1. Introduction

Alkali reactivity was first noted in various publications dated to 1916 when the reaction between feldspar and sodium carbonate had been reported, which led to the formation of new structures that disrupted the stone structure. The degradation of concrete as a result of this reaction between the alkalis included in cement and some natural aggregates was first registered in the United States. In 1922, a similar case occurred at the New River Hydropower Station (Virginia, USA) in only ten years after the construction. 1940 saw the published results of research [1] reporting the "alkaline reaction" (the alkali–aggregate reaction, AAR) as a result of using opal-containing fractions of the aggregate to erect a dam in California. These cases initiated a large number of studies conducted in the United States in order to identify causes and take appropriate measures.

In 1947, paper [2] described a reaction between alkalis and silicate acid (the alkali–silica reaction, ASR). In 1952, this reaction was described in the United States [3]. The cited studies described only the existence of the problem, without offering variants to resolve it.

The issue of studying the process of interaction between alkalis from cement compositions and reactive aggregates has remained relevant in the modern world, and has become even more important. The reserves of conditioned, the so-called "inert", aggregates are rapidly utilized. At the same time, the market offers a large amount of material at a reduced price; testing it reveals that its composition contains reactive components. The problem relates to that most of the manufacturers of building materials do not pay attention to a deep analysis of the aggregate characteristics when accepting it. They only determine fractional composition and moisture content. This leads to that the risks of getting a low-quality concrete mixture are increasingly high. Another issue related to the progress of aggregate alkaline corrosion is that the destructive processes do not manifest themselves immediately, but after a while, when a structure is already...
under operation and its replacement is a very complex and costly affair. At present, there are no effective approaches to restoring the characteristics of a concrete structure exposed to the aggregate alkaline corrosion.

The relevance of research in the proposed field is predetermined by that the increasing specific share of substandard aggregates in the market of building materials poses significant threats to life of people and to the functioning of the economy. Therefore, the issue of neutralizing these threats at the technological level is extremely urgent and important.

2. Literature review and problem statement

The results from experimental research into the "alkali-active aggregate" reaction, reported by different authors [4], allow us to formulate the basis of the AAR reaction mechanism:

- cement itself [5], admixtures to concrete [6], and the external aggressive environment [7] are the sources of alkalis [8];
- the permissible alkali content in the Portland cement (recalculated for Na₂O-equivalent (Na₂O+0.658 K₂O) is limited to a magnitude of 0.6 % [9];
- for the case of using mixed cements, this indicator may reach 2 % [10];
- the expansion process is accompanied by osmotic pressure, which is created by viscous-fluid (plastic) alkali-metal silicate gel, formed as a result of reaction process [11]. The gel works as a semipermeable membrane, through which the OH⁻, K⁺, Na⁺ ions can penetrate a reaction surface – the active aggregate [12]. First, the silicates of alkaline metals fill the surrounding porous space, and only then the expansion pressure appears [13];
- an important role in the described processes belongs to the presence of free Ca(OH)₂ in cement stone, which initially increases membrane permeability [14]. It then promotes the formation of additional quantity of alkalis due to exchange reactions between Ca(OH)₂ and the salts of alkaline metals. These salts were introduced to the composition of concrete with different additives (plasticizers [15], hardness boosters, anti-frost additives, etc.) [16];
- minimizing the expansion effect is achieved by introducing various active mineral additives to the cement composition. These additives can be both of secondary [17] and volcanic origin (limestone with amorphous silica content [18], zeolites [19], perlite, tuff, etc. [20]).

They can also be produced by humans (fuel ash, metallurgical slag, micro silica, etc.) [21]. However, the cited study also contained certain shortcomings. The effect of application of such additives is mainly based on their reactivity in relation to the alkali metal hydroxides [22]. This contributes to a uniform distribution of reaction products in concrete, thus preventing dangerous attacks by alkali on large reactive aggregate. Second, the pozzolanic additives bind the free ions of Ca²⁺. This contributes to the reduction of CaO to SiO₂ ratio and stabilizes the binding of Na⁺ and K⁺ when forming C–S–H. Such an understanding of the ASR mechanism was accepted by scientists over many years as the basis for the development of recommendations for preventing the harmful effects of the reaction. However, that made it impossible to substantiate the use of new cements (alkali-activated ash and slag cements, geocements, geopolymers, alkaline Portland cements, etc.), whose alkali content is much higher than that in traditional cements [23]. At the same time, the necessity of application of new cements is predetermined by the modern state of human development, the lack of minerals and the necessity to reduce environmental load from industry.

However, there are known attempts to explain the processes of active aggregate corrosion in the presence of alkalis not only in terms of the quantitative content of alkalis and free Ca(OH)₂. Thus, authors of [24] studied the role of Al₂O₃, which occurred as the result of dissolution of feldspar; they found that an increase in the ratio of Al₂O₃/SiO₂ during AAR changes its character from the destructive to constructive. These results were confirmed by work [25].

By advancing earlier studies, paper [26] described the less harmful effect exerted by alkalis for the case when vitreous slag is added to the Portland cement. This can be explained not only by the lower permeability of cement pastes, but also by the ability of slag to bind the ions of alkaline metals into insoluble hydroalumosilicates [27]. This is evidenced by the possibility to form, in the contact zone, alkaline or hybrid alkaline-alkaline-earth hydroalumosilicates, depending not only on the type of aggregate, but also the composition of the hydroalumosilicate alkaline component [28].

It was concluded that regulating the content of Al₂O₃ in cement composition by introducing additives containing active Al₂O₃ makes it possible to prevent the destructive nature of ASR reaction in concretes [29]. It can also be used for the alkaline Portland cement [30].

Thus, an analysis of literary sources has revealed the importance of the issue of aggregate alkaline corrosion in concrete and has shown that the problems related to interaction between the active aggregate and alkaline cements had been insufficiently studied. Current theory of the corrosion mechanism does not allow the use of alternative cements. A theoretical possibility of avoiding such a problem by using additives that contain aluminum compounds has been noted. That would make it possible to avoid the processes of aggregate alkaline corrosion in real structures, as the reaction could be directed not towards the destruction of the cement stone, but its compaction and strengthening. Another important issue that has not been previously documented is the establishment and substantiation of a new, fundamentally different mechanism of the “alkali-active silica” reaction in the presence of metakaolin, which suggests an opportunity of using unconventional cements.

3. The aim and objectives of the study

The aim of this study is to establish patterns of change in the structure of a contact area and in the processes of self-healing of the concretes based on the alkaline Portland cement using active aggregates. This would make it possible to predict the development of destructive processes and to prevent them by means of technical and technological measures.

To accomplish the aim, the following tasks have been set:

- to conduct a comparative study in order to define the specificity of the progress of corrosion processes “alkalis-reactive aggregates”, which occur in concretes made with the use of conventional and alkaline Portland cements;
- to examine the possibility to prevent destructive processes in concrete with an elevated content of alkalis by introducing to a cement composition the Al₂O₃-containing additives, specifically, metakaolin;
- to investigate shrinkage deformations in the developed compositions.
4. Materials and methods to study a change in the contact area and properties of alkaline concretes

The conventional Portland cement (OPC), the class of strength 42.5N (according to EN 197-1:2011 IDT classification), was used in our study as an aluminosilicate component of the alkaline Portland cement. The specific surface of the Portland cement was 320...350 m²/kg by the Blaine's device.

To study ASR, natural basalt was used as reactive aggregate. Glass rods, cast from a basalt melt, were used to model and investigate ASR in a concrete contact area.

Sodium silicate was used in the form of a solution with silicate module $M_S=2.87$ and density $\rho=1,300$ kg/m³ as the alkaline components.

Metakaolin was used as an active mineral additive. The content of a metakaolin additive was 15 % by the weight of cement. The specific surface of metakaolin was 1,860 m²/kg.

The chemical composition of raw materials is given in Table 1.

The contact area of cement with the aggregate and “cement stone – basalt rod” was studied using the scanning electron microscope-analyzer REMMA-101A (Ukraine). To investigate the transition area, we prepared special microsections by cutting a thin section of the material followed by coating with copper. In addition, we studied the distribution of chemical elements in the contact zone by using the microanalyzer microscope REMMA-101 A.

Hydration products in the contact zone “cement stone – basalt rod” were examined using an X-ray analysis at the automated diffractometer XRD-6000 (Shimadzu, Japan). We applied CuKα-radiation with a wavelength of 1.54 Å and the arc graphite monochromator; voltage in a tube, 40 kV; current, 30 mA; continuous scanning mode; angular range of the study, 20°, from 5 to 90°; sample rotation speed, 30 rpm. The diffractograms were decoded using the ICCD PDF2+–2003 database (The International Centre for Diffraction Data) and the software Match V.1.9a (Crystal Impact). Models to study the contact area were prepared with a sodium silicate volume ratio to the content of cement=0.4. The content of alkalis (Na₂O+K₂O) in the composition of cement was 4.42 % by weight. Active Al₂O₃ participates in the process of forming the structure in the contact area “cement stone – aggregate”. This conclusion is also confirmed by the results from a physical-chemical analysis of the model system “cement stone – basalt rod”.

5. Results of studying a change in the contact area and properties of the examined concretes

5.1. Studying a change in strength and deformation characteristics

The results of change in the strength characteristics and deformations of samples are given in Table 2.

As one can see from an analysis of the represented data, the magnitude of deformations during expansion of the samples tends to decrease when active Al₂O₃ in the composition of metakaolin is added to the cement composition. Active Al₂O₃ actively participates in the process of forming the structure in the contact area “cement stone – aggregate”. This conclusion is also confirmed by the results from a physical-chemical analysis of the model system “cement stone – basalt rod”.

### Table 1

<table>
<thead>
<tr>
<th>Chemical composition of raw materials</th>
<th>Oxide content, % by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
</tr>
<tr>
<td>Natural basalt</td>
<td>50.2</td>
</tr>
<tr>
<td>Glass rods</td>
<td>50.0</td>
</tr>
<tr>
<td>Portland cement</td>
<td>21.8</td>
</tr>
<tr>
<td>Metakaolin</td>
<td>55.1</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>No.</th>
<th>Cement composition</th>
<th>Compressive strength/bending, MPa, after, days</th>
<th>Deformations of shrinkage (−)/expansion (+), mm/m, after, days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>28</td>
<td>90</td>
</tr>
<tr>
<td>1</td>
<td>Portland cement+H₂O</td>
<td>72.3</td>
<td>74.3</td>
</tr>
<tr>
<td>2</td>
<td>Portland cement+H₂O+MK</td>
<td>67.0</td>
<td>64.2</td>
</tr>
<tr>
<td>3</td>
<td>Portland cement+SS</td>
<td>80.3</td>
<td>109.7</td>
</tr>
<tr>
<td>4</td>
<td>Portland cement+SS+MK</td>
<td>104.4</td>
<td>119.8</td>
</tr>
</tbody>
</table>

Note: SS – sodium silicate, $M_S=2.87$ and $\rho=1,300$ kg/m³; MK – metakaolin additive – 15 % by the weight of cement.

5.2. Physical-chemical examination of the microstructure of cement stone

Taking into account the results from an X-ray phase analysis, we examined the phase composition of hydrated dispersions in the concrete's contact zone based on cement composition No. 1 (Table 2), shown in Fig. 1. Curve 2. The phase composition is represented by the following reaction products: $Ca_2Si_2H (6CaO·3SiO_2·H_2O) (d=0.335; 0.284; 0.246; 0.237; 0.225; 0.180 nm)$, $Ca_2SiH (2CaO·SiO_2·H_2O) (d=0.284; 0.270; 0.246; 0.190; 0.180 nm)$, $Ca_2SiO_3 (3CaO·2SiO_2·H_2O) (d=0.56; 0.284; 0.184 nm)$. We also recorded reflexes
matching Ca(OH)$_2$ ($d$=0.487; 0.311; 0.261; 0.193; 0.18 nm), CaCO$_3$ ($d$=0.303; 0.229; 0.21; 0.193; 0.188 nm. We also observed weak reflexes related to Ca$_2$H$_4$ (2CaO·Al$_2$O$_3$·4H$_2$O) ($d$=0.717; 0.376; 0.266; 0.258; 0.246 nm). No X-ray amorphous phase of the calcium-silicate gel, which can be formed in the contact area and weaken it [16], has been recorded.

However, based on the distribution of elements in the contact area and considering a relatively high level of expansion (+0.44 mm/m), such a probability may exist. This conclusion is confirmed largely by the increased content of Ca and Si in the contact area (Fig. 2). As shown in the microphotographs (Fig. 2, a), the contact area is not “acute” and clean, thereby confirming this assumption.

The use of alkaline Portland cement (Table 2, Composition No. 3) leads to a change in the phase composition of new structures in the model in the contact area (Fig. 1, Curve 5). Consequently, cement hydration tends to deepen, which is evident from the lower intensity of the initial diffraction lines. There is a redistribution of the composition of new structures in the direction of synthesis of more low-base calcium hydrosilicates, the type of CSH(I) ($d$=0.283; 0.270; 0.247; 0.179 nm) and tobermorite ($d$=0.56; 0.307; 0.299; 0.283; 0.227; 0.208; 0.183 nm). The lines relating to Ca(OH)$_2$ are completely absent. The content of Ca$^{2+}$ and Si$^{4+}$ in the contact area sharply reduces, while the content of Al$^{3+}$ and Na$^+$ slightly increases (Fig. 3). This allows us to draw a conclusion about the synthesis of sodium and mixed sodium-calcium hydroalumosilicates, which is confirmed by results from the diffractograms in Fig. 1. The lines relating to Na$_2$O$\times$Al$_2$O$_3$$\times$4SiO$_2$$\times$2H$_2$O ($d$=0.56; 0.343; 0.293; 0.252; 0.174 nm) and 2Na$_2$O$\times$2CaO$\times$5Al$_2$O$_3$$\times$10SiO$_2$$\times$10H$_2$O ($d$=0.654; 0.467; 0.353; 0.283; 0.270 nm) are clearly identified along curve 5.
The acquisition of experimental data on a change in the characteristics (Table 2) and composition of new structures, metakaolin to the alkaline Portland cement (Table 2, Composition No. 4) has been recognized as ineffective, because it does not significantly affect the diffraction pattern (Fig. 1, Curve 4).

At the same time, as shown by Fig. 4, the content of the Ca\(^{2+}\) ions and, therefore, the hydroxide ions, tends to decrease in the contact area; this eliminates to a larger degree the risk of developing corrosive processes on the contact zone, which have harmful destructive consequences.

This correlates well with the clean (non-diffusion) contact area (Fig. 3). Similarly, this is confirmed by data in [37], according to which the presence of active aluminum in the composition of the Portland cement stone reduces the relative concentration of alkalis in a porous fluid. In the presence of alkalis, it is impossible to rule out the adaptive transformation of clay minerals in the contact zone into the more stable zeolite-like new structures. The introduction of

The expansion of the contact area through the formation of the above-mentioned hydration products is clearly observed in the microphotographs. Therefore, taking into account results from determining the physical and mechanical properties, there is a constructive nature in the corrosion of the contact zone “cement stone – basalt rod”. Introducing a metakaolin additive to conventional Portland cement (OPC) without alkaline activation (Table 2, Composition No. 2) has been recognized as ineffective, because it does not significantly affect the diffraction pattern (Fig. 1, Curve 4). At the same time, as shown by Fig. 4, the content of the Ca\(^{2+}\) ions and, therefore, the hydroxide ions, tends to decrease in the contact area. This eliminates to a larger degree the risk of developing corrosive processes on the contact zone, which have harmful destructive consequences.

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determined from the results of a physical-chemical study of the microstructure of cement, have allowed us to assume the mechanism of the “alkali-active silica-metakaolin” reaction (Fig. 6).

1 – formation of alkaline ions or their introduction from outside and diffusion to the reaction point:

\[ \text{Na}_2\text{SO}_4 + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \times 2\text{H}_2\text{O} + 2\text{NaOH} \] (Na⁺, OH⁻).

\[ \text{Na}_2\text{O} \times \text{nSiO}_2 \times 2\text{mH}_2\text{O} + \text{Ca(OH)}_2 + \text{CaO} \times \text{nSiO}_2 \times 2\text{mH}_2\text{O} + \text{kNaOH}; \]

2 – formation of silicate gel of alkali metals: 2\text{NaOH} + amorphous \text{SiO}_2 \times \text{mH}_2\text{O} → \text{Na}_2\text{SiO}_3 \times \text{mH}_2\text{O};

3 – metakaolin addition: \text{Al}_2\text{O}_3 \times 2\text{SiO}_2;

4 – formation of alkaline and alkaline-alkaline-earth (hybrid) hydroalumosilicates:

\[ \text{Al}_2\text{O}_3 \times 2\text{SiO}_2 + 2\text{NaOH} + \text{mH}_2\text{O} \rightarrow \text{Na}_2\text{O} \times \text{Al}_2\text{O}_3 \times 2\text{SiO}_2 \times 2\text{mH}_2\text{O} + \text{H}_2\text{O}; \]

\[ \text{Al}_2\text{O}_3 \times 2\text{SiO}_2 + \text{Na}_2\text{SiO}_3 \times \text{mH}_2\text{O} \rightarrow \text{Na}_2\text{O} \times \text{Al}_2\text{O}_3 \times \text{nSiO}_2 \times \text{mH}_2\text{O}. \]

Comparison of the conventional aggregate reaction mechanism in the presence of alkalis [31] with the proposed one allow us to note certain differences. The process of structure formation in conventional compositions is characterized by the formation of an outer zone of contact of film. This film consists of calcium hydrosilicates and gel of alkaline metals capable of swelling/expanding under this film and creating the strains/deformations in concrete (destructive process). In the cement modified with metakaolin, due to the reaction between metakaolin and alkalis, the concentration of the OH⁻, Na⁺ and K⁺ ions can be reduced to non-critical values, and, consequently, concrete does not expand. The result of the pozzolanic reaction is the formation of an outer zone of contact with the microstructure of cement, have allowed us to assume the mechanism of the “alkali-active silica-metakaolin” reaction (hybrid) hydroalumosilicates: Being resilient, the latter compact and strengthen the contact area by enhancing its micro-hardness and strength (the so-called self-healing of structure).

Our study reveals the essence of the course of aggregate alkaline corrosion processes both in the system of conventional Portland cement and in the alkaline Portland cement. The results obtained have allowed us to suggest a new mechanism for the progress of such corrosion, as well as methods to control it for various binders. This eliminates the shortcomings of conventional approaches that are associated with the existing issue about using non-traditional cements. The established patterns could be applied, at certain adjustment, to corrosion processes of various types of active aggregates.

Further research could address the identification of influence from the composition formulation of alkaline cements on the process of aggregate alkaline corrosion. In addition, one must investigate a possibility to control corrosion in the already hardened cement stone.

7. Conclusions

1. Comparative studies have been conducted to determine the specificity of corrosion processes “alkalis-reactive aggregates”, which occur in concretes made with the use of conventional and alkaline Portland cements. It has been shown that the use of the alkaline Portland cement is characterized by a 3 – 4-time smaller shrinkage of artificial stone compared to the conventional Portland cement and by the considerably higher strength indicators (exceeding 100 MPa) in the long term. We have established patterns in the active aggregate corrosion processes depending on the type and composition of a cement system. The most effective in terms of strength is the use of sodium silicate as the alkaline component. At the same time, such systems are characterized by elevated parameters of shrinkage.

2. A possibility to prevent destructive processes in concrete with an elevated content of alkalis by introducing metakaolin to the cement composition has been explored. It has been shown that introducing a metakaolin additive in the amount of 15 % in order to replace part of cement makes it possible to control the structure-forming processes in the contact zone “cement stone – active silica”, thereby changing the character of new structures towards creating stable zeolite-like new structures and hybrid hydroalumosilicates.

3. We have studied deformations of shrinkage in the developed compositions based on the conventional and alkaline Portland cements. It has been shown that the introduction of metakaolin makes it possible to reduce the indicators for system expansion from 0.44 to 0.01 mm/m, thereby maintaining the defect-free structure of cement stone and concrete.

References


Technology organic and inorganic substances


