THE COURSE OF THE ALKALI-AGGREGATE REACTION IN THE PRESENCE OF LITHIUM NITRATE

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Lithium nitrate is recognized as a chemical compound capable of inhibiting the alkali-silica aggregate reaction. The extent to which the reaction is inhibited or limited is affected by the amount of the applied lithium compound and by the kind of reactive aggregate that has been used. In the case of the polymineral aggregate this process is particularly complex, as the alkali-silicate reaction may be accompanied by other alkali-aggregate reactions, i.a. the alkali-carbonate reaction. The paper presents the results of the investigation on the effect of lithium nitrate on the course of the alkali - reactive gravel aggregate reaction. The investigation was conducted in accordance with ASTM 1260 standard. The investigation results showed that lithium nitrate, when applied in appropriate amount, inhibits the process of mortar samples expansion. The appearance of spalls in the samples modified with a lithium compound indicates the occurrence of two reaction types: alkali-silica and alkali-carbonate.

INTRODUCTION

The interaction between aggregate and cement paste enhances concrete strength and thus its functional properties. On the other hand, the interaction between aggregate and paste is known to have negative effects as well. One should mention here the reaction between aggregate and alkalis (present in cement), which cause concrete expansion and cracking. The most significant alkali-aggregate reactions are alkali-silica reaction and alkali-carbonate reaction, which are caused by different factors [1, 2].

There are several methods of preventing the destructive reaction occurring between alkali and aggregate, such as the application of cement with very low alkali content or cement containing puzzolana additives. Reference sources indicate also that one of the methods of inhibiting the reaction is introducing lithium compounds into the material [3,4]. The paper attempts at evaluating the effect of the lithium nitrate additive on the course of the alkali-aggregate reaction for mortar samples prepared from reactive gravel aggregate and from Portland cement with varied alkali content.

The alkali-silica and alkali-carbonate reactions

The alkali-silica reaction occurs between aggregate containing reactive silica in its amorphous or poorly crystalline form, and alkali contained in the concrete pore solution. In the case of the alkali-silica reaction the reactive components include i.a. opal, obsidian, cristobalite, tridymite, chalcedon, hornstone, quartz, metamorphic quartz in the state of stress.

Reactive components reacting with alkali produce an expanding sodium-potassium-calcium silicate gel. There are several hypotheses with regard to the destruction of concrete by the products of alkali-silica reaction. It is believed that for concrete destruction to take place the necessary condition is the presence of reactive silica, as well as sodium, potassium and calcium ions. It is assumed, i.a. that the process of rims appearing around reactive aggregate particles contributes to concrete destruction. The rims are formed as a result of the sodium-potassium gel being enriched with calcium ions. As hydrozol, sodium and potassium ions can further pass through the rim around the aggregate particulates, the process of further silica depolymerization is observed. This leads to building up of considerable pressure in the aggregate grain, entailing the occurrence of cracks in the cement paste surrounding the grain [5].

Another destructive reaction is the alkali - dolomitized limestone one. In this case it is the swelling of clay minerals, present in carbonate rocks, that is responsible for concrete destruction. For the process to occur it is necessary that dolomite decomposition should take place first, even though the decomposition alone does not induce expansion. Nevertheless, the dolomite decomposition causes the formation of a network of pores and capillaries through which water gets easier access to clay minerals [1]. Some scientists claim, however, that it is the presence of a small amount of reactive silica that

accounts for concrete destruction in the case of carbonate aggregates, and thus they attribute an important role to the alkali-silica reaction here [6, 7].

The effect of lithium nitrate on the course of alkali-silica reaction

The first attempts to inhibit the destructive alkali-reactive aggregate reaction by using lithium compounds were taken in the middle of the 20th century by McCoy and Cadwell [8]. The results of the further investigation revealed that lithium compounds such as LiOH, LiCl, LiF, Li_2SO_4, $LiNO_3$, Li_2SiO_3, Li_2CO_3 are the most effective ones in this process. It was also discovered that the minimum molar ratio of lithium ions to alkali ions, necessary to inhibit the destructive reaction, is 0.74. The amount of the introduced lithium compound is determined, however, by the amount of the applied aggregate and by its reactivity level, as well as by the kind of the lithium compound. Diamond and Ong [9], among others, claimed that the inappropriate amount of the applied lithium, especially lithium carbonate or lithium hydroxide, may cause concrete destruction. The phenomenon results probably from the increased pH of the concrete pore solution. Kawamura's works related to this issue [10] demonstrate that increasing the amount of the applied lithium compounds to 1.5 % can inhibit the expansion. It was also discovered that among the analysed lithium compounds, it is the lithium nitrate $LiNO_3$ [11, 12] that has the greatest potential to inhibit the alkali-aggregate reaction. In comparison with lithium fluoride, carbonate or hydroxide, this compound does not raise the pH value, does not have a negative effect on the material's freeze resistance or its mechanical properties, and it does not evoke drying contraction [13].

Unfortunately, the effects of lithium nitrate on the course of reaction are not thoroughly explained. There is a hypothesis, according to which the inhibiting effects that lithium has on the alkali-silica reaction is connected with the increased stability of the reactive silica, due to a lower pH of the paste pore solution after the application of lithium compounds.

Another mechanism is based on increasing the aggregate stability by changing the chemical composition of the pore solution. Lawrence and Vivian [14] state that the solubility of silica is determined by the type of cation present in the hydroxide. The greatest extent of dissolution is achieved with the application of potassium hydroxide, with sodium hydroxide giving a smaller effect and lithium hydroxide – the smallest one. Further investigation showed that as the size of the hydrated cation grows, the silica washability decreases. The size of the hydrated ions grows in the following order: $K^+ < Na^+ < Li^+$. In the case of lithium, its hydrated ion is bigger than the hydrated ions of potassium or sodium, which contributes to a greater silica stabilization and thus limits the formation of the expansive sodium-potassium-calcium silicate gel.

It is also postulated that the increased silica stability is connected with the emergence of a layer formed by a lithium compound with silicon in its crystalline form (lithium silicate crystals) or its amorphous form (gel) on the surface of silica aggregate. An insoluble layer formed on the grain surface provides a barrier protecting silica from the further attack by alkalis [15].

Another hypothesis does not link the diminished negative reaction effects with the increased silica stability. It claims, however, the emergence of crystalline or amorphous compounds containing lithium. Since the lithium ion is the smallest cation in the first group of the periodic table, it has a smaller radius in comparison with a sodium or potassium cation and simultaneously, a denser surface charge, therefore it becomes faster incorporated into the alkali-silica gel than sodium or potassium ions. The alkali-silica gel enriched with lithium cations takes the form of a less expansive or non-expansive product [16].

The theory of a double layer formed on or near the surface of the aggregate grains should also be dealt with. This layer is composed of negatively charged molecules of the silica gel and positively charged layer of ions in the paste. The thickness of both layers depends on the kind of ions that form them, on the charge of both layers and on the pore solution composition. Since the hydrated lithium ion is larger than sodium or potassium ions, it should cause the largest gel expansion. Lithium ions are apparently immediately absorbed by the cement hydration products and are not available for the hydrated alkali gel [17].

Another likely mechanism assumes that in this case the presence of lithium ions has an increasing effect on the level of silica solubility. A stronger repulsion of colloidal silica molecules prevents its polymerization, which in turn limits the formation of expansive alkali-silica gel [18].

The effect of lithium nitrate on the course of the alkali-carbonate reaction

The effect of lithium nitrate on the course of the alkali-carbonate reaction has not been fully explained as well. Some scientists maintain that lithium compounds can serve as a factor distinguishing the alkali-silica reaction from the alkali-carbonate reaction [19, 20]. The results of the conducted investigation show that introducing lithium ions balanced by hydroxyl ions (in the form of fluoride, hydroxide or lithium carbonate) leads to increasing expansion level. Alkali hydroxides, causing the process of dedolomitization, lead to the formation of brucite, calcium carbonate and the carbonate of an alkali element. The reaction proceeds according to the formula (1).

$$CaMg(CO_3)_2 + LiOH \rightarrow CaCO_3 + LiCO_3 + Mg(OH)_2$$

$$(1)$$
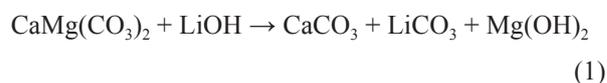
It is noteworthy to mention the fact, that the dedolomitization alone does not result in swelling but causes the volume decrease by 5.1 %. Additionally, products can crystallize in voids, or concrete cracks without inducing the cracking process. As mentioned above, it is maintained that the negative influence of lithium compounds is linked with loosening of concrete structure and with the fact that water has an easier access. At the same time, lithium carbonate produced in this reaction can lead to the volume growth by 48.87 % [21].

In the case of applying lithium nitrate the destruction of material connected with the pessimum effect should not take place, which is linked with the fact that pH does not grow after introducing lithium nitrate into the mix. Moreover, lithium ions introduced into the mix are balanced almost entirely by nitrate anions and only to a small extent by hydroxyl ions [22].

EXPERIMENTAL

Materials and methodology

Mortar samples were prepared according to the ASTM 1260 standard [23]. Portland cement CEM I with a chemical composition presented in Table 1 was applied. The applied cement was characterized by alkalinity reaching 0.66 % of the sodium equivalent. The post-glacial gravel aggregate was used as a reactive aggregate. The lithium compound used for mortar modification was lithium nitrate (analitically pure).

Nine series of mortars were made. The composition of mortar samples is presented in Table 2. A1,B1 and C1 series are reference series which were not modified with lithium nitrate.

The levels of alkali content were maintained at: 0.66 %, 0.9 % and 1.1 % of sodium equivalent.
The appropriate alkali participation was achieved by adding potassium sulphate into the mortar mix. The nitrate content expressed as the percentage of cement mass corresponded to the molar ratio Li/Na+K = 0.74. W/c ratio coefficient = 0.47.

The sample expansion investigation was conducted through a lengthened period of 30 days.

The samples of A1-C2 series were kept in 1 M solution of NaOH at the temperature of 80°C. The samples of A3-C3 series were kept in NaOH and LiNO$_3$ solution at the temperature of 80°C, with the molar ratio of Li/Na+K ions in the solution kept at the level of 0.74. X-ray analysis of mortar samples with lithium nitrate was conducted for cement with varied alkali content. The microstructure investigation was conducted by means of electron scanning microscopy with the microanalysis of X-ray radiation (SEM/EDS).

Gravel aggregate characteristics

Pastes were prepared from post-glacial gravel aggregate. According to the chemical analysis conducted in accordance with the PN-92/B-06714-46 standard [24], the content of the reactive aggregate included in the gravel aggregate was approximately 49 %. The results of the petrographic and X-ray analyses revealed that the reactive aggregate components include organodetritic sparite-micrite limestone, metamorphic quartz-pyroxene shale with opal binder, quartz-glauconite sandstone with clay-carbonate binder including some chalcedon, and quartz grains in the igneous rock (feldspar-biotite granite). The X-ray analysis revealed also a small amount of dolomite and the presence of clay minerals: illite and kaolinite.

RESULTS

The results of the investigation on the expansion of the modified and non-modified samples are presented in Figures 1 to 3 respectively.

The observed expansion values for samples of all the series A1-C2 exceed the value of 0.2 % (aggregate reactivity threshold), both for the reference samples and for those modified with lithium nitrate. The increase of the alkali content in mortar samples does not have a significant influence on the observed expansion values.

Table 1. Chemical composition of cement.

Material	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	K$_2$O	Na$_2$O	TiO$_2$	LOI	N.s.p.	Na$_2$Oeq
Cement	20.20	4.80	3.00	61.70	1.80	2.70	0.78	0.15	0.45	3.00	1.00	0.66

LOI - loss of ignitron, N.s.p. - parts non-soluble in HCl and Na$_2$CO$_3$

Table 2. The composition of mortar samples.

Series designation	A1	B1	C1	A2	B2	C2	A3	B3	C3
% Na$_2$Oe in the mortar	0.66	0.9	1.1	0.66	0.9	1.1	0.66	0.9	1.1
% LiNO$_3$ in the mortar	–	–	–	1.1	1.5	1.8	1.1	1.5	1.8
Solution for keeping samples			NaOH					NaOH+LiNO$_3$	

The samples with the alkali content of approximately 0.9 % manifested the highest expansion value. In the case of the samples modified with lithium nitrate one could observe a large number of cracks and spalls. The conducted X-ray analysis of the spalls revealed the presence of small amounts of magnesium hydroxide and ettringite, and considerable amounts of quartz and calcspar (Figure 4).

Figure 4. X-ray analysis of spalls obtained from mortar samples modified with lithium nitrate.
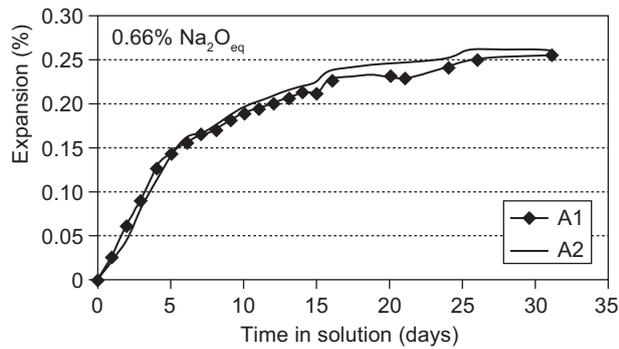
Figure 1. The expansion of mortar samples of the A1 series (without the lithium additive) and of the A2 series (with the lithium additive).
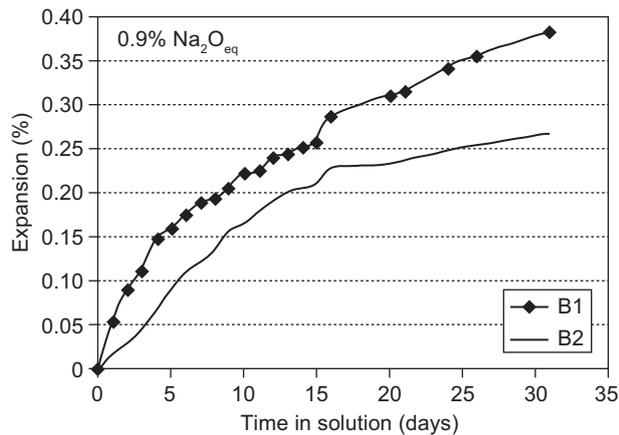
Figure 2. The expansion of mortar samples of the B1 series (without the lithium additive) and of the B2 series (with the lithium additive).
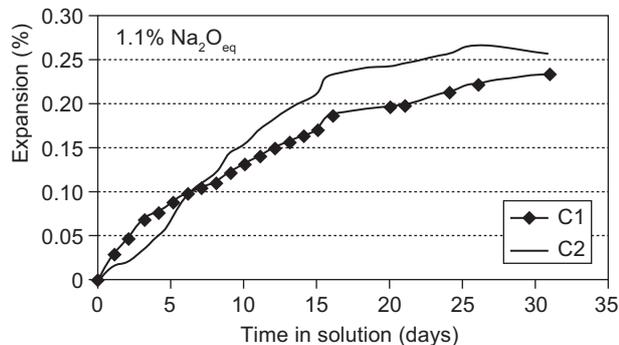
Figure 3. The expansion of mortar samples of the C1 series (without the lithium additive) and of the C2 series (with the lithium additive).

a)

b)

Figure 5. The alkali-silica gel observed on the surface of aggregate grains in the C2 sample; a) SEM ×2000, b) Gel composition (EDS).

In the samples modified with lithium nitrate (C2) one could observe the appearance of an amorphous alkali-silica gel rich in sodium and calcium (Figure 5) as well as the appearance of a crystalline form of the gel with a lower content of Ca ions than the amorphous form, but with a similar content of Na ions (Figure 6).

In the case of samples modified with lithium nitrate, kept in the solution of sodium hydroxide with lithium nitrate, the expansion process did not occur (Figure 7). In this series, however, mortar samples had spalls on their surface, which were nevertheless finer and appeared in a smaller number than in the case of the samples of A2-C2 series. One could also notice a small number of fine cracks.

When subjected to a microscopic analysis, the spalls from an A3 sample revealed a crack network, and the grain surface – a product rich in Ca and Na ions, with a smaller participation of Si than in the case of mortar samples with lithium additive (series A2-C2) (Figure 8).

The analysis of some amount of the mortar collected from the inside of the C3 mortar sample (lithium nitrate in the mortar and in the solution) revealed the presence of a crystalline product rich in Ca, Si, Al, with a small number of Na and K ions (Figure 9). Products with a smaller content of potassium ions and a larger content of sodium, aluminum, magnesium and iron ions are located at the ridge of voids (Figure 10).

a)
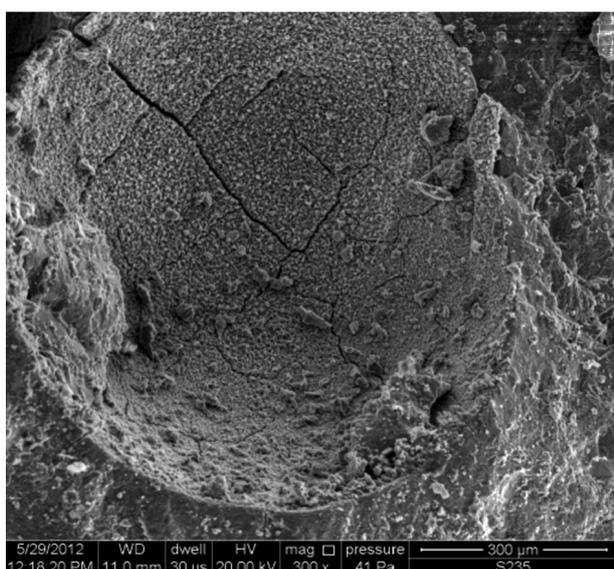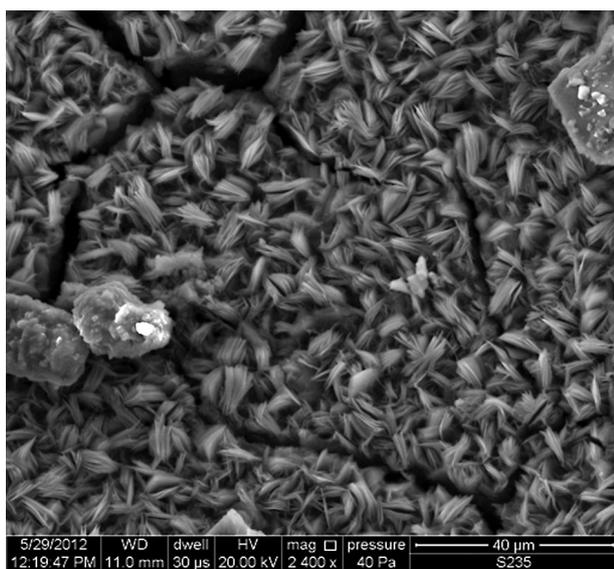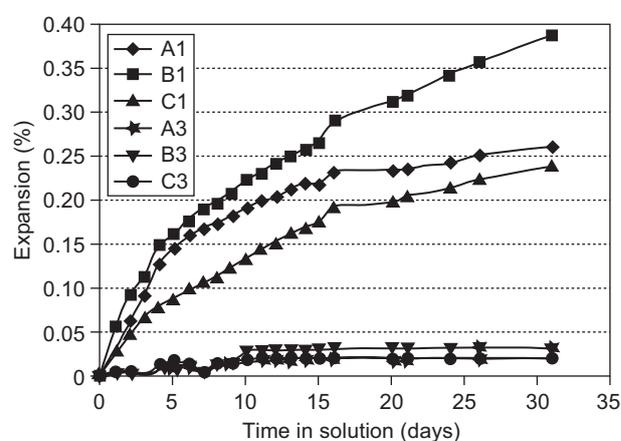
Figure 7. The expansion of mortar samples of A1-C1 series (without lithium additive) and A3-C3 series (with the additive of lithium nitrate in the mortar and in the solution).

b)
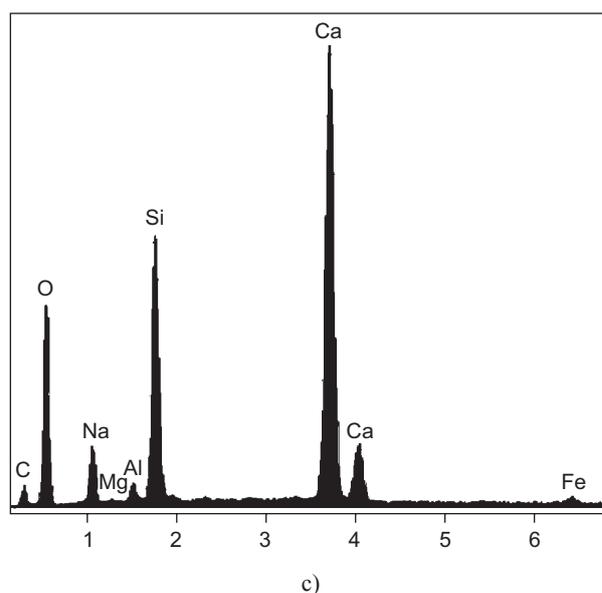
c)

Figure 6. A void in the cement paste filled with the products of the alkali-silica reaction. The sample C2; a) SEM ×300, b) SEM ×2400, c) Gel composition (EDS).
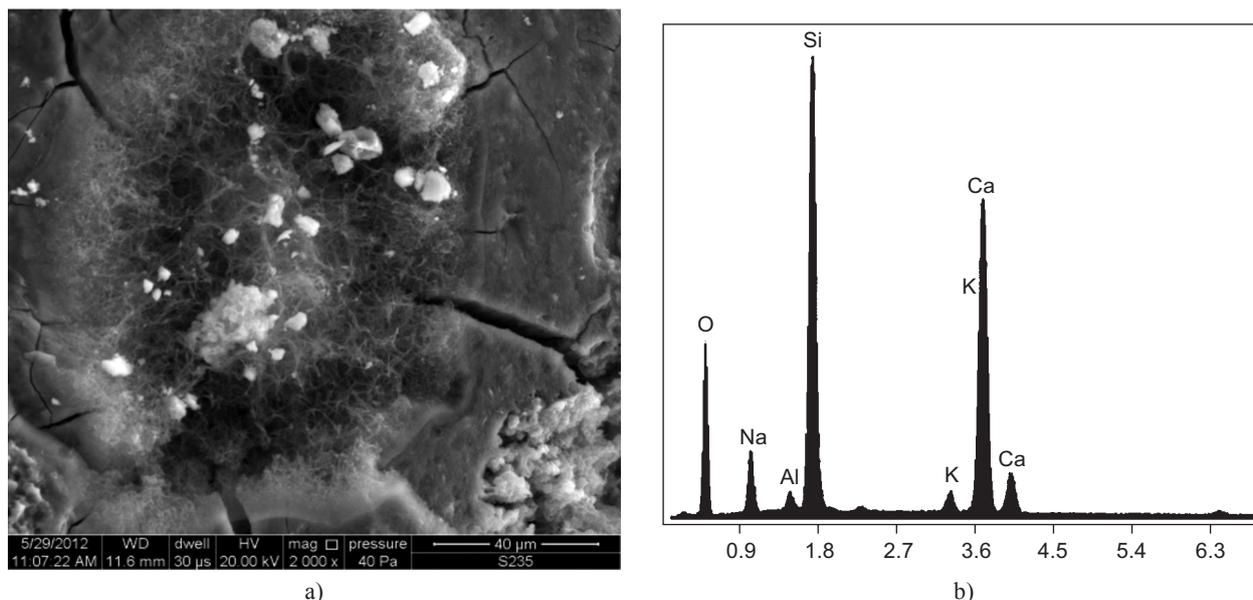
Figure 8. The alkali-silica gel observed in an A3 sample; a) SEM ×6000, b) Gel composition (EDS).

DISCUSSION

The conducted investigation revealed that there is no linear dependence between expansion values for mortar samples with varied alkali content. Neither did the applied lithium compound in the form of nitrate influence the decrease of expansion level of samples with reactive gravel aggregate and alkali content at the level of 0.66, 0.9, 1.1 % of Na_2O_{eq} (series A2-C2). In the samples of A2-C2 series a considerable expansion and appearance of spalls were observed. X-ray analysis of the spalls revealed the presence of brucite and ettringite. The emergence of brucite indicates the alkali-carbonate reaction. Probably, in the microcracks resulting from the alkali reaction emerged a secondary ettringite, which, being an expansive product, led to the appearance of a spall. One may suppose that the amount of lithium nitrate was too small to inhibit the alkali-silica reaction. A significant number of lithium ions (app. 40 %) can be bound in the cement hydration products. Thus the process results in a limited effectiveness of lithium ions, present in smaller numbers in the pore solution. The presence of lithium ions in the solution is necessary to build them into the alkali-silica gel. In addition, there is a risk that in the samples investigated with an accelerated test in high temperature lithium may be washed away.

The analysis of the applied gravel aggregate showed that the alkali-silica reaction is also accompanied by the alkali-carbonate reaction. Judging by the results of the investigation on the effect of lithium compounds on the course of the alkali-carbonate reaction [21], one could expect that lithium nitrate will increase the mortar sample expansion. However, in the case of the samples of the A3-C3 series, the expansion process did

not take place, but there appeared a small number of spalls. The lack of sample expansion can be explained by the fact that lithium ions, being included in the alkali-silica gel, decrease its expansive properties. The kind of the emerging gel depends on the content of calcium and lithium ions. According to the theory postulated by Feng [11] as the content of lithium ions in the sample increases, so does its participation in the Ca–Na–K–Si gel, with calcium content being low.

With lithium content progressively decreasing, the gel becomes gradually enriched with calcium ions, until finally with a lack of lithium in the mix the gel becomes expansive. However, in the case of the analysed samples this theory is not confirmed as the analysed gel contains a significant number of calcium ions. Unfortunately lithium is too light an element and it cannot be detected by means of the scanning electron microscopy with the X-ray radiation microanalysis (SEM/EDS). It may be supposed that the emerging gel as well as the crystalline form create dense non-absorbing water layers, not characterized by high mobility [25]. On the basis of the X-ray analysis results it may be stated that introducing lithium compounds into samples affects the extent of silica washability. The analysed gels in the samples of the series A3-C3 contain smaller amounts of silica than the alkali-silica gels observed in the samples of the series A2-C2.

The appearance of considerable amounts of iron in the gel (sample C3) may be connected with the release of iron from the aggregate as a result of dissolution or transformation of minerals containing iron and easily complexed in the solution of alkali hydroxides. At the same time, a high content of calcium ions in the products filling voids in the presence of sodium and potassium

ions can indicate the presence of calc-spar produced in a reaction between portlandite and sodium hydroxide – the product of dedolomitization with sodium hydroxide. Whereas the analysed sample series did not undergo expansion, there appeared small spalls. Supposedly, this phenomenon is connected with the crystalization of lithium carbonate, the production of which is the effect of lithium hydroxide interacting with mortar. The presence of lithium hydroxide can be explained by the fact that lithium ions were not fully balanced by nitrate ions. Moreover, the solution in which samples were kept manifested a high content of sodium hydroxide. It should also be remembered that the very dedolomitization is not

an expansive process but the production of solid lithium carbonate leads to the growth in volume of 48.67 %. The issue of evaluating the effect of lithium on the course of alkali-gravel aggregate reaction requires further investigation. It should be added that ASTM C1260 method may not be appropriate for defining the effect of lithium compounds. The conditions in which the experiment was conducted, i.e. high temperature and a considerable content of sodium hydroxide in the solution may result in a different effect of lithium compounds on the course of the alkali reaction than in the case of real structures.

CONCLUSIONS

Based on the above study the following hypotheses could be proposed:

1. The addition of lithium nitrate can suppress the expansion caused by the alkali- aggregate reaction,

2. The X-ray elemental analysis of the microregions indicates that the gel formed in the lithium-modified samples contains a significant number of calcium ions. There are cracks in the superficial layer, but no expansion was observed. It could be suggested that the modified samples contain the alkali silica gel,

3. The inhibition of the alkali-gravel aggregate reaction by lithium compounds is a difficult process due to the fact that the alkali-silica reaction may be accompanied by the alkali-carbonate reaction.
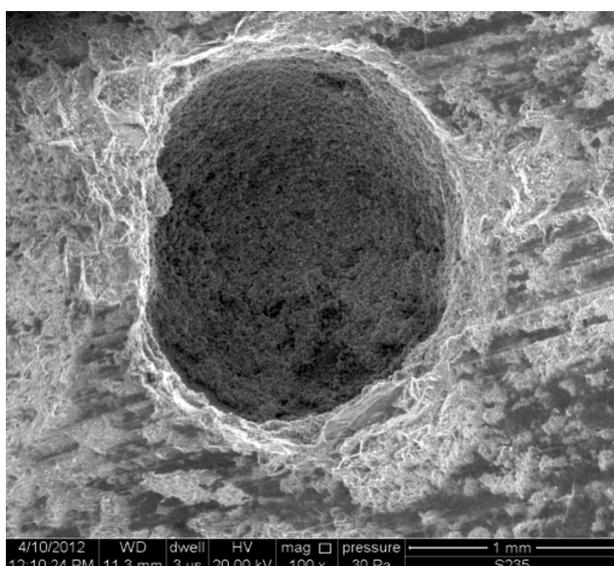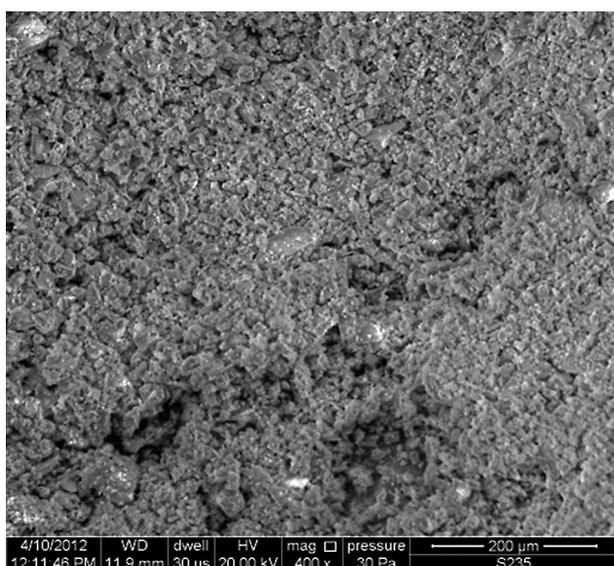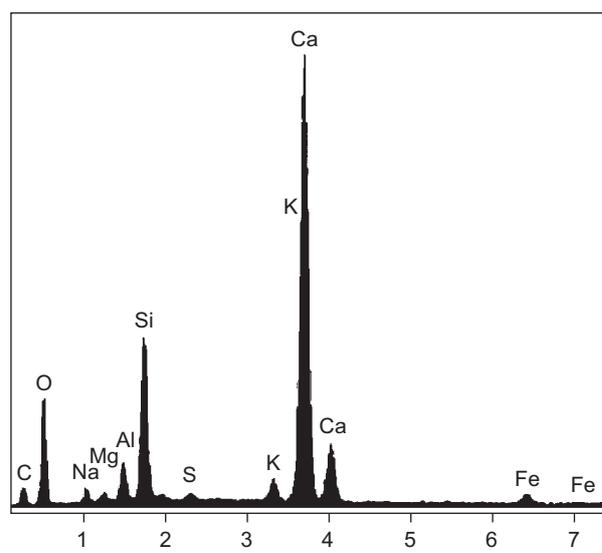
Figure 9. A avoid in the cement paste filled with a crystalline reaction product (sample C3); a) SEM ×100, b) SEM ×400, c) Gel composition (EDS).
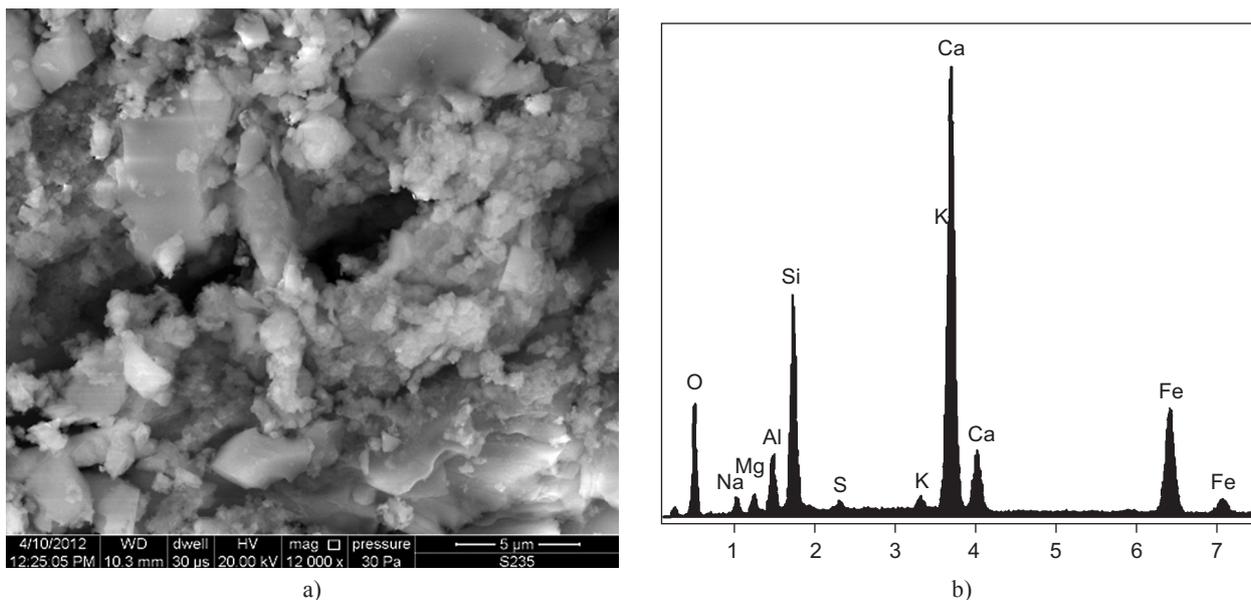
Figure 10. A reaction product at the edge of a void (sample C3); a) SEM ×12000, b) Gel composition (EDS).

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