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PROPRIEDADES DOS LIGANTES DE ESCÓRIA ALCALINA BASEADOS EM RESÍDUOS INDUSTRIAIS

PROPERTIES OF SLAG-ALKALI BINDERS BASED ON INDUSTRIAL WASTE

ИССЛЕДОВАНИЕ СВОЙСТВ ШЛАКОЩЕЛОЧНЫХ ВЯЖУЩИХ КОМПОЗИЦИЙ НА ОСНОВЕ РАЗЛИЧНЫХ ДОБАВОК ОТ ИХ СОСТАВА

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RESUMO

Para estudar os processos de interação e formação da composição de fases em ligantes de escória alcalinos à base de cinzas volantes, a solução de ingrediente alcalino foi proporcionada após 28 dias de envelhecimento e após tratamento térmico, cura a vapor ou assentamento em condições naturais. Os produtos de interação de escórias e mistura de sulfato de sódio com aditivos altamente básicos foram estudados. Sua composição de fases foi determinada pelo tipo de escória, aditivos e condições de ajuste. O aumento na densidade da solução de ingrediente alcalino de 1.100 para 1.300 kg/cm³ resultou em uma resistência à compressão 1.7-2 vezes maior do aglomerante, que é de 30.7, 47.1 e 45.9 MPa, dependendo do módulo de vidro líquido. Quando a mistura de sulfato de sódio foi introduzida na fórmula, a resistência à compressão das amostras curadas por vapor foi 7–22% maior do que a das amostras expostas ao tratamento térmico seco. A força dos ligantes de escória alcalina baseados em cinzas volantes dependiam da finura das cinzas volantes. As fórmulas de ligação desenvolvidas podem ser usadas para a preparação de concretos de alta resistência e materiais de construção.

Palavras-chave: *ligantes de escória alcalina, aditivos, escória de fósforo, vidro líquido, resistência à compressão, atividade de ligação, cinzas volantes.*

ABSTRACT

To study the processes of interaction and formation of the phase composition in slag-alkali binders based on fly ash, the alkaline ingredient solution was proportioned after 28 days of aging and after heat treatment, steam curing or setting in natural conditions. The products of interaction of slags and soda-sulfate mixture with highly basic additives were studied. Their phase composition was determined by the type of slag, additives, and setting conditions. The increase in density of alkaline ingredient solution from 1,100 to 1,300 kg/cm³ resulted in a 1.7–2 times higher compressive strength of set binder, which is 30.7, 47.1 and 45.9 MPa, depending on the liquid glass module. When the soda-sulfate mixture was introduced into the formula, the compressive strength of the steam-cured samples was 7–22% higher than that of the samples exposed to dry heat treatment. The strength of slag-alkali binders based on fly ash depended on the fineness of fly ash. The developed binding formulas can be used for the preparation of high-strength concretes and building materials.

Keywords: *slag-alkali binder, additives, phosphorous slag, liquid glass, compressive strength, binding activity, fly ash.*

АННОТАЦИЯ

Для исследования процессов взаимодействия и образования фазового состава шлакощелочных вяжущих композиций на основе золы-уноса был проведен подбор состава раствора щелочного компонента в 28-суточном возрасте после тепловой и тепловлажностной обработки, а также после твердения в естественных условиях. Изучение продуктов взаимодействия шлаков и содосульфатной

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смеси в сочетании с высокоосновными добавками показало, что их фазовый состав определяется видом шлака, добавки и условиями твердения. Увеличение плотности раствора щелочного компонента с 1100 до 1300 кг/см³ приводит к повышению предела прочности при сжатии камня, вяжущего в 1,7–2 раза, что в зависимости от модуля стекла составляет 30,7, 47,1, 45,9 МПа. Результаты показали, что при тепловлажностной обработке, когда в состав компонента вводили содосульфатную смесь, предел прочности образцов при сжатии на 7–22% выше, чем у образцов, подвергнутых тепловой обработке. Установлено, что прочность шлакощелочных вяжущих на основе золы-уноса, зависит от дисперсности золы-уноса. Разработанных шлакощелочных вяжущих композитов можно использовать для приготовления высокопрочных бетонных растворов и материалов для строительного производства.

Ключевые слова: *Шлакощелочные вяжущие, добавки, электротермофосфорный шлак, жидкое стекло, прочность при сжатии, активность вяжущих, зола-унос.*

1. INTRODUCTION

Given the rapid development of the construction industry and the expansion of new industrial and civil construction in Kazakhstan, the demand for building materials is increasing. Research and engineering of constructional and heat-insulating materials using secondary resources is especially relevant. Kazakhstan has immense raw material resources in the form of wastes from the metallurgical, petrochemical, mining, fuel and power-generation industries, and their utilization in the composition of building materials is a priority of the national economy.

Light-weight concrete, having low density and rather high strength, has found a wide range of applications due to its useful qualities; small consumption of raw materials being one of them. This is one of the lightest building materials, with low thermal conductivity and good soundproofing properties. However, the increased quality requirements for lightweight concrete set the task to further improve its constructional, operational, technological, and strength properties. The use of industrial wastes as slag-alkali binders, having high activity and generating structure-forming elements, can improve strength, stress-related performance, and durability of lightweight concrete. The aim of this study is to obtain high-strength slag-alkali binders with various additives, having increased adhesiveness to organic aggregates in lightweight concrete.

Slag-alkali binders are hydraulic binding agents, obtained by fine grinding of granulated slags and various mineral additives. When mixed with solutions of alkali metal compounds, such binder enters into an alkaline reaction hardens in air and water. It has been experimentally proven that the properties of hydraulic binders, along with compounds of alkali-earth metals, are inherent to alkali metal compounds (Bisenov *et al.*, 2005; Bazhenov 2003; Bazhenov *et al.*, 2006; Bazarbaeva 2010; Vysotsky and Tsarik, 1993; Volzhensky and Chistov, 1991; Glukhovsky *et al.,* 1981; Goncharov *et al.,* 2000, 2002; Goncharov, 1999; Dvorkin, 1993; Danilovich and Skanavi, 1988; Kapustin *et al.*, 2000). These conclusions can be well confirmed by the behavior of systems, in which sodium hydroxide and sodium silicate and non-silicate salts that give an alkaline reaction were used as the alkaline ingredient. As a result, alkaline binders fundamentally changed the idea of the role of alkaline oxides in the synthesis of artificial stone. They have defined modern ways of creating new, highly efficient binding systems and improving the properties of regular cements. That is why the attempts to use alkali metal compounds in combination, for example, with slags or Portland cement, were limited to using them in small quantities as activating additives, not to disturb the hydraulic ability of the calcium binder system. In particular, liquid glass and alkaline carbonates were introduced into Portland cement as anti-frost and plasticizing agents in an amount less than 0.5–2.5% by weight of Portland cement. As the slag-alkali binder hardens, calcium oxide in the slag and alkaline ingredients enter into a cation exchange reaction, releasing free alkali, which contributes to the predominant occurrence of low-base hydrated calcium silicates. Simultaneously with them, non-stoichiometric sodium hydrogarnates and sodium-calcium hydroaluminosilicates are formed. These compounds are similar to natural minerals, and this gives the binder good physical and mechanical properties and favors the development of effective composite materials on their basis.

The studies of the relationship between the formation of slag-alkali binder structure and the ability to control the properties of such binders showed that to obtain slag-alkali binders with predominantly identical properties, regardless of the composition, it is necessary to adjust the basicity of the binder system to the optimum level (Bisenov *et al.*, 2005, Glukhovsky *et al.,* 1981;

Goncharov, 1999; Dvorkin, 1993; Danilovich and Skanavi, 1988; Kapustin *et al.*, 2000; Korneyev *et al.*, 1999, 2002; Kasimov *et al.*, 1989; Rybyev, 2007; Suleimenov, 1996; Isakulov, 2009, 2011; Akulova *et al.*, 2013a, 2013b, 2014a, 2014b; Sokolova *et al.*, 2017; Isakulov and Zhiv, 2014; Issakulov *et al.*, 2010). To do this, one can add Portland cement clinker. It was established (Bisenov *et al.*, 2005) that the greatest amounts of added quickly hydratable cementing minerals, free from gypsum, serve as mineralizers, which can control structure formation in slag-alkali binders. Portland cement clinker in the amount of 1–5% by weight of slag made it possible to equalize the strength of set binder, based on blast-furnace slags. One of the most convenient properties of slag-alkali binders is that they can be used for the production of concrete containing an increased amount of clay and dust particles in the aggregates, which eliminates the need to concentrate the aggregates. Importantly, substandard raw materials of various mineral composition of both artificial and natural origin can be used in materials based on these binders. That is why developing new slag-alkali binders, based on industrial waste, and studying their properties and interaction with organic aggregates are relevant today. This paper reports the development of slag-alkali binder, containing fly ash, with increased adhesion to the organic constituents in concrete.

2. MATERIALS AND METHODS

Phosphorous slag of the Shymkent Production Association (Shymkent, Kazakhstan) and electric arc furnace slag of the Aktobe Metallurgical Plant (Aktobe, Kazakhstan) were used for experimental research. Slags were ground to powders with a specific surface of 320–330 m^2/kg. Sodium silicate and a soda-sulfate mixture (waste products from caprolactam production) were used as alkaline ingredients. The active mineral additive was fly ash from the Actobe CHP (Aktobe, Kazakhstan), which meets the requirements of national standard GOST 10181-2000. Fly ash from Aktobe CHP had the following properties: specific surface – 2,550 cm^2/g; absorption activity – 32 mg/g; true density – 2,000 kg/m^3; bulk density – 955 kg/m^3. The chemical composition of fly ash is given in Table 1.

In order to control the structure formation in the binder, alkaline ingredients were prepared in the form of aqueous solutions. The composition of alkaline ingredients by volume is given in Table 2.

The Portland cements were tested in accordance with national standard GOST 25820-2000. The compressive (bending) strength was determined on cube-shaped samples, having 100 mm on edge, in accordance with GOST 7473-2010. The mobility of paste was determined using a Suttard viscometer. The normal density and the setting time were determined according to national standard GOST 31108-2003. The thermal conductivity of slag-alkali samples was studied using the ITP-MG-4 device in accordance with GOST 7076-99. The ultimate strength in bending and tensile strength was determined on 40x40x160 mm bar-shaped samples using the IP-2710 device. The phase composition of the alkali binder was determined by X-ray phase analysis. The radiographic survey was performed with the DRON-3 diffractometer. The test samples were prepared in the form of fine powders of optimal mass applied in a thin layer on the surface of frosted glass. The interval of diffraction angles was from 2 to 32º. The obtained X-ray patterns were interpreted with reference to the standard X-ray patterns of mineral ingredients.

To study the processes of interaction and formation of the phase composition of slag-alkali binders based on fly ash, we proportioned the composition of the alkaline ingredient solution. The slag-alkali binder was prepared by mixing ground slag with alkaline ingredient solutions. The alkaline ingredient was introduced together with the gauging water in the form of a solution with a density of 1,100–1,300 kg/m^3. The binder strength was determined according to national standard GOST 7473-94. The normal consistency and the setting time were determined according to GOST 25820-2000. The samples were condensed for 3 minutes on the BC-1 vibrating plate. The tests were performed on samples after steaming and hardening in natural conditions.

Also, we made an attempt to create a slag-alkali binder with the active mineral additive—high-calcium fly ash from the Aktobe CHP. The main physicochemical processes of interaction between the ingredients and the phase composition of the products, formed during these processes, were examined. When studying the composition based on fly ash, phosphorous slag, soda-sulfate mixture and the active additive, the samples aged for 28 days after heat treatment, steam curing, and hardening in natural conditions. To determine the setting time and the strength gain, the slag-alkali binder samples of different age were exposed to steam curing in a special drying chamber. The steam curing was carried out at 60–100 °C at atmospheric pressure for 12–14 hours.

We examined the composition of slag-alkali binders with active mineral additive high-calcium fly ash, based on phosphorous slag and soda-sulfate mixture, that solidified in normal conditions and after heat treatment and steam curing (Table 3).

Table 3. *Composition of slag-alkali binders*

	Ingredient	wt %
1	Phosphorous slag	45–67
2	Soda-sulfate mixture	8
3	Active mineral additive high-calcium fly ash	25–50

To compare the results, we examined the composition of slag-alkali binders with other mineral active additives high-calcium fly ash and sodium disilicate, which solidified in normal conditions and after heat treatment (Table 4).

Table 4. *Composition of slag-alkali binders*

	Ingredient	wt %
1	Phosphorous slag	45–67
2	Sodium disilicate	8
3	Active mineral additive high-calcium fly ash	25–50

To study the effect of the alkaline ingredient density on the strength of the set binder, liquid glass with different silicate modules (M_s) was used. According to (Bisenov *et al.*, 2005; Bazhenov 2003; Bazhenov *et al.*, 2006; Bazarbaeva 2010; Vysotsky and Tsarik, 1993; Volzhensky and Chistov, 1991; Glukhovsky *et al.,* 1981; Goncharov *et al.,* 2000, 2002; Goncharov, 1999; Dvorkin, 1993; Danilovich and Skanavi, 1988; Kapustin *et al.*, 2000; Korneyev *et al.*, 1999, 2002; Kasimov *et al.*, 1989; Rybyev, 2007; Suleimenov, 1996; Isakulov, 2009, 2011; Akulova *et al.*, 2013a, 2014a) binding compositions based on fly ash and such alkaline ingredients as Na_2SO_4 and Na_2CO_3 do not harden in normal conditions and when steamed. The compositions of slag-alkali binders, consisting of such active mineral additives as high-calcium fly ash (50 wt %) + phosphorous slag (42 wt %) + liquid glass (8 wt %), with different silicate modules, were investigated at solution densities from 1,100 to 1,300 kg/cm^3.

It is known (Bisenov *et al.*, 2005; Bazhenov 2003; Bazhenov *et al.*, 2006; Bazarbaeva 2010; Vysotsky and Tsarik, 1993; Volzhensky and Chistov, 1991; Glukhovsky *et al.,* 1981; Goncharov *et al.,* 2000, 2002; Goncharov, 1999; Dvorkin, 1993; Danilovich and Skanavi, 1988; Kapustin *et al.*, 2000, Korneyev *et al.*, 1999, 2002; Kasimov *et al.*, 1989; Rybyev, 2007; Suleimenov, 1996; Isakulov, 2009, 2011; Akulova *et al.*, 2013a, 2013b, 2014a, 2014b; Sokolova *et al.*, 2017; Isakulov and Zhiv, 2014; Issakulov *et al.*, 2010) that it is possible to control the process of structure formation in slag-alkali binder systems by selecting an alkaline ingredient with controllable dissociation. The dissociation rate on the ingredient's nature, temperature conditions, alkaline medium (pH), and dispersed medium. Researchers (Bisenov *et al.*, 2005; Bazhenov, 2006; Glukhovsky *et al.,* 1981; Goncharov *et al.,* 2000, 2002; Goncharov, 1999; Dvorkin, 1993; Danilovich and Skanavi, 1988; Kapustin *et al.*, 2000; Korneyev *et al.*, 1999, 2002; Kasimov *et al.*, 1989; Rybyev, 2007; Suleimenov, 1996; Isakulov, 2009, 2011; Akulova *et al.*, 2013a, 2014a) also showed that the introduction of low-module liquid glass and salts Na_2SO_4, NaCl to slag-alkali binder systems, based on slags with $1 < \hat{I}_0 < 1$, increases the rate of strength development at the early stages of hardening and in final activity.

To study the effect of the content of complex alkaline ingredients on the strength and the setting time of the slag-alkali binder, a soda-sulfate mixture was used in the form of an aqueous solution with a density of 1,200 kg/cm^3, which was added to the liquid glass with silicate module M_s-3. To compare the results, we also tested binders on the basis of fly ash with phosphorous slag without soda-sulfate mixture, with liquid glass only. The effect of the soda-sulfate mixture on the compressive strength of set binder was also considered for the binder based on phosphorous slag. The research also included the investigation of binder compositions based on phosphorous slag when gauging fly ash with an alkaline ingredient consisting of liquid glass and an aqueous solution of the soda-sulfate mixture at the ratio 50:50. Two types of heat treatment were used: heat treatment at a temperature of up to 80 °C for 12–14 hours (heating of samples without steam) and steam curing in standard mode at 60–100 °C at atmospheric pressure. In order to avoid intensive evaporation of moisture, the molds with samples were tightly sealed.

It is known (Bisenov *et al.*, 2005; Bazhenov 2003; Bazhenov *et al.*, 2006; Bazarbaeva 2010; Vysotsky and Tsarik, 1993; Volzhensky and Chistov, 1991; Glukhovsky *et al.,* 1981; Goncharov *et al.,* 2000, 2002; Goncharov, 1999; Dvorkin, 1993; Danilovich and Skanavi, 1988; Kapustin *et al.*, 2000; Korneyev *et al.*, 1999, 2002; Kasimov *et al.*, 1989; Rybyev, 2007; Suleimenov, 1996; Isakulov, 2009) that it is possible to control the process of structure formation in alkaline binders by adjusting the glass composition or mixing slags of different basicity and structure, as well as by microcalculating a part of the dispersed phase by creating an organic or mineral composition on their surface. When developing the binder, phosphorus slag was ground into a powder with a specific surface of 50–56 µm. Soluble sodium silicate and soda-sulfate mixture (waste products from caprolactam production) were used as alkaline ingredients. Fly ash with a specific surface of 2,550 cm^2/g from Aktobe CHP was used as an active mineral additive. The slag-alkali binder was prepared as follows: dry fly ash was thoroughly mixed with dry ground phosphorous slag, then gauged with an alkaline ingredient solution (soda-sulfate mixture + liquid glass). For the study, we developed the following composition of the slag-alkali binder: active mineral additive high-calcium fly ash (50 wt %) + phosphorous slag (42 wt %) + alkaline ingredient consisting of the co-sulfate mixture and liquid glass at the ratio 50:50 (8 wt %). The effect of the active mineral additive (fly ash) on the compressive strength of set binder was studied. It was revealed that there is a dependence of the binder strength on the fineness of fly ash. It is known (Bisenov *et al.*, 2005; Bazhenov 2003; Bazhenov *et al.*, 2006; Bazarbaeva 2010; Vysotsky and Tsarik, 1993; Volzhensky and Chistov, 1991; Glukhovsky *et al.,* 1981) that the principal amount of the vitreous phase is concentrated in the smallest (less than 56 µm) fraction, i.e., in quartz of 56–105 microns. The finer the fraction of ash, the more melted particles it contains and the higher the strength properties of the set binder. The characteristics of raw materials show that the residue of fly ash on sieve 008 is 21 %. Taking into account the results of the above tests, we conducted experiments in parallel to study the effect of coarse fractions (> 800) on the binder strength. For this, ash of the following specific surface was used:

1) initial fly ash (S_{sp} – 300 m^2/kg);

2) fly ash (S_{sp} – 360 m^2/kg);

3) fly ash (S_{sp} – 410 m^2/kg).

The specific surface of fly ash was modified by adding coarse fractions to ash, sieved through sieve 008. To study the effect of phosphorus slag content on the strength characteristics of set slag-alkali binder, active mineral additive (fly ash) and phosphorus slag, gauged with an alkaline ingredient solution, were used (Tables 5 and 6).

For a better understanding of the influence of the content of slags and aluminosilicate ingredients in the slag-alkali binder, the binder composition was optimized. In the result, it was observed that the silicate module of the alkaline ingredient, the density of the alkaline ingredient, the solvent-solid ratio and the content of phosphorous slag in the slag-alkali ingredient have the greatest influence on the properties of the slag-alkali binder. By reducing and increasing the content of the alkaline ingredient and reducing the silicate module of the alkaline solution, the slag content in the aluminosilicate ingredient can be reduced, which is a criterion for obtaining optimal slag-alkali solutions.

The density and the silicate modulus of the alkaline ingredient have the greatest effect on the binder strength. At the same time, their joint influence can be expressed by the pairing effect. When the content of phosphorous slag in the aluminosilicate ingredient is 50 %, the solution-slag ratio is 0.32, the density of the alkaline ingredient is 1,300 kg/m^3, and the silicate module of the alkaline ingredient is 3.0, one can obtain binders with the M500 grade activity. In order to obtain M500 grade binders at the same slag content, one needs an alkaline ingredient with the silicate module of 2.0, the density of 1,300 kg/m^3 and the solution-slag ratio of 0.36. The obtained results confirm the previous findings that with increased content of phosphorous slag in the aluminosilicate ingredient, the strength increases. Therefore, it was decided to choose the maximum content of phosphorous slag in the aluminosilicate ingredient of 50%, i.e., 50% fly ash + 50% phosphorous slag.

The most important characteristics of binders, which determine the basic properties of concrete based on them, include the setting time and strength variation kinetics. These properties, in turn, depend mainly on the type of aluminosilicate ingredient, as well as on the type and density of the gauging liquid. These characteristics were examined on the compositions of studied binders, taking into account their optimality in terms of strength. The setting time of binders based on fly ash and phosphorous slag was studied using the gauging silicate solutions with various densities.

3. RESULTS AND DISCUSSION

The X-ray analysis of the products of the interaction of the binder, consisting of fly ash and phosphorous slag, gauged with the alkaline ingredient, consisting of an aqueous solution of sodium liquid glass and soda-sulfate mixture, showed that these products were calcite and low-basic calcium hydrosilicates, such as gyrolite.

The IR spectroscopic study of samples, based on high calcium fly ash, showed (Figure 1, Curve 1) that the aqueous solution of sodium liquid glass and the soda-sulfate mixture was alkaline; the position and the shape of the main band of stretching vibrations of silica-oxygen bonds changed (Figure 1, Curve 2). This indicates the almost complete interaction of the alkaline solution with fly ash, as a result of which boron, along with silicon, belongs to the fourth coordination of anionic groupings.

The integrated study of physicochemical interaction of binders based on high-calcium fly ash showed that the phase composition of binders was determined by the type of alkaline ingredient and additive. It was established that formulas, based on fly ash, had binding properties and the phase composition of the set product determined the nature of these properties.

As the density of the alkaline ingredient solution increased, its concentration increased as well. This increased the strength of the set slag-alkali binder. When the density of the alkaline ingredient solution was 1,100 kg/cm^3, the strength of the set binder was 16.3, 26.5 and 22.9 MPa, respectively, for sodium silicate solutions with M_s 3, 2 and 1. If the density of the alkaline ingredient solution was increased from 1,100 to 1,300 kg/cm^3, the compressive strength of the set binder improved by 1.7–2 times, which was 30.7, 47.1 and 45.9 MPa, depending on the module. If the silicate module of liquid glass was reduced to 2, the strength improved by up to 1.5 times as compared to the tests with a similar density of the solution. However, if M_s was decreased to 1, no strength gain was observed as compared with the formulas with sodium disilicate.

The introduction of the soda-sulfate mixture as an additive significantly intensified the slag glass hydration, apparently, due to its chemical composition. Soda-sulphate mixture also contributed to the formation of fibrous calcium hydrosulfoaluminates, which serve as additional reinforcement and compact the stone structure. The results showed that during the steam curing, when the soda-sulfate mixture was introduced into the formula, the tensile strength of the samples under compression was 7–22% higher than that of the samples exposed to heat treatment. The increase in the soda-sulfate mixture content in the alkaline ingredient up to 75% by volume improved the strength of the set binder. Thus, the compressive strength of the set binder, based on liquid glass, was 31.1 and 38.3 MPa, respectively, for samples exposed to steam curing and heat treatment. The strength of the samples, based on 75% soda-sulfate mixture, was 45.1 and 47.7 MPa, respectively. At the optimum ratio of the soda-sulfate mixture to the liquid glass (75:25), the setting time became nearly 7 times longer as compared with the control sample.

The samples prepared on fly ash (S_{sp} = 360–410 m^2/kg) had a compressive strength of 60–100% higher than the samples prepared on initial fly ash. It was found that the strength of unburned alkali binders based on fly ash, like other mineral binders, depends on the fineness of fly ash (Table 5).

As the tests showed, with a higher content of phosphorous slag, the compressive strength of slag-alkali binders increases and reach 47.7 MPa (Table 6).

The obtained optimal formulas of slag-alkali binders, with different densities and silicate modules of the alkaline ingredient, and their properties are given in Table 7. Therefore, the use of fly ash to obtain a binder with the strength of 46–64 MPa appears to be efficient. It was confirmed that it is possible to adjust the properties of ash-based and ash-slag-alkali-based binders. At the same time, binders of the same grade can be obtained by adjusting the formula of the binder by changing some ratios.

The binder grade can be adjusted within a wide range to obtain slag-alkali wood concretes.

It was established that as the solution density increases, the binder setting time becomes longer. When the density of liquid glass was 1,300 kg/m^3, the binder would set instantaneously, i.e., it is hard to examine it. By reducing the density of liquid glass to 1,100 kg/m^3, the initial setting lasted 3 minutes, and the final setting, 5 minutes. When the density of liquid glass was 1,300 kg/m^3 with silicate module M_s 1, the initial setting lasted 7 minutes, and the final setting, 10 minutes. The experiments showed that the ash-alkali binders were quick-setting with all gauging liquids. At that, the initial setting occurred after 1 hour 45 minutes, and the final setting, after 6 hours (Table 8). According to the results of the above studies and experiments, it can be argued that slag-alkali binder, based on fly ash, are quick-setting. It is known that reducing substances of organic aggregates greatly increase the setting time of binders; therefore, slag-alkali binders can be recommended in the production of lightweight concrete. The kinetics of changing the strength of the developed binder formulas compositions depends on their composition, processing conditions, and the setting mode. The change in the strength of the set slag-alkali binder samples, which hardened in natural conditions or were exposed to heat treatment, was investigated on dry-cured samples that aged for 28–360 days. The results of the tests with binder formulas, which included fly ash and sodium disilicate and hardened in natural conditions (Table 9), indicated that these binders had the compressive strength of 43.0 MPa after 28 days and 45.3 MPa after 360 days.

The same formula, after 28 days of aging and heat treatment, had the compressive strength of 43.8 MPa, which indicates that heat treatment improves the binder strength (see Table 9).

By day 360, the compressive strength of wood-concrete reached 48.5 MPa. The binder, consisting of fly ash and phosphorous slag in proportion 1:1 by weight, had strength 57.0 MPa after heat treatment and 63.9 MPa after 360 days of aging. The same formula, set in natural conditions, had strength 50.0 MPa after 28 days of aging, and 61.2 MPa after 360 days (Table 9).

At that, the strength of 360-day old slag-alkali binders increased by 1.2–1.5 times in comparison with the initial strength, which indicates long-lasting structure formation. The strength gain in these binders can be explained by their formula and setting conditions.

Previous studies have proven (Bisenov *et al.*, 2005; Bazhenov 2003; Bazhenov *et al.*, 2006; Bazarbaeva 2010; Vysotsky and Tsarik, 1993; Volzhensky and Chistov, 1991; Glukhovsky *et al.,* 1981; Goncharov *et al.,* 2002; Goncharov, 1999; Kapustin *et al.*, 2000) that the properties of hydraulic binders, along with compounds of alkali earth metals, are inherent in compounds of alkali metals.

These conclusions can also be supported by our experimental data. We used sodium hydroxide and sodium silicate and non-silicate salts, which give an alkaline reaction, as the alkaline ingredient. The aluminosilicate system includes clay minerals, which, by the chemical and mineralogical composition and the articulation of main structural elements, sufficiently comprise all types of clay (the most widely used raw material), and which can be used both in formulas of hydraulic alkali binders and substandard aggregates.

Studies (Glukhovsky *et al.,* 1981; Goncharov *et al.,* 2002; Goncharov, 1999) have shown that the compound on the basis of kaolinite is formed at low-temperature treatment (373–573 °K) if non-silicate salts of alkali metals, such as sodium carbonate, are added as the alkaline ingredient.

Our experiments also confirm the fact that with slag-alkali binders new compounds can be obtained, similar to natural sodalites of the carbonate-sodalite type, which resemble nepheline hydrate. The presence of the source raw materials (for example, hydromica), an excess of silica, or its introduction with kaolinite and montmorillonite, and the heat treatment and steam curing intensify the processes of physicochemical interaction. Based on the established regularities, we developed slag-alkali binders based on alkali metal compounds, engineered the production technology, and described their physicomechanical properties.

Binders based on alkali aluminosilicates are obtained by grinding glasses, sintered masses or calcinates of natural and synthetic substances, in which the ratio between basic oxides must be 1:1, and by gauging alkali metal compounds with solutions that give an alkaline reaction (Bisenov *et al.*, 2005; Bazhenov 2003; Bazhenov *et al.*, 2006; Bazarbaeva 2010; Vysotsky and Tsarik, 1993; Volzhensky and Chistov, 1991; Glukhovsky *et al.,* 1981).

Our data is also consistent with the above studies. We obtained binding formulas based on highly active additives that set in natural conditions, and after heat treatment and steam curing. Their activity depends on the basicity of the silicate ingredient, the type of alkaline ingredient, and the setting conditions. Thus, the theoretical foundations of the setting of hydraulic alkali binders are fundamentally different from those of ordinary hydraulic binders, since they contain neither lime nor cement clinkers. The strength gain during setting occurs due to the formation of alkali aluminosilicate structures, which by mineral composition imitate natural minerals such as micas and zeolites, and their water resistance and durability are determined by analogy with the latter. In this system, the ratio between new (alkali) and traditional (alkali-earth) binding substances may vary greatly. Such binders are fundamentally different from known calcium binders, which are not considered as an independent ingredient of hydraulic binders due to their very high solubility as compared to alkali-earth binders. When slag-alkali binder sets, there occurs a cation exchange between calcium oxide in the slag and alkaline ingredients. It results in the formation of free alkali, which contributes to the predominant formation of low-base calcium silicates. Simultaneously with them, there appear sodium hydrogarnates of variable composition and sodium-calcium hydroaluminosilicates. These compounds are similar to natural minerals, which gives the binder good physical and mechanical properties. It should be noted that the above binder formulas are quick-setting. However, if M_s is reduced to 1, the setting time is somewhat longer. Most likely, this is caused by good stability of liquid glass with a lower silicate module, which has a higher charge on the surface of the particles against the coagulating effect of ash ions Ca^{+2}. When studying the composition of fly ash, it was determined that unburned particles of coal are concentrated in large fractions of ash. Equally metamorphosed unburned fuel particles are present in the ashes of all solid fuels. If the combustion process is proper, their number is small; in other cases, their content may reach 20% or more. The organic matter, transformed in the furnace, differs from its initial state and converges in the form of coke and semi-coke with a very low hygroscopicity, yielding volatile substances. It can be assumed that the coarse fractions and the unburned part of fuel, remaining in fly ash, impair the quality of the latter.

It was found that the binder systems based on phosphorus slag have great strength. This can be explained by the fact that granulated phosphorus slag, as a more active ingredient of the system, produces enough hydrates to give strength to slag-alkali binders. One can also make a tentative conclusion that alkali systems based on silicate alkali salts should be preferred because they have higher potential as compared to non-silicate alkali salts, such as Na_2SO_4 and Na_2CO_3. It was also established that soda-sulfate mixture in slag-alkali binders based on phosphorus slag increases the strength of up to 45%. In addition, the introduction of the soda-sulfate mixture in the binder formula significantly reduces the binder cost as compared to that based on industrial liquid glass.

4. CONCLUSION

The physicochemical processes in binders with active mineral additives based on high-calcium fly ash were studied. The phase composition of the binder formulas is determined by the type of alkaline ingredient and additive. As the developed binders set, low-basic tobermorite hydrosilicates and alkali new growths appear. Fly ash-based formulas have binding properties, and the phase composition after setting determines the nature of these properties, and the strength of unburned alkali binders with added fly ash depends on the fineness of fly ash and the particle size distribution. The density and the silicate module of the alkaline ingredient have the greatest effect on the strength of the slag-alkali binder, and the optimal slag content is equal to the content of phosphorous slag in the aluminosilicate ingredient, i.e., 50% fly ash + 50% phosphorous slag. The binders with active mineral additives, such as high calcium fly ash and phosphorous slag, at the ratio 1:1 by weight have compressive strength from 57.0 to 63.9 MPa after heat treatment, which indicates that the heat treatment improves the binder strength gain.

The study set forth scientifically based solutions for the production of high-strength composite slag-alkali binders, which can be used in lightweight concrete. Importantly, the findings agree with other studies that addressed the structure formation of modified composite concretes based on slag-alkali binders. The proposed technology allows using composite slag-alkali binders in the production of lightweight concrete, to intensify the setting processes in binders, and to increase their strength by 50–70% with moderate cement consumption, thus supporting to waste-free production.

5. ACKNOWLEDGMENTS

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Table 1. *Chemical composition of fly ash*

Loss on ignition, % wt	Oxides content, % wt						
	SiO_2	Al_2O_3+TiO_2	Fe_2O_3	CaO	MgO	NaO_2	SO_2
7.33	48.3	23.92	5.94	9.0	1.9	0.18	0.52

Table 2. *Composition of alkaline components by volume*

Alkaline ingredient	Content of alkaline ingredient solution (l)	Density of alkaline ingredients (kg/m^3)	Content of alkaline ingredient solution (l)	Density of alkaline ingredients (kg/m^3)
Soluble sodium silicate, μ_c=2.6	0.5	1,300	0.75	1,300
Soda-sulphate mixture (l)	0.5	1,200	0.25	1,200

Table 5. *Effect of fly ash fineness on compressive strength of set binder*

Specific surface of fly ash (m^2/kg)	Gauge	Compressive strength (MPa)
300	Liquid glass	45.2
350	Liquid glass	45.1
400	Liquid glass	41.5
410	Liquid glass	40.3
300	Soda-sulfate mixture + Liquid glass	47.7
350	Soda-sulfate mixture + Liquid glass	45.5
400	Soda-sulfate mixture + Liquid glass	42.0
410	Soda-sulfate mixture + Liquid glass	40.6

Table 6. *Effect of phosphorus slag content on compressive strength of set binder*

Aluminosilicate ingredient		Alkaline ingredient		Solution-slag ratio	Compressive strength (MPa)
Fly ash (%)	Phosphorus slag (%)	Gauge	Density (kg/m^3)		
–	100	Liquid glass	1,3	0.28	40.2
25	75		1,3	0.30	47.1
50	50		1,3	0.34	47.7
75	25		1,3	0.35	32.1
100	–		1,3	0.38	31.0
–	100	Sodium disilicate	1,25	0.28	45.0
25	75		1,25	0.31	46.1
50	50		1,25	0.36	40.7
75	25		1,25	0.38	36.4
100	–		1,25	0.40	32.6

Table 7. *Optimal formulas and strength properties of slag-alkali binders, depending on the density and silicate module of the alkaline ingredient*

Formula	Solvent-solid ratio	Density (kg/m^3)	Silicate module (M_s)	Phosphorous slag content (%)	Fly ash content (%)	Compressive strength (MPa)
1	0.32	1,100	1.0	50	50	46
2	0.34	1,200	2.0	50	50	49
3	0.36	1,300	3.0	50	50	55
4	0.32	1,300	3.0	50	50	64
5	0.34	1,200	2.0	50	50	61
6	0.36	1,100	3.0	50	50	57
7	0.32	1,100	1.0	50	50	59
8	0.34	1,300	3.0	50	50	48
9	0.36	1,300	3.0	50	50	61

Table 8. *Setting time of slag-alkali binders*

Slag-alkali ingredient		Gauge		Setting time (min)	
		Ingredient	Density (kg/m^3)	Initial	Final
1	Fly ash	Liquid glass	1,1	3 min	5 min
2	Fly ash	Liquid glass	1,2	7 min	10 min
3	Fly ash	Liquid glass	1,3	instant	instant
4	Fly ash	Soda-sulfate mixture + Liquid glass	1,1	15 min	23 min
5	Fly ash 50% + Phosphorous slag 50%	Soda-sulfate mixture + Liquid glass	1,2	22 min	34 min
6	Phosphorous slag 50 %	Soda-sulfate mixture + Liquid glass	1,3	24 min	35 min

* Normal density is 28–38%.

Table 9. *Compressive strength of slag-alkali binders depending on their composition, treatment, and aging*

Formula	Setting condition	Slag-alkali ingredient	Compressive strength (MPa)	
			28 days	360 days
1	In natural conditions	Fly ash + Sodium disicate	43.0	45.3
2	After heat treatment	Fly ash + Sodium disicate	43.8	48.5
3	In natural conditions	Fly ash + phosphorous slag	50.0	61.2
4	After heat treatment	Fly ash + phosphorous slag	57.0	63.9

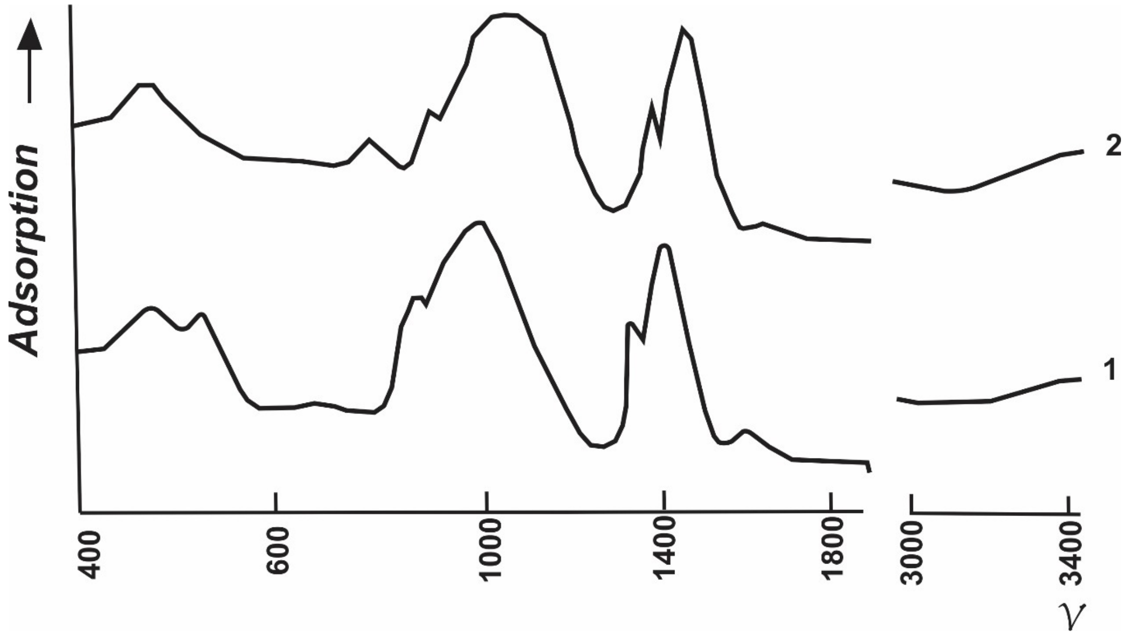

Figure 1. *IR spectroscopic study of samples, based on high calcium fly ash: Curve 1 – aqueous solution of sodium liquid glass; Curve 2 – same with soda-sulfate mixture added*