UDK 67.017:666.762.1:661.34
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 51(6)1005(2017)

BASIC PHYSICAL, MECHANICAL AND ELECTRICAL PROPERTIES OF ELECTRICALLY ENHANCED ALKALI-ACTIVATED ALUMINOSILICATES

OSNOVNE FIZIKALNE, MEHANSKE IN ELEKTRIČNE LASTNOSTI ELEKTRIČNO IZBOLJŠANIH, Z ALKALIJAMI AKTIVIRANIH ALUMINOSILIKATOV

Lukáš Fiala[1], Miloš Jerman[1], Pavel Rovnaník[2], Robert Černý[1]

[1]Czech Technical University, Faculty of Civil Engineering, Department of Materials Engineering and Chemistry, Thákurova 7, 166 29 Prague 6, Czech Republic
[2]Brno University of Technology, Institute of Chemistry, Faculty of Civil Engineering, Žižkova 17, 602 00 Brno, Czech Republic
fialal@fsv.cvut.cz

Prejem rokopisa – received: 2017-05-04; sprejem za objavo – accepted for publication: 2017-07-28

doi:10.17222/mit.2017.051

Alkali-activated aluminosilicates (AAAs) with electrically conductive admixtures are promising competitors to the cement-based materials enhanced in the same way. The electrical conductivity of these materials dramatically increases with a sufficient amount of admixtures, which broaden their possible applicability. Electrically optimized materials are typically used in self-heating, self-sensing or magnetic-shielding systems. However, an increase in the amount of admixtures can negatively affect the compressive or flexural strength and can lead to an increase in the porosity. Therefore, it is crucial to experimentally determine the mechanical properties in order to decide whether an electrically enhanced material is applicable in the building industry. In this research, basic physical, mechanical and electrical properties of AAAs with three types of electrically conductive admixtures in different dosages are studied. Typical representatives of spherical inclusions, carbon black (CB), graphite powder (GP) and carbon fibers (CF) as fibrous fillers, are tested. The experimental results reveal that AAAs with CB dosages higher than 4 % are promising materials that could be utilized in self-heating systems due to their sufficiently high electrical conductivity.

Keywords: alkali-activated aluminosilicates, electrically conductive admixtures, compressive strength, flexural strength, electrical conductivity

Z alkalijami aktivirani aluminosilikati (AAA) z električno prevodnimi dodatki so obetavni konkurenti materialov, ki izboljšani na enak način, temeljijo na cementu. Električna prevodnost teh materialov se drastično povečuje z zadostno količino takšnih dodatkov, ki razširjajo njihovo možno uporabnost. Tipična praktična uporaba električno optimiranih materialov je v samoogrevanju, samozaznavanju ali magnetno-zaščitnih sistemih. Vendar lahko povečanje količine dodatkov negativno vpliva na tlačno ali upogibno trdnost in lahko povzroči povečanje poroznosti. Zato je ključnega pomena, da določimo eksperimentalno mehanske lastnosti, da bi se odločili, ali se naj električno ojačan material uporablja v gradbeništvu. V tem prispevku so preučevane osnovne fizikalne, mehanske in električne lastnosti AAA s tremi vrstami električno prevodnih dodatkov v različnih doziranjih. Eksperimentalni rezultati kažejo na dejstvo, da so AAA z odmerki CB, višjimi od 4 %, obetavni materiali, ki bi jih lahko uporabili v sistemih za samoogrevanje zaradi dovolj visoke lastne električne prevodnosti.

Ključne besede: aluminosilikati, aktivirani z alkalijami; električno prevodne dodajne mešanice, tlačna trdnost, upogibna trdnost, električna prevodnost

1 INTRODUCTION

Alkali-activated aluminosilicates (AAAs, often also denoted as geopolymers) are promising competitors to the cement-based materials due to their good mechanical properties, chemical resistance and enhanced fire resistance.[1,2] Moreover, other AAA benefits that cannot be overlooked are economic aspects and their environmentally friendly nature.[3,4]

Alkaline activators as components of cementing materials date back to 1930, when Kuhl investigated the setting behavior of mixtures of ground slag powder and caustic potash solution. The first extensive laboratory study on clinkerless cements consisting of slag and sodium hydroxide was performed in 1940s by A. O. Purdon.[5] Further detailed observations of AAAs were performed by V. D. Glukhovsky[6] who aimed at investigating the binders used in ancient Roman and Egyptian constructions and concluded that they were composed of calcium aluminosilicate hydrates similar to the ones of Portland cement, which explained their durability. Based on these observations, Glukhovsky developed a new type of binders, the so-called soil cement, which consists of aluminosilicates mixed with alkalis-rich industrial wastes. Another study carried out by R. Malinowski[7] revealed the fact that the restoration of ancient constructions with the materials based on Portland cement leads to their disintegration after 10 years, which is much lower compared to the durability of the original material.

A further qualitative enhancement of AAAs represented by an increased electrical conductivity can be achieved with an addition of electrically conductive

admixtures, which was already observed for the cement-based materials.[8–10] With an appropriate amount of such admixtures, at around the percolation threshold, an electrically conductive network is built up in the solid matrix. Therefore, the electrical conductivity significantly increases and naturally electrically non-conductive materials become electrically conductive, which broadens their practical utilization. Such materials can then be used in many practical ways, e.g., in self-heating[11] or self-sensing[12] systems.

In the past, various electrically conductive admixtures based on metallic particles or fibers, such as nickel powder (NP) and steel fibers (SF), or on carbon-based materials, such as carbon black (CB), carbon fibers (CF), carbon nanotubes (CNT) or graphite powder (GP) were studied. A comprehensive review of widely used admixtures suitable for self-sensing concrete was given by B. Han et al.[13]

In this paper, the basic physical, mechanical and electrical properties of reference AAAs and several types of electrically enhanced AAAs with different dosages of conductive admixtures, namely, carbon black (CB), carbon fibers (CF) and graphite powder (GP) are studied. The main aim is to determine the relation of the amount of electrically conductive admixtures with the electrical conductivity, the compressive strength and the flexural strength and to identify the most appropriate AAA mixes that allow satisfactory electrical and mechanical parameters.

2 EXPERIMENTAL PART

The studied AAA materials were based on SMŠ 380 produced by Kotouč Štramberk s.r.o. It is a dry, granulated blast-furnace slag with a fineness of 380 $m^2\ kg^{-1}$ fulfilling the requirements of ČSN EN 197-1. The second component, the Britesil C205 waterglass with the SiO_2/Na_2O molar ratio equal to 2.07, was used for the alkali activation. The filler was represented by three normalized CEN fractions of the quartz sand (PG1, PG2, PG3) produced by Filtrační písky, Ltd., Czech Republic, which complies with ČSN EN 196-1. The particle size distribution of the used sand is given in **Figure 1**.

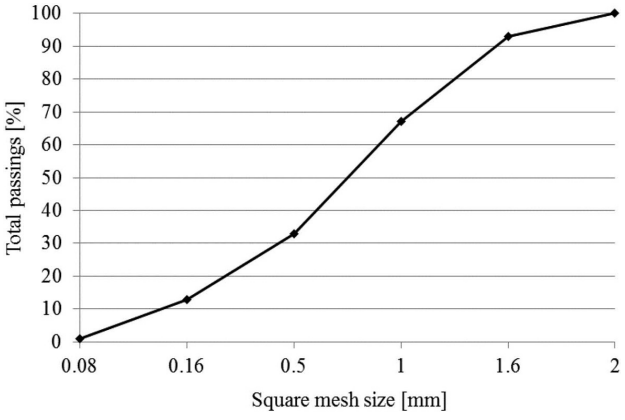

Figure 1: Particle size distribution of the Chlumský reference sand

Within the study, fifteen different types of AAA samples were prepared: the reference sample without any conductive admixture, samples with CB in amounts of (0.89, 2.22, 4.44, 6.67 and 8.89) % of mass fractions, samples with CF in amounts of (0.56, 1.11, 1.67 and 2.22) % of mass fractions, and samples with GP in amounts of (1.78, 3.33, 4.44, 6.67 and 8.89) % of mass fractions. The compositions of the analyzed AAA mixes are given in **Tables 1–3**.

The samples were prepared as follows: Firstly, waterglass was mixed with water. The solution was then mixed with the suspension of an electrically conductive admixture. CB was incorporated into the mixture in the form of a 20 % mass-fraction homogenized suspension (relative to the slag mass), GP in the form of 10 % mass-fraction and 20 % mass-fraction suspensions and CF in the form of a 5 % mass-fraction suspension. Optionally, additional water was added to ensure good workability of the mix. Other components were added in the following order: slag, a fine fraction of sand (PG1), a medium-coarse fraction of sand (PG2), a coarse fraction of sand (PG3). The final mixture was put into 40 mm × 40 mm × 160 mm molds and vibrated. The samples were demolded after 24 h, cured in water for additional 28 d and dried in an oven.

Table 1: Compositions of the reference AAA mixture and AAA mixtures with CB

Component/ Admixture	Refe-rence	CB 0.89 %	CB 2.22 %	CB 4.44 %	CB 6.67 %	CB 8.89 %
Slag (g)	450	450	450	450	450	450
Waterglass (g)	90	90	90	90	90	90
Sand PG1 (g)	450	450	450	450	450	450
Sand PG2 (g)	450	450	450	450	450	450
Sand PG3 (g)	450	450	450	450	450	450
Admixture suspense (%)	0	20	20	20	20	20
Amount of suspense (g)	0	20	50	100	150	200
Additional water (g)	0	190	170	130	90	105

Table 2: Compositions of the AAA mixtures with CF

Component/ Admixture	CF 0.56 %	CF 1.11 %	CF 1.67 %	CF 2.22 %
Slag (g)	450	450	450	450
Waterglass (g)	90	90	90	90
Sand PG1 (g)	450	450	450	450
Sand PG2 (g)	450	450	450	450
Sand PG3 (g)	450	450	450	450
Admixture suspense (%)	5	5	5	5
Amount of suspense (g)	50	100	150	200
Additional water (g)	150	100	50	0

Table 3: Compositions of the AAA mixtures with GP

Component/ Admixture	GP 1.78 %	GP 3.33 %	GP 4.44 %	GP 6.67 %	GP 8.89 %
Slag (g)	450	450	450	450	450
Waterglass (g)	90	90	90	90	90
Sand PG1 (g)	450	450	450	450	450
Sand PG2 (g)	450	450	450	450	450
Sand PG3 (g)	450	450	450	450	450
Admixture suspense (%)	10	10	20	20	20
Amount of suspense (g)	80	150	100	150	200
Additional water (g)	140	70	130	90	50

As the fundamental physical material characteristics, the bulk density ρ_v (kg m^{-3}), the open porosity Ψ (–) and the matrix density ρ_{mat} (kg m^{-3}) were measured using the water-vacuum-saturation method. In the first step, the samples were dried in a drier to remove the majority of the physically bound water. Subsequently, the samples were placed into a desiccator. In three hours, the air was evacuated with a vacuum pump from the desiccator. The samples were then kept under water for 24 h. From the mass of water-saturated sample m_w (kg) and the mass of immersed water-saturated sample m_a (kg), volume V of the sample was determined, and the basic physical properties were calculated.

Mechanical properties were measured on three samples with dimensions of 40 mm × 40 mm × 160 mm according to the Czech Standard ČSN EN 196-1 (**Figure 2**). At first, three samples of each mixture were cured in a water bath for 28 d. Then the flexural strength was determined with the three-point-bending test. The span length between supports was 100 mm, and the loading rate was 0.15 mm/min. The compressive strength was then determined on six halves of the prisms from the previous flexural-strength tests.

Electrical properties were determined on samples with dimensions of 40 mm × 40 mm ×10 mm cut from 40 mm × 40 mm × 160 mm prisms. In order to achieve good contact of the tested materials with the measuring apparatus, two lateral sides (40 mm × 40 mm) playing the role of electrodes were painted with a conductive-carbon paint produced by SPI Supplies, together with a copper adhesive tape that was connected to the conductors. The samples dried in an oven were put into the dessicator for a couple of days in order to achieve dry state with no residual water. Finally, the electrical resistance was determined with a Fluke 8846A 6-1/2 digit precision multimeter in a 4-electrode configuration (**Figure 3**) and the electrical conductivity was calculated with respect to the shape ratio of the samples.

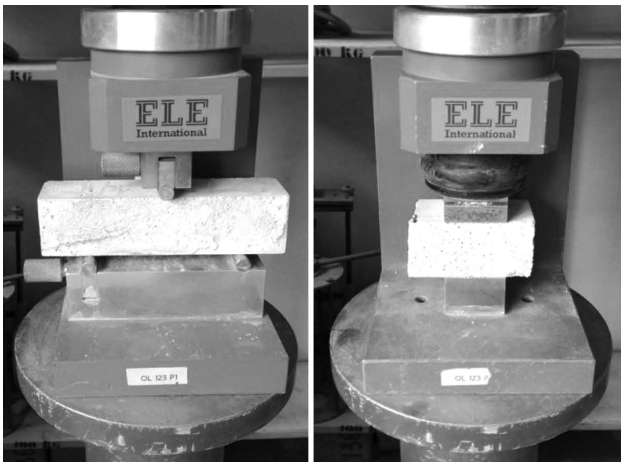

Figure 2: Three-point bending and compressive-strength experiment

Figure 3: Electrical-resistivity measurements

3 RESULTS AND DISCUSSION

The basic physical properties are presented in **Figures 4** to **6**. The bulk density of the reference material (**Figure 4**) was 2164 kg m^{-3}. It decreased with the increasing amount of all the tested electrically conductive admixtures. In the case of CB, the decrease was in a range of 3.3–8.7 % compared to the reference material. The highest decrease of 8.7 % was observed for the AAAs with 8.89 % of CB. Concerning the AAA samples with CF and GP, the decrease in the bulk density was in ranges of 3.1–4.9 % and 2.9–4.5 %, respectively.

The matrix density (**Figure 5**) was highest for the reference material (2673 kg m^{-3}). Concerning the AAA

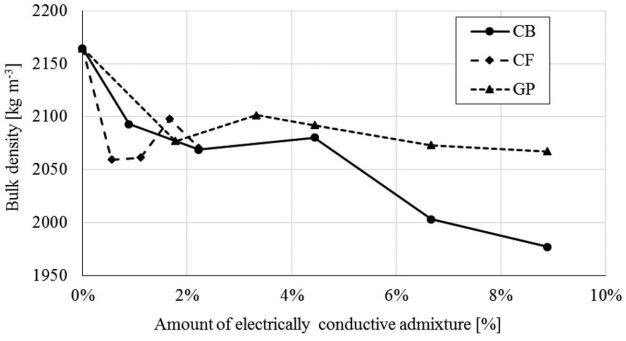

Figure 4: Bulk density of electrically enhanced AAAs

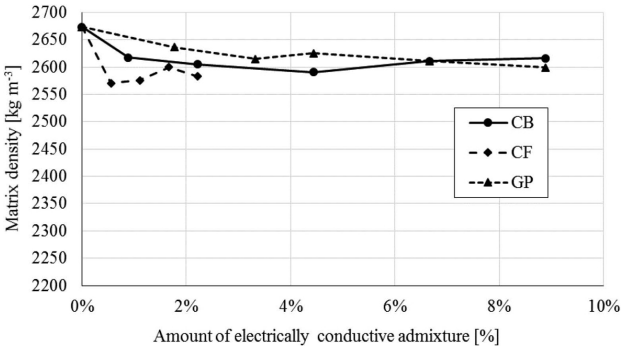

Figure 5: Matrix density of electrically enhanced AAAs

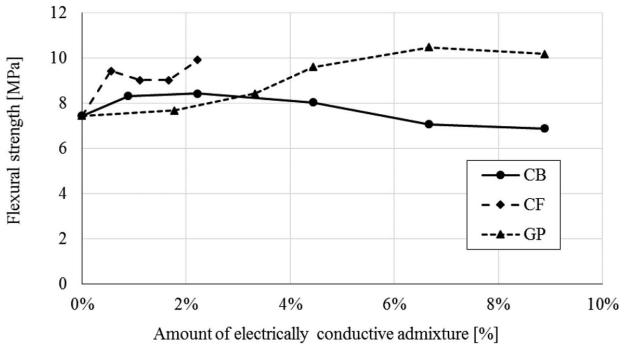

Figure 7: Flexural strength of electrically enhanced AAAs

mixtures with electrically conductive fillers, the samples with a GP admixture exhibited a higher matrix density (2599–2636 kg m^{-3}) compared to the samples with CF and CB. In the case of the samples with CB, the matrix density ranged between 2590–2618 kg m^{-3}. In the case of CF, the decrease was higher than for the reference material and the matrix density ranged between 2570–2600 kg m^{-3}. The maximum decrease (3.9 %) was observed for the samples with 0.56 % of CF admixture.

The total open porosity of the mixtures ranged between 0.193–0.244 % (**Figure 6**). A significant increase in the porosity was observed for the AAA mixtures with 6.67 % of CB and 8.89 % of CB.

The dependence of the flexural strength on the amount of electrically conductive admixtures is presented in **Figure 7**. The flexural strength of the reference AAAs was 7.43 MPa and it slightly increased up to 8.03 MPa for the 4.44 % CB dosage for the materials with a CB admixture (an 8 % increase compared to the reference AAAs). For higher dosages of the CB filler, the flexural strength decreased to 6.88 MPa (a 7.4 % decrease compared to the reference AAAs). In the case of the CF admixture, the flexural strength was higher than that of the reference AAAs, which was due to the fibrous nature of such an admixture. The increase to the maximum of 9.9 MPa (a 33.2 % increase compared to the reference AAAs) was observed for the mixture with CF in the amount of 2.22 %. GP exhibited a systematic increase in the flexural strength of up to 10.47 MPa (40.9 % compared to the reference AAAs) for 6.67 % of GP and then a slight decrease to 10.17 MPa (a 36.9 % increase compared to the reference AAAs) was observed for GP in the amount of 8.89 %.

The dependence of the compressive strength on the amount of electrically conductive admixtures is presented in **Figure 8**. The highest compressive strength equal to 66.38 MPa was observed for the reference AAAs. With the increase in the amount of electrically conductive admixtures, a decrease in the compressive strength was observed. The electrically conductive admixtures reduced the workability of the mixes and therefore a higher amount of the mixing water led to a higher total open porosity, which negatively affected the above mechanical property. Comparing the types of admixture, CF exhibited the lowest maximum decrease of 58.67 MPa for the samples with CF in the amount of 1.11 % (an 11.6 % decrease compared to the reference AAAs), 24.77 MPa for the samples with CB in the amount of 6.67 % (a 62.7 % decrease compared to the reference AAAs) and 37.34 MPa for the samples with GP in the amount of 6.67 % (a 43.7 % decrease compared to the reference AAAs).

The electrical conductivity of the reference AAA material was 1.27 × 10^{-6} S m^{-1}. Such a material is practically electrically non-conductive. The electrical conductivity of the samples with any type of the studied electrically conductive admixtures increased compared to the reference material (**Figure 9**). However, the increase was by just about one order of magnitude (10^{-5}) and remained constant for all the dosages of the CF and GP admixtures. In the case of CB, the electrical conductivity increased significantly by about three and half

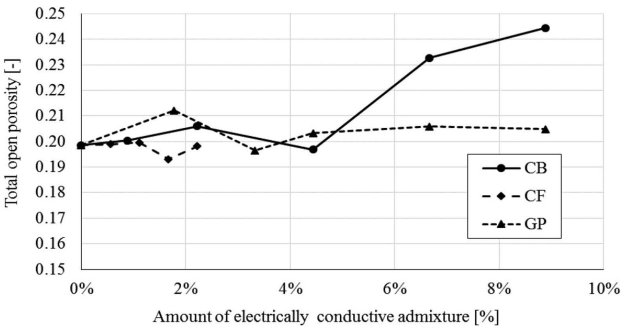

Figure 6: Total open porosity of electrically enhanced AAAs

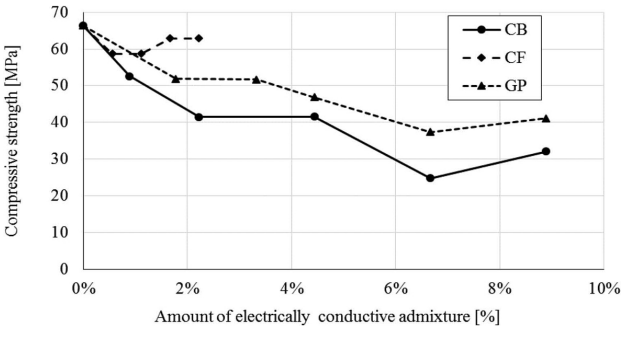

Figure 8: Compressive strength of electrically enhanced AAAs

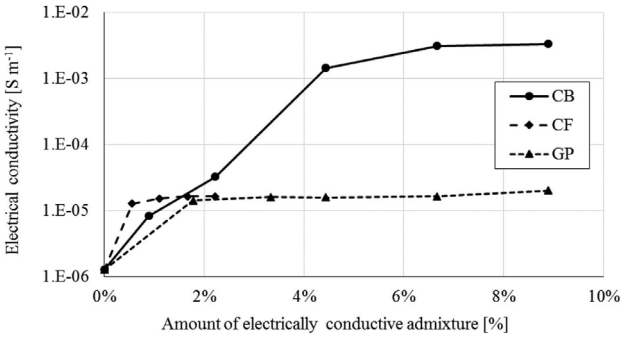

Figure 9: Electrical conductivity of electrically enhanced AAAs

orders of magnitude with the percolation threshold close to 4 % of CB.

4 CONCLUSIONS

Fifteen different AAAs were analyzed in the study, namely the reference AAAs and the AAAs with CB, CF and GP admixtures in different dosages. Basic physical properties represented by the bulk and the matrix density were determined by means of the water-saturation method. The total open porosity was then calculated with respect to the determined basic physical properties. Mechanical properties were measured according to the Czech Standard ČSN EN 196-1 on different types of samples (reference samples and the samples with a given dosage of electrically conductive admixture). Electric properties represented by the electrical conductivity were determined by measuring the electrical resistance in a 4-electrode set-up and calculating the electrical conductivity with respect to the shape ratio of the samples.

The highest increase in the electrical conductivity of about three and half orders of magnitude was observed for the samples with the CB admixture in an amount higher than 4 %, which is promising in terms of possible applications in self-heating systems. The total open porosity of the AAA samples with 4.44 % of CB remained at the same level as for the reference sample. The total open-porosity increase of about 17 % and 22.6 %, respectively, was observed in the case of the AAA samples with 6.67 % and 8.89 % of CB. The increased total open porosity negatively influenced the flexural and compressive strength of the AAAs with a 6.67 % dosage of CB; a decrease in the flexural strength of about 4.8 %, to 7.07 MPa, and a decrease in the compressive strength of about 62.7 %, to 24.77 MPa, were observed. For the AAAs with an 8.89 % dosage of CB, the strengths decreased by 7.4 %, to 6.88 MPa, and 51.7 %, to 32.03 MPa. The decrease in the compressive strength of these materials is particularly significant. However, with respect to the enhancement of electrical properties and the fact that CB is a waste product, such a material can find applications in building practice. In the case of the AAAs with CF and GP admixtures, electrical properties were not enhanced significantly, and the electrical conductivity increased by just about one order of magnitude. However, the AAAs with a CF admixture exhibited an increased flexural strength and only a low decrease in the compressive strength when compared to the reference AAAs.

Based on the results presented in this paper, the AAAs with a CB admixture exhibited the best electrical properties. Therefore, they are promising candidates in the field of smart materials. These materials will be subjected to a deeper investigation in terms of their applicability for self-heating elements.

Acknowledgment

This research was supported by the Czech Science Foundation, under project No. 16-00567S.

5 REFERENCES

[1] J. Davidovits, Geopolymers and geopolymeric materials, Journal of Thermal Analysis, 35 (**1989**) 2, 429–441, doi:10.1007/BF01904446

[2] J. Davidovits, Geopolymers – inorganic polymeric new materials, Journal of Thermal Analysis, 37 (**1991**) 8, 1633–1656, doi:10.1007/BF01912193

[3] P. Marc, I. Costescu, Industrial wastes used in pavement layers, Journal of Environmental Protection and Ecology, 14 (**2013**) 1, 187–195

[4] T. Kim, S. Tae, C. U. Chae, K. Lee, Proposal for the Evaluation of Eco-Efficient Concrete, Sustainability, 8 (**2016**) 8, 705–724, doi:10.3390/su8080705

[5] A. O. Purdon, The action of alkalis on blast furnace slag, Journal of the Society of Chemical Industry, 59 (**1940**), 191–202

[6] V. D. Glukhovsky, Soil Silicates, Gostroyizdat Ukrainy Publishing, Kiev, USSR, 1959

[7] R. Malinowski, Concretes and mortars in ancient aqueducts, Concrete International, 1 (**1979**) 1, 66–76

[8] P. Xie, P. Gu, J. J. Beaudoin, Electrical percolation phenomena in cement composites containing conductive fibers, Journal of Materials Science, 31 (**1996**) 15, 4093–4097, doi:10.1007/BF00352673

[9] M. Chiarello, R. Zinno, Electrical conductivity of self-monitoring CFRC, Cement & Concrete Composites, 27 (**2005**) 4, 463–469, doi:10.1016/j.cemconcomp.2004.09.001

[10] J. Song, D. L. Nguyen, C. Manathamsombat, D. J. Kim, Effect of fiber volume content on electromechanical behavior of strain-hardening steel-fiber-reinforced cementitious composites, Journal of Composite Materials, 49 (**2015**) 29, 3621–3634, doi:10.1177/0021998314568169

[11] J. P. Won, C. Kim, S. Lee, J. Lee, R. Kim, Thermal characteristics of a conductive cement-based composite for a snow-melting heated pavement system, Composite Structures, 118 (**2014**), 106–111, doi:10.1016/j.compstruct.2014.07.021

[12] F. Azhari, N. Banthia, Cement-based sensors with carbon fibers and carbon nanotubes for piezoresistive sensing, Cement & Concrete Composites, 34 (**2012**) 7, 866–873, doi:10.1016/j.cemconcomp.2012.04.007

[13] B. Han, S. Ding, X. Yu, Intrinsic self-sensing concrete and structures: A review, Measurement, 59 (**2015**), 110–128, doi:10.1016/j.measurement.2014.09.048