



The role of lithium compounds in mitigating alkali-gravel aggregate reaction



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HIGHLIGHTS

- Factors that affect the reactivity of polymineral glacial gravel aggregates were determined.
- The benefits of lithium nitrate to mitigate alkali-aggregate reaction were evaluated.
- The microstructure of the reaction products in mortars modified with lithium nitrate was studied.

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ABSTRACT

Alkali reaction with reactive aggregates is an example of concrete internal corrosion. Cracks and damage to elements of a concrete structure are the result of the formation of an expansive alkali-silica gel. One of the ways to minimise the effects of this damaging reaction is to use lithium compounds as an admixture to concrete mixes. Lithium ions are believed to reduce the reaction between the alkalis and aggregate or minimise damaging expansivity by modifying chemical composition of the reaction products.

This paper presents the results from the tests carried out on mortars from reactive polymineral gravel with lithium nitrate according to the modified ASTM C1260 standard and ASTM C227. The findings show that lithium ions decrease mortar expansion until it reaches the levels markedly lower than those set out in the standards. A considerable reduction in the number of microcracks may indicate either lower swelling capacity of the gels or reduced reactivity of the aggregate, leading to the reduction in the quantity of damaging expansive products.

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1. Introduction

One of the causes of concrete deterioration is the reaction between siliceous aggregates and alkalis in the cement. Reactive aggregates contain reactive forms of silica which enter into reaction with sodium and potassium hydroxides quickly – opal, tridymite, cristobalite, acid volcanic glass – and those which react slowly – chalcedony, cryptocrystalline quartz and strained quartz [1]. Alkali reactivity of aggregates depends on their geological origin, mineralogical composition and texture. Identification of the factors that affect the gravel reactivity is difficult, and due to its polymineral character, qualitative and quantitative analyses of reactive constituents have to be performed to be able to choose proper methods for reducing reactivity potential. Gravel aggregate

are commonly used in concrete, thus the minimisation of the alkali-aggregate reaction effects is critical [2].

The idea that lithium compounds can be used to mitigate negative effects of the aggregate reaction with sodium and potassium hydroxides first appeared in the 1950 s. Having conducted a comprehensive investigation on the inhibition potential of over 100 different compounds, McCoy and Caldwell reported lithium compounds to be most effective [3]. Worldwide interest in the lithium-bearing compounds has found lithium nitrate, used as a replacement for mineral admixtures, to have the highest effectiveness in preventing negative effects of alkali-aggregate reaction [4–7]. It has been demonstrated that this neutral and well soluble salt does not raise the pH value of the solution in the concrete pores, thus eliminating the risk of the pessimum effect [8]. Inappropriate doses of lithium ions in the form of lithium carbonate and lithium hydroxide lead to increased expansion and are deleterious to concrete, as observed by Diamond and Ong [9], Kawamura and Fuwa [10] during their studies of mortars containing LiOH and Li₂CO₃. The lithium compound introduced ions introduced into the

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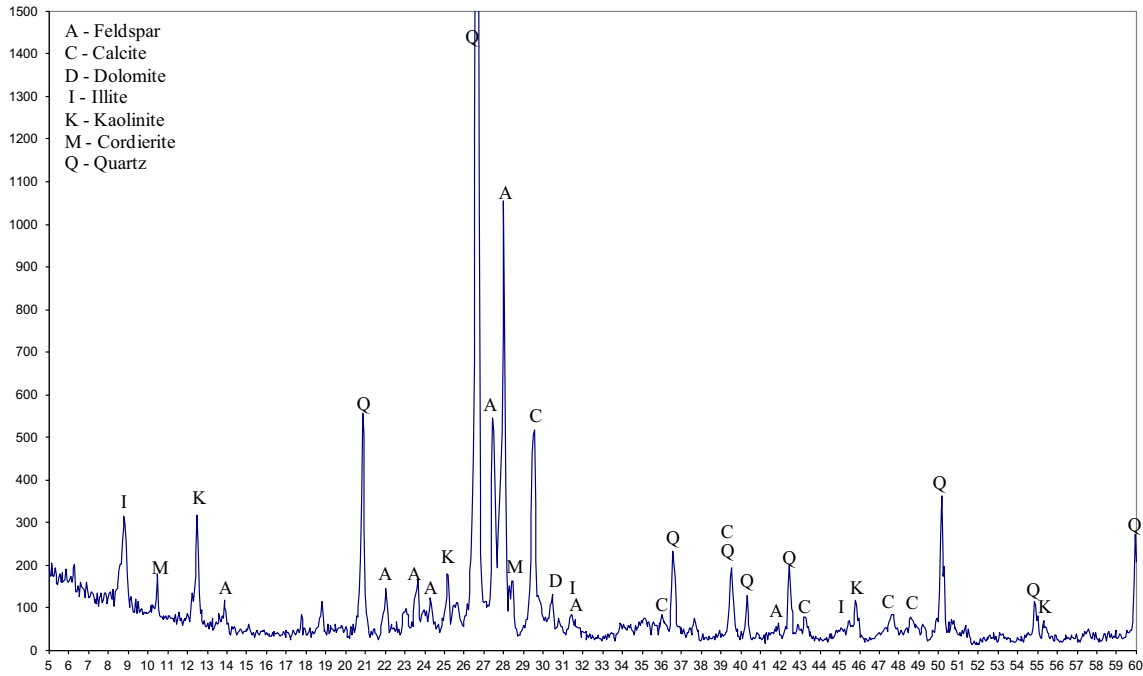


Fig. 1. XRD diffraction pattern of gravel aggregate.

concrete mix is thus of great importance. According to Feng et al., the effectiveness of lithium ions may vary for aggregates with different reactivity levels [11].

Several mechanisms of the reaction in the presence of lithium ions have been proposed. Some of them are based on increased stability of silica due to reduced pH of pore solutions or a change in their chemical composition [12]. It is presumed that amorphous or crystalline products containing silicon and lithium may form on the surface of reactive silica grains [13], acting as a protective barrier against Na⁺ and K⁺ ions. Other reaction mechanisms, not related to the Li⁺ induced increase in silica stability, focus on the modification of the resulting gel products with lithium ions, rendering the modified gels less capable of swelling than traditional gels [13,14]. Crystalline lithium silicate may also form on the surface of the reactive silica. The literature reports the effect of Li⁺ ions on the increased solubility of silica, which remains in the solution and prevents the gel from swelling [15].

2. Materials and methods

2.1. Aggregates

Polyminerall glacial gravel aggregates, 0/16 mm, from the northern regions of Poland were used. Fig. 1 shows the results of the X-ray analysis. The aggregates tested contain large amounts of quartz, calcite and plagioclase series with albite and anorthite, and lower amounts of clay minerals (illite, kaolinite) and dolomite.

Mass loss results from the aggregate fraction measurements conducted according to PN-92/B-06714-46 [16] and the results for silica leachability according to ASTM C289 [17] classify the gravel aggregate as potentially reactive (PN-92/B-06714-46) and reactive (ASTM C289) (Fig. 2a, b).

Those aggregate grain types, identified in macroscopic observations, which showed the greatest mass loss in the potential reactivity evaluation were subjected to a petrographic analysis. The following reactive components were found using an optical microscope: organodetrritic sparite – micrite limestone, metamorphic quartz pyroxene shale with opal cement, quartz – glauconite sandstone with clay-carbonate binder including some chalcedony, and quartz grains in feldspar – biotite granite. Three main constituents, chalcedony, opal and strained quartz, are probably responsible for the reactivity of the aggregate. Table 1 shows the analysis of the quantitative composition of minerals in the aggregate.

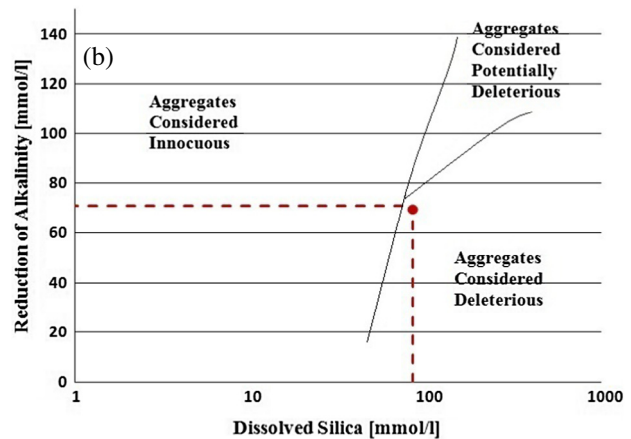
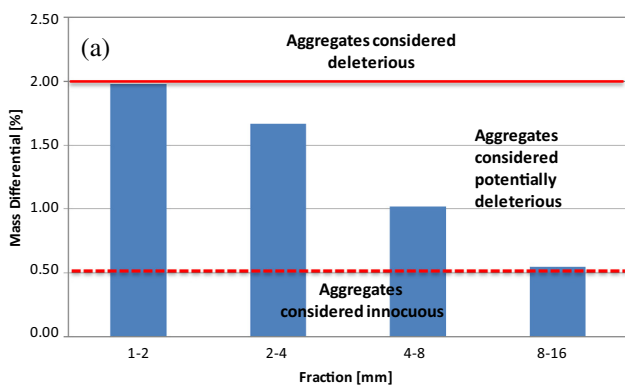


Fig. 2. Reactivity Of Gravel Aggregate According To Specifications (a) PN-92/B-06714-46 (b) ASTM C289-94.

Table 1
Reactive components in polymineral aggregate.

Rock type	Reactive constituent	Content [%vol.]
Quartz glauconitic sandstone	Chalcedony	2.1
Feldspathic granite with biotite	Quartz	15.7 ^a
Quartz pyroxene shale	Opal cement	47.0
Organodetritric sparite – micrite limestone	Quartz	0.1

^a Strained quartz.

2.2. Cement

Portland cement CEM I 42,5R containing 0.66% Na₂O_e was used. Table 2 shows the chemical composition of the cement.

2.3. Test methods

To evaluate the potential reactivity of the gravel aggregate, the accelerated ASTM C1260 method was used together with the long-term ASTM C227 method [18,19]. The grain composition was prepared from the mechanically crushed gravel aggregate according to the requirements outlined in ASTM C1260 and ASTM C227. The bars with dimensions 25 × 25 × 250 mm were made with and without lithium nitrate. The lithium nitrate was added to the mix with the mixing water in the molar ratio of lithium ions to alkali ions [Li]/[Na + K] kept to 0.74 [11]. The bars were immersed in the solution with the [Li]/[Na + K] molar ratio as in the mortar bars (ASTM C1260) at 80 ± 2 °C and above the water table at 38 ± 2 °C (ASTM C227). The measurements were taken for 14 days in the accelerated method and at 14, 30, 60, 90, 180, 270 and 360 days in the long-term method. The microstructure of the resultant reaction products was studied under the scanning electron microscope with X-ray microanalysis.

3. Test results

3.1. Mortar expansion test

Fig. 3a, b and Table 3 present the results of the expansion tests for mortars modified with lithium nitrate and for non-modified mortars.

In the mortars without lithium nitrate, analysed using the short-term method, expansion exceeds the aggregate reactivity threshold of 0.1% after 14 days. High values of linear expansion were also recorded in the long-term method, which confirms the reactivity of the aggregate used. Higher linear expansion of the gravel aggregate mortars recorded in the accelerated method may result from different storage conditions. In the ASTM method

Table 2
Cement chemical composition.

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	TiO ₂	LOI	Cz. n.r.
Cement	20.20	4.80	3.00	61.70	1.80	2.70	0.78	0.15	0.45	3.00	1.00

LOI – loss on ignition, Cz.n.r. – HCl and Na₂CO₃ – insoluble parts.**Table 3**
Expansion of mortars with gravel aggregate at 14 days according to ASTM C1260 and at 360 days according to ASTM C227.

Method	Measurement time [days]	Mortar expansion [%]	
		Reference sample	Sample with LiNO ₃
ASTM C1260	14	0.215	0.014
ASTM C227	360	0.122	0.033

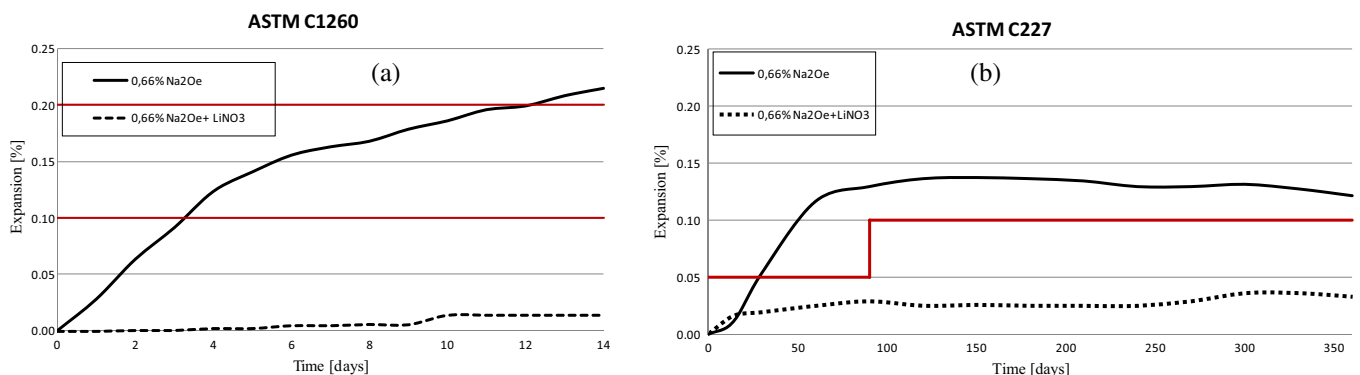
C1260, the bars are subjected to high temperatures and external source of sodium hydroxide for a relatively short time. In the long-term method, the action of corrosive factors is “milder” owing to the lack of external alkali source, lower temperature and markedly longer exposure time.

In the mortars made with lithium nitrate admixture, elongation of the samples was limited to the safe level of up to 0.1% in the short-term method and 0.05% (up to 90 days) and 0.10% (after 90 days) in the long-term method. Expansion was reduced by about 93% in the mortars with gravel aggregate and lithium nitrate in the accelerated method, and by about 73% in the long-term method. To prevent washing the lithium ions out of the cement paste, the immersion solution was reinforced with lithium nitrate with the [Li]/[Na + K] molar ratio maintained at the same level as in the mortar bars. The differences in the percentage of expansion reduction in the two methods may result from the modification of the composition of the immersion solution.

3.2. Mortar microstructure

Microstructural observations of mortars without lithium compounds showed considerable quantities of microcracks in the samples tested using both methods (4a–b) (Fig. 4). The gels formed in the particles contained large amounts of sodium and potassium.

Fig. 5 presents the findings from the observations of the microstructure of the mortars made with lithium nitrate. These mortars had much lower cracks in the region of aggregate particles and cement paste, compared with the control samples. The silicate hydrate gels showed lower contents of sodium at a variable content of calcium (Fig. 5a, b). The products of the alkali-aggregate reaction, filling the microcracks in the aggregate, contained small amounts of sodium and potassium (Fig. 5d).

**Fig. 3.** Expansion progress over time for mortars made with gravel aggregate, with and without lithium nitrate: (a) ASTM C 1260, (b) ASTM C227.

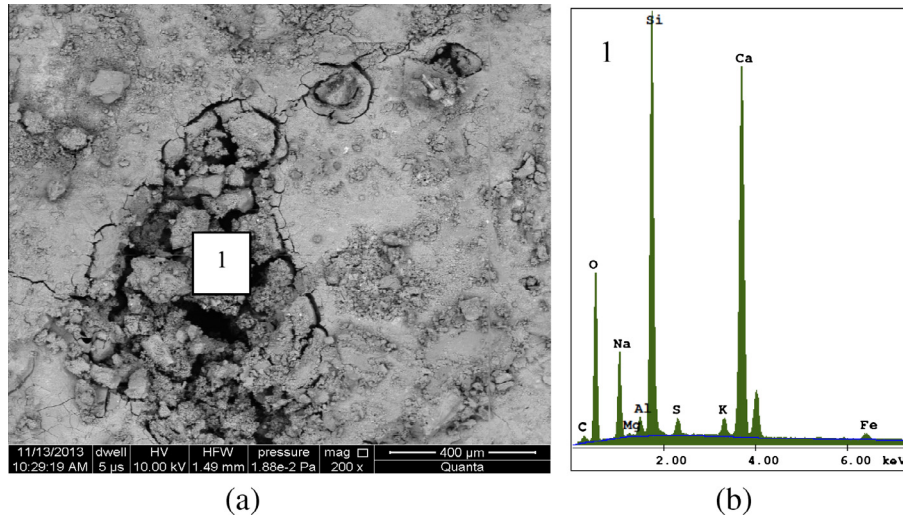


Fig. 4. Mortar samples without lithium nitrate, accelerated method, (a) microstructure and cracks, (b) X-ray microanalysis at point 1.

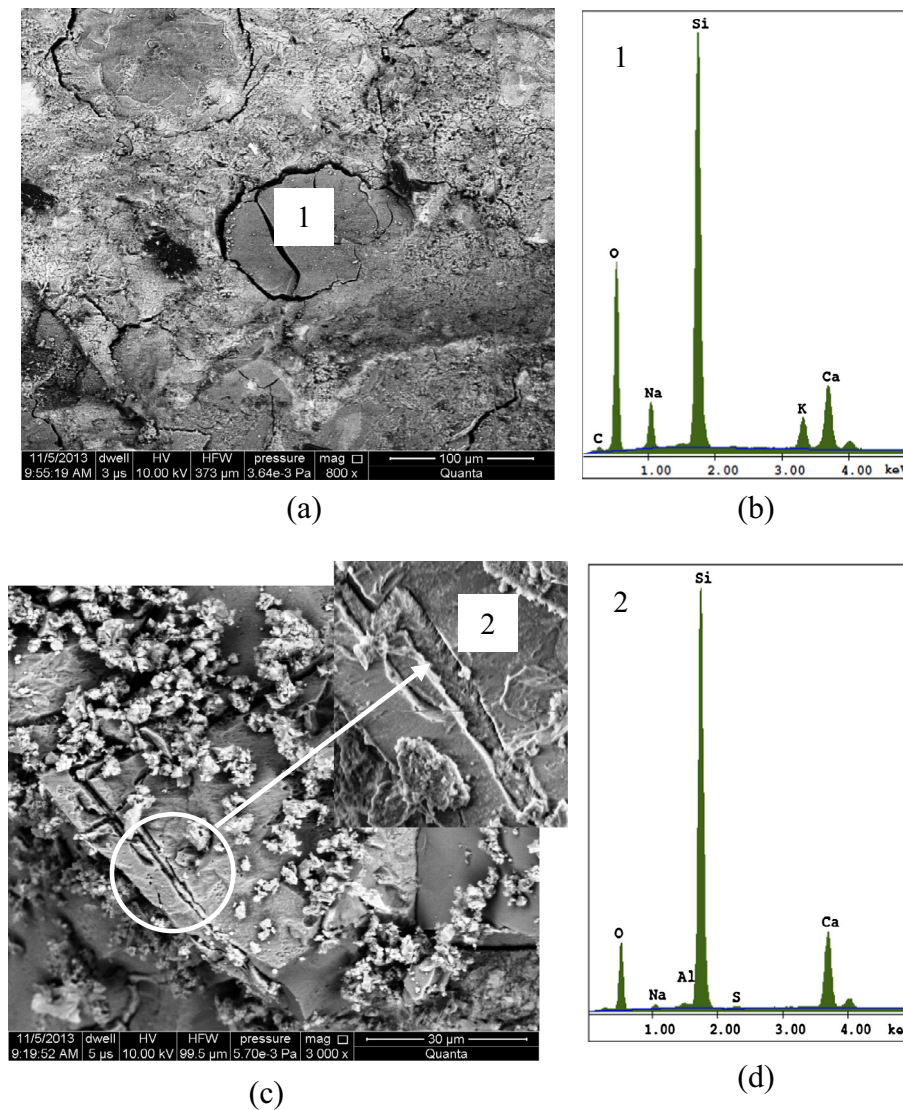


Fig. 5. Mortar samples with lithium nitrate, accelerated method, (a) resultant cracks on aggregate particles, (b) X-ray microanalysis at point 1, (c) gel filling the microcracks in aggregate, (d) X-ray microanalysis at point 2.

4. Conclusions

1. The gravel aggregate used in this study reacted with the alkalis because expansion of the mortars exceeded the threshold of potential reactivity specified in ASTM C1260 and ASTM C227. Lithium compounds are effective inhibitors of expansion of mortars made with reactive gravel aggregates.
2. Products of aggregate reaction with sodium and potassium hydroxides filled the area of the aggregate, and the sodium-potassium-calcium silicate gel contained large amounts of sodium and potassium.
3. An addition of lithium nitrate in the molar ratio of Li/(Na + K) at the level of 0.74 helped decrease the expansion of mortars made with reactive gravel aggregate until it reached the safe, non-destructive level.
4. The differences between percentage reduction of expansion in the accelerated and long-term methods may result from the modification of the immersion solution composition. In the modified ASTM C1260 test method, due to the presence of lithium nitrate in the solution in which the mortar bars were stored, lithium leaching was limited and expansion decreased to 0.014%.
5. In the mortars with lithium nitrate, alkali content in the gel was small probably because the remaining lithium ions incorporated in the structure of the resultant products limit the sorption of sodium and potassium ions, thus contributing to the decrease of their swelling properties.
6. Further studies are necessary to better understand the mechanism of lithium compounds effect because available methods, for example, X-ray microanalysis, fail to analyse both the content and distribution of lithium due to its light weight.

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