CENTER OF EXCELLENCE FOR AIRPORT TECHNOLOGY

TECHNICAL NOTE

TECH NOTE NO: 36

TITLE: pH of Potassium Acetate Deicing Solution

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Abstract

The pH of potassium acetate deicing solution increased from about 10 to above 14 when the solution is mixed with a small amount of calcium hydroxide. Experiments were performed to understand the reason for this increase. There was no formation of a precipitate that might cause such an increase in pH. Experimental results suggest that the high pH may be due to a high hydroxide ion activity coefficient, but model calculations do not support this conclusion.

Introduction

This work is part of a project on the influence of potassium acetate deicing solution on alkali-silica reaction in concrete. The alkali-silica reaction occurs when silica dissolves in high pH solution, followed by formation of a hydrous alkali-silica gel that absorbs large amounts of water and swells, generating localized stresses that cause the concrete to crack and producing expansion. The reaction is usually initiated by portland cement with a high content of alkali (sodium and potassium). As the cement hydrates, the pore solution develops an alkali hydroxide concentration typically about 1 M and a pH typically about 13.8. The potassium acetate deicing solution is about 5-6 M CH_2COOK (hereafter abbreviated KAc). The solution has a pH about 10-11. But with the addition of a small amount of hydroxide, say in the form of calcium hydroxide, the pH increases to well above 14. The objective of the current study was to explore whether the high pH of deicing solution after the addition of calcium hydroxide is due to precipitation of a calcium acetate phase (which is not expected from solubility considerations) or reflects a very high hydroxide ion activity coefficient (γ_{OH}) due to the very high ionic strength of the solution. For this purpose, we measured the change in pH and the chemical composition when deicing solution was mixed with various amounts of calcium hydroxide or potassium hydroxide.

Experiment results and discussion

1. Different amounts of calcium hydroxide (2-g, 5-g, and 10-g) were mixed with 50-mL deicing solution or reagent-grade KAc solution prepared at the same concentration, about 6.3 M. The pH of all deicing solutions increased from an initial value of 11.1 to above 14.2 in 24 hours, and the pH of all KAC solutions increased from an initial value of 9.7 to about 14.2 in 24 hours (as shown in Figure 1). The result suggest that the increase in pH produced when hydrated cement is mixed with KAc deicing solution is due solely to the hydroxide ion normally found in the hydrated cement pore solution.

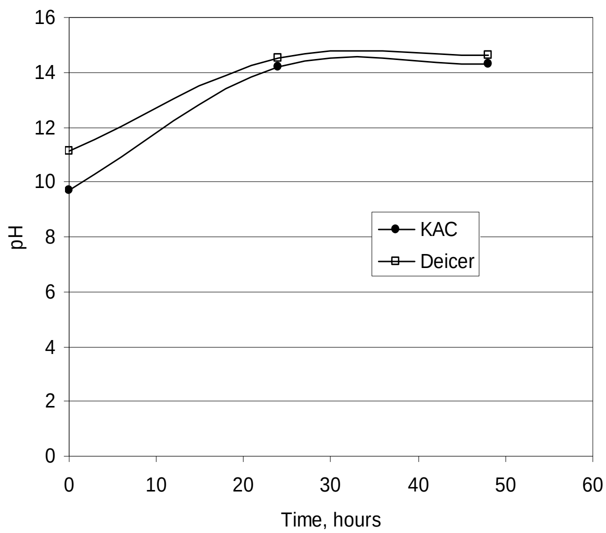

Figure 1. pH versus time after the reaction between Ca(OH)2 and KAc or Deicing solution.

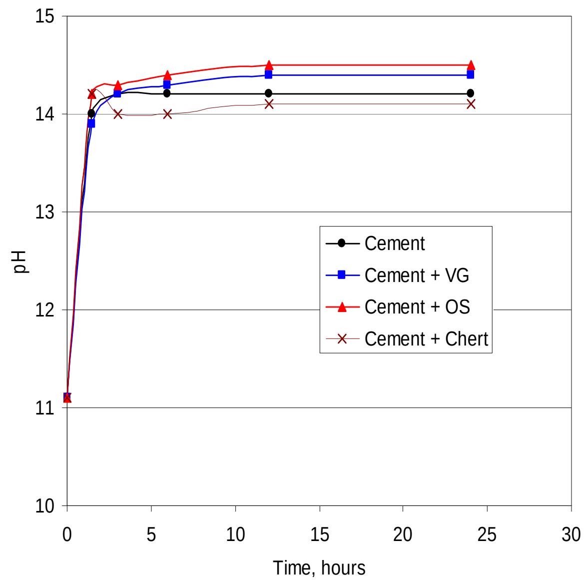

Figure 2. pH versus time after reaction between $Ca(OH)_2$, aggregate, and deicing solution. VG is vycor glass and OS is Ottawa sand.

2. The solution samples after the reaction between 5-g calcium hydroxide and 50-mL deicing solution or 6.3-M KAc solutions were analyzed[1] for the amounts of acetate, sodium, calcium and pH. Acetate concentration was found to be very low in the solid residue after reaction, indicating no precipitation. Concentration of Ca^{2+} was still low after reaction, indicating little dissolution of $Ca(OH)_2$. The calcium concentration was lower than theoretically required to produce such a high pH value (using an assumed activity coefficient of 1). Therefore, the increase of pH was not due to dissolution of $Ca(OH)_2$ or precipitation of acetate.

[1] Performed by the Water Management and Resource Center (WMRC) at University of Illinois.

Table 1. Composition of deicing and KAc solutions after reaction with $Ca(OH)_2$

Solution	Ions	Before reaction, mol/L	After reaction, mol/L
Deicer + $Ca(OH)_2$	Ac^-	~6.20	7.12
	K^+	~6.20	6.28
	Ca^{2+}	0	0.013
KAc+ $Ca(OH)_2$	Ac^-	~6.10	6.78
	K^+	~6.10	5.46
	Ca^{2+}	0	0.02

Table 2. Composition of solid residue after the reaction between $Ca(OH)_2$ and deicing or KAc solutions

Solid (per 1g)	Ions	Before reaction, mg	After reaction, mg
Deicer + $Ca(OH)_2$	Ac^-	0	32
	K^+	0	145
	Ca^{2+}	541	314
Deicer + $Ca(OH)_2$	Ac^-	0	33
	K^+	0	136
	Ca^{2+}	541	297

3. In a similar experiment, mixtures of 5-g calcium hydroxide and 50-mL 6.3-M KAc solution were prepared and allowed to react, then filtered and the [K^+], [Ca^{2+}], organic carbon, total carbon and alkalinity were analyzed[2]. The concentration of Ca^{2+} was still low after reaction, indicating little dissolution of $Ca(OH)_2$. There was a small amount of Ac^- in the solid after reaction, which probably came from evaporation of the solution. The very low concentration of OH^- confirmed that the high pH probably reflects the very high ionic strength.

Table 3. Composition analysis of 5-g $Ca(OH)_2$ and 50-mL KAc solution

	K^+	Ca^{2+}	Ac^-	OH^-	CO_3^{2-}
Solution, M	5.21	0.00225	6.61	0.026	N/A
Solid, mol per 1 Kg	2.72	7.75	1.19	N/A	[4.21]

4. The solid residue after the reaction between $Ca(OH)_2$ and deicing solution or 6.3-M KAc solution was analyzed by X-ray diffraction (XRD). The results, shown in Figures 3 and 4, indicate that the solid after reaction contained mainly $Ca(OH)_2$ and KAc.

[2] Also in the WMRC.

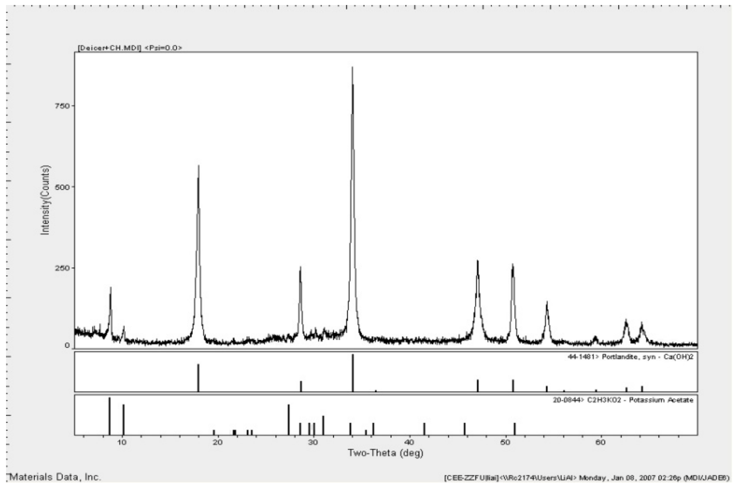

Figure 3. XRD analysis of the solid residue after the reaction between $Ca(OH)_2$ and deicing solution.

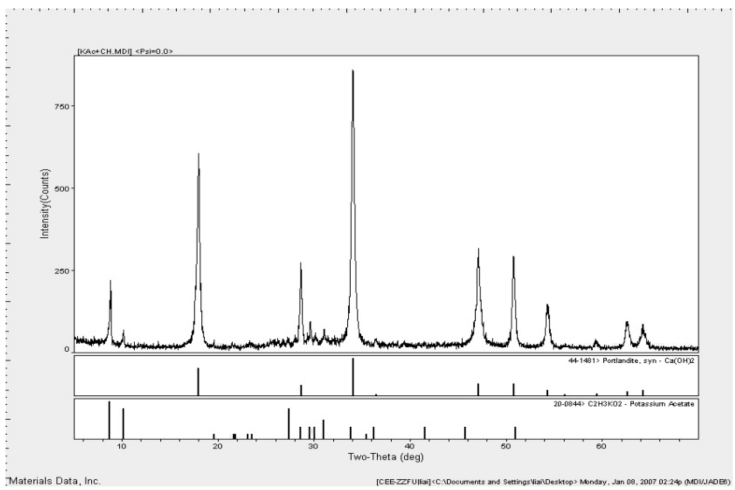

Figure 4. XRD analysis of the solid residue after reaction between $Ca(OH)_2$ and deicing solution.

5. 13-mL filtrate solution produced from the reaction between deicing solution and $Ca(OH)_2$ was titrated, with the pH being measured as function of added water. The initial pH was about 14.5. The measured values (blue) were greater than the calculated values (black), which assumed that γ=1. The difference between the measured and the calculated values decreased steadily and progressively with addition of water. There is no sharp drop in pH that would indicate a chemical reaction (dissolution or precipitation). Rather, the steady decrease in pH suggests that the initial pH is high because the small concentration of hydroxide ion has been amplified by the very high activity coefficient

resulting from the very high ionic strength of the deicing solution and that this activity coefficient approaches unity with addition of water. The titration curve supports the hypothesis that the increase of pH was due to the very high concentration ionic strength in the KAc deicing solution.

6. Mixtures were prepared of deicing solution or doubly distilled (DD) water and

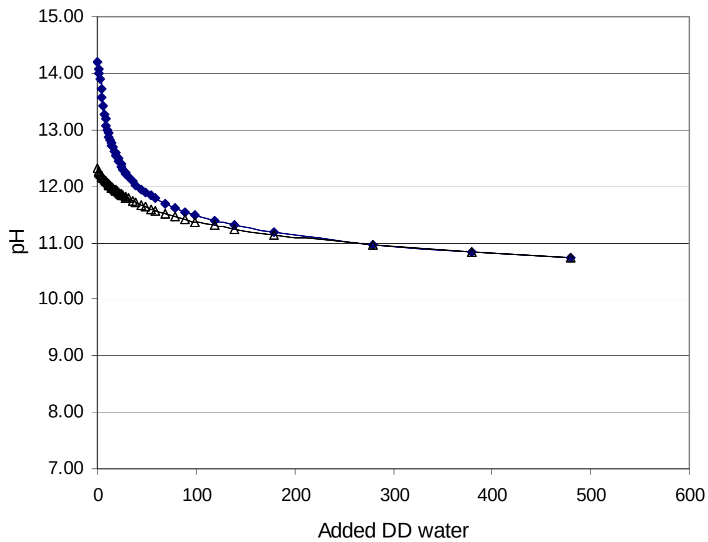

Figure 5. pH titration curve for 13-mL solution after reaction with $Ca(OH)_2$.

solutions with different concentrations of NaOH or KOH. The pH was measured as function of concentration of added OH^-. The test results are shown in Figure 6 and 7 for deicing solution (blue) or DD water (black). The pH of the deicing solution was much higher than the pH of water at the same concentration of hydroxide ion. The measured pH levels were also very high even when the alkali hydroxide concentration was low. For example, the pH of 0.091-M NaOH in deicing solution was 14.3, and the pH of 0.11-M KOH in deicing solution was 14.7. In addition, there was no sharp rise in pH that would indicate chemical reaction (dissolution or precipitation). Therefore, the high pH appears to reflect the very high ionic strength of deicing solution.

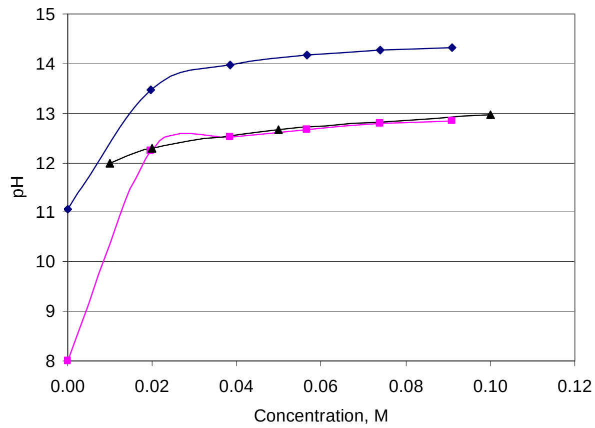

Figure 6. pH as function of NaOH concentration in water (black) or deicing solution (blue). The purple curve is the theoretical pH in water.

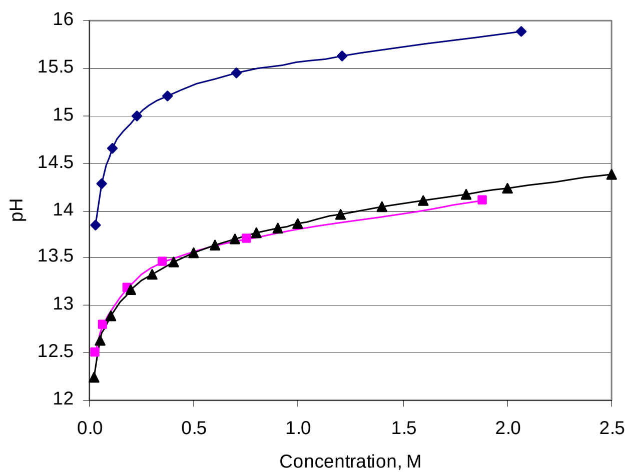

Figure 7. pH as function of concentration of KOH in water (black) or deicing solution (blue). The purple curve is the theoretical pH in water.

The activities of OH^- calculated from the measured values of pH and $[OH^-]$ versus the concentration of NaOH or KOH are shown in Figures 8 and 9, respectively. The test results indicate that, as a general rule, the activity coefficient of OH^- increased with its concentration. These activity coefficient values are extremely high.

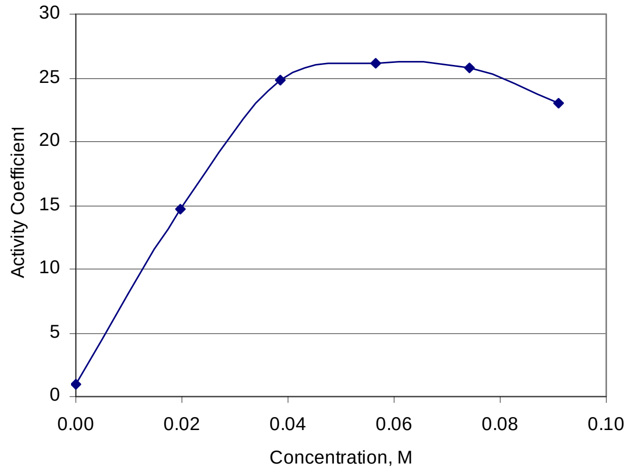

Figure 8. Hydroxide ion activity coefficient versus concentration of NaOH in 6.3-M deicing solution.

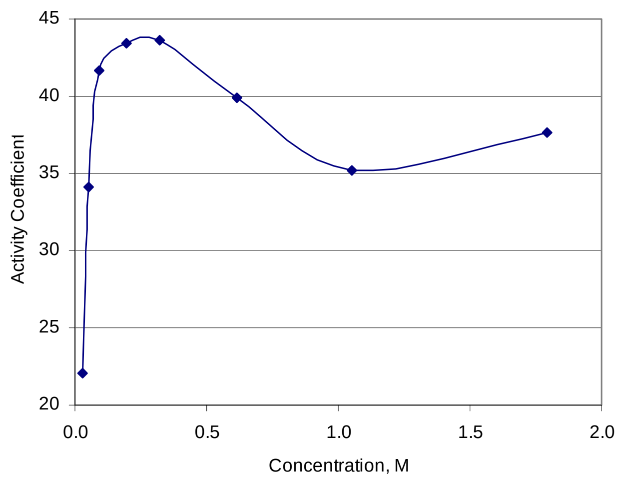

Figure 9. Hydroxide ion activity coefficient versus concentration of KOH in 6.3-M deicing solution.

7. In another set of experiments, 5-g samples of aggregate were mixed with 5-g cement powder and 50-mL deicing solution and pH was measured. Three aggregate materials were tested: vycor glass and chert, both known to be reactive with alkali, and Ottawa sand, known to be nonreactive with alkali. The pH of the solutions after reaction increased from about 11.1 above 14.0 for all three aggregates.

8. A modified quick chemical test (ASTM C289) was performed for Ottawa sand and Vycor glass in a solution of 6.3-M KAC to which a small amount of NaOH was added. Solutions were filtered and analyzed for pH and dissolved silica. The initial pH was 13.5, which is the pH of the 1-M NaOH solution used in C289. The solutions after reaction showed negligible dissolved silica and marked decrease in pH. The test results demonstrated that both Ottawa sand and Vycor glass did not pursue any deleterious reaction in such a solution, probably because the small amount of NaOH required to produce the initial pH was consumed with little aggregate dissolution. More consideration is required on how we might measure the chemical changes associated with these reactions.

9. Some modeling was done to compute the activity coefficient of OH^- in KAC/KOH solution. A standard chemical potential model (the Pitzer equations) was used. The model produced activity coefficient values between 1 and 1.2, much lower than that computed from measured pH and $[OH^-]$ values (about 30). This result raises some uncertainty about whether high activity coefficient is responsible for the high pH.

Discussion

It is not possible to conclude from this work whether the high pH observed when concentrated KAc solution is mixed with calcium hydroxide is due to a high hydroxide ion activity coefficient. Experimental results suggest this is the case, but model calculations do not. If it is the case, then this behavior may not be specific to KAc, but rather it may be general in such highly concentrated deicing solutions.

Conclusions

When a small amount of $Ca(OH)_2$ was added to concentrated KAc solution, the pH increased from about 10 to more than 14. Similar results were obtained when concentrated KAc solution was mixed with Portland cement and aggregate. There was no evidence of CaAc precipitation that might cause such an increase in pH. Experimental results suggest that the high pH may be due to a high hydroxide ion activity coefficient, about 30, though values computed using a standard chemical potential model were much lower, about 1-1.2. Thus this work has demonstrated that the deicing solution shows a strong increase in pH when mixed with calcium hydroxide or portland cement but has not shown the reason for the increase.