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3.1. Introduction

The development of infrastructure leads to an increase in the demand for natural resources, which are limited, and the building industry in particular consumes a huge amount of raw materials for the production of building materials. Ordinary Portland Cement (OPC) will remain a key player in the future, although its production is energy demanding and contributes to the ongoing increase in global CO_2 emissions. There are two possible ways of reducing the negative impact of the building industry. One way is to utilize secondary raw materials as supplementary cementing materials, among which blast furnace slag is the most effective at reducing CO_2 footprint (Keun-Hyeok 2015). The other way is to utilize alkali-activated concrete. This type of material is even more effective in reducing CO_2 emissions and energy consumption. Different sources show that the global warming potential of alkali-activated concrete is approximately 40–70% lower than that of OPC concrete (McLellan 2011, Keun-Hyeok 2013).

Alkali activation was introduced and brought into practice by Gluchovsky (Gluchovsky 1959). It is a reaction of siliceous material which contains a highly reactive vitreous phase (blast furnace slag, fly ash, metakaolin, silica fume etc.) with alkali activator, usually alkaline hydroxide, silicate or carbonate, which is added either in the form of a solution or a soluble solid. Davidovits who working on numerous aluminosilicate-based formulations from early 1980s named these materials ‘Geopolymers’ (Davidovits 1982). The mechanical properties and application possibilities of alkali-activated materials, especially with slag as aluminisilicate precursor, are very similar to those of OPC concrete. However, in contrast to OPC-based binders, these materials offer superior properties such as higher corrosion resistance against acid or sulphate attack (Bakharev 2005, Rovnaníková 2002) and also higher resistance to elevated temperatures and fire (Rovnaník 2013, Lyon 1997). The major disadvantage is increased shrinkage. This effect is caused by both autogenous and drying shrinkage and finally results in volume contraction, micro-cracking and the deterioration of tensile and bending properties (Shi 2006).

Multi-walled carbon nanotubes (MWCNTs) exhibit extraordinary mechanical properties, with the Young's modulus of an individual nanotube being around 1 TPa and tensile stresses being in the range of 65–93 GPa (Belytschko 2002). MWCNTs are thus the most promising nanomaterials for enhancing the mechanical fracture properties of building materials, and their resistance to crack propagation. Some problems have appeared connected with the aggregation of MWCNTs, which reduces the efficiency of single nanotubes. Nevertheless, effective dispersion can be achieved by applying ultrasonic or high shear rate mechanical dispersion with the use of a surfactant (Konsta-Gdoutos 2010-1).

The main aim of this work is to apply MWCNTs as a shrinkage reducing admixture for alkali-activated materials. Regarding the properties of MWCNTs, they have a great potential to reduce the cracking tendency of silicate-based materials caused by autogenous and drying shrinkage, which is one of the essential problems arising during the practical application of materials in the building industry (Sanchez 2010, Konsta-Gdoutos 2010-2).

Since microcracks have a strong negative effect on mechanical performance, the efficiency of MWCNTs as a potential nanoscale reinforcement and shrinkage reducing agent can be monitored by the fracture behaviour of the composite material and by acoustic emission methods. In this study, fracture testing and acoustic methods were applied to determine the performance of MWCNTs in mortars with three different types of basic binder: alkali-activated slag, fly ash geopolymer and metakaolin geopolymer.

3.2. Materials and methods

The alkali-activated materials were composed of basic aluminosilicate precursor and water glass as alkaline activator. Among plenty of reactive aluminosilicate materials three basic and the most common commercially available were chosen. Two of them are considered secondary raw materials (granulated blast furnace slag, coal fly ash) and one is primary product (metakaolin). The chemical composition of aluminosilicate precursors together with the fineness is introduced in Table 3.1. A commercial sodium silicate solution with SiO_2/Na_2O = 1.6 and 43 wt% of dry mass was used as an activator. Quartz sand with a maximum grain size of 2.5 mm was used as aggregate. Multi-walled carbon nanotubes (Graphistrength® CW 2-45, Arkema, France) were used as received. Since MWCNTs are commonly not water-soluble, the received MWCNTs already contained 55% of carboxymethyl cellulose as a dispersing agent. Carbon nanotubes were used in the form of 1 and 5% dispersions. In order to prepare the aqueous dispersions, the procedure prescribed by the producer was followed. MWCNT pellets were dissolved in hot water and dispersed bundles of MWCNTs were further disintegrated by mechanical homogenizer (3 h at 14000 rpm).

Table. 3.1. Chemical composition and characteristics of aluminosilicate precursors

Material	Slag	Fly ash	Metakaolin
SiO2 (%)	39.66	49.82	55.01
Al2O3 (%)	6.45	24.67	40.94
Fe2O3 (%)	0.47	7.05	0.55
CaO (%)	40.12	3.91	0.14
MgO (%)	9.50	2.68	0.34
Na2O (%)	0.33	0.70	0.09
K2O (%)	0.55	2.78	0.60
d10 (μm)	5.2	9.1	3.4
d50 (μm)	15.5	60.7	6.3
d90 (μm)	38.3	200.4	11.6

The mixture composition is given in Table 3.2. The MWCNT content was 0.05, 0.10, 0.15, and 0.20% of the weight of the solid aluminosilicate, and the results of the tests were compared with a reference mixture, which was prepared without MWCNTs but following the same procedure. The mixtures were cast into 40 × 40 × 160 mm prismatic moulds and left to set. The curing process differed for different types of basic material. Metakaolin and fly ash geopolymer specimens were covered with plastic sealant directly after casting to keep moisture in the fresh material. Meanwhile metakaolin geopolymer was treated only at ambient temperature, the moulds with fly ash geopolymer were kept at first at ambient temperature for 3 days and then heated at 60 °C for 24 h. After demoulding the hardened specimens were stored in the laboratory conditions (22 ± 2 °C, φ = 45 ± 5%) till the age of 28 days. Alkali-activated slag set within 24 hrs and the hardened samples were immersed in water for 27 days, then pulled out of the water and allowed to dry spontaneously under ambient conditions for 24 hrs prior to fracture testing. Samples are identified with the following designation: (aluminosilicate matrix) (percentage of MWCNTs). For example, sample of fly ash geopolymer with 0.1% of MWCNTs is identified as FAG 0.10.

Experiments were carried out on a Heckert FP 10 mechanical testing machine with the measuring range 0–2000 N. During the experiment, the three-point bending test was performed on specimens with a central edge notch cut to about 1/3 of specimen depth. The load span was 120 mm. The effective crack extension method was used to evaluate a load–deflection (*F*–*d*) diagrams. The *F*–*d* diagram was used for the calculation of elasticity modulus from the first (almost linear) part of the diagram, and for the calculation of effective fracture toughness and specific fracture energy. The effective fracture toughness values were determined using the Effective Crack Model (Karihaloo 1995), which combines linear elastic fracture mechanics and the crack length approach. Estimations of fracture energy values according to the RILEM method were calculated using a 'work of fracture' value (RILEM 1985). Informative compressive strength values were also determined for all specimens on the fragments remaining after the fracture experiments had been performed.

Table. 3.2. Mix composition of alkali-activated materials with MWCNTs

Material	Component	MWCNTs content				
		0%	0.05%	0.10%	0.15%	0.20%
AAS	Slag (g)	450				
	Sodium silicate (g)	180				
	Sand (g)	1350				
	1% MWCNTs (g)	0	22.5	45	67.5	90
	Water (ml)	95	72.5	50	27.5	5
FAG	Fly ash (g)	350				
	Sodium silicate (g)	280				
	Sand (g)	1050				
	1% MWCNTs (g)	0	17.5	35	52.5	70
	Water (ml)	70	52.5	35	17.5	0
MKG	Metakaolin (g)	350				
	Sodium silicate (g)	350				
	Sand (g)	1050				
	1% MWCNTs (g)	0	17.5	35	52.5	70
	Water (ml)	120	103.5	85	67.5	50

The initiation of cracks during the fracture tests was also monitored via the acoustic emission (AE) method. AE is the term for the noise emitted by materials and structures when they are subjected to stress. Stresses can be mechanical, thermal or chemical in nature. The noise emission is caused by the rapid release of energy within a material due to events such as crack formation that occur under applied stress, generating transient elastic waves which can be detected by piezoelectric sensors. In this case the AE method detects and characterizes the development of the fracture cracking process and only evaluates the damaging activity while it is occurring (Grosse 2008). A guard sensor eliminated mechanical and electrical noise. Four acoustic emission sensors were attached to the surface of the specimen with beeswax (Fig. 3.1). Acoustic emission signals were recorded by DAKEL XEDO measuring equipment with four IDK-09 acoustic emission sensors with a 35 dB preamplifier.

When monitoring the cracking tendency of AAS mortar during hardening, fresh slurry was placed into a cylindrical mould. A steel waveguide was then inserted into the slurry and the AE sensor was attached to its free end with beeswax (Fig. 3.1). The intensity threshold of the signals that were detected was set to 0.8 V with 30 dB gain. This allowed us to eliminate background noise and record only the emissions produced due to the cracking of the material.

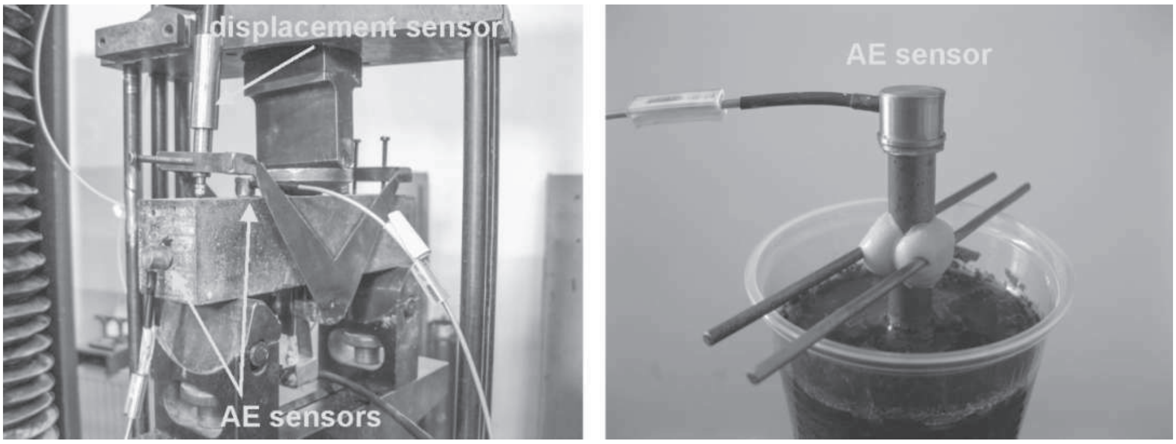

Fig. 3.1. Fracture test configuration in testing machine (left), measurement of AE activity during hardening (right)

3.4. Results and discussion

Basic mechanical and fracture parameters (mean values) of alkali-activated materials are listed in Table 3.3. Alkali-activated slag exhibits the best mechanical properties among all three tested materials, and the values are comparable with those observed for Portland cement mortars (Rovnaník 2008). On the other hand, fly ash geopolymer showed the lowest values of compressive strength, modulus of elasticity and fracture toughness. Only in case of fracture energy, the minimum value was reached with metakaolin geopolymer.

Table. 3.3. Mechanical and fracture parameters of reference alkali-activated materials

Material	Compressive strength	Elasticity modulus	Fracture toughness	Fracture energy
	MPa	GPa	MPa $m^{1/2}$	J m^{-2}
AAS	61	14	0.81	34.9
FAG	11	6	0.25	27.0
MKG	42	15	0.42	7.6

The effect of MWCNTs on the different mechanical fracture properties (mean values and standard deviations) of tested alkali-activated materials is introduced in Figs. 3.2–3.5. All parameters are presented as relative values with respect to average values of the reference materials set as 100%. Addition of MWCNTs has a positive effect on the compressive strength of all composites (Fig. 3.2). The best improvement was observed for the composite based on fly ash geopolymer, because the strength increased with addition of 0.05%, 0.10%, and 0.15% MWCNTs by 30%, 50%, and 70%, respectively. Generally, addition of 0.20% MWCNTs led to a rather decreasing effect on the compressive strength of all materials.

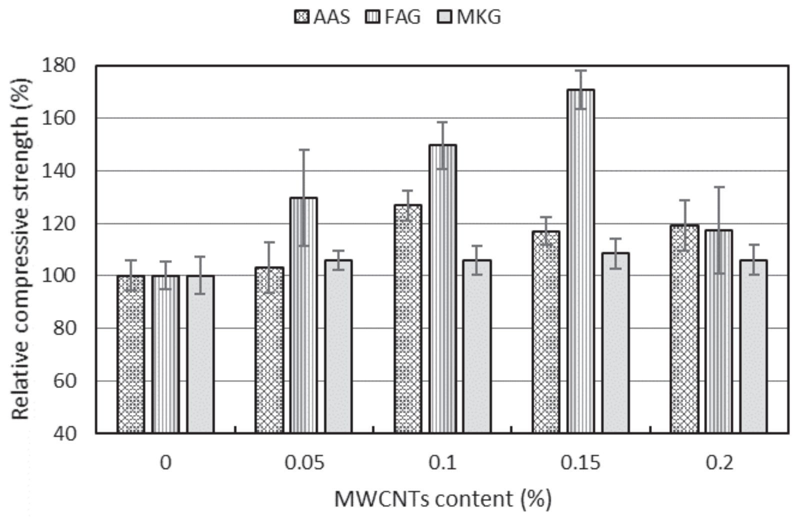

Fig. 3.2. Relative compressive strength values of alkali-activated aluminosilicate composites with various amounts of MWCNTs

When the values of elasticity modulus were compared, it turned out that MWCNTs remarkably contribute to the stiffness of AAS and FAG composites but the stiffness of MKG decreased instead (Fig. 3.3). The highest values were reached for AAS composite where even 0.05% MWCNTs was responsible for an increase in elasticity modulus of alkali-activated slag by 30% but further addition had a negligible effect. The values for the FAG composite follow similar trend as compressive strength with maximum observed for the composite containing 0.15% of MWCNTs. However, the increase was not as significant as in the case of compressive strength. On the other hand, the modulus of elasticity was reduced by up to 10% in case of MKG material, which means that MWCNTs have rather negative effect on the stiffness of metakaolin-based geopolymer materials.

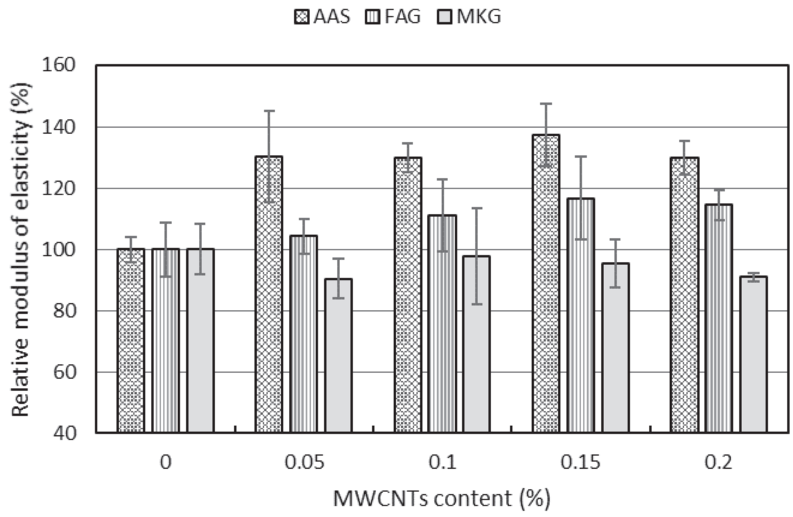

Fig. 3.3. Relative modulus of elasticity values of alkali-activated aluminosilicate composites with various amounts of MWCNTs

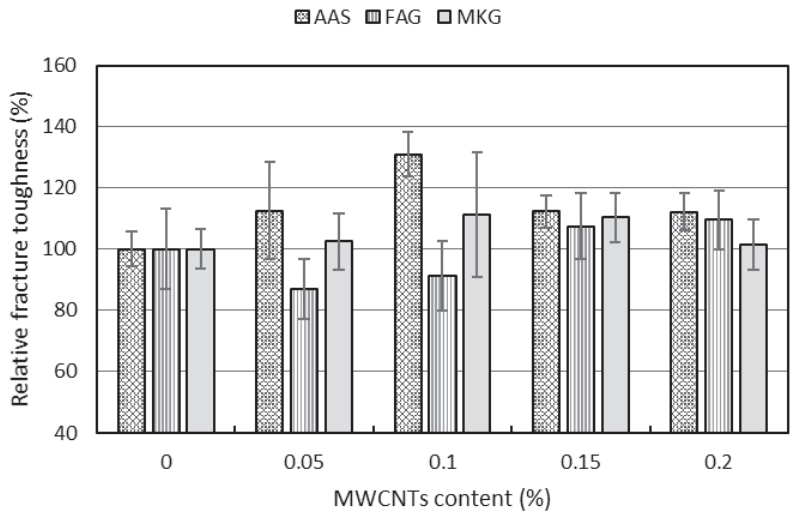

Fig. 3.4. Relative fracture toughness values of alkali-activated aluminosilicate composites with various amounts of MWCNTs

Values of effective fracture toughness of composites with MWCNTs were generally higher than those observed for reference samples with exception of fly ash geopolymer containing 0.05 and 0.10% MWCNTs (Fig. 3.4). In this case the effective fracture toughness decreased by 13 and 9%, respectively. A slight increase by 7 and 10% was detected in case of the mixtures having 0.15 and 0.20% of MWCNTs. Addition of nanotubes to MKG material improved the effective fracture toughness by 11% at its maximum which was reached for the mixture with 0.10% MWCNTs. Unfortunately, this composite showed also the highest coefficient of variation. The best improvement of the effective fracture toughness was achieved for AAS composite mixtures for which the values increased by 12–31%.

The comparison of the relative fracture energy values of alkali-activated aluminosilicate composites with various amounts of MWCNTs is presented in Fig. 3.5. This parameter exhibited the highest variability, especially in case of materials with FAG and MKG matrix. Meanwhile MWCNTs caused an improvement in fracture energy of MKG by up to 35% with 0.15% addition, they had rather adverse effect on other two composites. However, the fracture energy of pure MKG is surprisingly much lower than in case of FAG or even AAS samples. Concerning the variation coefficients, we can assume that the fracture energy of FAG is not influenced much by the addition of MWCNTs. In case of AAS, the fracture energy considerably increased only for 0.10% addition. However, with respect to high coefficients of variation of some results, it can be suggested that it follows similar trend as was observed for the fracture toughness.

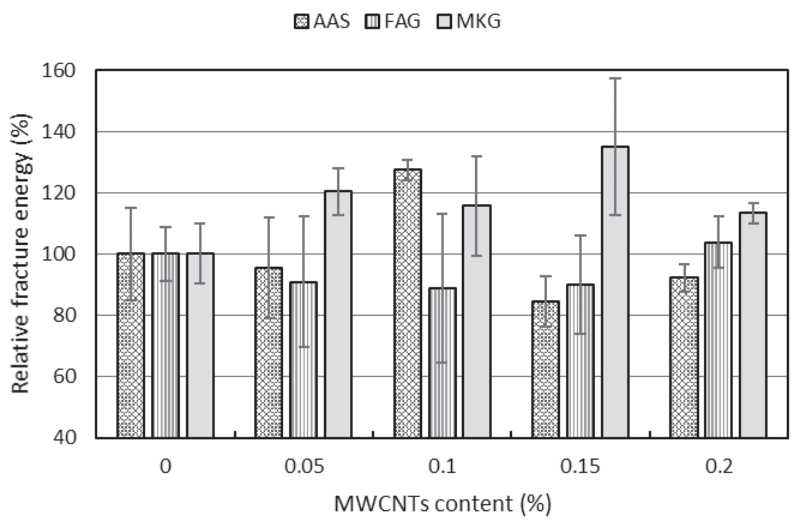

Fig. 3.5. Relative fracture energy values of alkali-activated aluminosilicate composites with various amounts of MWCNTs

Acoustic emission signals which were received during the three-point bending testing of the specimens were analysed. The attention was focused on three basic parameters: the amplitude, duration and energy of the AE signals (Figs. 3.6–3.8 – mean values and standard deviations). Different types of cracks generate different AE signals, and these differences can be related to the properties of the material (Iwanami 1997, Li 1995). Once the AE transducer captures a signal over a certain level, an AE event is recorded. The amplitude of AE signals, which is the greatest voltage measured in a waveform. This is an important parameter in AE inspection because it determines the detectability of the signal. Signals with amplitudes below the operator-defined minimum threshold are not recorded. A higher amplitude indicates the formation of a larger and more significant crack (Iwanami 1997). Amplitude values of all mixtures varied between 2489 and 3775 mV. FAG composites exhibited much higher amplitudes than AAS or MKG. However, while 0.15 and 0.2% MWCNTs caused rather significant decrease in amplitude, the variation in values of AAS and MKG composites was quite small.

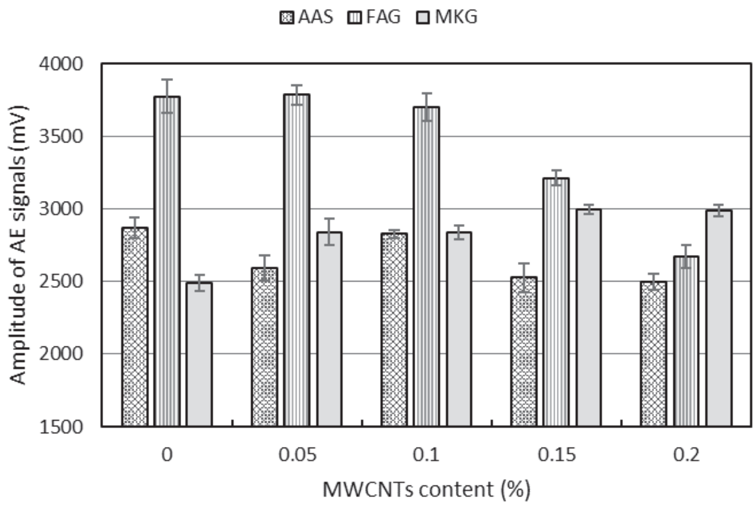

Fig. 3.6. Amplitude of AE signals of alkali-activated aluminosilicate composites with various amounts of MWCNTs detected during fracture test

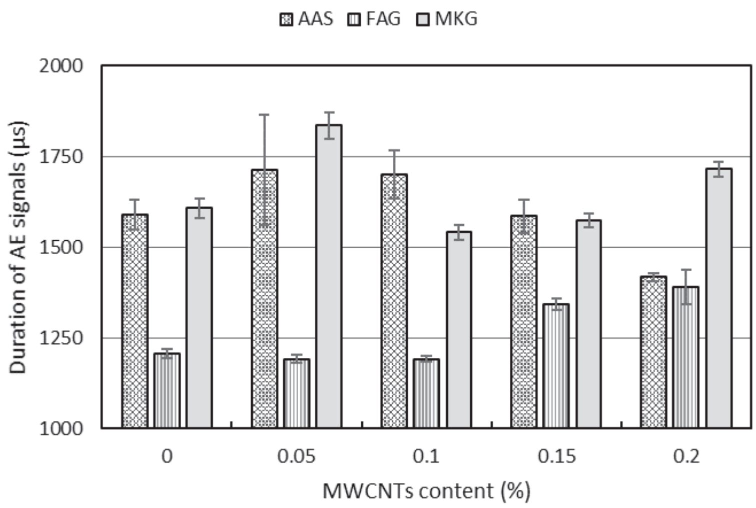

Fig. 3.7. Duration of AE signals of alkali-activated aluminosilicate composites with various amounts of MWCNTs detected during fracture test

The duration of an AE signal is the time difference between the crossing of the first and last threshold. As in case of amplitude, the duration of AE signals measured for FAG samples was completely different from those of AAS and MKG. FAG samples exhibited lower values which slightly increased with 0.15 and 0.20% MWCNTs. In case of AAS and MKG, the addition of carbon nanotubes at lower dosage increased the time of duration but with higher amounts of nanotubes it was reduced.

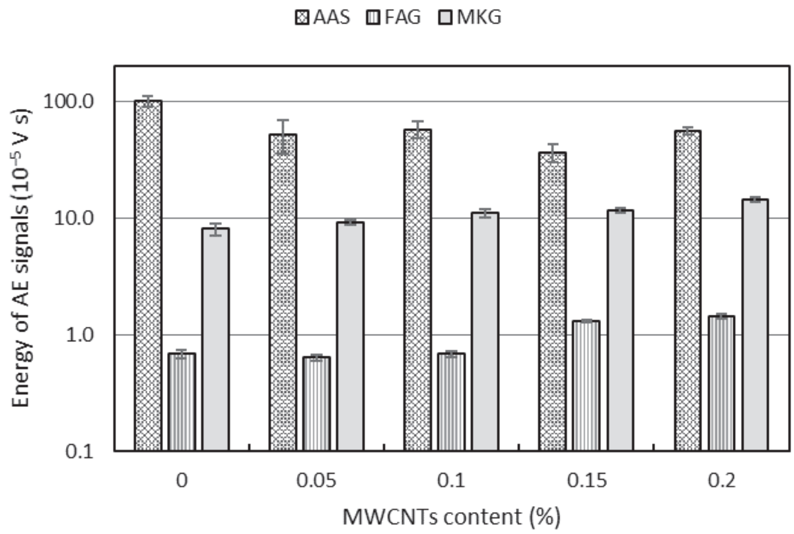

Fig. 3.8. Energy of AE signals of alkali-activated aluminosilicate composites with various amounts of MWCNTs detected during fracture test (in logarithmic scale)

The acoustic emission method was also used to monitor the hardening process of alkali-activated aluminosilicate mortars. In order to evaluate the formation of microcracks during hardening, we focused on the most commonly-used AE parameter, which is the number of signals overshooting a preset limit. ‘Number of overshoots’ refers to the number of pulses emitted by the circuitry measuring the signal voltage that exceed the threshold for a given time interval. The number of microcracks in the specimen can be inferred directly from such AE activity. Since the most important processes which are involved in the formation of hard structure occur at an early age, Figs. 3.9–3.11 show the cumulative number of AE signals over time during the first 6–10 days after mixing. Addition of MWCNTs to AAS material does not bring too much improvement in reduction of cracking during hardening process. In the first four days, the number of AE signals of composites with MWCNTs even exceeded the one achieved with the reference sample. However, in longer period some improvement can be observed because the curve for AAS has still increasing trend even after 7 days whereas with MWCNTs only few new signals were detected irrespective of MWCNTs amount.

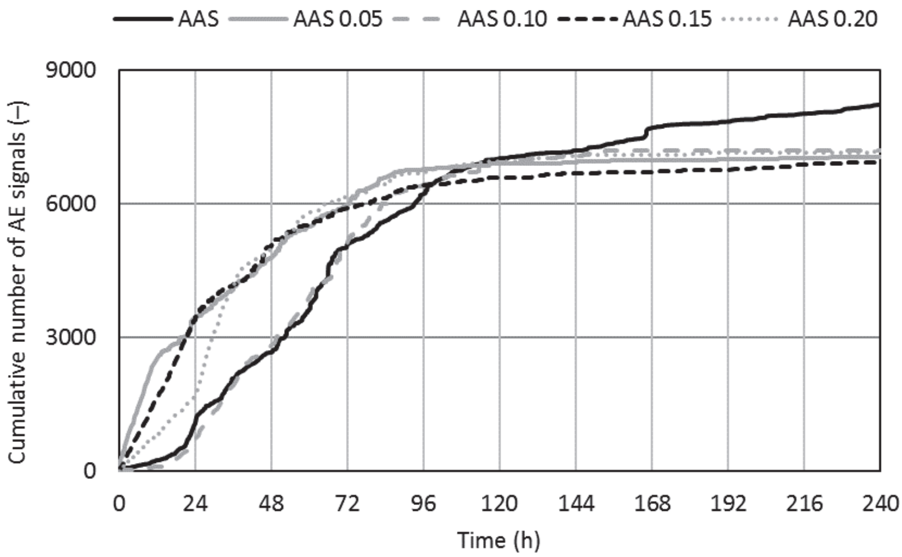

Fig. 3.9. Cumulative number of AE signals recorded during hardening of AAS mortars with MWCNTs

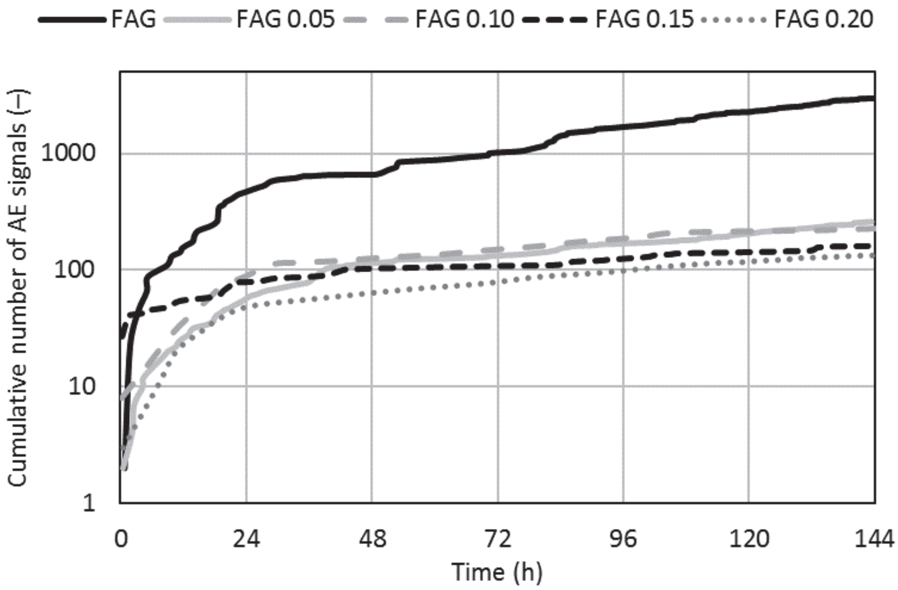

Fig. 3.10. Cumulative number of AE signals recorded during hardening of FAG mortars with MWCNTs (in logarithmic scale)

Remarkable improvement in cracking tendency was observed for FAG and MKG. The cracking tendency of FAG during hardening is much lower than for AAS and the application of MWCNTs helped reducing the number of AE signals by one order within the first three days (Fig. 3.10). However, similarly to AAS the amount of MWCNTs had negligible effect on the number of detected AE signals. Reference MKG material showed the highest number of AE signals within the first 6 days of the measurement but addition of MWCNTs had an essential influence on the reduction of signal (Fig. 3.11). It is also the only material for which the amount of MWCNTs had a significant effect on the number of signals. Application of just 0.15% MWCNTs was able to reduce the number of signals by three orders and in case of MKG 0.20 mixture the first event was detected at the age of 5 days.

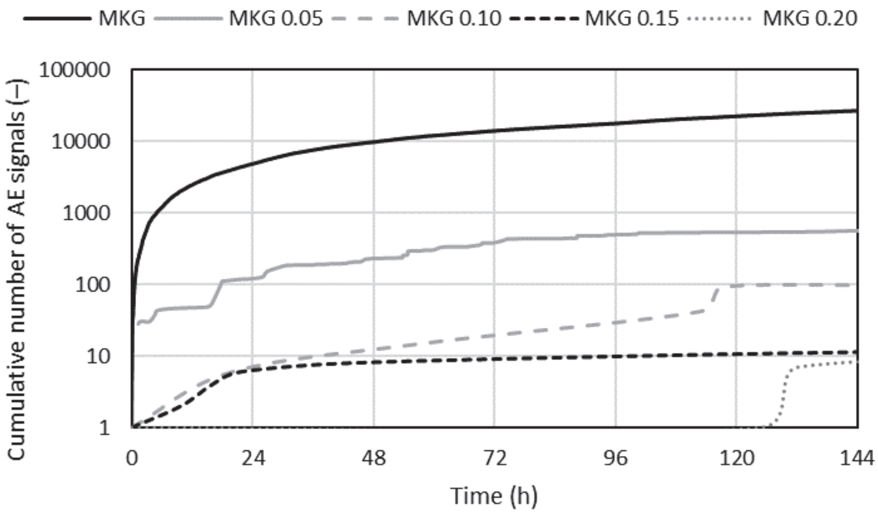

Fig. 3.11. Cumulative number of AE signals recorded during hardening of MKG mortars with MWCNTs (in logarithmic scale)

3.5 Conclusions

MWCNTs have been considered the most promising nanomaterial for enhancing the mechanical properties of building materials. In this research, MWCNTs were used for the improvement of mechanical fracture properties and the reduction in ability microcracks formation of three different types of alkali-activated aluminosilicate materials: alkali-activated slag, fly ash and metakaolin-based geopolymer. The tested materials exhibited totally diverse properties but the addition of MWCNTs had a positive effect on most of the determined parameters. Application of MWCNTs in AAS had the most positive effect on the improvement of elasticity modulus and fracture toughness whereas the best improvement in compressive strength was achieved with FAG. Finally, MWCNTs had the highest increase in fracture energy and showed the highest reduction of the microcracks formation during the process of hardening. We also noticed that the best improvement was achieved with 0.1 or 0.15% of MCNTs and higher dosage showed rather adverse effect. Therefore, the maximum amount of 0.15% of MWCNTs would be recommended to reach optimum properties.

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