

INFLUENCE OF POZZOLANA ON C₄AF HYDRATION AND THE EFFECTS OF CHLORIDE AND SULFATE IONS ON THE HYDRATES FORMED

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This study investigated the influence of natural pozzolana additive on the hydration of C₄AF (aluminoferrite) and the effects of chloride and sulfate ions on the hydrates formed. In the samples, 25% (by weight) of the C₄AF was replaced with pozzolana. The mixture was then hardened for 28 days in water, soaked in a saturated NaCl solution for 3 months, and then soaked in a 5% Na₂SO₄ solution for 3 months at 20°C. It is estimated that under normal conditions, pozzolana additive accelerates the formation of CO₃²⁻-AFm (monocarboaluminate) and gibbsite, however, impede the formation of cubic aluminum hydrates. Also, part of the amorphous SiO₂ penetrates into the structure of hydrates of C₄AF and initiates the formation of hydrated aluminosilicate (gibbsite). Monocarboaluminate affected by NaCl becomes unstable and takes part in reactions producing Ca₂Al(OH)₆Cl·2H₂O (hydrocalumite-M). After samples were transferred from a saturated NaCl solution to a 5% Na₂SO₄ solution, hydrocalumite-M was the source of aluminates for the formation of ettringite. In samples with pozzolana additive, the hydrated aluminosilicate and gibbsite compounds that were formed remained stable in an environment containing chloride and sulfate ions and retarded the corrosion reaction of C₄AF hydrates.

INTRODUCTION

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]. It is therefore reasonable to assume that a non-negligible proportion of the phases in actual cement will be associated with Fe phases. However, the AFm and AFt phases have received little attention. Moreover, the role of iron under aggressive conditions in cement has not been fully determined. 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]. The first minerals formed in the absence and presence of CaSO₄ are the poorly organized AFm and AFt phases, respectively. Both types of phase contain Al³⁺ and Fe³⁺ and tend to undergo further changes to form hydrogarnet phases.

Aluminates are one of the major compounds involved in cement corrosion reactions. Studies of the effect of chloride on the durability of cement stone are important in countries with access to the sea, because they have structures (jetties, quays, etc.) influenced by

sea water. In 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 cement structures (road shoulders, gutters, sidewalks, etc.).

Chloride ions influence the durability of cement stone, and it was found to be related to the reaction between aluminous compounds and Cl⁻ ions [4, 5]. Moreover, the long-term use of NaCl can initiate and/or accelerate alkali-silica reaction (ASR) by supplying additional alkalis to concrete [6, 7]. It was estimated that the primary compound formed is a Friedel's salt [8, 9]. Friedel's salt is a chloride-containing calcium aluminate hydrate. It has the composition 3CaO×Al₂O₃×CaCl₂×10H₂O. There is an interest in Friedel's salt due to its role as a diffusion barrier against chloride ion, which causes corrosion of steel that is embedded in concrete [10,11]. Also, AFm and aluminum hydrates interact with CO₂, which is always present in the environment [12]. It has been established that AFm group minerals containing Cl⁻ or CO₃²⁻ ions are formed [13]. When a concrete structure is exposed to different environments, its life span is drastically reduced. The most important variable is the resistance

of hardened cement to chemical attack by sulfate and chloride solutions, while under some conditions, the ferrite phase, usually not considered to be involved in sulfate attack reactions, may become more reactive, thus leading to release of aluminate and ferrite ions that can subsequently participate in formation of ettringite [14, 15]. Field experience and laboratory studies have also shown that the sulfate resistance of concrete to expansive ettringite damage is improved by limiting the water–cement ratio and by lowering the C₃A content of the clinker [16]. This realization resulted in research to develop a sulfate resisting clinker, primarily by replacing the C₃A clinker phase by the alumina-poor, ferrite-rich C₄AF. The amount of ettringite (AFt-phase) formed in the hydration of this cement is significantly reduced and - as the ferrite phase is the main source of Al³⁺ - this phase contains significant amounts of Fe³⁺, replacing Al³⁺ in its crystalline lattice. As the hydration of the ferrite phase is rather slow, distinct amounts of it may be present even in mature pastes. Upon contact with sulfate ions from an external source this fraction of the ferrite phase may react to yield ettringite. This reaction is associated with an expansion, however the expansiveness of this, iron-doped, AFt phase is rather small [16]. Existing research on the effect of a chloride solution on sulfate corrosion is quite scarce; more research is therefore needed.

In order to reduce the corrosion reactions of cement stone, pozzolana additives can be used [17-20]. Diverse and conflicting opinions can be found in the literature on the addition of pozzolana containing limestone. Scientists consider the effect of limestone on cement to be physical, taking into account the increase in strength [21, 22] or plasticizing effect [23]. Moreover, the addition of pozzolana to neat cement pastes and mortars reduces the diffusion coefficient of chloride ions [22].

Lithuania contains abundant natural pozzolana, which consists of amorphous SiO₂ and finely dispersed CaCO₃. The aim of this work was to investigate the influence of pozzolana on the hydration process of C₄AF and the effect of Cl⁻ and SO₄²⁻ ions on the hydrates formed.

EXPERIMENTAL

Samples (20 × 20 × 20 mm) were formed of (1) pure C₄AF and (2) C₄AF with 25% (by weight) replaced by pozzolana. The ratio of water to C₄AF was 0.4. During the first day, the samples were kept in moulds at 20 ± 1°C and 100% humidity. After 24 hours of formation, the samples 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 20°C, and then to a 5% Na₂SO₄ solution and stored there for a further 3 months at 20°C. Hydration of samples was stopped using acetone.

C₄AF was obtained as a result of the synthesis of limestone (99.0% CaCO₃), technically pure Al₂O₃ (99.0%), and Fe₂O₃ (99.0%) in a stoichiometric mixture in a Nabertherm HTC 03/16 furnace. The synthesis was carried out by burning this mixture at 1350°C for 2 h. X-ray powder diffraction (XRD) analysis of the material thus obtained indicated that it was pure C₄AF, free of any XRD-detectable impurities. The content of free calcium, determined by Franke's method, amounted to 0.0%. The specific surface area of pozzolana is 350 m²/kg, and that of C₄AF is 320 m²/kg (by the Blaine method). The composition of pozzolana is given in Tables 1 and 2 (loss on ignition, 16.97%; hydraulic activity, 220 mg CaO/g).

Table 1. Oxide composition of pozzolana.

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

Table 2. Mineral composition of pozzolana.

Component	Amount (wt.%)
Amorphous (SiO ₂ ·nH ₂ O)	22.2
Ancerite (Ca(Fe,Mg,Mn)(CO ₃) ₂)	1.3
Calcite (CaCO ₃)	36.1
Cristobalite (SiO ₂)	19.2
Muscovite (KAl ₂ (AlSi ₃ O ₁₀)(F,OH) ₂)	4.1
Plagioclase (NaAlSi ₃ O ₈)	1.1
Quartz (SiO ₂)	12
Tridymite (SiO ₂)	4

The XRD data were collected with a DRON-6 powder X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered CuK_α radiation, operating voltage 30 kV and emission current 24 mA. The step-scan covered the angular range 5-60° (2θ) in steps of 2θ = 0.02°.

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 handlers and crucibles of Pt–Rh. At a heating rate of 15°C/min, the temperature ranged from 30°C to 1000°C under the nitrogen atmosphere.

Infrared (IR) spectra have been measured using a PerkinElmer 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 $4000\text{--}400\text{ cm}^{-1}$ with a spectral resolution of 1 cm^{-1} .

Scanning electron microscopy (SEM) (FEI Quanta 200 FEG) coupled with energy dispersive X-ray spectrometry (EDS) was performed using an accelerating voltage of 20 kV, a working distance of 10 mm for SEM observation, and a 200-s accumulation time for EDS analysis.

The pozzolanic activity was assessed using the modified Chapelle method [24]. This test consisted of placing the 1.000 g of mineral admixture and 1.000 g of calcium oxide in a water volume of 250.0 ml. The solutions were kept for 16 h in an oven at $90\text{ }^\circ\text{C}$. 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.

The influence of pozzolana on the hydration of C_4AF under normal conditions

XRD analysis of C_4AF samples hydrated in water for 28 days (Figure 1) showed patterns characteristic of unhydrated C_4AF (d -spacing: 0.725, 0.264, 0.205, 0.193, 0.181 nm, etc.), C_3AH_6 (d -spacing: 0.514, 0.445, 0.336 nm, etc.), and gibbsite ($Al(OH)_3$) or $Fe(OH)_3$ (d -spacing: 0.485, 0.437, 0.432 nm, etc.). Together with these compounds, $CaCO_3$ (d -spacing: 0.304, 0.250 nm) and $CO_3^{2-}\text{-AFm}$ ($Ca_4Al_2O_6CO_3\cdot 11H_2O$) (d -spacing: 0.758, 0.379 nm, etc.) were identified as a result of interaction with environmental CO_2 . The main difference in the XRD patterns of the C_4AF samples with pozzolana additive was more intense diffraction peaks, characteristic of $CaCO_3$ and $CO_3^{2-}\text{-AFm}$, because $CaCO_3$ is the main compound of pozzolana. It can be assumed that the $CaCO_3$ contained in the pozzolana

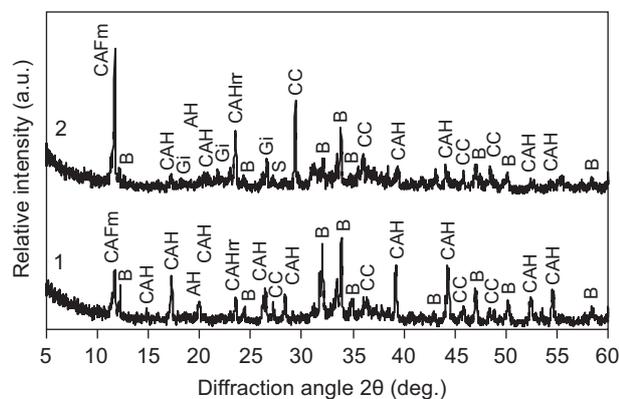


Figure 1. XRD patterns of samples cured for 28 days in water. 1 - pure C_4AF ; 2 - C_4AF with pozzolana additive. Abbreviations: B - $4CaO\cdot Al_2O_3\cdot Fe_2O_3$, CAH - $Ca_3Al_2O_6\cdot 6H_2O$, AH - $Al(OH)_3$, CC - $CaCO_3$, CAFm - $Ca_4Al_2O_6CO_3\cdot 11H_2O$, Gi - $CaAl_2Si_2O_8\cdot 4H_2O$, S - SiO_2 .

initiated the formation of monocarboaluminate. $CaCO_3$ reacts with hydration products of C_4AF and forms monocarboaluminate, and very weak diffraction patterns characteristic of ordinary cubic C_3AH_6 were identified in the XRD curve of samples with pozzolana (Figure 1, curve 2). Also in this sample, the formation of a new compound-hydrated aluminosilicate (gismondine), $CaAl_2Si_2O_8\cdot 4H_2O$ (d -spacing: 0.334, 0.427, 0.725, 0.185 nm)-was observed. Presumably, the formation of this compound was affected by other main compound of pozzolana: amorphous SiO_2 .

In the DSC curves of C_4AF samples (Figure 2), three significant endothermic peaks at $154\text{ }^\circ\text{C}$, $294\text{ }^\circ\text{C}$, and $737\text{ }^\circ\text{C}$ were observed. The endothermic peak at $154\text{ }^\circ\text{C}$ was mainly due to the dehydration of $CO_3^{2-}\text{-AFm}$, and the endothermic peak at $294\text{ }^\circ\text{C}$ is characteristic of the dehydration of cubic aluminum hydrate (C_3AH_6) [25, 26]. The endothermic peaks at $737\text{--}751\text{ }^\circ\text{C}$ indicate $CaCO_3$ decomposition [20]. During this process, the pure C_4AF sample lost 4.5 wt.% of its mass, and the sample with pozzolana lost 7.7 wt.%. DSC analysis of the samples with pozzolana indicated increasing endothermic effects at $153\text{ }^\circ\text{C}$, characteristic of the dehydration of monocarboaluminate. It should be noted that the endothermic peak of C_3AH_6 ($\sim 300\text{ }^\circ\text{C}$) was not obtained in the samples with pozzolana (Figure 2); however, an endothermic peak at $261\text{ }^\circ\text{C}$, characteristic of the dehydration of gibbsite, was identified [20].

The same data were confirmed by FT-IR analysis. The sharp band at a wavelength of 3670 cm^{-1} indicates the existence of cubic hydrates [27]. The IR spectrum of samples with pozzolana additive (Figure 3, curve 2) showed much less intense absorption bands, characteristic of this compound. Monocarboaluminate was detected in the IR spectrum of both samples (Figure 3). $CO_3^{2-}\text{-AFm}$ was described by double split bands, $\nu_3\text{-CO}_3^{2-}$ ($1481\text{--}1366\text{ cm}^{-1}$) [12, 27]. Absorption at the 1481 cm^{-1} frequency range was overlapped by a band characteristic of $CaCO_3$ (1423 cm^{-1}), so only a weak absorption shoulder could be seen in the samples with

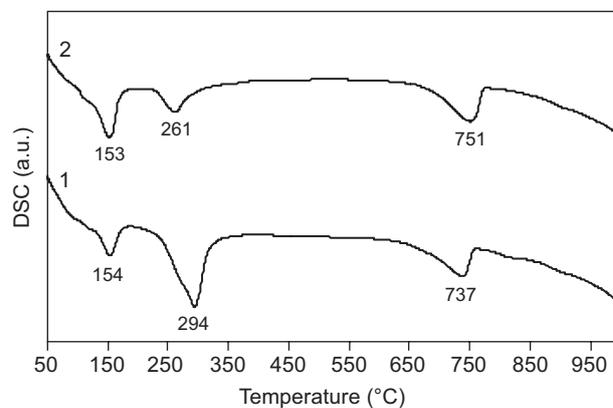


Figure 2. DSC curves of samples cured for 28 days in water: 1 - pure C_4AF ; 2 - C_4AF with pozzolana additive.

pozzolana. It should be noted that new absorption bands in the range 1107–967 cm^{-1} , characteristic of the Si–O band, were seen in the samples with pozzolana [27]. This may be related to incorporation of part of the amorphous SiO_2 into the structure of C_4AF hydrates.

In summary, it can be concluded that under normal conditions, pozzolana additive accelerates the formation of CO_3^{2-} -AFm and gibbsite but impedes the crystallization of cubic aluminum hydrates. Also, a part of the amorphous SiO_2 penetrates into the structure of hydrates of C_4AF and initiates the formation of hydrated aluminosilicate (gismondine).

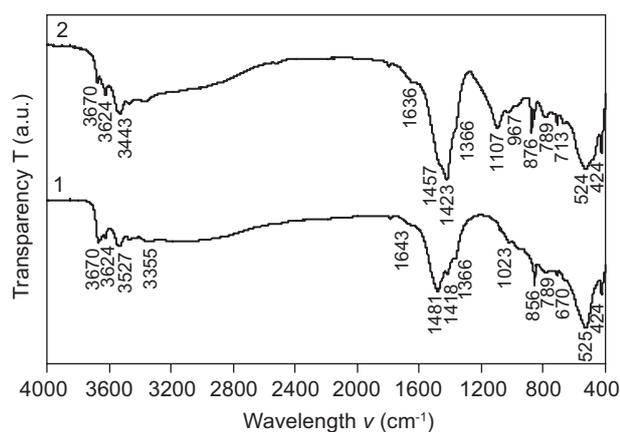


Figure 3. FT-IR spectra of samples cured for 28 days in water: 1 - pure C_4AF , 2 - C_4AF with pozzolana.

The influence of pozzolana on C_4AF hydrates in a saturated NaCl solution

After 28 days of hydration in water, samples were transferred to the saturated NaCl solution and stored there for 3 months. Diffraction peaks characteristic of regular C_4AF hydrates and CO_3^{2-} -AFm were not identified by the XRD analysis in either sample (Figure 4). On the other hand, formation of hydrocalumite-M ($\text{Ca}_2\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$; d -spacing: 0.790, 0.395, 0.288 nm) and halite (NaCl) (d -spacing: 0.282, 0.199 nm) was found. These peaks were more intense in the pure C_4AF samples. Moreover, in the XRD analysis, curves still had diffraction peaks characteristic of CaCO_3 and $\text{Al}(\text{OH})_3$. It should be noted that in samples with pozzolana, diffraction peaks that were characteristic of gismondine were also observed.

DSC curves of C_4AF and C_4AF with pozzolana samples were similar after soaking in the saturated NaCl solution (Figure 5). Endothermic peaks were identified at $\sim 140^\circ\text{C}$ and $335\text{--}350^\circ\text{C}$, and an exothermic peak was identified at $650\text{--}665^\circ\text{C}$, characteristic of chloride aluminates [25, 28], which are slightly more intense in the C_4AF samples. The endothermic peaks at $250\text{--}270^\circ\text{C}$ and $694\text{--}720^\circ\text{C}$ indicate the decomposition of $\text{Al}(\text{OH})_3$ and CaCO_3 , respectively. During decomposition of CaCO_3 , the sample of C_4AF lost 5.0 % of its weight, and

sample with pozzolana lost 6.87 wt.%. Mass changes showed an increasing amount of CaCO_3 (compared with samples cured for 28 days in water) in the samples of pure C_4AF . Because there can be no interaction of the samples with environmental CO_2 in a saturated NaCl solution, this phenomenon can be explained by the release of CO_3^{2-} ions from -AFm as it is affected by the Cl^- ions. Unbound CO_3^{2-} ions react with Ca^{2+} ions contained in the hardening system and produce a larger amount of CaCO_3 . On the other hand, in the samples with pozzolana, a decrease in the amount of CaCO_3 showed the participation of this compound (from pozzolana) in the hydration reactions, even in a saturated NaCl solution. This means that the different properties of CaCO_3 formed due to penetration of Cl^- into CO_3^{2-} -AFm and CaCO_3 added with pozzolana. An endothermic peak at 154°C due to the dehydration of CO_3^{2-} -AFm was not identified. Thus, CO_3^{2-} -AFm becomes unstable in the saturated NaCl solution and crystallizes in to hydrocalumite-M.

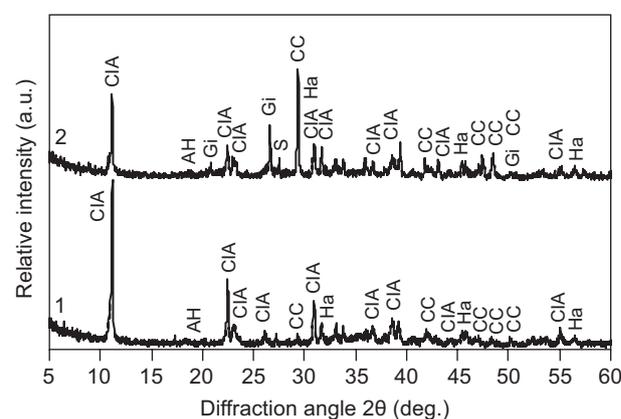


Figure 4. XRD patterns of samples cured for 3 months in a saturated NaCl solution: 1 - pure C_4AF ; 2 - C_4AF with pozzolana additive. Abbreviations: CIA - $\text{Ca}_2\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$, Ha - NaCl, AH - $\text{Al}(\text{OH})_3$, CC - CaCO_3 , Gi - $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$, S - SiO_2 , CAH - $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$.

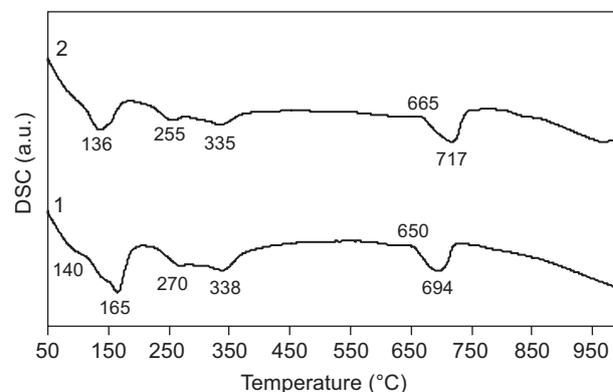


Figure 5. DSC curves of samples cured for 3 months in a saturated NaCl solution: 1 - pure C_4AF ; 2 - C_4AF with pozzolana additive.

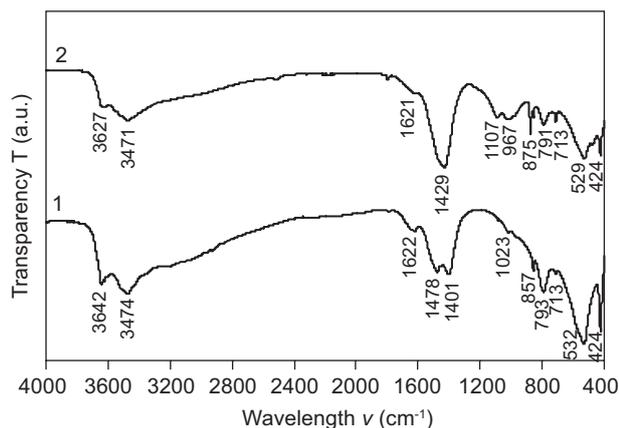


Figure 6. FT-IR spectra of samples cured for 3 months in a saturated NaCl solution: 1 - pure C_4AF ; 2 - C_4AF with pozzolana additive.

FT-IR data curves are shown in Figure 6. Bands characteristic of monocarboaluminate ($1481\text{--}1366\text{ cm}^{-1}$) and cubic aluminohydrates (3670 cm^{-1}) were not identified in either sample. On the other hand, the band vibration corresponding to H-O-H influenced by chloride at $3470\text{--}3475\text{ cm}^{-1}$ was determined [29]. These absorption bands were more intense in the pure C_4AF samples than in the samples with pozzolana. It should be noted that absorption bands in the range 1107 and 967 cm^{-1} , characteristic of the Si-O band, remained in the curves of the samples with pozzolana.

These studies indicated that regular C_4AF hydrates and monocarboaluminate affected by saturated sodium chloride solution become unstable and take part in reactions producing hydrocalumite-M. Under these conditions, gibbsite and gismondine remain stable in samples with pozzolana.

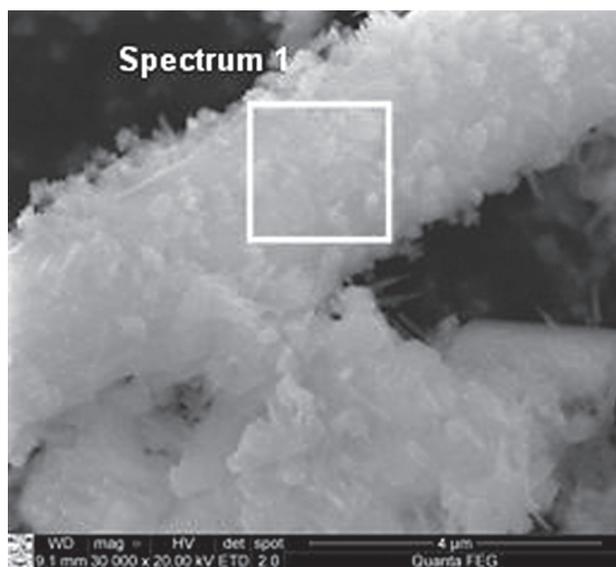
The influence of pozzolana on C_4AF hydrates in a Na_2SO_4 solution after treatment in saturated NaCl

In the next stage of investigation, all samples were transferred from saturated NaCl to a 5% Na_2SO_4 solution. After samples were kept there for 3 months, SEM-EDS analysis indicated the formation of needle-shaped Fe-*ettringite* crystals (Figure 7) with a minor content of Fe (Table 3) in both samples.

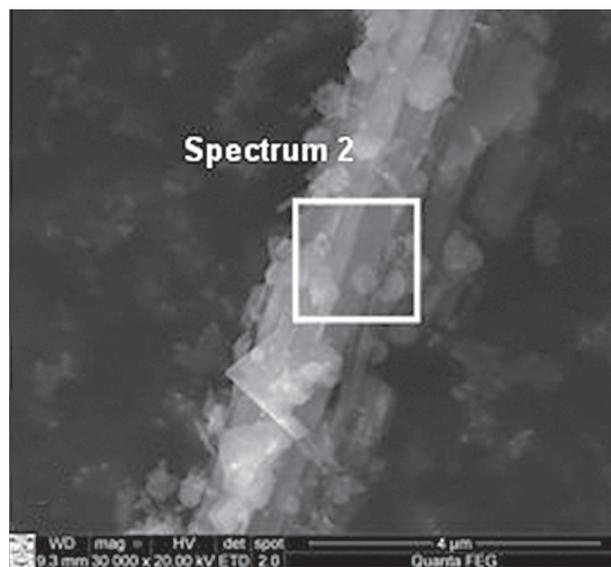
Table 3. Composition by element of C_4AF (spectrum 1) and C_4AF with pozzolana (spectrum 2) samples cured for 3 months in a saturated NaCl solution and 3 months in a 5% Na_2SO_4 solution.

Element	Atomic wt. %	
	Spectrum 1	Spectrum 2
Ca	7.4	8.4
Al	2.0	1.9
S	2.9	3.0
C	24.2	29.9
O	63.0	56.5
Fe	0.5	0.3

Diffraction peaks characteristic of *ettringite* (d -spacing: $0.971, 0.561, 0.387, 0.256\text{ nm}$) were identified by the XRD analysis in both samples (Figure 8). After treatment in a saturated NaCl solution, no C_3AH_6 was identified in either sample, and *ettringite* formed in a different way than it did after soaking in a 5% Na_2SO_4 solution alone (the classical mechanism). Peaks characteristic of hydrocalumite-M were observed in XRD



a)



b)

Figure 7. SEM of C_4AF (a) and C_4AF with pozzolana (b) samples cured for 3 months in a saturated NaCl solution and 3 months in a 5% Na_2SO_4 solution.

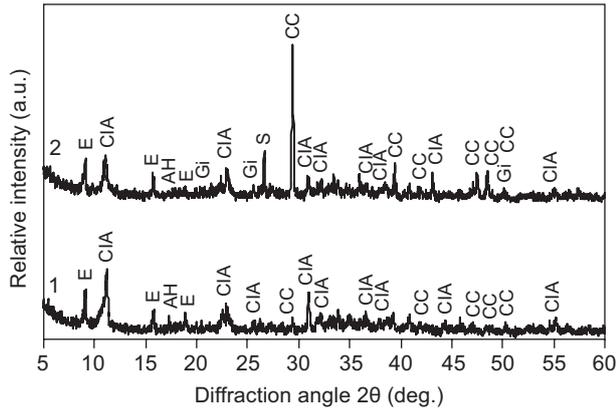


Figure 8. XRD patterns of samples cured for 3 months in a saturated NaCl solution and 3 months in a 5% Na₂SO₄ solutions: 1 - pure C₄AF; 2 - C₄AF with pozzolana additive. Abbreviations: E - Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O, CIA - Ca₂Al₂O₆Cl₂·10H₂O, AH - Al(OH)₃, CC - CaCO₃, Gi - CaAl₂Si₂O₈·4H₂O, S - SiO₂.

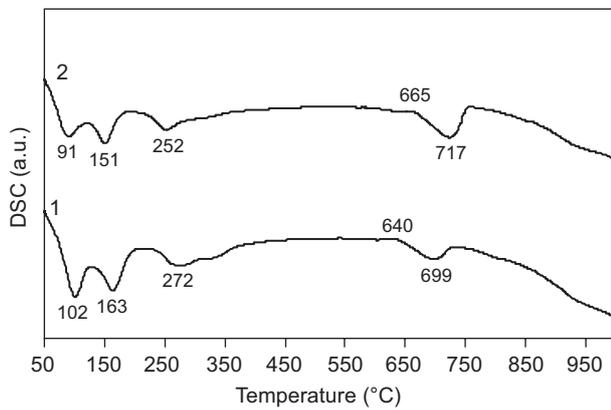


Figure 9. DSC curves of samples cured for 3 months in a saturated NaCl solution and 3 months in a 5% Na₂SO₄ solution: 1 - pure C₄AF; 2 - C₄AF with pozzolana additive.

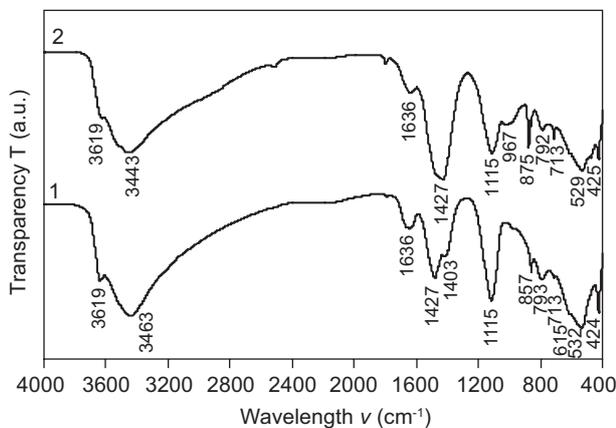


Figure 10. FT-IR spectra of C₄AF (1) and C₄AF with pozzolana (2) samples cured for 3 months in a saturated NaCl solution and 3 months in a 5% Na₂SO₄ solution.

analysis curves, but the intensity of these diffraction peaks was much less than it was after samples were kept in a saturated NaCl solution. The intensity of the diffraction peaks of hydrocalumite-M decreased with the formation of ettringite, showing that hydrocalumite-M is the source of aluminates for the formation of ettringite. Gibbsite was identified in both samples even after treatment in the saturated NaCl solution and in a 5% Na₂SO₄ solution (the same as after treatment in the saturated NaCl solution alone). It is important to note the identification of gismondine in the C₄AF samples with pozzolana, which is clear evidence of the stability of this compound in the 5% Na₂SO₄ solution.

These observations are well supported by the evidence obtained from DSC-TG curves (Figure 9). The broad endothermic peak between 80°C and 105°C can be attributed to the presence of ettringite (the first step of decomposition of ettringite) [30]. The mass loss of this compound was 6.4% in the pure C₄AF samples and 4.8% in the samples with pozzolana. The main thermal effects characteristic of hydrocalumite-M (at 335-350°C and 650-665°C) were very slight, which confirms previous findings. Under these conditions, the remaining endothermic peaks at 250-270°C and 694-724°C indicate the presence of Al(OH)₃ and CaCO₃, respectively.

The same trend was determined in the data obtained with FT-IR analysis (Figure 10). More intense absorption bands due to vibration of SO₄²⁻ (1115 cm⁻¹) characteristic of ettringite [31] were seen in the pure C₄AF samples. It is important to note that the absorption band characteristic of Si-O at 1107 cm⁻¹ was overlapped by absorption bands characteristic of ettringite, but the band at 967 cm⁻¹ remained present in curves of the samples with pozzolana.

These results indicate that gibbsite and gismondine remained stable in the samples with pozzolana under all conditions examined.

CONCLUSIONS

1. It was estimated that under normal conditions, pozzolana additive accelerates the formation of CO₃²⁻-AFm. Hydrated aluminum-silicate (CaAl₂Si₂O₈·4H₂O), however, impedes the crystallization of cubic aluminum hydrates.
2. Regular C₄AF hydrates and CO₃²⁻-AFm affected by saturated NaCl solution become unstable and take part in reactions producing hydrocalumite-M (Ca₂Al₂O₆Cl₂·10H₂O). Under these conditions, gibbsite and hydrated aluminum-silicate (gismondine) remain stable.
3. After samples are transferred from a saturated NaCl solution to a 5% Na₂SO₄ solution, hydrocalumite-M is the source of aluminates for the formation of ettringite.
4. In samples with pozzolana additive, the hydrated alumino-silicate and gibbsite compounds that are

formed remain stable in an environment containing chloride and sulfate ions and retard the corrosion reaction of C₄AF hydrates.

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