b) curves of samples hydrated for 48 hours (1 - Brownmillerite cement; 2 - Brownmillerite cement with opoka; 3 - Portland cement).

The effect is expected to increase the heat output due to the reaction of pozzolans with calcium hydroxide, moreover the increase of nuclear sites to accelerate CSH formation. The dilution effect expected to decrease the heat output due to the dilution in the main cement compounds (C_3S). The acceleration effect of opoka on C_3S hydration appears as the shift of beginning of the onset climbing of the acceleratory period (second peak) in the BC with opoka samples (Figure 2a). This effect clearly appears in Figure 2b for BC with opoka, as the heat difference with respect to the pure BC paste is positive for these mixes after the induction period. This was further confirmed by the plotting the total heat evolved with time in Figure 2b. The maximum peak of heat flow effect attributed to C_3S hydration is reached in 26 h 31 min. of BC with opoka samples, while only 32 h 17 min. - of pure BC. However, calorimeter data shows much slower hydration of BC with respect to the Portland cement.

Mercury porosimetry has been used, to measure the total pore volume and pore size distribution. It was observed that addition of opoka in BC decreased the total porosity of hardened cement paste (Figure 3a): total porosity of BC was 40.20 %, while 37.83 % of BC samples with opoka. Moreover, opoka decreased the

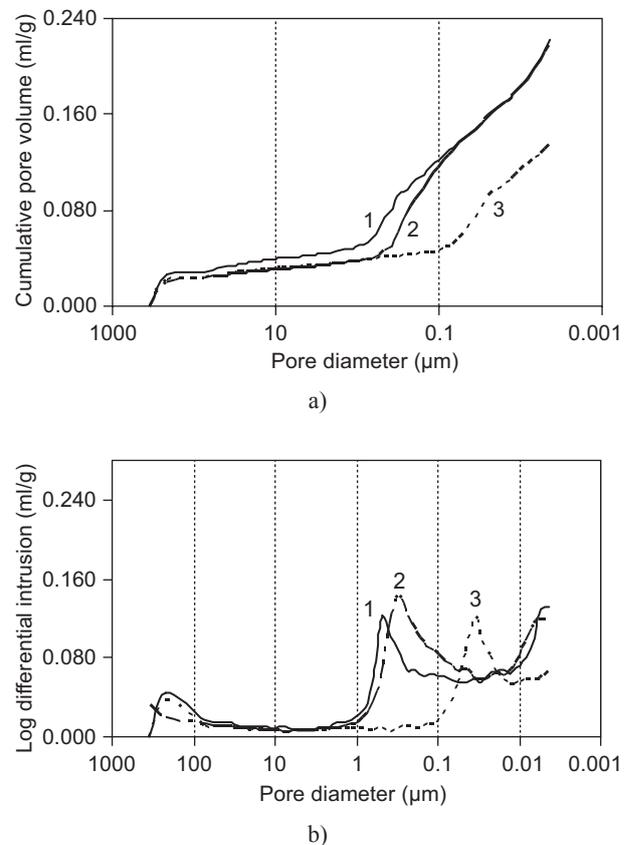
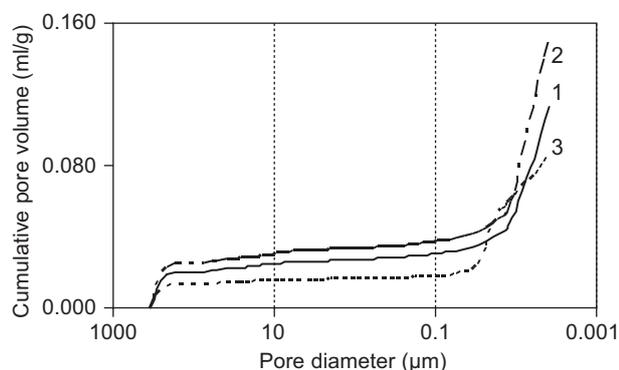


Figure 3. Cumulative pore volume (a) and pore size distribution (b) of samples after 2 days of hydration in water (1 - BC; 2 - BC with opoka; 3 - OPC).

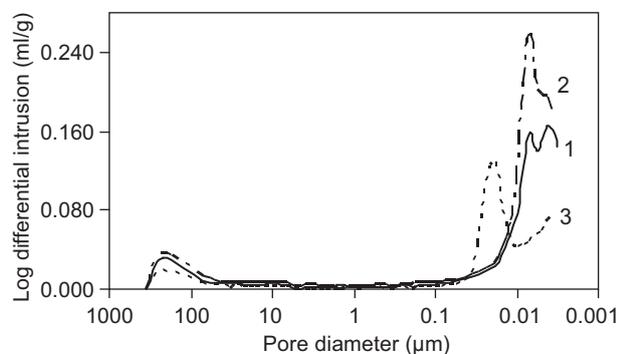
width of threshold pores (Figure 3b): width of threshold pores in the pure BC samples was $0.47 \mu\text{m}$, and in the samples with opoka - $0.30 \mu\text{m}$. However, the total porosity of OPC paste was identified much lower (26.75 %) to compare with BC samples. These results confirm the faster hydration of OPC then BC or BC with opoka.

After 28 days of hydration in the respect of 2 days the lower total pore volume was identified in all samples (Figure 4): total porosity of BC = 23.60 %; of BC with opoka = 28.14 %; of OPC = 18.18 %. But the threshold pore width of BC and BC with opoka samples were obtained much smaller ($0.007 \mu\text{m}$) than of OPC ($0.019 \mu\text{m}$) (Figure 4b). Larger pores contribute to mass transport by diffusion, ion migration, capillarity, and permeability, whereas smaller pores aggravate diffusion process and ion migration. Therefore, the reduction of pore size causes the diffusion of chloride ions into cement stone to be mitigated. The results of Diamond S. research shows the influence of threshold pore width on the resistance of cement pastes to aggressive environment [18, 19].

XRD analysis of BC and BC with opoka samples hydrated in water for 28 days (Figure 5) showed patterns characteristic of unhydrated C_4AF (d -spacing = 0.731 ; 0.366 ; 0.264 nm), while $\text{Ca}_{1.5}\text{SiO}_{3.5} \cdot x\text{H}_2\text{O}$ (d -spacing = 0.304 ; 0.279 ; 0.182 nm) and CO_3^{2-} -AFm ($\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3 \cdot 11\text{H}_2\text{O}$) (d -spacing: 0.758 ; 0.379 nm)



a)



b)

Figure 4. Cumulative pore volume (a) and pore size distribution (b) of samples after 28 days of hydration in water (1 - BC; 2 - BC with opoka; 3 - OPC).

were identified only in the samples with opoka. Opoka promotes the formation of calcium hydrosilicates in the BC paste. Moreover, it can be assumed that the CaCO_3 contained in the pozzolana initiated the formation of monocarboaluminate - CaCO_3 reacts with hydration products of C_4AF .

Less intense diffraction peaks, characteristic of Portlandite were identified in the BC samples with opoka, presumably, this effect was affected by other main compound of pozzolana: amorphous SiO_2 . The same data were confirmed by FT-IR analysis. The sharp band at a wavelength of 3644 cm^{-1} indicates the existence of Portlandite. The IR spectrum of samples with opoka additive (Figure 6) showed less intense absorption bands, characteristic of this compound.

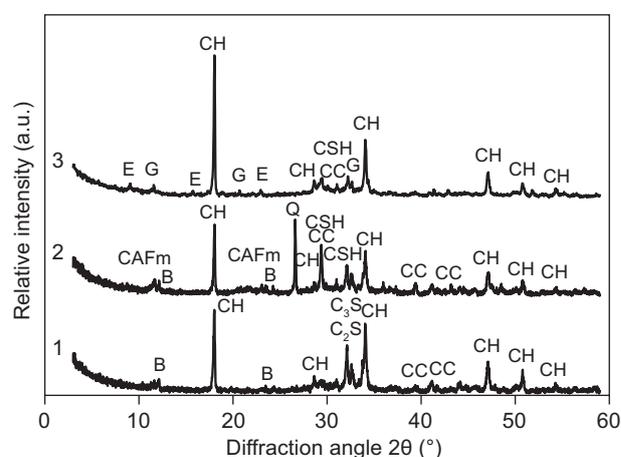


Figure 5. X-ray patterns of samples cured for 28 days under normal conditions (1 - BC; 2 - BC with opoka; 3 - Portland cement; indexes: CC - CaCO_3 , CAFm - $\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3 \cdot 11\text{H}_2\text{O}$, CH - $\text{Ca}(\text{OH})_2$; Q - SiO_2 ; C_3S - $3\text{CaO} \cdot \text{SiO}_2$; CSH - $\text{Ca}_{1.5}\text{SiO}_{3.5} \cdot x\text{H}_2\text{O}$; E - $(\text{CaO})_3(\text{Al}_2\text{O}_3)(\text{CaSO}_4)_3 \cdot 32\text{H}_2\text{O}$; G - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

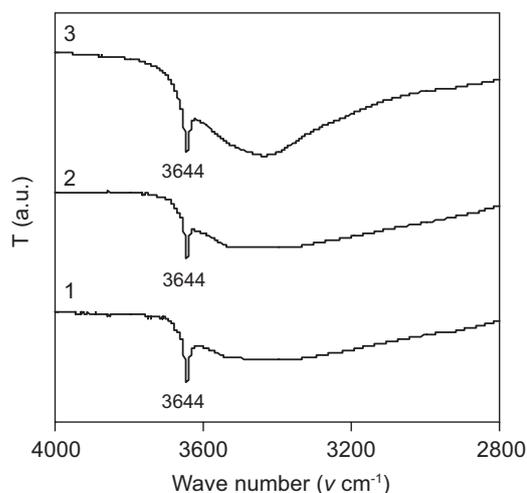
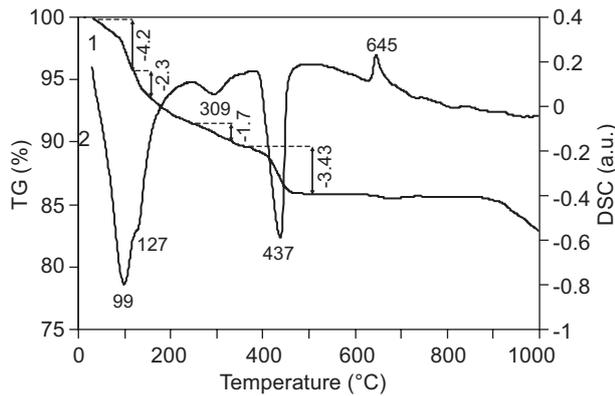


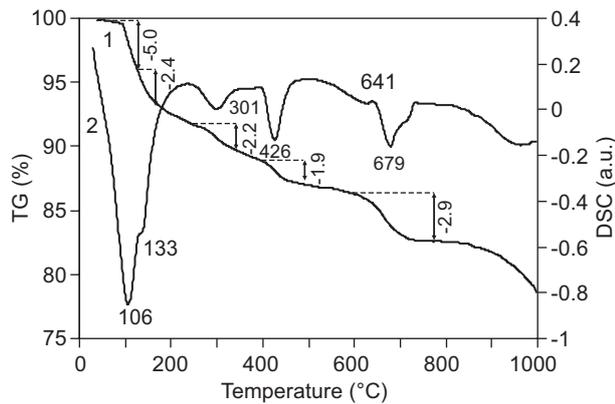
Figure 6. FT-IR curves of samples cured for 28 days under normal conditions (1 - BC; 2 - BC with opoka; 3 - Portland cement).

formed in the OPC with opoka (Figure 9b). The greater formation of Friedel's salt in samples with opoka can be explained by higher amounts of monocarboaluminate (invoked by opoka), which can react with chloride to form Friedel's salt.

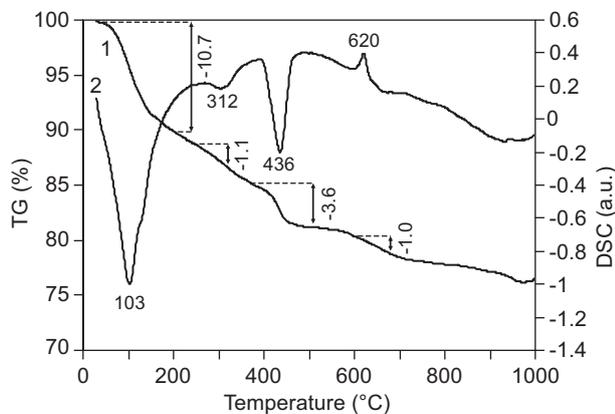
The mass loss of the pure BC (3.4 wt. %) and OPC (3.6 wt. %) samples during the endothermic effect characteristic of Portlandite (at approximately 430°C) after curing in NaCl solution for 3 months (Figure 9.) remained almost the same as after 1 month (28 days)



a) BC



b) BC with opoka



c) Portland cement

Figure 9. TG (1) and DSC (2) patterns of samples cured for 28 days and 3 months in a saturated NaCl solution.

of hydration in water (~3.6 wt. %) (Table 6), whereas the mass loss of the samples with opoka decreased from 3.05 wt. % (Table 6) after 1 month in water to 1.9 wt. % (Figure 9c) after 3 months in the saturated NaCl solution. Thus, it can be concluded that in the samples with opoka Portlandite reacted with amorphous SiO_2 (pozzolanic reaction) even in the saturated NaCl solution.

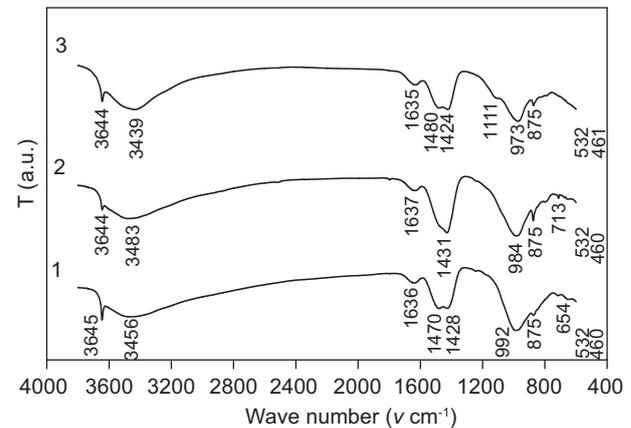


Figure 10. FT-IR patterns of samples cured for 28 days and 3 months in a saturated NaCl solution (1 - BC; 2 - BC with opoka; 3 - Portland cement).

FT-IR analysis showed pretty much similar spectrum for all samples (Figure 10). The main difference between them was that the peak intensity characteristic of Portlandite (3644 cm^{-1}) was weaker in samples of BC with opoka than in samples of BC or OPC.

The FT-IR spectrum characteristic of Friedel's salt consists of absorption peaks where wave numbers are 3636 cm^{-1} , 3480 cm^{-1} (ν_{OH}), 1621 cm^{-1} (δ_{H_2O}), 785 cm^{-1} , 620 cm^{-1} , and 532 cm^{-1} ($-O$ and $-O-H$ vibration) [22]. Only the peak at 532 cm^{-1} is not covered by the absorption ranges of other cement minerals; thus, the existence of the absorption band at 532 cm^{-1} is evidence of the formation of Friedel's salt in all samples treated in the saturated NaCl solution.

CONCLUSION

- It was estimated that under normal conditions, pozzolana additive accelerates the hydration of calcium silicates and initiates the formation of CO_3^{2-} -AFm in the brownmillerite rich cement. However, the hydration of Brownmillerite cement with opoka additive is still slower to compare with hydration of Portland cement.
- Opoka decreases total porosity and threshold pore diameter of Brownmillerite cement paste after two days of hydration. After 28 days of hydration threshold pore diameter became smaller even to compare with threshold pore diameter of Portland cement.

● Opoka additive promotes the formation of Friedel's salt in Brownmillerite samples treated in saturated NaCl solution, because CO_3^{2-} -AFm affected by saturated NaCl solution become unstable and takes part in reactions producing Friedel's salt.

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