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Carbon nanotube reinforced alkali-activated slag mortars

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HIGHLIGHTS

- Application of MWCNTs in alkali-activated slag binders is introduced.
- Dosage of MWCNTs has a significant effect on the mechanical fracture properties of AAS composites.
- Acoustic emission method was used to monitor the hardening process of AAS mortars.
- Optimum dosage to obtain the best performance lies around 0.10% of MWCNTs.

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ABSTRACT

The paper reports on a study of the effect of multi-walled carbon nanotubes (MWCNTs) when used as dispersed reinforcement on the fracture properties and microstructure of alkali-activated slag mortars. The amount of MWCNTs added varied in the range of 0.05–1.0% of the mass of slag. Mechanical and fracture properties were determined using fracture tests carried out on 40 × 40 × 160 mm specimens with a central notch. The observed parameters were compressive strength, modulus of elasticity, effective fracture toughness and specific fracture energy. Specimen response during fracture tests was also monitored by means of acoustic emission, and this method was also used for the determination of cracking tendency due to autogenous and drying shrinkage occurring during the hardening process. It is shown that the addition of up to 0.2% of MWCNTs improves the fracture properties of alkali-activated slag. Although a higher dosage of MWCNTs reduced the number of microcracks observed by acoustic emission, the mechanical properties of the slag deteriorated due to the less effective dispersion of the MWCNTs and the formation of bundles.

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 [1]. 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 [2–4].

One of the most common and intensively studied alkali-activated materials is alkali-activated slag (AAS). It is composed of finely ground granulated blast furnace slag and alkaline activator. Alkaline hydroxides, carbonates and especially silicates (water glass) are known to be the most effective activator for this type of material [5,6]. The mixture sets to form a very stable product and its properties depend on a number of factors such as the chemical and mineralogical composition of the slag, the type, composition and dosage of alkali activator, curing conditions, etc. The mechanical properties and application possibilities of AAS are very similar to those of OPC concrete. However, in contrast to OPC-based binders, AAS offers superior properties such as higher corrosion resistance against acid or sulphate attack [7–11] and also higher resistance to elevated temperatures and fire [12–16]. Its major disadvantage is increased shrinkage. This effect is caused by both autogenous and drying shrinkage and finally results in volume

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contraction, micro-cracking and the deterioration of tensile and bending properties [5].

Autogenous shrinkage is a basic property of CSH gel, which is a predominant binding phase; however, due to its different character, the shrinkage that affects AAS is more severe than in the case of OPC. Autogenous shrinkage increases with the increasing amount of Na_2O in the activator and it becomes more evident in the case of water glass activated materials as opposed to NaOH or Na_2CO_3 activated ones [17]. Drying shrinkage is even more severe because it acts unevenly and causes cracking especially in the surface layer, which is then responsible for the deterioration of the mechanical properties and decreasing serviceability of the structure. It depends not only on the nature of the material itself, but also on exterior conditions such as curing temperature, relative humidity, drying rate, etc. Collins and Sanjayan [18] used a crack-detection microscope to examine the cracking of AAS concrete. When the concrete specimens were cured in a water bath they did not notice any visible surface cracks. However, specimens cured under 50% relative humidity conditions had lots of cracks within one day. The average crack width is three times greater than for OPC concrete [19]. One possible way to reduce shrinkage is via the application of shrinkage reducing admixtures (SRA), which are commonly used for OPC concrete. The effect of SRA on alkali-activated slag was studied by Palacios and Puertas [20]. They observed that polypropylenglycol-based admixture reduces autogenous shrinkage by 85% and drying shrinkage by 50% in waterglass-activated slag mortars, but the effect strongly depends on curing conditions. However, the SRA retards the alkali activation of slag, with longer delays at higher dosages of admixture.

The main aim of this work is to apply multi-walled carbon nanotubes (MWCNTs) as a shrinkage reducing admixture for AAS-based mortars. 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 [21,22].

Carbon nanotubes 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 [23]. 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 [24].

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 AAS mortars.

Table 1
Mixture compositions.

Component	Slag (g)	Water glass (g)	MWCNTs (g)	Aggregate (g)	Water (ml)
AAS	450	180	0	1350	95
AASC 0.05	450	180	22.5[a]	1350	72.5
AASC 0.10	450	180	45[a]	1350	50
AASC 0.15	450	180	67.5[a]	1350	27.5
AASC 0.20	450	180	90[a]	1350	5
AASC 0.50	450	180	45[b]	1350	62
AASC 1.00	450	180	90[b]	1350	32

[a] 1% dispersion of MWCNTs.
[b] 5% dispersion of MWCNTs.

2. Experimental methods

2.1. Materials

The alkali-activated slag mortars used in the tests were composed of granulated blast furnace slag and water glass. Slag supplied by Kotouč, s.r.o. (CZ) was ground to a fineness of about 380 $m^2\ kg^{-1}$ (Blaine). The average grain size of the slag obtained by laser granulometry was d_{50} = 15.5 μm and d_{90} = 38.3 μm, indicating that 50% or 90%, respectively, of all grains is smaller than a given value. The slag was neutral with a basicity coefficient $M_b = (CaO + MgO)/(SiO_2 + Al_2O_3)$ equal to 1.08, and its chemical composition was (wt%): SiO_2 (39.66), Al_2O_3 (6.45), Fe_2O_3 (0.47), CaO (40.12), MgO (9.50), Na_2O (0.33), K_2O (0.55), MnO (0.65), SO_3 (0.72). A commercial sodium silicate solution (Vodní sklo, CZ) 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 (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 14,000 rpm).

2.2. Sample preparation

Seven different mixtures of alkali-activated slag mortars were prepared (see Table 1). The MWCNT content was 0.05, 0.10, 0.15, 0.20, 0.50 and 1.0% of the weight of the slag, 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 hardened specimens were immersed in water for 27 days, then pulled out of the water and allowed to dry spontaneously under ambient conditions for 24 h prior to fracture testing.

2.3. Testing procedure

2.3.1. Fracture tests

Experiments were carried out on a Heckert FPZ 10/1 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. A load–deflection (*F–d*) diagram was recorded and used for the calculation of elasticity modulus from the first (almost linear) part of the *F–d* diagram, and for the calculation of effective fracture toughness and specific fracture energy. The *F–d* diagrams for selected specimens (one for each type of material) are shown in Fig. 1.

The modulus elasticity value was determined according [25] using following formula:

$$E_c = \frac{P_i}{4B\delta_i}\left(\frac{S}{W}\right)^3\left[1+\frac{5qS}{8P_i}+\left(\frac{W}{S}\right)^2\left\{2.70+1.35\frac{qS}{P_i}\right\}-0.84\left(\frac{W}{S}\right)^3\right] + \frac{9}{2}\frac{P_i}{B\delta_i}\left(1+\frac{qS}{2P_i}\right)\left(\frac{S}{W}\right)^2 F_1(\alpha_0),$$

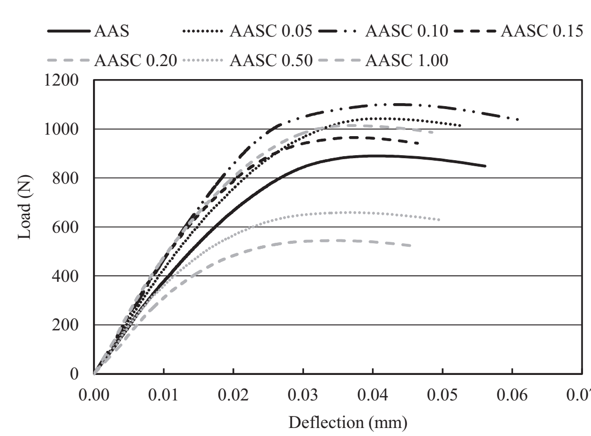

Fig. 1. Load vs. deflection diagrams for selected three-point bended notched specimens.