

Development of Preventive Method for Caking at Freezing Temperatures of Road Salt

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We studied the inhibition of sodium chloride dihydrate precipitation, and established a preventive method for caking at freezing temperatures using additives. The solubility of sodium chloride is fairly constant above 0.5 °C, but it decreases in proportion to the decrease in temperature below 0.5 °C. The crystals precipitating under this condition are sodium chloride dihydrate. The amount of precipitate increases in proportion to the decrease in temperature, and shows a rapid rate of increase below -5 °C. On the addition of other chemicals, the solubility of sodium chloride decreased in proportion to the increase in the concentration of additives. This effect was significant since the hydration enthalpy ($-\Delta H$) also increased. The amount of sodium chloride dihydrate precipitates also decreased in proportion to the increase in the concentration of additives, with a corresponding increase of the hydration enthalpy. Caking at freezing temperatures was prevented by adding substances having hydration enthalpies greater than that of the sodium ion. This effect was significant since the hydration enthalpy also increased.

1. INTRODUCTION

Sodium chloride in the presence of water transforms to sodium chloride dihydrate below 0.1 °C, which has the formula $\text{NaCl} \cdot 2\text{H}_2\text{O}$. Precipitation of sodium chloride dihydrate on the surface of sodium chloride particles will result in solid bridging at these contacts, thus cementing the particles together. The outcome is that it is very difficult to handle such caking aggregates. In northeastern Japan in the winter of 1993, road salt caked at freezing temperatures in large quantities, and a solution to this problem was demanded. Therefore, we studied the inhibition of sodium chloride dihydrate precipitation, and established a preventive method for caking at freezing temperatures using additives.

2. MATERIALS AND METHODS

2.1. Additives

The additives and their hydration enthalpies are shown in Table 1.

2.2. Experimental method

The experimental method is shown in Figure 1.

Table 1

Additives and their hydration enthalpies

Additive	Hydration enthalpy of M^+ $-\Delta H (\text{kJ} \cdot \text{mol}^{-1})$
KCl	320
CsCl	259
MgCl_2	1908
AlCl_3	4690
MgSO_4	1908

Hydration enthalpy of Na^+ is $-404 \text{ kJ} \cdot \text{mol}^{-1}$.

Additive solution (0.5 °C) 0.02 ~ 0.8 mol/100g H_2O

— NaCl

Solution saturated with NaCl

— NaCl (25g/100g H_2O)

Stir 72h (-5 or -15 °C)

Sampling

Solution

K, Cs, Mg, Ca, Al, Cl, SO_4

Precipitated matter

Measurement of weight

K, Cs, Mg, Ca, Al, Cl, SO_4

Figure 1. Experimental method

A solution saturated with sodium chloride was prepared by dissolving sodium chloride into an additive solution in a beaker at 0.5 °C. More sodium chloride was added to this solution (25g/100gH₂O), and then the beaker was sealed with film made of polyvinyliden chloride. The solution and precipitated matter were analyzed after stirring for 72h at -5 or -15 °C. The reagents used were of a special purity grade made by Wako Pure Chemical Ind. Ltd..

2.3. Analytical method

The amount of sodium chloride dihydrate precipitates was calculated using equations in Table 2. Equation No.1 was based on the supposition that all of the water lost from the solution transforms into sodium chloride dihydrate. Equation No.2 was based on the supposition that all the water originating from precipitated matter above 0.5 °C came from sodium chloride dihydrate.

Table 2

Calculation equations of NaCl · 2H₂O

1. Equation from analytical value of solution

$$S = \frac{262.2 (W_0 - (100 A_0/C_A - A_0 - N))}{W_0}$$

2. Equation from weight of precipitated matter

$$S = \frac{2.622 H (X - Y)}{W_0}$$

S: Amount of NaCl · 2H₂O precipitate (g/100gH₂O)

W₀: Initial weight of H₂O (g)

A₀: Initial weight of additive (g)

N: Final amount of dissolved NaCl (g)

C_A: Final concentration of additive (%)

X: Final weight of precipitated matter (g)

Y: Weight of solid matter at 20 °C (g)

H: Concentration of H₂O in filtrate at 20 °C (%)

2.622: NaCl · 2H₂O/2H₂O

Potassium, magnesium, calcium, chloride ions and sulfate ions were analyzed by method for salt analysis¹⁾. Aluminium was analyzed by plasma emission spectroscopic analysis. Cesium was analyzed by atomic absorption spectroscopic analysis.

The caking strength was measured by the

following method. Ground salt (65g) containing 3% water was packed into a cylindrical vessel and pressed at 20kg·cm⁻². The vessel was kept for 48h at -15 °C. Then, the breaking load of caking aggregates was measured.

Sodium chloride dihydrate was observed using a microscope (Nikon Co., Ltd. OPTIPHOTO-POL). The precipitated matter was identified using an X-ray diffractometer (Rigaku Co., Ltd. Rint-Ultima) at -15 or 20 °C.

3. RESULTS

3.1. Effect of additives on solubility of sodium chloride

Relationships between additive concentration and sodium chloride solubility are shown in Figures 2 ~ 7. The same relationship at 0.5 °C is shown in Figure 8 for comparison.

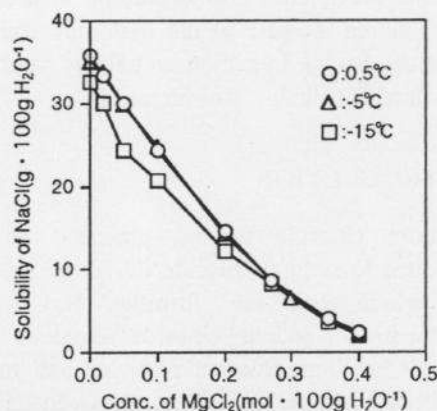


Figure 2. Relationship between concentration of MgCl₂ and solubility of NaCl

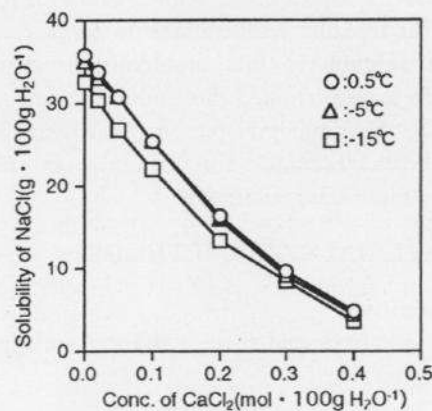


Figure 3. Relationship between concentration of CaCl₂ and solubility of NaCl

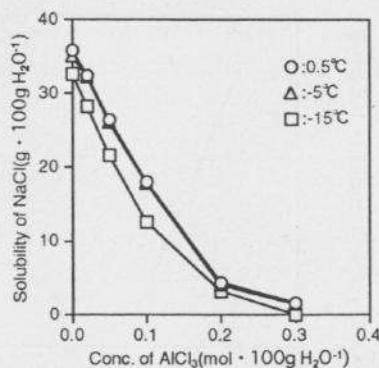


Figure 4. Relationship between concentration of AlCl_3 and solubility of NaCl

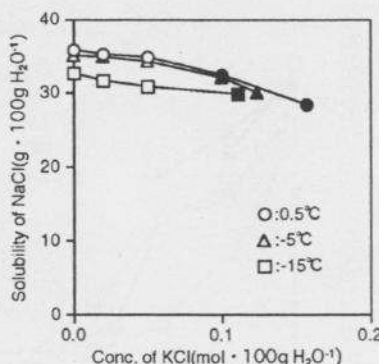


Figure 5. Relationship between concentration of KCl and solubility of NaCl
●▲■ : Precipitated KCl

We have classified the pattern of change of sodium chloride solubility into three groups based on the obtained results.

- 1) Chlorides of a cation whose hydration enthalpy is greater than that of the sodium ion.
- 2) Chlorides of a cation whose hydration enthalpy is less than that of the sodium ion.
- 3) Magnesium sulfate.

As shown in Figures 2 ~ 4, in the No.1 group, when the concentration of additives increased, the additives did not precipitate and the solubility of sodium chloride decreased suddenly in proportion to the increase in the concentration of additives. When temperature decreased from 0.5 °C to -5 °C, the solubilities of sodium chloride decreased negligibly for all concentrations of additives. When temperature decreased from 0.5 °C to -15 °C, the solubility of sodium chloride decreased considerably for low concentrations of additives, but negligibly for high concentrations of additives.

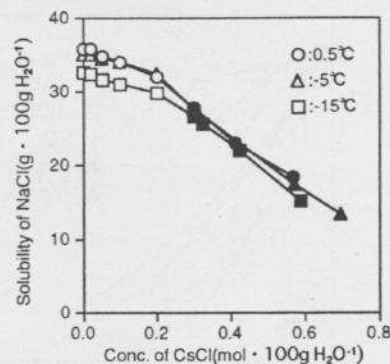


Figure 6. Relationship between concentration of CsCl and solubility of NaCl
●▲■ : Precipitated CsCl

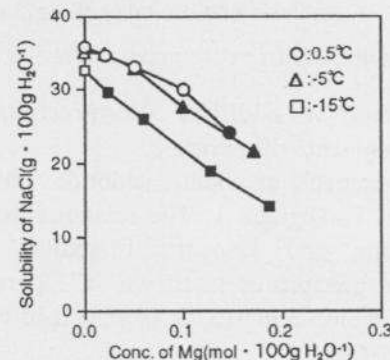


Figure 7. Relationship between concentration of Mg and solubility of NaCl (Added MgSO_4)
●▲■ : Precipitated Na_2SO_4

As shown in Figures 5 and 6, in the No.2 group, when the concentration of additives increased, the additives precipitated, and the solubility of sodium chloride decreased gently in proportion to the increase in the concentration of additives.

As shown in Figure 7, in magnesium sulfate, when the concentration of magnesium sulfate increased, sodium sulfate n-hydrate precipitated, and the magnesium sulfate concentration under which sodium sulfate n-hydrate begins to precipitate decreased in proportion to the decrease in temperature. When sodium sulfate n-hydrate precipitated, the solubility of sodium chloride decreased suddenly in proportion to the increase in the concentration of magnesium sulfate.

As shown in Figure 8, the effect where the solubility of sodium chloride decreased in proportion to the increase in the concentration of additives was significant since the hydration enthalpy of cation also increased. This tendency

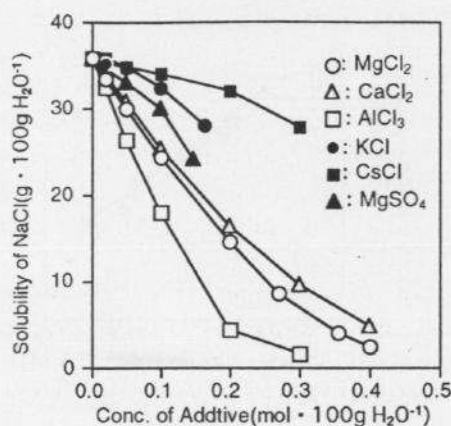
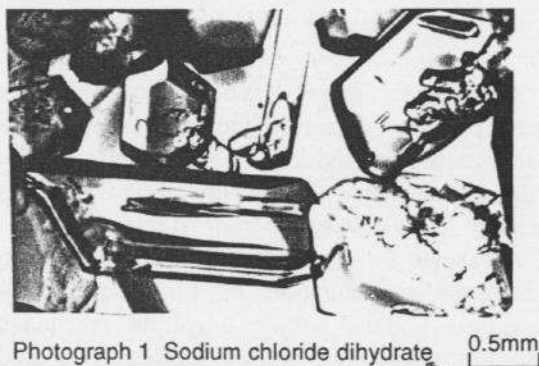


Figure 8. Relationship between concentration of additives and solubility of NaCl at 0.5°C

was the same at different temperatures.

3.2. Effect of additives on precipitation of sodium chloride dihydrate

A micrograph of sodium chloride dihydrate is shown in Photograph 1. The relationship between temperature and amount of sodium chloride dihydrate precipitates is shown in Figure 9. The same relationship at -15 °C is shown in Figure 10 for comparison.



Photograph 1 Sodium chloride dihydrate 0.5mm

As shown in Photograph 1, the crystals of sodium chloride dihydrate were monoclinic in flat plates with certain edges beveled. They transformed into sodium chloride as soon as temperature increased.

As shown in Figure 9, the sodium chloride dihydrate precipitates increased suddenly below -5 °C. This was similar to the sudden decrease of the solubility of sodium chloride below -5 °C. As shown in Figure 10, the sodium chloride dihydrate precipitates decreased in proportion to the increase

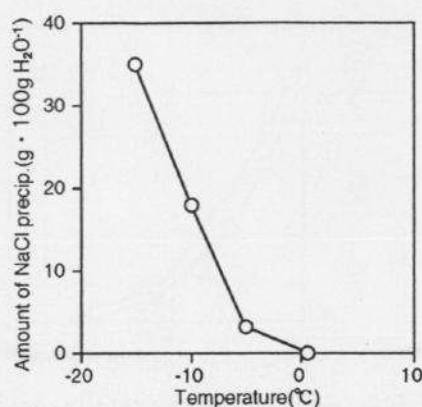


Figure 9. Relationship between temperature and amount of NaCl · 2H₂O precipitates

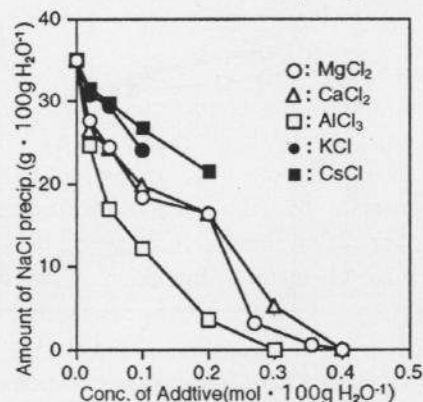


Figure 10. Relationship between concentration of additives and amount of NaCl · 2H₂O precipitates

in the concentration of additives. This effect is significant since the hydration enthalpies of the cations also increased. The precipitation of sodium chloride dihydrate was prevented by adding the chloride of aluminium, magnesium and calcium, whose hydration enthalpies are greater than that of the sodium ion.

3.3. Effect of additives on caking strength

The relationship between the concentration of additives and caking strength is shown in Figure 11.

The caking strength decreased in proportion to the increase in the concentration of additives for compounds of cations whose hydration enthalpies are greater than that of the sodium ion. However, the caking strength did not decrease on increasing the additive concentration for compounds of cations whose hydration enthalpies are less than that of the sodium ion.

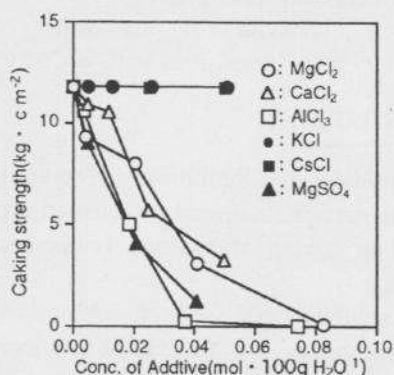


Figure 11. Relationship between concentration of additives and caking strength at -15°C

4. DISCUSSION

The solubility of sodium chloride and the amount of precipitates of sodium chloride dihydrate in the solution of additives decreased in proportion to the increase in the concentration of additives. This appears to be influenced by the decrease in the number of water molecules in bulk as a consequence of hydrate formation from ions of additives and water molecules in the solution.

We will discuss the additives of chloride below. When the hydration enthalpies of cations are greater than that of the sodium ion, the additives do not precipitate on increasing the additive concentration because the affinities of cations for water are greater than that of sodium ion. Then the number of water molecules in the bulk decreases, as does the solubility of sodium chloride. In the case of a high concentration of additives, the solubility of sodium chloride is very low at 0.5°C (transformation point) since there are fewer water molecules in the bulk than in the case of a low concentration of additives. When temperature decreases from 0.5°C to -15°C , the solubility of sodium chloride decreases negligibly and sodium chloride dihydrate precipitates negligibly.

When hydration enthalpies of cations are less than that of the sodium ion, the phenomena could be explained as follows. At a low concentration of additives, the solubility of sodium chloride decreases gently in proportion to the decrease in the number of water molecules in the bulk. At a high concentration of additives, the additives precipitate with sodium chloride since the affinities

of cations for water are less than that of the sodium ion. The solubility of sodium chloride decreases gently in this case. Decreases in the amount of sodium chloride dihydrate precipitates are less than in the case where hydration enthalpies of cations are less than that of the sodium ion, since the variance of sodium chloride solubilities between 0.5°C and -15°C is large.

In the case of magnesium sulfate, the phenomena are complex since the kinds of ions increase. Umano et al.²⁾ reported that sulfate ion precipitates as a sodium sulfate depending upon the temperature and concentration of chloride ions at the freezing concentration of sea water. The amount of sodium sulfate precipitates increases in proportion to the decrease of the temperature and the increase of the chloride ion concentration. Our results are in agreement with the results of Umano et al. In the case of a low concentration of magnesium sulfate, when the temperature decreases from 0.5°C to -5°C , sodium chloride dihydrate precipitates slightly. As temperature decreases further, the precipitate changes to sodium sulfate n-hydrate. The temperature at which the precipitate changes to sodium chloride n-hydrate decreases in proportion to the decrease of magnesium sulfate concentration. The amount of sodium chloride dihydrate precipitates is less than in the case of magnesium chloride, since the precipitate changes to sodium sulfate n-hydrate. In the case of a high concentration of magnesium sulfate, sodium chloride dihydrate negligibly precipitates since sodium sulfate n-hydrate precipitates above -5°C . We have observed that magnesium sulfate n-hydrate becomes a gel including the whole solution at -15°C . Therefore, we believe that this compound cannot cause caking, and that the caking strength is lower than in the case of magnesium chloride, since the amount of sodium chloride dihydrate precipitates is small.

Of the chlorides, sodium chloride solubility and the amount of sodium chloride dihydrate precipitates decrease in proportion to the increase of the hydration enthalpies of cations. The hydration enthalpy is a value which indicates the bonding strength between an ion and a water molecule, so this indirectly influences the decrease of water molecules in the bulk. The hydration

number, which is the number of water molecules bonding with an ion through hydration, directly influences the decrease of water molecules in the bulk. The hydration number was measured by various methods, but results differed depending on the measuring method. We assume that the number of water molecules in the bulk decreases due to hydration with the added ions, and the solubility of sodium chloride decreases with the decrease of water molecules in the bulk. Hence, we calculated the hydration numbers of additive ions based on this assumption, and show them in Table 3. Okada et al.³⁾ have reported that there is no distinct domain of a hydration structure on the chloride ion. Therefore we assume that the hydration number of chloride ion is 0. And the hydration numbers calculated from the measured nuclear magnetic resonance (NMR)^{4,6)} and obtained by Ulich⁷⁾ is shown in Table 3 for comparison.

Table 3
Hydration number of various ions

Ion	Hydration number		Ulich ⁷⁾
	this report	by NMR	
K	5.3	3.0 ⁴⁾	6
Cs	3.4	3.0 ⁵⁾	—
Mg	18	6.0 ⁶⁾	9
Ca	16	6.0 ⁴⁾	6
Al	28	6.0 ⁶⁾	—

As shown in Table 3, the hydration numbers obtained in this work are greater than those calculated from the measured NMR, and they are close to the hydration numbers obtained by Ulich. The hydration number calculated from the measured NMR indicates the number of water molecules which have interact directly with ions. Ulich considered that the loss of the degree of freedom of water molecules due to the formation of hydration ions is equal to that of the water molecules due to freezing. Consequently, he obtained the hydration number by dividing of the hydration entropy of the ion by the solidification entropy of water ($-25\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). This hydration number is the number of water molecules which indicate various strengths of interaction with ions. Therefore, we believe that the effects of decreasing the sodium chloride solubility and the sodium

chloride dihydrate precipitates are revealed by the "hydration" behavior of the water molecules undergoing mild interactions with added ions.

5. CONCLUSION

We studied the inhibition of sodium chloride dihydrate precipitation, and established a preventive method for caking at freezing temperatures using additives.

The solubility of sodium chloride is fairly constant above 0.5°C , but it decreases in proportion to the decrease in temperature below 0.5°C . The crystals precipitating under this condition are sodium chloride dihydrate. The amount of precipitate increases in proportion to the decrease in temperature, and shows a rapid rate of increase below -5°C .

On the addition of other chemicals, the solubility of sodium chloride decreased in proportion to the increase in the concentration of additives. This effect was significant since the hydration enthalpy ($-\Delta H$) also increased. The amount of sodium chloride dihydrate precipitates also decreased in proportion to the increase in the concentration of additives, with a corresponding increase of the hydration enthalpy. Caking at freezing temperatures was prevented by adding substances having hydration enthalpies greater than that of the sodium ion. This effect was significant since the hydration enthalpy also increased.

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