Sokoltsov V.,
Tokarchuk V.,
Sviderskyi V.

INFLUENCE OF SILICONS OF DIFFERENT STRUCTURES ON THE HYDRATION OF COMPOSITIONAL CEMENTS

Об'єктом дослідження є цемент, який містить в своєму складі кремнезем різної структури. Збільшення об'ємів випуску композиційних цементів призводить до необхідності пошуку нових активних мінеральних добавок. На даний момент вибір мінеральних добавок проводиться без урахування стану, в якому знаходиться силікатна складова, тому потрібна розробка певних критеріїв для цілеспрямованого підбору можливих матеріалів. Це дозволить знизити витрати трудових та фінансових ресурсів на проведення відповідних досліджень.

Як відомо, силікати можуть знаходитися в кристалічному, аморфному та скловидному стані, тому реакційна здатність різних добавок, навіть при однаковому хімічному складі, також може суттєво відрізнятися. Було запропоновано вивчити вплив структури кремнезему на процеси гідратації та властивості цементів.

Досліджено вплив кремнезему в різному фазовому стані (кристалічному, аморфному та скловидному) на процеси тверднення та фізико-механічні властивості композиційних цементів. Встановлено, що ступінь кристалічності кремнезему суттєво впливає на нормальну густоту цементного тіста. Так, введення кристалічного кремнезему підвищує нормальну густоту на 0,1–1,1 %, аморфного на 12,3–136,1 %, скловидного на 11,2–56,2 %, у порівнянні з бездобавочним цементом. Строки тужавлення цементного тіста змінюється несуттєво.

В ранні строки тверднення швидкість падіння міцності найвища при введенні аморфного кремнезему. Наприклад, при введенні 10 мас. % кристалічного кремнезему відмічається деяке зростання міцності зразків, у порівнянні з бездобавочним цементом на 8,2 %. Така ж кількість добавки аморфного кремнезему знижує міцність на 33 %, скловидного кремнезему – на 19,2 %. Ця тенденція зберігається і при збільшенні вмісту добавок.

Отримані результати досліджень дозволяють зробити висновок, що найбільш доцільно використовувати при виробництві композиційних цементів мінеральні добавки, які містять в своєму складі кремнеземисті фази в кристалічному і скловидному стані.

Ключові слова: *кремнезем різної структури, композиційний цемент, строки тужавлення, нормальна густота, процеси гідратації.*

1. Introduction

One of the stages of production of Portland cement is the process of burning the raw mix of a certain composition at a temperature of 1400 °C. The resulting material (clinker) is the most expensive component in cement and its quantity directly affects the final cost of the product. In addition, a significant amount of carbon dioxide is released during the firing of the raw mix, which is harmful to the environment. These factors lead to the need to reduce the content of the clinker component in the cement. This can be achieved by using additives that contain silicates or aluminosilicates. The most commonly used granulated blast furnace slag, fly ash, flask, tripoli powder, tuff and others [1, 2]. These additives have proven themselves well in the manufacture of general purpose cements. But with the introduction of a significant amount of these additives in composite cements, there is a significant slowdown in curing in the early stages of hardening and reducing the grade strength of cements. This is due to the fact that the silicate component of these additives has a different structure and, accordingly, the processes of hydration during the hardening of cement with various additives have certain differences.

As it is known, silicates can be in a crystalline, amorphous and glassy state; therefore, the reactivity of various additives, even with the same chemical composition, can also differ significantly [3].

Cement production requires a significant amount of raw materials, which leads to the need for a constant search for new types of mineral additives, while it is important to know what the structure of their silicate component is most effective. Therefore, the study of the influence of the crystalline state of silica on the processes of cement hydration and their properties is relevant.

2. The object of research and its technological audit

The object of research is cement, which contains silica of various structures.

In the production of Portland cement use a variety of mineral additives. Existing DSTU provide for the use of granulated blast furnace slag, fly ash, limestone and pozzolanic materials [4]. These are traditional additives that have gained considerable experience. Using them allows not only to reduce the cost of cement, but also to improve the operational properties of the latter. Usually, in the composition of cements for general construction purposes, the content of such additives does not exceed 20–25 wt. %.

A somewhat different situation in the production of composite cements, where the content of additives can be up to 80 wt. %. Such «dilution» of clinker changes the nature of the processes of hydration and significantly reduces the rate of curing with such cement, especially in the early stages of hardening. In addition, composite cements are characterized by extended setting times and increased values of normal density. In order to prevent these phenomena, regulatory documents require the use of two types of additives:

1) necessarily granulated blast furnace slag (18.0–60.0 wt. %), which is distinguished by its hydraulic activity [5];

2) to choose: pozzolanic materials, fly ash or limestone (10.0–40.0 wt. %).

Thus, the content of the clinker component can be from 20.0 to 60.0 wt. %.

Pozzolanic additives include natural materials that, in the presence of water, bind with lime at a temperature to form insoluble compounds. These additives are quite different in origin and in structure. The effect of these additives on the properties of composite cements has not been studied sufficiently and it is advisable to consider the effect of silica of various structures on the basic characteristics of cement and the characteristics of the processes of their hardening.

3. The aim and objectives of research

The aim of research is studying the effect of silica additives of various structures on the hydration processes and physico-mechanical properties of composite cements for general construction purposes.

To achieve this aim it is necessary to solve the following tasks:

1. To study the nature of the effect of silica additives with a structure of varying degrees of orderliness on the processes of cement hardening.

2. To investigate the effect of silica additives on the physico-mechanical properties of cements.

3. To identify the factors affecting the characteristics of hardening of cement, depending on the type of silicate admixture.

4. Research of existing solutions of the problem

Currently, in the production of cements used a significant amount of silicate additives of various origins. The most typical of them have a different structure and origin and are predominantly represented by silica: hydrate (amorphous), glassy or with a crystalline structure.

By the type of substance, it determines the mechanism of $Ca(OH)_2$ binding, active mineral additives are divided into three groups [6].

The first group includes additives whose activity is determined by the presence of amorphous silica – diatomite, Tripoli powder, and flask (silica in them in an aqueous, active form) [7]. The ability of the mixture of hydraulic additives of the first group in the interaction with $Ca(OH)_2$ to harden is based on the properties of active aqueous silica, is in an amorphous state, actively react with calcium hydroxide to form low-base hydrosilicates.

Additives of the second group contain products of roasting of clay substances: burnt rocks, fly ash, clay [8].

Additives of the third group are benches (ash, tuff, pumice). Their hydraulic activity is determined by water, enters the glass structure as OH groups, which increase the reactivity to interact with $Ca(OH)_2$ during the formation of hydrosilicates and calcium hydroaluminates [9, 10]. In addition to the glass phase, most of the above materials contain a crystalline component, which is represented by silicate minerals.

Many authors have proposed various additives that have pozzolanic properties. Thus, the authors of [11, 12] present data on the effect of ash from burning rice straw and maize, but these works do not explain the hydraulic activity of the resulting additive.

The works [13, 14] are devoted to the possibility of using ash from the burning of wood waste and sewage sludge in the production of cements, but without analyzing the mineralogical composition of the materials obtained in the combustion process.

It should be noted that the majority of studies are aimed at studying the effect of various silicate-mixing additives on the properties of ordinary Portland cements. The authors of [15] present the results of studies of the effect of mineral additives (zeolite, ash and slag and fly ash) as components of cement, but in a range of concentrations that do not allow to predict their use in the production of composite cements.

Thus, the results of the analysis allow to conclude that the influence of the structure of silicate mineral additives on the properties of composite cements has not been studied sufficiently.

5. Methods of research

The effect of additives on the physico-mechanical properties of cements was investigated in terms of the normal density and setting time of cement paste, as well as strength indicators at different times of hardening. The processes of hydration and hardening of cement were studied using X-ray and derivatographic methods of analysis.

6. Research results

To determine the effect of crystalline, glassy and amorphous silica additives on the physico-mechanical characteristics of cements, mixed binders containing from 10 to 90 (every 10) wt. % of additives are investigated. Strength characteristics are determined on samples that are hard in normal conditions for 1, 3 and 28 days.

It has been established that silica additives of different structure ambiguously influence the normal density and setting time of the cement. Thus, with an increase in the content of crystalline silica in the composition of the binder, there is only a slight increase in the normal density from 25.0 to 26.5 % (Fig. 1).

Amorphous silica in the composition of composite cements leads to a significant increase in water demand – with an increase in the dosage of the additive from 10 to 90 wt. %. The normal density of cement paste increases from 28.0 to 59.0 %. The increase in water demand with the introduction of amorphous silica can be explained by the high absorption capacity of the additive amorphous silica itself.

The effect of glassy silica on the physico-mechanical characteristics of cements differs from the previous ones: with an increase in its content, the normal density of the cement paste increases much more slowly compared to amorphous silica, but more rapidly with crystalline.
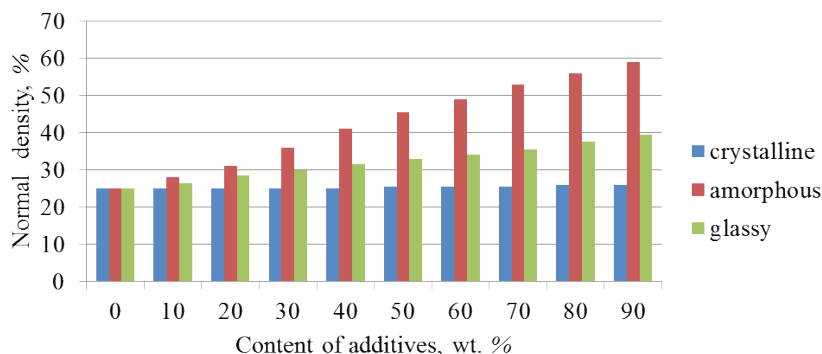
Fig. 1. Normal density of cement paste depending on the content of additives

The effect of the selected additives on the setting time is also different from each other. The introduction of crystalline silica into the composition of the binder is characterized by a monotonous lengthening of the time of both the beginning and the end of the setting, which may be due to a decrease in the proportion of cement in the composition of the binder (Table 1).

Table 1

The setting time of cement with silica additives of various structures

The content of the additive, wt. %	The setting time of cement, hour-min, with the addition of silica					
	crystalline		amorphous		glassy	
	start	finish	start	finish	start	finish
0	0–36	1–23	0–44	1–19	0–50	1–35
10	0–49	1–34	0–41	1–03	0–46	1–30
20	1–18	1–40	0–33	0–49	0–44	1–25
30	1–37	1–50	0–31	0–43	0–39	1–21
40	1–33	1–57	0–27	0–56	0–35	1–15
50	2–00	2–56	0–21	0–38	0–31	1–05
60	2–07	2–47	0–17	0–31	0–27	0–50
70	2–31	3–20	0–19	0–36	0–21	0–43
80	2–20	3–21	0–14	0–41	0–18	0–35
90	0–36	1–23	0–44	1–19	0–50	1–35

The effect of amorphous silica on the setting time is somewhat different: increasing the dose to 70 wt. % significantly reduces the setting time. This may be due to the high absorption capacity of amorphous silica and, as a result, the formation of a larger amount of silica gel and reduced mobility of the dough. Some delay in setting in materials containing 80–90 % of the additive is most likely due to the low cement content of the binder.

The effect of glassy silica on the physico-mechanical characteristics of cements differs from the previous ones. With an increase in its content, the normal density of cement paste increases much more slowly compared to amorphous silica. In addition, with an increase in the content of glassy silica, the setting time monotonically reduced.

If compare the strength of cements with various additives, it is possible to conclude that after 1 day of normal hardening, the strength of cements with the addition of crystalline silica, with all its concentrations, is higher than amorphous (Fig. 2).

The rate of decrease in strength with the same increase in the content of amorphous silica is significantly higher (Fig. 1). Moreover, the introduction of 10 wt. % of crystalline silica leads to a certain increase in the strength of the samples, compared to 8.2 % non-additive cement. While the same amount of amorphous silica additive reduces strength by 33 %.

The introduction of glassy silica does not lead to such a significant reduction in the strength of cements, as with the introduction of amorphous silica. So, with its content of 10 wt. % loss of strength is 19.2 %.

Interestingly, in the entire studied range of the content of additives, cements with the addition of crystalline silica have the highest strength. Most likely this is due to the fact that crystalline particles play the role of microfiller, which somewhat increases the strength.

The explanation can be the results of derivatographic and X-ray phase analysis methods. The intensity of the thermoelectric effect in the low-temperature region decreases when going from a composition with amorphous silica to glassy and crystalline silica is well explained by the different chemical activity of the additives used.

The main new formation, when cement is hydrated in the presence of an acidic additive, is low-base calcium hydrosilicates, which are formed in a gel-like state. Therefore, it is possible to conclude that in the presence of highly active amorphous silica the amount of such products will be greatest. Conversely, inert crystalline silica, practically does not participate in the process of formation of low-basic calcium hydrosilicates, which causes a decrease in the intensity of the dehydration effect of the gel-like component.

This is confirmed by the difference in the mass loss of the systems when heated:

– the smallest (about 7 %) – in cements with the addition of crystalline silica;

– slightly higher (about 8.5 %) – with the addition of glassy silica;

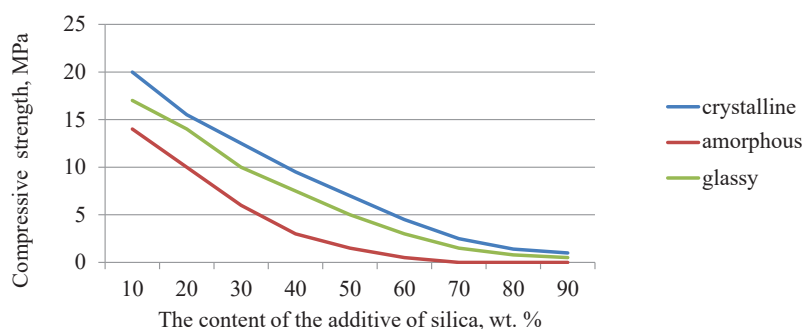– the largest (about 13 %) – the composition with the addition of amorphous silica.

Fig. 2. The effect of silica content of different degrees of crystallinity on the strength of cement at the age of 1 day

On diffractograms of samples that were solid for 1 day, the intensity of the reflections of calcium hydroxide decreases upon transition from a composition with glassy silica to a composition with crystalline, and then with amorphous silica. The general view of the X-ray diffraction pattern of the latter significantly differs from the other two by a significantly smaller number and a reduced intensity of all reflexes, indicating a high rate of hydrolysis of the clinker component with the almost complete absence of crystalline tumors. This is in full accordance with the results of the determination of the strength characteristics – the mechanical strength of the samples with amorphous silica is the smallest.

After 3 days of hardening, the picture does not change much: the rate of decrease in cement strength with increasing amounts of additives of amorphous silica in the composition of the binder is significantly higher compared with its glassy and crystalline varieties (Fig. 3).
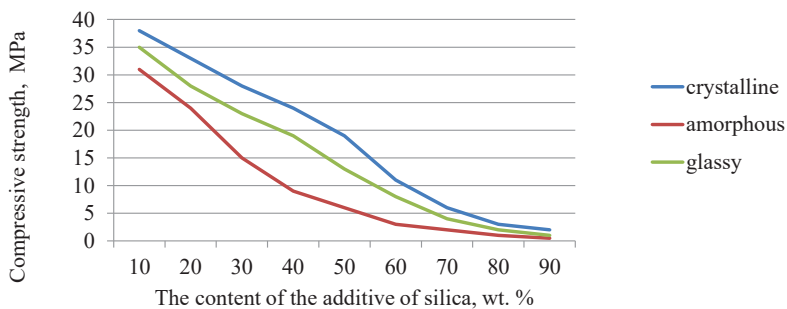
formation intensifies in the binder-based stone with the addition of glassy silica, and the mass loss is significantly increased. This may be due to the increased activity of the glassy component under the action of calcium hydroxide.
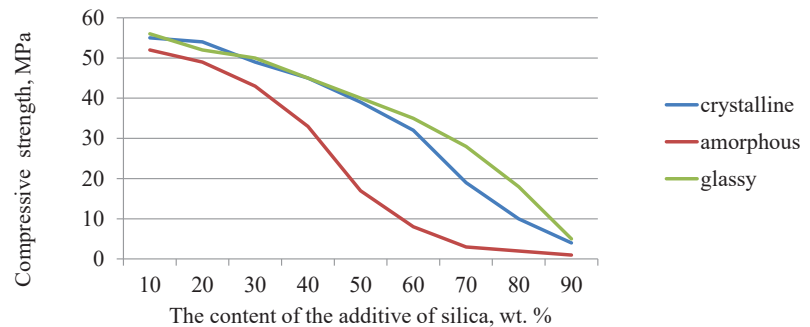

Fig. 4. The effect of silica content of different degrees of crystallinity on the strength of cement at the age of 28 days

Fig. 3. The effect of silica content of different degrees of crystallinity on the strength of cement at the age of 3 days

The results of thermogravimetric analysis are consistent with the above: the mass loss of compositions with the addition of glassy silica increased in relation to their change after one-day hardening due to the development of the hydration process. Especially significantly they increased when heating in the low-temperature region. The mass loss of the system with the addition of crystalline silica is higher than it took place after 1 day of hardening. Their growth is not as large as in the composition with the addition of glassy silica.

A general view of the radiographs of cements, hardened for 3 days, is very similar to those considered above after 1 day of hardening.

Marked dependence persists with longer curing (28 days). At the same time, the fact that with the dosage of additives more than 40 wt. % the reduction in the strength of cement with amorphous silica is significantly greater than in other materials.

After 28 days of hardening, the strength of the binders with the addition of silica in the glassy state was either equal to or greater than the strength of the samples with the addition of crystalline silica, in contrast to the data at 1 and 3 days of hardening (Fig. 4).

The results of derivatographic analysis (DTA) of cements, which were hard for 28 days under normal conditions, indicate that the process of calcium hydrosilicate

On the X-ray diffraction pattern of the composition with crystalline silica, the intensity of reflections of Portlandite in the region of large angles became less, which agrees well with the assumption made above about the active process of lime binding in calcium hydrosilicates. It should be noted that, regardless of the hardening time of systems with the addition of crystalline silica, the intensity of reflections of the quartz component remains almost unchanged. This is an additional confirmation of the extremely low chemical activity of crystalline silica, which practically does not participate in the process of neoplasm synthesis.

On the radiograph of cements with the addition of glassy silica, the intensity of the peaks of the main clinker minerals is less than with the addition of crystalline silica, which indicates its greater activity.

Fundamentally different from those described is the nature of radiographs of cement, contains the addition of amorphous silica. The structure becomes even more amorphous, the minimal intensity of the reflections of the clinker minerals indicates an almost complete hydrolysis of the anhydrous phases (this is in good agreement with the data of DTA on the reduction of calcium hydroxide content). However, there are no pronounced diffraction peaks of crystalline new formations. This clearly indicates the predominant formation of hydrates in the form of X-ray amorphous products and is in good agreement with the results of determining the strength characteristics of the cement stone. In particular, with the introduction of an amorphous silica additive, a sharp drop in the strength of the cement stone is observed.

In general, it can be argued that with the introduction of crystalline silica, the smallest drop in the strength of cement occurs, especially in the early periods of hardening, amorphous – more, and cements with the addition of glassy silica occupy an intermediate position. This suggests that it is most expedient to use as an active mineral additive in the production of composite cements additives containing in its composition silica phases in a crystalline and glassy state.

7. SWOT analysis of research results

Strengths. The obtained results allow to explain the nature of the influence of silica of various structures on the processes of hydration, hardening and properties of composite cements. This will allow to search for potential pozzolanic additives with lower labor and financial costs and in a shorter time. In addition, the proposed conclusions can be used in the production of special cements due to the possibility of regulating certain characteristics by introducing appropriate additives.

Weaknesses. Studies are carried out on model systems and can't take into account all the features of real materials, therefore, after the selection of promising additives, additional research is still necessary.

Opportunities. Production volumes of composite cements are increasing worldwide, which leads to a reduction in stocks of traditional active mineral additives. In addition, as studies have shown, not all additives that are traditionally used in the production of conventional cements are suitable for the production of composite cements. Therefore, the results obtained will allow to search for new additives with lower costs.

Threats. When introducing research results, manufacturers will not incur additional costs.

8. Conclusions

1. It is shown that the introduction of additives of crystalline silica practically does not affect the normal thickness of the cement paste, but monotonously lengthens the setting time, which is associated with a reduction in the content of clinker in the composition of the binder. And the introduction of glassy silica additives leads to a monotonous increase in the water demand of the cement paste (by 11.2–56.2 wt. %).

With the introduction of amorphous silica significantly increases the water requirement (by 12.3–136.1 wt. %) due to the high absorbency of the additive itself. This explains the reduction of the setting time of cement with this additive: the formation of silica gel during the binding of water with amorphous silica reduces the mobility of the cement paste.

2. Different effects of crystalline, glassy, and amorphous silica additives on the strength characteristics of cement stone have been established: during all the hardening periods studied, the strength of samples with amorphous silica turns out to be significantly less than with crystalline and glassy silica. At the same time, with an increase in the hardening time and the dosage of the additive, the difference in strength indicators increases. This may be due to:

1) with the mechanical strengthening of the system with the introduction of solid particles of quartz sand;

2) with the absorption of water by amorphous silica and a corresponding decrease in the rate of cement hydration;

3) with different chemical activity of additives, changes the phase composition of tumors.

3. It is revealed that the main factor determining the nature of the processes of hardening of cements with additives is the degree of orderliness of the structure of their silicate component.

In the early stages of hardening, the rate of drop in strength is highest with the introduction of amorphous silica. For example, when enter 10 wt. % of crystalline silica shows a slight increase in the strength of the samples, compared with 8.2 % non-additive cement. The same amount of amorphous silica additive reduces strength by 33 %, glassy silica – by 19.2 %. This trend continues with increasing content of additives.

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Sokoltsov Vladimir, Engineer, Department of Chemical Technology of Composite Materials, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Ukraine, ORCID: http://orcid.org/0000-0003-1811-4527, e-mail: xtkm@kpi.ua

Tokarchuk Volodymyr, PhD, Associate Professor, Department of Chemical Technology of Composite Materials, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Ukraine, ORCID: http://orcid.org/0000-0001-8620-954X, e-mail: tokarchuk.volodya@ukr.net

Sviderskyi Valentin, Doctor of Technical Sciences, Professor, Department of Chemical Technology of Composite Materials, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Ukraine, ORCID: http://orcid.org/0000-0002-2246-3896, e-mail: xtkm@kpi.ua