Influence of whitening additives on the properties of decorative slag-alkaline cements

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Abstract. Traditional decorative cements are made on the basis of white cements and the demand for them is constantly growing. But such cements have all the disadvantages of clinker cements, namely, high energy intensity and high price. An alternative may be slag-alkali cements having higher physical and mechanical characteristics and lower price. Therefore, these studies were aimed at choosing such additives that would have the maximum whitening properties and would enhance the stabilization of bleaching processes during hydration and hardening of slag in the presence of alkalis, to determine the simultaneous effect of three additives on the whiteness and physical-mechanical characteristics, as well as to determine the optimal the content of these additives in slag-alkali decorative compositions. In this work, as a result of the studies performed, the possibility of obtaining effective slag-alkali white cements as the basis for the production of decorative concrete with acceptable economic characteristics is proved. The influence of each of the bleaches on such characteristics of decorative slag-alkali cements as strength, setting time, whiteness is established. Methods for optimizing compositions are identified.

1. Introduction

Decorative cements are used to increase the architectural expressiveness of buildings and perform finishing work. Demand for them and requirements for their operational characteristics are constantly growing [1]. Usually they are made on the basis of white cements [2]. However, such decorative cements have all the disadvantages of Portland cement, including high energy demand and high cost. They are not always able to provide a decorative ecological and comfortable coating with improved performance [3-5].

The use of decorative alkaline activated cements, in particular slag-alkali cements, can be an important alternative in the production of white and non-ferrous cements. In addition, they are able to demonstrate a number of special properties цвета color stability, durability, high strength and adhesion, etc. [6-12]

The problem associated with the use of slag-alkali cements as a basis for decorative cements with high whiteness (70...95%) is the instability of the chemical composition of slags and the acquisition of green color in the process of hydration of slag-alkali cement due to the oxidation processes of sulfide compounds present in slag [13].

In previous studies in this direction [14-17], insufficient attention was paid to the influence of individual additives and their interaction on the decorative and physic-mechanical properties of slag-alkali cements.

Therefore, these studies were aimed at choosing such additives that would have the maximum whitening properties and enhance stabilization of bleaching processes during hydration and hardening of slag in the presence of alkalis, to determine the simultaneous effect of three additives on the whiteness and physic-mechanical characteristics, as well as to determine the optimal the content of these additives in slag-alkali decorative compositions.

2. Raw materials and research methods

In the studies, two blast furnaces granular slags were used, which significantly differed in the content of iron oxides. The chemical composition of the slag is presented in Table 1.

Table 1. Composition of blast furnace granulated slag.

Slag	The content of oxides, % of the mass										M_b
	SiO_2	Al_2O_3	CaO	MgO	FeO	SO_3	MnO	TiO_2	roasting losses	Σ	
Dnieper	37,90	6,85	45,35	5,21	0,31	2,6	0,11	0,35	1,34	100,02	1,13
Kryvyi Rih	39,2	5,1	47,14	4,42	1,65	1,72	0,16	–	0,6	99,99	1,16

To compare the influence of grinding conditions on the whiteness of cement, slag was ground both in a conventional ferrous metal mill with steel grinding bodies, and in a mill with alubite (high alumina) grinding bodies and a lining. The degree of grinding of the slag was 4650...4770 cm^2/g according to Blaine.

Non-hygroscopic sodium metasilicate ($Na_2O·SiO_2·5H_2O$) in powder form was used as the alkaline component of slag-alkali cements.

TiO_2, $CaCO_3$ (90%) and kaolin of class KH 84 (84%) were used as whitening additives.

To produce 4×4×16 cm beam samples of 1:3 composition from a mixture of normal consistency, standard sand of the Gusarovskoye field, Kharkov region, was used.

All components were mixed in standard Hobart mixers.

Technological and physic-mechanical properties of slag-alkali cements were determined in accordance with state standards in force in Ukraine.

The whiteness of the samples was determined using an NS810 spectrophotometer with a wavelength range of 400...700 nm. For comparison, we used a sample of Ral 9016 with a brightness of L = 98,85. Samples from cinder-base alkali cement test of normal density were studied after 28 days of hardening.

To optimize the composition of decorative cements, ease of processing the obtained data and create a mathematical model of the experiment in the form of regression equations, we used the mathematical design of the experiment in the form of a full factorial experiment 3^3, which traditionally has proven itself in scientific research.

3. Research Results and Discussion

3.1. Study of basic physical-mechanical characteristics and whiteness

First, studies were carried out on the effect of bleaching additives on the degree of whiteness of the compositions and on their physical and mechanical properties using a full factorial experiment. Factors, the boundaries of their variation, and the experimental matrix with response functions are presented in Table 2 and Table 3.

The Dnieper slag, ground in an ordinary steel mill and therefore partially contaminated with metal grinding media, and the Dnieper slag, ground in a mill with alubite grinding media and a lining, were used.

Table 2. Source data

№	Factors	Units	Codes	Factor Variation Levels		
				–1	0	+1
1	TiO_2 content	%	X1	0	4	8
2	Kaolin content	%	X2	0	7	14
3	$CaCO_3$ content	%	X3	0	12	24

Table 3. Full factorial experiment matrix.

№	Plan matrix in codes			Plan matrix in physical terms			Strength $R_{str.}$, MPa, after, days			Setting start time, min.	Degree of whiteness, %	
	X1	X2	X3	TiO_2 %	kaolin %	$CaCO_3$ %	2	7	28		milling in a steel mill	milling in alubite mill
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	67,5
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

Note. The amount of metasilicate in the compositions – 10%, slag – Dnieper.

As a result of processing the data in Table 3, we obtained regression equations for three responses – strength after 28 days (R_{28}), the start time of setting (τ) and degree of whiteness (W) when grinding slag in a mill with alubite grinding media:

$$R_{28} = 49,85–1,81\cdot X_1–3,65\cdot X_2–3,57\cdot X_3+0,47\cdot X_{11}–1,23\cdot X_{22}+1,27\cdot X_{33}+0,5\cdot X_{12}–2,48\cdot X_{13}–0,75\cdot X_{23}$$
$$\tau = 40,17+3,1\cdot X_1–3,3\cdot X_2–10,3\cdot X_3–1,28\cdot X_{11}+3,72\cdot X_{22}+3,72\cdot X_{33}–1,13\cdot X_{12}–3,63\cdot X_{13}+1,88\cdot X_{23}$$
$$W = 83,16+9,92\cdot X_1+2,11\cdot X_2+3,01\cdot X_3–5,16\cdot X_{11}+1,79\cdot X_{22}+0,69\cdot X_{33}–1,0\cdot X_{12}–1,63\cdot X_{13}+1,53\cdot X_{23}$$

The strength of the samples after 28 days was in the range 38,6...57,0 MPa, the onset of setting – 33...69 minutes, the degree of whiteness – 64,3...94,4%.

Diagrams of strength, setting start time and whiteness are presented in Fig. 1...Fig. 3. For the convenience of their construction, each 3-factor equation was divided into three pseudo 2-factor equations with X3 ($CaCO_3$) – 0%, 12% and 24%

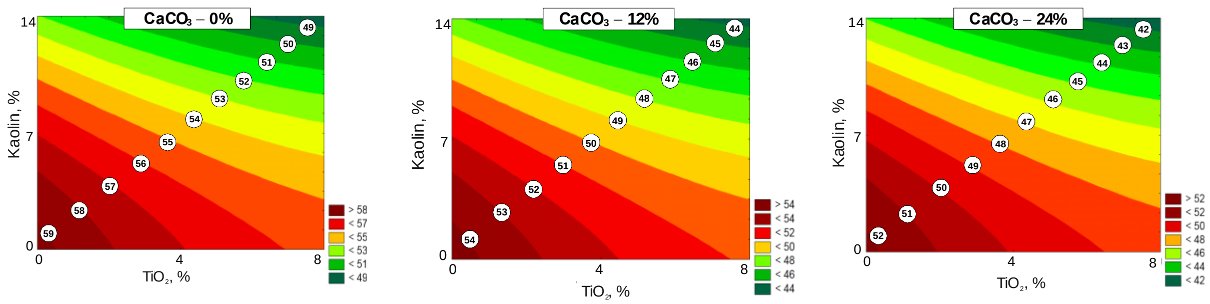


Figure 1. The isolines of the strength of slag-alkali compositions after 28 days

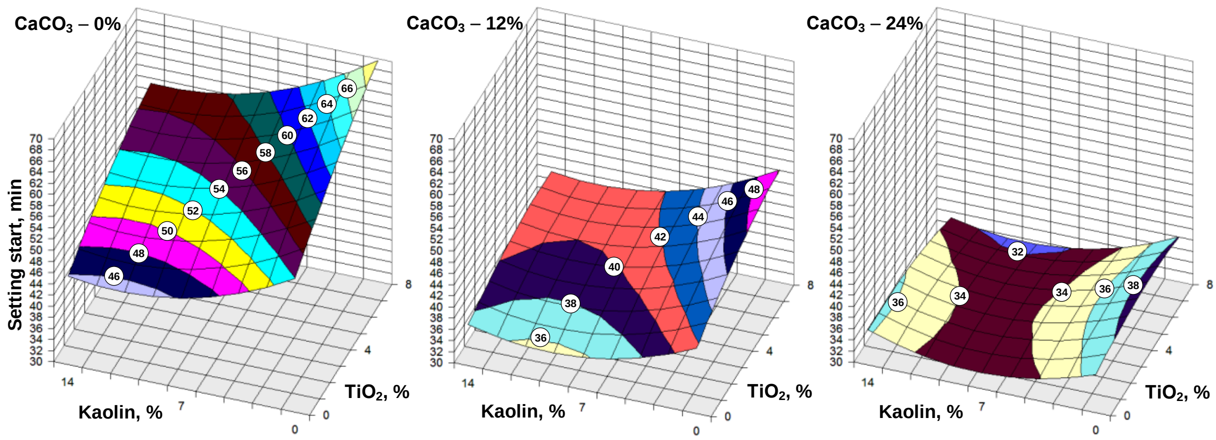


Figure 2. Isosurfaces and isolines of the start time of setting slag-alkali compositions.

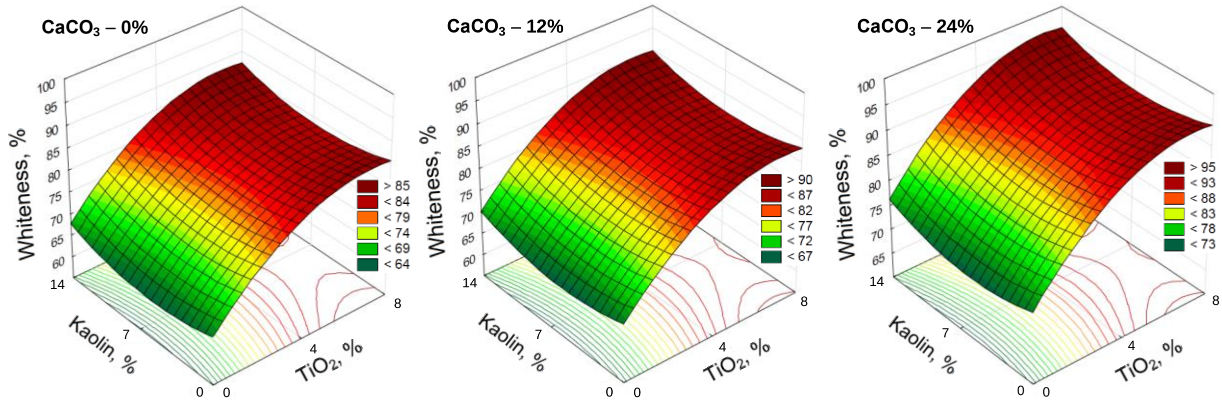
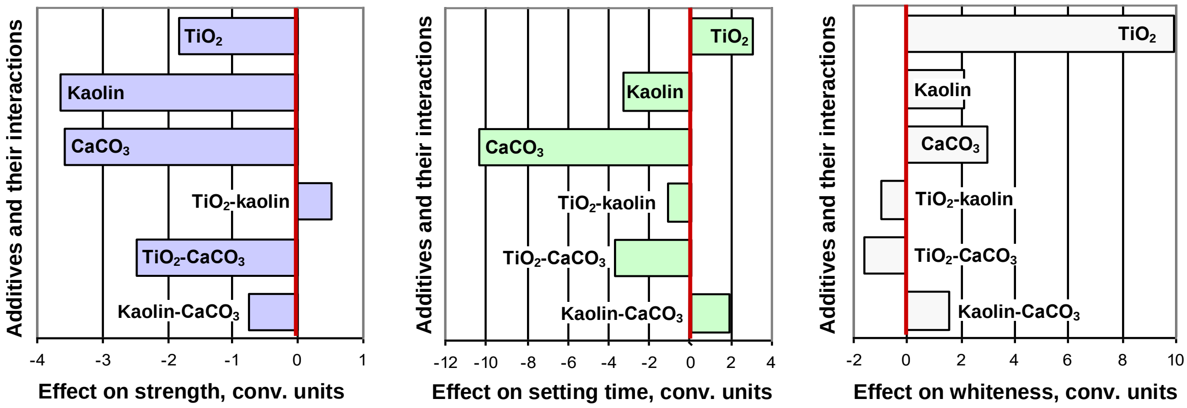


Figure 3. Isosurfaces and isoline whiteness of slag-alkali compositions after 28 days of hardening.

Slag-alkali decorative cements had good dynamics of hardening in the early stages and after 2 days showed a strength of 25,2...39,0 MPa.

Depending on the degree of whiteness, white clinker cement is divided into three grades: 1 (premium) – 80...95%, 2 grade – 75%, 3 grade – 68%. Therefore, based on these requirements, most of the slag-alkaline compositions, even after grinding the slag in a steel mill, can be attributed to the decorative, as they had a degree of whiteness of – 70%.

As a result of the regression analysis of the obtained equations, the significance of each of the coefficients of the equation (the so-called Pareto effects) is determined, that is, the influence of each of the factors and their interaction on the response functions. The results are presented in Fig. 4.



a *b* *c*

Figure 4. The degree of influence of whitening additives on the properties of slag-alkali decorative cements: *a* – on compressive strength; *b* – on setting start; *c* – on whiteness.

As can be seen from Fig. 4, *a*, all individual whitening additives do not contribute to the increase in strength. The greatest negative effect on the strength of slag-alkali cement compositions has kaolin, slightly less than – $CaCO_3$ and the smallest – TiO_2. The interaction of factors X1 and X2 (TiO_2 and kaolin) contributes to a slight increase in strength.

If kaolin and $CaCO_3$ shorten the setting time, then TiO_2 (X1) and the composition of kaolin with $CaCO_3$ (interaction of factors X2 and X3) somewhat contribute to their increase (Fig. 3, *b*).

From the point of view of increasing whiteness, the most positive effect is exerted by TiO_2, then $CaCO_3$ and the least influence is влияние kaolin (Fig. 3, *c*). The interaction of factors X1 and X2 (TiO_2 and kaolin) and X1 and X3 (TiO_2 and $CaCO_3$) somewhat impair whiteness.

3.2. The effect of iron oxides on whiteness

Checking the effect of iron oxides was carried out as follows. As a control composition, composition N° 4 (see table 3) based on the Dnieper slag was adopted, where the amount of FeO was 0,35% (Table 1). For comparison, the same composition N° 4 was used, but based on Kryvyi Rih slag, where the amount of FeO was 1,65% (Table 1). The third point was composition N° 4 on Kryvyi Rih slag, where additional FeO was added to the total amount of 3,3%. The research results are presented in Fig. 5. The mathematical dependence of whiteness on the FeO content was expressed by the regression equation shown in the graph.

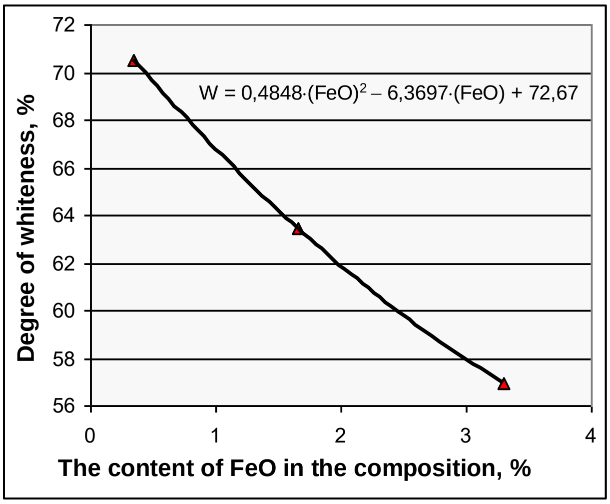


Figure 5. Effect of FeO additive on the whiteness of slag alkaline cement.

3.3. The effect of sulphide compounds of slag's

In the initial stages of hardening, slag-alkaline compositions may acquire a blue-green color. In the literature [13], this is associated with the formation of compounds of the type $FeSO_4 \cdot 7H_2O$ and this was the basis for concerns about the possibility of obtaining white decorative cements on their basis. But if slag-alkali concrete is exposed to air, then its surface quickly and substantially "bleaches", obviously, due to carbonization [18]. The introduction of whitening additives in its composition completely eliminates the risks of painting the surface in undesirable colors and shades.

3.4. Economic aspect.

If we compare the cost of bleaches, then it roughly corresponds in such a way – "$CaCO_3$: kaolin : TiO_2" as 1:6:12. That is, the most expensive component is TiO_2 and therefore systems with a significant TiO_2 content are economically inefficient.

Analyzing Table 3 and evaluating the effectiveness of the compositions from the point of view of their economy, it can be said that slag-alkali compositions make it possible to significantly reduce or completely abandon the use of TiO_2. So, for example, in compositions N° 2 and N° 4, TiO_2 is generally absent, but due to only kaolin and $CaCO_3$, a whiteness of 70,5...79,8% and a strength of 46,2...56,0 MPa are ensured. And in warehouses N° 11...15 with a quantity of TiO_2 4%, a degree of whiteness of 80,8...87,1% and a strength of 45...54,7 MPa are ensured. Therefore, titanium dioxide can be used to trim compositions, and as the main bleaches use cheaper kaolin and $CaCO_3$.

4. Conclusions

Thus, as a result of the studies, the possibility of obtaining effective slag-alkali white cements, as the basis for the production of decorative concrete based on them, with acceptable economic characteristics, has been proved. The influence of each of the bleaches is established, the role of FeO on the deterioration of the whiteness of decorative compositions is indicated. Methods for optimizing compositions are identified. The high activity of slag-alkali cements allows the introduction of bleaching additives in the amount of 25% or more without significant deterioration of physical and mechanical characteristics.

Further work will be directed to deeper physical and chemical studies, the study of the catalytic effect of TiO_2 (both conventional and anatase) on the restoration of whiteness during operation, the effect of the dispersion of bleaches on decorative properties, the establishment of the interaction of bleaches with dyes in highly alkaline environments, the study of white stability and non-ferrous slag-alkali cement to the effects of UV and heat-moisture treatment of concrete and to perform long-term tests to establish the durability and operational characteristics of white and colored slag-alkali cements.

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