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High-Performance Alkali-Activated Cement Concretes for Marine Engineering Applications

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Additional information is available at the end of the chapter

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Abstract

The contribution covers results of studies on the alkali-activated cement concretes intended for marine engineering applications. Such properties as strength, wear, corrosion, freeze-thaw, weather resistance and many others have been studied, and the results are reported and discussed in detail. The obtained results suggested to draw a conclusion on high potential of the alkali-activated cement concretes for marine engineering applications, since in their performance properties these concretes are highly advantageous over other concretes used as marine concretes and big savings can be expected in the future due to the longer span of service life. The results are supported by long-term observations in real conditions. The above advantages are attributed to more perfect micro- and macrostructure of the alkali-activated cement stone. The authors have summarized their own experience and results collected by PhD and DSc students under their supervision dedicated to assessment of durability of these concretes, in particular, for marine engineering applications. In order to bring these advanced materials into practice of construction worldwide, two *rilem* (International Union of Laboratories and Experts in Construction Materials, Systems and Structures) committees have been founded: “Alkali-activated Materials” (2010–2013) and “Durability Testing of Alkali Activated Materials” (2013–ongoing).

Keywords: alkaline activation, cement, concrete, marine engineering

1. Introduction

Marine concretes are used for making concrete structures that are permanently or from time to time immersed in sea water. In accordance with service conditions in sea water, these marine

concretes are classified into those that work under water, above water and concretes for zones of alternate level of sea water.

The requirements for marine concrete structures vary depending upon location (zone) of service of the concrete in structures (**Table 1**) [1, 2].

Requirements for concretes	Massive structures						Non-massive structures		
	Outer zone			Inner zone					
	Zones relatively water level								
	Under water	Alternating level of sea water	Above water	Under water	Alternating level of sea water	Above water	Under water	Alternating level of sea water	Above water
Water resistance	+	+	+	+	+	–	+	+	+
Water impermeability	+	+	+	+	+	–	+	+	+
Freeze-thaw resistance	–	+	+	–	–	–	–	+	+
Low heat of hydration	+	+	+	+	+	+	–	–	–
Weather resistance	–	+	+	–	+	+	–	+	+
Corrosion resistance	+	+	+	+	+	+	+	+	+
Abrasion resistance	+	+	–	+	+	–	+	+	–

Table 1. Requirements for marine concretes vs. service conditions.

Especially, strict requirements are applied to marine concretes working in the zone of alternating sea level and the “above water” zone of the outer sides of the marine concrete structures.

Compressive and flexural strength at the age of 28 or 60 or 180 days are main characteristics of concretes intended for contemporary marine structures. Usually, concretes with compressive strength of 40–50 MPa are used as marine concretes.

Among the most important characteristics of marine concretes which determine durability are: freeze-thaw resistance, water permeability, resistance to corrosive exposure of sea water (marine environment), weather resistance, protective properties of concrete with regard to corrosion of reinforcement, abrasion resistance, etc.

As a rule, these requirements are met through a proper concrete mix design and by taking measures on protection of concrete and reinforcement in order to guarantee service life reaching 50 years.

On the other hand, one of the main criteria of global sustainable development concept is an issue of durability (lifespan of concrete over 100 years).

Existing widely used cements due to a four-phase principle of compositional build-up and hydration product phase composition are not able to guarantee such durability of concretes.

That is why the only way to proceed is to use alternative cements. The alkali-activated cements represent one of such alternatives (**Table 2**) [3, 4].

Cement type	Early strength	Durability	Chemical resistance
Portland cement	++	++	+
Blended cement	+	+++	++
High alumina cement	+++	+	+++
High sulphate cement	+	++	+++
Sulphoaluminate cement	+++	++	+++
Alkali activated cement	+++	+++	+++

Note: (+) low, (++) medium, (+++) high.

Table 2. Comparative properties of various cements.

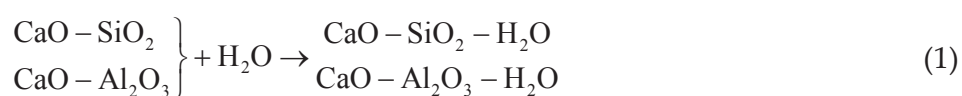
High efficiency of the alkali-activated cement concretes is proved by a vast experience collected from over 50-year use in structures for marine engineering, hydro-engineering, road and agricultural construction as well as residential, industrial, public buildings all over the world [5].

2. General information on alkali-activated cements

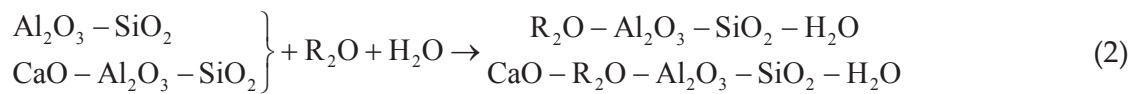
As long ago as in 1957, Viktor Glukhovsky, a scientist from Kiev (USSR, Ukraine), has discovered that compounds of alkali metals (Li, Na, K, Rb, Cs), the elements of the first group of the Periodic Table, could exhibit hydraulic binding properties similar to those of alkali earth metals (Mg, Ca, Sr, Ba), the elements of the second group [3].

As a result, an idea of creation of cementitious materials has been transformed as the following:

“Old scheme” (portland cement, high-alumina cement)



“New scheme” (alkali-activated cement) (AAC)



where R—Na, K, Li, Rb, Cs.

The idea of using these systems as cementitious materials was based, first of all, on geological data about sodium-potassium-calcium aluminosilicate compounds, which have the higher stability and resistance to atmospheric reagents and are widely present in the Earth's Crust. Second, this idea was based on the results of experimental studies, which proved that alkali hydroxides and salts of alkali metals came into interaction with clay minerals, aluminosilicate glasses and crystalline substances of natural and artificial origin with the formation of water-resistant alkaline and alkaline-alkali earth aluminosilicate hydration products analogous to natural minerals of the zeolite and mica types [6, 7].

A classification proposed by Pavel Krivenko in [8] is based on characteristic features of hydration products of the alkali-activated cements, the “edge” variants of which may be represented by the compounds of two types: alkaline aluminosilicate hydrates of the system $\text{R}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and alkali earth silicate hydrates of the system $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$.

A variety of mixed alkaline-alkali earth aluminosilicate hydrates may fall within these “edge” variants. A cement stone hydration product phase composition is determined by constituent raw materials (**Table 3**).

Cement type	Initial solid phase	Alkali content (R ₂ O), %	Hydration product	
portland cement	portland cement clinker	< 0.6	0%	100%
alkali activated portland cement	portland cement clinker+ R ₂ O	1...5		
blended alkali activated portland cement	portland cement clinker+ additive (metallurgical slag, ash, basalt) + R ₂ O	2...5		
alkali activated slag cement	metallurgical slag + R ₂ O	4...8		
alkali activated ash cement	ash—product of coal combustion	5...10		
geocement	clay + R ₂ O	10...20	100%	0%

Table 3. Mineralogical composition of cement hydration products vs. type of initial aluminosilicate component.

Strength classes of the alkali-activated cements (compressive strength at age of 28 days) are designated in the national standard of Ukraine DSTU B V.2.7-181:2009 “Cements, alkaline” [9]. High properties of the alkali-activated cement stone are attributed to its structure, which is

different from that of portland cement, considerably lower solubility of hydration products and absence in them of $\text{Ca}(\text{OH})_2$ and calcium sulphoaluminate hydrates [10, 11].

3. Alkali-activated cement concretes

3.1. Strength properties

According to the national standard of Ukraine [12], heavyweight and super heavyweight alkali-activated cement concretes are designated in classes in compressive strength at standard age (28 days).

In compressive strength, the alkali-activated cement concretes are designated, similar to EN-206, as below:

C8/10; C12/15; C16/20; C20/25; C25/30; C30/37; C35/45; C40/50; C45/55; C50/60; C55/67; C60/75; C70/85; C80/95; C90/105; C100/115; C110/125.

In flexural strength, the alkali-activated cement concretes are designated as below:

in axial tension: $C_t 0.8$; $C_t 1.2$; $C_t 1.6$; $C_t 2.0$; $C_t 2.4$; $C_t 2.8$; $C_t 3.2$; $C_t 3.6$; $C_t 4.0$.

in tensile bending strength: $C_{tb} 0.8$; $C_{tb} 1.2$; $C_{tb} 1.6$; $C_{tb} 2.0$; $C_{tb} 2.4$; $C_{tb} 2.8$; $C_{tb} 3.2$; $C_{tb} 3.6$; $C_{tb} 4.0$; $C_{tb} 4.4$; $C_{tb} 4.8$; $C_{tb} 5.2$; $C_{tb} 5.6$; $C_{tb} 6.0$; $C_{tb} 6.4$; $C_{tb} 6.8$; $C_{tb} 7.2$; $C_{tb} 7.6$; $C_{tb} 8.0$; $C_{tb} 8.4$; $C_{tb} 8.8$.

where C_t is the characteristic strength in axial tension (MPa) and C_{tb} is the characteristic tensile bending strength (MPa).

As a rule, tensile strength of coarse aggregates in the alkali-activated cement concrete constitutes 10–20% of compressive strength, depending upon type and density of alkaline activator and alkali-activated cement composition.

Strength of the alkali-activated cement concretes is kept under control, chiefly, by a proper choice of alkaline activator and its content. The greatest effect on strength characteristics is made by soluble sodium silicates. The alkali-activated cement concretes made using sodium silicates have high compressive strength reaching 120–140 MPa. They have close values of compressive strength measured on cubes not depending upon a modulus of basicity and slag content. This is especially clearly expressed in the steam-cured alkali-activated cement concretes. A conclusion was drawn that the lowering of the slag content in the concrete mix from 500 to 300 kg per 1 m^3 , the alkaline activator represented by sodium silicates, would affect early strength gain and has no any effect on values of final compressive strength. Strength of the alkali-activated cement concretes made using sodium carbonate as alkaline activator varies between 45 and 80 MPa. Type of slag also affects strength gain, and this is especially clearly expressed in the alkali-activated cement concretes that hardened in normal conditions, which continue to attain strength at the later ages. With decrease in blast-furnace slag basicity and slag content, the strength of these concretes will decrease by 10–15 MPa. The highest compressive strength (116–123 MPa) is characteristic of the steam-cured alkali-activated cement concretes made using neutral blast-furnace slags and low-modulus sodium silicates (silicate

modulus $M_s = 1-2$). Strength of the steam-cured alkali-activated cement concretes increases with decrease in silicate modulus of sodium silicate and is higher than that of the concretes that hardened for 28 days in normal conditions. The concretes hardening in normal conditions, similar to steam-cured concretes, exhibit the highest compressive strength in case of using neutral slags and low-modulus sodium silicates. The alkali-activated acid slag cement concretes have rather slow early strength gain. However, after two years the strength has increased by 2–2.6 times. High-modulus sodium silicates are not recommended for the alkali-activated cement concretes in which acid slags are used and for hardening in water. The above combination of cement components can be used under condition that basicity of the binding system will be increased by introduction of high-basic additives [13, 14].

As follows from Ref. [15], not depending upon slag characteristics and nature of alkaline activator, the alkali-activated cement concretes continue to gain strength steadily in normal conditions, in the air and in water even after they have already gained a 28-day strength.

3.2. Water permeability

Water permeability is the most widely used key characteristic of permeability of concrete and is expressed as the highest pressure of water at which water still does not penetrate into the test specimen and this characteristic is called a “filtration coefficient”. This coefficient is expressed as a quantity of liquid penetrating through a unit of cross section per unit of time at head gradient of 1.

The alkali-activated cement concretes, to which more strict requirements (low water permeability and high corrosion resistance) are applied, are classified with regard to water permeability as the following: W2; W4; W6; W8; W10; W12; W14; W16; W18; W20; W25; W30 (W – water permeability, pressure in atm) [12].

Specific features of pore structure of the alkali-activated cement concretes, their high water retaining capacity and lack of segregation in the alkali-activated cement concrete mixtures result in possibility to design concretes with the lower water permeability [16].

Density of the alkali-activated cement concretes increases, and water permeability decreases with time and depends upon chemical-mineralogical composition, slag fineness, and cement content (Tables 4 and 5).

Characteristics of water permeability	Slag fineness (m ² /kg) (measured by Blaine)				
	230	300	420	510	600
Pressure at which filtration occurs (MPa)	2.5	3.7	4.1	4.3	3.6
Filtration coefficient ($K_f \cdot 10^{-13}$) (cm/s)	4.7	3.1	0.6	0.1	0.9

Table 4. Water permeability of alkali-activated slag cement stone vs. slag fineness.

Concrete mix design (%)		w/c	Water adsorption (%)	Compressive strength (MPa)	Pressure at which filtration is observed (MPa)	Filtration coefficient (cm/s)
Slag	Sand					
15	85	0.60	8.3	30.1	0.4	1.3×10^{-6}
20	80	0.40	7.2	39.7	0.8	5.3×10^{-7}
25	75	0.36	4.1	45.5	1.8	0.8×10^{-10}
30	70	0.33	3.7	56.7	3.4	0.4×10^{-11}

Table 5. Water permeability of fine aggregate alkali-activated slag cement concretes vs. slag content.

Strength gain and decrease in water permeability of the alkali-activated cement concrete depend upon the cement content: with the cement content reaching 20%, a decrease in water permeability while hardening of the concrete specimens in high humidity conditions has been reported: by 20 times after 1 year and as much as by 200 times after 5 years. The concretes with the cement content between 25 and 40% at this age were dense enough not to allow water to penetrate into them even at pressures of 4–5 MPa [15].

Water permeability of the alkali-activated cement concretes decreases in case of using aggregates with properly selected particle size distribution providing minimum void content. So, the lowest value ($K_f = 0.9 \times 10^{-12}$ cm/s) corresponds to void content of 32.3%. Water permeability of the alkali-activated cement concretes can be improved by addition of clays, which, participating in the structure formation processes, increase density of the concrete. A determining role is played by mineralogical composition of clays. The fine aggregate alkali-activated cement concrete with the highest density was produced using sands containing 10% of coal and mining wastes. Glauconite clay, in its action on water permeability, is similar to kaolinite clay, and its maximum allowed quantity is 5%. The use of bentonite clay is found to be of no favour due to its coagulation during mixing with alkaline activator solutions.

Filtration coefficient of the alkali-activated cement concretes made using aggregates containing up to 15% of clay, at the initial test ages, due to its slow interaction with alkaline activators, remained rather high ($K_f = 3 \times 10^{-9}$ cm/s). However, after 1 year it has decreased by 5–7 times, after 5 years by 20 times. The decrease in water permeability can be provided by application of special techniques of mixing, in particular, under vibration which was found to decrease filtration coefficient by 25–30 times compared to mixing in traditional mixers.

The most favourable conditions which allow for to reach similar low water permeability, as those of the concretes hardened in normal conditions, are: steam curing in closed moulds at $T = 373$ K with a temperature rise for 3–4 h and isothermal heating for 4 h. The longer isothermal curing has no sense since a density of the concrete does not change.

According to long-term test results, strength, density, and water permeability of the alkali-activated cement concretes tended to improve with time (**Figure 1**) not depending upon applied curing conditions, but with the higher rate when the concrete specimens were allowed to cure in water and in high humidity conditions.

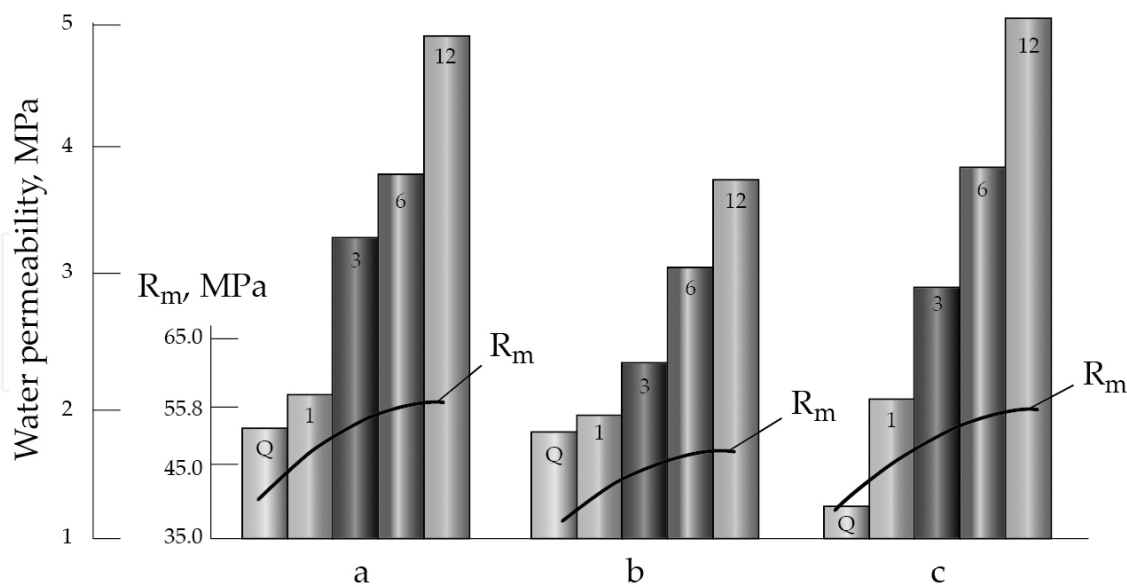


Figure 1. Compressive strength gain (MPa) and water permeability (MPa) of alkali-activated cement concretes vs. cure conditions: **a**—high humidity; **b**—dry; **c**—in water and cure regimes: Q—after steam curing; 1, 3, 6, 12—at age of 1, 3, 6, and 12 months, respectively.

Due to specific features of a capillary pore structure, water permeability of the alkali-activated cement concretes remained almost unchanged and still rather low after attacks of cyclic unfavourable conditions: heating-cooling, wetting-drying, freezing-thawing (**Table 6**). Water permeability as a function of concrete structure is the most important physical characteristic defining degree of deterioration under exposure of various aggressive environments, since corrosion processes start at the interfacial surface of external environment and concrete and proceed inward the concrete-reaching pores and capillaries.

Water permeability of the alkali-activated cement concrete can be improved by optimization of its composition with application of conventional techniques.

Composition no	Heating-cooling			Wetting-drying			Freezing-thawing		
	Cycles								
	50	100	200	50	100	200	50	100	200
Permeability expressed as pressure (MPa)									
1	1	8	7	13	15	14	15	17	16
2	5	5	4	9	10	11	11	12	13

Notes

- Concrete mix design (composition no. 1), 1 m³: ground granulated blast-furnace slag—500 kg, ultrafine (desert) sand—300 kg, coarse aggregate (5/20)—1175 kg, and sodium metasilicate (density = 1220 kg/m³)—200 l.
- Concrete mix design (composition no. 2), 1 m³: portland cement—500 kg, river sand—300 kg, coarse aggregate (5/20)—1175 kg, and water—200 l.

Table 6. Changes in water penetration of alkali-activated slag cement concrete after cyclic exposures.

3.3. Corrosion resistance in mineral environments

Durability of the alkali-activated cement concrete in mineral salt solutions is affected by ion composition, concentration and exposure conditions and is predetermined by specific features of micro- and macrostructure affected by slag composition, type and quantity of alkaline activator, as well as by cure conditions. The alkali-activated cement concretes exhibit high resistance in solutions of magnesium chlorides and nitrates considerably exceeding those of sulphate-resisting portland cements [17].

Resistance of the alkali-activated cement concretes in sulphate solutions is determined by cations of sulphate salts as well as by alkali-activated cement composition. In sodium sulphate solutions, the alkali-activated cement concretes, not depending upon alkali-activated cement composition, are not subjected to deterioration. This is attributed to lack of conditions for the formation of insoluble corrosion products.

Sulphates of polyvalent metals (magnesium, manganese, aluminium, nickel, copper, zinc, etc.), as well as those of ammonia that form insoluble (silicate hydrates, hydroxides) or volatile (ammonia) compounds, are more aggressive environments. These compounds react actively with the alkali-activated cement stone solid phase with the formation of gypsum dehydrate. A degree of aggressiveness of these sulphate compounds is determined by properties of cations, permeability of corrosion products and pH-values of the formed hydroxides.

Depending upon properties of cation, resistance of the alkali-activated slag cements in sulphate solutions decreases in the following sequence: $\text{Na}^+ > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Al}^{3+} > \text{NH}_4^+ > \text{Mg}^{2+} > \text{Mn}^{2+}$ [18].

Nos Alkaline activator		Coefficient of corrosion resistance after immersion, duration in months							
		3% concentration				6% concentration			
		1	3	6	12	1	3	6	12
1	Sodium hydroxide	1.02	1.00	0.63	0	1.15	–	–	–
2	Sodium carbonate	1.10	0.74	0.65	0	1.18	0.42	0.29	0
3	Sodium metasilicate	1.01	1.04	1.24	0	1.49	0.43	0.27	0
4	Sodium disilicate	1.37	1.28	3.60	1.35	1.51	1.40	2.87	1.07
5	Sodium silicate (Ms = 3.0)	2.97	4.49	9.90	3.09	3.62	9.05	13.96	2.50

Table 7. Corrosion resistance of alkali-activated slag cement concretes made with various alkaline activators in MgSO_4 solutions.

Corrosion of the alkali-activated cement stone in MgSO_4 -solutions takes place similar to corrosion of portland cement stone: occurrence of cracks, mainly perpendicular to a longitudinal axis of a specimen, curvature of the specimen, increase in linear dimensions and volume, deterioration.

At equal densities of alkaline activators, the corrosion resistance of the alkali-activated cements in MgSO_4 solutions tends to improve depending upon a type of alkaline activator in the following sequence: $\text{NaOH} < \text{Na}_2\text{CO}_3 \approx \text{Na}_2\text{SiO}_3 < \text{Na}_2\text{Si}_2\text{O}_5 < \text{Na}_2\text{O} \cdot 2.65\text{SiO}_2$ (Table 7).

An alkaline activator solution content to slag content ratio affects corrosion resistance in MgSO_4 solutions. The higher is this ratio, the lower is the corrosion resistance due to the higher porosity and higher is the permeability of the resulted stone.

Heat-treated alkali-activated cement concretes made with sodium silicate ($M_s = 1-3$) have the lower resistance compared to that of similar concretes that hardened in normal conditions. The use in this case of non-silicate compounds of alkali metals has positive effect on corrosion resistance of the alkali-activated cements in MgSO_4 solutions.

In general, the comparative test results of the alkali-activated, portland and sulphate-resisting portland cements showed that in the conditions of full immersion, the alkali-activated cement concretes had higher resistance in the solutions of sodium sulphates ($K_{r24} \geq 1$), magnesium chloride, and nitrate and had similar corrosion resistance in marine environment to that of sulphate-resisting cement ($K_{r24} \geq 0.55$. Where: K_r —ratio of strength of a specimen exposed to aggressive environment to that of a specimen stored in water; $_{24}$ —a number of months).

Analysis of specific deterioration of the alkali-activated cement stone and known types of corrosion suggested that alkali-activated cement hydration products were represented by four groups of substances varying in resistance in aggressive environments:

- the most easily dissolved — “free” (unbound) alkaline activator;
- less dissoluble compared to alkalis, but relatively easily dissoluble substances of the sodium silicate or calcium-sodium silicates types that are present in a gel-like state;
- relatively resistant to dissolution calcium silicate hydrates and calcite;
- the most poorly dissoluble crystalline calcium silicate hydrates and sodium aluminosilicate hydrates.

Prevalence of one of these or those groups in the cement hydration products determines variations in corrosion resistance.

3.4. Corrosion resistance in organic environments

Corrosion resistance of the alkali-activated slag cement concretes in organic environments is dependent upon an alkali-activated cement composition, character of pore structure of the resulted concrete as well as reactivity of aggressive environments.

Corrosion resistance expressed by K_r was measured on the specimens made from alkali-activated and portland cement concretes 24 months after immersion in hydrocarbon media (kerosene, diesel, mineral oil, petroleum) and water as reference medium (K_{r24}) (Table 8). A conclusion was drawn that corrosion resistance of the alkali-activated cement concretes was higher than that of portland cement concretes. This is explained by formation of the concrete

structure with the lower capillary porosity and continuation of hydration processes in the alkali-activated cement in organic environments [19].

Aggressive environment			Variations of K_{r24} after storage in the conditions of full immersion of concrete specimens made from	
Name	pH	Acidity measured by titration (mol/l)	Alkali-activated cement	Portland cement
Gasoline	–	0.0005	0.98...0.99	0.98...0.99
Benzene (benzole)	–	0.0007	0.96...1.00	0.70...0.90
Kerosene	–	0.0008	0.92...0.99	0.60...0.78
Mineral oil	–	0.0011	0.64...0.96	0.50...0.70
Diesel	–	0.0009	0.72...0.94	0.50...0.67
Sulphur-bearing crude	–	0.0013	0.5...0.97	0.56...0.40
Animal fat	–	0.0500	0.56...0.97	Destroyed
Solution of sugar 30% concentration	–	0.0100	0.68...1.18	0.30...0.64
Pickle (saline) solution of meat processing factory	–	–	0.68...1.18	0.30...0.64
Acetic acid of 10% concentration	2.80	–	0.25...0.45	0.15...0.24
Milk acid of 10% concentration	3.45	–	0.3...0.79	0.20...0.35

Table 8. Resistance of fine aggregate alkali-activated cement and portland cement concretes in various organic environments after 24 months.

Depending upon the alkaline activator used, resistance of the alkali-activated cement concretes in aggressive petroleum environments increases in the following sequence: NaOH > soda-alkali melt (by-product of chemical industry) > Na_2CO_3 > Na_2SiO_3 > $\text{Na}_2\text{O}_2\text{SiO}_2$.

High-molecular organic environments are less aggressive for the alkali-activated cement concretes. After 24 months of storage of the specimens in pickle (saline) solution, animal fat and 30% concentration solution of sugar, the resistance was more than by three times higher compared to that of portland cement concrete.

Resistance of the alkali-activated cement concrete in low-molecular compounds (glycerine, acetic and milk acids) is comparable to that of portland cement concrete and somewhat exceeds it. This may be attributed to the lower solubility of hydration products of the alkali-activated cements and lack of $\text{Ca}(\text{OH})_2$, high-basic calcium silicate and aluminate hydrates in the hydration products.

Thus, on the contrary to conventional cements, the alkali-activated cements exhibit the higher physico-mechanical properties such as strength, water permeability, corrosion resistance. The alkali-activated cements possess a complex of the above properties and can be classified as cements with polyfunctional properties.

3.5. Biodegradability and bio-fouling

Capability with regard to biodegradability and bio-fouling was tested according to the following: the specimens were stored in solution of sulphuric acid (pH = 3–4) [20].

After exposure to aggressive environment, the concrete specimens were tested to determine compressive and flexural strength characteristics.

When a ratio of strength after testing to that before testing is higher than 0.8, the cements are classified as corrosive resistant cements. Test results are given in **Table 9**.

Concrete class	Compressive/flexural strength (MPa) after					
	3 months		6 months		9 months	
	Normal curing	In sulphuric acid	Normal curing	In acid solution	Normal curing	In sulphuric acid
C45/50	53.4/11.4	50.5/10.7	54.7/9.6	60.6/11.1	60.7/10.6	55.6/10.5
C100/115	122.6/12.1	105.4/11.0	113.1/10.3	93.2/12.1	115.8/12.0	105.8/12.0

Table 9. Strength variations after exposure of aggressive environment.

From given results, both concretes under study showed stability of strength properties even after storage in aggressive environment for 9 months. So, it is clear that the alkali-activated slag concretes are resistant to biodegradability and bio-fouling.

3.6. Chloride diffusion

Replacement of portland cement with blast-furnace slag suppresses chloride diffusion in the hardened cement pastes, mortars and concretes [20]. Other study [5] has indicated that the addition of alkalis to blended portland slag cement not only increased cement strength but also decreased chloride diffusion in the cement paste significantly (**Figure 2**). The other clear trend is that diffusion rate of chloride decreases with increase in slag substitution.

The developed diffusion cell test is often used to measure the apparent diffusivity of Cl^- through hardened cement pastes and concrete. Chloride diffusion test on both the F-cement (a variety of alkali-activated cement) and portland cement pastes indicated that the diffusion rate of Cl^- through F-cement pastes is about 30–40 times slower than that through portland cement pastes for a given water-to-cement or water-to-slag ratio (**Table 10**). It was also noticed that cracks of 10–50 microns wide, induced by drying below 50% relative humidity, did not show any influence on the Cl^- diffusion rate of the specimens. However, the specimens with cracks wider than 50 microns running through the specimens had much higher Cl^- diffusion rate [20].

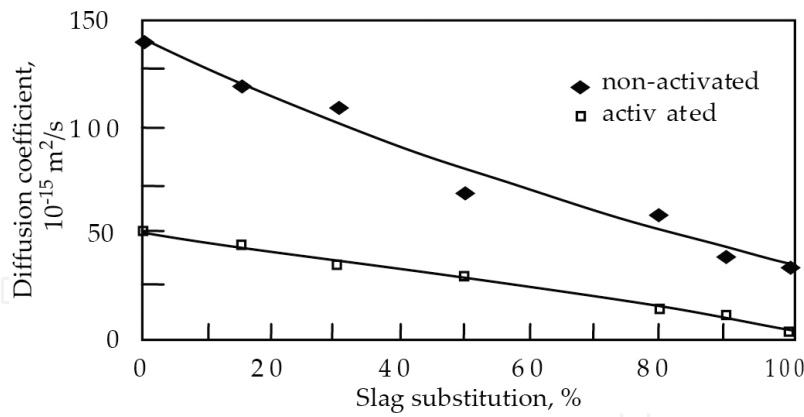


Figure 2. Effect of alkaline activation on chloride diffusion in portland slag cement.

Nos	Cement paste	Water to cement (slag) ratio	Diffusion coefficient (cm^2/s)
1	Portland cement	0.23	321×10^{-12}
2	Alkali-activated slag cement	0.23	75×10^{-12}
3	Portland cement	0.35	6390×10^{-12}
4	Alkali-activated slag cement	0.35	240×10^{-12}

Table 10. Chloride permeability test results of various cements [20].

Age	Voltage—30 V; time—24 h						
	No	I0/mA	T0/	If/mA	Tf/	L/cm	Dfucc/ $\times 10^{-12}$
3 days	CH1	21.9	23.8	17.8	22.5	1.33	2.91
	CH2	29.1	23.7	28.0	21.4	1.53	3.37
	CH3	29.5	23.5	19.2	22.2	1.55	3.42
	Mean						3.23
7 days	CH1	22.8	25.9	16.4	23.7	1.27	2.78
	CH2	18.6	25.8	15.8	23.6	1.22	2.67
	CH3	23.6	25.5	21.7	23.8	1.37	3.01
	Mean						2.82
28 days	CH1	16.8	24.2	20.3	22.8	0.81	1.71
	CH2	19.4	24.1	16.4	22.8	0.79	1.66
	CH3	21.7	23.9	20.8	22.7	1.04	2.53
	Mean						1.71

Notes: I0, T0, initial current (T); If, Tf—final current (T); L—diffuse depth; Dfucc—diffusion coefficient.

Table 11. Chlorine ions diffusion parameters [20].

Analysis of the obtained results showed that all concretes had good resistance to chloride ions penetration. According to ASTM standard, such properties are characteristic of exclusively for polymer concretes. Thus, it is possible to predict high durability of all tested concretes.

Dependences between chloride diffusion and age of concrete are shown in **Table 11**.

3.7. Freeze-thaw resistance

A key factor affecting durability of a cement stone is its pore structure which determines, in particular, its freeze-thaw resistance. For example, frost destruction of water-saturated portland cement stone takes place, chiefly, during spasmodic freezing of microcapillary water during a period starting from ice formation and until $T = 253\text{ K}$.

Frost destruction of the water-saturated alkali-activated cement stone occurs when the remaining portions of microcapillary moisture get frozen at temperatures below $T = 223\text{ K}$.

At temperatures of 243 K , the alkali-activated cement stone is subjected to residual deformations; after cooling to $T = 233\text{ K}$, the residual deformations were 0.01 mm/m , after cooling to $T = 213\text{ K}$ — 0.15 mm/m (**Figure 3**) or of about 10% of residual deformations after freezing to 173 K and thawing [21].

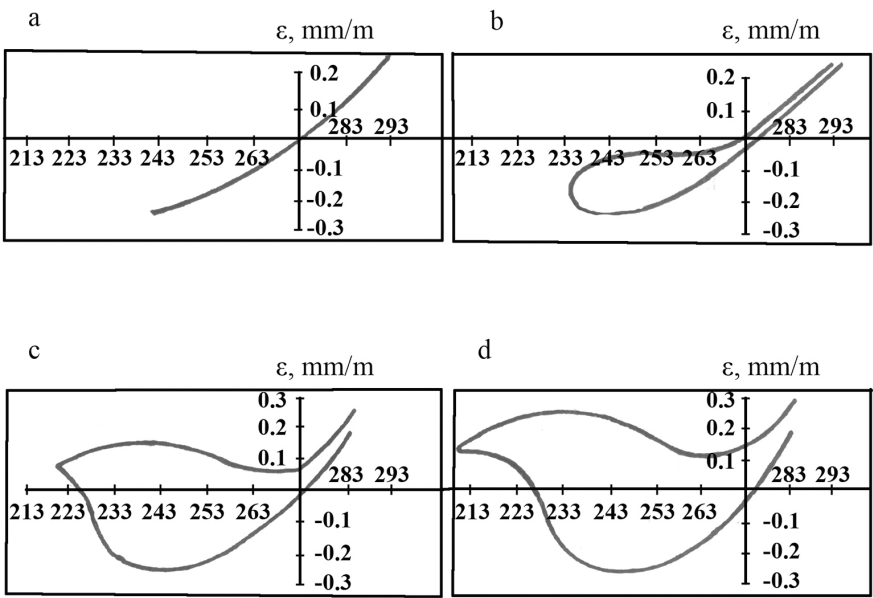


Figure 3. Deformations of alkali-activated slag cement concrete (water-to-slag ratio = 0.3) under attacks of freezing-thawing: **a**— $T = 243\text{ K}$; **b**— $T = 234\text{ K}$; **c**— $T = 219\text{ K}$; **d**— $T = 212\text{ K}$.

Differences in mechanism of temperature-induced deformations of the water-saturated portland cement and alkali-activated cement stones are attributed to the presence in the capillaries of the latter of true solutions of strong electrolytes, the lowering of the freezing temperature and promoting step-by-step removal of water due to freezing. Mechanism of water removal from a pore space of the alkali-activated cement stone is different from that in portland cement stone, thus determining a difference in the rate of their deformations in the

process of cooling and heating. Pore liquid in portland cement stone capillaries gets frozen spasmodically with elimination of meniscus and in the capillaries of the alkali-activated cement stone step-by-step, with maintaining the meniscus in a frozen state, resulted in the lowering of temperature of precipitation (settling-out) of eutectic mixtures.

A freezing temperature of pore liquid is largely determined by a type of alkaline activator. For example, in case of potash a freezing temperature of the eutectic mixture is 237 K, in case of soda only 270.9 K. The other reason causing different behaviour of the frozen water-saturated specimens from portland cement and alkali-activated slag cement concretes is attributed to specific features of their pore structure; in particular, the alkali-activated cement stone is characteristic of the increased microcapillary porosity.

A temperature of ice formation in the alkali-activated cement concretes is shifted to the region of the lower temperatures, since contents of fine pores (3–8 nm) in the alkali-activated cement stone are somewhat higher than those in portland cement concrete.

The alkali-activated cement concretes made with soluble sodium silicates have the highest freeze-thaw resistance, high density and strength. Their freeze-thaw resistance, depending upon production technology and other factors affecting strength characteristics, is 300–1300 cycles [22].

3.8. Weather resistance

Alternate (cyclic) wetting-drying, carbon dioxide and temperature variations are among factors associated with weather exposure.

Long-term cyclic wetting-drying will increase irreversible shrinkage deformations and deterioration of the concrete structure and may cause in the future loss of its load carrying ability.

Alternate wetting-drying of the alkali-activated cement concretes has no effect on its compressive strength: after 50 cycles of wetting-drying, a compressive strength of the alkali-activated cement concrete made with sodium carbonate of technical grade (commercial product) in solution has lowered by 4%, with sodium metasilicate—by 1.5% [13].

Strength properties of the alkali-activated cement concrete exposed to alternating atmospheric conditions can be improved through regulation of rate of crystallization of a gel phase, adjustment of the hydration product phase composition and directed synthesis of the materials with a required pore structure. The influence of these factors on durability of the artificial stone is evident and may be taken in account in choosing the appropriate process parameters for manufacture of the alkali-activated cement concrete with desired physico-mechanical characteristics.

Weather resistance was tested according to the prescribed testing procedure [23]. The specimens were immersed in water for 4 h and then dried at temperatures of 378–383 K for 15 h.

Three characteristics were studied: compressive and flexural strength and mass changes after testing. Test results are given in **Tables 12** and **13**.

Sample No	Drying-wetting				Normal curing			
	C70/85		C100/115		C70/85		C100/115	
	Flex.	Comp.	Flex.	Comp.	Flex.	Comp.	Flex.	Comp.
After 75 cycles (MPa)								
Sample no 1	8.2	76.9	11.0	116.3	9.9	50.9	10.8	103.0
Sample no 2	7.1	75.6	9.9	113.8	9.8	46.4	11.7	110.1
Sample no 3	6.4	74.5	10.0	116.3	9.0	48.1	11.2	105.3
Mean strength	7.2	75.7	10.3	115.5	9.6	48.5	11.2	106.1
After 100 cycles (MPa)								
Sample no 1	8.7	88.1	11.4	115.1	9.5	51.3	11.6	113.1
Sample no 2	8.5	87.1	12.1	117.8	9.1	52.3	11.8	108.5
Sample no 3	7.6	88.2	12.1	115.6	9.7	58.0	11.8	110.2
Mean strength	8.3	87.8	11.9	116.1	9.4	53.9	11.7	110.6
After 150 cycles (MPa)								
Sample no 1	7.4	83.3	11.1	119.1	8.2	48.9	11.9	112.9
Sample no 2	7.8	79.3	10.4	120.9	10.1	44.2	11.9	113.6
Sample no 3	8.5	83.3	11.5	117.3	8.5	46.7	11.6	110.7
Mean strength	7.9	82.0	11.0	119.1	8.9	46.6	11.8	112.4
After 200 cycles (MPa)								
Sample no 1	9.2	86.7	11.0	110.1				
Sample no 2	8.2	92.2	11.5	125.1				
Sample no 3	8.1	85.1	9.0	112.4				
Mean strength	8.5	88.0	11.3	113.9				

Table 12. Residual strength characteristics of alkali-activated slag cements concretes vs. curing conditions.

Test results showed that both concretes passed 200 cycles without any sign of deterioration.

3.9. Wear resistance

Wearing can be classified into three categories: abrasion, erosion and cavitation [20].

Specific features of wear in abrasion of the alkali-activated cement stone are attributed to its mineralogical and phase compositions, size of crystals and specific surface of a solid phase. Due to intensive processes of structure formation, a time-based approach to assessment of this characteristic was applied.

Tests were carried out according to a standard procedure on cube specimens ($70 \times 70 \times 70$ mm). A standard river sand was used as an abrasive material. Wear in abrasion was expressed as changes of mass and linear dimensions of the specimens subjected to wear. The results of wear in abrasion of the alkali-activated slag cement concrete are reported in (Table 14) [24].

	C70/85		C100/115	
	Before	After	Before	After
After 75 cycles (g)				
Sample no 1	559.0	558.0	562.0	560.0
Sample no 2	561.0	560.0	562.0	556.0
Sample no 3	563.0	563.0	570.0	564.0
Mean mass	561.0	560.3	564.7	560.0
Mass change (%)	0.125		0.832	
After 100 cycles (g)				
Sample no 1	553.0	555.0	562.0	559.0
Sample no 2	564.0	567.0	578.0	571.0
Sample no 3	558.0	561.0	573.0	573.0
Mean mass	558.3	561.0	571.0	567.7
Mass change (%)	-0.484		0.578	
After 150 cycles (g)				
Sample no 1	554.0	555.0	578.0	572.0
Sample no 2	553.0	554.0	563.0	555.0
Sample no 3	555.0	558.0	571.0	561.0
Mean mass	554.0	555.7	570.7	562.7
Mass change (%)	-0.307		1.402	
After 200 cycles (g)				
Sample no 1	567.0	562.0	573.0	568.0
Sample no 2	564.0	559.0	566.0	561.0
Sample no 3	562.0	556.0	562.0	560.0
Mean mass	564.3	559.0	567.0	563.0
Mass change (%)	0.939		0.705	

Table 13. Mass changes of alkali-activated slag cement concretes.

Wear resistance of the alkali-activated slag cement concrete decreases with its compressive strength increase. This dependence can be approximated to a linear one and described by the following expression [25]:

$$W = C - K \cdot R_m \quad (3)$$

where W is the wear of concrete in abrasion, g/cm^2 ; C , K is the dimensionless coefficients; R_m is the compressive strength of concrete measured on cubes (MPa).

Sodium carbonate				Sodium silicate			
Normal conditions		Steam curing		Normal conditions		Steam curing	
Compressive strength (MPa)	Wear in abrasion (g/cm ²)	Compressive strength (MPa)	Wear in abrasion (g/cm ²)	Compressive strength (MPa)	Wear in abrasion (g/cm ²)	Compressive strength (MPa)	Wear in abrasion (g/cm ²)
35.0	0.470	33.0	0.550	37.5	0.462	40.0	0.497
37.0	0.437	34.0	0.547	44.5	0.441	42.0	0.484
47.5	0.450	41.0	0.540	59.5	0.465	61.5	0.455
52.5	0.394	48.5	0.490	65.0	0.420	64.0	0.418
54.5	0.420	51.0	0.470	66.5	0.377	67.5	0.423
62.0	0.358	59.0	0.453	80.0	0.379	83.5	0.362
67.5	0.330	60.5	0.430	88.5	0.368	89.5	0.375

Table 14. Wear in abrasion of alkali-activated slag cement concretes vs. compressive and curing conditions.

Wear in abrasion of the alkali-activated cement concrete tends to reduce with time, especially until the age of 180 days, that is, during a period of intensive structure formation. Analyzing the results of measurements of wear of the alkali-activated cement concrete specimens for a period of 24 months suggested to reveal a correlation between age of the alkali-activated cement concrete and express it mathematically [24]:

$$W = \frac{W^{28}}{0.61gT} \quad (4)$$

where W is the wear of concrete in abrasion, g/cm²; W^{28} is the same, at age of 28 days; and T is the age of concrete, days.

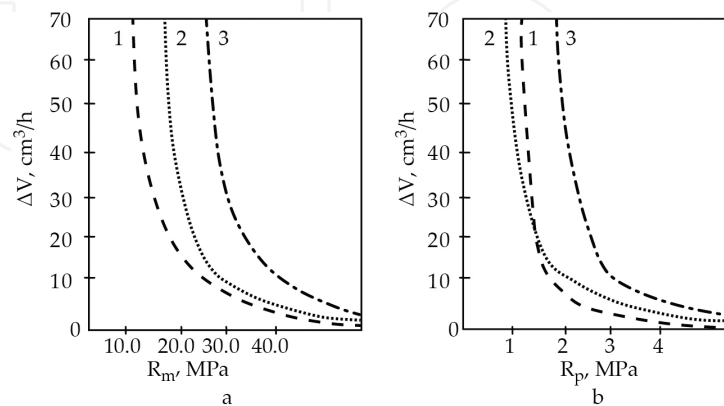


Figure 4. Correlation between the rate of cavitation-induced degradation of various concretes vs. compressive (a) and tensile strength (b): 1—fine aggregate alkali-activated cement concrete; 2—fine aggregate portland cement concrete; 3—coarse aggregate portland cement concrete.

The alkali-activated cement concretes exhibit not only high wear resistance in normal service conditions, but are resistant to cavitation damage (**Figure 4**). Cavitation resistance of the alkali-activated cement concrete, expressed as specific mass change of the concrete per unit of time (measured rate of deterioration, cm^3/h), correlates well with strength characteristics and is described by a hyperbolic-type equation.

Cavitation-induced wear (cavitation damage) on concrete surface is most common in case of spillway in dams. This leads to cracks on the concrete surface which further increases the risk of damage to concrete due to sulphate attack, freeze-thaw, alkali-silica reaction and other means. Cavitation damage occurs on concrete surface when discontinuity or irregularities is encountered in the path of high velocity water flow.

According to Ref. [16], cavitation resistance of the alkali-activated cement concrete structures working in the zones of wave-cut/break is higher than that of portland cement concretes. In high humidity service conditions, the alkalis that are present in the alkali-activated cement stone allow for self-healing of the zones of stress concentrations and strengthening of the alkali-activated cement concrete due to “renewal” (re-start) of the processes of hydration and hardening resulting in densification of the concrete structure and filling of its defects (pores, etc.) with hydration products (**Table 15**).

Curing/exposure conditions	Alkali activated slag cement concrete			Portland cement concrete		
	Strength (MPa)		Wear (cm^3/h)	Strength (MPa)		Wear (cm^3/h)
	Compressive	Tensile bending		Compressive	Tensile bending	
28 days in normal conditions (after steam curing)	50.00	4.00	8.27	40.50	4.40	6.36
	39.00	4.00	9.11	30.00	2.80	12.25
180 days in sweet water	53.50	6.14	6.21	43.00	5.20	6.21
	41.50	5.40	7.38	32.40	3.30	10.36
180 days in sea water	55.60	8.24	5.42	41.50	4.13	6.43
	45.00	7.23	5.96	28.60	3.18	11.34

Note: Fine aggregate alkali-activated slag cement concrete (soluble sodium carbonate as alkaline activator).

Table 15. Wear caused by cavitation (cavitation resistance) of alkali-activated cement and portland cement concretes vs. curing/exposure conditions.

Thus, durability of the alkali-activated cement concretes, assessed in terms of endurance and wear resistance, is comparable and even exceeds that of portland cement concretes, especially in unfavourable (extremely severe) service conditions.

3.10. Corrosion due to alkali-aggregate reaction (AAR-induced corrosion)

One of the reasons associated with concrete durability is an alkali-aggregate reaction (AAR), which is a reaction between alkali of cement and alkali-susceptible aggregate. Rate of this

reaction is determined by a type and quantity of alkalis, and type and content of reactive silica. In case of the alkali-activated cements, which contain alkalis in much higher contents compared to that of portland cements, this problem is important. For this, a number of research projects have been performed [26–28], which showed a possibility to keep the AAR under control with a so called “positive” effect. The results of study showed that it could be possible due to introduction into the cement or concrete composition of aluminate-containing additives, in the presence of which a destructive (“negative”) process of corrosion converts into a constructive (“positive”) one. This is attributed to binding of the corrosion products with the formation of the alkali-activated aluminosilicate hydrates according to the following scheme:



The resulted compound forms a dense and strong cage (shell) around the aggregate thus preventing corrosion processes.

This conclusion coincides well with the results of the following experiment: the metakaolin additive in a quantity of 15% was introduced into the cement composition to minimize influence of the destructive processes in the interfacial transition zone.

The influence of additive type on expansion deformations is shown in **Figure 5**. As follows from **Figure 5a**, non-admissible high expansion deformations were observed in the concretes made from portland cement with the increased content of Na_2O (1.3%) and from the alkali-activated portland cement with the Na_2O content of 2.5% in which andesite rock was used as coarse aggregate.

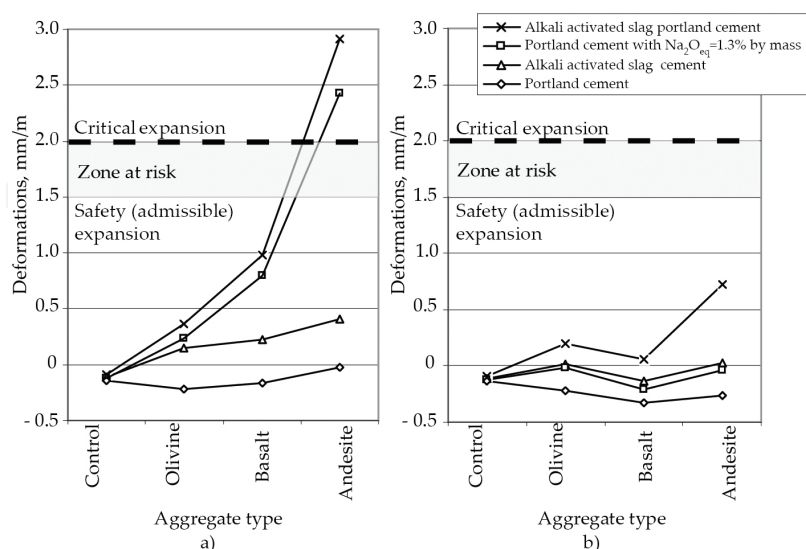


Figure 5. Influence of aggregate type (olivine, basalt, andesite) and metakaolin additive on deformations of the concrete specimens: **(a)** without additive; **(b)** with the metakaolin additive (15%); curing conditions—28 days of continuous steam curing at $T = 343 \text{ K}$ and relative humidity = 100%.

Corrosion products in the interfacial transition zone and microcracks occurring in the aggregates of the concretes made using portland cement with the increased contents of Na_2O and the alkali-activated slag portland cement are clearly seen in the electron microscope images. On the contrary, the use of the alkali-activated cements is not at any risk, and the interfacial transition zone “cement stone—alkali-susceptible aggregate” remained clear.

The introduction of the additive will allow to shift all concrete compositions not only from the zone of not allowable critical expansion and deterioration, but also from the zone of risk, not depending upon a cement type and aggregate type. The interfacial transition zone in this case is clear and without sign of corrosion. This may be attributed to the fact that conditions required for synthesis of alkaline zeolite-like aluminosilicate hydrates of the general formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot n\text{H}_2\text{O}$ are created in the interfacial transition zone in the presence of reactive Al_2O_3 in a strongly alkaline medium, that is, the alkali starts to bind very quickly.

The alkali-activated cement stone has low deformation expansions even without the meta-kaolin additive. This may be attributed to high contents of reactive Al_2O_3 in the glass phase of the slag.

4. Practical experience

Theoretical data in combination with those obtained experimentally that have been collected by a scientific school headed by Professor Viktor Glukhovsky (currently is headed by Professor Pavel Krivenko) allowed as early as in 1958 to launch first pilot scale production of the alkali-activated cement concrete products and to continue in 1962 with industrial-scale production of a number of concrete small-size building elements and structures.

The majority of alkali-activated slag cement concrete structures manufactured in 1960s was intended for hydro-engineering, in particular, marine engineering application that work in extreme service conditions (corrosive exposure of running waters, alternate freezing-thawing in winter, wetting and drying in summer, etc).

Regular continuous observations over the alkali-activated cement concrete small-size building elements and structures showed their higher performance properties compared to those of portland cement concretes as reference (**Tables 16–18**).

From these tables, performance properties of these concretes tended to increase during the whole period under review. This may be attributed to permanent deepening of the hydration processes, resulted in the formation of low basic calcium silicate hydrates and zeolite-like water-resistant final products of the alkaline as well as mixed (alkaline- alkali earth) composition. Low water permeability and high resistance of the alkali-activated cement concretes in aggressive environments can be explained by nature of their hydration products [17, 29].

The results of chemical analysis showed that quantities of free (unbound) alkalis in the alkali-activated cement concretes varied from 0.3 to 0.5%. A pH-index inside the alkali-activated slag cement concretes was 12.7–12.9. This is an evidence of presence in these concretes of an alkaline

medium which is required for the further flow of processes of hardening in the alkali-activated cements as well as for passivation of reinforcement steel. The alkalis are released in very small quantities. This is attributed to the increased density of the alkali-activated slag cement concrete, closed porosity and nature of hydration products.

Structure (small-size building element)	Mnfg year	Aggregate	Alkaline activator	Initial strength (MPa)	Test results (1973)	
					Freeze/thaw resistance (cycles)	Strength (MPa)
Cast-in-situ facing concrete covering of main irrigation channel (under water level)	1962	Heavy sandy loam	Na ₂ CO ₃	15	900	42.60
The same, above water	1962	The same	Na ₂ CO ₃	15	900	40.00
Pre-stressed precast concrete elements of irrigation system	1964	Sea sand (fineness modulus = 0.9...1.1)	Na ₂ CO ₃	25	700	59.50
Precast concrete piles	1964	The same	Na ₂ CO ₃	30	600	71.80
Cast-in-situ road pavement	1965	The same	Na ₂ CO ₃	10	250	47.60
Cast-in-situ breakwater massive elements	1965	The same	Na ₂ CO ₃	30	570	62.00
Prefabricated pavement slabs	1965	The same	Na ₂ CO ₃	25	437	67.00
Centrifuged pipes (<i>d</i> = 100 mm)	1966	River sand (fineness modulus = 1.65)	Na ₂ CO ₃	30	–	83.00
Large-size wall blocks	1967	Waste of shell rock	Na ₂ CO ₃	10	300	31.30

Table 16. Performance properties of alkali-activated cement concretes after long-term service in various exposure conditions.

Type of concrete	Design compressive strength (MPa)	Compressive strength (MPa) after exposure in sea water during			
		1 year	3 years	5 years	7 years
Slabs of embankment					
Alkali activated slag cement (alkaline activator—sodium carbonate)	40.0	40.0	47.8	53.8	57.0
Portland cement	39.0	39.0	38.5	Destroyed	
Slabs immersed in sea water (under layer of biomass)					
Alkali activated slag cement (alkaline activator—sodium carbonate)	40.0	40.0	59.6	60.1	61.4
Portland cement	39.0	39.0	47.6	51.6	50.0

Table 17. Performance properties of alkali-activated cement slag concretes after service in sea water (Black Sea, Odessa, Ukraine).

Large-scale production of the alkali-activated cement concretes in the USSR showed their high efficiency. Cost savings (30–40%) were achieved due to the use of by-products and waste materials, as well as longer span of service life, especially in extreme conditions. These alkali-activated materials are in line with principles of global sustainable development: near-zero carbon dioxide emissions, low-energy consumption (no high temperature processes), preservation of natural resources, etc.

Structure (small-size building element)	Age of concrete (years)	Water permeability (MPa)	
		Initial (1 month after placing)	After service
Cast-in-situ concrete facing of main irrigation channel (under water level)	12	0.6	1.8
Chutes, pre-stressed, precast	9	1.0	2.0
Pre-stressed precast concrete elements of irrigation system			
Massive (large-size) water breaks, precast blocks	8	0.8	2.0
Cast-in-situ breakwater massive elements			
Slabs in service under layer of biomass	8	0.8	2.0
The same, isolated from biomass	8	0.8	2.0

Table 18. Water permeability of alkali-activated slag cement concretes after long-term service.

5. Conclusions

Numerous studies held on alkali-activated cement concretes supported by test results showed that they could work successfully with high efficiency in various structures withstanding extreme service conditions (alternate freezing-thawing, aggressive environments, dynamic and static loads, etc.). In their performance properties (freeze-thaw resistance, water permeability, corrosion resistance, etc.), the alkali-activated cement concretes are superior to portland cement ones and can be recommended for marine engineering applications, especially for so called “responsible use” structures that are in service in extreme weather conditions and under exposure of alternating loads and aggressive environments.

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