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The Efficiency of SiO_2 Based Materials in Granulated Artificial Aggregates

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ABSTRACT

This paper reports on the development of a new type of low cost artificial aggregates based on granulated reactive silica (AAGS) for application in lightweight concrete. The functional principle of AAGS is based on the formation of polysilicate solutions under heat treatment (up to 80 °C) and migration of these solutions into the porous space of concrete under the thermal gradients, resulting in strengthening of inter-porous space. Developed AAGSs are based on low cost local raw materials, which may contain different amounts of amorphous silica. The activity coefficient (AC) and amorphous silica content are used to evaluate the performance of raw materials by suggested accelerated method.

Silica components with different genesis are investigated and ranked according to their AC. It is found out that chemogenic and biogenic siliceous rocks with a low degree of diagenetic transformations, which are mostly represented by CT-opals (a low-temperature nanoscale modification of tridymite and crystobalite, such as diatomite, tripoli and opoka) are the most highly active raw materials for AAGS. All tested siliceous materials including natural and artificial components are divided into three groups: highly active (with AC of 51–100%), active (with AC of 21–50 %) and low-active (with AC of 5–20 %). Based on theoretical and experimental studies, the requirements for AAGS raw materials are developed.

INTRODUCTION

The production of efficient construction materials and products using local raw materials and energy-saving technologies is the main direction for the development of the construction industry. Lightweight concrete based on lightweight aggregates obtained with low temperature processing technology is an attractive product [1–4]. The developed artificial aggregate based on silica raw material (AAGS) is an example of such effective materials [4, 5].
It has been proposed that under thermal gradients, the liquefied silica-alkali phase diffuses from the silica grains into the cement matrix and densifies the aggregate contact zone (Fig. 1) [5]. Also, the developed aggregate and concrete can be produced by autoclave treatment [6, 7]. This research is focused on the synthesis of the AAGS with generic formula «SiO_2–ROH», where R is an alkali metal ion using steam treatment. The aim of this work is to evaluate the raw materials of different origin for the production of effective AAGS and the development of an express method of determining the performance of different raw materials.

EXPERIMENTAL PROGRAM

The following reactive silica raw materials from Russia and Belarus are used in this research: opoka (Alekseevskoe deposit, Mordovia); diatomite diasile powder (diatomaceous

earth, «Diamix» state corporation, Ulyanovsk Region); expanded perlite (Open JSC «Betonprom», Belgorod Region); tripoli (Fokino deposit, Bryansk Region); perlite (Mukhor-Talinskoe deposit, Buryat Republic); tripoli (Stal'noe deposit, Belarus); opoka (Korkino deposit, Chelyabinsk Region). In this study, selected clay minerals are used to investigate the effect of clay minerals present as silica rocks. Fly ash (supplied from Novo-Troitsk power station, Orenburg Region) and finely crystalline quartz are also used in the experimental program. For comparison, silicic acid is used as a model system. The alkaline solution of NaOH is used as an alkaline component.

By design, the AAGS must provide the leaching of amorphous silica and formation of the solutions of polysilicates. The activity coefficient is proposed as an integral performance characteristic of raw materials. To determine the activity coefficient, an accelerated method is developed. This method is suitable for the analysis of raw materials to obtain the AAGS with optimal performance. The sample of silica raw material is crushed to pass through the sieve with mesh size of 0.315 mm and then placed in a conical flask that is then filled with a 30% solution of NaOH. This concentration is chosen to provide a sufficient alkali amount to react with siliceous component. The flask is tightly sealed with ground-in stopper to prevent the ingress of air. The obtained suspension is stirred in a shaking table for 10 min and subjected to heat treatment at 90 ºC in a steam chamber for 2 hours. Treated suspension is filtered and the mineral residue is washed with distilled water for three times, and then dried to a constant weight. The filtered fluid is then dried and its quantitative chemical composition is determined.

The activity coefficient K_A is calculated according to the equation:

$$K_A = \frac{m_1 - m_2}{m_1} \times 100, \% \quad (1)$$

where:

m_1 – the weight of initial silica material; m_2 – the weight of dried mineral residue after the steam treatment.

The silicate modulus (i.e. molar ratio of SiO_2/R_2O) is determined using the Babushkin method by estimating the alkaline oxide content by titration [10]. Liquid glass with a density of 1.38 is used for the titration. 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-vise method using the following equation:

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

where

n – molecular ratio of R_2O/SiO_2, which is equal to 1.032 and 1.568 for sodium and potassium silicates, respectively;

γ_g – specific density of the residue, g/cm^3;

K – empirical coefficient to estimate the solid residue in the silicate; the coefficient value is taken according to sodium silicate modulus [11];

x – alkaline oxide content.

RESEARCH RESULTS AND DISCUSSION

According to the developed accelerated method the raw materials of various genetic types are analyzed and ranked by the activity coefficient and the silicate modulus (Table 1).

Table 1. The Activity Coefficients and the Silica Modulus of Raw Materials

Raw materials	$K_{A,}$ %	Silicate modulus
Silicic acid	76.0	4.11
Opoka (Alekseevskoe deposit, Mordovia)	40.5	2.92
Diatomite Diasile, powder (Diamix, Ulyanovsk Region)	40.1	2.89
Tripoli (Fokino deposit, Bryansk Region)	39.2	2.82
Opoka (Korkino deposit, Chelyabinsk Region)	25.4	1.83
Enriched kaolin (Rifey, Chelyabinsk Region)	16.3	1.17
Expanded perlite (Betonprom, Belgorod Region)	15.6	1.12
Tripoli (Stal'noe deposit, Belarus)	12.1	0.87
Perlite (Mukhor-Talinskoe deposit, Buryat Republic)	8.4	0.61
Volcanic glass (Gyumushskoe deposit, Armenia)	7.8	0.56
Montmorillonite (Gumbrskoe deposit, Georgia)	6.0	0.43
Fly-ash (Novo-Troitsk power station, Orenburg Region)	4.5	0.32

The application of the accelerated method enabled to rank the silica raw materials by using the activity coefficient as: highly active, with K_A = 51–100%; active, with K_A= 21–50%; and little active, with K_A= 5–20%. Thus, chemo-sedimentary and biogenic siliceous rocks with a low degree of diagenetic transformations which are mostly represented by CT-opals (the low-temperature nanoscale modification of tridymite and cristobalite) such as diatomite, tripoli and flask have the highest activity (Table 1). Factors that reduce the activity of silica materials are related to the presence of high-temperature modifications and significant concentrations of crystallized silica. Based on the obtained results, the silicate modulus of polysilicate solution depends on K_A of raw materials, which is determined by the content of crystobalite-tridymite opalescent components. It should be noted that with decreasing K_A, and hence, the silica modulus, the amount of alkali in the AAGS nucleus must be reduced to maintain the optimal value of silicate module.

Based on theoretical and experimental research the following requirements for the silica raw materials for effective AAGS are developed:

– The activity coefficient of silica material should be at least 15%;

– The silicate module of formed polysilicates must be at least 1, since, at lower values, the cement paste possesses low strength and water resistance.

To prove that the activity of raw materials during the steam treatment is affected by the amount of silicon dioxide in the amorphous phase, the chemical composition of silica raw materials and solid residue of silica-alkali compound is determined before and after steam treatment and the resulting phase composition is calculated based on XRD results (Table 2). In

Table 2 the number above the line shows the amount in the source component, and below the line – the amount in the dry residue of silica materials after the steam treatment with alkali. It can be observed that the most considerable crystal phase gain of 43.5% is observed for the Diatomit Diasile specimen, which had the maximal initial amorphous material content (99.1%). The least crystallization gain of 10-13% is observed for the group of perlites and tripoli (Belarus). Opoka specimens had intermediate values of the crystal phase gain, at the level of 21-25%, Table 2.

Table 2. The Chemical Composition of Raw Silica Materials and Steam Treated Materials

Silica based raw materials	**Oxide composition, % before/after steam treatment**									**Amorphous phase, %**
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	R_2O	SO_3	LOI	
Silicic acid	99.90	–	–	–	–	–	–	–	–	100.0
(reference)	99.51	–	–	–	–	–	0.20	–	–	100.0
Opoka	86.50	4.60	3.62	0.98	0.78	0.35	2.70	0.29	0.27	83.1
(Mordovia)	77.50	7.66	5.33	1.57	1.13	0.58	7.30	0.01	0.04	57.9
Diatomit Diasile	81.08	5.63	2.67	0.01	0.68	0.32	1.33	0.05	7.50	99.1
(Ulyanovsk)	73.17	8.30	3.94	0.01	1.00	0.47	1.96	0.07	11.06	55.6
Opoka	76.30	8.40	3.10	2.20	1.00	0.20	1.70	–	7.10	76.0
(Chelyabinsk)	71.24	10.19	3.76	2.67	1.21	0.24	2.06	–	8.62	54.3
Tripoli	74.20	7.20	2.40	6.60	1.10	–	0.60	–	8.60	96.5
(Bryansk)	64.71	9.73	3.24	8.92	1.49	–	0.81	–	11.10	57.3
Expanded	75.50	12.50	0.70	1.60	–	–	–	–	9.70	98.9
perlite	72.16	14.20	0.80	1.82	–	–	–	–	11.02	86.4
Perlite	74.00	14.00	2.60	2.10	–	–	2.36	–	8.01	98.9
(Buryat Republic)	61.34	18.62	3.46	2.79	–	–	3.14	–	10.65	87.5
Tripoli	56.87	6.10	2.30	18.10	1.36	0.24	2.25	0.18	12.58	34.5
(Belarus)	48.14	6.49	2.45	19.26	1.45	0.26	2.39	0.19	13.38	24.1

Trial AAGS are produced using the opoka (Alexis field, Mordovia), considering the recommended amount of alkali in the nucleus. Analysis of the results demonstrates that, after the steam treatment, the content of the silicon dioxide in amorphous phase is reduced in all materials, while the concentration of other oxides increases, as demonstrated by Fig. 1.

The results of XRD investigation of the changes in the mineral composition of core AAGS after steam treatment with alkalis demonstrated that opoka which is presented mostly by low-temperature-based nano-dimensional modifications of tridymite and crystobalite has the highest activity coefficient among the investigated natural silica materials (Fig. 1).

The use of XRD enabled better understanding of the interaction of alkalies with reactive silica minerals and formation of sodium polysilicates. It is observed that the presence of alkalis, under thermal gradients, cause the dissolution of amorphous silica as demonstrated by reduction of CT-opal reflections (Fig. 1) and the formation of mobile polysilicates, enabling their subsequent migration through the AAGS shell into the contact zone.

CONCLUSIONS

The use of the developed accelerated method for determining the activity of silica components enables to specify the best raw materials for the developed AAGS. The application of the developed method enables the selection of raw materials to achieve the optimal level of

impregnation of lightweight concrete with sodium polysilicate and, therefore, the improved performance.

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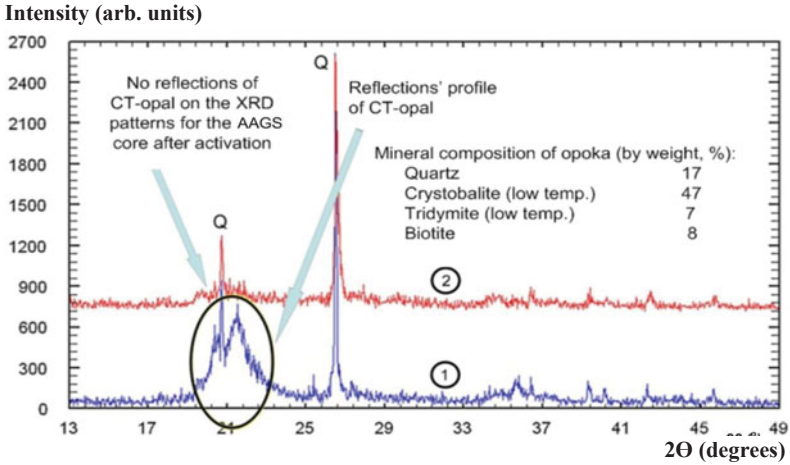

Figure 1. The phase composition of AAGS core before (1) and after (2) steam treatment:

CT – crystobalite-tridymite bearing opals; Q – quartz

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