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High Corrosion Resistant Ash Alkali Activated Cements

Abstract

This paper covers the results of development of corrosion resistant ash alkali cements based on regulation of phase composition of the hydration products by changing the alkali content, content of calcium-containing cement components resulting in the increase strength and density of the cement stone. The results suggested to conclude that the cement compositions with predominance in the hydration products of weakly soluble low basic hydrosilicates of calcium, hydroaluminates minerals similar to natural hydroaluminates exhibited the highest corrosion resistance. The results of comparison suggested to draw a conclusion that the alkali activated cements Types ШЦЕМ III-400 and ШЦЕМ V-400, according to National Standard DSTU B V.2.7 had high corrosion resistance compared to that of ordinary cements allowing to recommend the developed cements for the concretes intended for aggressive environments, inclusive of sodium and magnesium sulphates and chlorides.

1 Introduction

With the increase in volumes of construction a first-priority issue is how to ensure their durability. Durability of concrete structures is dependent upon service conditions and, among many other factors, by characteristics of the cement used for making concrete. Of special interest is durability of corrosion resistant concretes for their intended use. Until now there is no unified solution for the concrete mix design that would meet all needs with regard to corrosion resistant concretes.

The most important characteristics which determine corrosion resistance of concretes are: type of cement and its mineralogical composition, composition of hydration products, water to cement ratio (W/C), type of admixtures and aggregate, pore structure, etc. In the corrosion resistant concrete mix the following factors should be taken into account: service conditions and exposure conditions.

The alkali activated cements based on granulated blast-furnace slags and fly ash have been developed by a scientific school headed by Professor V.D. Gerasimov. These are the cements that can be successfully used for making corrosion resistant concrete. The alkali activated cement concretes have high strength properties (40-100 MPa), frost resistance (1000 cycles), water penetration (W10-W50), high corrosion resistance in different mineral and organic environments [4, 5].

Further research work allowed to develop fly ash alkali activated cements in which fly ash content reached 90% [6-9]. These fly ash alkali activated cements are an important alternative to portland cements containing fly ash in a quantity of up to 30%, since in their physical-mechanical properties are similar to the portland cements.

the fly ash alkali activated cement stone is characterized by the higher weather resistance, frost- and corrosion resistance.

Material and methods of examination

The composition of the concrete without admixtures was constant in all experiments. The calcium fly ash class F (under ASTM C 618), ground to a specific surface of 800 m²/kg by Blaine, sodium carbonate and sodium metasilicate pentahydrate as alkaline activator were used as basic raw materials. Ordinary portland cement (OPC) Type I (commercial product with a specific surface of 380 m²/kg) and blast-furnace slag (specific surface 450 m²/kg) were taken as additional cement constituents. Chemical composition of raw materials is shown in Table 1.

Chemical composition of raw materials

Material	SiO ₂ , %	Al ₂ O ₃ , %	Fe ₂ O ₃ , %	CaO, %	MgO, %	SO ₃ , %	Na ₂ O, %	K ₂ O, %	LOI, %
Fly ash	51.08	24.8	13.67	3.12	1.83	0.08	0.60	1.90	1.50
OPC	23.4	5.17	4.12	64.13	0.88	0.55	0.41	0.33	0.20
Slag	40.0	5.91	0.32	46.9	5.87	1.62			

The fly ash alkali activated cements under study, they were: alkali activated pozzolanic cement (M30) and alkali activated composite cement (M30) were prepared from the preliminary separately ground fly ash and slag, OPC, and alkaline activator and plasticizer in a ball mill. The slag portland cement M400 (M30) (III/A), according to Ukrainian classification [14] was taken as reference. The composition of the alkali activated cements under study is given in Table 2.

Composition of the fly ash alkali activated cements under study

Cement Type	Composition, % by mass				
	Fly ash	OPC I-500	Slag	Alkaline activator	Plasticizer
M30	66.2	28.4		Na ₂ CO ₃ -4.7	0.75
M30	54.2	8.9	26.2	Na ₂ CO ₃ -4.7 Na ₂ SiO ₃ ·5H ₂ O-5.3	0.7

The frost resistance of the fly ash alkali activated cements under study was determined according to recommendations given in [10] by measuring strength variations of the specimens placed in aggressive environments (10%- and 5%- solutions of sodium sulfate (Na₂SO₄), 4%- and 2%-solutions of magnesium sulfate (MgSO₄), concentrated sulfuric acid). The specimens were kept for 3 days in normal conditions, then, for 25 days in aggressive environment of technical grade. The test ages were: 30, 60, 90 and 180 days.

The corrosion resistance was expressed by a coefficient of corrosion resistance calculated as a ratio between a flexural strength of the specimen after 12 months in aggressive environment and flexural strength of the specimen after 12 months in water. According to above recommendations the cement is considered to be a corrosion resistant if the coefficient of corrosion resistance for storage for 12 months is equal or higher than ($>$)0.8.

3 Results and discussion

At the first stage of the study, main physical-mechanical characteristics of the alkali activated cements have been determined (Fig.1). The results of test suggest to draw a conclusion that the developed cements fall within the ranges of strength requirements for the alkali activated cements ЛЦЕМ III and ЛЦЕМ III/A-400 (their compressive strength was 38.4- 41.3 MPa).

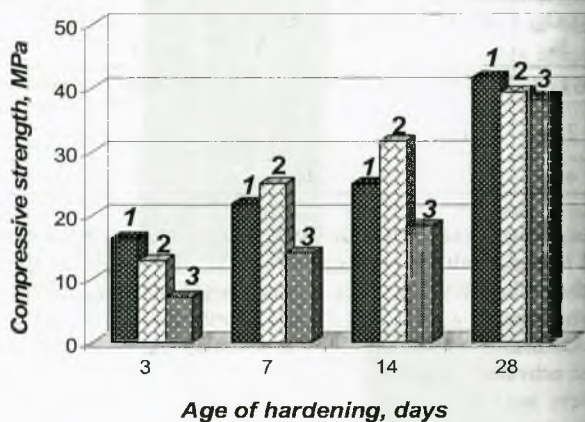


Figure 1
Compressive strength of the cements under study: 1 – ЛЦЕМ III; 2 – ЛЦЕМ III/A-400; 3 – ШПЦ III/A-400.

The results of study of corrosion resistance (Fig.2, a, b, c, d, e, f.) suggest that all cements under study after long-term storage in aggressive environment at the age of 30 days have increased their strength properties comparing to the cement/ This can be attributed to the deepening of the hydration process. At the age of 2-3 months strength of the majority of the cements under study is lowering. So, at the age of 6 months, the cement ШПЦ III/A-400 has lower strength compared to the fly ash alkali activated cements ЛЦЕМ III and ЛЦЕМ III/A-400. Thus, the cement ШПЦ III/A-400 could not be considered as corrosion resistant (Fig 3)

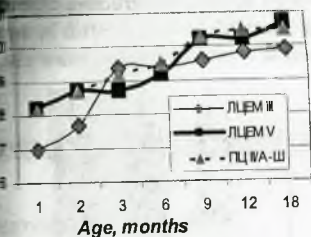


Figure 2a

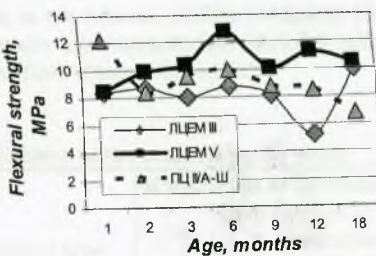


Figure 2b

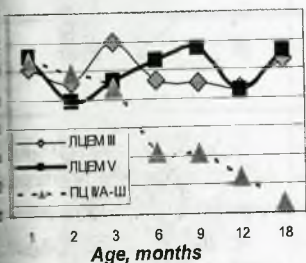


Figure 2c

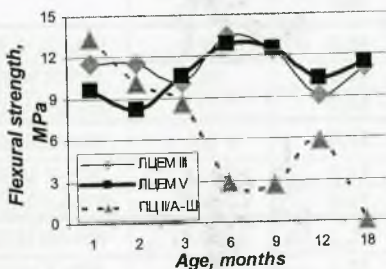


Figure 2d

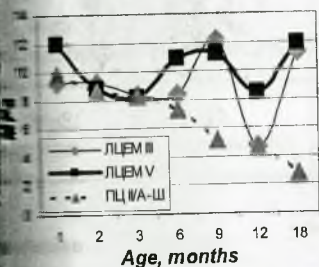


Figure 2e

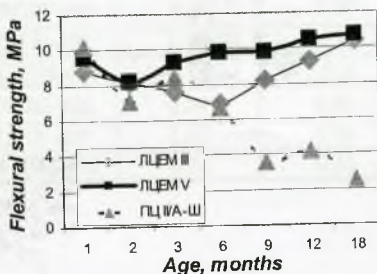


Figure 2f

flexural strength of the cement under study vs. age (storage in aggressive environment): (a) water of technical grade; (b) sea water; (c) Na_2SO_4 concentration- 5%); (d) Na_2SO_4 (concentration- 10%); (e) MgSO_4 concentration- 4%); (f) MgSO_4 (concentration- 4%).

calculated coefficients of corrosion resistance (Table 2) suggested to draw a conclusion that the developed fly ash alkali activated cements (ЛЦЕМ III-400 and ЛЦЕМ V-400) have much better resistance against aggressive environment compared to OPC. So, at the age of 9 months, the coefficient of corrosion resistance of these cements did not lower below 1 and at the age of 12 months the developed composite ЛЦЕМ V-400 had good flexural strength (the coefficient of corrosion resistance was higher), and the coefficient of corrosion resistance of the developed cement ЛЦЕМ III-400 declined below critical level only in sea water and magnesium sulfate

with concentration of 4%. This result can be explained by a constructive character of combined alkaline-sulfate activation of the fly ashes [11].



Figure 3a



Figure 3b

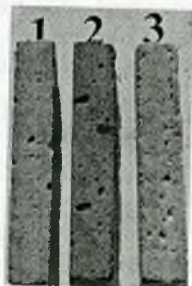


Figure 3c

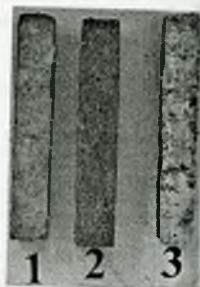


Figure 3d



Figure 3e

Photos of the specimens after 1 year-storage in aggressive environment: (a) 4% Na_2SO_4 ; (b) 5% Na_2SO_4 ; (c) 10% Na_2SO_4 ; (d) 2% MgSO_4 ; (e) 4% MgSO_4 .
1 - ЛЦЕМ III-400; 2 - ЛЦЕМ V-400; 3 - ШПЦ III/A-400.

Analyzing the coefficients of corrosion resistance (Table 3) suggested the conclusion corrosion resistance of the developed fly ash alkali activated cement study is directly proportional to a quantity of the calcium-containing constituents. Thus, with regard to the calcium-containing cement

Corrosion resistance decreases as follows: ЛЦЕМ V < ЛЦЕМ III < ШПЦ III/A-400.
 In regard of different aggressive environments, the corrosion resistance decreases as follows: sea water < sodium sulfate < magnesium sulfate.

3

Results of corrosion resistance of the cements under study

Aggressive environment	Cement type	Coefficient of corrosion resistance (Ks) after storage in aggressive environment, days		
		90	180	365
Sea water	ЛЦЕМ III-400	0.95	0.84	0.83
	ЛЦЕМ V-400	1.39	0.99	1.22
	ШПЦ III/A-400	1.05	0.85	0.85
Na ₂ SO ₄ (concentration- 5%)	ЛЦЕМ III-400	1.0	0.95	0.88
	ЛЦЕМ V-400	1.16	1.13	1.05
	ШПЦ III/A-400	0.45	0.45	0.29
Na ₂ SO ₄ (concentration- 10%)	ЛЦЕМ III-400	1.45	1.29	0.93
	ЛЦЕМ V-400	1.40	1.23	1.11
	ШПЦ III/A-400	0.31	0.26	0.09
MgSO ₄ (concentration- 2%)	ЛЦЕМ III-400	0.9	1.27	0.84
	ЛЦЕМ V-400	1.18	1.10	0.91
	ШПЦ III/A-400	0.77	0.5	0.55
MgSO ₄ (concentration- 4%)	ЛЦЕМ III-400	0.74	0.85	0.94
	ЛЦЕМ V-400	1.07	0.96	1.13
	ШПЦ III/A-400	0.71	0.35	0.5

Conclusion

Results of study suggested to conclude that in corrosion resistance the developed fly ash alkali activated cements, they are: alkali activated pozzolanic and alkali activated slag cements exhibit the higher corrosion resistance compared to the slag portland cements and can be successfully used in making corrosion resistant concretes for the use in aggressive environments.

Results of study suggested to conclude that the fly ash alkali activated cements ЛЦЕМ III and ЛЦЕМ V-400 exhibit high corrosion resistance (Ks = 1.04...1.39 after 12 months of storage in aggressive environments) and the developed composite cement ЛЦЕМ V-400 has the higher characteristic.