DEVELOPMENT OF NEW CHLORIDE GROUP DEICING/ANTI-FREEZING AGENTS

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1 Astract

The chloride group (calcium chloride dihydrate, sodium chloride, magnesium chloride hexahydrate) has occupied most of the deicing/anti-freezing agents currently used. The reasons are that they have high snow/ice melting capability and low price in the chloride group. In recent years, there has been talk about the influence on the environment by deicing/anti-freezing agents. When the above agents are spread on the street, there are some problems such as the corrosion of metal materials like the parts of a car or a guardrail, and other problems such as the degrading of concrete. Further, the reduction of the amount of the agents spread is required in order to reduce the influence on the environment.

As a result of a study in our company, in order to solve these problems, we found that the following methods are effective.

① By mixing a little addition of the amino-acid compounds into the chloride group deicing/anti-freezing agents, metal corrosion and concrete degradation could be controlled up to about 15% and 70%, respectively. In case of mixing some kind of grain grounds, corrosive of metal materials could also be controlled up to 80%.

② The lab examination proved that the mixing two kinds of chloride group agents was improved snow/ice melting capability. As a result, the total amount of the mixed agents spread could be less than the amount of each agent spread.

2 Introduction

The deicing /anti-freezing agents (Agents) are sprinkled in order to prevent the traffic accidents from a freezing road surface. The chloride group Agents (calcium chloride dihydrate, sodium chloride, magnesium chloride hexahydrate) have a large thaw / melting-ice capacity, and they are low priced. The calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) has a freezing point as low as –55℃, and it has an exothermic reaction of –285 J/g. Consequently, an appearance of the deicing effect is quick (Immediacy effect). On the other hand, the freezing point of the sodium chloride (NaCl) is comparatively high at –21℃, and it has an endothermic reaction of +87 J/g. Although an appearance of the effect is slow, it is durable (Durability effect). Moreover, the freezing point of magnesium chloride ($MgCl_2 \cdot 6H_2O$) is -33℃, and it has an exothermic reaction of –61 J/g. It is seen to have a middle effect between $CaCl_2 \cdot 2H_2O$ and NaCl. The chloride groups Agents demonstrate the excellent function in maintaining a road surface from freezing in winter. However the influence on the environment of metal corrosion, concrete degradation, inhibition of plant growth and water-quality aggravation, etc. have been problematic[1)2)].

In Tokuyama Corporation, in order to solve the above-mentioned problems, research and development has been undertaken from two viewpoints. The 1st examined the effect of an additive agent for the purpose of reducing the environmental influence of the Agents themselves. Consequently, for the concrete degradation control, it found out that glycine was effective[3)]. The 2nd method, the winter road surface monitoring system[4)], was developed from the idea that the amount of the used Agents can be decreased by managing road surface clearance and then clarifying the amount of Agents sprayed on a winter road surface. In this paper, the 1st method, covers two points ①Paying attention to the metal corrosion by spraying the Agents, the anticorrosive effect was observed by lab experiments. And the anticorrosive effect was investigated by the real road-spraying test. ②The deicing effect of the mixed Agents of $CaCl_2 \cdot 2H_2O/NaCl$ was investigated, and the possibility of curtailment of the spraying amount was examined.

3 The Effect of The Anticorrosion Agents

3-1 The Research of Anticorrosive effect

3-1-1 The Method of Lab Examination

3wt%-$CaCl_2$ (NaCl) aqueous solutions that added the additive agents (anticorrosive) of predetermined quantity was adjusted. These solutions were made to 25±1℃, and pH was measured. Weight of test pieces (SS400, 60×40×2.5 mm) were measured after degreasing in IPA. Subsequently, these test pieces were dipped in each aqueous solution. After seven days, rust adhering to the test pieces was removed by sandpaper, and the weight was measured.

As for the capability evaluation of the anticorrosive, the amount of corrosion (MDD) and the anti-corrosion ratio was determined by the following formula.

$$\mathrm{MDD} = \frac{\text{Weight reduction of test piece(mg)}}{\text{Area of test piece(dm}^2\text{)Lapsed time(day)}}$$

Anti-corrosion ratio (%) = (A-B) / A × 100

A : MDD (in $CaCl_2 \cdot 2H_2O$).

B : MDD (in $CaCl_2 \cdot 2H_2O$ with anticorrosive).

3-1-2 Experiment Result

As for the anticorrosion of the Agents, it is also important not to have a bad effect on the environment (animals and plants). Then, the anticorrosion effect of the substances shown below were investigated.

① Phosphate group, Silicate group : It is known as corrosion inhibitor, such as an iron pipe.

② Phytic acid : It is used as an inactivation agent of metal ion.

③ Rice bran : Raw material of phytic acid.

④ Another natural substance : soybean cake, rice less and rapeseed oil.

(1) The anticorrosion effect of a phosphate group and a silicate group

The corrosion amount of test pieces for $CaCl_2$ and NaCl solution were 16.3 MDD and

19.0 MDD, respectively (Table 1 1', 2'). It turns out that the corrosion rate of NaCl is a little quicker than $CaCl_2$.

The anticorrosion effect of phosphate groups and silicate groups are shown in Table 1. About phosphate groups, phosphates other than sodium tripolyphosphate ($Na_5P_3O_{10}$) showed the anticorrosion effect (No.1-6). In the phosphate groups more than 50% anticorrosion ratio were sodium dihydrogenphoshate ($NaH_2PO_4 \cdot 2H_2O$, No.1), di-sodium hydrogenphoshate ($Na_2HPO_4 \cdot 12H_2O$, No.2) and sodium hexametaphosphate (No.4). When adding the phosphate to the $CaCl_2$ solution, pH has an acidity of 4.6〜6. Moreover, when these phosphates were added to the $CaCl_2$ solution, white precipitation was generated. Although calcium phosphate was formed, it was shown to have an anticorrosion effect also in the heterogeneous state. Next, the relationship between the additional amount of the phosphate and the anticorrosion amount was investigated (Fig. 1). In Figure 1, The addition 1wt% of $NaH_2PO_4 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 12H_2O$ was seen to be the optimum ($NaH_2PO_4 \cdot 2H_2O$: 69%, $Na_2HPO_4 \cdot 12H_2O$: 67%). On the other hand, in the case of hexametaphosphate, even if 1〜5wt% of the addition showed about an 80% anticorrosion ratio and the additional amount increased, the effect did not decrease.

About sodium silicates ($Na_2O \cdot nSiO_2$)[5], the anticorrosion effect was not obtained in the same little addition as the phosphate. However, with increasing the additional amount from 5 to 10 times, the anticorrosion effect of $Na_2O \cdot 3.2SiO_2 \cdot nH_2O$ (Be'=41 15℃), $Na_2O \cdot 2SiO_2$ (crystallinity SKS-6 ; made in Clariant Tokuyama Ltd.) and $Na_2O \cdot 2SiO_2 \cdot nH_2O$ (amorphous SKS-6/H_2O ; made in Clariant Tokuyama Ltd.) were obtained regardless of the kind of sodium silicate (No.7-11). When influence of the mole ratio (n) of $Na_2O \cdot nSiO_2$ was examined (No. 8, 10), the anticorrosion effect of $Na_2O \cdot 2SiO_2$ (anticorrosion ratio=56%) was superior to $Na_2O \cdot 3.2SiO_2$ (anticorrosion ratio =28%) by about 2 times. This is because the sodium silicates of n= 2 have strong alkalinity (pH=11). Next, we investigated the difference between crystallinity and amorphous nature (No. 10, 11). There is no difference in the anticorrosion ratio, and both showed about 60% of the value. These sodium silicates reacted with calcium chloride like the already described phosphate, and generated white precipitation. The relationship between the additional amount of sodium silicate and the anticorrosion ratio is

Table 1 The anticorrosion effect of a phosphate group and a silicate group

No.	Agents[1)] (3wt%)	Anticorrosive	Additional amount[3)] (wt%)	pH	MDD (mg/dm^2 day)	Anticorrosion ratio (%)
1'	A	non	non	9.39	16.3	-
2'	B	non	non	7.84	19.0	-
1	A	$NaH_2PO_4 \cdot 2H_2O$	1	4.69	5.1	69
2	A	$Na_2HPO_4 \cdot 12H_2O$	1	5.78	5.4	67
3	A	$Na_3PO_4 \cdot 12H_2O$	1	10.34	15.0	8
4	A	Sodium polyphosphate	1	5.96	3.1	81
5	A	Sodium hexametaphosphate	1	9.42	15.2	7
6	A	$Na_5P_3O_{10}$	1	9.63	17.1	-5
7	A	n=3.2[2)]	1	9.45	16.0	2
8	A	n=3.2	5	9.69	11.7	28
9	A	n=3.2	10	9.64	10.4	36
10	A	n=2 (crystallinity)	5	11.08	7.2	56
11	A	n=2 (amorphous)	5	11.01	6.7	59

1) A: $CaCl_2$, B: NaCl

2) $Na_2O \cdot nSiO_2$

3) (Anticorrosive/Agents)×100

shown in Figure 2. The optimum additional amount for the sodium silicates were also like the phosphate. When there was the sodium silicate of n= 2, 5wt% of addition was effective. When it was $Na_2O\cdot 3.2SiO_2$, 10% of addition was effective.

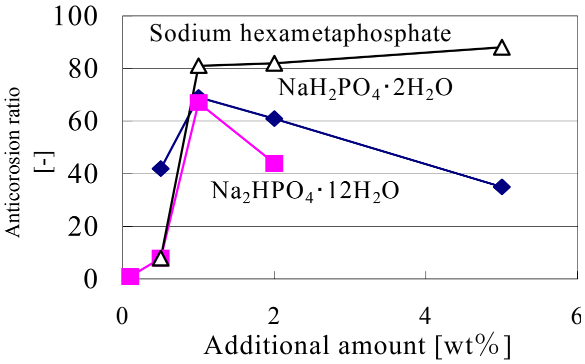


Fig. 1 The relationship between additional amount of phoshate and anticorrosion ratio (3%-$CaCl_2$, 25℃)

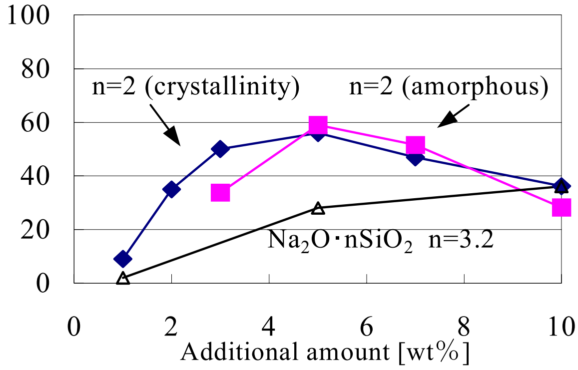


Fig. 2 The relationship between additional amount of silicate and anticorrosion ratio (3%-$CaCl_2$, 25℃)

(2) The anticorrosion effect of the phytic acid and the natural products

The anticorrosion effect of phytic acid used as an inactivation agent of metal ion is shown in Table 2. Only when there were few additions (0.4 - 1.0wt%) of the phytic acid, about 50% of the anticorrosion effect was seen (No.1,2). When there were many additions of the phytic acid, shortly after putting the test piece into the solution, the small blister was seen on the test piece. That is, the corrosion was promoted (No.3). The pH of the aqueous solution has a strong acidic nature, and it turned out that it changes acidity with the increase in the addition (0.4wt%→5wt%) of the phytic acid (pH=2.9→1.68). Subsequently, the anticorrosion effect of phytic acid with raw rice bran[6)] was investigated (No.4-6). When the addition of rice bran was 5wt%, the greatest anticorrosion effect of 84% was shown, and it turned out that rice bran was superior to the phytic acid. The pH of the aqueous solution had weak acidity (5.58). From this result, it was suggested that the active composition of rice bran is not only a phytic acid. Moreover, when it was added in NaCl solution (No.7), 72% of anticorrosion was shown. Although the anticorrosion effect (No.8-10) of soybean cake, rice less and rapeseed oil of other natural products were investigated, there was nothing superior to rice bran.

Table 2 The anticorrosion effect of the phytic acid and the natural products

No.	Agents[1)] (3wt%)	Anticorrosive	Additional amount (wt%)	pH	MDD (mg/dm^2 day)	Anticorrosion ratio (%)
1	A	phytic acid[2)]	0.4	2.9	7.7	52.9
2	A	phytic acid	1	2.45	7.9	51.6
3	A	phytic acid	5	1.68	19.5	-19.6
4	A	rice bran	1	8.36	11.5	29
5	A	rice bran	5	5.58	2.6	84
6	A	rice bran	10	4.87	5.1	69
7	B	rice bran	5	6.81	4.6	72
8	A	soybean cake	10	9.2	13.4	18
9	A	rice less	10	6.59	15.2	6
10	A	rapeseed oil	10	7.84	6.6	60

1) A: $CaCl_2$, B: NaCl 2) phytic acid: 50%aq.

3-2 The Real Road-Spraying Examination

3-2-1 The Method of Examination

From the result of the laboratory examination, when the influence on the natural environment, anticorrosion effect and price etc. were taken into consideration, we judged that rice bran excelled most as an anticorrosive. Then, the Agents (Photo. 1) with molding rice bran (2-3 mm) was adjusted. The real road-spraying examination was performed in two areas of Gifu Prefecture's Gujo and Toyama Prefecture's Toyama City. Test pieces were installed in the spraying part of each Agent. Then effect of the Agents spraying was investigated looking at the following conditions. The evaluation of a corrosion amount was performed by the same method as the 3-1-1term.

Conditions :

① Used Agents

Gifu Prefecture : $CaCl_2 \cdot 2H_2O$/Rice Bran=95/5 (wt%)

Toyama Prefecture : $CaCl_2 \cdot 2H_2O$/NaCl/Rice Bran=47.5/47.5/5 (wt%)

② Test pieces (60 mm × 38 mm × 2 mm)

3 kinds ; SS400, Zn plating steel material and paint steel material (epoxy paint).

③ Installation Places (Three Places)

- The part which sprinkles the anticorrosive entering Agents.
- The part which sprinkles $CaCl_2 \cdot 2H_2O$ or NaCl (Ref.).
- The part which does not sprinkle the agents.

* Install each N= 6-10 test pieces.

④ Installation method

It is fixed to a guardrail by a string (Photo. 2).

⑤ Spraying term

Gifu Prefecture : January 13, 2001 to February 9

Toyama Prefecture : February 6, 2001 to April 4

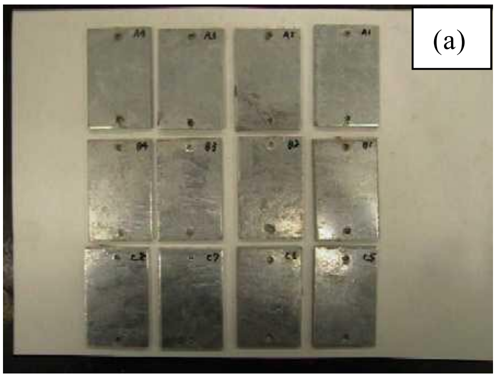
Photo.1 The Agents with molding rice bran

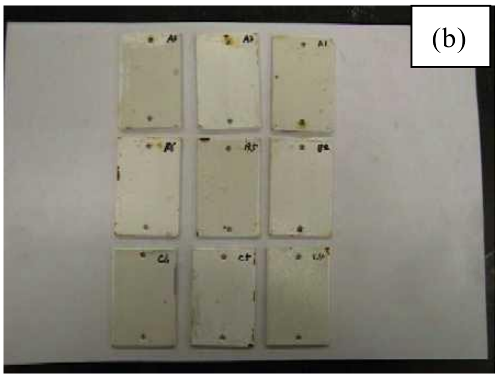
Photo. 2 Installation places of test pieces

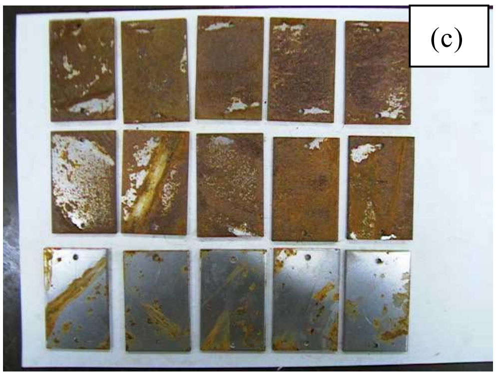
3-2-2 The Result of Real Road-Spraying Examination

The results of real road-spraying examination are shown in Table 3, Figure 3 and 4.

There was no corrosion of the test pieces of Zn plating in the examination of the spraying in Gifu Prefecture. About the test pieces with epoxy paint, corrosion was seen at only the crack portion (photo. 3). About SS400, it was the corrosion of 1.2 MDD (13 days after) and 1.7 MDD (28 days after) in the Agents non-sprinkled area. And in the $CaCl_2 \cdot 2H_20$ sprinkled area, it turned out that the corrosion was promoted by the influence of $CaCl_2 \cdot 2H_20$ (52MDD (13 days later), 40 MDD (28 days later)). On the other hand, in the area which sprinkled the Agents containing rice bran, MDD was 34 (13 days later) and 25 (28 days later), and became smaller than the $CaCl_2 \cdot 2H_20$ sprinkled area. It turned out that there were about a 40% anticorrosion ratio.







(a) Zn plating steel material
(b) epoxy paint steel material
(c) SS400 (steel)
top : $CaCl_2$ sprinkled area
middle : rice bran entering Agents sprinkled area
under : no sprinkled area

Photo. 3 The corrosion state of test pieces

There was no corrosion in the Zn plating test pieces also in the spraying examination of Toyama Prefecture. Also about test pieces with epoxy, corrosion was seen only at the crack. About SS400, the corrosion accelerated from 3.3 MDD (18 days later) to 16.2 MDD (53 days later) in the non-sprinkled area of the Agents (Fig. 4). This cause is considered because the place of the spraying test was close to the sea. The corrosion was accelerated similarly in the NaCl sprinkled area in the second half of the examination, and MDD after 53 days was 42.9. The corrosion amount of the salt spraying area was 2.6 times the non-sprinkled area. On the other hand, the MDD of the sprayed area of Agents containing rice bran was 11.2 (18 days later) and 24.4 (53 days later). The anticorrosion ratio of the Agents containing rice bran was at about 40%.

Table 3 The result of real road-spraying examination

		Gife Prefecture		Toyama Prefecture	
Condition	Term Spraying amount Spraying method Traffic	January 13, 2001 to February 9 2～3T／day(total 57T) Sprinkler vehicle (4T) 200～300 car／hr		February 6, 2001 to April 4 1～2T／day(total 36T) Sprinkler vehicle (2T) 800～1000 car／hr	
MDD (SS400)		13 days later	28 days later	18 days later	53 days later
	Agents with rice bran	34	25	11	24
	$CaCl_2$ or NaCl	52	40	14	43
	non-sprinkled	1.2	1.7	3.3	16
	Anticorrosion ratio (%)	35	39	21	44
Zn plating Epoxy paint		no corrosion It corroded to a crack.		no corrosion It corroded to a crack.	

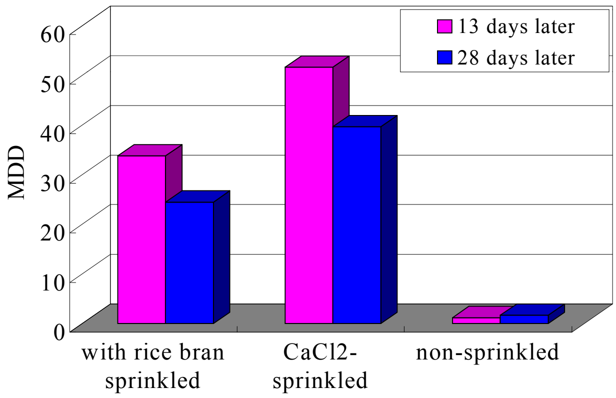


Fig. 3 Anticorroson effect of Agents with rice bran (Gife Pre.)

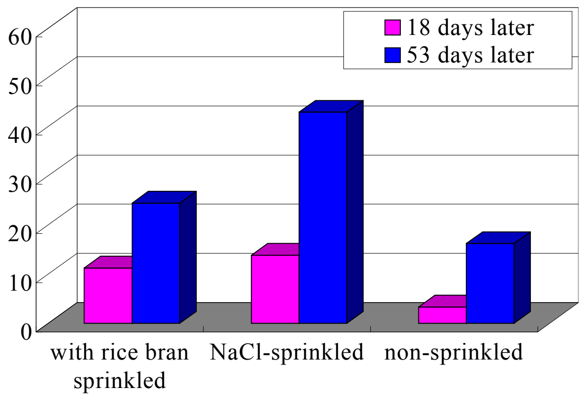
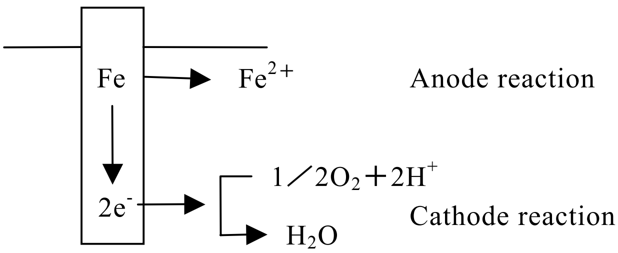


Fig. 4 Anticorrosion effect of Agents with rice bran (Toyama Pre.)

3-3 Consideration

Generally metal corrosion happens by two reactions shown in Figure 5. Therefore, oxygen is needed for corrosion reaction. The difference in the anticorrosion ratios between the lab examination and the real road-spraying examination is also considered to be the influence of oxygen. That is, in the laboratory test performed in the aqueous solution, the moving of oxygen to a metal surface became a rate-determining step. Therefore, the corrosion reaction is inhibited. On the other hand, In the real road-spraying examination, since so much oxygen is always in the air, it can be said that the corrosion reaction is promoted. Furthermore, it is thought that the real road-spraying examination was influenced by traffic, the weather, etc.



Dissolved oxygen of water ：5～6mg／L

Fig. 5 Model of metal corrosion

4 The Thaw Effect of $CaCl_2 \cdot 2H_2O$/NaCl Mixed Agents

4-1 Experiment Operation

The melting-ice capacity of $CaCl_2 \cdot 2H_2O$, NaCl and 1:1 mixtures was clarified. And the possibility of curtailment of the amount of the Agents spraying was examined.

4-1-1 Indoor Melting-Ice Examination

200 g of water was put into the plastic envelope with a diameter of 110 mm, and it was frozen(-10℃). Then, with temperature held at a constant -10℃, each Agent of 10 g was uniformly sprinkled, and the weight of the liquid (water) obtained within the fixed time was measured.

4-1-2 Frictional-Resistance Measurement of Road Surface

Each Agent was sprinkled on the road surface (20 g/m^2, 3×30 m), and the road surface resistance was measured to every fixed time. Road surface resistance was measured from the deceleration when slamming the brake on an automobile driving at 20km/h.

4-1-3 Temperature Measurement of Road Surface

After sprinkling each Agent on a road surface (100 g/m^2), the temperature reduction of a road surface was recorded in the thermal graph (2000 type made from AVIO), and the durability of the Agents was investigated.

4-2 Experiment Result

4-2-1 Result of Indoor Melting-Ice Examination

A Duration change of the melting ice amount after $CaCl_2 \cdot 2H_2O$, NaCl and 1:1 mixtures sprinkled is shown in Figure 6. The exothermic reaction of $CaCl_2 \cdot 2H_2O$ was very large at first in melting the amount of ice. It was very excellent in the Immediacy effect. Moreover, although NaCl did not have Immediacy effect, the amount of melting ice increased linearly with the progress of time. It was excellent in the Durability effect. The mixed Agents of $CaCl_2 \cdot 2H_2O$ and NaCl showed the middle melting-ice capability, and it turned out that the Immediacy effect (after 10 minutes) increase by about twice that of NaCl, and the Durability effect (after 180 minutes) increases about 1.2 times that of $CaCl_2 \cdot 2H_2O$.

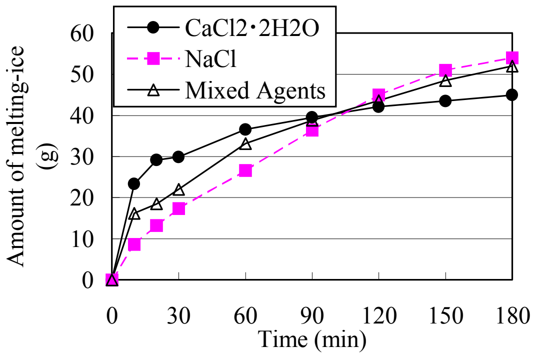


Fig. 6 The result of indoor melting-ice examination
(－10℃, ice:200 g, Agents:10 g)

4-2-2 Result of Frictional-Resistance Measurement of Road Surface

A Duration change of the road surface resistance after $CaCl_2 \cdot 2H_2O$, NaCl and 1:1 mixtures sprinkled is shown in Figure 7.

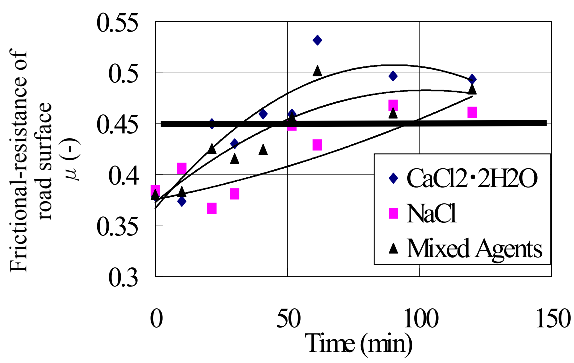
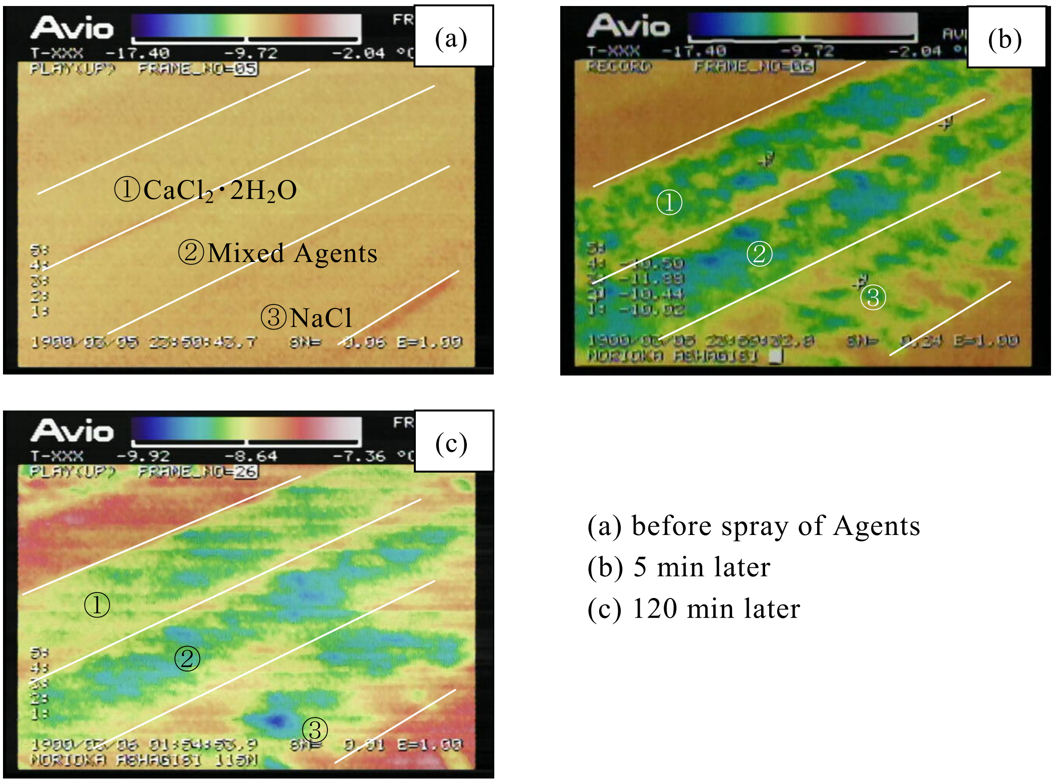


Fig.7 The result of frictional-resistance measurement of road surface

When μ value of a vertical axis is bigger than 0.45, it is the range in which ABS system of an automobile does not operate. And it is shown that the road surface frictional resistance improves. When $CaCl_2 \cdot 2H_2O$ was sprinkled, it went into the range that ABS does not operate for about 30 minutes. NaCl required no less than 90 minutes (3 times) for reaching a level equivalent to $CaCl_2 \cdot 2H_2O$. Since the 1:1 mixed Agents became $\mu = 0.45$ in 50 minutes, it was suggested that there is the Immediate effect.

4-2-3 Result of Road Surface Temperature Measurement

A Duration change of the road surface temperature after $CaCl_2 \cdot 2H_2O$, NaCl and 1:1 mixed Agents were sprinkled is shown in Figure 8(a)-(c). The black segment of the figure shows that the road surface temperature fell. That is, that the thaw effect happened. As for $CaCl_2 \cdot 2H_2O$ and the mixed Agents, road surface temperature fell immediately after spraying. When $CaCl_2 \cdot 2H_2O$ was sprinkled and 2 hours passed, the temperature of the road surface was equal to the perimeter (non-sprinkled zone). However, the fall in the road surface temperature by spraying of the mixed Agents and NaCl remained constant. This result suggests that, as for the mixed Agents and NaCl, the thaw effect is maintained after 120 minutes, too.



(a) before spray of Agents
(b) 5 min later
(c) 120 min later

Fig. 8 The result of road surface temperature measurement

4-3 Consideration

About the Immediacy effect, the mixed Agents was superior by to 2～3 times that of NaCl from the result of melting-ice examination and road surface frictional-resistance measurement. If the mixed Agents are used when the Immediate effect is demanded in the area of the NaCl spraying, the amount of Agents sprayed can be decreased by half. From the result of the road surface temperature measurement, the melting-ice effect of the mixed Agents continued after 2 hours, too. Therefore, when the Durability effect is required in the area of $CaCl_2 \cdot 2H_2O$ spraying, it is thought the spraying amount or the times of spraying can be reduced. From such a result, it is thought that use of the mixed Agents is the best method of enabling the curtailment of the amount of spraying.

5 Conclusion

From the result of the laboratory examinations and the real road-spraying tests, it turned out that it is effective to add 5wt% rice bran as the suppression method of a metallic corrosion. In the laboratory test, the anticorrosion effectiveness of about 80% was obtained. On the other hand, in the real road-spraying examination, it was an anticorrosion effectiveness of 40%. This cause was the influence of dissolved oxygen (3-2-3 term). Moreover, it was thought that uneven factors, such as a snow-coverage situation, a sprinkling method and traffic, also influenced the effectiveness.

By measurement of the indoor melting-ice examination, the frictional-resistance of the road surface and the road surface temperature, the thaw/melting-ice capacity of $CaCl_2 \cdot 2H_2O$, NaCl and 1:1 mixed Agents was investigated. Consequently, it turned out that the melting-ice capability balance of the Immediacy effect (about 2～3 times of NaCl) and the Durability effect (about 1.2 times of $CaCl_2 \cdot 2H_2O$) became better. And the total amount of melted ice increases by about 15% by using mixed Agents of $CaCl_2 \cdot 2H_2O$ and NaCl when it was compared with using each chloride independently. Therefore, it is thought that using the mixed Agents can reduce the amount of Agents sprayed.

6 A Future Measure

- For the purpose of the improvement of the anticorrosion effectiveness on the real road, the mixed method (dispersibility, soluble improvement) of rice bran will be examined.
- The simple mixed Agents of $CaCl_2 \cdot 2H_2O$ and NaCl were used in this report. Aiming at further improvement in the Immediacy effect and the Durability effect, we will prepare the one granular Agent that has NaCl in a nucleus and has $CaCl_2$ in an outer layer. And effectiveness of the one granular Agent will be investigated.

7 Reference

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