Method for Detection of Chemical Reactions Between Concrete and Deicing Chemicals

HENRY J. GILLIS, JI-WON JANG, PAUL W. WEIBLEN, AND IWAO IWASAKI

An attempt was made to develop methods that can be used to detect chemical reactions between concrete and deicing chemicals and to determine if they actually occur. The results collected to date provide clear evidence of chemical reactions between concrete and the corrosion-inhibiting deicing salts. The different amounts of precipitates (chemical reaction products) found in the test cells are dependent on the type and the concentration of corrosion-inhibiting deicing salts.

Concrete degradation occurs through a variety of chemical and physical processes. Concrete may be degraded in three different ways distinguished by the prevalent signs of destruction (1,2) such as (a) decomposition of concrete by lime leaching, (b) chemical exchange reactions between hardened cement constituents and a solution, and (c) the accumulation, crystallization, and polymerization of reaction products.

It is well known that the use of deicing salts causes rebar corrosion in concrete and leads to structural failures. Corrosion inhibitors are mixed with plain rock salt (sodium chloride) to reduce or prevent rebar corrosion in concrete. Even though some reports (3–8) indicate the possibility of concrete degradation by deicing chemicals, the effects of the corrosion-inhibiting deicing salts and salt substitutes on concrete degradation are not well understood, and methods for determining the effects of the corrosion-inhibiting deicing salts and salt substitutes on concrete degradation are not available.

The result of previous research (9) suggest that the corrosion-inhibiting deicing salts interact with concrete and produce precipitates through a chemical reaction. If certain ions in the corrosion-inhibiting deicing salts that function as inhibitors are lost by precipitation, the effectiveness of the corrosion-inhibiting deicing salts on rebar corrosion could drop significantly. On the other hand the formation of precipitates in cracks may act as a barrier to the penetration of the salt solutions, thereby acting as an inhibitor. Alternatively some of the precipitates may form in the microcracks or pores of concrete and facilitate the propagation of cracks.

In the investigation described here an attempt was made to develop methods that can be used to detect chemical reactions between concrete and deicing chemicals and to determine if they actually occur.

H. J. Gillis, Office of Materials, Research and Engineering, Minnesota Department of Transportation, Maplewood, Minn. 55109. J.-W. Jang and P. W. Weiblen, Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minn. 55455. I. Iwasaki, Central Research Institute, Mitsubishi Material Corporation, 1-297 Kitabukuro-cho, Omiya, Japan.

EXPERIMENTAL

Concrete slabs and cone-shaped concrete samples were designed to accelerate the deterioration of concrete in corrosion-inhibiting deicing salt and salt substitute solutions. The physical and chemical changes of the cone-shaped concrete samples are being monitored by visual examination and chemical and mineralogical analyses in an on-going research program.

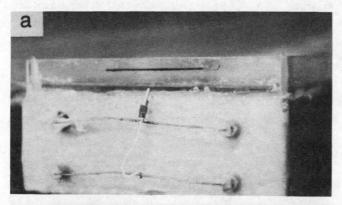
Concrete Slab Samples

Concrete slabs $[30 \times 30 \times 15 \text{ cm} (12 \times 12 \times 6 \text{ in.})]$ [Figure 1(a)] were fabricated by using a 1.5-m³ (2-yd³) mix (183 \times 183 \times 183 cm) consisting of Portland Cement-Concrete [313 kg (691 lb)] with coarse [797 kg (1,757 lb)] and fine [523 kg (1,154 lb)] aggregates. The bottom halves of all of the slabs were cast from the mix as delivered, and the top halves were cast after adding 9 kg (20 lb) of NaCl to the remaining mix. After casting the slabs were placed in a moist room for a period of 28 days and were then dried in a chamber maintained at a temperature of 43 to 49°C (110 to 120°F) for 45 days. The air content determined by the linear transverse test was 13 percent. Originally the slabs were made for rebar corrosion testing with 3 percent solutions of corrosion-inhibiting deicing salts and salt substitutes.

Concrete slab samples ponded with 3 percent corrosioninhibiting deicing salts and salt substitute solutions for 484 days were visually examined for rust stains, concrete cracks, and the roughness of the concrete surfaces caused by the corrosion-inhibiting deicing salts.

Cone-Shaped Concrete Samples

Cone-shaped concrete samples [Figure 1(b)] were made by mixing 374 kg (825 lb) of Type III cement, 635 kg (1,400 lb) of sand (Minnesota DOT Specification 3126), and 635 kg (1,400 lb) of quartzite meeting the CA-70 grade (Minnesota DOT Specification 3137). A paper mold was used to make the cone-shaped concrete samples. The cone shape of the samples was chosen to provide a large surface area exposed to the corrosion-inhibiting deicing salt solutions and to accelerate the chemical reactions at the tip. The physical changes in the concrete samples could readily be recognized at the tips. The concrete samples were placed in a moist room for 28 days after fabrication and were then air dried. The compressive strength of the concrete samples was 63.4 MPa (9,190 lb/in²).



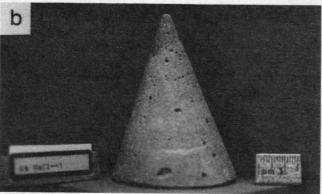




FIGURE 1 A concrete slab sample (a) and a cone-shaped concrete sample (b) in test cell for concrete degradation by corrosion-inhibiting deicing salts and salt substitutes (c).

The bottoms of the cone-shaped concrete samples were cut with a water-cooled diamond saw to make samples of uniform dimensions. The samples were cleaned with a Dayton 3Z856 sand blaster and graded Ottawa sand (ASTM C109) under 0.4 MPa (60 lb/in²) of air pressure. The distance between the sand blaster nozzle and the samples was kept constant. The average dimension of the samples was a 5.08-cm (2-in.) bottom diameter by a 6.4-cm (2.5-in.) height. The initial dimension of each sample was measured by using a dial caliper, and the weight was measured with a Sartorius balance. The average weight of the samples was 120 g (0.26 lb).

Deicing Chemical Solutions

For the slab tests, CMA, Domtar, sodium formate, and plain salt were mixed into city water at a concentration of 3 percent. Plexiglas dams [Figure 1(a)] were bonded to the top surfaces of the slabs with silicone rubber, and the solution levels were kept constant on each slab.

For the cone-shaped concrete samples two corrosion-inhibiting deicing salts (A and B) and plain sodium chloride were mixed with deionized water at concentrations of 3, 6, and 20 percent (Table 1). The corrosion-inhibiting deicing salt solutions were filtered to remove insoluble constituents.

The concrete samples were immersed in individual polyethylene jars [Figure 1(c)] containing 500 ml of a corrosion-inhibiting deicing salt or plain sodium chloride solution. Three-milliliter solution samples are being collected periodically from the jars (test cells) to examine the chemical changes of the test solutions.

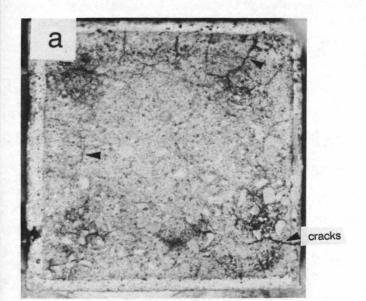
RESULTS AND DISCUSSION OF RESULTS

Concrete Cracks and Rust Stains on Slab Surfaces by Corrosion-Inhibiting Deicing Salt and Salt Substitute Solutions

Figure 2 shows typical slab surfaces after 484-day ponding with 3% CMA and Domtar solutions. Numerous concrete cracks and rough concrete surfaces were found on the slabs tested with the solutions. A summary of the average crack length and the average area of yellow rust stains of three slabs caused by rebar corrosion

TABLE 1 Chemical Compositions of Corrosion-Inhibiting Deicing Salts Used in Cone-Shaped Concrete Test Cells

	Ca	Mg	Na	K	P	SO ₄	CI
Deicing Salt A	0.35	2.71	27.64	0.03	2.36	2.14	52.01
Deicing Salt B	0.40	0.01	36.95	0.01	2.14	2.35	56.25
NaCl	0.00	0.00	39.00	0.00	0.00	0.003	60.00
Deionized water	0.00	0.00	0.00	0.00	0.00	0.00	0.00



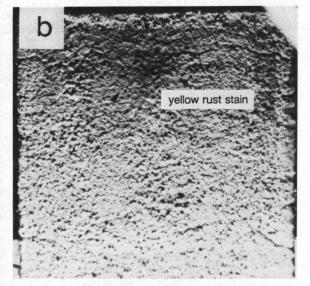


FIGURE 2 Top surfaces of concrete slabs showing (a) numerous concrete cracks and (b) yellow rust stain.

is shown in Figure 3. The slabs tested with CMA and sodium formate solutions contained cracks [Figure 3(a)] but did not show any yellow rust stains on their surfaces [Figure 3(b)]. On the other hand the slab surfaces tested with salt (NaCl) solutions showed signs of rebar corrosion in concrete, but no cracks were observed (Figure 3). Figures 2 and 3 indicate that the cracks in the concrete slabs were created by both rebar corrosion and chemical reactions between deicing chemicals and concrete. These results made it of interest to investigate the concrete degradation caused only by chemical reactions between the deicing media and concrete.

Precipitates in Corrosion-Inhibiting Deicing Salt Solutions

To evaluate the effects of the chemical reaction between corrosioninhibiting deicing salts and concrete, the cone-shaped concrete sam-

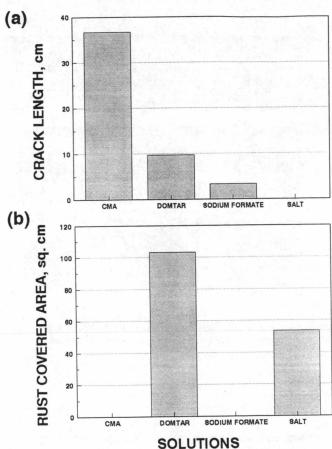


FIGURE 3 Average concrete crack length (a) and average area of yellow rust stains (b) caused by 3 percent corrosion-inhibiting deicing salts and salt substitute.

ples were placed in the 3, 6, and 20 percent corrosion-inhibiting deicing salt and plain sodium chloride solutions. After leaving the concrete samples in the test solutions for a day various amounts of precipitates were found in the test cells depending on the type and the concentration of corrosion-inhibiting deicing salts. Figures 4 and 5 show that the precipitates were formed by chemical reactions between the concrete and the corrosion-inhibiting deicing salts. The precipitates were observed on the concrete sample surfaces, at the bottoms of the test cells, or both. However, no precipitates were found in the test cells containing NaCl (Figure 6) and deionized water (Figure 7). For Deicing Salt A (Figure 4) the amount of precipitates increased with an increased concentration of corrosion-inhibiting deicing salt. For Deicing Salt B (Figure 5) the amount of precipitates decreased with an increased concentration of corrosion-inhibiting deicing salt. It appears that the amount of precipitates increased with time in all cases.

The chemical changes in the test solutions as well as the physical changes in the concrete samples are being monitored as a function of time. The results collected so far provide clear evidence of chemical reactions between concrete and the corrosion-inhibiting deicing salts. The impact of the chemical reactions on concrete degradation can be understood by determining the chemical and mineralogical changes in the concrete caused by the corrosion-inhibiting deicing salts. The chemical changes in the solutions provide part of the necessary information on changes in

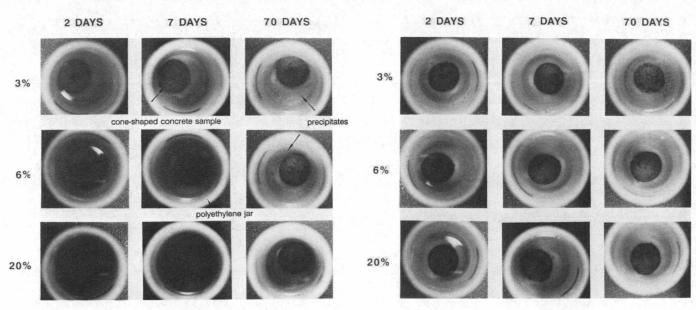


FIGURE 4 Top views of test cells containing 3, 6, and 20 percent corrosion-inhibiting Deicing Salt A. Precipitates increased with increased concentration and as a function of time.

FIGURE 6 Top views of test cells containing 3, 6, and 20 percent NaCl. No precipitate found after 70 days.

the chemistry and bonding strength of concrete, but the mineralogy of the precipitates must also be determined. The precipitates are being collected from the test cells for quantitative and qualitative chemical and mineralogical analyses to define the chemical reactions.

The physical changes in the concrete samples after 400 days of reaction have not been significant enough (i.e., a minimum of 15 percent weight and dimension changes) to determine the extent of changes by the corrosion-inhibiting deicing salt solutions. The

physical properties (volume changes on dry-wet and freeze-thaw cycling) of the precipitates will be determined at a later date.

CONCLUSIONS

The results collected to date provide clear evidence of the chemical reactions between concrete and the corrosion-inhibiting deicing salts. The different amounts of precipitates found in the test

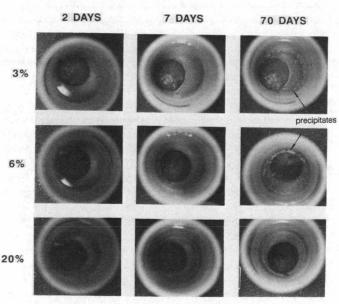


FIGURE 5 Top views of test cells containing 3, 6, and 20 percent corrosion-inhibiting Deicing Salt B. Precipitates decreased with increased concentration.

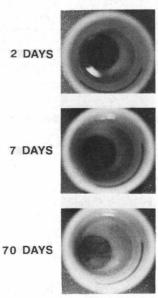


FIGURE 7 Top views of test cells containing deionized water. No precipitate found after 70 days.

However further research is necessary to understand the mechanisms of concrete degradation by corrosion-inhibiting deicing salts. The concrete in the cone-shaped concrete samples are expected to show significant physical changes resulting from the corrosion-inhibiting deicing salts with time. The precipitates must be collected from the test cells for quantitative and qualitative analyses to identify the degree of chemical reaction, the chemical elements involved in the reactions, and the mineralogy of the precipitates. The volume changes in the precipitates in dry-wet and freeze-thaw cycling will indicate the impacts of the precipitates on microcracks in concrete.

ACKNOWLEDGMENTS

The authors express appreciation to the Office of Maintenance and the Office of Materials, Research and Engineering of the Minnesota Department of Transportation, for support of the research.

REFERENCES

 Tayor, H. F. W. Cement Chemistry. Academic Press Limited, London, England, 1990, pp. 377-408.

- Biczok, I. Concrete Corrosion and Concrete Protection. Hungarian Academy of Science, Budapest, 1964.
- Ryell, J., and P. Smith. Case Histories of Poor Concrete Durability in Ontario Highway Structures. A Symposium in Honor of Thorbergur Thorvaldson. In Performance of Concrete: Resistance of Concrete to Sulphate and Other Environmental Conditions (E. G. Swenson, ed.), University of Toronto Press, Ontario, Canada, 1968, pp. 180-204.
- Gillott, J. E. Effect of Deicing Agents and Sulphate Solutions on Concrete Aggregate. Quarterly Journal of Engineering Geology, Vol. 11, 1978, pp. 177-192.
- Pitt, J. M., M. C. Schluter, D. Y. Lee, and W. Dubberke. Sulfate Impurities from Deicing Salt and Durability of Portland Cement Mortar. In *Transportation Research Record 1110*, TRB, National Research Council, Washington, D.C., 1987, pp. 16-23.
- Crumpton, C. F., B. J. Smith, and G. P. Jayaprakash. Salt Weathering of Limestone Aggregate and Concrete Without Freeze-Thaw. In *Trans*portation Research Record 1250, TRB, National Research Council, Washington, D.C., 1989, pp. 8-16.
- Gunter, M., T. Bier, and H. Hilsdorf. Effect of Curing and Type of Cement on the Resistance of Concrete to Freezing in Deicing Salt Solutions. Proc., Katharine and Bryant Mather International Conference, Concrete Durability, Atlanta, Ga., Vol. 1, American Concrete Institute, Detroit, Mich. (ACI SP-100), 1987, pp. 877-899.
- Dubberke, W., and V. J. Marks. The Effect of Deicing Salt on Aggregate Durability. In *Transportation Research Board 1031*, TRB, National Research Council, Washington, D.C., 1985, pp. 27-34.
- Jang, J. W., and I. Iwasaki. Effect of Salt Additives on Rebar Corrosion.
 Final Report. Minnesota Department of Transportation, June 1993.

Publication of this paper sponsored by Committee on Corrosion.