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MIX DESIGN OF ACID RESISTANT ALKALI ACTIVATED MATERIALS FOR RECONSTRUCTION OF THE BUILDING CONSTRUCTIONS DAMAGED BY THE WAR

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Abstract

The paper covers the results of development of alkali activated materials stable in the acid environment. Such materials can be used as main materials for reconstruction of the residential and industrial buildings, influenced by the acid pollution or exploitation conditions. It was shown possibility to obtain alkali activated cement able to be use in normal hardening conditions, meeting the requirements for normal cements (compressive strength up to 60 MPa, initial setting time over 45 minutes, coefficient of acid resistance over 0.8). Such results provide possibilities to develop acid resistant repairing mixes for reconstruction and various applications.

Keywords*: Alkali-activated cement; Reconstruction; Acid resistance; Damaged structures.*

Introduction

The question of restoration of historical buildings rises up with a new force because of the war in Ukraine. A lot of studies investigated questions of restoration of different types of buildings: historical [1-2], medical, cultural [3-5], etc. However, one branch of the question is still in need of attention – restoration of the parts of the buildings which are in exploitation under aggressive environment (different types of pipes, drainages, ovens, and other constructions. Traditional cement- or lime-based materials could not provide necessary characteristics of corrosion resistance, moreover, acid resistance.

There are some acid resistant materials on the market, but they are mostly based on the liquid glass bases, making the technology quite difficult and also providing material with good acid resistance, but not a water-resistant, that could be a problem for the further exploitation. That is why the problem rises sharp to obtain material with good or excellent properties of acid resistance, but also with high water resistance and able to be cast and hardened in normal conditions.

Among the different binding materials, the most appropriative seems to use alkali activated materials [6-9], which are well-known with their high service properties and excellent special properties including corrosion and acid resistance [10-16]. A lot of types of alkali activated cements are able to be hardened in normal conditions [17] and also have high

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characteristics of resistance in aggressive media [18-24]. And one more important thing, alkali activated systems are creating new formations with high durability, which are very similar to the structure element of ancient constructions [24-28].

The mentioned above makes it possible to predict, that according to the results of previous studies [29-34] it is possible to provide mix design of alkali activated cement, which will be able to harden in normal conditions and have a good acid resistance due to modification of mixes by alumina and silica source containing materials [35, 36]. The main goal of the study is to investigate acid resistant properties and acid resistance of the cementitious materials.

Materials and methods

As a main alumina silicate component of alkali activated cement was used ground granulated blast furnace slag (GGBS) from «DMZ», Kamenske (Ukraine), grounded to the specific surface = 430m^2/kg by Blaine and modulus of basicity Mo = 1.11. Oxides content in precent: SiO_2 – 38.95, TiO_2 – 0.47, Al_2O_3 – 6.88, Mn – 0.21, MgO – 5.76, CaO – 46.93, Fe_2O_3+ FeO – 0.37, K_2O+Na_2O – 0.43.

As a supplementary alumina silicate component source was used dehydrated kaolin (metakaolin (MK)) from Glukhiv ($Al_2O_3·2SiO_2$) with specific surface = 1800m^2/kg. Oxides content in percent: SiO_2 – 55.1, Al_2O_3 – 35.4, MgO – 0.92, CaO – 3.91, Fe_2O_3+ FeO – 4.27, SO_3 – 0.33, loss of ignition – 0.07.

As an alumina silicate component source with technogenic origin was used red mud – waste of the alumina production by Bayer method. Specific surface is 1500m^2/kg. Oxides content in percent: SiO2 – 19.58, TiO_2 – 6.23, Al_2O_3 – 17.5, Mn – 0.03, MgO – 0.17, CaO – 10.4, Fe_2O_3+ FeO – 37.9, K_2O+Na_2O – 7.7, P_2O_5 – 0.19, SO_3 – 0.3.

As a source of silica aspen was used (SiO_2 (MT)).

As an alkaline component sodium meta silicate pentahydrate was used $Na_2SiO_3·5H_2O$ (MC) in the dry powder state.

As an aggressive environment were used solutions of sulfuric acid (H_2SO_4) in two concentrations: 5 and 35%.

Mathematical planning of the experiment was done by using statistical software and Office Excel.

Acid resistance was determined by:

− express method by boiling of the specimens of cement paste during 1 hour in 35% solution of aid (H_2SO_4). As criteria were chosen parameters of surface, mass loses and residual strength after boiling;

− by storying of the mortar specimens in 5% solution of sulfuric acid (H_2SO_4) for 30 days, after 28 days of normal hardening. Acceptance criteria were chosen: surface, residual strength after test and expanding deformations.

Results and Discussions

The first step to obtain acid resistant alkali activated hybrid cement is to study recipe factors, influencing the development of acid resistant new formations. To provide formation of stable hydro silicate and zeolite-like fazes, characterized by high acid resistance and hydraulic properties, it is necessary to determine correct coexistence of oxides in the system. To meet this, there were proposed to study the raw of the compositions in the system $Na_2O – CaO – Al_2O_3 – SiO_2 – H_2O$, where oxides content will be varying within the ranges:

- CaO 5-10% by mass;
- Na_2O up to 2.0 by mass;
- Al_2O_3 10-30% by mass;
- SiO_2 50-70% by mass.

To obtain this, as a Si source were used metakaolin (MK) and aspen (trepel, MT) in the different combinations. Maximal content of MK is 40% by mass, and for MT – 20% by mass.

To provide alkali activated cement mix design to obtain acid resistant properties the study of influence of MK and MT on rheological properties had been done.

As an object of the study was taken alkali activated cement in the system "GGBS – alkaline component" (control composition) and complex cement compositions in the system "GGBS – MK – MT – alkaline component". Sodium metasilicate was taken as an alkaline component.

Using the cement paste, taken by mixing with water, were tested paste of normal consistence of the cement (PNC) and setting times. These properties were investigated using a three-factor experiment. Factors and limits of their variation are presented in Table 1.

Table 1. Source data

No	Factors	Units	Codes	Factor Variation Levels		
				-1	0	1
1	Sodium meta silicate pentahydrate $Na_2SiO_3·5H_2O$ (MC)	%	X1	8	10	12
2	Metakaolin (MK)	%	X2	0	20	40
3	Aspen content (SiO_2(MT))	%	X3	0	10	20

Table 2 shows experimental matrix with response functions and results of the study.

Table 2. PNC and setting time test results of acid resistant alkali activated cements

No	Plan matrix in codes			Plan matrix in physical terms, %			GGBS, %	PNC, %	Setting time, min	
	X1	X2	X3	MC	MK	MT			initial	final
1	1	1	1	12	40	20	28	37.5	175	300
2	-1	1	1	8	40	20	32	44.5	180	345
3	1	-1	1	12	0	20	68	28	80	185
4	-1	-1	1	8	0	20	72	30	125	245
5	1	1	-1	12	40	0	48	36	50	145
6	-1	1	-1	8	40	0	52	39	65	150
7	1	-1	-1	12	0	0	88	20.5	25	35
8	-1	-1	-1	8	0	0	92	21.5	30	50
9	1	0	0	12	20	10	58	31.1	55	145
10	-1	0	0	8	20	10	62	33.3	130	200
11	0	1	0	10	40	10	40	36	120	280
12	0	-1	0	10	0	10	80	24.5	60	100
13	0	0	1	10	20	20	50	36.5	150	350
14	0	0	-1	10	20	0	70	29.5	70	140
15	0	0	0	10	20	10	60	33.5	115	225

Using mathematic modelling tool were set the dependences between setting times of the cement and his composition (Fig. 1).

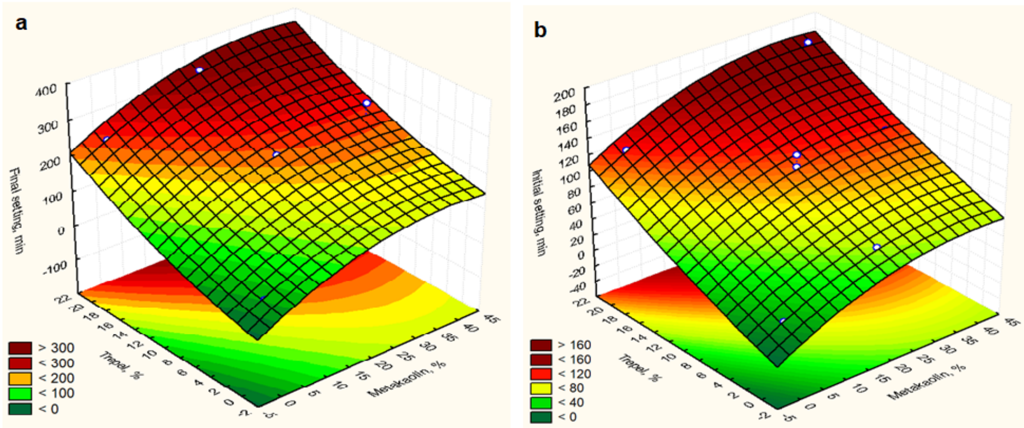

Fig 1. Influence of composition of alkali activated cement on:
a) initial setting; b) final setting of the systems with MK and MT admixtures.

According to the obtained results, control composition with MC content 12% by mass of the cement (composition 7) is characterized by PNC 20.5initial and final setting times 25 and 35 min correspondingly. Control composition with MC content 8% by mass of the cement (composition 87) is characterized by higher PNC - 21.5% and initial and final setting time 30 and 50 min correspondingly.

Additional introduction of MK and MT leads to the significant increasing of PNC and longer setting times. The optimal way is joint introduction of 20% of MK and 10% of MT with 10% of alkaline component content. This way PNC is 31.1%, and initial and final setting times 55 and 145 min correspondingly.

Increasing of MK content to 40% and MT to 20% by mass in one system (composition 2) leads to the high-water content (PNC = 44.5%), which influence negatively on physical-mechanical and exploitation properties of the composition.

Also optimal are compositions with selective introduction of one admixture (MK in the quantity 20% or MT – 10% by mass) and, correspondingly, increasing of alumina silicate content.

Compressive strength of the compositions was determined on the cube specimens 40 mm height, prepared from the standard mortar. Results of the study are given in Table 3.

Table 3. Experimental matrix with response functions and strength characteristics of acid resistant alkali activated cements at the age 28 days off normal hardening

No	Plan matrix in codes			Plan matrix in physical terms, %			GG BS, %	W/C ratio	m, g	R_c, 28 days, MPa	Mean density kg/m³
	X1	X2	X3	MC	MK	MT					
1	1	1	1	12	40	20	28	0.52	130	0.84	1992
2	-1	1	1	8	40	20	32	0.53	138	1.0	2172
3	1	-1	1	12	0	20	68	0.43	143	52.5	2219
4	-1	-1	1	8	0	20	72	0.44	156	47.8	2375
5	1	1	-1	12	40	0	48	0.43	143	1.6	2242

No	Plan matrix in codes			Plan matrix in physical terms, %			GG BS, %	W/C ratio	m, g	R_c, 28 days, MPa	Mean density kg/m^3
	X1	X2	X3	MC	MK	MT					
6	-1	1	-1	8	40	0	52	0.46	141	1.5	2180
7	1	-1	-1	12	0	0	88	0.33	150	53.65	2359
8	-1	-1	-1	8	0	0	92	0.34	148	43.4	2313
9	1	0	0	12	20	10	58	0.41	142	25.3	2195
10	-1	0	0	8	20	10	62	0.42	143	21.2	2242
11	0	1	0	10	40	10	40	0.41	128	1.6	1977
12	0	-1	0	10	0	10	80	0.36	154	39.8	2453
13	0	0	1	10	20	20	50	0.43	139	5.4	2198
14	0	0	-1	10	20	0	70	0.43	146	38.5	2271
15	0	0	0	10	20	10	60	0.41	140	22.8	2135

Basing on the obtained results and mathematic modelling there were taken diagrams of dependence of strength from the cement mix design (Fig. 2).

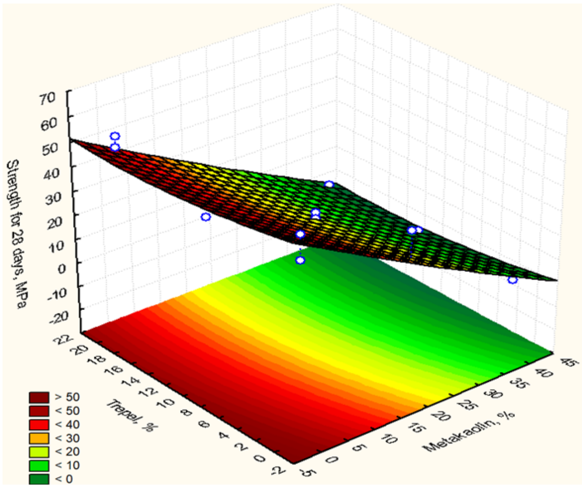

Fig. 2. Strength properties change in acid resistant alkali activated cements depending on MK and MT content

The compositions under study according to the mean density characteristics are laying within the 2200-2500kg/m^3 (Fig. 3).

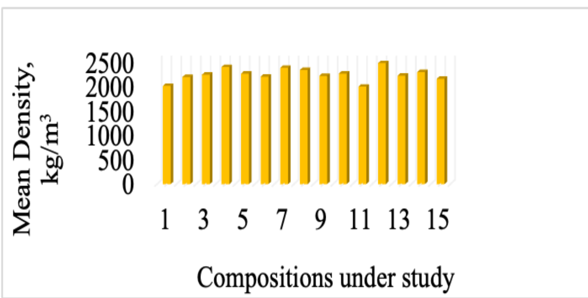

Fig. 3. Mean density of the compositions under study

Analysis of the obtained results had shown that high content of MK (40%) leads to the significant strength losses. At the same time, introduction of MT in the quantity 20% by mass generally have no influence on strength properties.

The lower strength loses comparing to the control compositions are observed for the systems with selected introduction of one admixture in the case of alkaline component content 10% by mass, namely: composition 12 with MT content 10% provides compressive strength at the age of 28 days 39.8MPa, and composition 14 with MK content 20% by mass – 38.5MPa.

Study of the acid resistance by accelerated method gave the possibility to preliminary estimate possibility of the composition under study to be used for the further optimization in the aim to obtain acid resistant materials with normal hardening.

As a test criteria were chosen surface, losses of compressive strength after tests and residual strength after tests.

Results of the study are given in Table 4.

Table 4. Test results of the cement paste specimens after steam curing

No	Component content, %				mass, g		Compressive strength 28 days, MPa		K_c	Δm, %
	MC	MK	MT	GGBS	before curing	after curing	before curing	after curing		
1	12	40	20	28	14.1	8.8	2	–	–	37.59
2	8	40	20	32	13.5	8.8	1	–	–	34.81
3	12	0	20	68	15.85	15.8	68.75	55.0	0.81	0.31
4	8	0	20	72	15.45	15.4	67.5	57.5	0.85	0.32
5	12	40	0	48	15.1	12.2	2	–	–	19.2
6	8	40	0	52	14.7	12.2	1.75	–	–	17.0
7	12	0	0	88	18.1	18.0	87.5	69.2	0.79	0.55
8	8	0	0	92	17.7	17.6	78.75	62.9	0.80	0.59
9	12	20	10	58	15.95	11.9	39.4	18.6	0.47	25.4
10	8	20	10	62	15.2	12.1	32.75	16.3	0.49	22.1
11	10	40	10	40	14.5	8.5	2	–	–	41.4
12	10	0	10	80	16.95	16.9	52.5	43.57	0.83	0.29
13	10	20	20	50	14.0	8.5	2.5	–	–	39.3
14	10	20	0	70	16.9	14.2	47.5	22.5	0.47	16.0
15	10	20	10	60	14.9	10.1	35.75	17.4	0.49	32.2

Analysis of the obtain results shows positive influence of MT introduction on the coefficient of acid resistance, when introduction of MT in the same quantity leads to the partial or total destruction of the material.

Thus, a way, additional content of MT from 10 to 20% makes it possible to obtain alkali activated cementitious systems with acid resistance coefficient Kc = 0.81-0.85. Mass loses after the tests are lower than 0.35%.

To determine possibilities of the cement compositions under study to be used as an acid resistant and their effectiveness in time, as an alternative to the express method was taken the standard test on acid resistance for the compositions under study, storying the specimens of the cement mortar in 5% solution of sulphuric acid (H_2SO_4) for 30 days, after 28 days of normal hardening. As a test criteria were chosen surface, residual strength after tests and shrinkage/expansion deformations.

Results of the study are given in Table 4 and on Figure 5.

Table 5. Experimental matrix with response functions and compressive strength characteristics after storying at 5% solution of H_2SO_4

No	Plan matrix in codes			Plan matrix in physical terms, %			GGBS, %	W/C ratio	$R_{стс}$, MP		ΔF, %
	X1	X2	X3	MC	MK	MT			60 days at normal conditions	30 days under aggressive environment	
1	1	1	1	12	40	20	28	0.52	1.4	0.8	42.8
2	-1	1	1	8	40	20	32	0.53	0.9	-	-
3	1	-1	1	12	0	20	68	0.43	51.85	20.6	60.3
4	-1	-1	1	8	0	20	72	0.44	51.3	33.7	34.3
5	1	1	-1	12	40	0	48	0.43	1.5	1.2	20.0
6	-1	1	-1	8	40	0	52	0.46	1.6	0.94	41.3
7	1	-1	-1	12	0	0	88	0.33	46.25	35.9	22.4
8	-1	-1	-1	8	0	0	92	0.34	42.6	19.4	54.5
9	1	0	0	12	20	10	58	0.41	2.78	1.4	49.6
10	-1	0	0	8	20	10	62	0.42	21.1	9.7	54.0
11	0	1	0	10	40	10	40	0.41	1.8	1.03	42.8
12	0	-1	0	10	0	10	80	0.36	42.8	19.8	53.7
13	0	0	1	10	20	20	50	0.43	2.8	1.4	50.0
14	0	0	-1	10	20	0	70	0.43	43.8	24.4	44.3
15	0	0	0	10	20	10	60	0.41	4.0	2.9	27.5

Results of the study had been shown that long-term storage of the specimens in aggressive media has a huge destructive influence on the structure of the cement stone in the compositions under study.

The higher negative influence was observed for the compositions with 40% of metakaolin. In the case of minimal content of alkali component, meaning 8%, deformation processes appearing in the structure of artificial stone are characterized by the shrinkage 4.86%, comparing to the control specimens, storying in the normal conditions.

So as for the rapid method of investigation, the lower loses of compressive strength are characterized for the compositions 12 with additional introduction of MT admixture (10% by mass) and composition 14 with additional introduction of metakaolin admixtures (20% by mass).

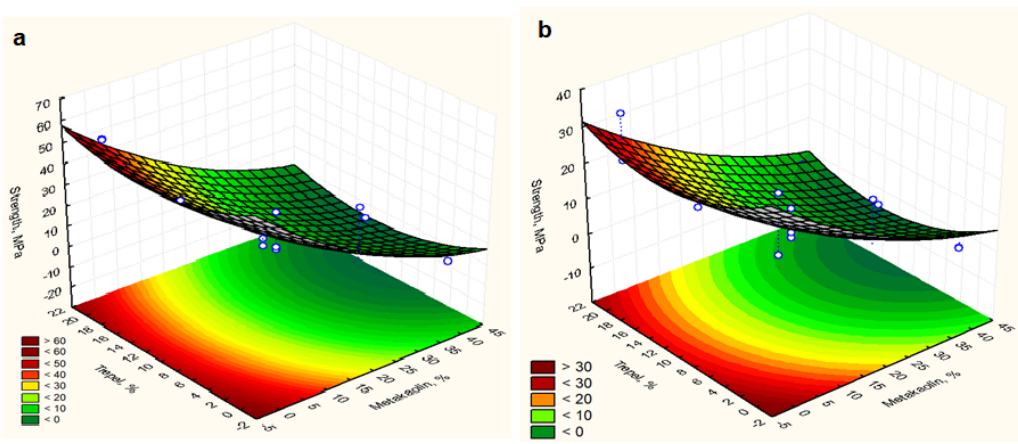

Fig. 4. Dependence of the strength characteristics of acid resistant alkali activated cements from the media: a) normal conditions, b) 5% solution of H_2SO_4.

Conclusions

It was shown possibility to obtain acid resistant materials, able to be hardening in normal conditions, for restoration of specific parts of historical buildings (tubes, ovens, etc.).

The most effective compositions from the point of view of corrosion resistance and residual strength are compositions with 20% of metakaolin and aspen both.

Shrinkage deformations of the optimal systems are low and making it able to be used for restoration.

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