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The Alkaline Reactivity of Opal in Mortars Modified with Lithium Nitrate

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Abstract

Preventing the destructive reaction between reactive aggregate and sodium and potassium ions in concrete pore solution is vital for the maintenance of concrete durability. There are several methods of preventing this adverse reaction, such as the application of cement with pozzolanic additives. Several papers also indicate the high efficiency of lithium compounds in mitigating the alkali-aggregate reaction.

The aim of this study was to determine the effect of lithium nitrate on the reaction between opal and alkali in mortar bars. The mortar samples contained alkalis of two different concentration levels.

Lithium nitrate was applied at a fixed molar ratio of lithium to sodium and potassium ions. Expansion studies were conducted in accordance with the methodology included in the ASTM C1260 standard. The modification of samples with lithium nitrate contributes to the decrease of expansion both for the low alkali cement and high alkali cement. The microstructure of mortar samples, both modified and non-modified with lithium nitrate, was examined and X-ray microanalysis was performed.

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1. Introduction

The application of lithium compounds to mitigate alkali silica reaction was first investigated by McCoy and Caldwell in 1950s [1]. Among over hundred lithium compounds such as LiCl, LiOH, Li₂CO₃, LiNO₃, Li₂SO₄ and the others, lithium nitrate was discovered to have the highest potential to inhibit the alkali silica reaction [2-3].

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Lithium nitrate is well soluble in water and does not increase pH in the pore solution. However, applying an insufficient amount of lithium ions can lead to the increase in the expansion level, due to the alkali-silica reaction, especially when the concentration of hydroxyl ions in pore solution increases. It can be attained when lithium ions are balanced by hydroxyl ions in pore solution. This effect was observed by Ong [4] when lithium ions were added in the form of carbonate or fluoride salt. In the case of applying lithium nitrate this effect does not occur because lithium ions introduced into the mix are balanced almost entirely by nitrate ions and only to a small extent by hydroxyl ions [5].

The effect of lithium nitrate on the expansion reduction is reliant on the amount of the applied salt. The amount of lithium nitrate which is inserted into the concrete or mortar depends mainly on two factors:

-the alkali content in cement expressed in lithium to alkali molar ratio. Usually, the sufficient amount of Li/Na+K equals 0.74, but a significant number of lithium ions, approximately 40%, can be bound in cement hydration products [6]

-the type and the structure of reactive aggregate. A highly reactive aggregate usually requires a higher Li/Na+K molar ratio in order to inhibit the expansion. The type of the aggregate is not the only factor, a significance role is also played by a textural structure. Feng and others discovered that the access of lithium ions to reactive form of silica is different when reactive particles are embedded in a dense matrix of nonreactive minerals. Thus, the more limited access to reactive silica, the less efficiency of lithium in inhibiting the alkali-silica reaction [7].

The mechanism in which lithium nitrate is effective against the alkali-silica reaction is still far from explanation. Several mechanisms have been proposed to explain the impact of lithium compounds on the alkali-silica reaction. Certain hypotheses refer to the fact that silica increases its stability due to the formation of a dense layer of lithium silicate on the surface of grains. Other hypotheses draw attention to the repolymerization of the ASR gel, still others to the modification of the sodium-potassium-calcium silicate gel with lithium ions leading to the emergence of non-expansive gel [8-10].

The paper presents the results of the investigation on the effect of lithium nitrate on the changes in alkaline reactivity of opal. In addition, the impact of the increased amount of alkali on the level of expansion and the structure formation of mortars modified by lithium nitrate were both investigated.

2. Materials and methods

The materials used for this study included Portland cement CEMI with chemical composition presented in table 1. The applied cement was characterized by alkali content of 0,66% of the sodium equivalent (Na_2O_e) and it was considered as low alkali cement. The high alkali cement was obtained by adding potassium sulphate to the mix water. The alkali content was increased to the value of 1,1% of Na_2O_e . Opal of the 0,5-1 mm fraction was applied in the amount of 6% of the aggregate mass, the aggregate included 94% of standard quartz sand with the grain size of 0-4mm.

Table 1. Chemical composition of cement

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO ₂	LOI	Cz.n.r.	Na_2O_{eq}
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 ignition

N.s.p. - parts non-soluble in HCl and Na_2CO_3

All mortar bars were prepared according to the ASTM C1260 standard [11]. Lithium nitrate was introduced with the molar ratios of 1,0 Li/Na+K ions. Mortar bars unmodified with lithium nitrate were also prepared. The samples were stored at the temperature of 80°C. Unmodified samples were kept in 1M NaOH and modified ones in NaOH and LiNO_3 solution with the same Li/Na molar ratio as in the mortar bars. Mortar samples expansion was examined to define the effect of lithium nitrate on the change of the opal aggregate reactivity.

The microstructure of samples was examined using the scanning electron microscopy with the X-ray microanalysis (SEM/EDX).

3. Results

3.1 Mortar samples expansion

Fig. 1. and Fig. 2. show the expansion testing results for unmodified samples and the samples modified with lithium nitrate. The expansion was measured for an extended period of 28 days.

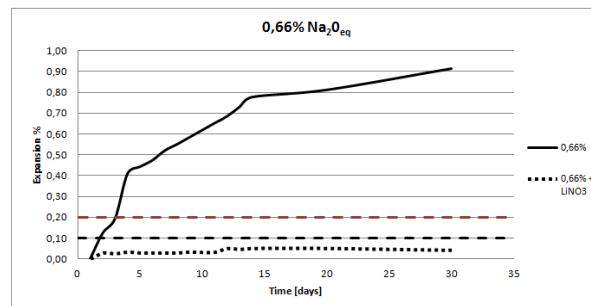


Fig. 1. Expansion of unmodified and lithium-additive-modified mortar samples for the low alkali cement.

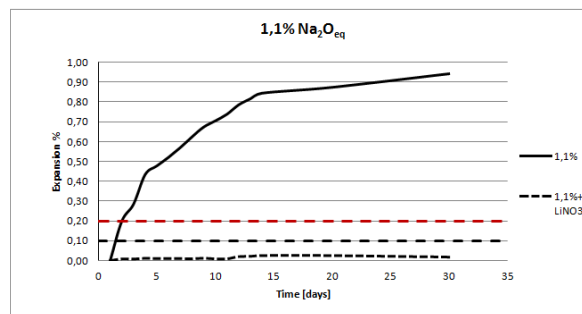


Fig. 2. Expansion of unmodified and lithium-additive-modified mortar samples for the high alkali cement.

During the extended period of 28 days, the unmodified mortar bars show significant level of expansion exceeding 0,9 %, both in mortars with high and low concentration of Na₂O_e. This value permitted the aggregate to be classify as reactive. The addition of lithium nitrate decreases the degree of expansion. In this case the modification of mortar bars with lithium nitrate changes the alkaline reactivity of opal and thus permits it to be classified as nonreactive aggregate. There is no significant difference between the alkali content in mortar bars and the level of expansion in lithium modified samples.

3.2 The microstructural analysis

The microstructure of modified and unmodified samples was analysed by means of scanning electron microscope with a high energy dispersive X-ray analyser. The specimens were covered by carbon. Fig. 3 shows images of alkali aggregate reaction products. The massive sodium-potassium-calcium silicate gel was found not only near the microcracking but also spread out over the surface. These gel contains considerable amount of Si, Na, Ca ions and a small amount of K ions.

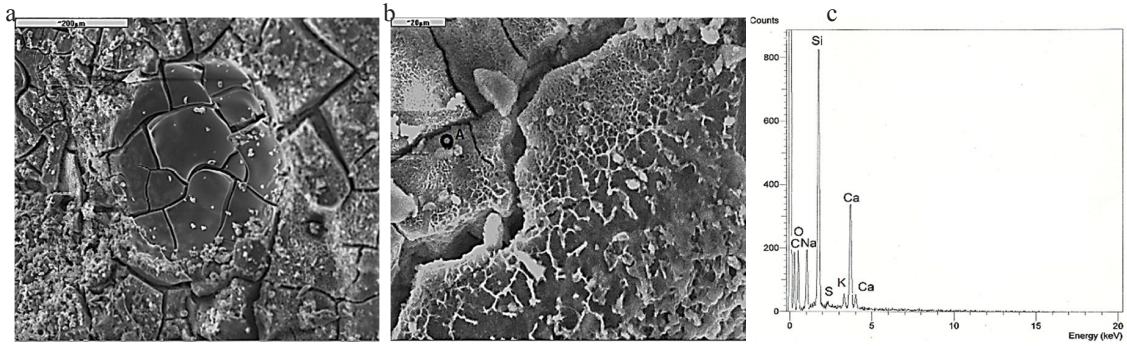


Fig. 3. Alkali silica reaction products in the non-modified samples with the high alkali content. (a)SEM x 200. (b) SEM x 1500. (c) EDX spectrum of analysis at location A

Fig. 4 shows the SEM images for sample modified with lithium nitrate. The cracks and ASR gel were not observed. Additionally, no lithium silicate crystallites were discovered. The microanalysis indicates that the form visible on the surface included a small amount of Na ions and a great amount of Si.

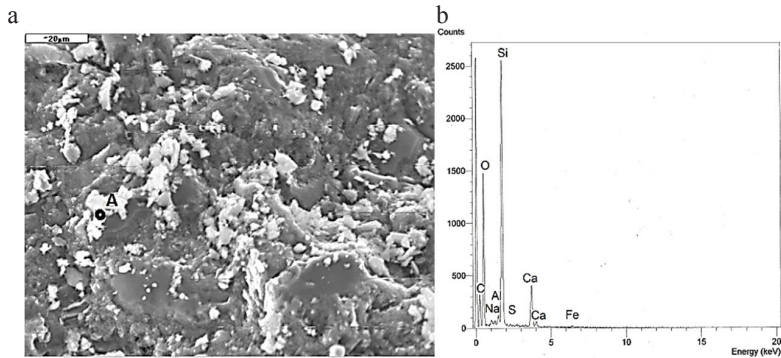


Fig. 4 Viewed of the microstructure in the samples with a low alkali content and modified with lithium nitrate. (a)SEM x 1000. (b) EDX spectrum of analysis at location A

Nevertheless, a great deal of sodium compounds appeared, especially in the voids. Sodium ions are probably bound with carbon dioxide forming sodium carbonate (Fig. 5). The SEM/EDX analysis revealed also the presence of calcium hydroxide, both on the surface and in the voids (Fig. 6).

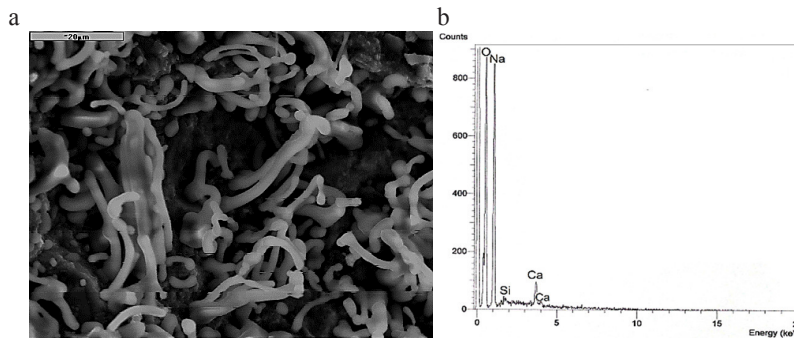


Fig. 5. The sodium-rich products of reaction in the sample prepared from high alkali cement and modified with lithium nitrate. (a) SEM x 1500. Bb) EDX analysis

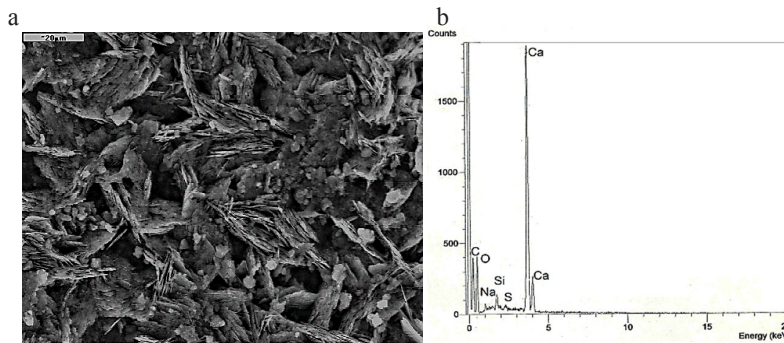


Fig. 6. A cement paste surface with portlandite crystals in the samples modified with lithium nitrate and with a low alkali concentration. (a) SEM x 1000. (b) EDX analysis

4. Discussion

The conducted investigation showed, that the expansion of mortar bars with opal aggregate is independent of the concentration of alkalis. In both series of mortar bars prepared from low alkali cement and high alkali cement the level of expansion exceeded the border value for the aggregate reactivity. When the lithium nitrate was inserted into mortar bars, the expansion process was exhibited. After 11 days the expansion increased slightly, so the measurement of expansion was extended to 28 days. The level of expansion in modified mortar bars reached the same value - not higher than 0,05%. The expansion degree was also independent of the initial alkali content in cement. It can be assumed that the lithium nitrate modification changed the alkaline reactivity of opal aggregate. The microstructure of samples was tested in order to comprehend the expansion mechanism in the unmodified mortar and a course of reaction in the modified samples. In unmodified samples series numerous microcracks were observed. The sodium potassium calcium silicate gel surrounds the opal aggregate and covers the surface near the microcracking. The cracks also radiate into the surrounding cement paste. The EDX analysis shows that expansive gel was composed of SiO_2 with high concentration of Na ions. The microstructure analysis of mortar samples modified with lithium nitrate did not reveal microcracking. The observed forms contained a small amount of Na and Ca ions, in addition the gel had a denser structure, so it was likely to have a lower capacity to absorb moisture from cement paste. In these samples characteristic forms of lithium silicates crystallites or expansive alkali silicate gel were not found. It can be assumed that the swelling capacity of alkali silica gel is changed in the presence of lithium ions and non-expansive or less expansive products are formed. A certain amount of portlandite was observed in emerging voids or on the surface. It indicates that calcium probably plays an important role in lithium-modified samples. Further work on the role of Ca ions in ASR reaction is clearly necessary. In the samples modified with lithium nitrate, with high alkali content, forms of sodium carbonate were observed. It is possible that sodium ions are not bound by ASR gel to the same extent as in traditional ASR gel and the place of sodium ions in reaction product is replaced by lithium ions. It is also possible that by precipitation of sodium carbonate the pH of pore solution is decreased to safe level. Unfortunately, lithium ions cannot be detected by SEM/EDX analysis.

5. Conclusions

Base on the above study the following conclusions can be proposed:

- 1) the expansion of mortar bars created with opal is suppressed by lithium nitrate addition,
- 2) the sufficient amount of lithium nitrate needed to inhibit expansion caused by the alkali silica reaction equals 1,0 (expressed as Li/Na molar ratio). The amount of lithium ions introduced into mortar bars is high due to the high reactivity of opal,
- 2) the alkali content in cement does not affect the linear changes in unmodified samples. The inhibition effect of lithium additive on ASR is also independent of the alkali content in cement,
- 3) the SEM/EDX analysis of unmodified samples indicates the presence of massive alkali silica gel rich in Na ions,

- 4) the observation of the bars with lithium addition proves that the created gel is rigid and includes smaller amount of Na ions compared with classic ASR gel,
- 5) in modified samples no microcracking or expansive sodium potassium calcium silicate gel were detected however, the Na rich-forms and portlandite in voids and on the surface were observed. No lithium silicate crystallites were detected. This indicates that lithium nitrate possibly has changed the structure of classic ASR gel and has created non-expansive or less expansive gel or has increased the stability of reactive silicon.

Acknowledgement

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