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Mechanism of preventing the alkali–aggregate reaction in alkali activated cement concretes

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ABSTRACT

Processes of structure formation taking place in the interfacial transition zone “cement paste – aggregate” have been studied on a variety of cement model systems. The results of this study suggest that, depending upon the contents of components capable of actively interacting with alkalis in the presence of reactive SiO_2 in the cement and aggregate, the processes taking place during an alkali-aggregate reaction could be constructive or destructive in character. So-called “constructive processes” are attributed to binding the corrosion reaction products with the formation of the alkaline aluminosilicate hydrates. The results of this study have been taken as a base in developing a mechanism of preventing the alkali–aggregate reaction in the alkali activated cement concretes through the introduction of additional quantities of Al_2O_3-containing substances.

1. Introduction

First observations of reactivity of the alkalis contained in some mineral constituents go back to 1916 when a geologist E.A. Stephenson has reported about a reaction between feldspar and sodium carbonate which resulted in the formation of a gel. Degradation of concrete as a result of this reaction between the alkalis contained in cement and some ground rocks was first observed in the USA. In 1922 similar deteriorations took place in the New River Hydropower Station (Virginia, USA) 10 years after it had been erected. In 1940 Stanton [1] has reported about an “alkaline reaction” (alkali–aggregate reaction, AAR) due to opal-containing fractions of the rocks used for the diverting dam in California. These deteriorations have initiated a number of extensive studies to be held in the USA to reveal causes for taking appropriate measures.

In 1947 a reaction between the alkali and silicic acid (alkali–silica reaction, ASR) was described by Bogue [2]. A few years later, in 1952 this reaction was described by Kuehl in his book, in which he made references to the data obtained in the USA [3].

Starting from 1950s this reaction is also known in Australia and since the mid of 1950s more and more countries (Canada, Iceland, South Africa and other countries) report about deteriorations of bridges, sleepers, dams, roads due to the ASR. Very often these deteriorations are attributed to other causes such as low frost resistance or other aggressive exposure. The losses were huge, which is why the problem became urgent and required prompt actions to be taken.

As a result of extensive studies and experimental works [3–6], basic fundamentals of the ASR mechanism have been formulated. These are:

- sources of alkalis are cement, concrete admixtures, outdoor aggressive environment;
- limit values of the alkalis ($Na_2O + 0.658\ K_2O$) contained in portland cement (expressed in terms of Na_2O-equivalent content) should be less than 0.6% by mass;
- expansion due to the ASR is associated with osmotic pressure from the aluminosilicate gel- a product of reaction between the active silica and alkali. This gel acts as a

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semi-permeable membrane, through which the OH^-, K^+, Na^+-ions can move in the direction towards the aggregate surface. The alkali metal silicates start to fill a surrounding pore space resulting in the expansion pressure;
- a free $Ca(OH)_2$ of the cement paste plays an important role. The alkali metal silicate gel itself is not able to produce great expansion pressure. However, the presence of calcium creates conditions promoting synthesis of a dense gel-like calcium silicate hydrate (CSH), which is present in the outer zone of reaction and acts as a semi-permeable membrane allowing an access of new portions of water, the Na^+ and OH^--ions to a place of reaction, but restricting a removal of the reaction products from the interfacial transition zone (ITZ), thus increasing pressure in the ITZ "cement paste – alkali-susceptible aggregate". This pressure may achieve 20 MPa [7] and the attained strength of the concrete in tension may reach only 3…5 MPa, thus resulting in microcracks and progressive degradation of concrete. Besides, the alkali which is released in the end of this reaction takes part in deterioration of the deeper layers of the alkali-susceptible aggregate grains. That is why, finally, an available content of the $Ca(OH)_2$ can serve to some extent as a restricting factor not allowing this reaction to damp. This can explain the reasons for more severe destructive effect in case of excessive quantities of the Na^+- and Ca^{2+}-ions compared to solely Na^+-ions;
- reduction of risk due to expansion is reached by introduction of active mineral additives of sedimentary and igneous origin (gaizes, zeolites, perlite, tuff, pumice, etc.) and those of man-made origin (fuel ashes, metallurgical slags, silica fume, etc.) in order to bind excessive quantities of calcium.

This problem becomes more and more serious since contents of alkalis in contemporary cements and concretes tend to increase due to the wider use of the cements with the higher quantities of sodium and potassium oxides as a result of high degree of cement kiln exhaust gas cleaning and return of the cement kiln dust back into the process. As a result, contents of alkalis in cements (in Na_2O_{eq}) tend to increase up to 1…2% by mass (against $\leqslant$0.6% by mass permitted under the standards). Also, of wider and wider use is a class of alkali activated cementitious materials (alkali activated slag cement, alkali activated portland cement, alkali activated slag portland cement, alkali activated pozzolana cement, geocement-based adhesives, etc.), the contents of alkalis in which (in Na_2O_{eq}) vary between 1.5% and 5% by mass [8–10]. And, at last, a quantity of alkalis in concrete tends to increase as a result of the wider use of chemical, mineral and organo-mineral additives containing alkalis.

For a long time the above views on the mechanism of ASR have been taken as a base for developing recommendations on how to prevent dangerous consequences of this reaction and to apply restrictions on a wider use of alkali activated cements which contain alkalis in much greater quantities, as is shown earlier, compared to those of traditional cements [11,12].

At the same time, some researchers have reported on the results of attempts to explain the processes of corrosion of alkali-susceptible aggregates in the presence of alkalis not only from the point of view of quantitative content of alkalis and free $Ca(OH)_2$. So, Malek and Roy [13] studied a role played by Al_2O_3 which is released from the feldspathoid stone through dissolution and found that with increase in the Al_2O_3 to SiO_2 ratio the ASR changes its character from a destructive for the constructive one. These findings coincide well with the results of the studies reported by Tang and Han [14]. Basing on them, Malek and Roy [15] draw a conclusion that elimination of hazardous effect of alkalis when a glassy slag was added to portland cement could be attributed not only to the lower permeability of slag pastes, but also to an ability of the slag to bind the alkali metal ions with the formation of insoluble alkaline aluminosilicate hydrates of the $Na_2O \cdot Al_2O_3 \cdot 5SiO_2 \cdot 5.4H_2O$ type. Further, the results of works reported in [16–19] showed that possible formation of the alkaline or mixed alkaline–alkaline earth aluminosilicate hydrates in the ITZ depended not only upon an aggregate type, but upon a composition of the aluminosilicate constituent of the alkali activated cement. A conclusion was made that by changing the Al_2O_3-content of the cement aluminosilicate constituent by introduction of the active Al_2O_3-containing additives the risk of destructive consequences of the ASR in the concretes made from the cements with high content of alkali could be brought to minimum.

The paper covers the results of study on behavior of aggregates from the alkali-susceptible rocks in the environment of various cement pastes, including the alkali activated cement pastes, and discusses ways of how to eliminate destructive processes in the concretes made from the cements with the increased alkali contents.

Moreover, a necessity of such studies was initiated by the increasing use of the alkali activated cements and concretes both in Ukraine and over the world.

2. Materials and examination techniques

Finely crushed dense rocks of polyfractional composition with the particle size between 0.5 and 10 mm were used in the study as potentially alkali-susceptible aggregates. Chemical composition of the selected aggregates is given in Table 1. A river quartz sand with a grading factor equal to 2 was used as fine aggregate in preparation of the reference specimens.

The following cements were used to study a behavior of the alkali-susceptible aggregates in the alkali activated cement concretes:

- portland cement Type ПЦ II/A-III with compressive strength = 400 kgf/cm^2 and 0.22% Na_2O_{eq} by mass (according to national standard of Ukraine);
- portland cement Type ПЦ II/A-Ш with compressive strength = 400 kgf/cm^2 and 1.3% Na_2O_{eq} by mass;
- alkali activated slag cement Type ШЦЕМ I (2.5% Na_2O_{eq} by mass);
- alkali activated slag portland cement Type ШЦЕМ IV (60% slag by mass) (2.5% Na_2O_{eq} by mass)
- alkali activated pozzolanic cement Type ШЦЕМ III-З (60% fly ash by mass) (2.5% Na_2O_{eq} by mass) [20].

Fineness of the cements under study expressed as a Blaine specific surface was 4400…4600 cm^2/g.

Chemical composition of the major cement constituents and metakaolin additive are given in Table 2.

Sodium carbonate and sodium metasilicate pentahydrate were used in the study as Na_2O_{eq}. They were introduced into the cement composition in dry form in the process of intergrinding and blending the cement constituents or in liquid form (aqueous solutions). Metakaolin was used as active mineral additive.

Water was used in preparation of the compositions in which the alkaline activator was introduced in dry form (W/C = 0.35–0.4).

Beam specimens (4 × 4 × 16 cm) were prepared for testing strength in compression and in flexure and prism specimens (2.5 × 2.5 × 28.5 cm) with copper bench marks – for testing deformations. The concrete mixture used in the experiments contained cement and aggregate taken as 1:2.25.

After 2 days the specimens were taken from the moulds and placed for further hardening in the corresponding conditions. A basic measurement was taken preliminary on the specimens intended for control of deformations (reference specimens). A device with indicating gage (division value = 0.01 mm) was used for taking measurements.

Table 1
Chemical composition of the aggregates used in the study.

Rock type	Chemical composition, % by mass								
	SiO_2	Al_2O_3	TiO_2	FeO	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Olivine	50.0	15.7	2.26	–	10.5	10.4	9.0	2.4	2.4
Basalt	50.4	12.5	2.5	9.4	8.5	9.3	5.7	2.2	0.9
Andesite	54.2	18.0	0.4	9.39		8.6	4.7	1.0	2.1
Perlite	72.8	12.5	0.11	0.9	3.4	1.07	0.17	2.1	4.5
Quartz sand	95.9	0.4	0.02	9.2	0.16	0.23	0.33	0.14	0.29

Table 2
Chemical composition of the cement constituents and metakaolin additive.

Constituent	Chemical composition, % by mass									
	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	SO_3	LOI
Granulated blastfurnace slag	40.0	5.91	0.32	0.50	5.87	46.98	0.64	0.5	1.62	–
Portland cement clinker	23.4	5.17	4.12	–	0.88	64.13	0.41	0.33	1.03	0.20
Fly ash	50.94	24.56	13.25	0.03	1.98	2.86	0.69	2.69	–	1.36
Metakaolin	55.05	35.4	4.27	–	0.92	3.01	–	–	0.28	0.07

Curing conditions for the specimens made with the alkali-susceptible aggregates were: $t = 38$ °C and RH $\approx 100\%$ (standard procedure), as well as long-term (for 28 days) continuous steam curing at $t = 70$ °C and RH = 100% (accelerated procedure) [21] and test ages were 14 and 28 days. When tested under the standard procedure, a critical expansion was >1 mm/m after 1 year, under the accelerated procedure- the results of measurements after 28 days were classified according to the following [22]:

(a) Expansion less than 1.5 mm/m – an aggregate is not alkali-susceptible one (no need to continue its testing).
(b) Expansion between 1.5 and 2.0 mm/m – an aggregate is alkali-susceptible (appropriate measures should be taken to reduce effect of reactive silica).
(c) Expansion higher than 2.0 mm/m – an aggregate is alkali-susceptible and is forbidden for the use in concrete (alternative aggregates should be selected).

Determination of fineness of raw materials and ready cements was done using a Blaine apparatus and expressed by a specific surface.

A full factorial experiment design with each factor having three distinct levels allowed to plot the isolines of shrinkage deformations depending upon quantity of the metakaolin additive and alkali content of the cement.

An expression proposed by Ladinsky was used to measure specific surface of the aggregate [23,24]

$$S = \left(16.5 \cdot \frac{K_{shape}}{1000}\right) \cdot (a + 2b + 4c + 8d + 16e + 32f) \qquad (1)$$

where K_{shape} is the coefficient reflecting the aggregate shape, that is a ratio of the largest size to the least size and a, b, c, d, e, f the residues on Sieves 2.5 (a); 1.25 (b); 0.63 (c); 0.315 (d); 0.16 (e);<0.16 (f), in%.

3. Results and discussion

3.1. Preliminary comparative analysis of alkali-susceptibility of the aggregates under study using various methods

First of all, a preliminary evaluation of the rocks under study with regard to their susceptibility/reactivity to alkali using various methods was done and its results are given in Table 3.

As it follows from Table 3, the results obtained using these methods correlate well.

Following the recommendations contained in [25], the aggregates can be classified as potentially alkali-susceptible ones if the soluble SiO_2-content in them is in excess of 50 mmol/l. Thus, analyzing data of Table 3, all rocks under study, with the exception of quartz sand and solid quartz, can be classified as *potentially alkali-susceptible ones*, and with regard to their susceptibility/reactivity to alkali they can be placed as the following: perlite > andesite > basalt > olivine > quartz sand > solid quartz.

A further comparative study was performed using these rocks on cement mortars with the application of two test procedures – the accelerated and standard ones, their results are shown in Fig. 1.

As it follows from Fig. 1a, the admissible contents of alkali ($Na_2O_{eq} \leqslant 0.6\%$ by mass) in portland cement are considered as not dangerous ones. According to basic measurements, no any expansion was found in all specimens, thus no need to apply appropriate technological measures or to introduce expansion-reducing additives.

The increase in the Na_2O_{eq}-content in the portland cement (reaching 1.3% by mass)(Fig. 1a) resulted in acceleration of the destructive processes in the ITZ and in case of the andesite rock as aggregate resulted in critical expansion values in excess of 2.0 mm/m (2.43 mm/m). The values of expansion of all other cements fall within the admissible limits.

The use of the alkali activated slag cements has no risk – in all cases the values of expansion (0.15...0.41 mm/m) are below the admissible values (Fig. 1a).

In case of the alkali activated slag portland cement (similar to portland cement with $Na_2O_{eq} = 1.3\%$ by mass), maximal and not admissible expansion values were found in the composition made with the andesite rock –2.9 mm/m (Fig. 1a).

Falling out of general regularity and standing aside are the results obtained in case of the perlite rock, which, despite its higher glass content, showed low values of expansion in all cements under study. This can be attributed to a fact that glass of the perlite rock contains active Al_2O_3 together with SiO_2, whereas the Al_2O_3 contained in other rocks is present in a crystalline form. Thus, the statement on alkali-reactivity of the rock containing more than 50 mmol/l of soluble silica (against 137.9 mmol/l of perlite) seems to be not valid (Table 3).Thus, summarizing these data allowed to accept for further studies the accelerated procedure which would provide rather useful

Table 3
Preliminary evaluation of susceptibility/reactivity to alkali of the rocks under study.

Rock type	Examination technique		
	Petrographical analysis	Chemical analysis	Phase analysis
	Glassy phase content, % by mass	Quantity of soluble SiO_2, mmol/l	Size of crystalline quartz of the rock, nm
Olivine	5–7	70.1	124.8
Basalt	17–19	92.3	114.1
Andesite	39–41	106.5	65.7
Perlite	95–97	137.9	12.0
Quartz sand	0.5–1	18.9	312.1
Solid quartz	–	–	390.0[a]

[a] Remark – according to [21].

information and validity of the results and above all, would allow to obtain the results within a short period of time.

3.2. Effect of the metakaolin additive on expansion of the concretes made with the alkali-susceptible aggregates

A metakaolin was added to the alkali activated cement composition in a quantity of 15% by mass in order to minimize a risk of destructive processes in the ITZ.

The effect of the metakaolin additive on expansion deformations of the concretes under study is shown in Fig. 2. As it follows from Fig. 2a, not admissible high expansions were found in the concretes made from portland cement with the increased content of Na_2O_{eq} (1.3% by mass) and from the alkali activated slag portland cement with $Na_2O_{eq} = 2.5\%$ by mass in case of the andesite rock as aggregate.

Reaction products in the ITZ and microcracks on the aggregates in the concretes from the portland cement with the increased content of Na_2O_{eq} (Fig. 3a–c) and from the alkali activated slag portland cement are clearly seen in the microphotographs (Fig. 5a). The use of the alkali activated slag cement is found to have no risk since the ITZ "cement paste – alkali-susceptible aggregate" remained clear (Fig. 4a and b).

Introduction of the metakaolin additive allowed to derive all concretes under study, not depending upon a cement type and aggregate type, not only from the zone of not admissible critical expansion and degradation, but from the zone at risk (Fig. 2a and b). The ITZ in this case is clear without any sign of corrosion (Figs. 3d, 4 and 5b). This may be attributed to the fact that the conditions are created in the ITZ for synthesis of the alkaline zeolite-like aluminosilicate hydrates of the general formula $Na_2O{\cdot}Al_2O_3{\cdot}mSiO_2{\cdot}nH_2O$, that is an intensive binding of the alkali in the presence of active Al_2O_3 and strongly alkaline environment.

Low expansion in case of the alkali activated slag cement even without the metakaolin additive can be attributed to the active Al_2O_3 contained in the slag glass along with the amorphous SiO_2.

The effect of the metakaolin and alkali contents on the rate of the ASR flow in the alkali activated slag portland cement concrete made with the andesite rock was studied with the help of a full factorial experiment design with each factor having three distinct levels [26]. Using a numerical model for the experiment design an adequate equation of regression has been produced. The results are shown in Fig. 6. As it follows from the figure, with increase in the alkali content the higher contents of the metakaolin are required to reduce expansion to admissible values. If to accept an expansion admissible value below 1/5 mm/m as recommended in [22], for the most typical contents of the alkali-activated cements falling within 2.5...4% by mass (calculated as Na_2O_{eq}), the metakaolin additive in quantities of 7...11% by mass seems to be enough.

The effect of the alkali activated cement type on development of the reaction in the ITZ was studied as well. The results are given in Table 4.

Comparing the expansion deformations of the alkali activated slag portland and the alkali activated pozzolanic (fly ash) cements allowed to draw a conclusion on better effect rendered by the fly ash contained in the cement composition on the ASR reduction. This can be attributed to the higher content of the active alumina of the fly ash compared to that of the slag (Table 2).

Moreover, by comparing effects of the active Al_2O_3-containing and active SiO_2-containing additives a conclusion can be drawn that the first listed additives are by 2 fold more effective ones compared to the latter additives. So, according to [27], 1 g of metakaolin can bind of about 1000 mg of lime, whereas ultrafine silica fume

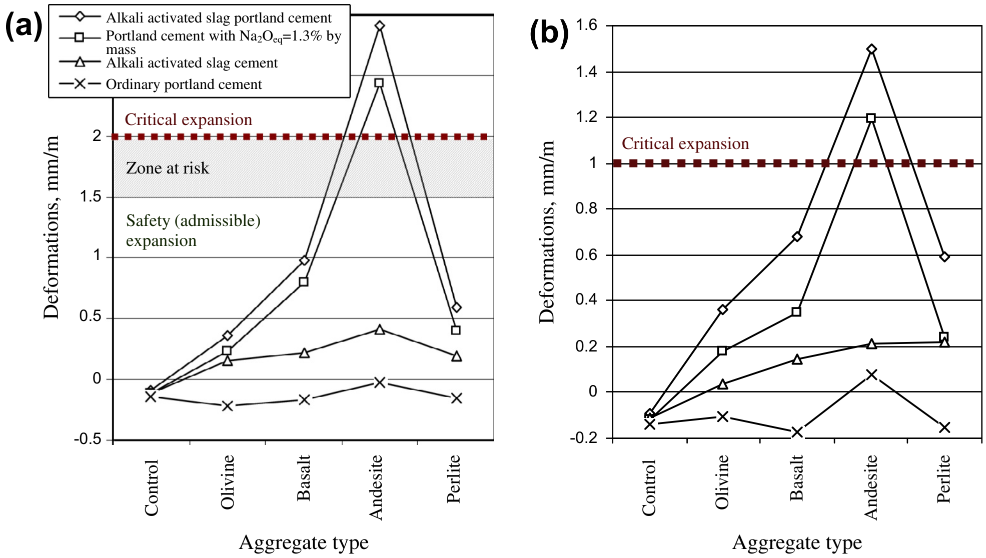

Fig. 1. Comparative test results obtained under: (a) Accelerated procedure (28 days of continuous steam treatment (*t* = 70 °C, RH = 100%)) at the age of 28 days; (b) Standard procedure (*t* = 38 °C, RH = 100%) at the age of 1 year.

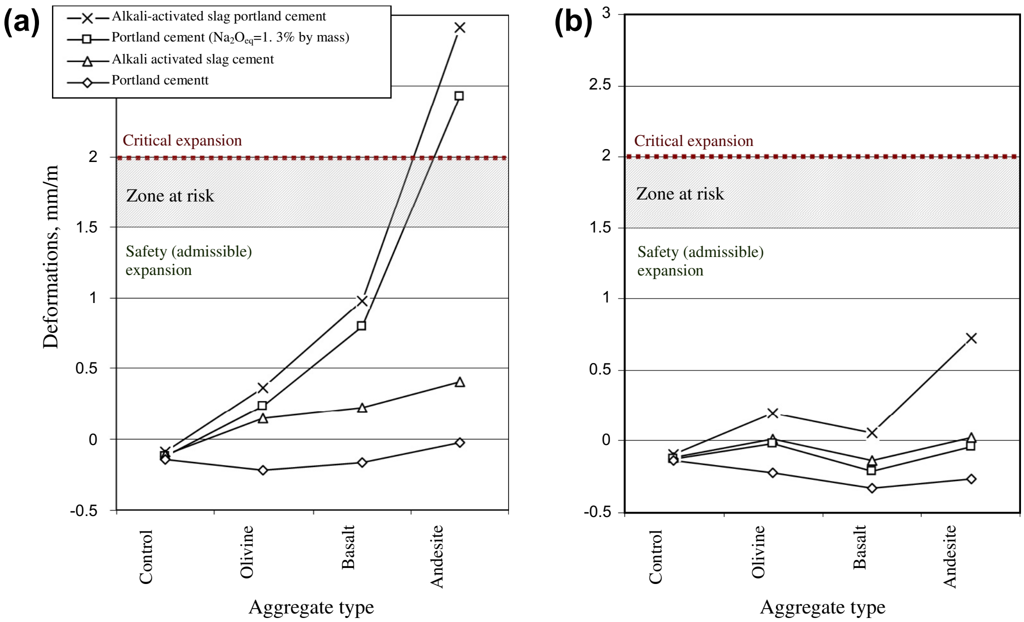

Fig. 2. Deformations of the concretes vs. aggregate type and metakaolin additive: (a) without metakaolin additive; (b) with metakaolin additive (15% by mass) (curing conditions–28 days of continuous steam treatment at $t = 70$ °C and RH = 100%).

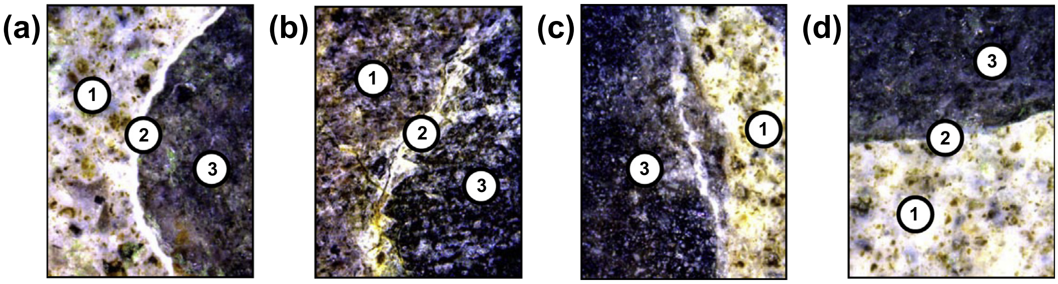

Fig. 3. The ITZ "cement paste – andesite" (cement: portland cement with the increased content of Na_2O_{eq} – 1.3% by mass): (a) cement without metakaolin additive; sign of corrosion in the ITZ; (b) cement without metakaolin additive; sign of corrosion and microcracks in the ITZ and cement paste; (c) cement without metakaolin additive; the ASR-exposed aggregate grain; (d) cement with metakaolin additive: (1) cement paste; (2) ITZ; (3) alkali-susceptible aggregate. *Scanning* electron microscopy images at ×500.

– only 350...450 mg. With regard to alkalis this difference is even more essential.

The results of study on effect of metakaolin and fly ash from the point of view of reduction of corrosion process in the ITZ "cement paste–alkali-susceptible aggregate" allowed to rate them as follows: metakaolin > fly ash.

3.3. Effect of aggregate grain size, type of the alkaline activator and method of its introduction into the concrete on development of the ASR

A sensitivity/reactivity of the alkali-susceptible aggregate to the ASR depending upon the aggregate grain size was studied as well. The results are given in Fig. 7. The grains of size 1.25...5 mm were

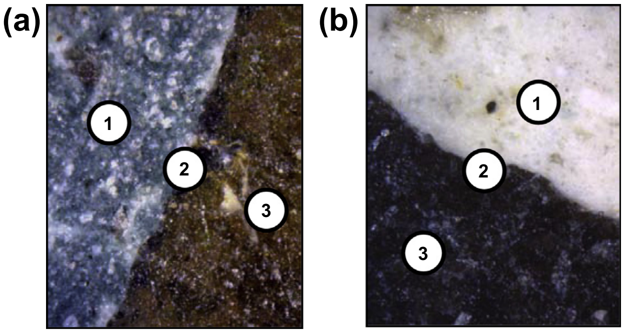

Fig. 4. The ITZ "cement paste – andesite" (cement: alkali activated slag cement with Na_2O_{eq} – 2.5% by mass) (a) cement without metakaolin additive; (b) cement with metakaolin additive: (1) cement paste; (2) ITZ; (3) alkali-susceptible aggregate. *Scanning* electron microscopy images at ×500.

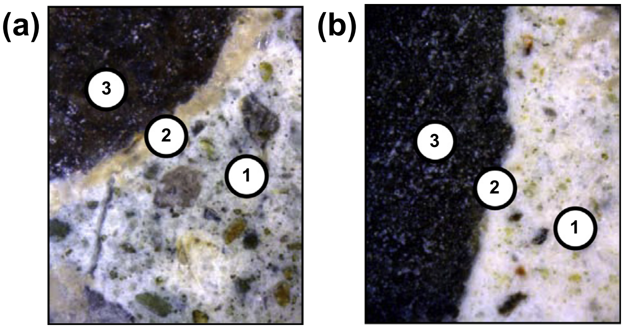

Fig. 5. The ITZ "cement paste – andesite" (cement: alkali activated slag portland cement with Na_2O_{eq} – 2.5% by mass) (a) cement without metakaolin additive; (b) cement with metakaolin additive: (1) cement paste; (2) ITZ; (3) alkali-susceptible aggregate. *Scanning* electron microscopy images at ×500.

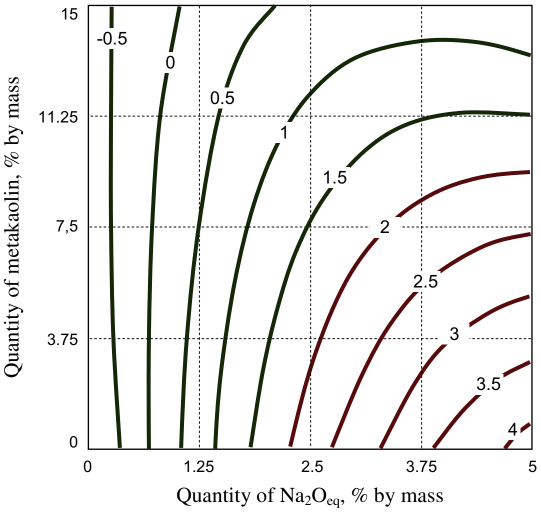

Fig. 6. Isolines of expansion deformations (mm/m) vs. quantities of metakaolin additive and alkali content of the cement (cement: alkali activated slag portland cement (portland cement clinker: slag = 40:60; aggregate – andesite).

found to be the most alkali-susceptible ones. The results of study suggested to conclude that fractions of the alkali-susceptible aggregates with the sizes <0.315 mm had no degradation effect on the ITZ "aggregate – cement paste" (Fig. 7a and b).

Then, in order to continue studies in this direction an interrelationship between the aggregate grain size, fineness of the aggregates expressed by a specific surface and their alkali-reactivity was established. The results are given in Fig. 8.

Maximal expansion was found in the concrete mixtures containing aggregates with particle sizes varying from 1.25 to 5 mm. This is to be taken into consideration in studying a susceptibility/reactivity of the aggregates to alkali and fine and dust-like fractions should be removed from the aggregates under study since they may skew the results.

From the other side, for concrete mixture designing and production this circumstance can play a positive role allowing to somewhat minimize risk of expansion.

Effect of a type of the alkaline activator on expansion is shown in Fig. 9. As it follows from the figure, the concrete compositions made with the sodium metasilicate showed somewhat lower values of expansion compared to those of the compositions made with the sodium carbonate. This may be attributed to the active SiO_2 present in the sodium metasilicate, which is capable at the early stages of hydration to bind partially free $Ca(OH)_2$ of the cement, thus resulting in the formation of not enough dense semi-permeable membrane composed from the CSH-gel and decrease in a quantity of the sodium silicate gel in the ITZ "cement paste-alkali-susceptible aggregate".

The results of study aimed to reveal effect of the method of introduction of the alkaline activator into the concrete mix, namely: in liquid form or in dry form, to other cement constituents with following mixing with water, suggested to establish that in both cases the values of deformations were similar.

3.4. Strength of the concretes made with the alkali-susceptible aggregates

Since a portion of alkali is bound by the metakaolin additive, strength of the concretes containing this additive at standard

Table 4
The ASR vs. alkali activated cement type (aggregate – andesite).

Metakaolin additive	Alkali activated pozzolanic cement (portland cement clinker: fly ash = 40: 60) Expansion, mm/m, after		Alkali activated slag portland cement (portland cement clinker: slag = 40: 60)	
	14 days	28 days	14 days	28 days
–	0.31	0.42	2.40	2.52
+	0.11	0.23	0.70	0.72

Remark: Curing conditions: 28 days of continuous steam treatment at $t = 70\ ^\circ C$ and RH = 100%.

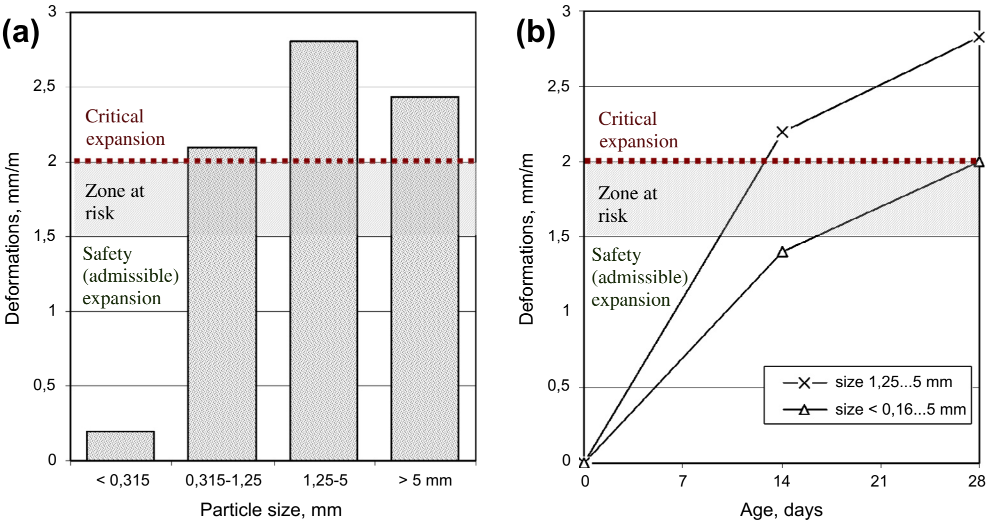

Fig. 7. The ASR development vs. particle size distribution of the aggregate under study: (a) effect of aggregate grain size on expansion of the concrete; (b) effect of polyfractional and monofractional compositions of aggregates (cement: alkali activated slag portland cement with $Na_2O_{eq} = 2.5\%$ by mass; curing conditions – 28 days of continuous steam treatment at $t = 70\ ^\circ C$ and RH = 100%; aggregate – andesite).

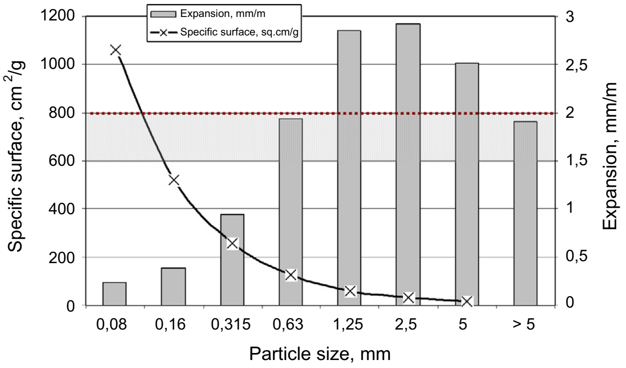

Fig. 8. The ASR development vs. aggregate grain size and specific surface (cement: alkali activated slag portland cement with Na$_2$O$_{eq}$ = 2.5% by mass; curing conditions – 28 days of continuous steam treatment at t = 70 °C and RH = 100%; aggregate – andesite).

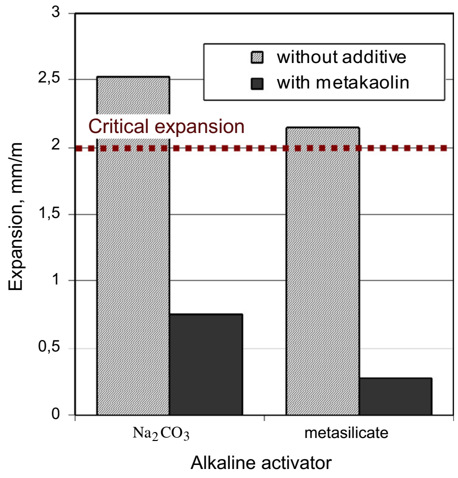

Fig. 9. Expansion of the alkali activated cement concretes vs. type of the alkaline activator (cement: alkali activated slag portland cement with Na$_2$O$_{eq}$ = 2.5% by mass; curing conditions – 28 days of continuous steam treatment at t = 70 °C and RH = 100%; aggregate – andesite).

specified ages can be somewhat lower (5…10%) compared to that of the concretes without the metakaolin additive. At the later ages (after 3…6 months), this difference is less and the higher strength is reported compared to that of the reference specimens due to deepening the hydration processes, synthesis of low-basic calcium silicate hydrates as well as synthesis of the zeolite-like and feldspar-like products.

The alkali metal oxides contained in the hydration products prevent their free migration to the surface, thus resulting in an essential reduction or complete elimination of the efflorescence on the surface of concrete and reinforced concrete structures.

3.5. Microstructure of the interfacial transition zone "cement paste – alkali-susceptible aggregate"

The elemental distribution in the ITZ "cement paste – alkali-susceptible aggregate" was studied. The results are given in Figs. 10 and 11.

The increase in content of the Ca in the ITZ "portland cement + -basalt" is an evidence of possible synthesis in this case of high-basic gel-like calcium silicate hydrates, the accumulation of which is found to increase the osmotic pressure and disturbance of the contacts between the aggregates and the cement paste (Fig. 10a). As it follows from the elemental distribution, the introduction of the metakaolin additive has reduced the calcium concentration in the ITZ (Fig. 10b). The increase in the Na and Al – concentrations, especially in the presence of the metakaolin additive, can serve as an indirect proof of possible synthesis of the alkaline aluminosilicate hydrates in the ITZ in case of the alkali activated slag cement (Fig. 11a and b).

Microhardness of the ITZ "cement stone – alkali-susceptible aggregate" shows if the ASR takes place. In case of the ASR-values of microhardness of the ITZ are low. The microhardness of the ITZ "cement paste – basalt bar" was studied with the help of a microhardness testing device and the results are given in Fig. 12.

The results of study allowed drawing a conclusion that the largest microhardness in the IT zones was in case of the alkali activated slag cement and the lowest – of portland cement. So, in case when the microhardness of the ITZ "portland cement – basalt bar" was equal to that of the cement paste and fell under the range of 640...660 MPa, that of the ITZ in case of the alkali activated slag cement was 3600...4100 MPa and the microhardness of the alkali activated cement paste was 3400…3600 MPa.

The obtained results coincide well with the below data of the X-ray phase analysis of the reaction products detected in the ITZ "cement paste – basalt":

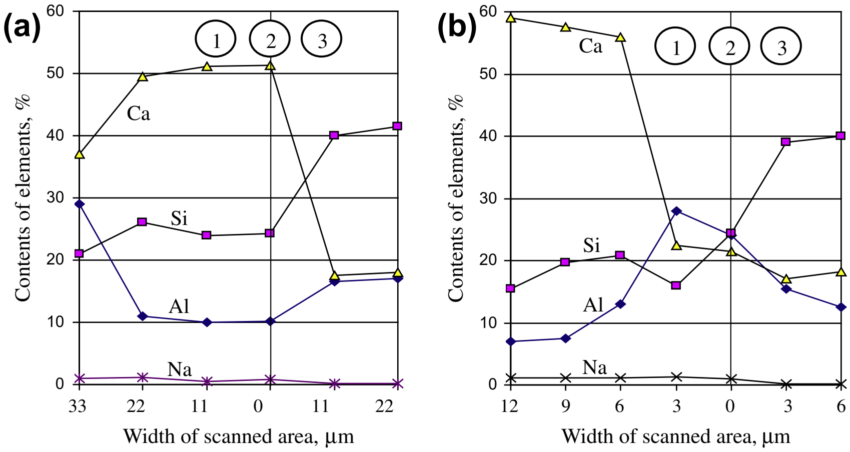

Fig. 10. Elemental distribution in the ITZ "cement (portland cement + water) – basalt bar": (a) without metakaolin additive; (b) with metakaolin additive: (1) cement paste; (2) ITZ; (3) basalt bar.

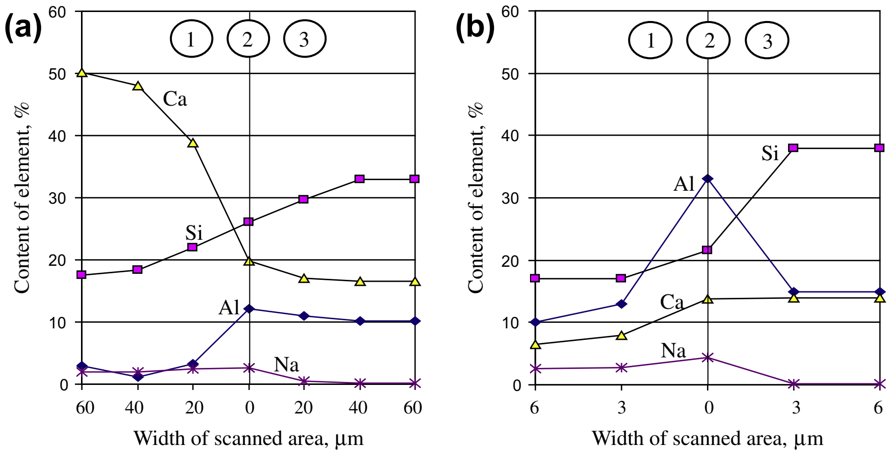

Fig. 11. Elemental distribution in the ITZ "cement stone – basalt bar" (cement: alkali activated slag cement (soluble glass as alkaline activator): (a) without metakaolin additive; (b) with metakaolin additive: (1) cement paste; (2) ITZ; (3) basalt bar.

"portland cement – basalt rock + H_2O"

- C_6S_3H (d = 0.335; 0.284; 0.246; 0.237; 0.225; 0.180 nm).
- C_2SH (d = 0.284; 0.270; 0.246; 0.190; 0.180 nm).
- C_3S_2H (d = 0.56; 0.284; 0.184 nm).
- $Ca(OH)_2$ (d = 0.487; 0.311; 0.261; 0.193; 0.18 nm).
- $CaCO_3$ (d = 0.303; 0.229; 0.210; 0.193; 0.188 nm).
- C_2AH_4 (d = 0.717; 0.376; 0.266; 0.258; 0.246 nm).

"portland cement – basalt rock + soluble glass"

- CSH(I) (d = 0.283; 0.270; 0.247; 0.179 nm).
- tobermorite (d = 0.56; 0.307; 0.299; 0.283; 0.227; 0.208; 0.183 nm).
- $Na_2O \times Al_2O_3 \times 4SiO_2 \times 2H_2O$ (d = 0.56; 0.343; 0.293; 0.252; 0.174 nm).
- $2Na_2O \times 2CaO \times 5Al_2O_3 \times 10SiO_2 \times 10H_2O$ (d = 0.654; 0.467; 0.353; 0.283; 0.270 nm).

"portland cement – basalt rock + soluble glass + metakaolin"

- CSH(I) (d = 0.283; 0.270; 0.247; 0.179 nm).
- tobermorite (d = 0.56; 0.307; 0.299; 0.283; 0.227; 0.208; 0.183 nm).
- $Na_2O \times Al_2O_3 \times 3SiO_2 \times 2H_2O$ (d = 0.653; 0.587; 0.436; 0.286; 0.219 nm).
- $Na_2O \times Al_2O_3 \times 4SiO_2 \times 2H_2O$ (d = 0.569; 0.343; 0.293; 0.251; 0.174 nm).
- $Na_2O \times 2CaO \times 5Al_2O_3 \times x10SiO_2 \times 10H_2O$ (d = 0.654; 0.467; 0.353; 0.285; 0.269 nm).

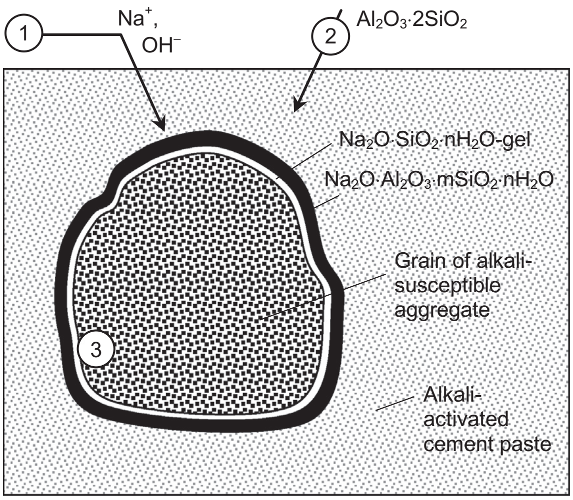

Fig. 13. Schematic representation of the ASR with the constructive effect of corrosion in case of the alkali activated cement stone: (1) diffusion of ions from the alkaline activator solution to a place of reaction; (2) the metakaolin additive; (3) ion exchange and ion reaction.

A schematic representation of the ASR taking place in case of the alkali activated cement paste with a "positive" effect of corrosion is given in Fig. 13.

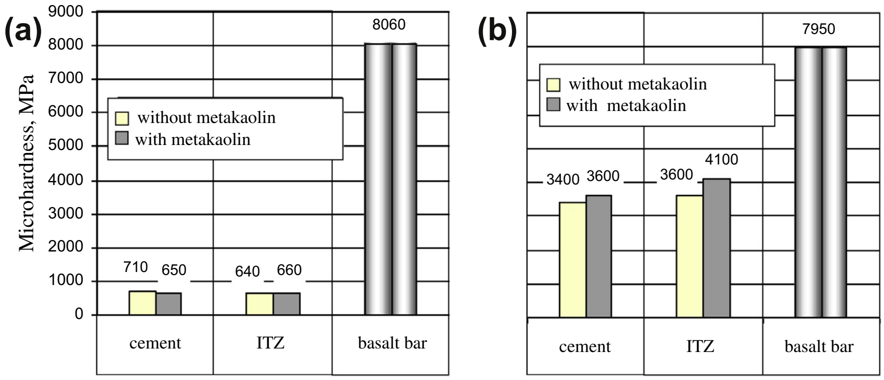

Fig. 12. Microhardness of the ITZ "cement stone – basalt bar": (a) portland cement + water; (b) alkali activated slag cement (soluble glass as alkaline activator).

The active alumina can get into the alkali-activated cement within the active mineral substances like granulated blastfurnace slag, fly ash or metakaolin.

As it follows from the scheme (Fig. 13), the alkali metal gel ($Na_2O{\cdot}SiO_2{\cdot}nH_2O$)- a product of reaction between the alkali and the alkali-susceptible aggregate- is an intermediate product and a consumable material (reserve) for synthesis of the zeolite-like ($Na_2O{\cdot}Al_2O_3{\cdot}mSiO_2{\cdot}nH_2O$) dense, sound and impermeable shell around the aggregate grains, which stops further development of the destructive reaction.

4. Conclusions

The results of the study suggest that alkali-susceptible aggregates could be used in the alkali activated cement concretes without any risk. Above all, the results showed that the active alumina (metakaolin and fly ash) in the alkali activated cements had a favorable effect allowing to effectively control the structure formation process in the interfacial transition zone "cement paste – alkali-susceptible aggregate" and to reduce expansion down to admissible levels or completely avoid it. This ensures reliability and durability of alkali activated cement concretes, and reinforced concrete products and structures, with respect to this form of deterioration.

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