

# THE INFLUENCE OF POZZOLANA TO THE TRICALCIUM ALUMINATE HYDRATION AND THE EFFECTS OF CHLORIDE IONS TO FORMED HYDRATES

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*Influence of natural pozzolana additive to the hydration of tricalcium aluminate and the effects of chloride ions to formed hydrates was investigated. In the samples 25 % C<sub>3</sub>A mass weight was replaced by pozzolana and they were hardened for 28 days at normal conditions, soaked in saturated NaCl solution, and stored there for three months at 20 °C. It is estimated that at normal conditions the additive of pozzolana has no substantial effect on the course of C<sub>3</sub>A hydration, but a part of amorphous SiO<sub>2</sub> penetrates into the structure of aluminium hydrates. Regular C<sub>3</sub>A hydrates and CO<sub>3</sub><sup>2-</sup> - AFm affected by NaCl becomes unstable and takes part in reactions producing Friedel's salt and a complex compound - hydrocalumite - Ca<sub>8</sub>Al<sub>4</sub>(OH)<sub>24</sub>(CO<sub>3</sub>)Cl<sub>2</sub>(H<sub>2</sub>O)<sub>1.6</sub>·(H<sub>2</sub>O)<sub>8</sub>. Pozzolana additive reduces the penetration of Cl<sup>-</sup> ions to the structure of C<sub>3</sub>A hydrates and impedes the formation of aluminium chloride hydrates. In samples with pozzolana additive a part of cubic aluminium hydrates, CO<sub>3</sub><sup>2-</sup> - AFm and C<sub>3</sub>A hydrate substituted with Si<sup>4+</sup> affected by chlorides remained stable.*

## INTRODUCTION

One of the cement compounds is tricalcium aluminate - C<sub>3</sub>A, content of which in Portland cement may be up to 15 % [1]. It is a key component of early cement hydration. C<sub>3</sub>A reaction with water is exothermic and very fast, it produces aluminium hydrates and compounds of the AFm, AFt phases [2].

On the other hand, aluminates are one of the major compounds involved in the cement corrosion reactions. Study of the effect of chloride on the durability of cement stone are actual in countries with access to the sea because they have constructions (jetties, quays, etc.) influenced by sea water. In countries with colder climates mixtures of sand and salt or saturated salt solution are used as deicing materials. It can have a significant influence on the durability of cement products - borders, sidewalks, etc.

Chloride ions has influence to cement stone durability, and it was found to be related to the reaction between the aluminous compounds and Cl<sup>-</sup> ions [3, 4]. It was estimated that the primary formed compound is a Friedel's salt [5, 6]. Also, AFm and aluminium hydrates interact with CO<sub>2</sub>, which is always present in the environment [7]. It is established that AFm group minerals containing Cl<sup>-</sup> ions are formed [8].

In order to reduce the corrosion of cement stone, C<sub>3</sub>A quantity in cement clinker is limited. Furthermore, pozzolana additives can be used [9, 10, 11]. On the

other hand, controversial diverse opinions can be found in the literature on addition of limestone. I. Soroka et al. consider the effect of limestone on cement to be only physical, taking into account the increase in strength and resistance to seawater [12]. The addition of limestone filler to neat cement pastes and mortars reduces the diffusion coefficient of chloride ions [13]. Many authors supported the view that the limestone acts as an active participant and some CaCO<sub>3</sub> during hydration of Portland cement (PC) is taken up into system and reacts with C<sub>3</sub>A [14-16]. Moreover, the influence of substitution of limestone for gypsum on setting time of Portland cement was examined [17, 18].

In Lithuania there is a big amount of natural pozzolana. Pozzolana consists of amorphous SiO<sub>2</sub> and fine dispersed CaCO<sub>3</sub>. The aim of this work is to investigate the influence of pozzolana on the hydration process of tricalcium aluminate and the effect of Cl<sup>-</sup> ions to the formed hydrates.

## EXPERIMENTAL

The chemical composition of pozzolana is (wt.%): SiO<sub>2</sub> - 41, Al<sub>2</sub>O<sub>3</sub> - 2.6, CaO - 29.8, Fe<sub>2</sub>O<sub>3</sub> - 1.53. Loss on ignition - 23.41, hydraulic activity is 180 mg CaO/g. Specific surface area of pozzolana is 350 m<sup>2</sup>/kg, while of C<sub>3</sub>A - 320 m<sup>2</sup>/kg by Blaine.

Tricalcium aluminate was obtained as a result of the synthesis of limestone (99.0 %  $\text{CaCO}_3$ ) and technically pure  $\text{Al}_2\text{O}_3$  (99.0 %) stoichiometric mixture in a Nabertherm HTC 03/16 furnace. The synthesis was carried out by burning the above mentioned mixture twice at 1370 °C for 3 h. Prior to the second burning, the material was crushed and ground in a laboratory mill. The XRD analysis of the sample of the material obtained indicated that it was pure tricalcium aluminate, free of any XRD-detectable impurities. The content of free calcium determined by means of Franke's method amounted to 0.11 %, so it had no fundamental influence on the course of experiments.

Samples (20×20×20 mm) were formed of pure  $\text{C}_3\text{A}$  and those where 25 % of  $\text{C}_3\text{A}$  mass weight was replaced by pozzolana. The water to  $\text{C}_3\text{A}$  ratio was 0.5. During the first day, the samples are kept in moulds at  $20 \pm 1$  °C and 100 % air humidity. After 24 hours of formation, the samples were transferred into water and stored there for 27 days at  $20 \pm 1$  °C. After that samples were transferred to the saturated NaCl solution and stored there for 3 months at 20 °C. Hydration of samples was stopped using acetone.

Scanning electron microscopy (SEM) (Oxford ISIS Leo 440 i) coupled with energy dispersive X-ray spectrometer (EDS) was performed using an accelerating voltage of 20 kV and a working distance of 10 mm for SEM observation and a 200 s accumulation time for EDS analysis.

The X-ray powder diffraction data (XRD) were collected with DRON-6 powder X-ray diffractometer with Bragg-Brentano geometry using Ni filtered  $\text{CuK}_\alpha$  radiation, operating voltage 30 kV and emission current - 24 mA. The step-scan covered the angular range 5-60° ( $2\theta$ ) in steps of  $2\theta = 0.02^\circ$ .

IR spectra have been measured by the spectrometer Perkin Elmer FT-IR system Spectrum X. Samples were prepared by mixing 1 mg of the sample in 200 mg of KBr. The spectral analysis was performed in the range  $4000 \div 400 \text{ cm}^{-1}$  with spectral resolution of  $1 \text{ cm}^{-1}$ .

Simultaneous thermal analysis (STA: differential scanning calorimetry - DSC and thermogravimetry - TG) was carried out on a Netzsch instrument STA 409 PC Luxx with ceramic sample handlers and crucibles of Pt-Rh. Heating rate of 15°C/min, the temperature ranged from 30°C up to 1000°C under the ambient atmosphere.

## RESULTS AND DISCUSSION

### Hydration of $\text{C}_3\text{A}$ and the effect of chloride ions to formed hydrates

XRD analysis of  $\text{C}_3\text{A}$  samples hydrated in water for 28 days indicated that regular  $\text{C}_3\text{A}$  hydrates were formed. X-ray pattern (Figure 1, curve 1) shows the peaks characteristic to  $\text{C}_3\text{AH}_6$  ( $d$ -spacing - 0.514; 0.445; 0.336 nm),  $\text{C}_2\text{AH}_8$  ( $d$ -spacing - 0.785; 0.287; 0.270 nm) and for

gibbsite ( $\text{Al}(\text{OH})_3$ ) ( $d$ -spacing - 0.485; 0.437; 0.432 nm). Together with these compounds,  $\text{CaCO}_3$  ( $d$ -spacing - 0.304; 0.250 nm) and  $\text{CO}_3^{2-}$ -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.) were identified.

After 28 days of hydration under normal conditions,  $\text{C}_3\text{A}$  samples were transferred to the saturated NaCl solution and stored there for 3 months. Peaks of main  $\text{C}_3\text{A}$  hydrates -  $\text{C}_3\text{AH}_6$  and  $\text{C}_2\text{AH}_8$  were not identified by the XRD analysis. There are also no diffraction maxima characteristics to  $\text{CO}_3^{2-}$ -AFm (Figure 1, curve 2). Among the hydration products Friedel's salt ( $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ ) ( $d$ -spacing - 0.789; 0.394; 0.288 nm) and a complex compound hydrocalumite with inserts of  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  ions ( $\text{Ca}_8\text{Al}_4(\text{OH})_{24}(\text{CO}_3)\text{Cl}_2(\text{H}_2\text{O})_{1,6} \cdot (\text{H}_2\text{O})_8$ ) ( $d$ -spacing - 0.792; 0.399; 0.385 nm) dominated. Also formation of halite ( $\text{NaCl}$ ) ( $d$ -spacing - 0.282; 0.199 nm) was observed. The basal reflections of  $\text{CaCO}_3$  ( $d$ -spacing - 0.304; 0.250 nm) were more intense than after keeping for 28 days in water (Figure 1, curve 1). It should be noted that in both experiment conditions the peaks typical to gibbsite ( $d$ -spacing - 0.485; 0.437; 0.432 nm) were observed.

The hexagonal hydrates and monocarboaluminate were detected in the IR spectrum of samples of tricalcium aluminate hydrated for 28 days at normal conditions (Figure 2, curve1) with split bands  $\nu_3$  -  $\text{CO}_3^{2-}$  ( $1417\text{-}1366 \text{ cm}^{-1}$ ), together with  $\nu_2$  -  $\text{CO}_3^{2-}$  ( $876 \text{ cm}^{-1}$ ) and  $\nu_3$  -  $\text{CO}_3^{2-}$  ( $713 \text{ cm}^{-1}$ ). The absorption band in the frequency range of  $1643 \text{ cm}^{-1}$  belongs to deformations  $\delta(\text{H}_2\text{O})$ , whereas 3368 and  $3007 \text{ cm}^{-1}$  to stretching  $\nu(\text{H}_2\text{O})$  vibration of free water interacting with carbonate group. The sharp band near  $3670 \text{ cm}^{-1}$  indicates the existence of cubic hydrates [19], and band near  $3542 \text{ cm}^{-1}$  is characteristic to inner O-H band deformations. Absorption maxima in the frequency ranges of 422, 533, 670,  $957 \text{ cm}^{-1}$  are attributed to the inner deformations of  $[\text{AlO}_6]^{3-}$ .

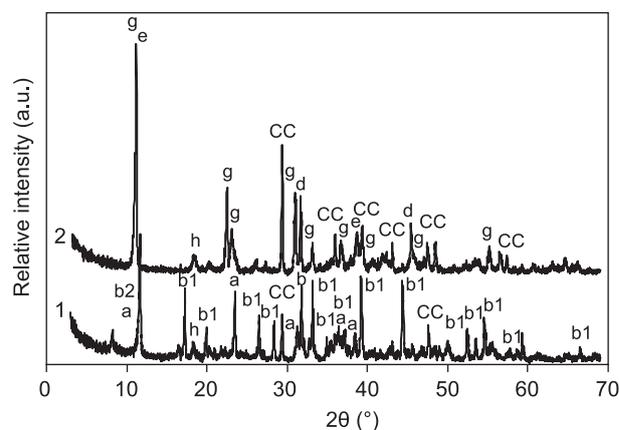


Figure 1. XRD patterns of tricalcium aluminate samples cured for: 1-28 days in normal conditions; 2-3 months in saturated NaCl solution; indexes: CC -  $\text{CaCO}_3$ , a -  $\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3 \cdot 11\text{H}_2\text{O}$ , b1 -  $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ , b2 -  $\text{Ca}_2\text{Al}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ , d - NaCl, e -  $\text{Ca}_8\text{Al}_4(\text{OH})_{24}(\text{CO}_3)\text{Cl}_2(\text{H}_2\text{O})_{1,6} \cdot (\text{H}_2\text{O})_8$ , g -  $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ , h -  $\text{Al}(\text{OH})_3$ .

After the transfer of samples to the saturated NaCl solution and keeping for 3 months (Figure 2, curve 2), absorption maxima in the frequency ranges of 423, 532, 790, 857, 976  $\text{cm}^{-1}$  characteristic to  $[\text{AlO}_6]^{3-}$  remain in the spectrum. Meanwhile the bands near 1423 and 1479  $\text{cm}^{-1}$

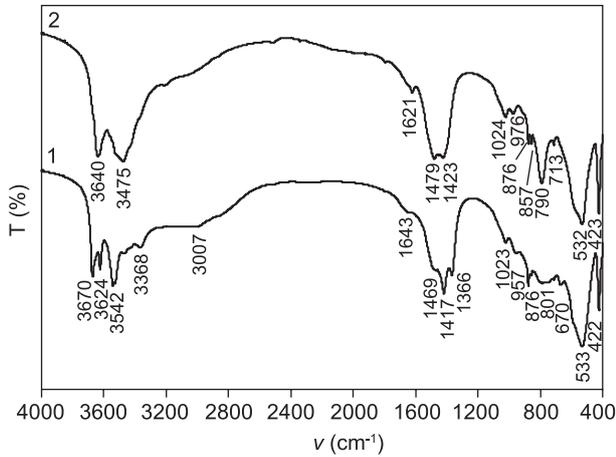


Figure 2. FT-IR spectra of tricalcium aluminate samples cured for: 1-28 days in normal conditions; 2-3 months in saturated NaCl solution.

indicate  $\nu(\text{CO}_3^{2-})$  vibrations in the  $\text{CaCO}_3$  compound, which confirms the continuing carbonation and the reduced stability of  $\text{CO}_3^{2-}$  - AFm. Absorption band in the range of 3475  $\text{cm}^{-1}$  is attributed to hydrogen-bonded water molecules in Friedel's salt [20, 21].

SEM images of  $\text{C}_3\text{A}$  samples hydrated in the water for 28 days show the conglomerates of indefinite structure (Figure 3, spectrum 1) and plate shaped crystals (Figure 3, spectrum 2), which size is about 3-7  $\mu\text{m}$ .

After soaking the samples in the saturated NaCl solution and keeping here for 3 months, SEM analysis also shows conglomerates of indefinite structure and plate shape crystals (Figure 4), with size about 10  $\mu\text{m}$ . It was identified by the EDS that in the plate shape crystals (Figure 4, spectrum 2) the amount of  $\text{Cl}^-$  and  $\text{Ca}/\text{Al}$  ratio is less than in the conglomerates of indefinite structure (Figure 4, spectrum 1). Also  $\text{Na}^+$  is inserted only into conglomerates of indefinite structure.

In thermal analysis curve of  $\text{C}_3\text{A}$  samples hydrated for 28 days under normal conditions (Figure 5) three significant endothermic peaks at 165, 300 and 742  $^\circ\text{C}$  and weak exothermic peak at 864  $^\circ\text{C}$  temperature are observed. Endothermic peak at 165 $^\circ\text{C}$  is mainly due

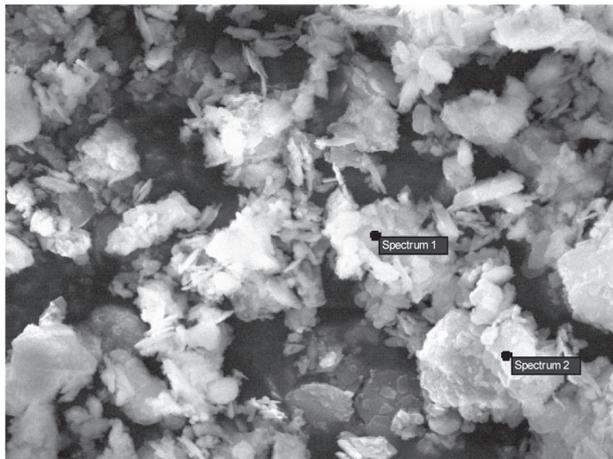


Figure 3. SEM micrographs and EDS curves of tricalcium aluminate samples cured for 28 days in normal conditions.

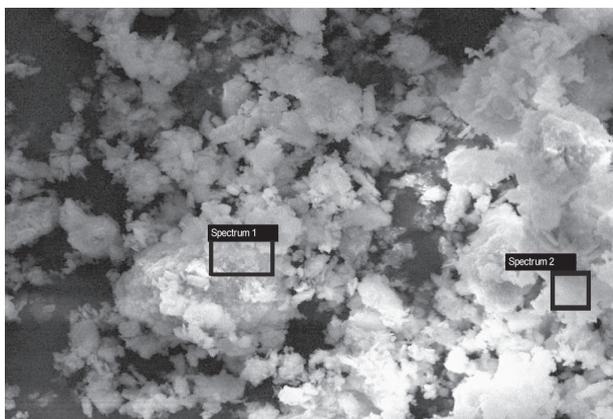


Figure 4. SEM micrographs and EDS curves of tricalcium aluminate samples cured for 3 months in saturated NaCl solution.



of this sharp band was affected by the fact that  $\text{CaCO}_3$  is a constituent of pozzolana. IR spectrum also maintained absorption maxima in the frequency ranges of 1107 and  $967\text{ cm}^{-1}$  characteristic to Si-O bonds.

SEM images of  $\text{C}_3\text{A}$  samples with pozzolana additive hydrated for 28 days at normal conditions (Figure 9) show crystals of similar microstructure like in the samples without additive.

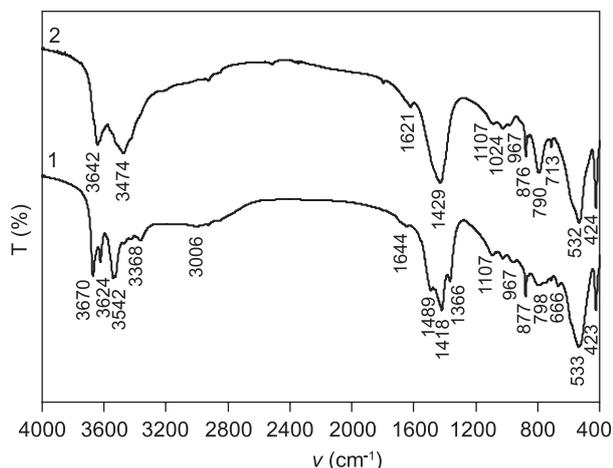


Figure 8. FT-IR spectra of tricalcium aluminate with pozzolana samples cured for: 1-28 days in normal conditions; 2-3 months in saturated NaCl solution.

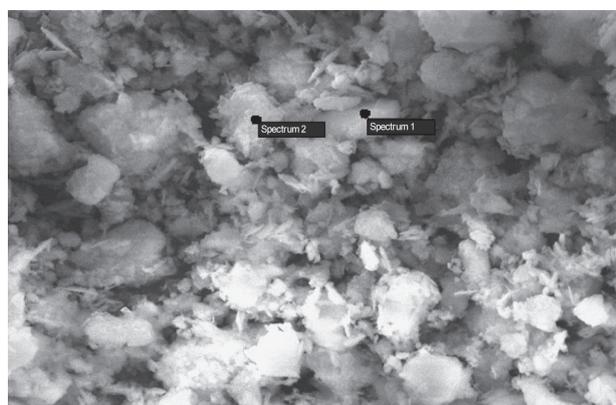


Figure 9. SEM micrographs and EDS curves of tricalcium aluminate with pozzolana samples cured for 28 days in normal conditions.

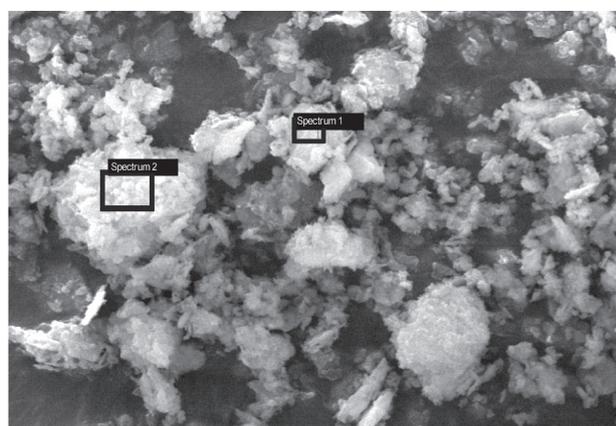
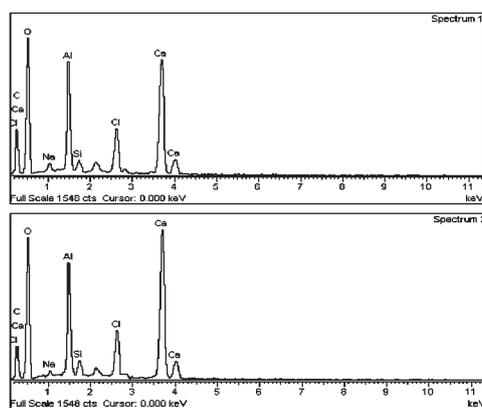
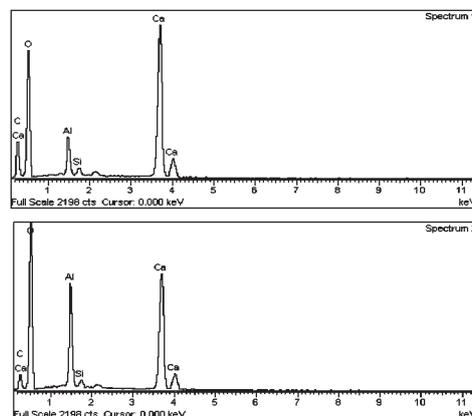


Figure 10. SEM micrographs and EDS curves of tricalcium aluminate with pozzolana samples cured for 3 months in saturated NaCl solution.

After soaking the samples into the saturated NaCl solution and keeping here for 3 months, only plate shape crystals are visible (Figure 10). EDS data indicate almost identical composition. It should be noted that amount of Cl is less than in samples without pozzolana additive. This data confirm that pozzolana additive reduces the penetration of  $\text{Cl}^-$  ions into the  $\text{C}_3\text{A}$  hydrates.

Thermogram of sample with pozzolana additive stored for three months in saturated NaCl solution (Figure 12) shows endothermic peaks at 136, 265°C and exothermic peak at 656°C, characteristic for Friedel's salt and a "shoulder" at 160°C, characteristic for hydrocalumite with inserts of  $\text{CO}_3^{2-}$  ions. Thermogram also shows the exothermic peak at  $\sim 800^\circ\text{C}$ , indicating the presence of  $\text{CO}_3^{2-}$  - AFm compound. The intensity of this exothermic peak is higher than with the sample after 28 days of hydration under normal conditions (Figure 11), but shifted towards the lower temperatures and the amount of mass loss decrease to 0.5 %. This compound was not observed by XRD method probably due to its low degree of crystallinity. In addition, thermogram maintains the endothermic peak at 300-305 °C, characteristic to cubic aluminium hydrate ( $\text{C}_3\text{AH}_6$ ), but its intensity is less than for the sample after 28 days of hydration under normal conditions (Figure 11).



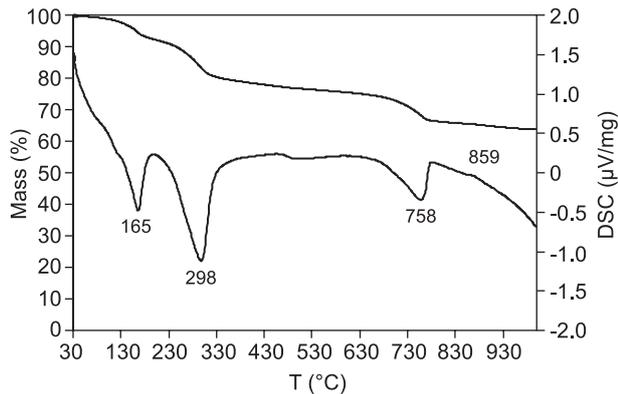


Figure 11. DSC–TG curves of tricalcium aluminate with pozzolana additive samples cured for 28 days in normal conditions.

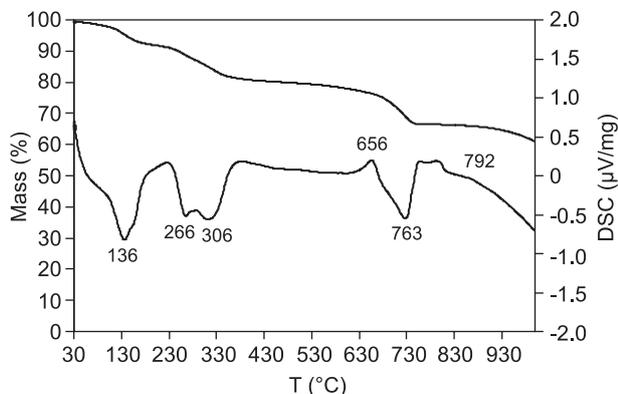


Figure 12. DSC–TG curves of tricalcium aluminate with pozzolana additive samples cured for 3 months in saturated NaCl solution.

## CONCLUSIONS

In normal conditions the additive of pozzolana has no substantial effect on the course of  $C_3A$  hydration, but a part of  $Si^{4+}$  ions penetrates into the structure of aluminium hydrates.

Regular  $C_3A$  hydrates and  $CO_3^{2-}$  - AFm affected by saturated NaCl solution become unstable and take part in reactions producing Friedel's salts and a complex compound – hydrocalumite with inserts of  $CO_3^{2-}$  ions.

Pozzolana additive reduces the penetration of  $Cl^-$  ions to the structure of  $C_3A$  hydrates and impedes the formation of aluminium chloride hydrates. A part of cubic aluminium hydrates,  $CO_3^{2-}$  - AFm and  $C_3A$  hydrate substituted with  $Si^{4+}$  remained stable under these conditions.

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