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To cite this article: L Galvankova *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **583** 012020

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# Stabilization of the ammonia in SNCR fly ash - the influence of tannins presence on the preparation of an autoclaved aerated concrete

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**Abstract.** Due to the legislative regulations on NO<sub>x</sub> emissions, a selective non-catalytic reduction (SNCR) technology had been introduced to a coal combustion process in power plants. The valuable by-product, fly ash, contains ammonia in the form of soluble salts, e.g. NH<sub>4</sub>HSO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. After mixing SNCR fly ash with cement, thanks to the rise of pH, the toxic ammonia releases and contaminates the working area, so the presence of these salts is undesirable in an autoclaved aerated concrete (AAC) manufacturing process. A possible solution is the conversion of soluble ammonium salts to an insoluble form. Tannins are a class of polyphenolic biomolecules, which react with the ammonium ions to form insoluble compounds. The AAC samples were mixed using SNCR fly ash and two different ammonium binding additives - pure tannic acid and the cost-effective animal food supplement containing chestnut tannins. The influence of additives on the hydration process of the starting mixture was studied by isoperibolic calorimetry. The results suggest that the cost-effective source of tannins retards the hydration. The presence of insoluble compounds was studied by the infrared spectroscopy.

## 1. Introduction

The strict regulations of nitrogen oxides (NO<sub>x</sub>) emissions induce the introduction of NO<sub>x</sub> control technologies to all industry levels. A significant amount of NO<sub>x</sub> emissions is produced in power plants during the combustion process, so the introduction of air pollution control technologies is inevitable. There are several technologies concerning NO<sub>x</sub> removal, but thanks to its efficiency and low capital expense, the selective non-catalytic reduction process (SNCR) plays an important role in European countries [1]. SNCR is a post-combustion technology for reducing NO<sub>x</sub> by injecting ammonia (NH<sub>3</sub>) or urea or other ammonia type reactant into the furnace at the determined location. The reactants selectively react with NO<sub>x</sub> at the temperature ranging from 875°C to 1150°C to produce nitrogen and water. Besides other factors, e.g. the NO<sub>x</sub> concentration in flue gas, reagent injection rate, etc., the temperature of the reaction is the most important parameter which affects the efficiency of the process [2]. By increasing the temperature above 1150°C, the reducing ammonia based reactant is oxidized results in additional NO<sub>x</sub> production. Below the 800°C, the temperature is too low to the reaction could proceed

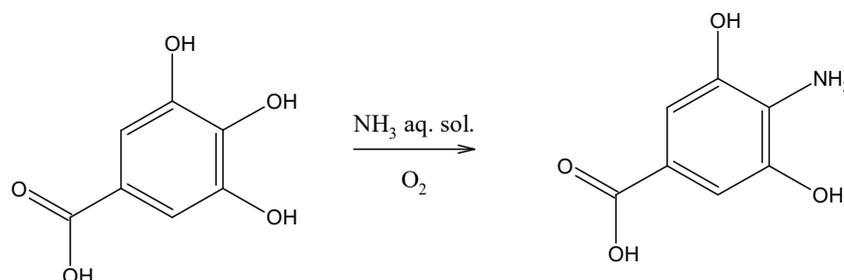


so the injected  $\text{NH}_3$  remains unreacted. Even if the temperature rises above  $870^\circ\text{C}$ , a part of  $\text{NH}_3$  does not react. The unreacted  $\text{NH}_3$  is so-called “ammonia slip” [3].

Besides the ammonia slip, the flue gas contains  $\text{SO}_3$  and water. These compounds react to form soluble ammonium salts, mainly ammonium bisulfate ( $\text{NH}_4\text{HSO}_4$ ) and ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) [4]. During the cooling process, these salts are absorbed on the surface of fly ash. Fly ash from coal-fired power plants is a useful secondary raw material partially re-used in building industry as a pozzolan material [5]. It is commonly used as a source of  $\text{SiO}_2$  instead of silica sand in lightweight building material - autoclaved aerated concrete (AAC) [6]. AAC has outstanding properties such as fire resistance, thermal and sound insulation and excellent manipulability. In past decades the fly ash AAC attracts attention thanks to the global interest in re-using of energetic by-products. Ammonia captured in the fly ash in the form of soluble salts could be released as an ammonium gas or could be leached to water. Under a highly alkaline environment, which is created when water is added to a system containing cement and lime ( $\text{CaO}$ ), the ammonium salts react with water and liberate ammonium gas as shown in the equation (1) [3]. The release of toxic gas during the production deteriorates the working place and could cause serious injuries. Dilmore and Neufeld [7] used the ammoniated fly ash after SCR (selective catalytic reduction) for the production of AAC. They conclude that using ammoniated fly ash as a source of  $\text{SiO}_2$  does not affect the mechanical properties of prepared AAC samples.

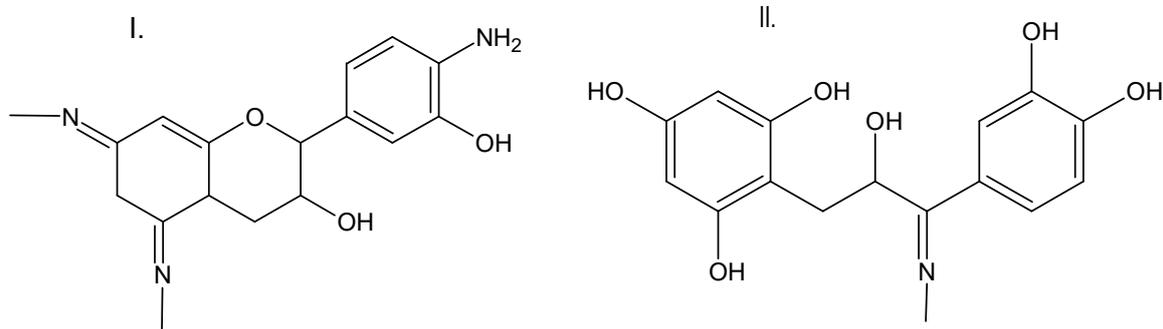


Tannins are a class of natural polyphenolic biomolecules that bind to and precipitate proteins and other organic compounds [8]. They are found in a variety of plants, mainly in wood and fruits. Tannin compounds could be divided into two main groups differing in chemical composition. Hydrolysable tannins are a mixture of simple phenols (gallic and ellagic acid) and could be hydrolysed by weak acids or bases to carbohydrates and phenolic acids. Condensed tannins are polymers formed by the condensation of flavans. The industrially produced tannins are mainly extracted from plants by hot water or other solvents. Tannins react with  $\text{NH}_3$  in water to form insoluble compounds. Hashida et al. [9] concluded that the amination of gallic acid and related polyphenols with pyrogallol nucleus is regioselective and proceeds only in the presence of  $\text{O}_2$  (figure 1). Amination of condensed tannins was studied by Braghiroli et al. [10]. The reaction with ammonia leads to multi-amination of phenolic hydroxy groups and cross-linking through the nitrogen bridges, which causes the gelation of the tannin/ammonia mixture in water. The possible reaction products are shown in figure 2. The amination of organic compounds in wood is used for a process called ammonia fuming, during which the colour of the wood changes. Miklečić et al. [11] concluded that the amount of water extractable tannin decreases rapidly after the ammonia fuming, while the amount of bonded nitrogen increases.



**Figure 1.** Reaction scheme of amination of gallic acid [9].

As was mentioned above, during the preparation of AAC the ammonium gas is released from the SNCR fly ash which deteriorates the working space. The possibility of binding the ammonia into the insoluble compound using natural tannins is examined. For this purpose, the extract from chestnut wood and pure tannic acid was used. The influence of these additives on the production of AAC was observed.



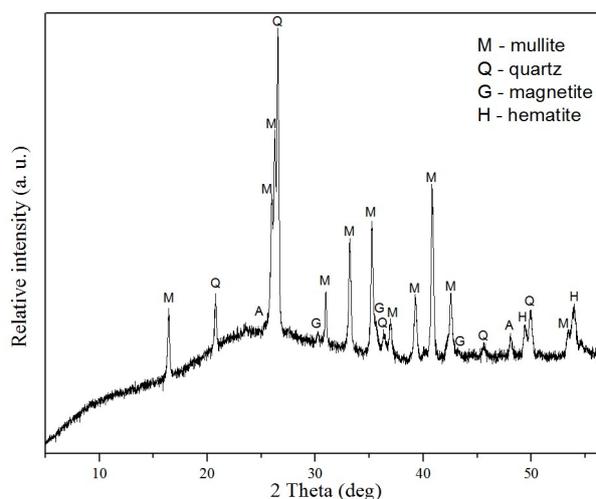
**Figure 2.** Two possible products of amination of condensed tannins [10].

## 2. Experimental

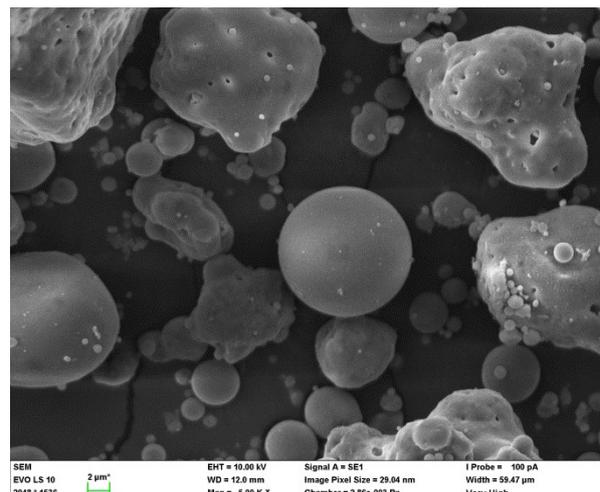
### 2.1. Starting materials

The coal fly ash from Počerady power plant was used as a source of  $\text{SiO}_2$ . The phase composition was determined by X-ray diffractometry analysis; the diffractogram is shown in figure 3. The main detected crystalline phases were mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ), quartz ( $\text{SiO}_2$ ), hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ). The morphology of fly ash particles was observed by scanning electron microscope (figure 4). The fly ash consists of spherical particles with diameter around  $10 \mu\text{m}$ . The total ammonium nitrogen in a raw fly ash was determined to 48 mg of  $\text{NH}_3/\text{kg}$  of fly ash.

As tannin additives, two sources were used. The first was the commercial dietary product for animals called Farmatan (F). It is a natural chestnut wood extract and the producer declares that there are 74 grams of chestnut tannin in 100 grams of Farmatan, the rest is a sweetener. As the second tannin source, the tannic acid (T, pharmaceutical purity, Lach-Ner) was used. Tannins were dissolved in water and mixed with the dry fly ash. After 24 hours the mixture was dried in a laboratory dryer and stored. The amount of added tannins differs from 0 (refer as reference) to 2 wt. % to the amount of fly ash. Except for the tannin enriched fly ash, the starting mixture was mixed from Portland cement (CEM I), quicklime (CL 90), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and aluminium powder. Additionally, the tap water at a temperature of around  $50^\circ\text{C}$  was used.



**Figure 3.** XRD pattern of raw fly ash.



**Figure 4.** SEM image of raw fly ash.

## 2.2. Isoperibolic calorimetry

The influence of tannin additives on the hydration process was studied by isoperibolic calorimeter constructed at Faculty of Chemistry, Brno University of Technology. The construction of the calorimeter is described elsewhere [12]. The mixture for isoperibolic calorimetry was made from 64.6 wt. % fly ash, 25.5 wt. % quicklime, 9.9 wt. % Portland cement. The w/b (water-binder) ratio was set to 0.55. Immediately after the mixing, the mixture was placed to the sealed container and the measurement was started. The samples are labelled according to the type and amount of tannin additive added to fly ash, e.g. sample C\_F0.5 corresponds to a sample prepared from fly ash with 0.5 wt. % of Farmatan.

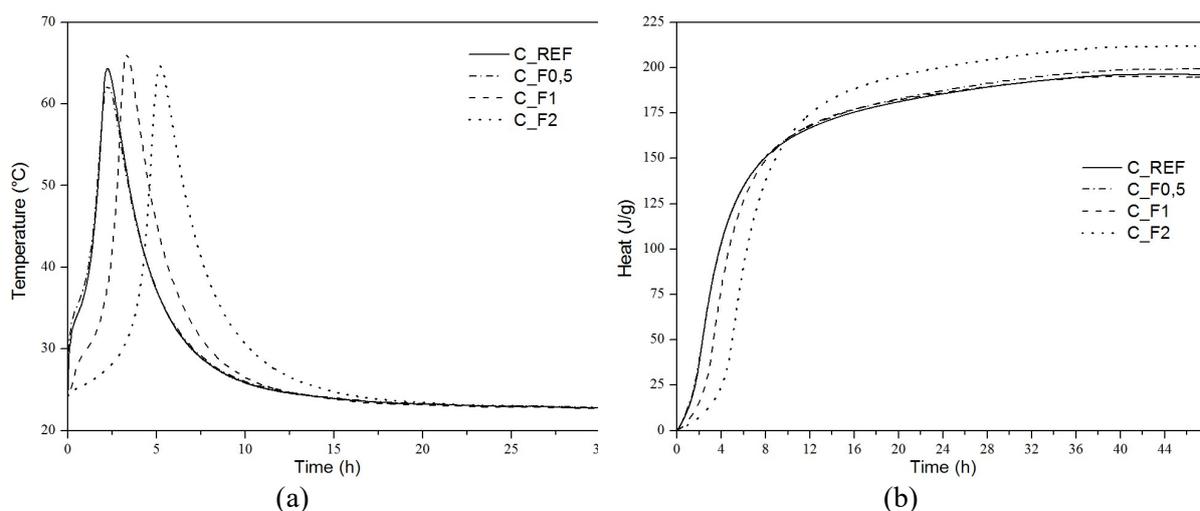
## 2.3. AAC manufacturing and characterization of products

The mixture for manufacturing of AAC blocks was made from 57.3 wt. % fly ash, 25.4 wt. % quicklime, 11.6 wt. % Portland cement, 5.7 wt. % gypsum and a trace of aluminium powder acting as foaming agent. The w/b ratio was set to 0.6. The prepared mixture was poured into iron moulds, where it expanded to its final volume. The hardened samples were removed from moulds after 24 hours and dried at 40°C for 24 hours. The prepared blocks were cured in a laboratory autoclave to obtain their final properties. The conditions of the hydrothermal reaction were set to 190°C and 1.2 MPa. The reaction was stopped after 8 hours and the prepared AAC blocks were stored and examined. The samples are labelled according to the same principle as the samples for calorimetry, but instead of C\_F0.5, it is A\_F0.5 as an autoclaved sample.

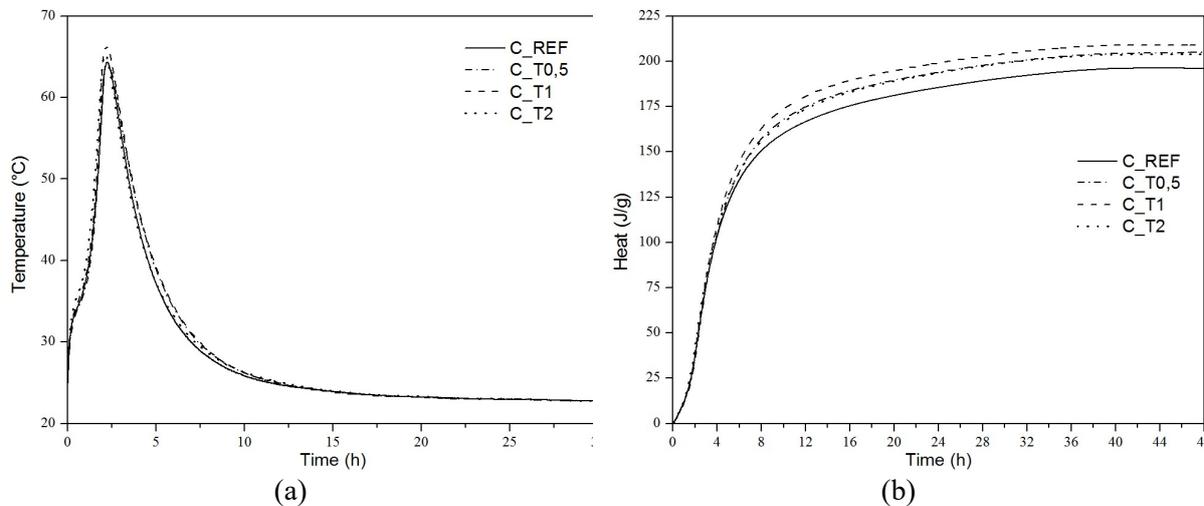
Phase composition of autoclaved samples were examined by X-ray powder diffraction (XRD) using X-ray diffractometer Empyrean (Pananalytical) with Cu K $\alpha$  radiation from 5 to 90° 2 theta and the step 0,013°. FTIR spectroscopic measurements were conducted on chosen samples using FTIR-ATR spectrometer iS50 from Thermo scientific. The total ammonium nitrogen (TAN) concentration in all autoclaved samples was determined according to an international standard ISO 7150-1 [13].

## 3. Results and discussion

The influence of the tannin additives to a cement-lime-fly ash system was examined by isoperibolic calorimetry. This method is suitable for a study of the evolution of heat during the hydration of silicate binders. The results are presented as a dependence of the temperature of the testing mixture placed in the sealed container on time (figure 5–6 a). The course of heat development during the hydration process was determined by integration of temperature curve and is shown in figure 5–6 b.

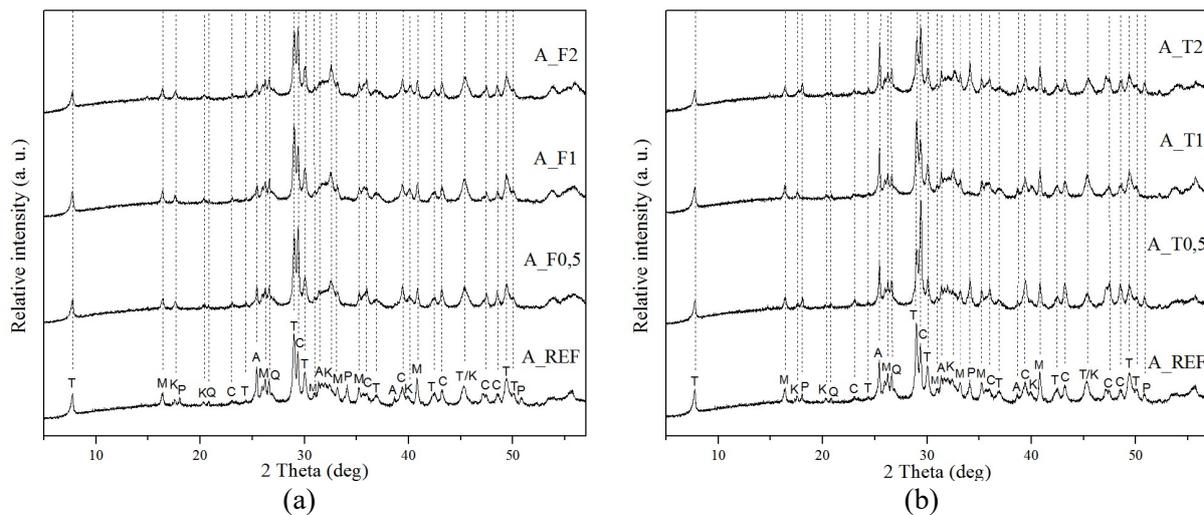


**Figure 5.** The results of isoperibolic calorimetry for samples prepared using Farmatan: (a) differential curves (b) integral curves.



**Figure 6.** The results of isoperibolic calorimetry for samples prepared using Tannic acid: (a) differential curves (b) integral curves.

An important advantage of calorimetry is the possibility to estimate the start of setting of the mixture. The results indicate that the addition of Farmatan in more than 1 wt. % delays the start of the setting. As was mentioned earlier, Farmatan consists of chestnut tannin and sugar. It is known, that sugars retard cement hydration [14]. After the addition of water, the main clinker minerals ( $C_3S$  and  $C_3A$ ), started to dissolve and after the saturation of the system with  $Ca^{2+}$  and  $SiO_4^{4-}$  ions, the C-S-H phase and portlandite are formed. In the presence of sugars, the  $Ca^{2+}$  ions form calcium complexes with sugars, which are bound to the  $C_3S$  surface and thereby slow down the nucleation of C-S-H phases [15]. In the sample containing 2 wt. % of Farmatan, the setting was delayed for about 3 hours. The amount of evolved heat in Farmatan samples is comparable with the reference. Contrary, when using pure tannic acid as a tannin additive, the hydration is not influenced in all studied samples. Because the chestnut tannin in Farmatan belongs to a group of hydrolysable tannins [16] same as the tannic acid, it can be stated that the delay in hydration in Farmatan samples is caused only by sugars. Pehanich et al. [17] suggested that tannins could act as cement hydration retardants, but this problem was not sufficiently examined until now.



**Figure 7.** XRD patterns of final AAC products with different tannin additive: (a) Farmatan (b) Tannic acid (T = Tobermorite, M = Mullite, K = Katoite, P = Portlandite, Q = Quartz, C = Calcite, A = Anhydrite).

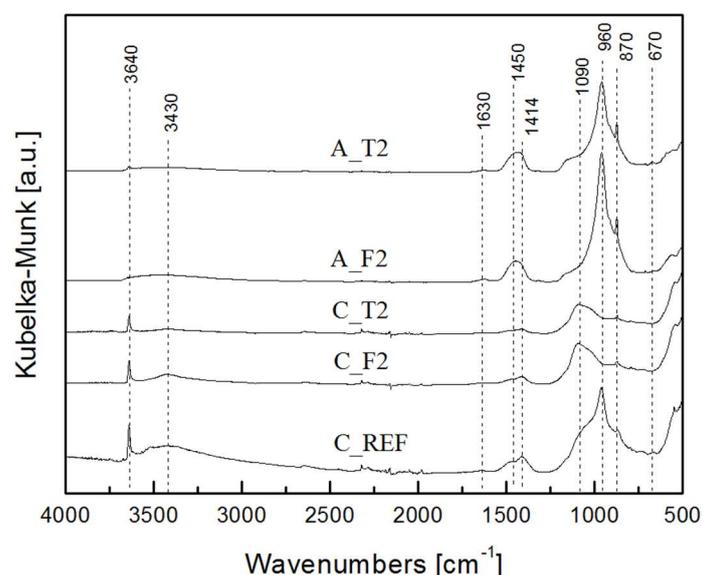
The phase composition of autoclaved samples was determined by XRD analysis. The diffractograms of all samples are shown in figure 7. During the hydrothermal reaction mineral tobermorite ( $\text{Ca}_5\text{Si}_6\text{O}_{17}\cdot 5\text{H}_2\text{O}$ ) is formed acting as a main binding phase in the AAC [6]. Besides tobermorite, katoite ( $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ ,  $x = 1.5-3.0$ ) was formed. There is a trace of unreacted CaO in a form of portlandite ( $\text{Ca}(\text{OH})_2$ ) and calcite ( $\text{CaCO}_3$ ). The unreacted phases from fly ash, mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ) and quartz ( $\text{SiO}_2$ ), were detected in all samples. The presence of unreacted gypsum in the form of anhydrite ( $\text{CaSO}_4$ ) was observed in all samples. Generally, this phase composition well agrees with the reported ones [6, 18]. There is no significant influence of the presence of tannin-based compounds to the final phase composition of prepared AAC samples.

Because the ammonium in fly ash is in the form of water-soluble salts, the amount of ammonium nitrogen in prepared AAC samples was measured. The results are presented in table 1. It is evident that there is no water extractable ammonium nitrogen in all samples, even in the reference sample without the tannin additives. This is probably caused by the fact that during the mixing phase of the starting mixture, the pH rise and the ammonium is released in the gas form, see equation (1). This problem was studied earlier [19], and the results are with good agreement with that obtained in this study. From the obtained results there is no possibility how to prove that the ammonium nitrogen reacts with tannin additives. It could be stated, that if the reaction proceeds the reaction products are not soluble in the water.

**Table 1.** The concentration of total ammonium nitrogen in autoclaved samples.

Sample	A REF	A F0.5	A F1	A F2	A T0.5	A T1	A T2
$C_{\text{TAN}}$ [mg of $\text{NH}_3$ /kg of fly ash]	0.66	0.28	0.27	0.35	0.39	0.52	0.49

The presence of different functional groups could be studied by Infrared microscopy (IR). Five samples were chosen for IR analysis, two samples after the calorimetry measurement and two samples of final AAC, all containing 2 wt. % of tannin additive and a calorimetry reference. The results of the IR analysis are shown in figure 8. The stretching vibrations of O–H groups in  $\text{H}_2\text{O}$  or possibly hydroxyls are characterized as broadband centered at around  $3400\text{ cm}^{-1}$  mainly in samples after calorimetry. The band at  $1630\text{ cm}^{-1}$  corresponds to the bending vibration of molecular water, probably in C–(A)–S–H structures. The sharp band at  $3640\text{ cm}^{-1}$  can be attributed to less strongly hydrogen-bonded water molecules in an interlayer of  $\text{Ca}(\text{OH})_2$ , which is consistent with the results obtained by Yu et al. [20]. The intensity of this band decreases in autoclaved samples because during the hydrothermal reaction the excess portlandite reacts with  $\text{SiO}_4^{4-}$  to form tobermorite and katoite. The bands at  $1400\text{--}1500\text{ cm}^{-1}$  and  $870\text{ cm}^{-1}$  can be attributed to asymmetric stretching of  $\text{CO}_3^{2-}$ . The presence of carbonates in autoclaved samples was detected by XRD, while in the samples after calorimetry, the unreacted portlandite probably undergo contamination of air  $\text{CO}_2$ . The most intense bands occurring in the range  $1100\text{--}900\text{ cm}^{-1}$  are attributed to asymmetrical stretching vibrations of silicate tetrahedra ( $\text{SiO}_4$ ). Yu et al. [20] assigned the different stretching bands of Si–O in calcium silicate hydrates. The band at  $960\text{ cm}^{-1}$  corresponds to Si–O stretching of  $\text{Q}^2$  sites. The intensity increase with the ordering of structure of C–S–H compounds. The broadening of this band towards higher frequency is due to the presence of  $\text{Q}^3$  and  $\text{Q}^4$  sites in  $\text{SiO}_2$  gel. The IR results of autoclaved samples are in good agreement with results obtained by Wu et al. [21], who performed an IR spectroscopy on AAC samples. The broadband centered at  $1090\text{ cm}^{-1}$  could be also attributed to stretching vibrations of C–N as R– $\text{NH}_2$ , but it could not be differentiated to which kind of stretching this band corresponds.



**Figure 8.** IR spectra of chosen samples.

#### 4. Conclusions

The influence of the addition of tannin-based additives to cement-lime-SNCR fly ash system was studied. Tannins react with ammonium ions in water to form insoluble compounds. Fly ash after SNCR is enriched by  $\text{NH}_3$  in a form of water-soluble salts ( $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ ). During the mixing phase, when the pH of the mixture rises, ammonium is released in a form of gas and deteriorates the working space.

Tannin additives were added to a starting mixture in a range from 0.5 to 2 wt. % to the amount of ammoniated fly ash. Two tannin additives were used; the cost-effective dietary product for animals containing chestnut tannin and sugar called Farmatan and pure tannic acid. Both additives belong to a group of hydrolysable tannins. The presence of Farmatan in a cement mixture causes delays in the start of the setting, probably thanks to obtained sugars in an additive. Sugars act as retarding agents. The pure tannic acid does not affect the hydration of the cement-lime-fly ash system. From this reason even if Farmatan is a low-cost material, it is not appropriate to use it as an ammonium binding additive in a cement-lime system. The effect of tannin additives to a final phase composition of the autoclaved aerated concrete using fly ash as a  $\text{SiO}_2$  source was not observed. The final composition of all prepared AAC samples was much alike. Unfortunately, the creation of insoluble ammonium compounds with tannins was not confirmed, because no suitable analytical method to prove the presence of  $\text{R-NH}_x$  was found.

#### Acknowledgements

This study was supported by the project of specific research FAST/FCH-J-18-5411 with the financial support of Brno University of Technology.

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