

## Influence of whitening additives on the properties of decorative slag-alkali cements and mortars

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Received 02 November 2022

Accepted 31 January 2023

Available on line 24 May 2023

**ABSTRACT:** The paper shows a comparative study of the influence of whitening additives (kaolin,  $\text{TiO}_2$  and  $\text{CaCO}_3$ ) on the production of decorative alkali-activated slag cement and mortars with a degree of whiteness of at least 70%; as well as their influence on the structure formation and evolution of physico-mechanical properties. According to results obtained, kaolin provides chemical bonding of  $\text{Na}^+$  into insoluble zeolite-like compounds; and  $\text{CaCO}_3$  densifies the structure and reduces shrinkage deformations. At the early stages of hardening (up to 7 days), the additions of kaolin and calcite, due to their significant amount (15 and 24%), reduces the compressive strength of the cement paste; nevertheless, at later ages (until 90 days) the difference in strength almost disappears. The high colourfastness and weather resistance of pigmented cements under the influence of ultraviolet radiation and freeze/thaw cycles has been established. A comparative assessment of the economic efficiency has shown that  $\text{CaCO}_3$  is the best cost-effective additive.

**KEY WORDS:** Alkali-activated slag cements; Colour stability; Pigments; Decorative cements; Freeze/thaw resistance; Behaviour.

**Citation/Citar como:** Krivenko, P.; Puertas, F.; Gots, V.; Helevera, O.; Rogozina, N. (2023) Influence of whitening additives on the properties of decorative slag-alkali cements and mortars. *Mater. Construcc.* 73 [350], e311. <https://doi.org/10.3989/mc.2023.319622>.

**RESUMEN:** *Influencia de aditivos blanqueadores en las propiedades de cementos y morteros de escorias activadas alcalinamente para fines decorativos.* Se presenta un estudio comparativo de la influencia de aditivos blanqueadores (caolín,  $\text{TiO}_2$  y  $\text{CaCO}_3$ ) en la producción de cementos y morteros decorativos de escoria activada alcalinamente con un grado de blancura de al menos el 70%; así como de los procesos de formación de estructuras cohesivas y de la evolución de las propiedades físico-mecánicas en los mismos. Según los resultados obtenidos, el caolín establece enlaces a través del  $\text{Na}^+$  en compuestos insolubles tipo zeolita; mientras que el  $\text{CaCO}_3$  densifica y la estructura y reduce las deformaciones por retracción. En las primeras etapas de endurecimiento (hasta 7 días), las adiciones de caolín y calcita, por su importante cantidad (15 y 24%), reducen la resistencia a la compresión de la pasta de cemento; sin embargo, a edades posteriores (hasta los 90 días) esa diferencia casi desaparece. Se ha establecido la elevada solidez del color y la resistencia a la intemperie de los cementos pigmentados bajo la influencia de la radiación ultravioleta y los ciclos hielo/deshielo. Se ha demostrado que el  $\text{CaCO}_3$  es el aditivo más rentable.

**PALABRAS CLAVE:** Cementos de escoria activada alcalinamente; Estabilidad del color; Pigmentos; Cementos decorativos; Resistencia hielo/deshielo; Comportamiento.

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## 1. INTRODUCTION

Production of Portland cement clinker is one of the most energy extensive and ecologically unfriendly production, and in order to meet the goals of global sustainable development, requires new more solutions (1-3). This is also important with regard to production of white cement clinker as a base for production of pigmented Portland cement.

Analysis of contemporary trends showed, that annual production of white clinker cements as a base of pigmented cement, is of about 35 million tonnes and continues to increase further by 8-10% per year in order to meet the growing demands of consumption market (4, 5). White Portland cement clinker is produced by firing until sintering of a raw mixture at the higher temperatures – 1500-1600°C compared to those required in the production of traditional Portland cement – 1400-1450°C (6).

White pure (high-quality) limestone sand and white kaolinite clays are necessary to use as raw materials for the manufacture of these cements. The following restrictions are applied to these raw materials: the content of contaminating not desirable oxides in raw limestones and clays are not allowed to exceed, for example,  $\text{FeO} < 0.15\%$ ,  $\text{Fe}_2\text{O}_3 < 1.5\%$ ,  $\text{Mn}_2\text{O}_3 < 0.03\%$ ,  $\text{Cr}_2\text{O}_3 < 0.01\%$ ,  $\text{MgO} < 3.0\%$ . Above all, special conditions are to be strictly followed in the production of these cements in order to escape the contamination of a raw mixture bimetallic iron in kilns with linings from magnesite bricks, and to use non-metallic grinding media in grinding operation.

In view of strict restrictions as to content of iron oxides in raw materials (being fluorites, they promote the formation of the melt), this circumstance makes the conditions for the sintering of clinker worse. For this reason, in order to improve the conditions for clinker formation, the fluxes-mineralizers such as fluorspar/sulphates ( $\text{CaF}_2$  and  $\text{CaSO}_4$ ) and sodium silicofluoride ( $\text{Na}_2\text{SiF}_6$ ) are added to the raw mixture (7).

In order to increase the degree of whiteness of the white cement clinker even with low contents of iron, the cement clinker is subjected to a special treatment—whitening (8-10), the essence of which is to reduce  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ . This helps to remove greenish colour and increases the degree of whiteness of the final cement. The calcination of clinker takes place in weakly reducing atmosphere and is followed by quick cooling and additional whitening. Also, special manufacturing apparatus—decolouriser, in which the cement clinker is subjected to short-term renewable exposure of gaseous medium without access of oxygen at 800-1000°C with a following quenching /cooling down to 200°C can be used. In the production of white cement, the process of whitening can be repeated many times.

All the above makes a manufacturing process quite complicated and results in a considerable increase in the cost of white cement production.

The alkali-activated cement can be considered as a real alternative to Portland cement since their manu-

facture is based on the chemical reaction of different wastes or by-products. From one part the use of wastes from the different process as the metallurgical industry, production of phosphor, energy generating industry (as granulated blast furnace slag, steel making, electro thermo phosphorus, non ferrous slags, ashes of heat power stations, etc.), and from the other some alkali-containing wastes that enable to produce an alkaline solutions. These cements have compressive strength reaching 40-120 MPa, high adhesion, durability, corrosion resistance and other special properties (6, 11-24).

Numerous research works have proved a possibility and feasibility of the production of white alkali-activated cements for decorative purpose using granulated blast furnace slags (13, 25-28). The pigmented cements reproduced by the addition to the composition of the alkali-activated slag cement of pigment alone or in combination with white kaolinite clay. The kaolinite clay acts as a structure-forming element of the cement matrix and at the same time acts as a whitening additive. However, a positive result as to the required degree of whiteness of the resulted cement (>70%) could be achieved only with the slags containing low contents of iron oxides (0.3- 0.4%).

Some attempts were taken to produce paints using the alkali-activated cements (29). A disadvantage of these paints is that after six months under exposure of weather conditions they lose their decorative properties because of the appearance on the surface of stains consisting of alkali metal compounds. In the studies reported in (22, 30), the reasons of efflorescence were analyzed, however, they did not show the ways on how to manage risk of efflorescence, which is a critical point for decorative materials.

The research works reported in (29, 31) studied a possibility to produce white alkali-activated slag cements based on blast furnace slags and alkaline compounds using titanium oxide, kaolin and calcium carbonate as whitening additives. However, the ways on how to manage whiteness of these cements depend on the chemical composition of the slag and it has not been studied until now. In the studies reported in (32) only one slag with a modulus of basicity ( $\text{CaO}+\text{MgO} / \text{Al}_2\text{O}_3+\text{SiO}_2$ )  $M_b = 0.91$  of unknown chemical composition was used in the production of the white alkali-activated slag cement. The influence of the contents of iron oxide of the slag on whiteness was not studied at all.

A decorative multicomponent cement based on Roman cement modified by alkalis, whitening, air entraining and plasticizing additives and admixtures is described in (33). Despite the fact that content of iron oxide varied in the composition of this cement within a range of 0.64-2.75%, their influence on decorative properties was not studied. Moreover, the achieved strength value sat an age of 28 days were too low (21.5-27.5 MPa), thus restricting their use only to obtain decorative plaster mixtures, and not for concretes.

Very few studies have been done for obtaining white and non-ferrous cements based on alkali-activated slag. In some

industrial wastes were used as pigments, but only for clinker cements, but not in alkali-activated slag cements (34-37).

The additive of CaCO<sub>3</sub> was also tried in some cement composition, including in the alkali-activated slag cements, but not as a whitening additive, but as a filler (38-40). The additive of TiO<sub>2</sub> to the clinker cement-based concrete sand mortars was tried, as reported in (41, 42), but not as a whitening additive; it was used as an antifungal and bactericidal additive to mortars or nano admixture to enhanced photocatalytic, hydrophobic and mechanical properties with the effect of self-cleaning of the surface and antimicrobial properties.

The use of the alkali-activated slag cement as a base in the production of pigmented cements was not considered by other researchers as alternative to white clinker cement.

The analysis held suggested to draw a conclusion the lack of information about the following problems associated with the production of white and pigmented alkali-activated cements:

- the influence of the FeO-content on whiteness of the decorative alkali-activated slag cements;
- behavior and influence of whitening additives (TiO<sub>2</sub>, kaolin, CaCO<sub>3</sub>) on decorative, physico-mechanical and performance properties of the decorative alkali-activated slag cements in the conditions of highly alkaline environment;
- adhesion of the white and pigmented alkali-acti-

- vated slag cement mortars to a substrate;
- shrinkage deformations;
- risk of efflorescence and capillary suction;
- water retaining characteristics;
- freeze/thaw resistance and weather resistance;
- stability of colour under exposure of ultraviolet radiation and in the conditions of steam curing.

Thus, it shows that this research line is relevant and is of scientific interest and novelty. A purpose of the present research was to make a comparative study on the influence of whitening additives on structure formation processes and evolution of physico-mechanical properties of the decorative alkali-activated slag cements depending upon the FeO-content of the composition of granulated blast furnace slag.

## 2. EXPERIMENTAL PART

### 2.1. Materials

Granulated blast furnace slags varying in the FeO-content were used as an aluminosilicate component of the alkali-activated slag cements. Chemical composition of the slags and other raw materials used in the study is given in Table 1. X-ray pattern of blast-furnace granulated slag D is shown in Figure 1.

TABLE 1. Chemical composition of raw materials.

Material	Oxide content, % by mass										Total	M <sub>b</sub> *
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	FeO	SO <sub>3</sub>	MnO	TiO <sub>2</sub>	Na <sub>2</sub> O	LOI.		
Slag D	37.9	6.85	45.35	5.21	0.31	2.6	0.11	0.35	1.13	1.34	101.15	1.13
Slag M	38.9	6.8	47.0	4.6	0.35	1.8	0.55	-	-	0.78	100.78	1.13
Slag T	43.0	7.0	43.5	6.3	0.42	-	0.05	0.26	-	0.5	101.03	1.00
Slag K	38.2	4.6	48.5	4.6	1.65	1.1	0.81	-	0.79	0.60	100.85	1.24
Kaolinite clay	48.77	30.94	2.62	0.8	-	-	-	0.25	-	13.06	96.44	-
Red mud	9.8	17.7	9.6	-	54.2	-	-	4.5	4.0	-	99.80	-

\*M<sub>b</sub> = CaO+MgO / Al<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub>

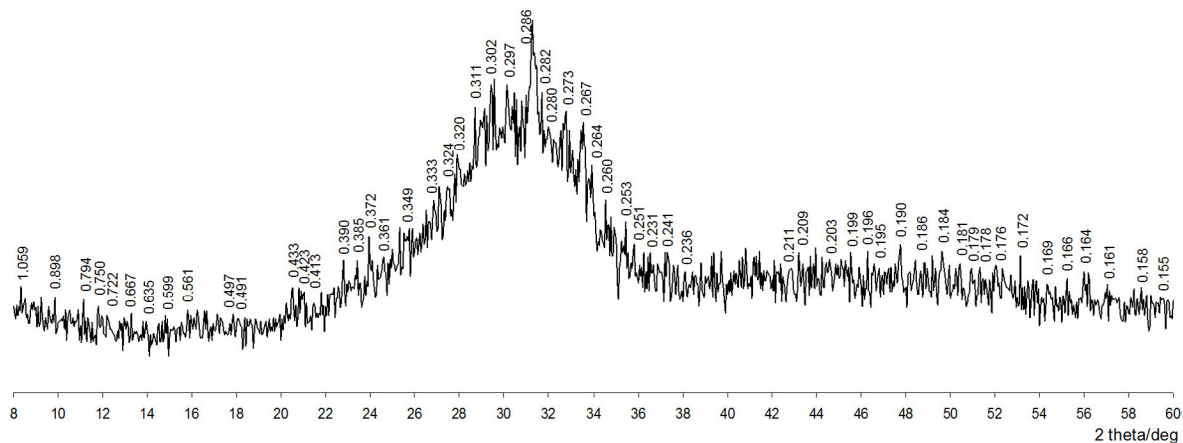


FIGURE 1. X-ray pattern of blast-furnace granulated slag D.

The mineralogical composition of slag D is represented by gehlenite  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  ( $d - 0.286$ ;  $0.241$ ;  $0.231$ ;  $0.176$   $\mu\text{m}$ ), merwinite  $\text{Ca}_3\text{MgSiO}_8$  ( $d - 0.264$ ;  $0.190$ ;  $0.186$ ;  $0.164$   $\mu\text{m}$ ), rankinite  $\text{Ca}_3\text{Si}_2\text{O}_7$  ( $d - 0.385$ ;  $0.320$ ;  $0.302$ ;  $0.291$ ;  $0.273$   $\mu\text{m}$ ), larnite ( $d - 0.28$ ;  $0.273$ ;  $0.260$ ;  $0.219$   $\mu\text{m}$ ) and some quartz ( $d - 0.423$ ;  $0.333$ ;  $0.184$ ;  $0.155$   $\mu\text{m}$ ).

All granular slags (except for slag T) belong to the main ones from  $M_b = 1.13$ - $1.24$  and are represented mainly by the vitreous phase, the content of which is 76-83%. Slag T with  $M_b = 1$  refers to neutral slags.

A specific surface area of the slags varied from 4300-4414  $\text{cm}^2/\text{g}$  by Blaine. The slags were ground in a ceramic mill with alubit (high alumina) grinding media and lining. For comparison, a steel mill was used.

Sodium metasilicate pentahydrate ( $\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 5\text{H}_2\text{O}$ ) in a form of a non-hygroscopic powder in a quantity of 10% by mass of the cement was used as an alkaline activator.

Quartz river sand was used as fine aggregate. Partial residues on sieves with openings of 0.63, 0.315 and 0.14 mm were 5.1%, 16% and 65%, respectively.

Titanium dioxide  $\text{TiO}_2$  (rutile); kaolin (whiteness – 84%) and calcium carbonate  $\text{CaCO}_3$  (whiteness – 90%) were used as whitening additives. In order to add colour, various pigments of mineral origin as well as red mud were used. The quantity of pigment was 5% by mass of the cement. About pigments the some characteristics are: Titanium dioxide  $\text{TiO}_2$  (rutile) with a particle size between 0.4-2  $\mu\text{m}$  and a whiteness  $\geq 95\%$ ; a delaminated kaolin with a whiteness  $\geq 84\%$ , an specific surface area 12-20  $\text{m}^2/\text{kg}$  and a particle size 0.4-10  $\mu\text{m}$  and plates of calcium carbonate  $\text{CaCO}_3$  with a whiteness –  $\geq 90\%$ , a particle size 9-20  $\mu\text{m}$ . To give colour, various pigments of mineral origin were used, as well as red mud. The amount of pigment was 5% by weight of cement.

Sodium carboxymethyl cellulose was used as a water retaining additive and an additive to prevent efflorescence.

## 2.2. Preparation and characterization of cement pastes and mortars

Technology-related and physico-mechanical properties of the alkali-activated slag cement pastes were determined in accordance with national standards and other normative documents acting currently in the Ukraine. Preparation of the cement pastes and mortars was done in accordance with the requirements described in (43). Optimization of the compositions of decorative slag-alkali cements was carried out according to the plans of full factorial experiments at three levels with three and two factors of type  $3^3$  and  $2^3$  (44).

Strength characteristics were determined in accordance with (45). Shrinkage and weather resist-

ance was determined in accordance with procedures that are described in (46). Freeze/thaw resistance was determined in accordance with (47). The second basic test method with freezing of the specimens at  $t = -20^\circ\text{C}$  in a 5%-solution of NaCl was applied. Stability of colour samples after normal condition and steam curing was determined under exposure of ultraviolet radiation – in accordance with Ukrainian national standard (48). Risk of efflorescence was evaluated in accordance with (49). Adhesion of the mortar to a substrate was determined in accordance with the procedure described in (50). The heat release of hydrated cement compositions was determined by the semi-diabatic (thermos) method in accordance with DSTU B V.2.7-289:2011 (EN 196-9:2010, MOD) using an installation, the schematic diagram of which is shown in Figure 2.

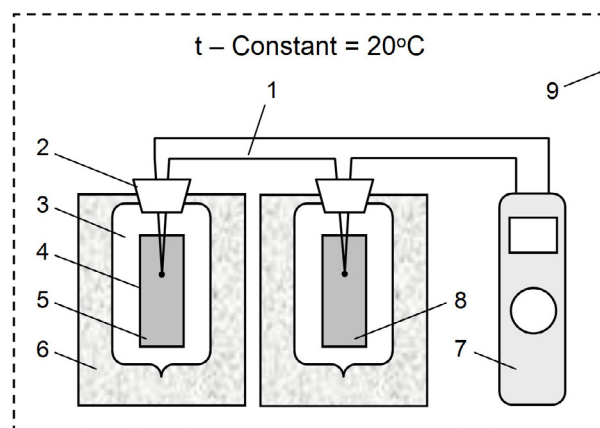


FIGURE 2. Scheme of the installation for determining the heat of hydration of cement by the thermos method: 1 – differential thermocouple; 2 – cork; 3 – Dewar vessel; 4 – a vessel for cement paste or mortar; 5 – cement paste or cement-sand mortar; 6 – thermal insulation; 7 – a device for recording indicators with a given frequency; 8 – model of cement paste; 9 – closed volume (thermostat) with thermally stabilized air temperature.

Determination of whiteness of the specimens was done using a spectrophotometer NS810 with a range of wavelengths of 400-700 nm. A Ral 9016 sample with whiteness index  $L = 98.85$  was used as reference sample. The specimens prepared from the alkali-activated slag cement paste of normal consistency after 28 days of hardening were studied in this test.

A phase composition of the slag sand quantity of glassy phase was determined using a X-ray device DRON-2 with a copper tube and nickel filtrate  $U = 42$  kW,  $I = 18$  mA, within the range of angles  $2\theta = 20$ - $62^\circ$ . Identification of the hydration products was done using data of computer data base PC-PDF, Version 2.13a, Copyright JCPDS – International Centre for Diffraction Data, the program “XPowder” and data base AMSCD, as well as information provided in (51, 52).

The images were taken using a scanning electron microscope (SEM) equipped with microprobe analyzer REMMA-102-02.

### 3. RESULTS AND DISCUSSION

#### 3.1. Optimization of the cement in degree of whiteness

At the first stage of optimization, the influence of whitening additives on the degree of whiteness of the cement and its physico-mechanical properties was studied using a full factorial design of experiment 3<sup>3</sup>. Factors/variables, levels of their variation

and experimental design matrix with functions of responses are shown in Table 2 and Table 3.

The slag D that was ground in a traditional steel mill and because of this was contaminated with metal from the grinding media, and the same slag that was ground in a ceramic mill.

As a result of the processing of the data of Table 3 the regression equations were produced under three responses – strength at 28 days of curing ( $R_{28}$ ), initial setting time ( $\tau$ ) and degree of whiteness ( $W$ ) for the case when the slag was ground in the ceramic mill:

$$R_{28} = 49.85 - 1.81 \cdot X_1 - 3.65 \cdot X_2 - 3.57 \cdot X_3 + 0.47 \cdot X_{11} - 1.23 \cdot X_{22} + 1.27 \cdot X_{33} + 0.5 \cdot X_{12} - 2.48 \cdot X_{13} - 0.75 \cdot X_{23} \quad [1]$$

TABLE 2. Input parameters of the 3-factor plan.

No	Factors/Variables	Units of measurement	Coded factors	Levels of variation		
				-1	0	+1
1	TiO <sub>2</sub> - content	%	X1	0	4	8
2	kaolin - content	%	X2	0	7	14
3	CaCO <sub>3</sub> - content	%	X3	0	12	24

TABLE 3. Matrix of full factorial design of experiment type 3<sup>3</sup>(slag D).

No	Matrix of design in coded form			Matrix of design in natural values			Compressive strength ( $R_{comp}$ ), MPa, at days			Initial setting time, min.	Degree of whiteness (W) after 28 days of normal curing, %	
											steel mill	ceramic mill
	X1	X2	X3	TiO <sub>2</sub> %	kaolin %	CaCO <sub>3</sub> %	2	7	28			
1	+1	+1	+1	8	14	24	25.2	30.4	38.6	33	88.4	94.4
2	-1	+1	+1	0	14	24	31.5	38.8	46.2	36	74.8	79.8
3	+1	-1	+1	8	0	24	29.7	40.2	46.4	38	83.5	89.1
4	-1	-1	+1	0	0	24	35.4	46.8	56.0	37	66.0	70.5
5	+1	+1	-1	8	14	0	32.5	41.0	52.2	57	83.0	88.6
6	-1	+1	-1	0	14	0	36.1	43.9	49.9	46	63.2	68.5
7	+1	-1	-1	8	0	0	35.9	46.2	57.0	69	83.7	89.4
8	-1	-1	-1	0	0	0	39.0	47.4	56.7	54	60.3	64.3
9	+1	0	0	8	7	12	31.4	39.5	48.5	42	82.2	87.9
10	-1	0	0	0	7	12	36.1	44.2	52.1	36	63.7	68.1
11	0	+1	0	4	14	12	31.8	39.2	45.0	40	81.4	87.1
12	0	-1	0	4	0	12	35.5	45.8	52.3	47	77.5	82.8
13	0	0	+1	4	7	24	30.1	39.4	47.5	34	81.2	86.9
14	0	0	-1	4	7	0	35.5	45.0	54.7	54	75.5	80.8
15	0	0	0	4	7	12	33.5	42.4	49.8	40	77.7	83.2

Remark. Quantity of sodium metasilicate – 10% by mass of the cement.



$$\tau = 40.17 + 3.1 \cdot X_1 - 3.3 \cdot X_2 - 10.3 \cdot X_3 - 1.28 \cdot X_{11} + 3.72 \cdot X_{22} + 3.72 \cdot X_{33} - 1.13 \cdot X_{12} - 3.63 \cdot X_{13} + 1.88 \cdot X_{23} \quad [2]$$

$$W = 83.16 + 9.92 \cdot X_1 + 2.11 \cdot X_2 + 3.01 \cdot X_3 - 5.16 \cdot X_{11} + 1.79 \cdot X_{22} + 0.69 \cdot X_{33} - 1.0 \cdot X_{12} - 1.63 \cdot X_{13} + 1.53 \cdot X_{23} \quad [3]$$

Strength values of the cements at 28 days of curing were within a range: 38.6-57.0 MPa, initial setting time: 33-69 min, and degree of whiteness: 64.3-94.4%. Diagrams of strength, initial setting time and whiteness are given in Figures 3-5. For easier plotting, each of 3-factor equations was divided into three pseudo 2-factor equation at X3 (CaCO<sub>3</sub>) – 0%, 12%, and 24%.

The decorative alkali-activated slag cement pastes showed good strength gain at the early ages and even at 2 days of curing (25.2-39.0 MPa).

Depending upon the degree of whiteness, white clinker cement is classified into three grades: 1 grade ≥ 80%, 2 grade ≥ 75%, 3 grade ≥ 70% (53). Coming from this classification, a majority of the white alkali-activated slag cements, even when the slag was ground in a steel and ceramic mill, can be considered as white cements since they had degree of whiteness ≥ 70% (see Table 3).

Analysis and processing of the obtained data (Table 3) showed, that in case of the slag D with the FeO-content of 0.31%, in order to achieve the degree

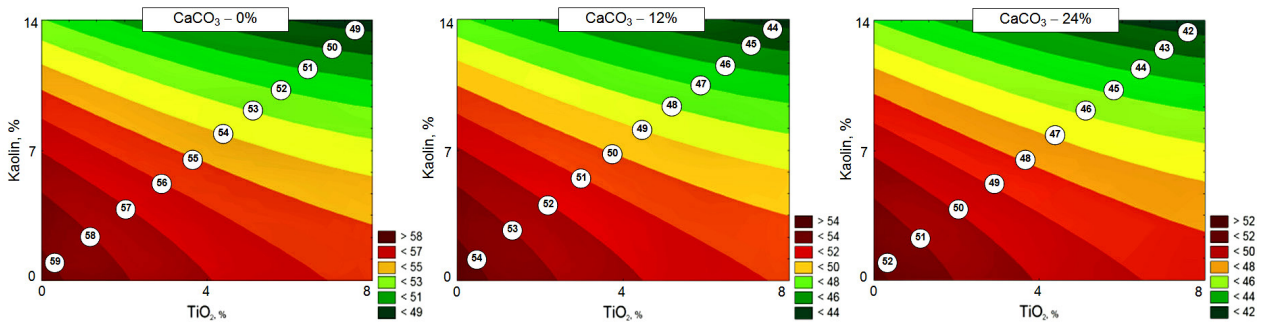


FIGURE 3. Isolines of equal strength of the alkali-activated slag cements at 28 days of curing.

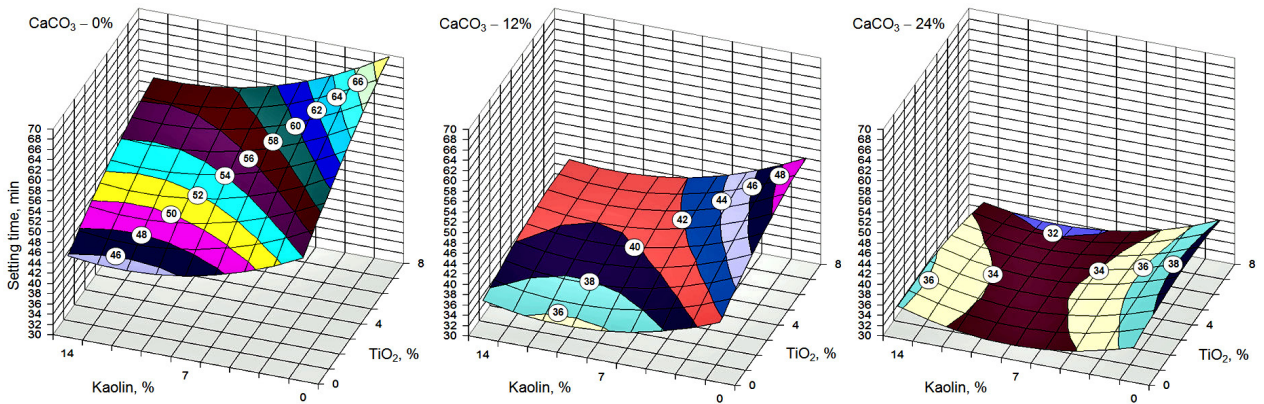


FIGURE 4. Isosurfaces and isolines of initial setting time of the alkali-activated slag cements.

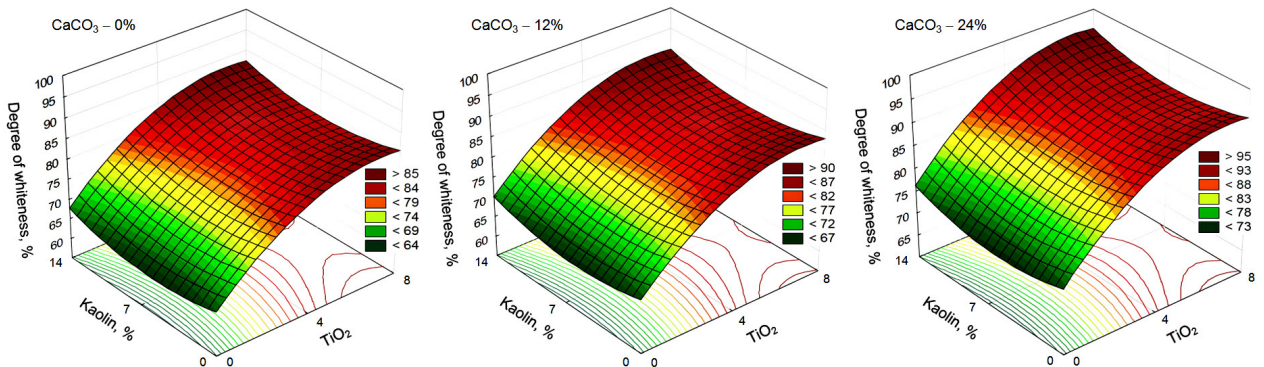


FIGURE 5. Isosurfaces and isolines of whiteness of the white alkali-activated slag cements at 28 days of curing.

of whiteness of the alkali-activated slag cement of at least 70% and class 42.5 R in compressive strength, the percentage (by mass) of each of the whitening additive should be: 5% for TiO<sub>2</sub>, 15% for kaolin and 24% for CaCO<sub>3</sub>.

**3.2. The influence of the FeO-content of the slag on the degree of whiteness of alkaline cement**

In order to study the influence of the FeO-content on the degree of whiteness of the alkaline cement, the slags M, T, and K with the FeO-contents of 0.35%, 0.42% and 1.65% by mass, respectively, were used side by side with the slag D. Moreover, an additional composition based on the slag K and with the added FeO in order to bring its total content to 2.95% was formulated. The results of the study are given in Figure 6. The mathematical dependence of the degree of whiteness (W) on the content of FeO was expressed by the regression equation presented in the figure. As it follows, FeO contained in the slag affects negatively the whiteness of the resulted cement.

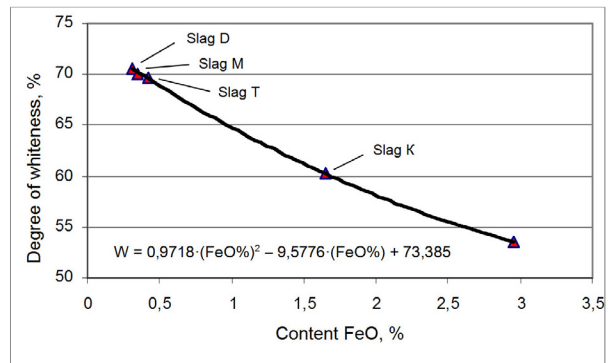


FIGURE 6. The influence of the FeO-content on the degree of whiteness of the alkali-activated slag cement.

**3.3. Optimization of the composition of the white alkali-activated slag cement depending upon the FeO-content of the slag**

In order to eliminate negative influence of FeO of the slag, the quantities of the whitening additives were chosen in such a way that to reach the degree of whiteness not less than 70%, not depending upon

TABLE 4. Input parameters of the 2-factor plans.

Factors/variables	Units of measurement	Coded factors	Levels of variations		
			-1	0	+1
FeO - content	%	X1	0.35	1.65	2.95
TiO <sub>2</sub> - content	%	X2	0	5	10
kaolin - content	%	X2	0	7.5	15
CaCO <sub>3</sub> - content	%	X2	0	12	24

TABLE 5. Matrix of full factorial design of experiment type2<sup>3</sup>.

No	Plan in coded form		Plan in natural values		Degree of whiteness (W), %	Plan in natural values		Degree of whiteness (W), %	Plan in natural values		Degree of whiteness (W), %
	X1	X2	FeO	TiO <sub>2</sub>		FeO	kaolin		FeO	CaCO <sub>3</sub>	
1	+1	+1	2.95	10	73.6	2.95	15	60.0	2.95	24	57.4
2	+1	-1	2.95	0	52.8	2.95	0	52.0	2.95	0	51.9
3	-1	+1	0.35	10	86.5	0.35	15	73.1	0.35	24	70.6
4	-1	-1	0.35	0	64.6	0.35	0	65.1	0.35	0	65.1
5	+1	0	2.95	5	61.6	2.95	7.5	56.0	2.95	12	54.7
6	-1	0	0.35	5	73.9	0.35	7.5	69.2	0.35	12	67.8
7	0	+1	1.65	10	80.9	1.65	15	67.8	1.65	24	65.5
8	0	-1	1.65	0	59.6	1.65	0	59.8	1.65	0	60.0
9	0	0	1.65	5	68.6	1.65	7.5	63.8	1.65	12	62.7

the chemical composition of the slags. Optimization of the cement composition was done with the help of plans a full factorial design of experiment type 2<sup>3</sup>. Factors, levels of variation and the results of the study are shown in Table 4, Table 5 and Figure 7.

Approximation of the data allowed to produce the equations of regression which adequately reflect the results of the experiment:

$$W(\text{FeO-TiO}_2) = 68.56 - 6.17 \cdot X_1 + 10.64 \cdot X_2 - 0.83 \cdot X_1^2 - 1.67 \cdot X_2^2 - 0.25 \cdot X_1 \cdot X_2 \quad [4]$$

$$W(\text{FeO-kaolin}) = 63.83 - 6.58 \cdot X_1 + 4 \cdot X_2 \quad [5]$$

$$W(\text{FeO-CaCO}_3) = 62.72 - 6.58 \cdot X_1 + 2.75 \cdot X_2 - 1.48 \cdot X_1^2 + 0.02 \cdot X_2^2 \quad [6]$$

The isosurfaces produced using these equations (see Figure 7) show that just the additive of TiO<sub>2</sub> is the best whitening additive and it allows to provide whiteness of the alkali-activated slag cement pastes reaching 87%.

As a result of the analysis of the obtained regression equations a factor of influence of each coeffi-

cient of the equation was assessed, that is the influence of each of the whitening additives on the degree of whiteness of the resulted cement. The results are given in Figure 8.

As it follows from Figure 8, a favorable influence of TiO<sub>2</sub> on the whiteness is considerably higher than the unfavorable influence of iron oxide. However, in the case of the additives of kaolin and CaCO<sub>3</sub>, the favorable influence is lower than the unfavorable influence of iron oxide, thus reducing their efficiency as whitening additives compared to that of TiO<sub>2</sub> and requiring more quantities to be added.

From the other side, the additives added in the increased quantities can deteriorate physico-mechanical and performance properties of the white alkali-activated slag cements. According to some authors (54), the addition of between 10-15% of kaolin by mass results in a mechanical strengths decline. This strength declines in the alkali-activated slag cements can be somewhat compensated due to the addition of 2-3% by mass of Portland cement or Portland cement clinker. However, in any case, the addition of kaolin in quantities exceeding 20%

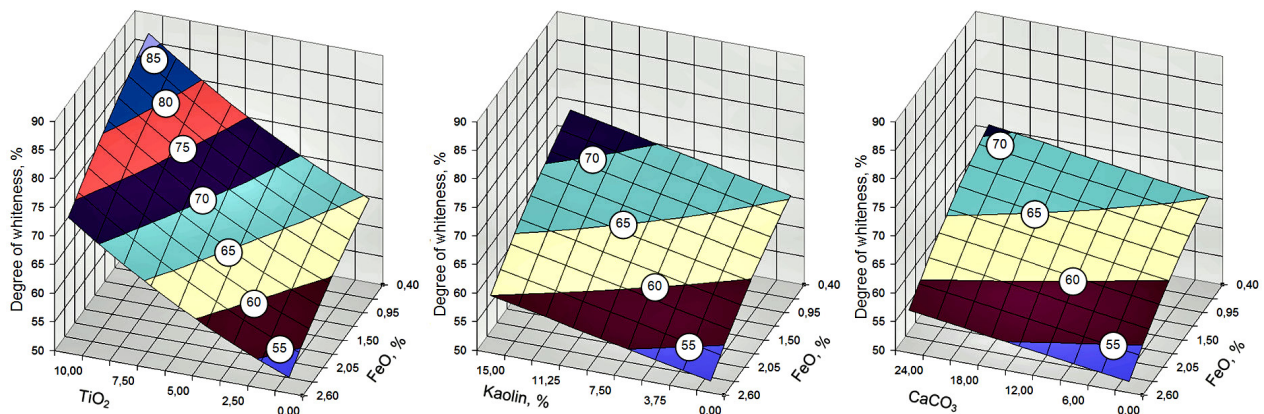


FIGURE 7. The degree of whiteness of the alkali-activated slag cement vs. quantity and type of whitening additive and FeO-content of the slag.

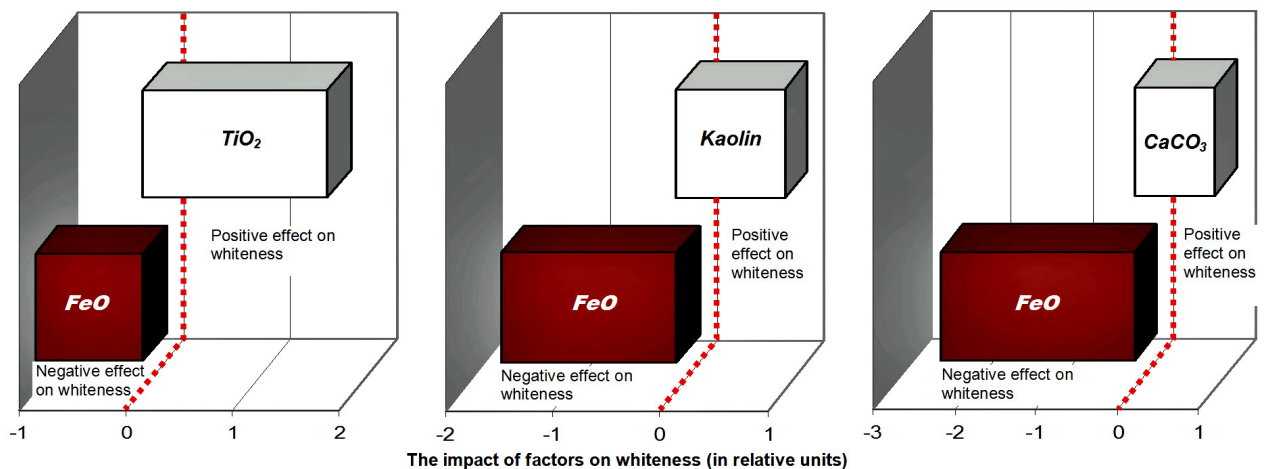


FIGURE 8. The degree of influence of various factors (whitener) on the whiteness of slag-alkali decorative slag cements.



by mass and  $\text{CaCO}_3$  in quantities exceeding 45% by mass in the composition of the alkali-activated slag cement is not desirable (see Figure 9). In case of the slag with the high FeO-content (higher than 1.65%) the additive of  $\text{TiO}_2$  alone or in combination with other additives should be used for whitening.

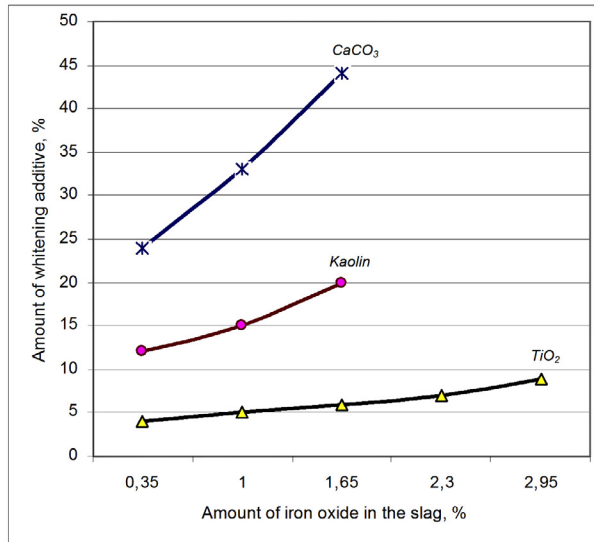


FIGURE 9. Quantities of the whitening additives required to achieve 70-72% degree of whiteness vs. FeO-content of the slag.

### 3.4. Structure formation processes in the white alkali-activated slag cement

#### 3.4.1. Phase composition and morphology of hydration products

According to the results of XRD analysis (Figure 10), a phase composition of the alkali-activated slag cements without whitening additives is presumably represented by C-S-H gel ( $d = 0.333; 0.307; 0.296; 0.281; 0.215; 0.187; 0.281; 0.182$  nm), xonotlite ( $d = 0.3871; 0.3061; 0.2021; 0.193$  nm) and calcite ( $d = 0.383; 0.302; 0.281; 0.227; 0.209; 0.191; 0.187$  nm).

The prevailing phases of the white cement with the 5% additive of  $\text{TiO}_2$  by mass are: calcite ( $d = 0.383; 0.303; 0.281; 0.21; 0.229; 0.209; 191; 0.187; 0.161; 0.152$  nm),  $\text{CaMg}(\text{CO}_3)_2$  ( $d = 0.536; 0.4; 0.362; 0.287; 0.267; 0.218; 0.177$  nm) and quartz ( $d = 0.425; 0.333; 0.182; 0.152$  nm),  $\text{TiO}_2$  ( $d = 0.324; 0.248; 0.23; 0.169; 0.162$  nm).

A phase composition of hydration products of the white cement with 15% kaolin by mass is presumably represented by C-S-H gel ( $d = 0.305; 0.28; 0.18$  nm), C-(A)-S-H(B) ( $d = 0.304; 0.28; 0.180$  nm), tobermorite ( $d = 0.333; 0.307; 0.297; 0.286; 0.214; 0.201; 0.182$  nm), calcite ( $d = 0.385; 0.303; 0.249; 0.228; 0.209; 0.192$  nm), weak diffractions of analcime ( $d = 3.43; 2.92; 0.286; 0.272; 2.52; 1.74$  nm)

and hydronepheline ( $d = 0.467; 0.435; 0.407; 0.385; 0.369; 0.343; 0.297; 0.283; 0.259$  nm). The quantities of analcime and hydronepheline, according to (6) tend to increase constantly in the long-term. Non reacted phases of the slag are represented by ghemite ( $d = 0.286; 0.242; 0.228$  nm) and quartz ( $d = 0.424; 0.333; 0.183$  nm). Diffractions lines ( $d = 0.435; 0.417; 0.385; 0.357; 0.309; 0.234$  nm) are characteristic of kaolinite.

The cement composition with 24%  $\text{CaCO}_3$  by mass is represented by CSH(B) ( $d = 0.304; 0.28; 0.180$ nm), presumably tobermorite gel ( $d = 0.305; 0.279; 0.18$  nm), tobermorite ( $d = 0.33; 0.307; 0.298; 0.285; 0.24; 0.214; 0.201; 0.183$  nm), calcite ( $d = 0.383; 0.303; 0.248; 0.228; 0.209; 0.192; 0.191$  nm), and quartz ( $d = 0.426; 0.334; 0.183; 0.152$  nm).

The study of the morphology of the hydration products (see Figure 11) showed that the following types of particles were visualized: plate-like crystals with layered structure, thread (string)-like crystals, spherulites and hexagonal plates, grains and aggregations of irregular shape. Microprobe analysis of elemental composition and the results of XRD analysis showed that the plate-like and thread (string)-like crystals are characteristic of low-basic calcium silicate hydrates; spherulites and hexagonal plates – aluminosilicate hydrates of alkaline and alkaline-alkali-earth composition; aggregation of irregular shape – various gels. The obtained microstructure of the resulted cement stone is homogeneous and without defects.

#### 3.4.2. The influence of additives on the migration of $\text{Na}^+$ -ion to the white alkali-activated slag cement pastes

Acceleration of the binding of the  $\text{Na}^+$ -ion in the alkali-activated slag cement pastes helps to prevent risk of efflorescences on its surface during service life. Homogeneity of distribution of the  $\text{Na}^+$ -ion from the surface of the cement pastes to its center was evaluated with the help of a scanning electron microscope (SEM) equipped with microprobe analyzer.

Figure 12 shows the alkali-activated slag cement pastes prepared without additives at 28 of curing. The elemental ( $\text{Na}^+$ -ion) distribution in the center (19.8% by mass) and on the surface (18.7% by mass) are very similar. This is evidence of the absence of critical mass transfer of  $\text{Na}^+$ -ion and its binding in insoluble compounds.

The elemental composition of the alkali-activated slag cement pastes with  $\text{TiO}_2$  is shown in Figure 13. With account of the  $\text{Na}_2\text{O}$ -content in the center (20.5% by mass) and on the surface (34.7% by mass). An assumption can be put forward that the whitening this additive ( $\text{TiO}_2$ ) does not prevent migration of free (non-bound) alkali to the surface.

The elemental composition of the alkali-activated slag cement pastes with kaolin is shown in Figure 14. Analysis of the elemental distribution of this

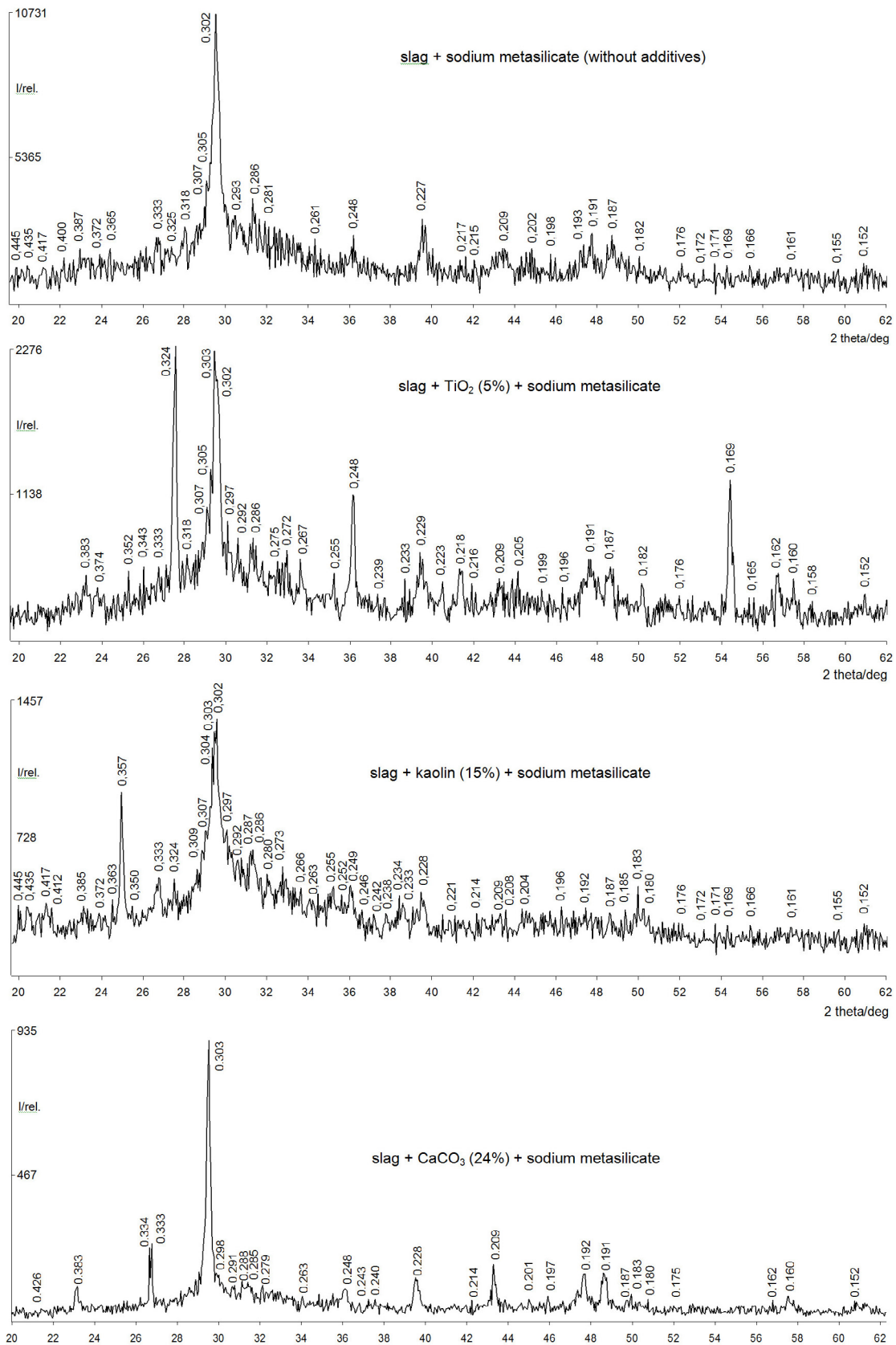


FIGURE 10. X-ray diffraction patterns of the white alkali-activated slag cement after hardening for 28 days.

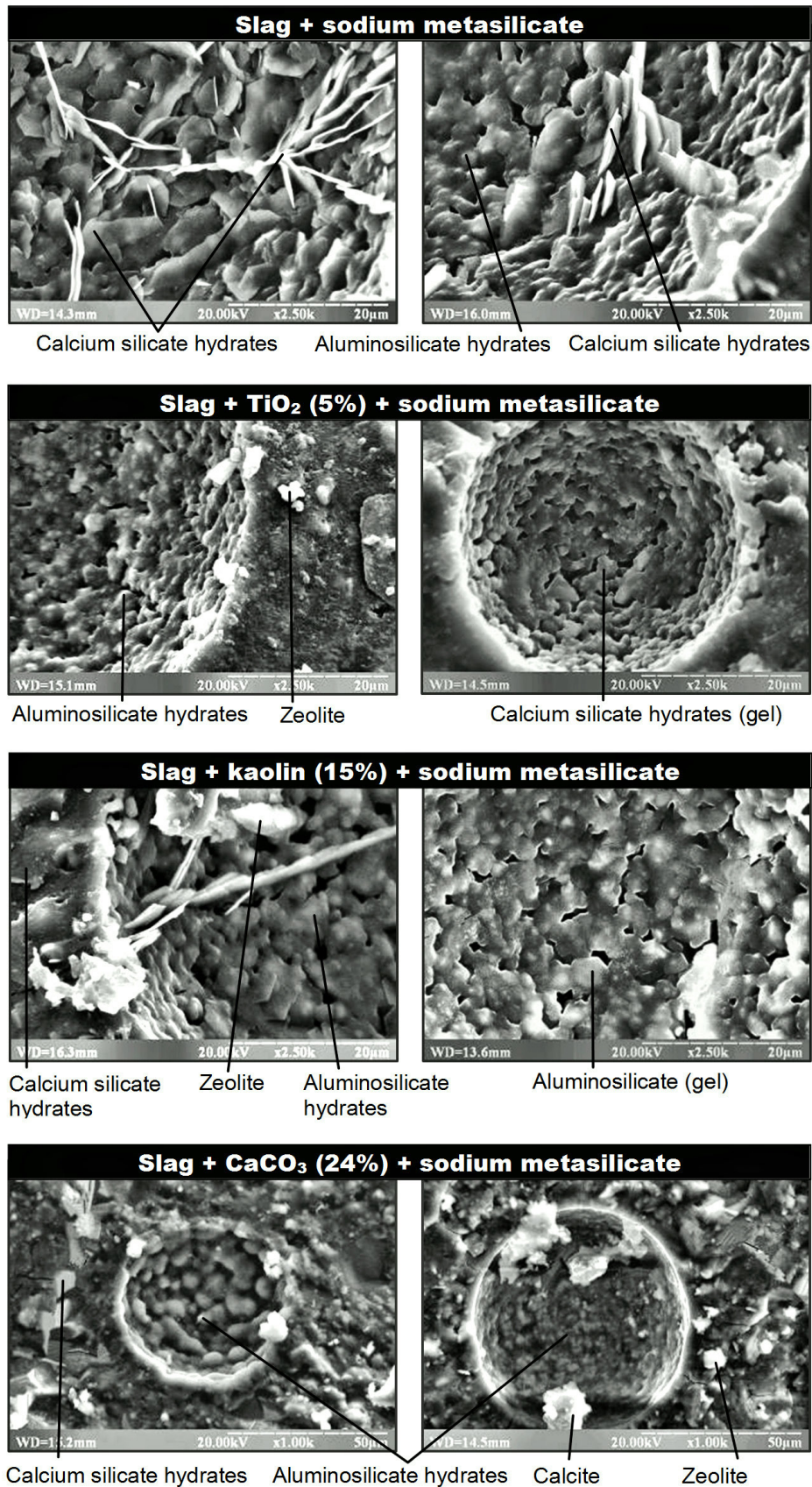


FIGURE 11. SEM images of a cleavage surface of the white alkali-activated slag cement stone after hardening for 28 days.



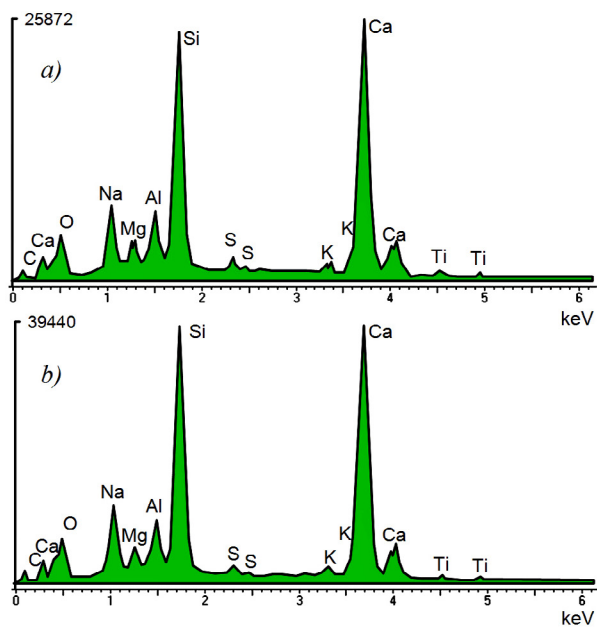


FIGURE 12. Elemental distribution in the alkali-activated slag cement pastes without additives after hardening for 28 days: *a* – in the center; *b* – on the surface.

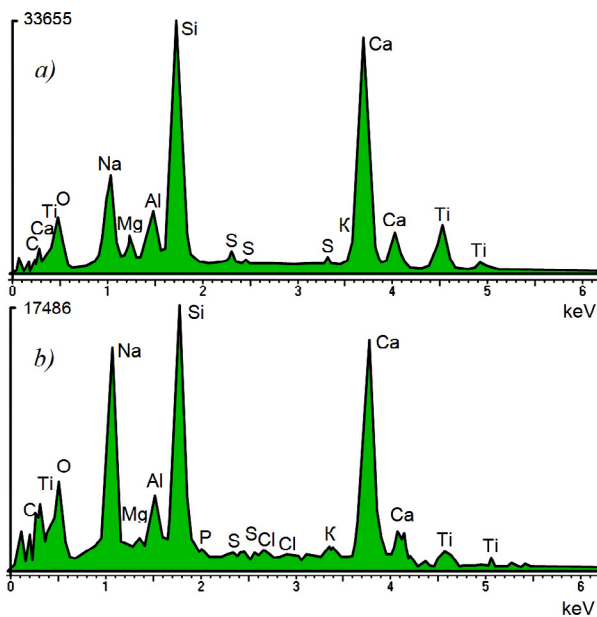


FIGURE 13. Elemental distribution in the alkali-activated slag cement pastes with  $\text{TiO}_2$ : *a* – in the center; *b* – on the surface.

paste shows that in the center and on the surface the kaolin affected positively the degree of binding of free alkali with the formation of insoluble aluminosilicate hydrates. Kaolin is known to possess weak acidic properties and for this reason, considerably increases its cation-exchange capacity in an alkaline medium (55). A quantity of  $\text{Na}_2\text{O}$  in the center (22.02% by mass) and on the surface (14.2% by mass) is evidence of the absence of mass transfer

of free alkali from the center to the surface. That was confirmed by XRD (see Figure 10) with the formation of aluminosilicate hydrates of analcime and hydronepheline; and also from the studies by SEM analysis (see Figure 11).

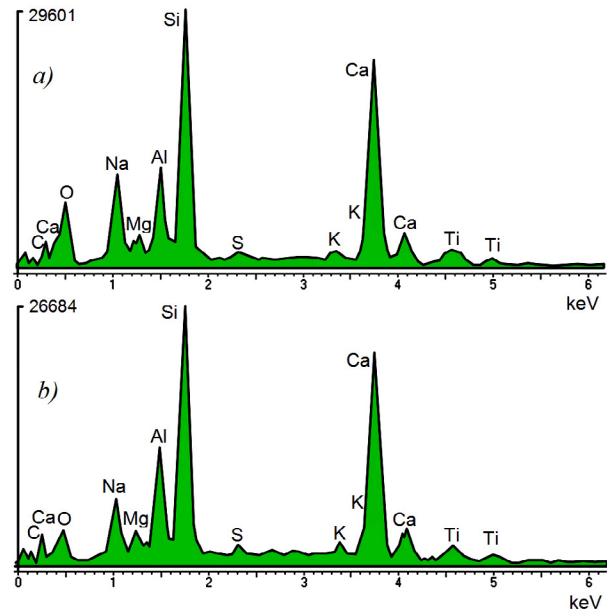


FIGURE 14. Elemental distribution in the alkali-activated slag cement pastes with kaolin: *a* – in the center; *b* – on the surface.

The elemental composition of the alkali-activated slag cement pastes with  $\text{CaCO}_3$  is shown in Figure 15. Quantities of  $\text{Na}_2\text{O}$  in the center (17.56% by mass) and on the surface (16.64% by mass) in the cement paste composition with  $\text{CaCO}_3$  is an evidence of the absence of mass transfer of alkali and its binding with the formation of aluminosilicate hydrate. This correlates well with the data reported in (40) on the deeper hydration processes taking place in the slag-containing cements in the presence of  $\text{CaCO}_3$ .

### 3.4.3. Heat release in the process of hydration of the pigmented alkali-activated slag cement

Curves of heat release of the white alkali-activated slag cement, depending upon its constituent composition, are represented in Figure 16.

When the cement composition is mixed with water, the heat starts to release almost immediately and its nature is connected with hemisorption processes, dissolution of the slag glass and formation of colloidal and crystalline products. A conclusion can be made that the higher quantities of the whitening additives in the cement composition the lower is a cumulative heat release. Peak of heat released is shifted from 7 or 8 h (the reference cement composition without additive) to 9 or 11 h (the compositions with the additives). This can be attributed, first of all, to



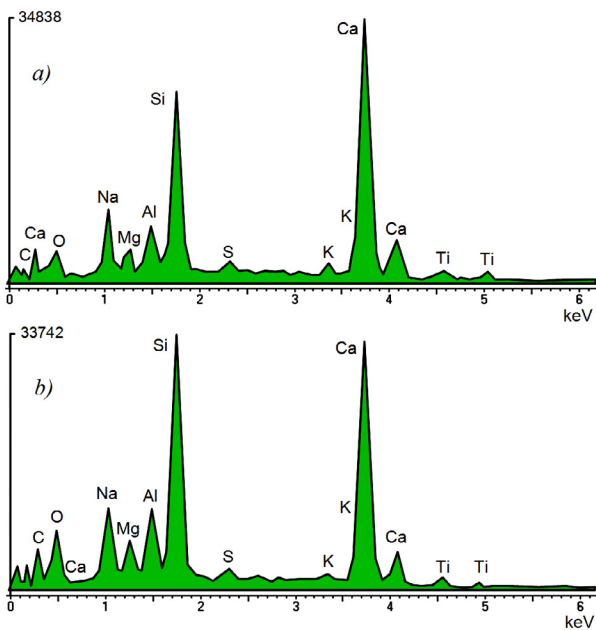


FIGURE 15. Elemental distribution in the alkali-activated slag cement pastes with  $\text{CaCO}_3$ : a – in the center; b – on the surface.

the lower contents of the slag in the cement composition. This is especially evident in the compositions with the additives of kaolin and  $\text{CaCO}_3$ . Accumulative heat release of the composition with the additive of  $\text{CaCO}_3$  (55.1 J/g) is higher than that of the composition with the additive of kaolin (44.0 J/g), though a quantity of the additive of  $\text{CaCO}_3$  – 24% is much higher compared to that of the additive of kaolin – 15%. This can, evidently, be attributed to the binding or absorption of some portions of alkali by kaolin and, as a result, the lower reaction ability of the liquid medium relatively to the slag.

### 3.5. Evolution of physico-mechanical and performance properties of the alkali-activated slag cements and mortars

#### 3.5.1. Compressive strengths

The influence of optimal quantities of the whitening additives strengthen standard-specified ages and in the long-term are given in Figure 17. As it see in

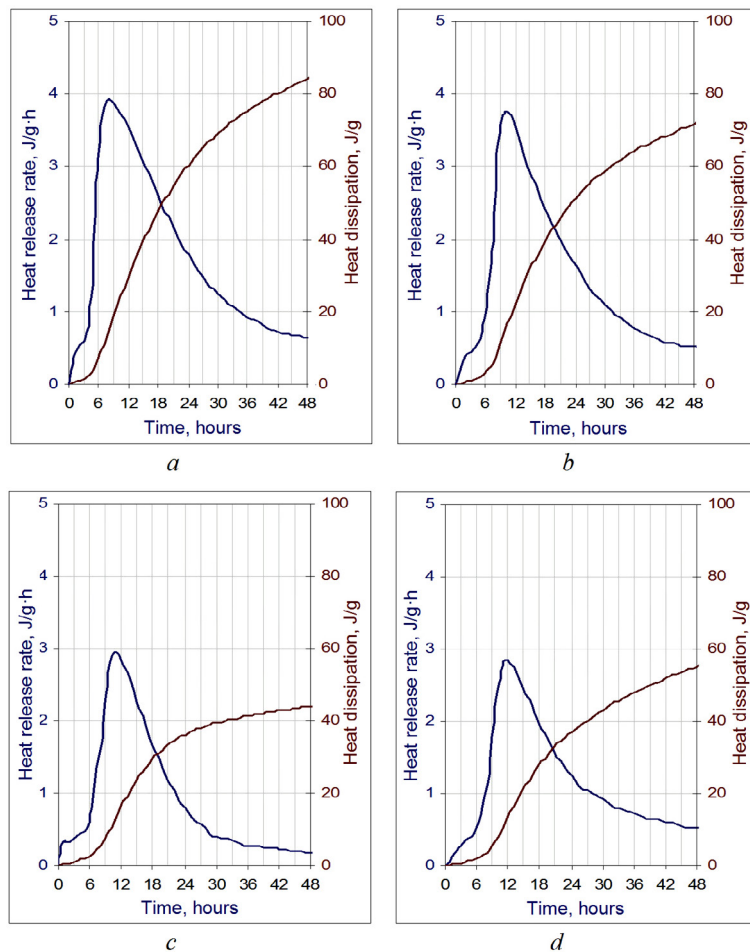


FIGURE 16. Heat release of the pigmented alkali-activated slag cement: a: cement paste without additives; b – “slag+ sodium metasilicate +  $\text{TiO}_2$  (5%) + pigment (5%)”; c – “slag+ sodium metasilicate+ kaolin (15% by mass) + pigment (5%)”; d – “slag+ sodium metasilicate +  $\text{CaCO}_3$  (24%) + pigment (5%)”. Quantity of sodium metasilicate – 10% of the cement by mass.

this Figure 17, the white alkali-activated slag cements have the values of compressive strength in the range 49.0-56.8 MPa at 28 days and 66.8-67.5 MPa at 180 days. All these white cements have good strength gain, and, judging by their strength at 2 days (35.0-37.0 MPa), can be considered as quick-hardening cements (class 42.5R or 52.5R, according to EN 197).

Kaolin possess weak acidic properties and for this reason in the conditions of a highly alkaline medium increases considerably its cation-exchange capacity (55). For this reason, it starts actively participate in structure formation processes with the formation of alkaline and alkaline-alkali-earth zeolite-like aluminosilicate hydrate (6), which guarantee the high performance properties of the final hardened cement pastes.

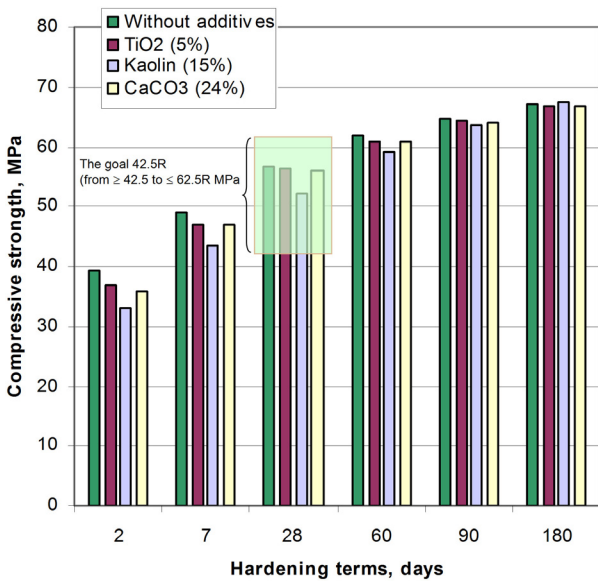


FIGURE 17. Influence of the whitening additives taken in optimal quantities on the compressive strengths of the white alkali-activated slag cement. Optimal quantities of the whitening additives, % by mass: TiO<sub>2</sub> – 5; kaolin – 15; CaCO<sub>3</sub> – 24.

On the contrary, to TiO<sub>2</sub> and CaCO<sub>3</sub>, kaolin acts not only as a whitening additive, but also as active mineral additive capable to affect considerably technology-related, physico-mechanical, and performance properties.

Since a part of alkali is bound by kaolin, strength values of the alkali-activated slag cement pastes at standard-specified ages are somewhat lower (by 10-11%) compared to those of the composition without additive. However, after 3 or 6 months, this difference disappears, and the high strength values are achieved due to the deepening of hydration processes, synthesis of low-basic calcium silicate hydrates, synthesis of analogs to zeolites and feldspars and absence of the processes of destruction.

On contrary to the additive of kaolin, TiO<sub>2</sub> is almost inert with regard to components of the alkali-activated slag cement. A small optimal quantity of this additive (approx. 5% wt.) almost does not affect the compressive strengths (Figure 17). Of interest is the influence of the additive of CaCO<sub>3</sub> on strength values. As it follows from Figure 17, despite large quantities of this additive (approx. 24% wt.) the strength of the alkali-activated slag cement pastes at 28 days was only by 1.5% lower compared to that of the cement composition without additive, and by the age of 180 days this difference practically not exist. This can be attributed to the following: known-in-the-art is that one of the methods of how to increase strength of concrete is to fill a cement matrix with mineral additives – finely dispersed mineral particles of various nature and fractional composition (54, 56, 57).

Finely dispersed carbonate rocks (58, 59) have certain chemical similarity with the alkali-activated slag cement and in size of particles, close to those of particles of the alkali-activated slag cement. Despite some chemical inertness, this circumstance, nevertheless, causes their interaction with hydration products of the alkali-activated slag cement as centers

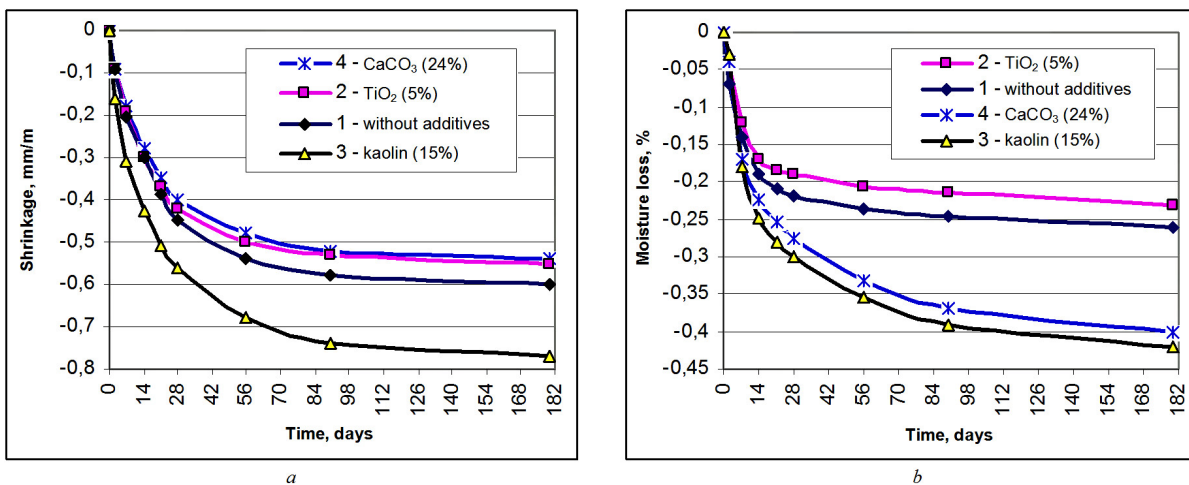


FIGURE 18. Influence of the whitening additives on shrinkage deformation (a) and moisture loss (b) in the long-term.

of crystallization or nucleation and enables to form crystal contacts. As a result, a more perfect microstructure is formed (60), thus ensuring the higher performance properties of the concretes and mortars.

### 3.5.2. Shrinkage deformations

Shrinkage deformations were measured on the prismatic mortar specimens 4×4×16 cm (cement : sand = 1:3); at RH of 60% and a temperature of 20±2°C. Side by side with taking measurements of shrinkage deformations, the values of moisture loss were measured.

The results obtained from measurements of shrinkage of the white alkali-activated slag cement mortars and moisture loss with optimal quantities of the whitening additives are given in Figure 18. A rather good correlation is observed between shrinkage and moisture loss, except for the mortar with the addition of CaCO<sub>3</sub>. The lowest values of shrinkage until stabilization were observed in the specimens with the additive of CaCO<sub>3</sub> – 0.54 mm/m. The compositions without additive and with TiO<sub>2</sub> have somewhat higher value of shrinkage – 0.55-0.60 mm/m. The highest value of shrinkage (0.77 mm/m) were observed in the compositions with the additive of kaolin (see Figure 18 a). Due to its small quantity (5% by mass) and chemical inertness, the additive of TiO<sub>2</sub> almost does not affect shrinkage. For this reason, the values of shrinkage deformation in the compositions without additive and with TiO<sub>2</sub> are very close.

The effect of kaolin on shrinkage is greater due to its higher content (15% by mass). This can be attributed to the fact that the alkaline cations of a liquid medium enter into interaction followed by peptization and following swelling of kaolin (61). Later, as soon as physical water leaves the specimen, a reverse process takes place, resulting in the higher value of shrinkage. This correlates well the values of moisture loss of the composition with the additive of kaolin obtained in the study (see Figure 18 b).

As was mentioned earlier, the lowest value of shrinkage deformation are measured in the compo-

sition with the additive of CaCO<sub>3</sub>, despite its high content in the cement composition – 24% by mass (Figure 18 a) and despite the fact that the values of moisture loss of this composition are among the highest values (Figure 18 b). This can be due to the following: high values of moisture loss are joined with higher content of calcium carbonate (24% by mass) and its finer particles. However, on contrary to kaolin, calcium carbonate is practically inert in an alkaline environment and is not subjected to peptization and following swelling. Besides, as was mentioned earlier, the particles of finely dispersed calcium carbonate can act as centers of crystallization and to form quickly a rigid crystal framework, which restrict shrinkage, and to fill a pore space of the cement stone and to form a denser and more rigid structure. For this reason, in this case, high values of moisture loss do not mean the higher shrinkage deformations.

### 3.5.3. Freeze/thaw resistance and weather resistance

The results of test of the white alkali-activated slag cement mortars for freeze/thaw resistance are given in Table 6. Mortar specimens 4×4×16 cm (cement : sand = 1:3) after hardening for 28 days curing were tested. The specimens contained 5% mineral pigment by mass. With the consideration of appropriateness, the testing was restricted by 150 cycles of freezing/thawing.

After 150 cycles of freezing/thawing (being equivalent to F200) the mass losses of the specimens were absent, the maximum compressive strength decline was 3.87%, scaling of the surface of the specimens was not observed. Thus, according to the results of the test represented in Table 6, all the mortars correspond in freeze/thaw resistance to brand F200.

The results of test of the pigmented alkali-activated slag cement mortar for resistance to wet/dry cycles are given in Table 7. Beam specimens 4×4×16 cm (cement : sand = 1:3) cured in normal conditions for 28 days were tested. The hardened specimens were exposed to alternate drying for 6 h at t = 105 ± 5°C and wetting (immersion into water)

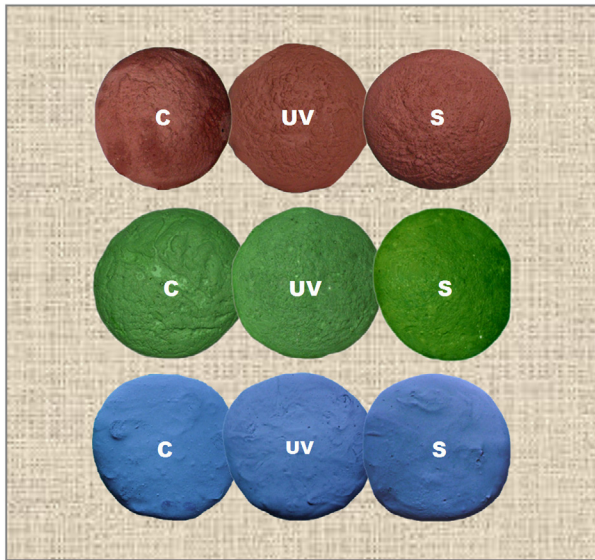
TABLE 6. Freeze/thaw resistance of the pigmented alkali-activated slag cement mortar vs. whitening additives.

Nos	Additive	Strength after 28 days, MPa	Compressive strength change, %, after freezing/thawing, cycles				Grade in freeze/thaw resistance
			45	75	100	150	
			F75	F110	F150	F200	
1	without additive	56.7	+1.21	+0.83	-0.52	-1.73	F200
2	TiO <sub>2</sub> (5%)	56.3	+1.0	+1.1	-0.68	-2.2	F200
3	kaolin (15%)	51.8	-0.42	-1.66	-2.42	-3.48	F200
4	CaCO <sub>3</sub> (24%)	56.0	-0.33	-1.85	-2.7	-3.87	F200

at  $20\pm 2^\circ\text{C}$  during 6 h. The strength was determined after a certain number of cycles. The cements are considered weather resistant, if after 100 cycles of alternate wet/dry, the strength decline of the specimens is less than 25%. As it follows from Table 7, a conclusion can be mortar composition have passed successfully test for weather resistance.

#### 3.5.4. Colour stability under exposure to ultraviolet radiation or steam curing

Colour stability was assessed in accordance with the testing procedure prescribed in the National standard of Ukraine DSTU B V.2.7-268:2011 Portland cement, colored. Technical specification (48) (see Figure 19).



**FIGURE 19.** Colour stability of the pigmented alkali-activated slag cement under exposure to ultraviolet radiation or steam curing: C – reference cement (not exposed); UV– cement exposed to ultraviolet; S – steam curing.

Colour stability of the pigmented alkali-activated slag cement was determined on disc-shaped specimens prepared from a cement paste of normal consistency in accordance with the Ukrainian national

standard DSTU B V.2.7-181:2009 (43). Two disc-shaped specimens prepared from each composition were stored in the air as reference samples, two disc-shaped specimens were subjected to steam curing, and two disc-shaped specimens – to ultraviolet radiation. Mineral pigments in a quantity of 5% by mass were used.

Irradiation of the disc-shaped specimens by ultraviolet rays is done with the help of a mercury-quartz lamp with a power of  $240\pm 20$  W for 48 hrs. The disc-shaped specimens were placed at a distance of 0.5 m from a source of ultraviolet radiation and a luminous flux was directed on the surface at an angle of  $45\pm 2^\circ$ .

Colour stability of the pigmented alkali-activated slag cement pastes was evaluated visually by comparing the colors of the disc-shaped specimens subjected to ultraviolet radiation or steam curing with colors of the reference disc-shaped specimens. As it follows from Figure 19, after exposure to ultraviolet radiation or steam curing the color almost did not change.

#### 3.5.5. Risk of efflorescence

Risk of efflorescence in the pigmented alkali-activated slag cement mortars was assessed under procedure of DSTU B V.2.7-69-98 (48) on specimens  $4\times 4\times 16$  cm (cement: sand = 1:3). After 28 days of hardening in normal conditions the mortar specimens were dipped in a container filled with distilled water to a depth of 4-5 cm and blown with air with



**FIGURE 20.** Risk of efflorescence in the pigmented alkali-activated slag cement mortars vs. the whitening additive: 1– reference sample (without additive); 2 –  $\text{TiO}_2$  (5% by mass); 3 – kaolin (15% by mass); 4 –  $\text{CaCO}_3$  (24% by mass). Content of pigment in mortar specimens (5% by mass).

**TABLE 7.** Weather resistance of the pigmented alkali-activated slag cement mortars vs. whitening additives.

Nos	Additive	Compressive strength of the dried specimens, MPa	Strength decline, %, after freezing/thawing, cycles			
			25	50	75	100
1	without additive	56.9	-2.0	-3.37	-4.64	-5.82
2	$\text{TiO}_2$ (5%)	56.5	-2.51	-3.85	-5.2	-6.46
3	kaolin (15%)	53.0	-3.84	-5.7	-7.33	-9.2
4	$\text{CaCO}_3$ (24%)	56.3	-3.04	-4.45	-5.9	-7.25



a temperature of about 25°C for a least of 3 h per day during 7 days.

A phenomenon of efflorescence on the open surface of the specimen was evaluated visually by the presence of salt deposits. As it follows from Figure 20, no salt deposits were observed.

In addition to standard test for the evaluation of the risk of efflorescence, other tests were also performed in the conditions of indoor and outdoor application. In order to model the exposure of various service conditions of indoor and outdoor application. Mortars (cement : quartz sand = 1:3; W/C = 0.46-0.53) were applied on a walls of the building from the outside to evaluate the exposure of appropriate weather factors in winter-spring-summer periods: (t = -15...+30°C, snow, rain, sun radiation, R.H. = 70-100%); and from the inside (t = 18-24°C, R.H. = 55-80%). The test period was 9 months. In order to prevent efflorescence, a water retaining additive (sodium carboxymethyl cel-

lulose), in a quantity of 0.25% by mass, was added in the decorative alkali-activated slag cement mortars. Test results are shown in Table 8 and Table 9.

From Table 8 and Table 9 is deduced that no salt deposits were formed on the decorative mortars tested in indoor and outdoor applications.

The use of red mud as pigment resulted in nice uniform terracotta color. Above all, according to (28, 62), the use of red mud allows to solve ecological problems, to increase strength of the alkali-activated slag cement due to the alkali contained in it, as well as to improve decorative characteristics of the resulted cement stone.

A final consideration from this study: the surface of the decorative mortars based on the white clinker cement usually have an inhomogeneous glossy surface, which is not acceptable from the point of use for decoration purposes, however, the hardened alkali-activated slag cement mortars have an uniform matte surface.

TABLE 8. Decorative alkali-activated slag cement mortars tested in outdoor application.












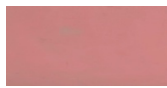








Pigment color	White alkali-activated slag cement with whitening additives			White clinker cement
	TiO <sub>2</sub>	kaolin	CaCO <sub>3</sub>	
Braun				
Yellow				-
Red mud (terracotta color)				-

TABLE 9. Decorative alkali-activated slag cement mortars tested in indoor application.

Pigment color	White alkali-activated slag cement with whitening additives			White clinker cement
	TiO <sub>2</sub>	kaolin	CaCO <sub>3</sub>	
Braun				
Yellow				-
Red mud (terracotta color)				-

### 3.5.6. Adherence tests to a substrate

Adherence tests were carried out in accordance with the methodology set out in EN 1542-1999 (50). A cement-sand mortar with a composition of 1:3 was applied to a concrete slab 30×30×10 cm. The concrete class of the slab was B20, and the water absorption of the slab was 6.2%.

After the mortar hardened, the samples were made on a concrete base in the form of cylindrical cores with a diameter of 5 cm in the amount of 5 pieces and were stored under laboratory conditions at a temperature of 20±2°C and relative humidity of the air about 65% for 27 days. The test of samples for separation from the base was carried out on a tensile testing machine FM-250 (Germany). The destruction occurred in the zone of contact of the mortar with the slab or with a partial detachment of the slab of concrete. The test results are presented in Table 10.

**TABLE 10.** Adherence (pull-out strength test) of the pigmented alkali-activated slag cement mortar to a concrete substrate vs. the whitening additives.

Reference (without additive)	Pull-out strength, MPa		
	TiO <sub>2</sub> (5% by mass)	kaolin (15% by mass)	CaCO <sub>3</sub> (24% by mass)
5.44	5.31	5.52	5.22

Remark. Further whitening additives, all compositions of the pigmented alkali-activated slag cement mortars contained 5% mineral pigment of red color by mass.

**TABLE 11.** Comparative costs of the whitening additives vs. content and content of iron oxide of the slag.

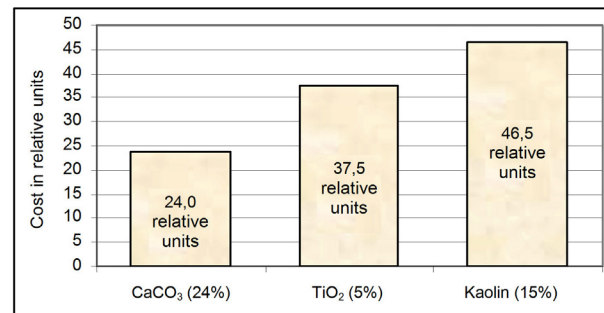
Whitening additive (cost in relative units)	Cost of the whitening additive, in relative units		
	FeO – 0.35% by mass	FeO – 1.65% by mass	FeO – 2.95% by mass
	5%	7%	9%
TiO <sub>2</sub> (7.5)	37.5 relative units	52.5 relative units	67.5 relative units
	15%	20%	
Kaolin (3.1)	46.5 relative units	65 relative units	–
	24%	45%	
CaCO <sub>3</sub> (1)	24 relative units	45 relative units	–

Remark. The top number (nominator) – a required quantity of the whitening additive (in % by mass), the bottom number (denominator) – cost of the whitening additive (in relative units).

### 3.6. Feasibility study of the use of whitening additives

Considering the amount of whitening additives used in this study and the requirements as whiteness of the alkali-activated slag cement (at level of 70-72%) and a class resistant 42.5R in compressive strengths, and having into account the iron oxide in the blast furnace slag, the economic efficiency of the three whitening additives used in this study are presented in Table 11 and Figure 20.

A comparative cost of the whitening additives at the content of iron oxide of 0.35% of the slag is given as an example in Figure 21.



**FIGURE 21.** Cost of the whitening additives vs. content. Content of iron oxide of the slag – 0.35% by mass.

According to these results, a conclusion can be made that the best choice in terms of cost is CaCO<sub>3</sub>, despite its high content. However, its use is restricted (≤ 45%) at the FeO-content of the slag ≤ 1.65% (Figure 9). Increasing the FeO content will require increasing of the CaCO<sub>3</sub> content, which will lead to a decrease of strength.

The additive of kaolin was found to be the most expensive solution and is restricted (≤ 20% by mass) at the FeO-content of the slag ≤ 1.65% (Figure 9). However, an advantage of kaolin is not only its whitening properties, but its chemical activity due to binding of free alkalis and synthesis of zeolite-like hydrates due to this a low risk of efflorescence.

In terms of cost, the additive of TiO<sub>2</sub> takes a position between kaolin and CaCO<sub>3</sub>, however, its potential as a whitening additives much higher and it can be used for the full range of the FeO-content of the slag (from 0.35% and up to 2.95%).

## 4. CONCLUSIONS

1. A comparative study of the influence of whitening additives, these are: TiO<sub>2</sub>, kaolin, and CaCO<sub>3</sub>, in order to produce white and pigmented alkali-activated slag cement and with the degree of whiteness of at least 70% and class 42,5R, in the compressive strength, on the structure formation properties and on the evolution

- of physico-mechanical and performance properties was performed.
- A conclusion was made that the principles to be laid in the compositional build-up of the white alkali-activated cement should take into account not only the influence of the whitening additives on the processes of whitening, but the FeO-content of the granulated blast furnace slag.
  - By using examination techniques such as calorimetry, X-ray diffraction analysis, scanning electron microscopy, microprobe analysis, a conclusion was made that the whitening additives used in the study make the processes of structure formation much deeper, resulting in a more complete binding of the Na<sup>+</sup>-ions in insoluble compounds, thus providing high durability. The additives of kaolin and CaCO<sub>3</sub> are found to be the most actively taking part in these processes eliminating risk of efflorescence and increasing color stability of the pigmented alkali-activated slag cement.
  - A comparative feasibility study of the use of the whitening additives depending upon the FeO-content of the granulated blast furnace slag suggested to conclude that the use of CaCO<sub>3</sub> is the most advantageous in terms of cost, however, its quantities are to be restricted by the FeO-content of the slag ( $\leq 1.65\%$  by mass). The additive of TiO<sub>2</sub> takes a position between CaCO<sub>3</sub> and kaolin, but its advantage is that the granulated blast furnace slags with the FeO-content up to 2.95% by mass can be used.

## ACKNOWLEDGMENTS

The authors are grateful to the Ministry of Education and Science of Ukraine for the financial support of the project (registration No. 1020U001010), which is being implemented at the expense of budget funding in 2021-2022.

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