**Magazine of Civil Engineering. 2019. 92(8). Pp. 96–105**
**Инженерно-строительный журнал. 2019. № 8(92). С. 96–105**

Magazine of Civil Engineering

ISSN 2071-0305

journal homepage: http://engstroy.spbstu.ru/

DOI: 10.18720/MCE.92.8

# Clinkerless slag-silica binder: hydration process and hardening kinetics

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**Keywords:** clinkerless binder, industrial waste, hydration, flocculation, hardening, phase composition, compressive strength

**Abstract.** The article discusses the results of experimental studies comply with modern approaches to the production of high-performance clinkerless binder in order to ensure the possibility of obtaining high-strength composites based on them, hardening under normal temperature and humidity conditions, with-out heat treatment. The binder, belonging to the class slag-alkaline binders, was obtained by grinding all components together in the presence of superplasticizers and a high content of silica fume. The laser granulometry method, XRD – method were used to estimate the particle size, phase composition of the original components and the clinkerless binder. The flocculation and hardening kinetics was evaluated by the penetrometric method and mechanical tests. The data of the phase composition change of the binder, plastic strength, features of mechanical behavior at different stages of hardening are obtained. As a result, the distinctive features of the main periods of heterogeneous processes of structure formation of the resulting binder are revealed. It was found that the high content of microsilica and particles with a diameter of $d$ ~ 1 ÷ 6 μm in the composition of clinkelrss binder, activated during grinding, allowed to increase their hydraulic activity. As a result, the speed of clinkelrss binder setting and hardening under normal temperature and humidity conditions corresponds to the speed of these processes for Portland cement. Setting rate and strength characteristics of clinkerless slag-silica binder meet the requirements for physical and mechanical properties of cement class 32.5 according to EN 197-1: 2000.

## *1. Introduction*

One of the key problems of modern materials science is the development of new types of effective cementitious materials, providing the creation of new generation concrete with high physical and mechanical characteristics and operational stability. At the same time, the high material and energy intensity of the production of clinker cement determines the need for the development and implementation of low- and clinkerless alternative types of binders.

Currently, in the class of clinkerless binders, the most studied in terms of properties, compositions, structure are slag-alkali binders. For more than 60 years of research in the classical works of Bozhenov P.I., Budnikov P.P., Volzhensky A.V., Glukhovsky V.D., Brandstetr J., Davidovits J., Malolepshi J., Sato K., Shi S., Skwara F., Wang S.D., and others the theoretical foundations of alkaline activation of slag were formed, the principles of controlling the processes of structure formation and hardening of slag-alkali binders were developed. As a result, the compositions of a wide range of these binders were developed, industrial technologies for the production of building products and structures based on them were created, the corresponding regulatory framework was formed. However, obtaining effective concretes based on slag-alkali

Slavcheva, G.S., Baidzhanov, D.O., Khan, M.A., Shvedova, M.A., Imanov, Y.K. Clinkerless slag-silica binder: hydration process and hardening kinetics. Magazine of Civil Engineering. 2019. 92(8). Pp. 96–105. DOI: 10.18720/MCE.92.8

Славчева Г.С., Байджанов Д.О., Хан М.А., Шведова М.А., Иманов Е.К. Бесклинкерное шлако-кремнеземистое вяжущее: параметры структурообразования и кинетика твердения // Инженерно-строительный журнал. 2019. № 8(92). С. 96–105. DOI: 10.18720/MCE.92.8

binders developed in the period of the 60–70s of the last century turned out to be possible only with their heat and moisture treatment used in a factory.

In modern realities, when the volumes of monolithic construction increase, the use of classic slag-alkali binders is rather limited. Therefore, modern research in the field of alternative clinkerless binders and, in particular, slag-alkali binders are associated with the possibility of obtaining high-strength composites based on them, hardening in normal temperature and humidity conditions, without heat treatment.

Two factors are the basis for obtaining a new generation of slag alkaline binders. Firstly, this is the use of binders of micro- and nanodispersed fillers with hydraulic activity. Secondly, it is the mechanochemical activation of binders during grinding.

The well-known developments of slag-alkali binders of the modern period [1–21] showed wide possibilities in comparison with clinker cement for controlling the composition, structure and properties of artificial stone building composites based on them. This is ensured by the introduction of mineral fillers and modifiers in the composition of these binders. The general and particular patterns of the influence of the material and particle size distribution, dispersion and surface potential of certain types of slag, mineral additives and alkaline additives on the structure formation and properties of paste and stone based on slag-alkali binders [1–14] were studied. Various works studied the effect on structure formation, hardening and the complex of properties of binding fly ash additives [15], waste sand [16], ground silica sand and micro-silica [17–18], zeolite-containing carbonate-silicon [19] and aluminum silicate [20] mineral additives. As a result, it was proved that it is the use of hydraulically active micro- and nanodispersed mineral modifiers that allows one to obtain binders that achieve strength up to 50 MPa without heat treatment.

However, the most effective ways of adding these modifiers (with joint or separate grinding), their optimal dosages, and also the rational dispersion of slag-alkali binders have not been clearly defined.

The results of experimental studies discussed in this article are correlated with modern approaches to obtaining highly effective clinkerless binders belonging to the class of slag alkaline. At the preliminary stage of research, the authors optimized, according to the criterion of strength, the composition of a new variety of cinder-alkaline binders based on granulated blast-furnace slag, silica fume, quicklime, two-water gypsum and powdery C-3 superplasticizer. Distinctive features of clinkerless slag-silica binder (CSSB) are:

1) obtaining by co-grinding all components in the presence of superplasticizer,

2) a high dosage of silica fume (20 %),

3) a high specific surface area of 900 $m^2$/kg.

The scientific approach to substantiating the composition and method of obtaining this binder is based on the implementation of the “top-down” nanotechnological principle [21]. It is believed that it is the joint grinding of all components that will provide a change in the energy state of the structure and, accordingly, the physical and/or physicochemical activity of surface and internal volumes of solid particles as they are being ground. In this case, the introduction of a superplasticizer as a surface-active substance during grinding will contribute to amorphization of the surface of binder particles, their saturation with structural defects of the nanoscale range. The achieved high specific surface area of the binder will determine the predominance of nano- and micro-sized particles in its composition. As a result, it is supposed to increase the rate of structure formation and hardening of the binder precisely due to nanotechnological activation of its components at the manufacturing stage, using the hydraulic potential of nano- and micro-sized particles at the hardening stage.

The aim of the work was to assess the applicability of clinkerless slag-silica binder (CSSB) as a hydraulic binder of normal hardening based on comprehensive studies of phase composition, structuration process and hardening. The objectives of the study included:

– assessment of the particle size distribution of the initial components and the CSSB obtained to evaluate the content of nano-and micro-sized particles in their composition;

– studying changes in phase composition of CSSB during hydration and structuration processes;

– assessment of flocculation and hardening kinetics of CSSB

## *2. Materials and Methods*[1]

The following raw materials were used to obtain clinkerless slag-silica binder:

– granulated blast-furnace slag from LLP “Arcelor Mittal” plant (Temirtau, Kazakhstan) with a lime factor of 0.75;

[1] The studies were conducted in the laboratory of the Collective Use Center Named After Professor Yu. M. Borisov (Voronezh State Technical University, Russia)

– microsilica of MKU-95 grade with a mass fraction of $SiO_2$ = 96.85 %;

– building lime of activity of 86.2 %;

– gypsum (gypsum dihydrate);

– powder superplasticizer S-3 based on naphthalenesulfonates.

The binder was obtained by dry joint grinding of raw materials. The ratio of the components is the know-how of the authors and is not published since the composition of the binder is at the patenting stage (patent application No 2018/0444.1 “Clinkerless binder from industrial wastes”, Kazakhstan).

Operational control of the binder dispersion by its specific surface area was carried out by the method of air permeation on the PSH-8A device. The granulometric compositions of the microsilica and binder were studied using the laser particle size analyzer ANALYSETTE 22 Nano Tec.

The structuration process, flocculation and hardening kinetics were studied in the “CSSB + water” system, W/CSSB = 0.3, which was assigned based on the standard normal consistency of fresh binder paste.

After mixing the CSSB with water, the flocculation process of fresh binder paste was controlled in two ways. The setting times were determined on a Vicat apparatus according to Russian State Standard GOST 30744-2001 “Cements. Methods of testing with using polyfraction standard sand”.

The setting kinetics was evaluated by the plastic strength index $P_{pl}$, determined using a universal penetrometer Geopocket S068. To determine the plastic strength, fresh binder paste was placed in a ring with a diameter of 150 mm and a height of 55 mm. The determination of plastic strength was performed by immersing a standard penetrometer plunger (6.4 mm) to a predetermined mark (to a depth of 5 mm). The readings were taken on an internal scale in kgf/cm$^2$, the value of plastic strength $P_{pl}$ was determined based on the fact that 1 kgf/cm$^2$ = 98.0665 kPa. Tests were carried out from the moment the mixture was prepared until the moment it began to set (determined using a Vicat apparatus) every 15 minutes. For each test period, 12 measurements were made.

The CSSB hardening kinetics was evaluated by testing samples – cubes 5×5×5 cm in size after 1, 3, 7, 14, 28 days of hardening under normal temperature and humidity conditions ($t$ = 20 °C, RH = 95 ± 5 %). The strength testing was carried out on a universal 4-column floor hydraulic test system INSTRON Sates 1500 HDS. As a result of the tests, the full diagrams “strain $\sigma$ – displacement $\Delta$” were obtained. According to the tests, the compressive strength and elastic modulus were determined. To ensure the statistical reliability of the results of physical and mechanical tests, the number of samples in the series was 6 pieces. The intra-series coefficient of variability of the test results was 7–10 %.

The phase composition of the clinkerless binder was controlled by the XRD-method (ARL X'TRA diffractometer, CuKα radiation ($\lambda$ = 1.541788 Å) after 1, 3, 7, 14, 28 days of hardening under normal temperature and humidity conditions. X-ray decoding and phase identification were carried out using PDWin 4.0.

## 3. Results

According to the laser granulometry data (Figure 1, Table 1), it was found that the composition of the clinkerless slag silica binder is characterized by polydispersity, with almost half of ultramicrodispersed particles (40 % with a diameter of $d$ ~ 1 ÷ 6 μm and 8 % with a diameter of $d$ < 1 μm). The granulometry of microsilica as the most dispersed initial binder component is characterized by a peaked distribution, that is, its composition is close to monodisperse, and is represented mainly by particles $d$ = 15.6 μm. A comparison of the granulometry of the CSSB with the granulometric composition of microsilica shows a significant increase in the ultramicrodispersed component as a result of grinding.

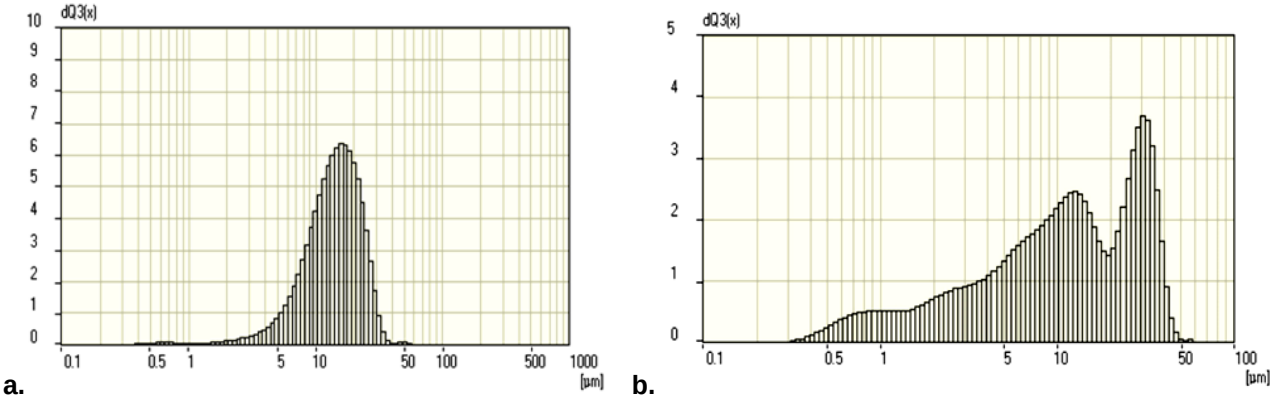


**Figure 1. Particles range of clinkerless slag-alkaline binder (a) and silica fume (b).**

***Table 1. Granulometry of clinkerless slag-silica binder and microsilica.***

| No | Name | Data (Analyzette22) | |
|---|---|---|---|
| | | $\omega$ particles, % | $d$, μm |
| 1 | Microsilica | 93 | 15.6 |
| | | 7 | ≤15.6 |
| 2 | Clinkerless slag-silica binder | 31 | 30 |
| | | 22 | 12 |
| | | 12 | 6 |
| | | 27 | 3 |
| | | 8 | ≤1 |

According to the data of X-ray diffractometry analysis (Figure 2), the slag, which is part of the clinkerless slag-silica binder, is traditionally X-ray amorphous, since there are no clearly defined intensity peaks for the X-ray diffraction pattern, but only blurry, low-intensity peaks, which blur into a halo, which is due to the high content of the glassy phase. However, in the X-ray diffraction pattern, several peaks can be distinguished, which correspond to one of the main crystalline phases of slag – the mellite phase $8CaO{\cdot}3Al_2O_3{\cdot}MgO{\cdot}5SiO_2$.

An analysis of the data of X-ray diffractometric studies of a clinkerless binder (Figure 3) showed that throughout the entire hardening time, a small initial phase of mellite is present in the studied system $8CaO{\cdot}3Al_2O_3{\cdot}MgO{\cdot}5SiO_2$. Its presence is natural, since according to the classical concepts formed in the works of the school of A.V. Volzhensky [22], the hydraulic activity of the slag phases decreases as follows: tricalcium silicate – calcium aluminoferrites – β-$2CaO{\cdot}SiO_2$ – main slag glass – acidic slag glass – mellite – β-$2CaO{\cdot}SiO_2$ – merwinite – monticellite – low basic aluminosilicates and calcium silicates. The amount of mellite phase is insignificant and it completely disappears by the twenty-eighth day of hardening.

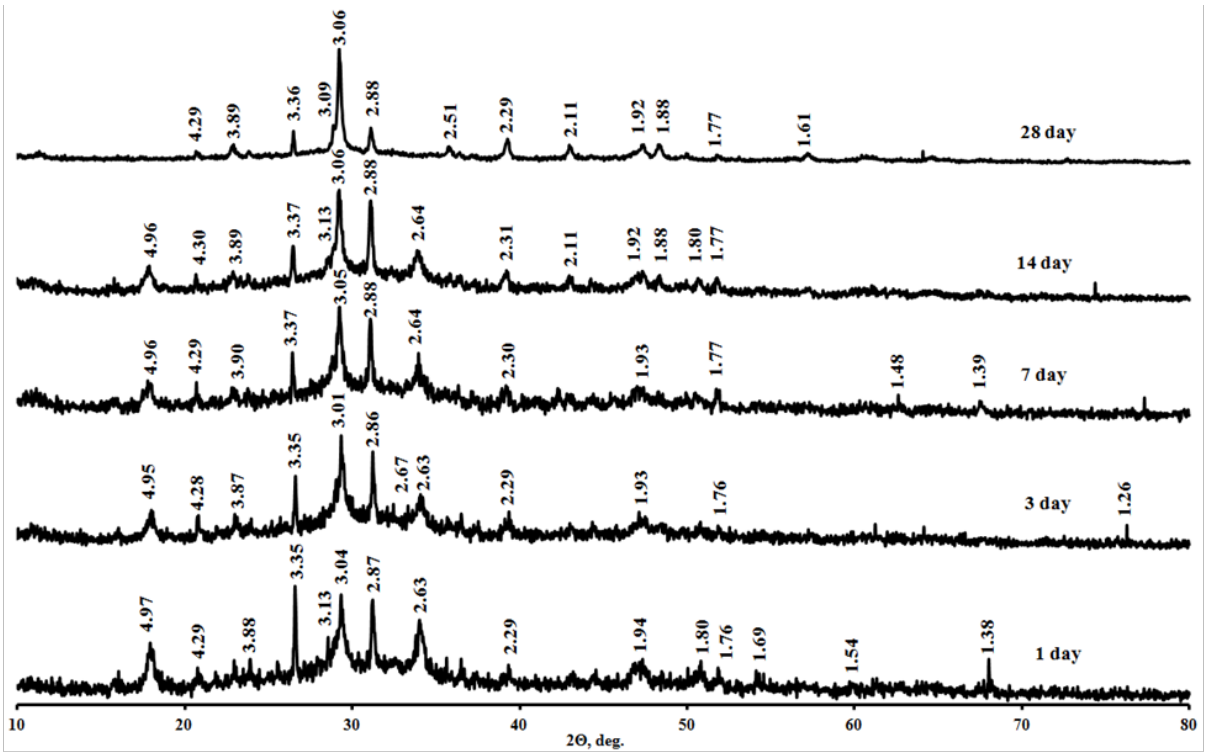


**Figure 3. XRD pattern of hardened system «clinkerless slag-silica binder + water» (W/CSSB = 0.3).**

Designations:

$6CaO{\cdot}4SiO_2{\cdot}3H_2O$ ($d$ = 4.31, 3.11, 2.26, 1.95, 1.76);

$2CaO{\cdot}SiO_2{\cdot}H_2O$ ($d$ = 3.34, 2.92, 2.25, 1.86, 1.75);

$(CaO)_x{\cdot}SiO_2{\cdot}zH_2O$ ($d$ = 4.92, 3.05, 2.93, 2.80, 1.83 );

$xCaO{\cdot}SiO_2{\cdot}zH_2O$ ($d$ = 3.07, 2.97, 2.80, 2.28, 1.83);

$CaO{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}4H_2O$ ($d$ = 4.91, 4.27, 3.34, 3.19, 2.70);

$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$ ($d$ = 4.98, 3.88, 1.90, 1.87, 1.76).

The hydrate neoplasms of the studied system are predominantly represented by high and low basic calcium hydrosilicates ($6CaO{\cdot}4SiO_2{\cdot}3H_2O$, $2CaO{\cdot}SiO_2{\cdot}H_2O$, $(CaO)_x{\cdot}SiO_2{\cdot}zH_2O$, $xCaO{\cdot}SiO_2{\cdot}zH_2O$), calcium

hydroaluminosilicate ($CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$). The content of these phases in the process of hydration and hardening of a clinkerless binder is constantly changing. So, on the first day of hardening, the phases of highly basic calcium hydrosilicates and the phase of calcium hydroaluminosilicate are predominantly seen in the system. The amount of these phases decreases over time. Low-basic tobermorite-like calcium hydrosilicates $(CaO)_x \cdot SiO_2 \cdot zH_2O$, $xCaO \cdot SiO_2 \cdot zH_2O$ appear in the studied system by the seventh day of hardening, while their content is constantly increasing. The ettringite phase is recorded only to the twenty-eighth day from the beginning of hardening. It is important to note that, in this system, the crystalline phase of portlandite is not observed at any moment of hardening ($Ca(OH)_2$).

According to the standard definition of setting time, the beginning of the setting of CSSB is fixed after 95 minutes, the end – after 150 minutes. Meanwhile, on the curve of the setting kinetics (Figure 4), one can clearly distinguish three periods:

1) 0–40 minutes is lack of a set of plastic strength;

2) 40–80 min is a slow increase in plastic strength;

3) 80–150 min is intensive growth of plastic strength until it reaches 387 kPa, corresponding to the end of the setting.

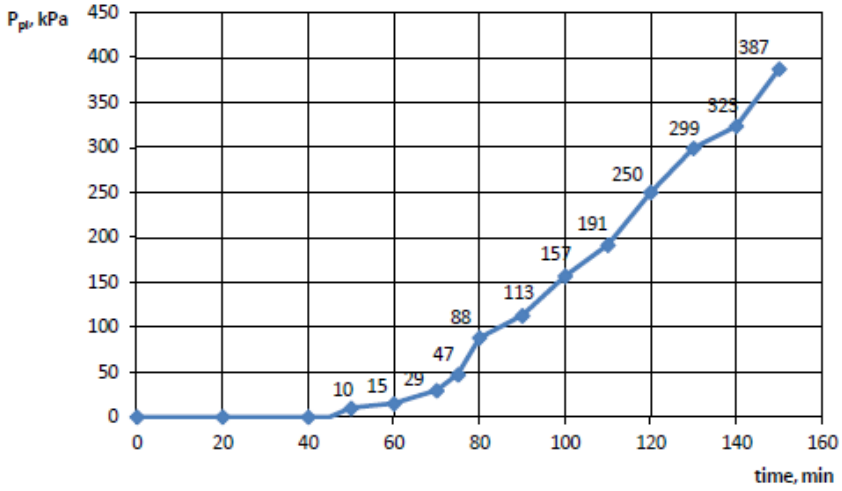


**Figure 4. Flocculation kinetics of fresh CSSB-paste.**

It was found that the appearance of the deformation diagrams (Figure 5) of the hardened binder paste differs significantly at different hardening times. So, at the age of 1 day, the elasticity zone is absent on the diagram, that is, the destruction occurs according to the pseudoplastic type. On the diagrams of deformation of samples, hardened for 3, 7, 28 days, the elastic zone is clearly fixed, the length of the de

scending branch of the diagram decreases. Thus, as hardening increases, rigidity increases and the plasticity of the system decreases. However, on the deformation diagrams of samples aged 14 days, the reappearance of the zone of plastic deformations was recorded, which corresponded to a temporary decrease in the modulus of elasticity. The kinetic curve of hardening (Figure 6) shows an intensive increase in strength up to 3 days of hardening, in the period of 3–14 days, strength increases by 30 %, and in the period of 14–28 days – almost by 2 times. It is important to emphasize that during the periods of 1–3 days and 14–28 days, a significant increase in the modulus of elasticity of the hardened binder paste occurs, it increases by 4 and 5 times, respectively (Table 2).

## *4. Discussion*

The hydration and hardening of CSSB differ from the traditionally distinguished stages of the hydration of cement systems.

Classically [23, 24], the process of hydration of Portland cement is divided into periods

– initial and pre-induction ($\tau$ = 0–30 min), when the rapid nucleation of particles of the primary hydrate CSH occurs;

– induction ($\tau$ = 30 min 2 hours) – the growth of CSH primary and secondary hydrate films on cement grains that block the flow of water to the clinker nodule and slow down the hydration and setting process;

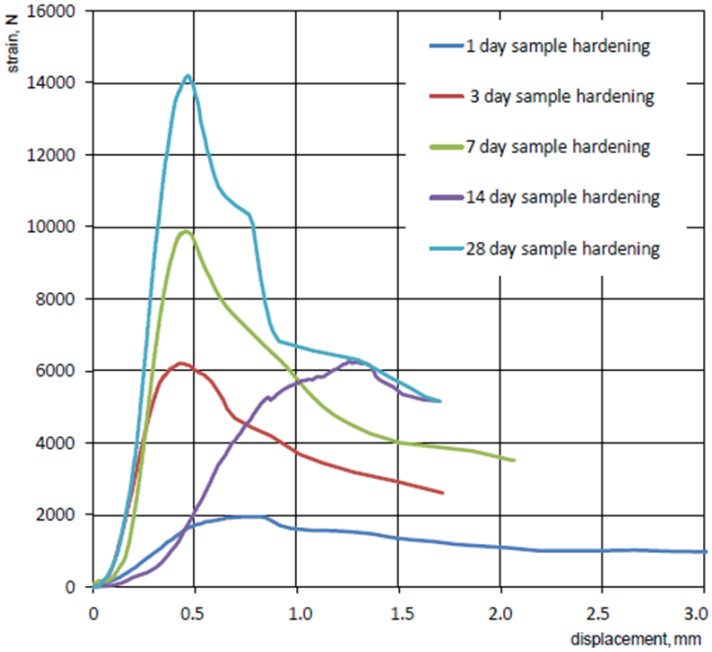


**Figure 5. Tested hardened CSSB pastes «strain $\sigma$ – displacement $\Delta$» experimental results.**

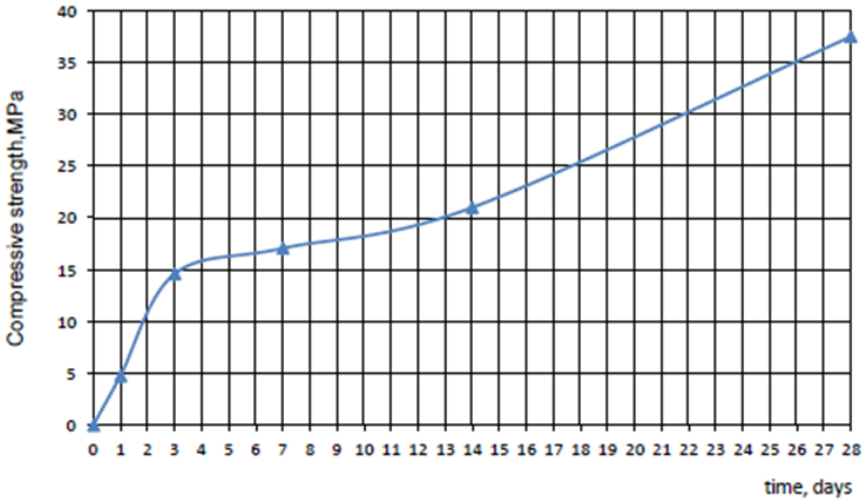


**Figure 6. Hardening kinetics of CSSB.**

***Table 2. Hardening kinetics data.***

| Time, days | 1 | 3 | 7 | 14 | 28 |
|---|---|---|---|---|---|
| Compressive strength, MPa | 4.7 | 14.6 | 17.1 | 21.0 | 37.5 |
| Young's modulus, MPa | 340 | 1390 | 1536 | 676 | 3398 |

– acceleration ($\tau$ = 2–12 hours) – agglomeration of primary and secondary hydrates of CSH, the formation of crystalline intergrowths, the process of mass crystallization of $Ca(OH)_2$, as a result of which the system sets and quickly hardens;

– deceleration (12 hours – 7 days) – hydration of $C_2S$, topochemical transformations of agglomerates of the secondary hydrate into the tertiary, about 30 % of cement enters the reaction by the age of about 7 days, as a result, this is the period of the most intensive increase in strength;

– slow interaction ($\tau \geq 7$ days) – recrystallization during spontaneous and self-organizing structure formation with the formation of a single three-dimensional structure of cementitious substance, which is accompanied by a slow monotonous increase in strength.

According to the obtained flocculation curve (Figure 4), the CSSB is characterized by practically the absence of an increase of plastic strength in the period up to 80 min from the moment of flocculation. It can be assumed that the reason for this is the slow dissolution of slag grains and the delay in the onset of hydration phases. Only after 80 minutes does the intensive growth of plastic strength begin, as a result, the setting onset time (150 minutes) corresponds to the standard range of setting onset time for Portland cement (120–160 minutes).

If for Portland cement, the acceleration period is associated with the formation of a spatial framework in the system as a result of mass crystallization of $Ca(OH)_2$, for CSSB the crystalline phase of portlandite is not observed even on the first day of hardening. During this period, highly basic primary calcium hydrosilicates $2CaO{\cdot}SiO_2{\cdot}H_2O$ prevail in hydration products, which are classified as a dendrite-like and amorphous morphological type, which leads to low strength of crystallization contacts [25]. Therefore, it is logical that by the first day of hardening the system has an anomalous deformation diagram for solids (Figure 5), low strength and modulus of elasticity.

In a period of 1 to 3 days of hardening of CSAB, the most intensive increase in the strength of the system and its elasticity occurs. The deformation diagrams clearly show the elasticity zone, which may be due to the formation of a crystalline framework from the phases of the secondary hydrates $6CaO{\cdot}4SiO_2{\cdot}3H_2O$ of fibrous-needle morphology, crystals of ettringite and AFt-phases, which ensure the greatest number and strength of contacts in a volume unit. The presence of secondary hydrates, a rapid increase in strength allows us to correlate this period with the period of deceleration of the hydration process.

However, further characteristics of the CSSB hardening process are significantly different from cement systems. In the period of 3–14 days, the strengthening of the system slows down dramatically, and the sample deformation diagram on the 14th day of hardening again acquires an anomalous character, characterized by a long plateau of pseudoplastic deformations. This is naturally accompanied by a decrease in the modulus of elasticity by more than two times with respect to its value at the age of 7 days. This may be due to the repeated mass formation of primary hydrates $2CaO{\cdot}SiO_2{\cdot}H_2O$. As a result, crystallization pressure can occur in the already formed crystalline framework, and the combination of $2CaO{\cdot}SiO_2{\cdot}H_2O$ crystals, as noted above, has a low strength of crystallization contacts.

In 14–28 days, there is an intensive increase in the strength and elasticity of the system, which can be correlated with the processes of self-organized structure formation [25]. In the hardening system, the content of low-basic tobermorite-like calcium hydrosilicates $(CaO)_x{\cdot}SiO_2{\cdot}zH_2O$, $xCaO{\cdot}SiO_2{\cdot}zH_2O$ increases, which have a fibrous-needle morphology and provide an increase in the energy of destruction due to a large number of randomly placed in the volume contacts and interfaces.

It is important to emphasize that during all hardening periods, the portlandite $Ca(OH)_2$ phase is absent in the composition of CSSB hydration products. This indicates that the solution very quickly reaches saturation with $HSiO_3^-$, $SiO_3^{2-}$, $H_2SiO_4^{2-}$, $Al^{3+}$, $AlO_2^-$ ions, which bind $Ca^{2+}$, $CaOH^+$ cations to hydrate compounds, preventing the crystallization of Portlandite $Ca(OH)_2$. Also, one of the least active slag phases, the mellite phase $8CaO{\cdot}3Al_2O_3{\cdot}MgO{\cdot}5SiO_2$, almost immediately disappears in the hydrated binder. On this basis, it can be argued that the resulting binder is characterized by high hydraulic activity. Most likely, this is ensured by the good solubility of ultramicrodispersed particles with a diameter of $d$ ~ 1÷6 μm with an amorphized surface, which is the result of mechanochemical activation during grinding in the presence of C-3 superplasticizer as a complex of surface-active substances.

## 5. Conclusions

1. The results of a comprehensive assessment of the characteristics of the clinkerless slag-silica binder and the parameters of its structure formation and hardening made it possible to confirm the effectiveness of nanotechnological activation of its components at the manufacturing stage, using the hydraulic potential of nano- and micro-sized particles at the hardening stage. It is the presence of an increased amount of microsilica and almost 50 % of ultramicrodispersed particles with a diameter of $d$~1 ÷ 6 μm in the composition of CSSB that made it possible to increase the hydraulic activity of the binder and ensure its setting and hardening speed under normal temperature and humidity conditions ($t$ = 20 ºC, $\mathrm{RH}$ = 95 ± 5 %), comparable to the rate of these processes for Portland cement.

2. As a result of studying the changes of CSSB phase composition during hydration and structuration processes, it was established that CSSB has high hydraulic activity. In the hardening system, the content of low-basic tobermorite-like calcium hydrosilicates $(CaO)_x{\cdot}SiO_2{\cdot}zH_2O$, $xCaO{\cdot}SiO_2{\cdot}zH_2O$ increases, which have a fibrous-needle morphology and provide an increase in the energy of destruction due to a large number of randomly placed in the volume contacts and interfaces.

3. CSSB is characterized by the onset of setting after 150 minutes, strength 17.1 MPa at the age of 7 days, 37.5 MPa at 28 days. The setting and strength indicators of the clinkerless slag-silica binder meet the requirements for physico-mechanical properties of cement grade 32.5 EN 197-1:2000 “Cement – Part 1: Composition, specifications and conformity criteria for common cements”. This allows us to recommend the resulting binder for the manufacturing building products and structures both in factory and in building conditions.

## 6. Acknowledgement

This research work has been financed by the Russian Foundation for Basic Research (RFBR), Project 19-38-50028.

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Инженерно-строительный журнал

ISSN 2071-0305

сайт журнала: http://engstroy.spbstu.ru/

DOI: 10.18720/MCE.92.8

# Бесклинкерное шлако-кремнеземистое вяжущее: параметры структурообразования и кинетика твердения

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**Ключевые слова:** бесклинкерное вяжущее, техногенное сырье, структурообразование, схватывание, твердение, фазовый состав, прочность

**Аннотация.** В статье рассматриваются результаты экспериментальных исследований, выполненные с целью обеспечения возможности получения высокопрочных композитов на основе бесклинкерного вяжущего, твердеющего в условиях нормальной температуры и влажности, без тепловой обработки. Разработанное авторами вяжущее, относящееся к классу шлако-щелочных, было получено путем совместного помола всех компонентов в присутствии суперпластификатора, его состав отличается от известных аналогов высоким содержанием микрокремнезема. Метод лазерной гранулометрии, XRD – метод были использованы для оценки размера частиц, фазового состава исходных компонентов и бесклинкерного вяжущего. Кинетика схватывания оценивалась пенетро-метрическим методом. Кинетика твердения оценивалась по результатам механических испытаний образцов через 1, 3, 7, 14, 28 суток твердения. В результате выявлены отличительные особенности основных периодов гетерогенных процессов структурообразования полученного вяжущего, отличительные особенности кинетики схватывания, механического поведения на разных этапах твердения в нормальных температурно-влажностных условиях. Установлено, что присутствие в составе повышенного количества микрокремнезема, и почти 50 % активированных при помоле частиц диаметром $d$ ~ 1 ÷ 6 μm позволило повысить гидравлическую активность вяжущего и обеспечить скорость его схватывания и твердения в нормальных температурно-влажностных условиях, сопоставимую со скоростью данных процессов для портландцемента. Показатель схватывания и прочностные показатели бесклинкерного вяжущего соответствуют требованиям к физико-механическим показателям цемента марки 32.5 согласно EN 197-1:2000.

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