UDC 666.973.6

O.O. Sihunov, A.O. Musina, A.O. Holovko, M.I. Bulatetskyi, O.P. Ryzhova

PHYSICOCHEMICAL PROCESSES DURING SOLIDIFICATION AND THE PECULIARITIES OF STRUCTURE FORMATION IN AERATED CONCRETES USING METALLIC SILICON AS A GAS GENERATOR

Ukrainian State University of Science and Technologies, Dnipro, Ukraine

The results of research on the structure and phase composition of non-autoclaved aerated concrete with a density of 550–750 kg/m^3 using metallic silicon as a gas generator are presented. The peculiarities of the structure formation of aerated concrete products and the mineralogical composition of their hydration products were investigated. It was established that increasing the content of metallic silicon in aerated concrete leads to an increase in the pore space of the compositions. The results of diffractometric and thermal analysis methods for establishing the phase composition of aerated concrete compositions with metallic silicon as a gas generator are also presented. Analysis of XRD patterns and derivatograms showed that the aerated concrete samples under investigation contain a binder component, obermorite ($5CaO\cdot6SiO_2\cdot5.5H_2O$); xonotlite ($6CaO\cdot6SiO_2\cdot H_2O$); α-dicalcium silicate hydrate ($2CaO\cdot SiO_2\cdot H_2O$); and hillebrandite ($2CaO\cdot SiO_2\cdot1.17H_2O$). It was established that increasing the amount of metallic silicon as a gas generator stimulates an increase in the content of hydrated phases in aerated concrete compositions.

Keywords: metallic silicon, aerated concrete, gas generator, phase composition, calcium hydrosilicates.

DOI: 10.32434/0321-4095-2024-155-4-69-78

Introduction

Currently, aerated concrete is one of the most common building materials used for the construction of civil and industrial buildings. This building material is an environmentally pure, efficient building material with a sufficient raw material base for its manufacture. In the simplest case, it consists of cement, filler, water and gas generator, has the properties, on the one hand, of stone, on the other hand, of wood. The combination of these properties makes aerated concrete an excellent building material. Due to increasing porosity of the material, the density of concrete is decreased and its thermal insulation properties are improved [1]. This is closely related to the construction and operational properties of products and enclosing structures: the weight of the walls, load on the foundation, vapor permeability, sorption moisture of the material, thermal insulation properties of the material, and specific heat energy consumption for heating buildings [2].

As is known from literary sources, the structure of aerated concrete is mainly represented by hydrated and silicon-containing components. The main hydrate phases formed in aerated concrete are calcium hydrosilicates, in particular tobermorite 11.3 Å ($5CaO\cdot6SiO_2\cdot5.5H_2O$) and xonotlite ($6CaO\cdot6SiO_2\cdot H_2O$) [3–8].

The purpose of the work is to study the process of structure formation and mineralogical composition of non-autoclaved aerated concretes with metallic silicon (Si_{met}) as a gas generator.

Experimental

We investigated samples of aerated concrete, which were made from the following materials: Portland cement clinker, gypsum stone, lime, river sand, metallic silicon and caustic soda. Tests of the compositions were carried out for several compositions (Table 1). The content of gypsum stone and caustic soda in the compositions is constant.

Table 1

Compositions of aerated concrete

Composition	The content of aerated concrete components, wt.%		
	cement	sand	lime
1	26	53	21
2	31	53	16
3	26	58	16

The phase composition of aerated concrete was determined by using complex X-ray diffraction (XRD) and differential thermal (DTA) methods. Identification of XRD peaks and endothermic and exothermic effects on DTA curves were carried out using reference data given elsewhere [4]. X-ray phase analysis was carried out based on powder diffractograms obtained on the automatic diffractometer «DRON-3» using an X-ray tube with a cobalt and copper anticathode. Differential thermal analysis of the samples was performed on a Q-1500D derivatograph of the Paulik-Paulik-Erdey system in the temperature range of 20–900^{0}C with a rate of temperature rise of 10 degrees·min^{-1}. The prepared samples of the material were crushed until they passed through the sieve No. 0063.

Results and discussion

Aerated concrete compositions with a density of 550–750 kg/m^3 have a uniform porous structure with predominant pore sizes from 0.2 to 1.8 mm. The pores existing in aerated concrete samples are mainly oval and round in shape. Interporous partitions have a uniform structure without cracks and other defects. A uniform distribution of pores of small and large sizes among themselves is observed.

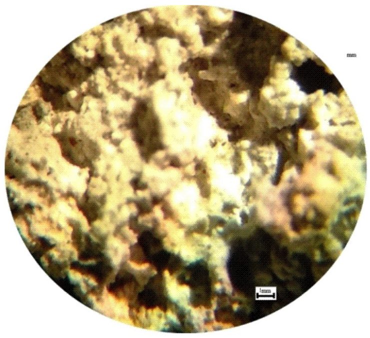
As a rule, non-autoclaved aerated concrete is mainly prepared using Portland cement. At the same time, it should be noted that the processes of setting and hardening of cement determine the mineral composition of neoplasms and the properties of porous products [9–12].

Analysis of the results on counting the number of interporous partitions and pores in aerated concrete, which has Si_{met} as a gas generator (Figs. 1–3), showed an increase in the content of pores in the composition structure with increasing the amount of gas generator. It should be obseved, in particular, the following:

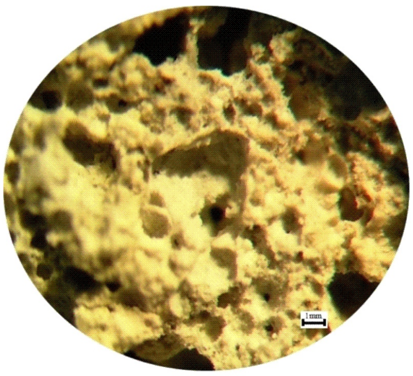
– the number of pores is about 45% when a Si_{met} content is 3 wt.% (Figs. 1a, 2a and 3c);

– the number of pores is about 53% when a Si_{met} content is 4 wt.% (Figs. 1b, 2b and 3b);

a



b



c

Fig. 1. Structure of non-autoclaved aerated concrete with Si_{met} as a gas generator (composition 1) at different contents of metallic silicon (wt.%): a – 3; b – 4; and c – 5

– the number of pores is about 69% when a Si_{met} content is 5 wt.% (Figs. 1c, 2c and 3c).

In order to establish the mineralogical (phase) composition of the developed aerated concrete composites, which contains Simet as a gas generator, X-ray phase analysis was carried out (Figs. 4–6).

Analysis of diffractograms showed that the investigated samples of non-autoclaved aerated concrete contain tobermorite 11.3 Å ($5CaO{\cdot}6SiO_2{\cdot}5.5H_2O$), α-dicalcium silicate hydrate ($2CaO{\cdot}SiO_2{\cdot}H_2O$), hillebrandite ($2CaO{\cdot}SiO_2{\cdot}1.17H_2O$) and xonothlite ($6CaO{\cdot}6SiO_2{\cdot}H_2O$). At the same time, it should be noted that some peaks of tobermorite and quartz peak 1.53 Å, hillebrandite and tobermorite peak 3.00 Å, tobermorite and xonotlite 2.25–2.27 Å and 1.81 Å are observed. In addition, the peaks at 3.30–3.31 Å, which are specific to quartz, are the most intense. Peaks of calcium hydrosilicates on radiographs of aerated concrete demonstrate the presence of poorly crystallized and lime-rich C-S-H-gel. When identified, it has the appearance of background lines [4].

Analysis of results presented in Fig. 7 showed that an increase in the amount of gas generator from 3 to 5 wt.% for compositions 1–3 leads to an increase in the content of tobermorite and xonotlite, which is accompanied by an increase in the intensity of their characteristic peaks. For example, the 1.81 Å peak increases from 11.57 to 26.30 (by 56%) for composition 1, from 11.67 to 14.4 (by 19%) for composition 2 and from 16.24 to 22.14 (by 27%) for composition 3. The specified dependence is also valid for the formation of α-dicalcium silicate hydrate. Thus, the intensity of the 4.20 Å peaks characteristic of α-dicalcium silicate hydrate increases with increasing Si_{met} as a gas generator from 13.05 to 22.5 (by 42%) for composition 1, from 10.63 to 29.00 (by 63%) for composition 2 and from 17.55 to 24.8 (by 29%) for composition 3. Analysis of XRD patterns in the presence of SiO_2 in the form of quartz did not show a clear relationship between the height of the peaks and the content of the gas generator.

The conducted X-ray phase analysis on the formation of the mineralogical composition of aerated concrete products is confirmed by DTA data shown on the example of one composition (composition 1) containing 3, 4 and 5 wt.% Si_{met} (Fig. 8).

The data of thermogravimetric analysis demonstrate that the weight losses of the samples containing 3, 4 and 5 wt.% of metallic silicon is 16–18 wt.%. Compositions in the temperature range of

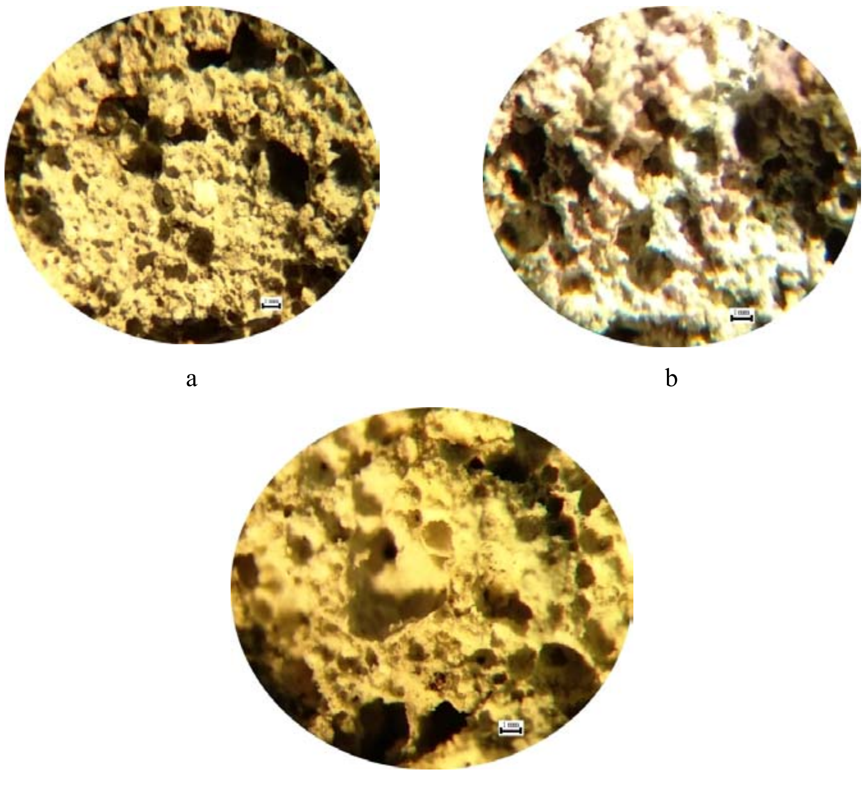
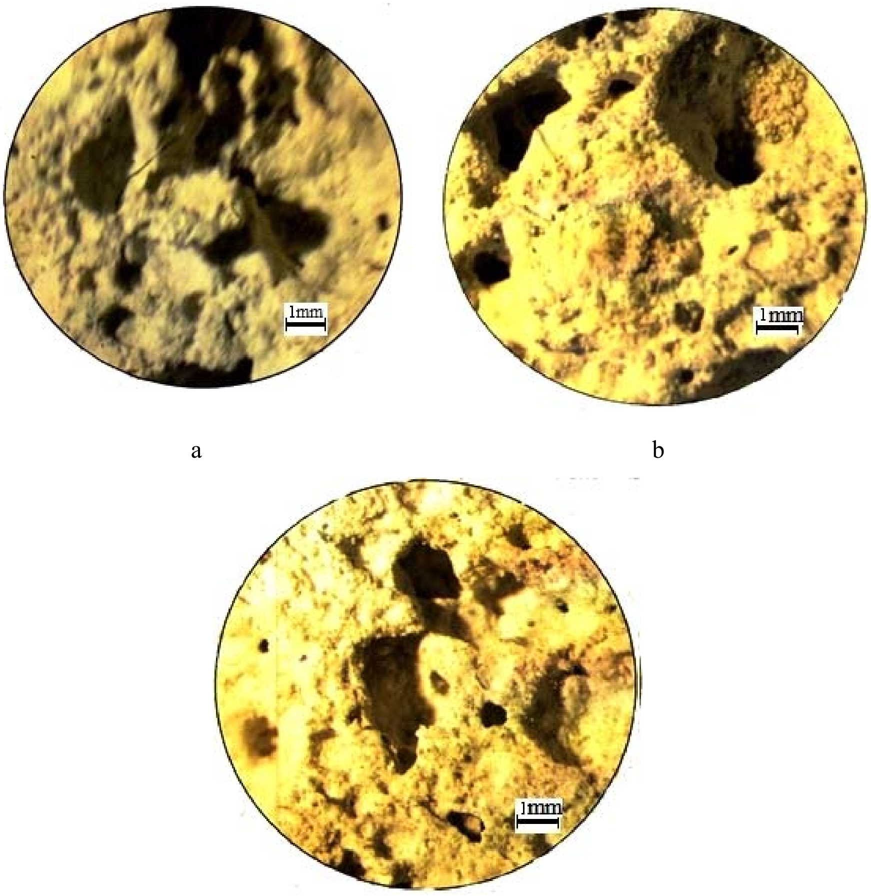


Fig. 2. Structure of non-autoclaved aerated concrete with Si_{met} as a gas generator (composition 2) at different contents of metallic silicon (wt.%): a – 3; b – 4; and c – 5



a b

c

Fig. 3. Structure of non-autoclaved aerated concrete with Si_{met} as a gas generator (composition 3) at different contents of metallic silicon (wt.%): a – 3; b – 4; and c –5

20–400^{0}C lose 31% of the total weight loss of the sample. Decreasing the sample weight at 460–500^{0}C can be explained by processes of oxidation and burning of organic compounds (stearic acid, surfactants) and removal of physically bound water. The main weight loss of the sample (65%) is observed in the temperature range of 460–810^{0}C. Dehydration of $Ca(OH)_2$ occurs, which is confirmed by the endothermic effect on DTA curves with a maximum at a temperature of 475–490^{0}C. The endothermic effect on thermograms with a maximum at a temperature of 570–580^{0}C corresponds to the dehydration of hillebrandite. In the temperature range of 750–860^{0}C, an endothermic effect is appeared on the DTA curves with a maximum at a temperature of 800–810^{0}C, which is associated with the formation of wollastonite.

Conclusions

Metallic silicon as a gas generator in the development of non-autoclave hardening porous concrete is a factor that allows creating a shallow porous structure of the material with sufficiently strong interpore walls. Increasing the content of metallic silicon in the range of 3–5 wt.% allows increasing the pore volume by 40–45%.

The use of modern methods of analysis made it possible to establish the phase composition of aerated concrete products with Si_{met} as a gas generator. It was established that the mineralogical composition of concrete as a binding component is mainly represented by the following hydrates: tobermorite ($5CaO{\cdot}6SiO_2{\cdot}5.5H_2O$), xonotlite ($6CaO{\cdot}6SiO_2{\cdot}H_2O$), α-dicalcium silicate hydrate ($2CaO{\cdot}SiO_2{\cdot}H_2O$) and hillebrandite ($2CaO{\cdot}SiO_2{\cdot}1.17H_2O$). Unbound quartz ($SiO_2$) is a non-binding component (a filler). A comparative analysis of investigations when developing porous concretes which have ferrosilicon ($FeSi_2$) [13] and metallic silicon as a gas generator showed the closeness of the mineralogical composition of hydrated neoplasms and the similar formation of the porous structure of the products.

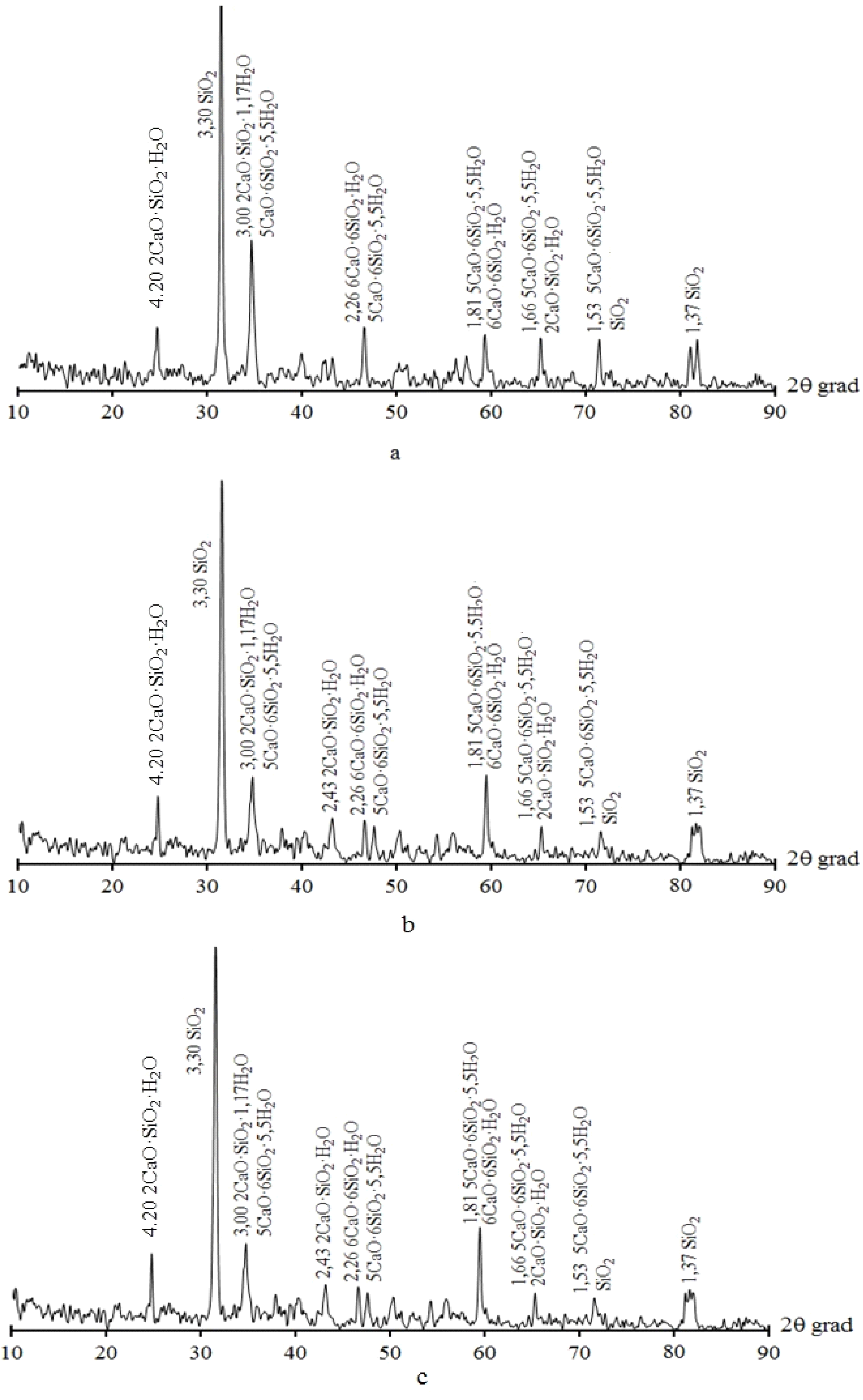


Fig. 4. XRD patterns of aerated concrete compositions (composition 1) using different contents of metallic silicon as a gasifier (wt.%): a – 3; b – 4; and c – 5

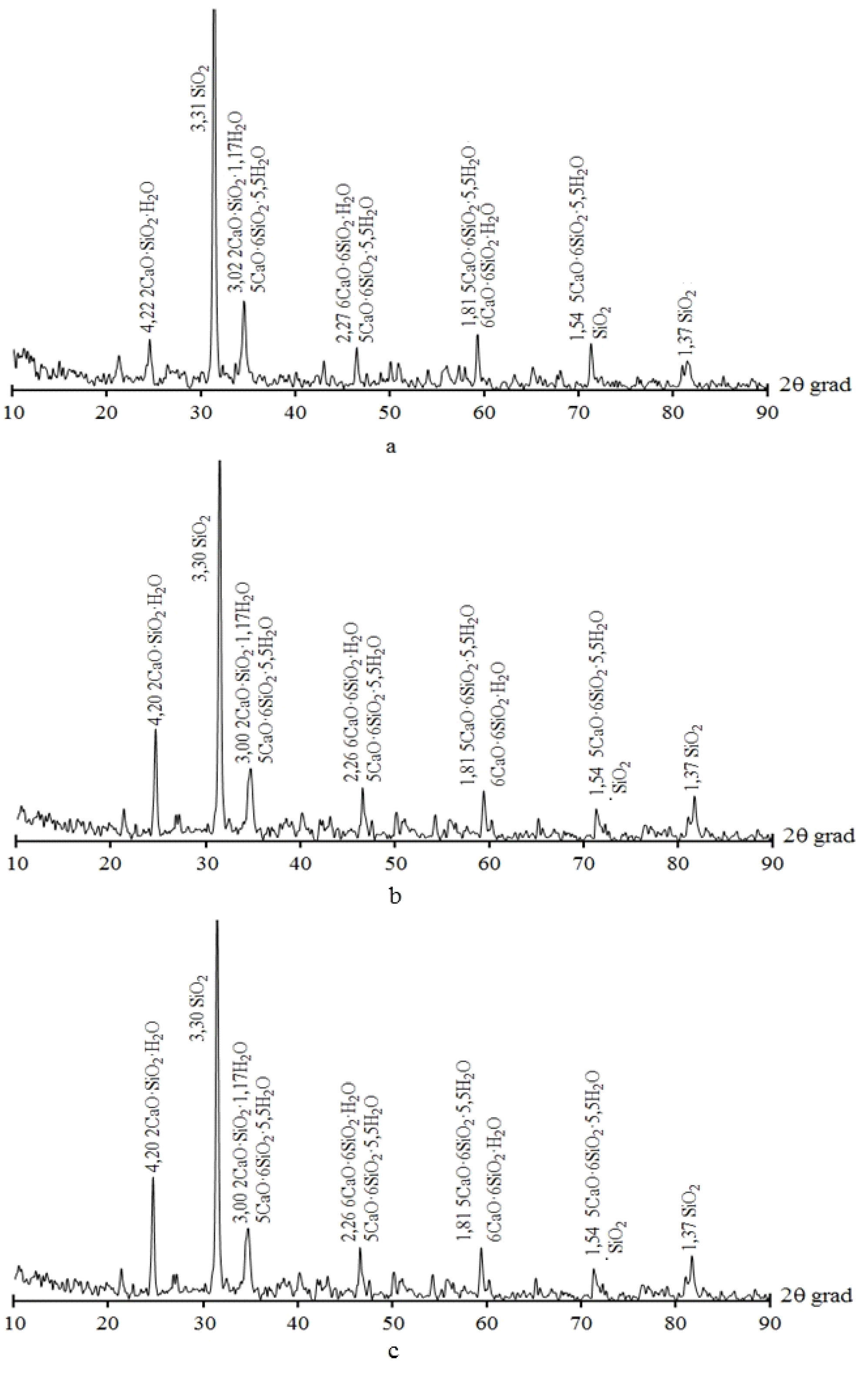


Fig. 5. XRD patterns of aerated concrete compositions (composition 2) using different contents of metallic silicon as a gasifier (wt.%): a – 3; b – 4; and c – 5

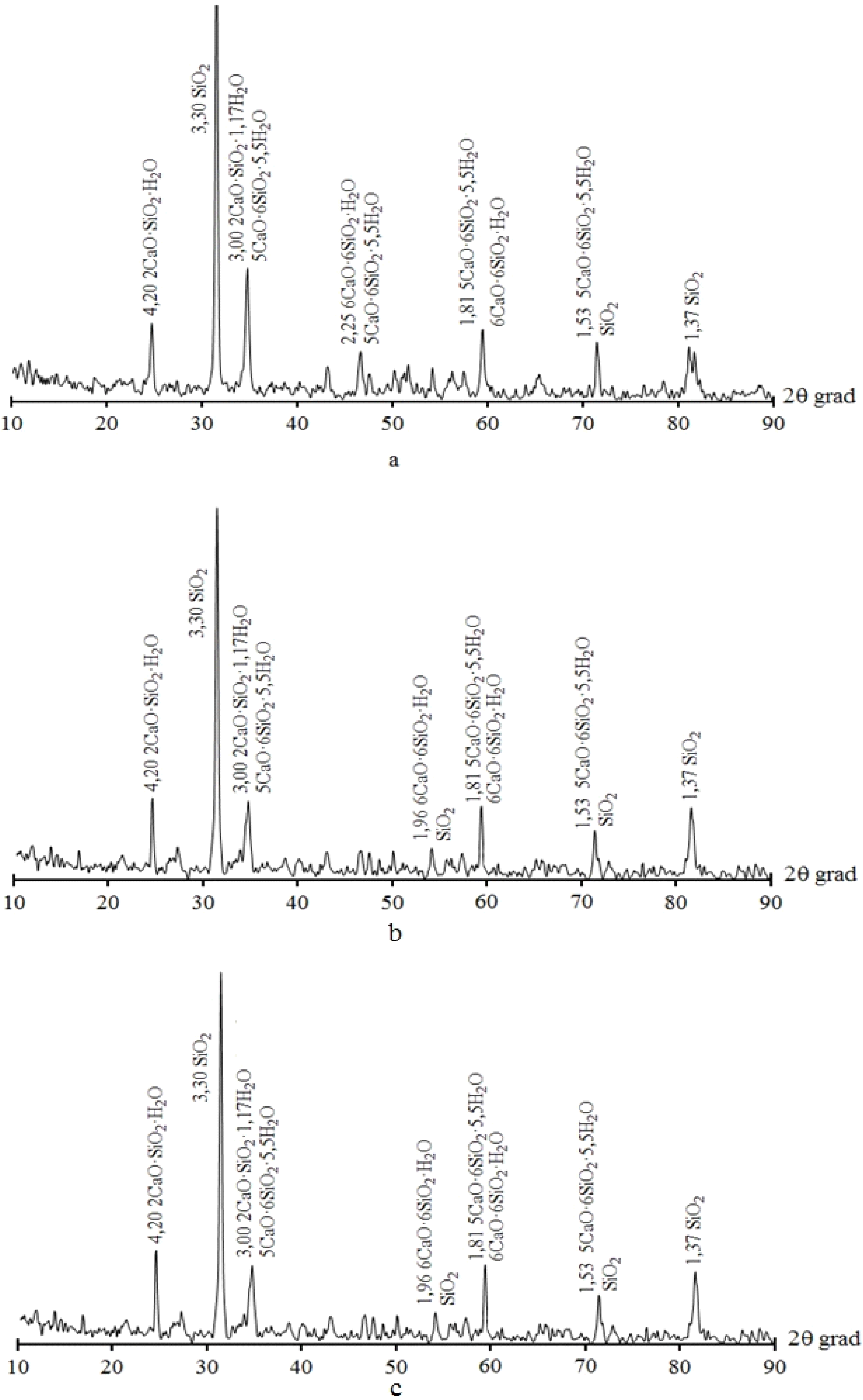


Fig. 6. XRD patterns of aerated concrete compositions (composition 3) using different contents of metallic silicon as a gasifier (wt.%): a – 3; b – 4; and c – 5

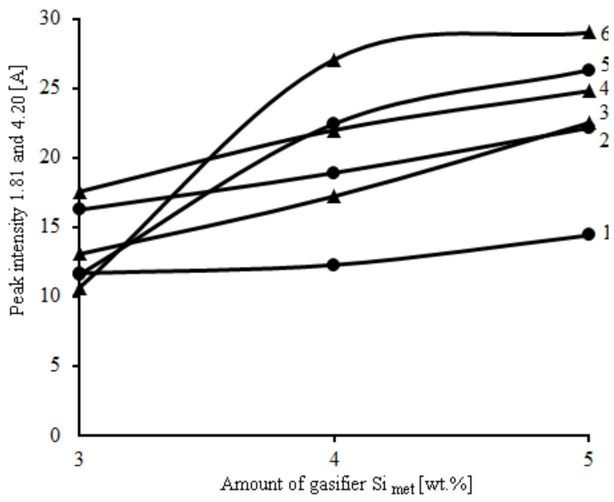


Fig. 7. Dependence on the content of calcium hydrosilicates on the amount of Si_{met} as a gas generator:
1 – tobermorite and xonotlite at 1.81 Å peak (composition 2); 2 – tobermorite and xonotlite at a peak of 1.81 Å (composition 3); 3 – α-dicalcium silicate hydrate at peak of 4.20 Å (composition 1); 4 – α-dicalcium silicate hydrate at peak of 4.20 Å (composition 3); 5 – tobermorite and xonotlite at 1.81 Å peak (composition 1); 6 – α-dicalcium silicate hydrate at peak of 4.20 Å (composition 2)

REFERENCES

1. *Korniyenko P.V.* Teoreticheskie osnovy obrazovaniya optimal'noi struktury yacheistogo betona // Nauka i Tekhnika Kazakhstana. – 2010. – No. 2. – P.81-89.

2. *Doslidzhennya* vplyvu dyspersnosti komponentiv gazobetonu na yogo osnovni budivelni vlastyvosti / Saley A., Sigunov A., Kravchenko T., Khmarska L. // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2015. – No. 5. – P.75-78.

3. *Identification*, generation of autoclaved aerated concrete pore structure and simulation of its influence on thermal conductivity / Chen G., Li F., Geng J., Jing P., Si Z. // Constr. Build. Mater. – 2021. – Vol.294. – Art. No. 123572.

4. *Gorshkov V.S., Timashev V.V., Savelyev V.G.* Metody fiziko-khimicheskogo analiza vyazhushchikh veshchestv. – M.: Vysshaya shkola, 1981. – 335 p.

5. *Thermodynamic* analysis of chemical reactions in the systems $FeSi-Ca(OH)_2-H_2O$ and $FeSi_2-Ca(OH)_2-H_2O$ / Musina A.O., Sihunov O.O., Kravchenko T.V., Hura A.O. // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2019. – No. 6. – P.136-143.

6. *Research* into influence of the electrolysis modes on the composition of galvanic Fe-Co-Mo coatings / Yermolenko I., Ved' M., Karakurkchi A., Proskurina V., Sknar I., Kozlov Y., Sverdlikovska O., Sigunov O. // East. Eur. J. Enterprise Technol. – 2017. – Vol.3. – No. 12(87). – P.9-15.

7. *Hordieiev Y.S., Karasik E.V., Zaichuk A.V.* Glass formation in the $MgO-B_2O_3-SiO_2$ system // Silicon. – 2023. – Vol.15. – P.1085-1091.

8. *Butt Yu.M.* Khimicheskaya tekhnologiya vyazhushchikh materialov. – M.: Vysshaya shkola, 1980. – 472 p.

9. *Qu X., Zhao X.* Previous and present investigations on the components, microstructure and main properties of autoclaved aerated concrete – a review // Constr. Build. Mater. – 2017. – Vol.135. – P.505-516.

10. *Modified* alumina cement with high service properties / Logvinkov S.M., Shabanova G.N., Korohodska A.N., Khrystych E.V. // China Refract. – 2016. – Vol.25. – No. 4. – P.1-5.

11. *Investigation* on properties of autoclave aerated concrete using different pre-curing and curing techniques / Khunt Y., Nathwani V., Patel H., Joshi T., Gandhi D. // Mater. Today Proc. – 2023. (in press).

12. *Size* distribution of pores and their geometric analysis in red mud-based autoclaved aerated concrete (AAC) using regression neural network and elastic mechanics / Dong M., Ma R., Sun G., Pan C., Zhan S., Qian X., et al. // Constr. Build. Mater. – 2022. – Vol.359. – Art. No. 129420.

13. *Processes* of structure and phase formation of aerated concrete of non-autoclave hardening containing ferrosilicon as a gasifier / Musina A.O., Sihunov O.O., Ryzhova O.P., Sverdlikovska O.S., Hura A.O. // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2021. – No. 6. – P.45-50.

Received 24.05.2024

ФІЗИКО-ХІМІЧНІ ПРОЦЕСИ, ЩО ВІДБУВАЮТЬСЯ ПРИ ТВЕРДІННІ, ТА ОСОБЛИВОСТІ СТРУКТУРОУТВОРЕННЯ ГАЗОБЕТОНІВ З ВИКОРИСТАННЯМ МЕТАЛЕВОГО КРЕМНІЮ ЯК ГАЗОУТВОРЮВАЧА

О.О. Сігунов, А.О. Мусіна, А.О. Головко, М.І. Булатецький, О.П. Рижова

Надано результати досліджень структури і фазового складу неавтоклавного газобетону щільністю 550–750 кг/м^3 з використанням металевого кремнію як газоутворювача. Досліджено особливості формування структури газобетонних виробів і мінералогічного складу продуктів їх гідратації. Встановлено, що зі зростанням вмісту металевого кремнію в газобетоні, спостерігається збільшення порового простору композицій. Надано результати дифрактометричного та термічного методів аналізу щодо встановлення фазового складу газобетонних композицій з металевим кремнієм як газоутворювачем. Аналіз рентгенограм і дериватограм показав, що зразки газобетону, що піддавалися дослідженням, містять в якості в'яжучої складової тобермори́т ($5CaO\cdot6SiO_2\cdot5,5H_2O$), ксонотліт ($6CaO\cdot6SiO_2\cdot H_2O$), α-гідрат двохкальцієвого силікату ($2CaO\cdot SiO_2\cdot H_2O$) та гіллебрандит ($2CaO\cdot SiO_2\cdot1,17H_2O$). Встановлено, що збільшення кількості металевого кремнію як газоутворювача стимулює підвищення вмісту гідратних фаз в газобетонних композиціях.

Ключові слова: металевий кремній, ніздрюватий бетон, газоутворювач, фазовий склад, гідросилікати кальцію.

Fig. 8. DTA curves of aerated concretes (composition 1), which contain Si_{met} as a gas generator in the amount: a – 3 wt.%; b – 4 wt.%; and c – 5 wt.%

PHYSICOCHEMICAL PROCESSES DURING SOLIDIFICATION AND THE PECULIARITIES OF STRUCTURE FORMATION IN AERATED CONCRETES USING METALLIC SILICON AS A GAS GENERATOR

O.O. Sihunov *, ***A.O. Musina, A.O. Holovko, M.I. Bulatetskyi, O.P. Ryzhova***

Ukrainian State University of Science and Technologies, Dnipro, Ukraine

* **e-mail: alsigunov@ukr.net**

The results of research on the structure and phase composition of non-autoclaved aerated concrete with a density of 550–750 kg/m^3 using metallic silicon as a gas generator are presented. The peculiarities of the structure formation of aerated concrete products and the mineralogical composition of their hydration products were investigated. It was established that increasing the content of metallic silicon in aerated concrete leads to an increase in the pore space of the compositions. The results of diffractometric and thermal analysis methods for establishing the phase composition of aerated concrete compositions with metallic silicon as a gas generator are also presented. Analysis of XRD patterns and derivatograms showed that the aerated concrete samples under investigation contain a binder component, obermorite ($5CaO \cdot 6SiO_2 \cdot 5.5H_2O$); xonotlite ($6CaO \cdot 6SiO_2 \cdot H_2O$); α-dicalcium silicate hydrate ($2CaO \cdot SiO_2 \cdot H_2O$); and hillebrandite ($2CaO \cdot SiO_2 \cdot 1.17H_2O$). It was established that increasing the amount of metallic silicon as a gas generator stimulates an increase in the content of hydrated phases in aerated concrete compositions.

Keywords: metallic silicon; aerated concrete; gas generator; phase composition; calcium hydrosilicates.

REFERENCES

1. Korniyenko PV. Teoreticheskie osnovy obrazovaniya optimal'noi struktury yacheistogo betona [Theoretical foundations for the formation of an optimal structure of cellular concrete]. *Nauka i Tekhnika Kazakhstana*. 2010; 2: 81-89. (*in Russian*).

2. Saley A, Sigunov A, Kravchenko T, Khmarska L. Doslidzhennya vplyvu dyspersnosti komponentiv gazobetonu na yogo osnovni budivel'ni vlastyvosti [Investigation on the influence of the dispersion of gas concrete components on main construction properties]. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2015; (5): 75-78. (*in Ukrainian*).

3. Chen G, Li F, Geng J, Jing P, Si Z. Identification, generation of autoclaved aerated concrete pore structure and simulation of its influence on thermal conductivity. *Constr Build Mater*. 2021; 294; 123572. doi: 10.1016/j.conbuildmat.2021.123572.

4. Gorshkov VS, Timashev VV, Savelyev VG. *Metody fiziko-khimicheskogo analiza vyazhushchikh veshchestv* [Methods of physicochemical analysis of binders]. Moscow: Vysshaya Shkola; 1981. 335 p. (*in Russian*).

5. Musina AO, Sihunov OO, Kravchenko TV, Hura AO. Thermodynamic analysis of chemical reactions in the systems $FeSi-Ca(OH)_2-H_2O$ and $FeSi_2-Ca(OH)_2-H_2O$. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2019; (6): 136-143. doi: 10.32434/0321-4095-2019-127-6-136-143.

6. Yermolenko I, Ved' M, Karakurkchi A, Proskurina V, Sknar I, Kozlov Y, Sverdlikovska O, Sigunov O. Research into influence of the electrolysis modes on the composition of galvanic Fe-Co-Mo coatings. *East Eur J Enterprise Technol*. 2017; 3(12(87)): 9-15. doi: 10.15587/1729-4061.2017.103100.

7. Hordieiev YS, Karasik EV, Zaichuk AV. Glass formation in the $MgO-B_2O_3-SiO_2$ system. *Silicon*. 2023; 15: 1085-1091. doi: 10.1007/s12633-022-01745-0.

8. Butt YuM. *Khimicheskaya tekhnologiya vyazhushchikh materialov* [Chemical technology of binders]. Moscow: Vysshaya Shkola; 1980. 472 p. (*in Russian*).

9. Qu X, Zhao X. Previous and present investigations on the components, microstructure and main properties of autoclaved aerated concrete – a review. *Constr Build Mater*. 2017; 135: 505-516. doi: 10.1016/j.conbuildmat.2016.12.208.

10. Logvinkov SM, Shabanova GN, Korohodska AN, Khrystych EV. Modified alumina cement with high service properties. *China Refract*. 2016; 25(4): 1-5.

11. Khunt Y, Nathwani V, Patel H, Joshi T, Gandhi D. Investigation on properties of autoclave aerated concrete using different pre-curing and curing techniques. *Mater Today Proc*. 2023. doi: 10.1016/j.matpr.2023.04.047.

12. Dong M, Ma R, Sun G, Pan C, Zhan S, Qian X, et al. Size distribution of pores and their geometric analysis in red mud-based autoclaved aerated concrete (AAC) using regression neural network and elastic mechanics. *Constr Build Mater*. 2022; 359: 129420. doi: 10.1016/j.conbuildmat.2022.129420.

13. Musina AO, Sihunov OO, Ryzhova OP, Sverdlikovska OS, Hura AO. Processes of structure and phase formation of aerated concrete of non-autoclave hardening containing ferrosilicon as a gasifier. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2021; (6): 45-50. doi: 10.32434/0321-4095-2021-139-6-45-50.