



Original Research Paper

Artificial aggregates based on granulated reactive silica powders

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ABSTRACT

This paper reports on the development of artificial aggregates based on granulated reactive silica (AAGS) powder materials activated by alkaline components. The alkali content was optimized depending on the properties of the reactive silica (RS) material. The best RS component for AAGS was determined to maximize the volume of synthesized soluble polysilicates. Additional research was conducted to evaluate the materials for the formation of a strong shell for AAGS. The effect of RS and AAGS composition on the structure of hardened cement composite was investigated.

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1. Introduction

Lightweight construction materials such as lightweight aggregate (LWA) concrete are in high demand because of their attractive mechanical performance and thermal insulating properties [1–4]. One of the most considerable disadvantages of LWAs that limits their application in concrete is related to a large volume of open pores and, therefore, high water absorption. Traditional LWAs are manufactured by firing at relatively high temperatures; therefore, conventional technology is characterized by a considerable energy consumption and dust emissions.

It is attractive to design a new type of aggregates which can provide the capability of improving the interface with cementitious matrix and reducing the water absorption while maintaining a low average density and thermal conductivity. Lightweight aggregates based on granulated powders (i.e. fly ash, aluminosilicates, reactive silica) which do not require firing in a kiln are the most promising materials for LWAs. Suitable diatomites, which occur as large fossil deposits in terrestrial environments can be used as a reactive silica (RS) material. This group of minerals, depending on the genesis, includes tripoli, opoka and others. These sedimentary rocks consist of the residue shells of diatoms, radiolarians, sponge spicules or small globules of opal-cristobalite particles. The annual production of diatomite in Russia is at the level of 80

thousand tons. The United States and China are the major manufacturers of diatomite with an annual production of 677 and 350 thousand metric tons, respectively [5].

The content of RS in these rocks can vary from 50% to 90%. The phase composition of RS minerals is mainly represented by opal (56–98%), cristobalite (<20%) and quartz (5–35%) [6].

Aggregates based on amorphous silica rocks have been used in LWA concrete [1]. The RS-alkali based LWA interact within the range of concrete curing temperatures (including steam curing) and result in a strong product. Under the concrete steam curing the grains of LWA are reduced due to the formation of soluble alkali-rich phases and, at the same time, the aggregate-cement paste contact zone is densified by alkali solution, Fig. 1 [7–9]. The main challenge related to proposed approach is related to some sensitivity of early age hydrating cement structure to internal stresses and possible induction of alkali-silica reaction when excessive quantities of alkalis are used. However, RS is a promising raw material for LWA when designed for prolonged action (to reduce the internal stresses) and when amorphous silica is incorporated into water-insoluble phases. This research was focused on investigation of the effect of a steam treatment of LWA concretes with artificial aggregates based on granulated reactive silica powders (AAGS) of genetic formula “SiO₂-ROH”, where R is an alkali metal ion. It was proposed that under thermal gradients the liquefied silica-alkali phase diffuses from the silica grains into cementitious matrix densifying the contact zone (Fig. 1).

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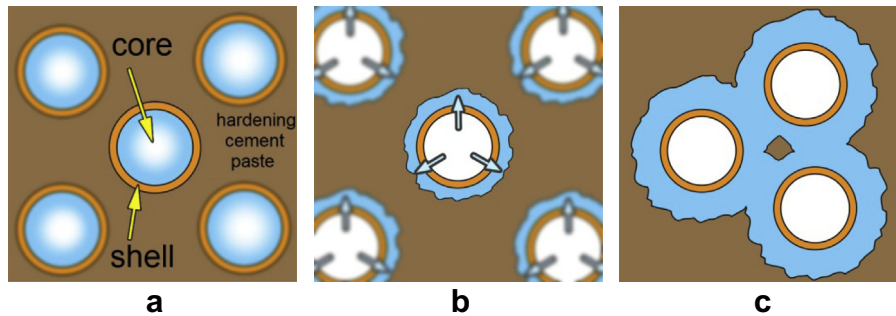


Fig. 1. The formation of AAGS based composite. (a) The initial structure. (b) Thermally induced diffusion. (c) The structure of hardened concrete with densified contact zone.

Table 1
Characteristics of lime.

Properties	Slaked lime	Unslaked lime
Content of active CaO + MgO (%)	>60	>80
Active MgO (%)	≤5	≤5
CO ₂ (%)	–	≤5
Unreacted grains (%)	≤11	–
Content of hydration water (%)	≤0.5	–
Slaking time (min)	–	≤8

On the first stage of thermally induced curing (Fig. 1a) the hydration of portland cement results in formation of a strong frame work around non-activated AAGS. Along with the hydration process (the second stage, Fig. 1b), an activation of AAGS's core is realized at a steam curing. At this stage, the diffusion of amorphous silica and formation of polysilicate solutions takes place followed by the densification of AAGS shell and concrete matrix. Further densification of AAGS contact zone (Fig. 1c) is realized with polymerization and polycondensation of newly-formed polysilicates.

2. Experimental program

2.1. Materials

The raw materials for AAGS included the range of alkali products: NaOH, Na silicate, Na fluorsilicate, quicklime, hydrated (slaked) lime, chalk and three types of portland cement: CEM II/A 32.5R (supplied by “Belgorod cement”), CEM I 42.5 (supplied by “Oskolcement”), CEM II/A 32.5H (manufactured by “Mordovcement”). The silica components for AAGS core included opoka (Aleksievskoe deposit, Mordovia) and tripoli (Stal’noe deposit, Belarus). The silicic acid (SiO₂·nH₂O) was used as a model system for investigation of a contact zone. The same types of portland cement were used to obtain the “model” cement paste and mortar for the study on contact zone. Fine sand (Ziborovskoe field, Belgorod

Table 2
Chemical composition of portland cement.

Type of cement	Chemical composition (%)						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	LOI
CEM II/A-S 32.5R	21.8	5.40	4.30	66.4	0.58	2.35	0.51
CEM I 42.5	21.52	5.83	4.50	66.03	0.57	2.42	0.30
CEM II/A 32.5	31.28	5.25	4.33	50.42	1.16	3.20	0.84

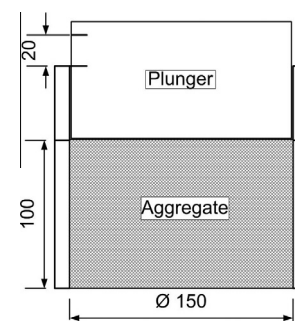


Fig. 3. The apparatus for testing of the crushing strength of aggregates.

region) with a fineness modulus of 1.4 was used as an aggregate for “model” mortars.

The properties of slaked lime and chemical composition of portland cement are presented in Table 1 and 2 respectively.

2.2. Test methods

The investigation of the cementitious matrix was performed using the methods of Infra-Red Fourier Transform Spectroscopy, FTIR (using FTIR Spectrometer VERTEX 70) and electron microscopy (High-Resolution Scanning Electron Microscopes Supra 50 VP and Dual Beam Electron Microscope Quanta 3D FEG). The

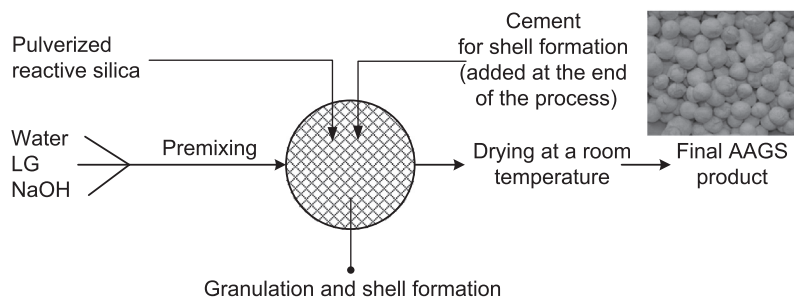


Fig. 2. The process of AAGS production.

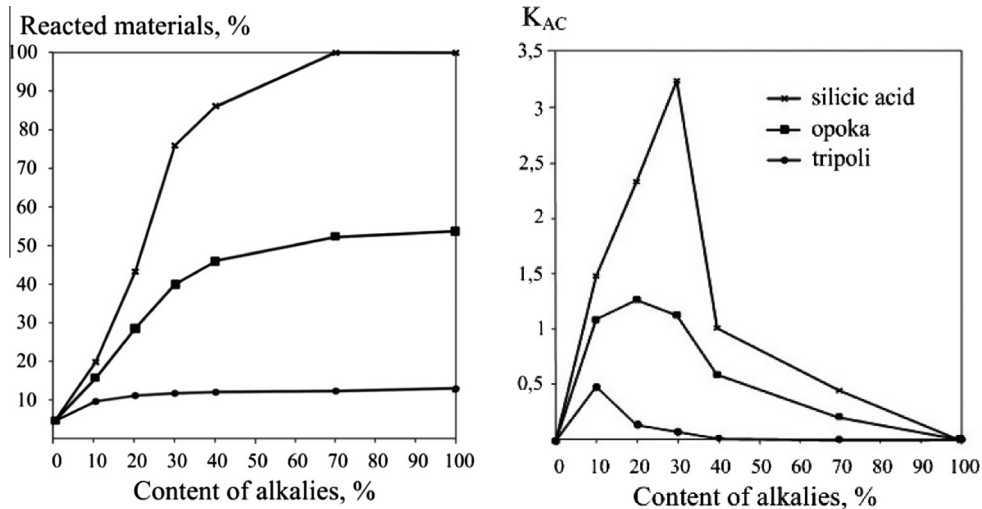


Fig. 4. The content of reacted material (left) and the K_{AC} (right) vs. alkali content.

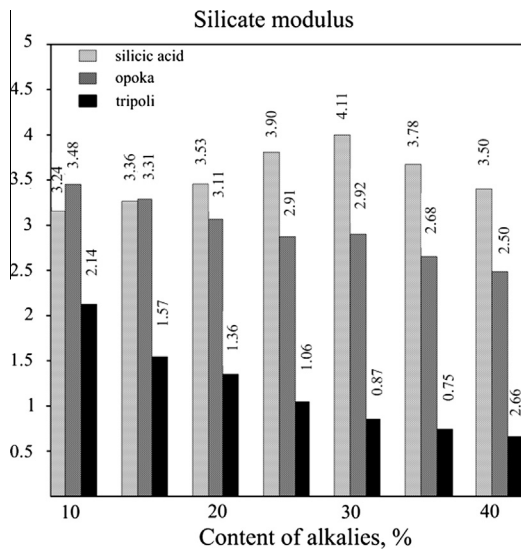


Fig. 5. The effect of alkalis on the silicate modulus.

reactivity of raw silica materials was investigated for the selection of composition of AAGS. This test included a 2-h steam treatment of silica raw materials mixed with different amounts of alkali (NaOH) at a temperature of 90 °C. Treated suspension was filtered, the mineral residue was washed with distilled water and dried to a constant weight. The dried residue was subjected to quantitative chemical analysis for calculation of silicate modulus. The silicate modulus (i.e. molar ratio of $\text{SiO}_2/\text{R}_2\text{O}$) was determined using the Babushkin methodology that is based on the estimation of alkaline oxide content by titration of aliquot portion of alkaline silicate solution [10]. Liquid glass with a density of 1.38 was used for the titration. Thus, the specific gravity, multiplied by the empirical coefficient K , corresponds to the total percentage of silicic acid, alkalis and impurities. The content of impurities in the liquid glass is assumed to be 2%. The silicate modulus is calculated by a step-wise method using the following equation:

$$m = n \frac{\gamma_g K - (x + 2)}{x} \quad (1)$$

where n is the molecular ratio of $\frac{\text{R}_2\text{O}}{\text{SiO}_2}$ which is equal to 1.032 and 1.568 for sodium and potassium silicates, respectively; γ_g the specific density of the residue, g/cm^3 ; K the empiric coefficient to estimate the solid residue in the silicate; the coefficient value is taken according to sodium silicate modulus [11]; x is the alkaline oxide content.

The amount of reacted material vs. alkali content of NaOH was determined and the coefficient of activity (K_{AC}), which indicates the amount of reacted material per a certain amount of alkali was calculated as:

$$K_{AC} = \frac{m_2 - m_1}{C_2 - C_1} \quad (2)$$

where m_1 and m_2 is the mass of the initial and the reacted RS material, kg; C_1 and C_2 is the mass of alkali at the initial and the final stages of test, kg.

The AAGS were obtained using a granulating disk. In this process, the powder materials are placed in a mixing plate and moisturized with a solution of alkalis such as sodium silicates. The agglomeration and granulation of the particles occur during the mixing process and leads to the formation of the core of the granules (Fig. 2).

The aggregate granules are enhanced by a stronger shell made of the following materials: sodium fluorosilicate, quicklime, hydrated lime, chalk and portland cement. After hardening, the resulting AAGS has a size of 3–10 mm.

According to the State Standard (GOST) 9758-86 “Porous Inorganic Aggregates for Construction: Test Methods” and BS EN 1097-2 2010 “Tests for mechanical and physical properties of aggregates. Methods for the determination of resistance to fragmentation”, the aggregates crushing strength is tested by crushing the aggregates in a cylinder (Fig. 3). The result is reported as the stress corresponding to the 20 mm penetration of plunger into the cylinder with aggregates (similar to BS EN 1097-2 2010 testing). The AAGS sample material was dried before the test to a constant weight. The same apparatus was used to determine the bulk density of the aggregate prior to the test.

3. Results and discussion

3.1. The composition of AAGS core

The composition of AAGS core was optimized by evaluation of the amounts of alkalis combined with RS during the steam treat-

Table 3
The properties of developed AAGS.

Batch ID	Composition, kg/m ³										Density (kg/m ³)	Bulk density (kg/m ³)	Water absorption (% by weight)	Compressive strength (MPa)
	Shell					Core								
	Opoka	Tripoli	NaOH	Liquid glass	Lime	Hydrated lime	Chalk	CEM I 42.5	CEM II/AS	Sodium fluorosilicate				
1	681	-	117	154	-	192	-	-	-	13.4	995	768	20.1	0.85
2	650	-	113	111	111	-	-	-	-	7.8	1114	861	22.3	0.90
3	531	-	86	87	-	-	314	-	-	22	1053	813	19.8	0.96
4	618	-	101	99	-	-	-	194	-	-	1123	867	7.2	1.47
5	-	660	112	112	-	177	-	-	-	13.2	981	758	20.2	0.85
6	-	618	106	106	113	-	-	-	-	8.4	1102	851	22.1	0.90
7	-	539	89	89	-	-	312	-	199	23.1	1045	807	19.7	0.96
8	-	603	97	97	-	-	-	-	-	-	1130	873	7.1	1.47
9	617	-	100	100	-	-	-	-	194	-	1107	861	5.0	1.42
10	-	603	96	96	-	-	-	-	199	-	1121	869	5.1	1.45

ment. Based on the test results the optimal alkali content was established at the inflex point on the curve of the reacted materials vs. alkali content (Fig. 4). This optimal content varies from 10% to 30%, depending on the type of RS materials.

The effect of alkalis and the type of silica on silicate modulus and the volume of reacted material were further investigated for the range of alkali contents from 10% to 40% (Fig. 5). The maximal values of the silicate modulus for investigated materials such as silicic acid, opoka, and tripoli were observed at different alkalinity levels of 30%, 20% and 10%, respectively.

To achieve the optimal performance of the AAGS and, in order to improve the impregnation of the cementitious matrix, the silica-alkali ratio was selected based on the volumes of reacted material and the coefficient of activity. The maximal values of the reacted materials and the coefficient of activity were obtained at a silicate modulus value above 1.5. This imposes the limitation on the alkali content enabling to avoid the loss of strength at early stages of hydration and to hinder the alkali-silica reaction during the service life.

3.2. Properties of the shell layer

The shell of AAGS has an important influence on the properties of LWA concrete. The mixture of lime and sodium silico-fluoride was proposed to form a strong shell layer, which is fixed on the surface due to presence of moisture supplied from the core. To control the physical and mechanical properties of the AAGS as well as to provide the impregnation of the contact zone, a number of materials for the shell were tested such as: lime, chalk and portland cement (Table 3).

Based on the obtained results, it is evident that the composition of the shell has a significant effect on the performance of the AAGS. The aggregates coated with portland cement had a better performance in terms of water absorption and compressive strength when compared with other materials (Table 3). Better performance of these compositions can be explained by the interaction of portland cement and sodium silicate compounds creating a strong impermeable monolithic shell around the core of the aggregate.

In zero-cement AAGS compositions strength is achieved by the polymerization of sodium silicate (which is a part of the core composition) and the adhesion of particles of lime or chalk on the surface. This process results in a shell of higher porosity (Table 3). As a result, these zero-cement coatings produce AAGSs with a higher value of water absorption and lower strength.

Three types of portland cement were tested in order to design the shell with the best water resistance (Table 4). The experiment involved testing of the model samples of cement paste which were mixed with a model alkaline core component consisting of sodium silicate, sodium hydroxide and water at a ratio of 1:1:2 (by weight), cured at normal conditions and tested after 28 days of curing.

The best residual strength after water exposure (defined by a residual strength coefficient) was demonstrated by the specimens based on slag cement (CEM II/A S). The improved performance can be explained by the interaction of slag cement and sodium silicates and formation of insoluble phases of sodium and aluminum polysilicates similar to those observed in alkali-activated slag cements [12]. However, these aggregates had the lowest initial strength. The optimized AAGS with slag cement shells had improved performance (e.g., lower water absorption) as demonstrated by compositions #9 and #10, Table 1.

3.3. Interaction with cementitious matrix

The use of XRD, FTIR spectroscopy and scanning electron microscopy enabled better understanding of the interaction of alkalis with reactive silica minerals and formation of sodium

Table 4
Properties of model shell compositions.

Specimen ID	Type of cement	Compressive strength (MPa)	Residual strength coefficient	Water absorption (%)
II-P3	CEM II/A P 32.5	20.77	0.56	4.05
I-P4	CEM I 42.5	22.90	0.58	7.88
II-S3	CEM II/A S 32.5R	18.60	0.86	5.17

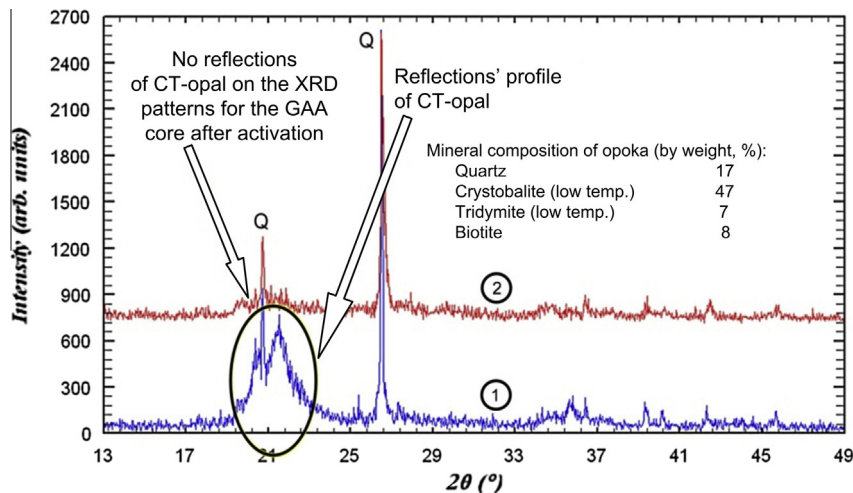


Fig. 6. The transformations of mineral composition of AAGS core due to thermal treatment: XRD before (1) and after heat treatment (2) for opoka: CT – cristobalite–tridymite bearing opals; Q – quartz.

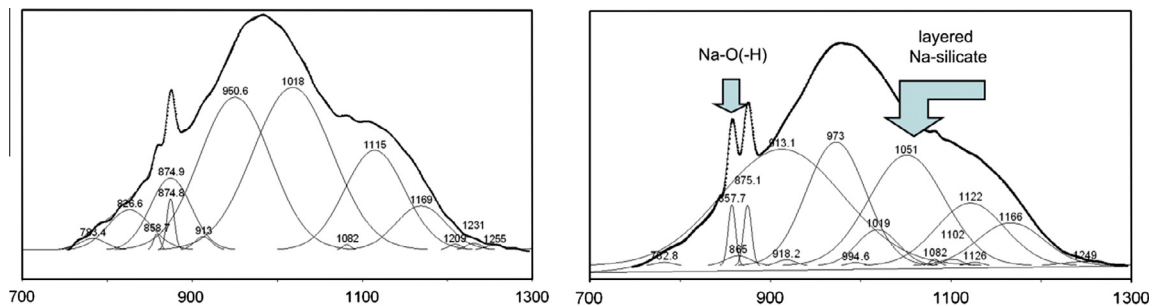


Fig. 7. The transformations within AAGS contact zone: IR spectra of bulk cement paste (left) and the effect of AAGS (right).

polysilicates (Fig. 6–8). It was observed that the presence of alkalis, under thermal gradients, cause the dissolution of amorphous silica as demonstrated by reduction of CT-opal reflections (Fig. 6) and the formation of mobile polysilicates, enabling their subsequent migration through the AAGS shell into the contact zone (as demonstrated by the presence of Na-silicates, Figs. 6 and 7). This process leads to the formation of new phases within the structure of hydrated cement, fine aggregates, and AAGS resulting in densification of the contact zone (according to Fig. 1).

To clarify the processes occurring due to the thermal activation of granules, a study of elemental composition of inter pore walls was conducted (Fig. 8). It can be observed that the shell of the aggregate is mainly represented by the interaction products of sodium silicates and lime. The contact zone of the AAGS shell and cementitious matrix (Fig. 8d) is characterized by the presence of carbon, which is the evidence of the AAGS carbonation, which were stored in open-air conditions. The aggregates contact zone in the “common” concrete is weak due to the wall effect and precipitation of portlandite crystals; however, the diffusion of sodium polysilicates from AAGS into the hydrating cement matrix enables to fill the inter pore spaces and cavities adjacent to the aggregate

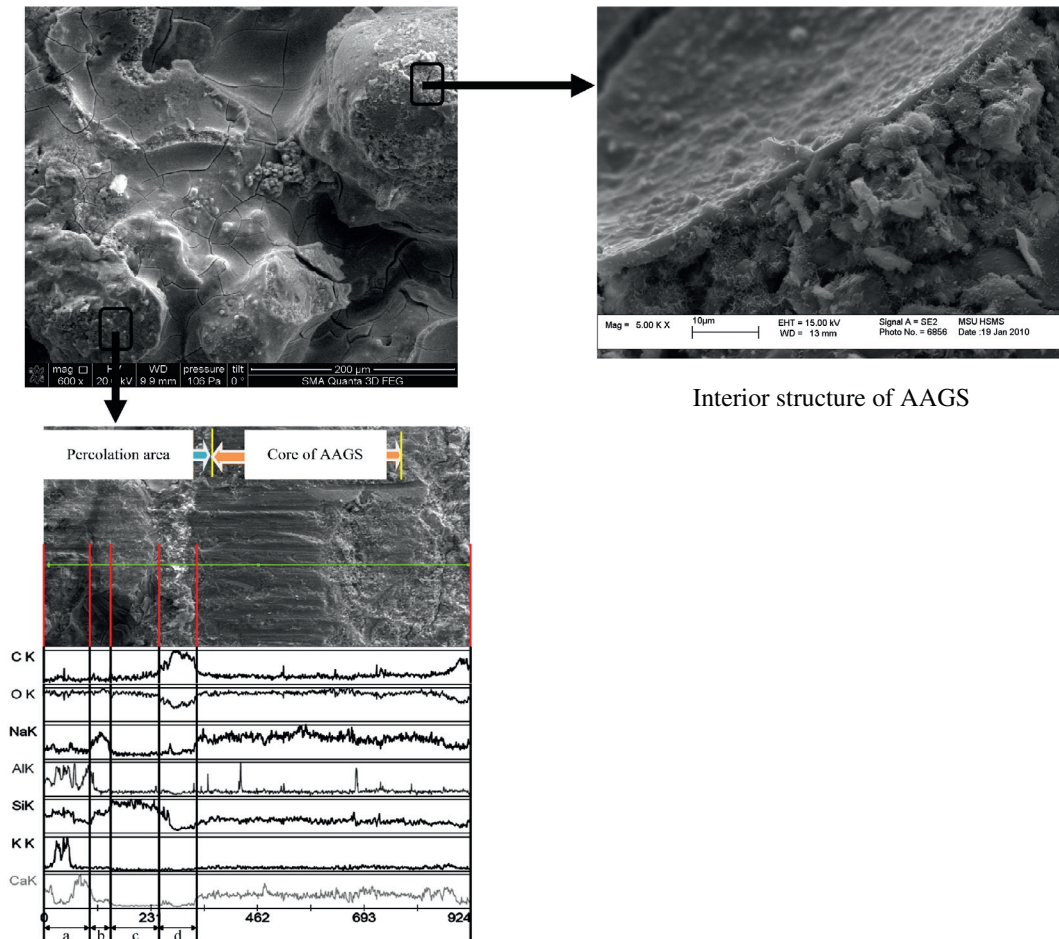
(zone 4, Fig. 8). Therefore, the increased intensity of the sodium ions within the contact zone is detected (Fig. 8b). Within the percolation area (Fig. 8a), the peaks of sodium silicates occur only locally, mainly within the zones of defected cement matrix.

4. Conclusions

This work demonstrated the feasibility of the production of artificial aggregates based on granulated SiO₂ reactive powders which are capable to interact with cementitious matrix and benefitate the contact zone in the LWA concrete.

The main components of the developed aggregates are the reactive silica powders from amorphized pozzolanic SiO₂ rocks. The optimal alkali content in the AAGS core can vary from 10% to 30% and can be selected according to the composition of pozzolanic rock (i.e., the amount of amorphous silica). It was demonstrated that slag cement is the most effective component for the AAGS shell designed for enhanced water-resistance.

According to the suggested mechanism, the use of steam treatment triggers the formation of sodium polysilicate solutions due to



Interior structure of AAGS

Fig. 8. Microstructure and the elemental composition of AAGS contact zone: a – hardened cement paste; b – contact zone; c – sand aggregate; d – carbonated surface of AAGS.

interaction of silica and alkalis within the core of the AAGS. As a result, the migration of this solution densities the cementitious matrix adjacent to the aggregate contact zone and leads to the formation of insoluble gel phases of polysilicates, sodium fluorides, as well as sodium or aluminum compounds within the porous space of the hardened phases on the surface of the cement and aggregate particles resulting in a strong monolithic AAGS-cementitious matrix composite with reduced porosity and low water absorption.

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