



INFLUENCE OF SODIUM AND POTASSIUM FORMATE ON THE ASR REACTIVITY OF GRANITE AGGREGATE

WPŁYW MRÓWCZANU SODU I POTASU NA PODATNOŚĆ KRUSZYWA GRANITOWEGO NA REAKCJĘ ALKALICZNĄ

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Abstract

Use of de-icing agents is necessary in winter to maintain appropriate quality of road and airport surfaces. Formate or acetate de-icing agents are safer for aircraft and the environment than the commonly used sodium chloride, but may cause an alkali-silica reaction in concrete. The study investigated the influence of sodium formate and potassium formate on the occurrence of ASR (alkali-silica reaction) in mortars with granite aggregate. Accelerated mortar-bar tests at 80°C using various de-icing agents were performed and detailed studies of the SEM-EDS microstructure were carried out.

Keywords: granite aggregate, alkali-silica reaction ASR, sodium formate, potassium formate, alkali-silica gel, microstructure

Streszczenie

Stosowanie środków odladzających jest niezbędne do zimowego utrzymania odpowiedniej jakości betonowych nawierzchni drogowych i lotniskowych. Środki odladzające na bazie mrówczanów lub octanów są bezpieczniejsze zarówno dla środowiska, jak i statków powietrznych niż powszechnie stosowany chlorek sodu, jednak mogą wywoływać reakcję alkaliczno-krzemionkową kruszywa w betonie. W pracy analizowano wpływ mrówczanu sodu i mrówczanu potasu na potencjał wystąpienia ASR (alkali-silica reaction) w zaprawach z kruszywem granitowym. Przeprowadzono badania ekspansji w 80°C z zastosowaniem różnych środków odladzających oraz przeprowadzono szczegółowe badania mikrostruktury SEM-EDS.

Słowa kluczowe: kruszywo granitowe, reakcja alkaliczno-krzemionkowa ASR, mrówczan sodu, mrówczan potasu, żel alkaliczno-krzemionkowy, mikrostruktura

1. INTRODUCTION

Due to climate conditions in Poland, it is necessary to use de-icing agents in winter to ensure appropriate quality of concrete road and airport pavements. Sodium chloride (NaCl) is commonly used for road pavement de-icing due to its effectiveness and low price. However chloride ions can negatively affect concrete pavements as well as the vehicles and the natural environment [1]. For de-icing of airport pavements, alternative agents are used: sodium and potassium formates or acetates [2]. Both formates and acetates are considered to be much

more environmentally friendly and they are not harmful to aircraft components. They are easily biodegradable, without emission of toxic products. Formates and acetates are more effective at lower temperatures in comparison to sodium chloride, they work quicker and last longer. The relatively high price is the factor that limits their use only to airport pavements.

Despite a number of advantages, premature damage near the expansion joints and cracks of the concrete airfield pavement has been noticed. There are a few studies describing the influence of de-icing

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agents based on organic salts on concrete durability, especially on alkali-silica reaction [3]. The harmful effects of formate and acetate de-icing agents have been reported by Giebson et al. [4]. They found that the acceleration of ASR by the use of organic salts was associated with an excess supply of alkali and the release of OH⁻ ions as a result of increased Ca(OH)₂ solubility. While Wang et al. [5] found no significant effect of acetate de-icing agents on the ASR acceleration in concrete. The influence of formates and acetates on the occurrence or acceleration of ASR is not clear. Therefore, it was necessary to perform research taking into account the available domestic aggregate deposits.

2. MATERIALS

Three granite aggregates (G1, G2, G3) from Polish mines were selected for testing. Granites aggregates are considered high-quality aggregates and are therefore widely used in concrete pavement construction. Due to the possibility of ASR, granite aggregates are classified as non-reactive [7] or potentially reactive [8] due to the presence of strained and microcrystalline quartz. In the analyzed granite aggregates, the content of reactive minerals was relatively low and ranged from 1.8% to 4.7% (strained quartz) [9]. Portland cement CEM I 52.5 R was used for mortar specimens preparation; the chemical composition is presented in Table 1.

Table 1. Chemical composition of cement determined by the XRF method, % wt.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	Na ₂ O _{eq}	LOI
CEM I 52.5 R	19.42	5.15	2.94	64.10	1.75	3.50	0.29	0.88	0.87	2.43

The water-cement ratio $w/c = 0.47$ and aggregate-cement ratio $a/c = 2.25$ were used. Crushing and

sieving of granite aggregate was performed according to RILEM AAR-2 [10].

3. TESTING METHODS

The expansion tests of mortars were performed according to the accelerated mortar-bar test RILEM AAR-2 [10]. The specimens (25 x 25 x 285 mm) were exposed to 1 M NaOH and 80°C for 28 days. The method was modified by the usage of deicing agents solutions: 50% HCOOK and 15% HCOONa. The concentration of the solution was related to the simulation of real conditions during defrosting of airport pavements [2]. Reference specimens stored in distilled water were also prepared.

The specimens after the accelerated mortar-bar test were cut into smaller parts (40 x 25 x 10 mm) and prepared for microscopic observations. The specimens were impregnated with epoxy resin, grinded on diamond discs (125, 75, 54, 18 and 9 μm) and polished on polishing pads with diamond pastes (6, 3, 1, 0.25 μm). The prepared specimens were sputtered with a carbon layer (~20 nm), then microscopic observations were performed on a JEOL JSM-6460LV scanning electron microscope (SEM) equipped with an X-ray energy dispersion (EDS) detector. The analysis was performed under high vacuum in the backscattered electron mode (Electron Backscatter Diffraction, EBSD). The SEM was operated with acceleration voltage set to 20 kV and a working distance of 10 mm.

4. RESULTS AND DISCUSSION

The expansion of mortar bars was different depending on the solution used. Results of the expansion over time were presented on Figure 1 and in Table 2. All specimens showed expansion below 0.1% after 14 days of exposure in a 1 M NaOH, which classified the aggregate as non-reactive according to RILEM AAR-2.

Table 2. Expansion [%] of mortar with aggregate G1, G2, G3 after 14 and 28 days of exposure in 80°C in different solutions (distilled water, sodium hydroxide, sodium formate, potassium formate)

Solution	G1		G2		G3	
	14 days	28 days	14 days	28 days	14 days	28 days
1 M NaOH	0.054 ± 0.002	0.097 ± 0.002	0.066 ± 0.002	0.134 ± 0.002	0.086 ± 0.03	0.108 ± 0.003
H ₂ O	0.001 ± 0.001	0.002 ± 0.001	0.003 ± 0.001	0.004 ± 0.001	0.002 ± 0.001	0.004 ± 0.001
15% HCOONa	0.004 ± 0.001	0.009 ± 0.001	0.008 ± 0.001	0.013 ± 0.001	0.006 ± 0.001	0.009 ± 0.001
50% HCOOK	0.323 ± 0.023	0.645 ± 0.032	0.430 ± 0.023	0.928 ± 0.018	0.459 ± 0.002	0.974 ± 0.001

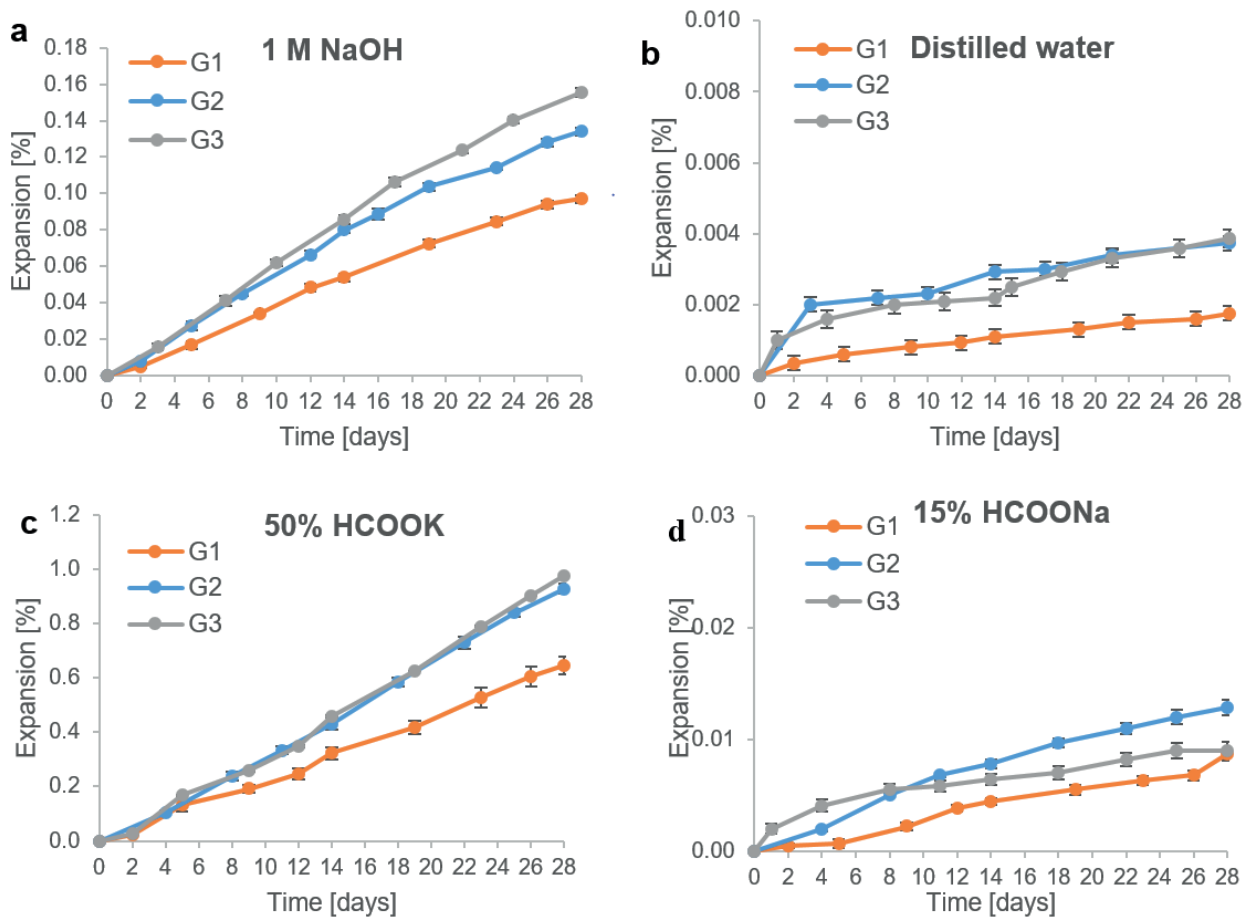


Fig. 1. Expansion of mortar bars with granite aggregate G1, G2, G3 in 80°C and (a) 1 M NaOH, (b) distilled water, (c) 50% HCOOK, (d) 15% HCOONa (the scales on the vertical axis differ due to a large variation of the results depending on the solution used)

The specimens stored in distilled water at 80°C showed negligible expansion from 0.002% to 0.004% after 28 days. Mortar bars showed no expansion potential under these conditions, similar to the exposure to 15% HCOONa (expansion after 28 days from 0.009% to 0.013%). Significant expansion was observed in the specimens immersed in 1 M NaOH (expansion after 28 days from 0.097% to 0.134%).

The greatest expansion was found for mortar bars immersed in 50% HCOOK, ranging from 0.645% to 0.997%. Specimens exposed to potassium formate were highly susceptible to alkali-silica reaction.

Microstructure observations on SEM-EDS confirmed the presence of ASR products in the mortar bars exposed to sodium formate and potassium formate. The results were shown in Figures 2-5.

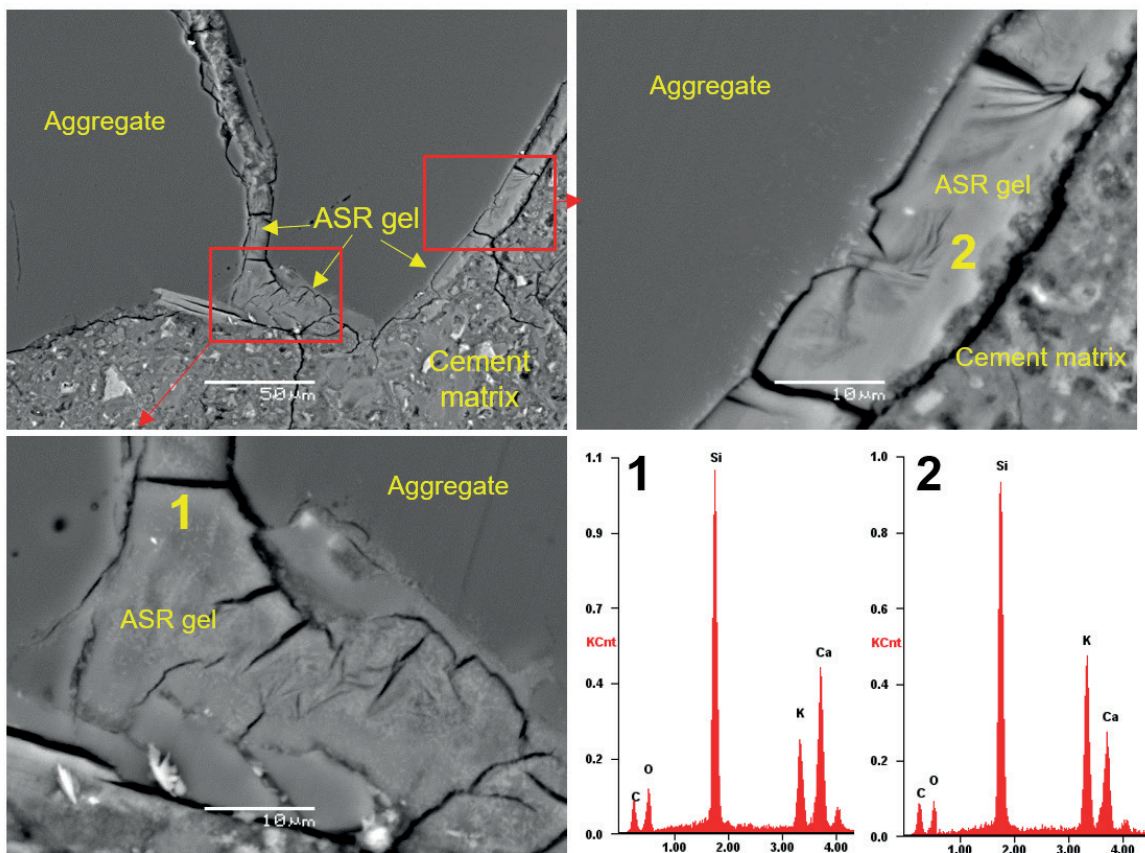


Fig. 2. The microstructure of the mortar with aggregate G3 after 28 days of storage at 80°C in 50% HCOOK, cracks in the aggregate grain filled with ASR gel (1) and ASR gel in the interfacial transition zone aggregate-cement matrix (2)

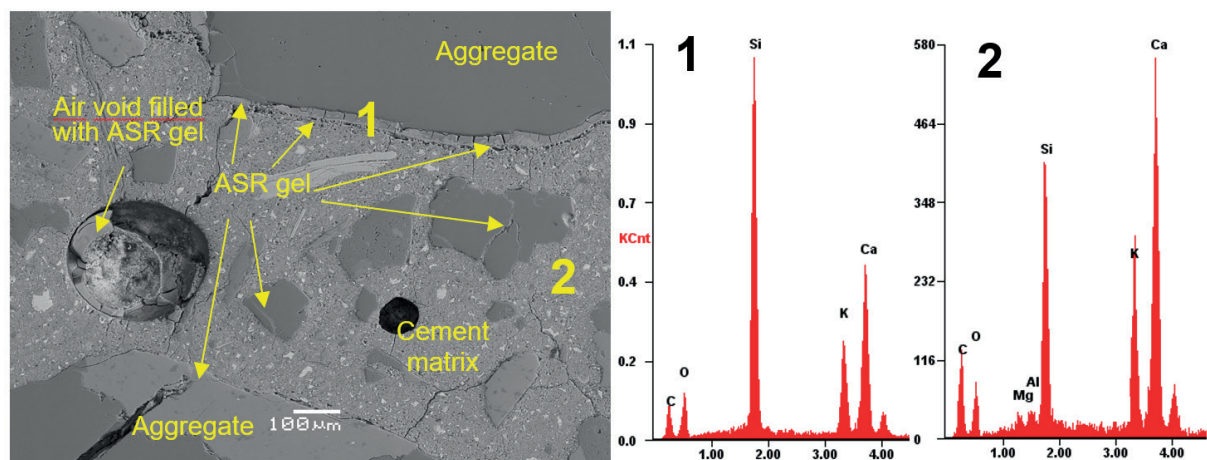


Fig. 3. The microstructure of the mortar with aggregate G2 after 28 days of storage at 80°C in 50% HCOOK, cracks in the aggregate grain filled with ASR gel, ASR gel in the interfacial transition zone between aggregate and cement matrix (1) air void filled with ASR gel, (2) cement matrix with increased potassium amount (2)

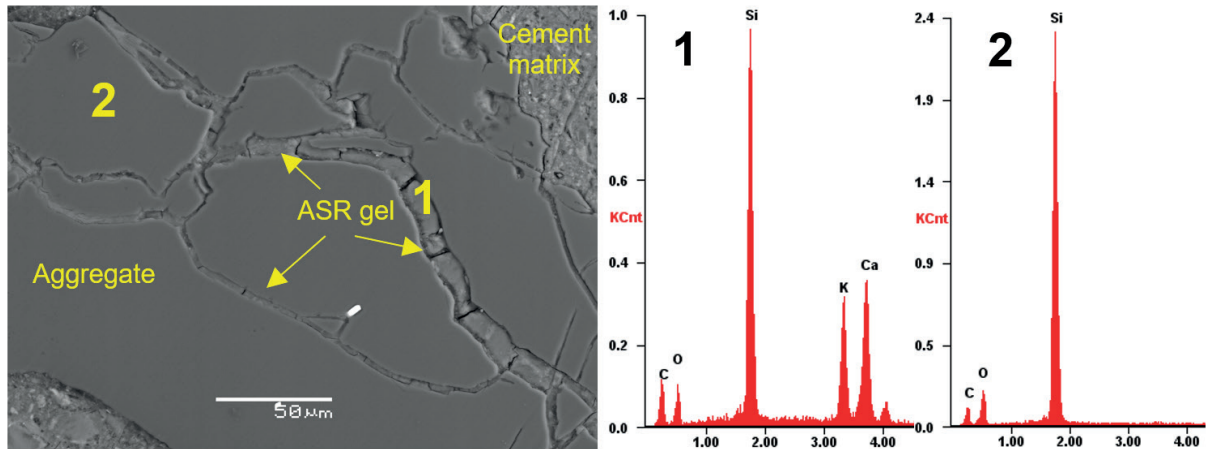


Fig. 4. The microstructure of the mortar with aggregate G1 after 28 days of storage at 80°C in 50% HCOOK, cracks in the aggregate grain filled with ASR gel (1), quartz (2)

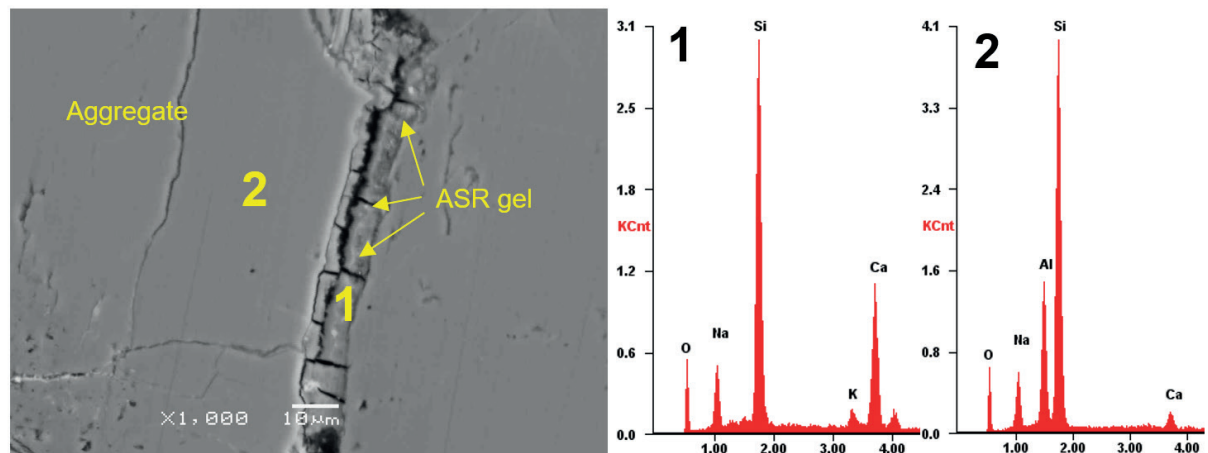


Fig. 5. The microstructure of the mortar with aggregate G2 after 28 days of storage at 80°C in 15% HCOONa, cracks in the aggregate grain filled with ASR gel (1), sodium feldspar (2)

No ASR reaction products were found in the specimens stored in distilled water. An abundance of ASR products was found in specimens exposed to 50% potassium formate. The gel was mainly found in the cracks in the aggregate grains and in the interfacial transition zone. Air voids partially or completely filled with ASR gel were also observed. In the mortar bars exposed to sodium formate, traces of ASR reaction products were found, the gel was recognized in the cracked aggregate grains.

An SEM-EDS microstructure analysis confirmed that the expansion of the specimens stored in a 50% potassium formate solution was related to the ASR reaction. The chemical composition of ASR gel identified in these samples was rich in potassium and was sodium-free. Despite a slight expansion of mortar bars immersed in a 15% sodium formate

solution, traces of ASR gel were identified in the microstructure, but in a much smaller amount than in the specimens stored in HCOOK. The ASR gel in the specimens tested in HCOONa contained both sodium and potassium ions, but was characterized by a higher content of Na.

Rangaraju et al. [11] found that the reactive aggregate exposed to potassium acetate showed high susceptibility to ASR. On the other hand, Wang et al. [5], despite the use of a high concentration of potassium acetate (54.5% by weight), did not find the presence of reaction products in concrete subjected to cyclic saturation and drying. Whereas, based on the performed research, it was found that the non-reactive aggregate in the mortar exposed to salts of organic acids, in particular potassium formate, showed a high potential for alkali-silica reaction. Thomas et al. [12]

investigated the possibility of reducing the degree of degradation of concrete treated with a 50% potassium acetate by using the addition of slag or fly ash. However, the effect was not satisfactory and allowed only for a slight delay in the reaction. The authors [12] confirmed the significant effect of potassium acetate on the degradation of concrete as a result of ASR, while in the performed research, the negative effect of potassium formate on the destruction of the mortar due to ASR was also found.

The chemical composition of the ASR gel depended on the de-icing agent used. The content expressed by the ratio of (Na+K)/Si was 0.4-0.6 for gel in mortar stored in potassium formate and 0.3-0.4 for mortar stored in sodium formate, but for specimens exposed to HCOOK, 100% of the alkali was potassium. According to Gholizadeh-Vayghan and Rajabipour [13] ASR gel which contains more alkali, shows greater expansion, which confirms the results obtained in this study and a much higher expansion

of mortars stored in HCOOK than in HCOONa. A more detailed analysis of the chemical composition and mechanical properties of the ASR gel will be the subject of further research related to this work.

5. CONCLUSIONS

Based on the conducted research, the following conclusions can be drawn:

- Formate-based de-icing agents promote the occurrence of ASR in granite aggregate.
- A microstructure analysis confirmed that the expansion of the mortars exposed to potassium formate was related to the presence of the ASR gel in the cracks in aggregate grains.
- Despite a slight expansion of mortar bars stored in sodium formate, the presence of ASR reaction products was found.
- The chemical composition of the gel, and thus its properties, depended on the type of de-icing agent used.

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