

# INFLUENCE OF ACETATE AND FORMATE BASED DEICERS ON ASR IN AIRFIELD CONCRETE PAVEMENTS

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## Abstract

In the past few years, the issue of external alkalis and their influence on ASR in concrete has become more important since several airfield concrete pavements showed ASR-distress related to the use of alkali-containing runway deicers based on acetates and formates. To assess the influence of external alkalis on ASR in pavement concretes, the cyclic climate storage has revealed as suitable performance-test. Especially deicers based on acetates and formates turned out to be extremely deleterious in concrete with reactive aggregates. Experiments with model pore solutions and cement pastes, as well as speciation calculations were performed to investigate possible mechanisms. The obtained results indicate that the solubility of portlandite in the cement paste is increased in presences of acetate and formate based deicers. Due to the additional release of  $\text{OH}^-$  from portlandite and the supply of alkalis, ASR can be initiated and accelerated highly in concretes with reactive aggregates. There are also indications for an interaction of other cement paste constituents with acetate and formate based deicers.

**Keywords:** airfield pavement concrete, deicer, acetate, formate, external alkali mechanism

## 1 INTRODUCTION

It has been suspected for some time now, that the action of alkali-containing deicers is capable of favoring an alkali-silica reaction (ASR) in concrete with reactive aggregates. The research in the past decades was mainly focused on NaCl [1, 2, 3]. For safety reasons, chloride-based deicers are not used on airfields in order to avoid corrosion damage to aircraft and airport equipment. Therefore, synthetic urea ( $\text{CH}_4\text{N}_2\text{O}$ ) was used as runway deicer for a long time. Deicers based on sodium and potassium acetate ( $\text{CH}_3\text{COOK}$ ) and later on also based on sodium and potassium formate ( $\text{HCOOK}$ ), were introduced in the USA as well as in Germany in the early 1990s. These deicers exhibit a large number of advantages over the synthetic urea. They are more environmentally friendly, since they are readily biodegradable, leaving behind only harmless, non-toxic residues and contain no nitrogen as well. They are also more effective at lower temperatures, work faster and longer and require fewer applications. In a while, acetate based deicers are also used for some highways and bridge decks, to benefit from the environmental advantages and prevent reinforced concrete structures from chloride-induced corrosion damage.

However, in the past few years severe ASR-distress occurred on airfield concrete pavements with increasing frequency. It is reported that about thirty U.S. military airfields around the world and at least eight commercial U.S. airports are affected [4, 5]. At the FIB (F.A. Finger-Institut für Baustoffkunde), a German runway was investigated that showed ASR-distress 5-7 years after the deicer was changed from urea to potassium acetate. Commercial deicer solutions contain about 50-55 % active components and minor amounts of corrosion inhibitors. To improve the effectiveness, solid deicers (e.g. sodium formate) and liquid deicers (e.g. potassium formate) are often used together. The application rates depend strongly on the weather situation and are usually about 10-60 g/m<sup>2</sup>. In Germany, there are approximately 40-50 days of deicing within every winter period and, if necessary, up to eight applications are done per day. So far, only a few studies became available that investigated the influence of these deicers on ASR in concrete.

Since 2001, an alternating climate test method (cyclic climate storage) is used at the FIB for accelerated simulation of Central European climatic conditions, in order to assess the durability of specific concretes for outdoor structures. Significant factors from environmental effects (drying, moistening, freezing and thawing, exposure to deicers) are simulated for this purpose by alternating temperature and moisture conditions in a special developed climate simulation chamber. A climate test program was especially developed for investigations into ASR for pavement concretes [6, 7]. After

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testing more than a hundred concretes, mostly job mixtures, with different cements and mostly with slow/late reacting aggregates, the results show clearly that a deleterious ASR can be initiated and highly accelerated in concretes with reactive aggregates exposed to alkali-containing deicers (Figure 1). It was found that externally supplied alkalis exceed the influence of the cement alkalis sooner or later. Low-alkali cements may delay the ASR, but are not capable of permanently preventing a deleterious ASR, if external alkalis are supplied and reactive aggregates are present [8]. To provide an explanation for these observations, investigations into the mechanisms were performed and are introduced below.

## 2 MATERIALS AND METHODS

### 2.1 Materials and experimental settings

Solubility experiments were performed using pure powders of  $\text{Ca}(\text{OH})_2$  (portlandite),  $\text{CH}_3\text{COOK}$  (K-acetate),  $\text{HCOOK}$  (K-formate),  $\text{Ca}(\text{CH}_3\text{COO})_2$  (Ca-diacetate) and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum) for comparison purposes. The used water was double distilled and freshly boiled to remove dissolved carbon dioxide. The deicing chemicals were mixed in different concentrations (0.05, 0.3, 1.5, 2.5 mol/l) into saturated solutions (200 ml) of portlandite with solid portlandite in excess. The experiments were done in a glove-box, using nitrogen as inert gas to avoid any possible degradation of the acetate and formate ions in contact with oxygen and to avoid precipitation of calcium carbonate as well. Furthermore, in a saturated solution (200 ml) of gypsum with solid gypsum in excess, K-acetate (0.05, 0.3, 1.5, 2.5 mol/l) was mixed. All solutions were sealed airtight in plastic vials and stored overnight at 20 °C. The solutions were analyzed by ICP-OES and the pH was measured by using an alkali-resistant glass electrode (Orion ROSS, 81-08). Selected solid residues were filtered, dried at 40 °C and analyzed by XRD, FT-IR and ESEM/EDS.

Cement pastes were made from two portland cements with different  $\text{Na}_2\text{O}_{\text{eq}}$  (0.44 and 0.81 wt%) and w/c of 0.42. After 7 days curing in airtight sealed vials at 20 °C, the hardened samples ( $\text{Ø}30$  mm, l=30 mm) were cyclical, every 14 days, vacuum-immersed in two commercial runway deicer solutions (K-acetate, K-formate) as well as in water for control. The vacuum immersion was done 5-times in series of decompression (15 minutes) and compression. After the vacuum immersion, the samples were sealed airtight in a plastic bag and stored at 40 °C for 14 days. Afterwards, the pore solution was squeezed out and analyzed by ICP-OES and cement paste samples were also examined by XRD and ESEM/EDS.

### 2.2 Methods for assessment and analysis

#### *Inductively coupled plasma-optical emission spectrometry (ICP-OES)*

About 20 ml of the solutions were filtered (0.45  $\mu\text{m}$ ) and sealed airtight in plastic vials. The solutions then were diluted (1:100) with nitric acid (1%) and about 100  $\mu\text{l}$  were injected in the argon-plasma of the spectrometer (Perkin-Elmer, Optima 3000). The element concentrations of K, Na, Ca and S were determined. The detection limits ranging from 0.02  $\mu\text{g/l}$  (Ca) to 30  $\mu\text{g/l}$  (S).

#### *X-ray powder diffraction (XRD)*

Solid residues were prepared in the glove-box by separation from the solution with a frit (40  $\mu\text{m}$ ) and rinse them with isopropanol and acetone. The residue was applied on a polyethylene sample holder, covered with a sheet of polypropylene and then discharged from the glove-box.

The cement paste samples were crushed dryly by hand with hammer and chisel and further on gently with a corundum mortar and pestle to obtain a coarse powder. The powder was rinsed with isopropanol and acetone in order to stop the hydration. Afterwards, the powder was dried for 30 minutes at 40 °C prior to gently grinding by hand with a mortar and pestle of corundum until all particles passed the 40  $\mu\text{m}$  sieve. About 1 g of the fine powder was applied on a polyethylene sample holder. The X-ray diffractometer (Siemens, D-5000) uses  $\text{Cu-K}_\alpha$  radiation of wavelength  $\lambda=0.154$  nm. Diffractograms were recorded from  $4-60^\circ 2\theta$ , in  $0.05^\circ 2\theta$  increments with 2.5 s counting time per increment.

#### *Fourier-transform infrared spectroscopy (FT-IR)*

Solid residues were prepared in the glove-box by separation from the solution with a frit (40  $\mu\text{m}$ ) and rinse them with isopropanol and acetone. Then, the residues were dried for 30 minutes at 40 °C and used as obtained for the analysis. Solutions were filtered (40  $\mu\text{m}$ ) and sealed airtight in a plastic vial. The samples were placed into the spectrometer (BioRad, FTS 175L) and the absorbance was determined from 400-4000  $\text{cm}^{-1}$ . For solutions, a pure water sample was recorded and subtracted from the sample spectra.

The environmental scanning electron microscope (Philips, XL 30 ESEM-FEG) equipped with EDS-detector was used to examine single phases and to determine their composition. Since samples do not need to be coated, they can be studied in situ without artifacts. Operating conditions were set to 25-10 kV and 10-3 Torr.

*Speciation calculation with PHREEQC*

Speciation calculations were performed using PHREEQC [9] to explain experimental results and to predict possible mechanisms. The WATEQF4-database and the supplementary reactions given in Table 1 were used for the modelling. The ion-association approaches according to Debye-Hückel and Davies were used to calculate activity coefficients in order to account for the non-ideality of aqueous solutions. These approaches will become unreliable with increasing ionic strength, so the ion-interaction approach according to Pitzer should be used preferably. However, the required parameters for the ion-ion interactions of interest were not available in the known literature.

### 3 RESULTS

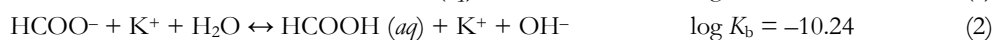
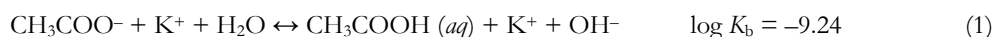
The initial pH of the saturated Ca(OH)<sub>2</sub> solutions at pH 12.5 immediately increased after addition of CH<sub>3</sub>COOK or HCOOK. Analysis of the resulting solutions by ICP-OES furthermore revealed an increased Ca concentration (Figure 2). The results of the XRD, FT-IR and ESEM/EDS analysis showed no new precipitation products in the solid residue. The FT-IR analysis of a saturated Ca(OH)<sub>2</sub> solution with addition of CH<sub>3</sub>COOK (2.5 mol/l) shows the same spectrum as a solution of CH<sub>3</sub>COOK (2.5 mol/l) alone. Compared to a solution of Ca(CH<sub>3</sub>COO)<sub>2</sub> (2.5 mol/l), there are only minor differences, mostly in intensity of the typical CH<sub>3</sub>COO<sup>-</sup> bands at 1553 cm<sup>-1</sup> and 1416 cm<sup>-1</sup> (Figure 3). For comparison, the pH in the saturated solution of CaSO<sub>4</sub>·2H<sub>2</sub>O increased only slightly after addition of CH<sub>3</sub>COOK, but the Ca concentration increased considerably (Figure 4).

For a saturated solution of Ca(OH)<sub>2</sub> with solid Ca(OH)<sub>2</sub> in excess and addition of CH<sub>3</sub>COOK, the speciation calculation shows an increasing pH that is strongly related to the formation of aqueous Ca-acetate complexes (Figure 5). At low acetate concentrations CaCH<sub>3</sub>COO<sup>+</sup> is the dominant complex, at higher concentrations Ca(CH<sub>3</sub>COO)<sub>2</sub> is more stable. Although the concentration of Ca<sup>2+</sup> is decreased, the total Ca concentration in the solution increases. With increasing addition of CH<sub>3</sub>COOK, the increase of pH and the total Ca concentration slows down. Compared to the total CH<sub>3</sub>COO<sup>-</sup> concentration (not shown in Figure 5), there are only a few percent of Ca-acetate complexes in the solution. Comparable results were obtained for HCOOK.

The ICP-OES analysis for the pore solutions of the vacuum-immersed cement paste samples showed an increase of the K concentration for the samples immersed in the deicer solutions (Figure 6). However, the pH was not as much affected than expected and even decreased for the high-alkali cement pastes (Figure 7). The Ca concentration is always higher in the cement pastes immersed in the deicer solutions than in water. At later ages, the Ca concentration increased especially in the low-alkali cement paste samples immersed in the CH<sub>3</sub>COOK-based deicer solution (Figure 8). The SO<sub>4</sub><sup>2-</sup> concentration (not shown) increased for both cement pastes treated with deicer solution, especially in case of HCOOK. The XRD-analysis (not shown) has revealed a decrease of the ettringite peak for the cement pastes exposed to the deicer solutions.

### 4 DISCUSSION

CH<sub>3</sub>COOK (2530 g/l at 20 °C) and HCOOK (3310 g/l at 20 °C) are extremely water-soluble salts of acetic acid (CH<sub>3</sub>COOH) and formic acid (HCOOH) respectively. Dissolved in water, the acetate/formate-ions behave according to the acid/base theory of Brønsted-Lowry as a base and absorb protons from water (Equation 1 and 2). Hence, aqueous solutions of CH<sub>3</sub>COOK and HCOOK are always slightly alkaline. The pH in such solutions can be calculated by using Equation 3. The smaller the pK<sub>b</sub> value the stronger the base, i.e. the greater its tendency to absorb protons. The equilibrium constants of Equation 1 and 2 indicate that only small amounts of the dissolved acetate and formate ions form acetic and formic acid.

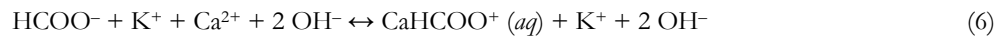


$$\text{pH} = 14.0 - 0.5 \cdot (\text{p}K_b - \log c) \quad (3)$$

with: pK<sub>b</sub> = -log K<sub>b</sub> = basicity constant

c = concentration of acetate/formate ions in an aqueous solution, [mol/l]

The speciation calculation for the saturated solution of  $\text{Ca}(\text{OH})_2$  with addition of  $\text{CH}_3\text{COOK}$  fits considerably well to the experimental results (Figure 9). For  $\text{HCOOK}$ , the mechanism is assumed to be the same, but at higher concentrations there are greater differences between speciation calculation and experimental results. This is probably caused by using ion-association approaches for the calculation of the activity coefficients, because with increasing ionic strength, the results will become progressively unreliable due to increasing ion interactions [10]. Furthermore, underlying uncertainties to the thermodynamic data also affect the calculation. Regardless of that, the formation of the Ca-acetate and Ca-formate complexes provides an fundamental explanation for the observed increase of pH and the total Ca concentration as well (Equation 4, 5, 6 and 7). Since  $\text{Ca}^{2+}$  is consumed for the formation of these complexes, more solid  $\text{Ca}(\text{OH})_2$  is dissolved to maintain the equilibrium (Equation 8). Consequently, the total Ca concentration and the pH increase in the solution.



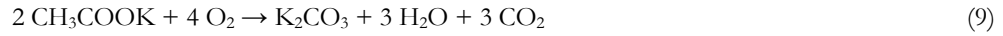
Because of the decreasing solubility of  $\text{Ca}(\text{OH})_2$  with increasing pH, there will be not enough Ca in the solution for a precipitation of solid  $\text{Ca}(\text{CH}_3\text{COO})_2$ . That is supported by the findings of the XRD, FT-IR and ESEM/EDS analysis, where no new precipitation products could be found [11]. However, the direct detection of the Ca-complexes turned out to be more difficult. The FT-IR analysis provided no indication for Ca-complexes in the solutions on the basis of peak shifts or appearance of new bands (Figure 3). But the speciation calculation shows that only small amounts of the Ca-complexes are formed, which may aggravate the detection. Furthermore, FT-IR is appropriate to identify organic ions, but not necessarily to which inorganic ions they are related to. An indirect verification provides the increased solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in pure water after addition of  $\text{CH}_3\text{COOK}$  (Figure 4). The solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in pure water (2.0 g/l at 20 °C) is comparable to  $\text{Ca}(\text{OH})_2$  (1.7 g/l at 20 °C), but in the  $\text{CH}_3\text{COOK}$  solution (2.5 mol/l), the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  increased about 9-times (21.9 g/l at 20 °C). The reason for this is again the formation of aqueous Ca-acetate complexes. But contrary to  $\text{Ca}(\text{OH})_2$ , a much higher Ca concentration is reached, because the pH increases only slightly, caused by the deprotonation of water (Equation 1), and consequently no  $\text{Ca}(\text{OH})_2$  will precipitate.

In a study from Diamond et al., even a pH of 15.1 was measured after addition of  $\text{Ca}(\text{OH})_2$  in a  $\text{CH}_3\text{COOK}$  solution of 50 wt%, which is a typical concentration (6.2 mol/l) of commercial runaway deicer solutions [12]. The existence of Ca-acetate complexes was confirmed in study by Frantz using Raman-spectroscopy [13]. It was found that in Ca-acetate solutions the concentration of the aqueous species  $\text{Ca}(\text{CH}_3\text{COO})_2$  increased with increasing addition of solid Ca-acetate to the solution and with increasing temperature. The solubility of  $\text{Ca}(\text{OH})_2$  in acetate solutions was investigated by Seewald et al. at high temperatures and pressures. It was found that the solubility of  $\text{Ca}(\text{OH})_2$  increased in acetate solutions due to the formation of the strong aqueous complex of  $\text{CaCH}_3\text{COO}^+$  which is accompanied by an pH increase. Only if the Ca-complex formation was considered in the speciation calculations, experimental results correlated with the calculations [14, 15, 16]. Already Taylor suggested, that organic compounds could attack concrete through complexing of  $\text{Ca}^{2+}$  and consequent dissolution of  $\text{Ca}(\text{OH})_2$ , but also of hydrated silicate and aluminate phases [17]. In a study of Dramé et al. a severe leaching-dissolution effect was observed on C-S-H-paste samples immersed in a Ca-Mg-acetate solution [18]. Degradation effects and altering processes on cement pastes exposed to acetate solutions were also reported in other studies [19, 20].

Concretes exposed to deicers based on  $\text{HCOOK}$  during the cyclic climate storage showed in the ESEM/EDS-analysis massive formations of tricarboaluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaCO}_3 \cdot 32\text{H}_2\text{O}$ ) in the surface near zone (Figure 9) [21]. Tricarboaluminate, the carbonate analogue of ettringite [17], was identified by the missing sulphur peak but increased carbon peak in the EDS spectrum [8]. This also indicates an interaction between  $\text{HCOOK}$  deicing solutions and ettringite.

It is well established that acetates and formates are degradable in contact with oxygen, but certain micro organisms are required to start the reactions (Equation 9 and 10). A degradation mechanism could not be found in the laboratory, but in fact takes places in the field. Due to the lower oxygen demand, degradation of formates occurs faster than of acetates. The rate of degradation increases with rising temperature, but high rates are already achieved at low temperatures [22]. It

is unknown so far, if degradation might be a significant mechanism that could affect ASR in the field. However, if degradation products would come into contact with a saturated solution of  $\text{Ca}(\text{OH})_2$ , poorly soluble  $\text{CaCO}_3$  will precipitate (Equation 11). Consequently, solid  $\text{Ca}(\text{OH})_2$  is dissolved to maintain equilibrium and the pH would also rise (Equation 8).



The cement paste experiments showed some deviating results from the solubility experiments. In fact, the K concentration increases clearly, indicating the ingress of the deicer solution into the cement paste. However, the pH did not increase for the high-alkali cement samples but decreases. At later ages, only a slight increase of the pH was observed for the low-alkali cement pastes. But generally, the pH and the Ca concentration for the samples immersed in the deicer solutions are higher than for the samples immersed in water. A problem with immersion-techniques is leaching, especially when small samples are used, what probably affected the obtained results, especially the decreasing pH. Also the  $\text{SO}_4^{2-}$  concentration increased for the samples immersed in the deicer solutions, especially in case of HCOOK. That would support the observed decomposition of ettringite by XRD-analysis, which could also be accompanied by the formation of tricarboaluminate, as observed by ESEM/EDS in concretes exposed to HCOOK-deicers during the cyclic climate storage but not found with XRD [21].

The general findings indicate that due to the higher solubility of portlandite in presence of acetate and formate based deicers, more  $\text{OH}^-$  ions are released and consequently the pH increases. This mechanism would clearly promote the attack of reactive aggregates (i.e. silica) and leads to an accelerated ASR in concrete. This also explains why low-alkali cements are not capable of permanently preventing an ASR in concrete exposed to acetate and formate based deicers, if reactive aggregates are used. The alkalis from the deicers alone would not necessarily cause an ASR, as long as the pH would stay low enough. But now, since solid portlandite is also present in concrete with low-alkali cement, more and more  $\text{OH}^-$  ions will be released gradually due to the increased solubility of portlandite in contact with the acetate and formate ions. If reactive aggregates were used, ASR will occur sooner or later. This was confirmed by results from the cyclic climate storage (Figure 11), which is used successfully as ASR performance-test [23].

## 5 CONCLUSIONS

Experiments with model pore solutions and cement pastes, as well as speciation calculations were performed to explain why deicers based on acetates and formates can initiate and highly accelerate ASR in concrete with reactive aggregates. The findings from the solubility experiments showed an immediate increase of the pH and of the Ca concentration in saturated solutions of  $\text{Ca}(\text{OH})_2$  after addition of  $\text{CH}_3\text{COOK}$  and  $\text{HCOOK}$  respectively, but no new reaction products were found. Only the speciation calculations indicate the formation of strong aqueous complexes of  $\text{CaCH}_3\text{COO}^+$ ,  $\text{Ca}(\text{CH}_3\text{COO})_2$  and  $\text{CaHCOO}^+$ ,  $\text{Ca}(\text{HCOO})_2$  respectively, resulting in an increased solubility of  $\text{Ca}(\text{OH})_2$ . Although Ca-complexes could not be found directly by any performed analysis, experiments with  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  support the theory of Ca-complex formation. The cement paste experiments showed some different results and new questions raised, but the findings were generally supported. Ultimately, two chemical mechanisms seem to initiate and accelerate the ASR in concrete with reactive aggregates exposed to deicers based on acetates and formates: (1) excess supply of alkalis and (2) release of  $\text{OH}^-$  ions due to the increased solubility of  $\text{Ca}(\text{OH})_2$ . These mechanisms are able to explain the general results found by the cyclic climate storage, including the observation that low-alkali cements may delay the ASR but can not prevent it permanently in concretes with reactive aggregates and exposed to deicers based on acetates and formates.

## 6 REFERENCES

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- [1] Chatterji, S., Thaulow, N., Jensen, A.D.: Studies of alkali-silica reaction. part 4. Effect of different alkali salt solutions on expansion, *Cement & Concrete Research* 17 (1987): 777–783
  - [2] Bérubé, M.A., Dorion, J.F.: Laboratory and field investigations of the influence of sodium chloride on alkali-silica reactivity, *Alkali-aggregate reaction in concrete*, Proceedings of the 11<sup>th</sup> ICAAR, Québec City, Canada (2000): 149–158

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- [3] Sutter L., Peterson, K., Touton, S., Van Dam, T., Johnston, D.: Petrographic evidence of calcium oxychloride formation in mortars exposed to magnesium chloride solution, *Cement & Concrete Research* 36 (2006): 1533–1541
- [4] Rangaraju, P.R., Sompura, K.R., Olek, J.: Investigation into potential of alkali-acetate based deicers in causing alkali-silica reaction in concrete, Department of Civil Engineering, Clemson University (2006)
- [5] Rangaraju, P.R., Olek, J.: Potential for acceleration of ASR in the presence of pavement deicing chemicals. IPRF Research Report (2007)
- [6] Stark, J., Seyfarth, K.: Performance testing method for durability of concrete using climate simulation. Proceedings of the 7<sup>th</sup> CANMET/ACI International Conference on Durability of Concrete, Montreal, Canada (2006): 305-326
- [7] Stark, J., Giebson, C.: Assessing the durability of concrete regarding ASR. Proceedings of the 7<sup>th</sup> CANMET/ACI International Conference on Durability of Concrete, Montreal, Canada (2006): 225-238
- [8] Stark, J., Seyfarth, K., Giebson, C.: Beurteilung der Alkali-Reaktivität von Gesteinskörnungen und AKR-Performance-Prüfung Beton. 16. Internationale Baustofftagung (ibausil), Tagungsbericht Band 2, Weimar (2006): 399-426
- [9] Parkhurst, D.L., Appelo C.A.J.: PHREEQC for Windows – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, Version 2.14.00 (PHREEQC-2 version 2.14.1-2217), Graphical user interface by Post, V.E.A. (2007), [http://wwwbrr.cr.usgs.gov/projects/GWC\\_coupled/phreeqc/index.html](http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html)
- [10] Anderson, G.: Thermodynamics of natural systems. Cambridge University Press, Second Edition (2005)
- [11] Goldbach, A.: Influence of runway deicers on ASR in airfield pavement concretes. Diploma thesis, Bauhaus-University Weimar, F.A. Finger-Institute for Building Materials Science (2006)
- [12] Diamond, S., Kotwica, L., Olek, J., Rangaraju, P.R., Lovell, J.: Chemical aspects of severe ASR induced by potassium acetate airfield pavement deicer solution. Proceedings of the 8<sup>th</sup> CANMET International Conference on Recent Advances in Concrete Technology, Marc-André Bérubé Symposium on Alkali-Aggregate Reactivity in Concrete, Montreal, Canada (2006): 261–277
- [13] Frantz, J.D.: Salts of aliphatic carboxylic acids: Raman spectra and ion pairing in hydrothermal solutions containing sodium and calcium acetates. *Chemical Geology*, Vol. 164 (2000): 1-20
- [14] Seewald, S.F., Seyfried, W.E.: Experimental determination of portlandite solubility in H<sub>2</sub>O and acetate solutions at 100-350°C and 500 bars: Constraints on calcium hydroxide and calcium acetate complex stability. *Geochimica et Cosmochimica Acta*, Vol. 55 (1991): 659-669
- [15] Shock, E.L., Koretsky, C.M.: Metal-organic complexes in geochemical processes: Calculation of standard partial molal thermodynamic properties of aqueous acetate complexes at high pressures and temperatures. *Geochimica et Cosmochimica Acta*, Vol. 57 (1993): 4899-4892
- [16] Shock, E.L., Koretsky, C.M.: Metal-organic complexes in geochemical processes: Estimation of standard partial molal thermodynamic properties of aqueous complexes between metal cations and monovalent organic acid ligands at high pressures and temperatures. *Geochimica et Cosmochimica Acta*, Vol. 59 (1995): 1497-1532
- [17] Taylor, H.F.W.: Cement chemistry, Thomas Telford Publishing, London (1997), 2<sup>nd</sup> Edition
- [18] Dramé, H., Beaudoin J.J., Raki, L.: A comparative study of the volume stability of C-S-H (I) and portland cement paste in aqueous salt solutions. *Journal of Materials Science*, Vol. 42, No. 16 (2007): 6837–6846
- [19] Santagata, M.C., Collepardi M.: The effect of CMA deicers on concrete properties. *Cement & Concrete Research* 30 (2000): 1389–1394
- [20] Lee, H., Cody, R.D., Cody, A.M., Spry, P.G.: Effects of various deicing chemicals on pavement concrete deterioration. Mid-Continent Transportation Symposium, Center for Transportation Research and Education, Iowa State University (2000): 151–155
- [21] Stark, J., Bellmann, F., Gathemann, B., Seyfarth, K., Giebson, C.: The influence of alkali-containing deicing agents on the alkali-silica reaction in pavement concretes for roads and airports. *ZKG international*, No. 11-2006 (Vol. 59): 74-82
- [22] Johnson, K.L.: Environmentally safe liquid runway deicer. Cryotech Deicing Technology, Iowa, (2006)
- [23] Stark, J., Seyfarth, K.: Assessment of specific pavement concrete mixtures by using an ASR performance-test, Proceedings of the 13<sup>th</sup> ICAAR, Trondheim, Norway, 2008

TABLE 1: Supplementary thermodynamic data for speciation calculations at 25 °C.				
Phases and Species	Formula	Reaction	log $K^{\circ}$	Reference
Portlandite	$\text{Ca}(\text{OH})_2 (s)$	$\text{Ca}^{2+} + 2 \text{OH}^-$	-5.19	[9]
Acetic acid	$\text{CH}_3\text{COOH} (aq)$	$\text{H}^+ + \text{CH}_3\text{COO}^-$	-4.76	[10]
Potassium acetate	$\text{CH}_3\text{COOK} (aq)$	$\text{K}^+ + \text{CH}_3\text{COO}^-$	+0.34	[10, 15]
Calcium monoacetate	$\text{CaCH}_3\text{COO}^+ (aq)$	$\text{Ca}^{2+} + \text{CH}_3\text{COO}^-$	-0.85	[10, 15]
Calcium diacetate	$\text{Ca}(\text{CH}_3\text{COO})_2 (aq)$	$\text{Ca}^{2+} + 2 \text{CH}_3\text{COO}^-$	-1.25	[10, 15]
Formic acid	$\text{HCOOH} (aq)$	$\text{H}^+ + \text{HCOO}^-$	-3.75	[10]
Potassium formate	$\text{HCOOK} (aq)$	$\text{K}^+ + \text{HCOO}^-$	-0.03	[10, 16]
Calcium monoformate	$\text{CaHCOO}^+ (aq)$	$\text{Ca}^{2+} + \text{HCOO}^-$	-1.40	[10, 16]
Calcium diformate	$\text{Ca}(\text{HCOO})_2 (aq)$	$\text{Ca}^{2+} + 2 \text{HCOO}^-$	-2.24	[10, 16]

<sup>1)</sup> Calculated by using  $\Delta_r G^\circ = -RT \ln K$  with data from the given reference

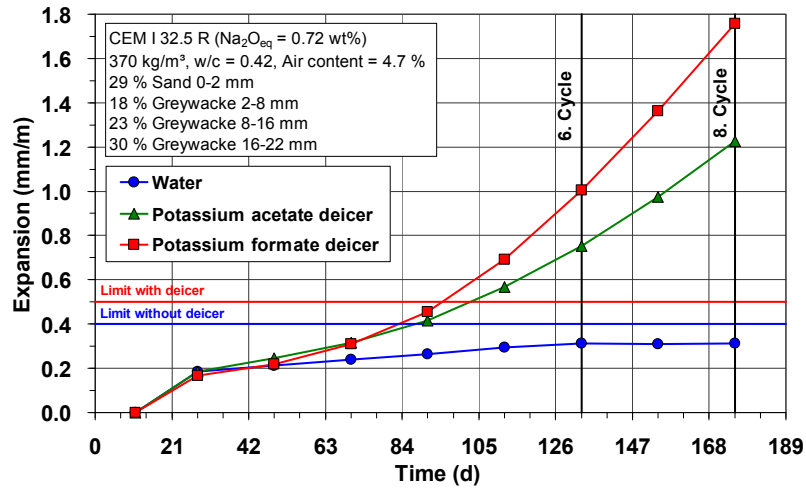


Figure 1: Expansion during the cyclic climate storage for a tested pavement concrete with reactive greywacke, exposed to deicer solutions and water (control)

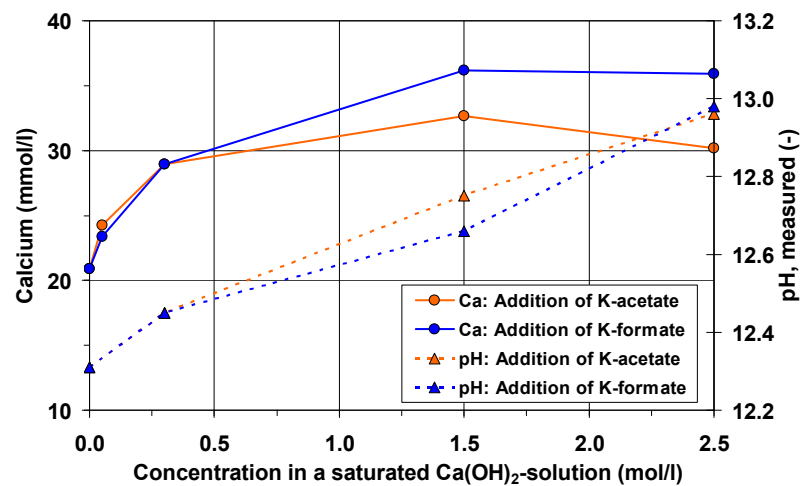


Figure 2: Increase of pH and Ca concentration in a saturated solution of  $\text{Ca}(\text{OH})_2$  with addition of  $\text{CH}_3\text{COOK}$  and  $\text{HCOOK}$  respectively

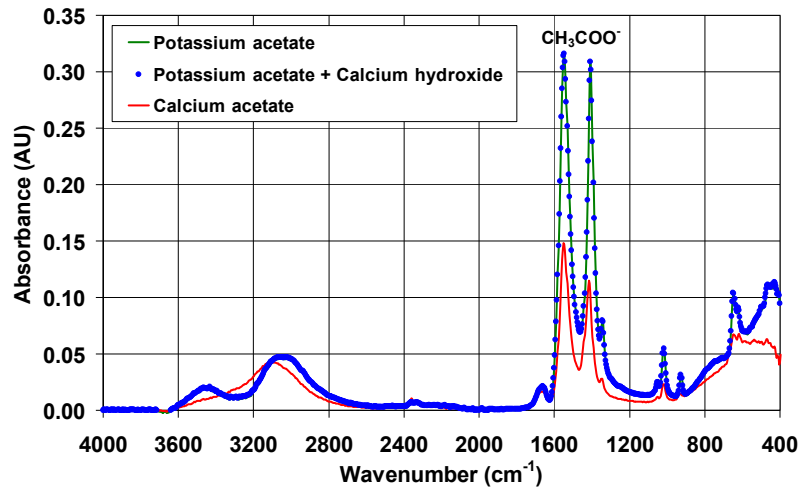


Figure 3: FT-IR spectra (water subtracted) from solutions (2.5 mol/l) of pure  $\text{Ca}(\text{CH}_3\text{COO})_2$ ,  $\text{CH}_3\text{COOK}$  and a saturated solution of  $\text{Ca}(\text{OH})_2$  with  $\text{CH}_3\text{COOK}$

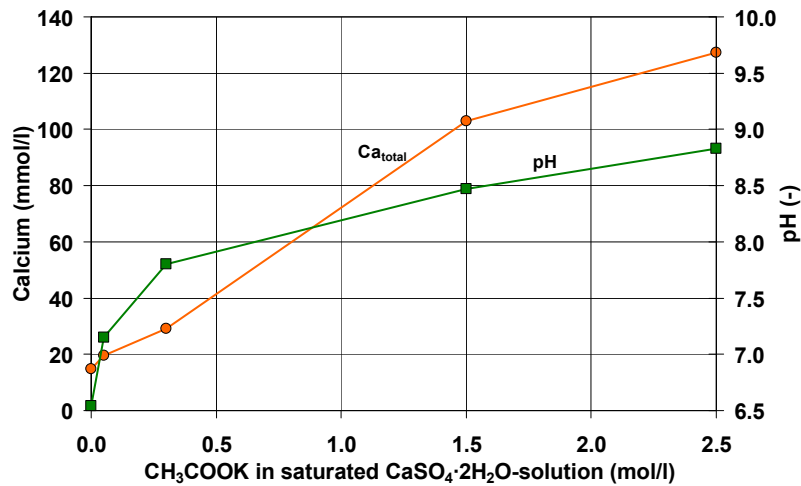


Figure 4: Increase of pH and Ca concentration in a saturated solution of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  with addition of  $\text{CH}_3\text{COOK}$

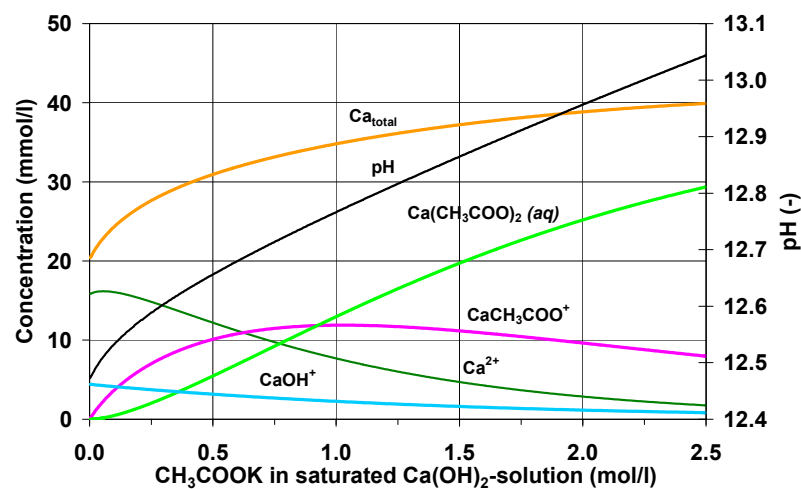


Figure 5: Calculated species distribution in a saturated solution of  $\text{Ca}(\text{OH})_2$  with addition of  $\text{CH}_3\text{COOK}$  at 25 °C



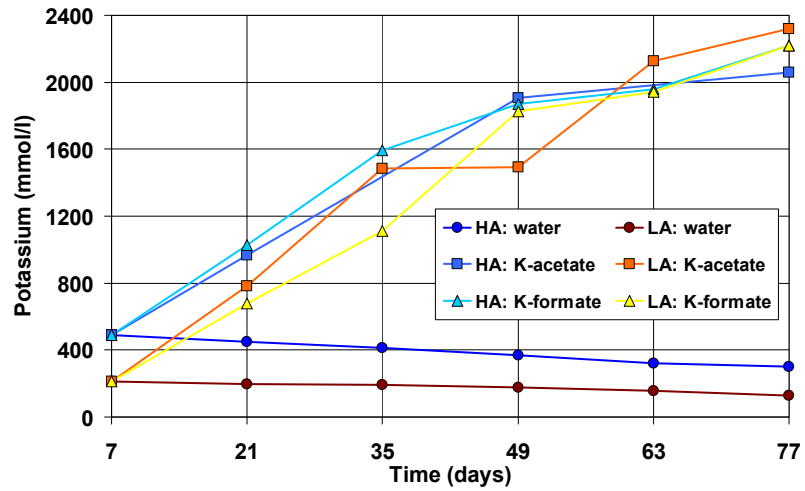


Figure 6: Pore solution analysis (potassium) for cement paste samples (HA = high-alkali cement, LA = low-alkali cement) after vacuum-immersion in water and two commercial deicer solutions

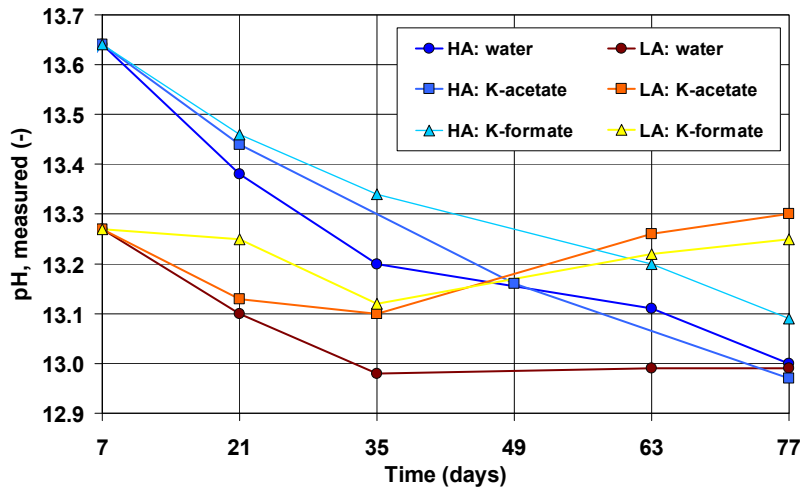


Figure 7: Pore solution analysis (pH) for cement paste samples (HA = high-alkali cement, LA = low-alkali cement) after vacuum-immersion in water and two commercial deicer solutions

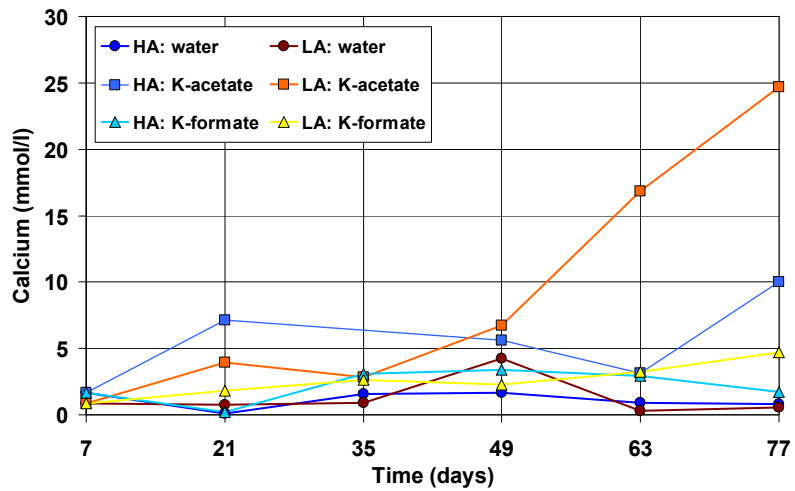


Figure 8: Pore solution analysis (calcium) for cement paste samples (HA = high-alkali cement, LA = low-alkali cement) after vacuum-immersion in water and two commercial deicer solutions

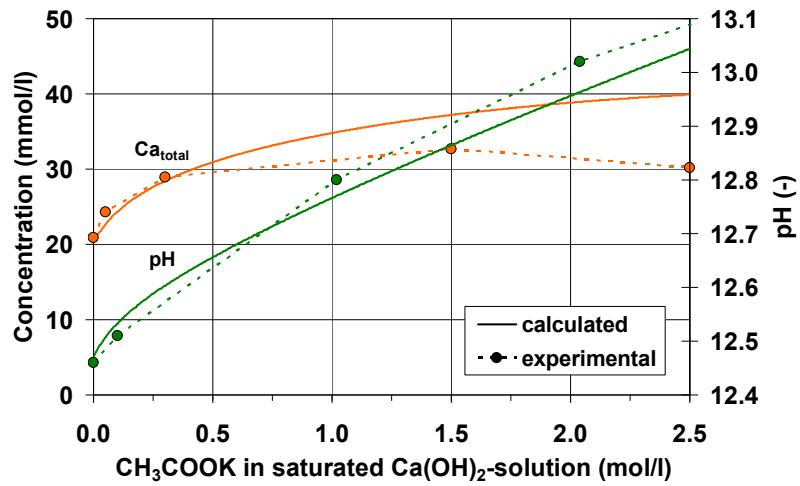


Figure 9: Calculated and measured pH and total Ca concentration in a saturated solution of  $\text{Ca}(\text{OH})_2$  with addition of  $\text{CH}_3\text{COOK}$  at 25 °C

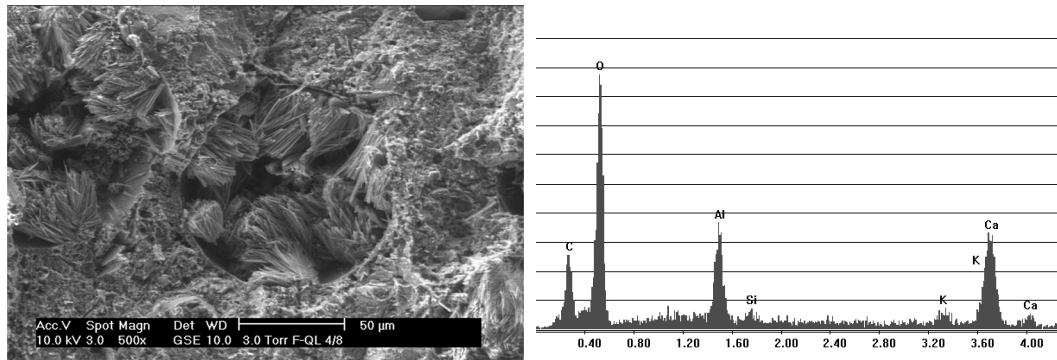


Figure 10: Tricarboaluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaCO}_3 \cdot 32\text{H}_2\text{O}$ ) in concrete air voids near to the concrete surface (3-5 mm) and EDS-spectrum, sample obtained from a concrete exposed to K-formate deicer solution during the cyclic climate storage

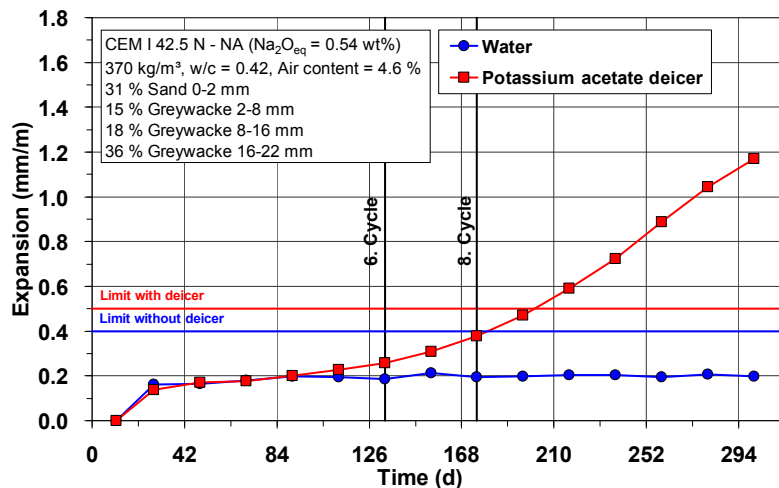


Figure 11: Expansion during the cyclic climate storage for a tested pavement concrete with reactive greywacke and low-alkali cement, exposed to a deicer solution and water (control)