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The evaluation of salt scaling of concrete by freeze and thaw test method with small sample and the effect of magnesium salt on salt scaling

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ABSTRACT

In order to evaluate resistance of salt scaling of concrete, the new evaluation test method with small amount of sample for short period of time was investigated in this study. Test method proposed was as follows: Mortar cured after 28 days was cut into cubes of 7mm. Various deicer solution of 40ml is poured into 100ml polypropylene vessels with three cubes of mortar (about 4g). Freeze and thaw cycles charged these vessels. After several cycles, these cubes were observed and sieved with 2.5mm. Each residue was weighed. The freeze-thaw resistance was evaluated by use of the residues of each sieve. The residue of each sample was also characterized by SEM and mercury porosimetry. The freeze-thaw resistance obtained by this new method was proved to coincide with those of ASTM C672 method. Deterioration process of specimen by freeze-thaw can be also observed by determination with each residue. Salt scaling resistance remarkably differs by the kind of deicers used. It was obtained that according to freeze-thaw cycles, crack proceeded from the surface to center of cubes through the transition zone between aggregate and cement paste by the deterioration of SEM image and pore structure of cubes residue. Salt scaling resistance with magnesium chloride, magnesium acetate and magnesium nitrate is proved be smaller than those with other deicers.

Keywords. Freezing-thawing method, Freezing-thawing resistance, Salt scaling, Magnesium salt, Evaluate resistance

INTRODUCTION

Repeated freezing and thawing action in snowy cold regions is an extremely serious issue that affects the durability of concrete. Deterioration phenomena are classified into four types, namely cracking, scaling, pop-out, and collapse(JCI 2008). Among these, cracking and scaling damage cases are especially frequent in actual structures. Cracking is the phenomenon wherein cracks occur owing to the expansion and constraint of concrete that is result of repeated freezing and thawing of the water inside concrete (deterioration of either the entirely or part of the concrete structure). On the other hand, scaling is the deterioration of concrete where in the paste-mortar structure delaminates in flakes from the surface of the concrete

Japan Industrial Standard(JIS 2010) prescribes JIS A 1148:2010 “Method of test for resistance of concrete to freezing and thawing” as the freeze-thaw test method, whereby a rectangular cube of concrete measuring 10x10x40cm is subjected to 300 cycles of freezing and thawing in the temperature of the concrete is assessed from the reduction in the dynamic modulus of elasticity of the concrete. This method is suitable for assessing the propagation of internal cracks.

On the other hand, JIS does not specify a standard for scaling assessment test methods. Overseas standards include ASTM C672 (ASTM 1998) in North America and Rilem CDF(Rilem 1996) in Europe. The ASTM C672 method, which requires specimens with surface area of at least 0.045m^2 and minimum thickness of 7.5cm, causes water absorption from the bottom surface of the specimens. Thus large-sized concrete specimens are required by both of these methods. These test methods were proposed in response to the increasing occurrence of concrete scaling as the result of the use of salt as a deicing agent on frozen roads for safety purposes.

Given the need to extend the life of concrete structures, the assessment of scaling deterioration is considered necessary in Japan too, but existing methods such as ASTM C672 should conduct many experiments. In terms of the test results, the focus of these methods is on the comparative assessment of scaling resistance, and considering the amount of labor involved, the payout in terms of useful materials science data is small. Therefore in this study, the authors decided to investigate an approach allowing the comparative and quick assessment of scaling susceptibility with simple and labor-saving methods using small-sized specimens. Test with the ASTM C672 method was additionally conducted under the same temperature conditions for the purpose of checking the consistency of the two sets of results. One of the merits of using small-sized specimens is that this allows direct observation of their state. This was taken advantage of to carry out observation of the pore size distribution and structure of the hardened mortar after the scaling test and determine differences in scaling deterioration phenomena according to the type and concentration of deicing agent.

EXPERIMENTAL METHOD

Materials and Mix Proportions. Commercially available ordinary Portland cement (density: 3.15 g/cm3) was used for the cement, and river sand from the Heigawa River in Miyako City, Iwate (density in saturated surface-dry condition: 2.66 g/cm3, fineness modulus: 2.78) for the fine aggregate. The specimens consisted of mortar without air entraining agent. Although scaling at the coarse aggregate boundary was a concern, this choice was made in order to extract the phenomena that take place in mortar in an environment treated with deicing agent. The water/cement/fine aggregate ratio by mass of 0.55:1:3 was used. After curing in moist air for 1 day, the specimens were demolded and water-cured for 27 days until testing.

Deicing Agents Used. The deicing agents used in this study were sodium chloride, calcium chloride, magnesium chloride, sodium acetate, calcium acetate and magnesium acetate. Tests were conducted using 3% (mass concentration) solutions of each deicing agent.

New Freeze-Thaw Test Method. ***Test specimens***. Table 1 gives an overview of the test method. Rectangular column specimens measuring 4x4x16cm were water-cured for 28days, and then the specimens were cut with a diamond cutter to form 7mm cubes for use as the test specimens. The test specimens were immersed in deicing agent solution, measuring the solution to achieve the solution to sample mass ratio of 10:1 in a polypropylene container with a capacity of 100ml and closed by a lid, and freeze-thaw testing was conducted. One set of four 7mm cube specimens (weighing approximately 3g each) was placed in the container and tested at one time.
Freeze-thaw test. The specimens were subjected to 1, 3, 5, 7 and 10 freeze-thaw cycles, each cycle consisting in placing the specimens in a freezer set at -20℃ for 12hours, then placing them in a room at 15℃ for 12 hours. After the designated number of cycles, the set of four specimens was taken out of the container, the specimens were separated from the deicing agent solution using 5B filter paper, and any remaining deicing agent was then washed off with distilled water. Next, the specimens were dried at the constant temperature of 40℃, size-sorted with sieves into particle sizes of 0.6, 1.2, and 2.5 mm, yielding a residual amount for each of these sizes. Tests conforming to ASTM C672 were also conducted. The test method was as previously reported (Oyamada 2009).

Table 1 Overview of new proposal freeze and thaw text method

Preparation of specimens	The same mixture of mortar used as ASTM C 672 is cast into JIS mortar form 4x4x16cm. 7mm cube samples are cut from JIS mortar by diamond saw.
Freeze and thaw test	100ml polypropylene vessels used. 4 cubes of mortar: 3% deicing agent solution ratio (1/10): 3vessels eaches Cycle number: 1, 3, 5, 7 and 10 Freeze and thaw condition: -20°C 12hours, 15°C 12 hours After freeze and thaw cycle, cube samples are remove from refrigerator.
Sample preparation and weighed	Samples were separated by filtration and washed off by distilled water and dried at 40°C, and were sieved by opening of 0.6, 1.2, 2.5mm and weighed by each residues.
Evaluation of sample	BEI image of polished surface of sample. Direct measurement of pore size distribution of sample by Hg porosimetry

Evaluation of Hardened Mortar. Under the new freeze-thaw test method, the hardened mortar subjected to freeze-and-thaw cycling was examined using an electron microscope to obtain backscattered electron images of the polished surface. Further, the pore size distribution in specimens collected in the 2.5mm sieve was measured using a mercury porosimetry.

RESULTS AND DISCUSSION

Assessment of Freeze-Thaw Resistance with New Freeze-Thaw Test.
Figure 1 shows the freeze-thaw test results obtained with the new freeze-thaw test method. These test results are for the 3% solution of each of the deicing agents. Almost no deterioration was observed in the case of distilled water, which was used for comparison purposes. On the other hand, delamination of mortar pieces from the surface was seen in all the samples that were immersed in a solution of deicing agent. The greater the number of cycles, the smaller the residual mass ratio tends to be.

Differences in the progress of delamination among the various deicing agents were observed, with major deterioration in the case of sodium salt, and a conspicuous amount of delamination as the number of cycles grew in the case of sodium chloride in particular. With regard to the sieve mesh, the larger the mesh, the smaller the residual amount ratio became, which further accentuated differences among the various deicing agent solutions. In this experiment, cubic specimens of 7mm per side were employed. Moreover, taking into consideration the need to remove any fine aggregate that broke off, 2.5mm was judged to be the optimum mesh size based on the results of the experiment.

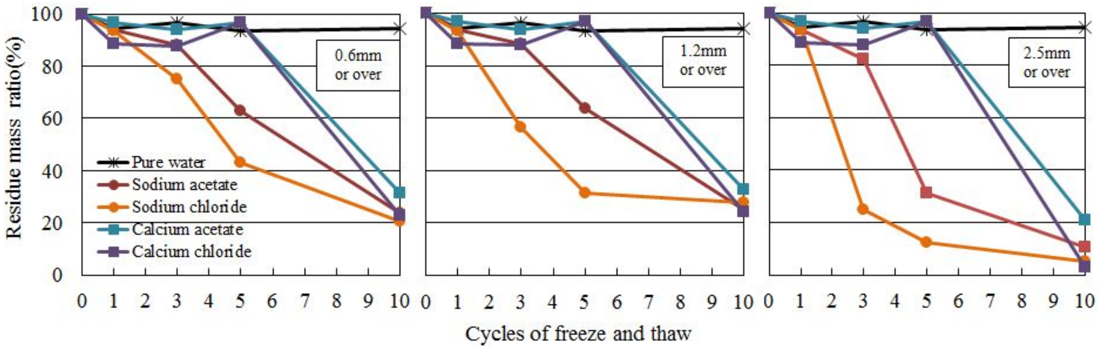


Figure 1 Freeze-thaw test results obtained with the new freeze-thaw test method

Figure 2 Appearance of specimens as the freeze-thaw test cycling progressed.

Figure 2 shows the appearance of specimens as the freeze-thaw test cycling progressed, taking sodium chloride and sodium acetate as examples. Although differences in deterioration state were seen within individual sets of four specimens , mortar pieces tended to come off mainly in the initial stage, and paste and coarse aggregate tended to delaminate independently in the later stage. At similar delamination amounts, for instance at 5 cycles for sodium acetate and 3 cycles for sodium chloride, no differences in the shape of delaminated pieces and residual test pieces were observed. The same applies for the other test pieces not shown in the figure: No differences in delamination state were seen in the case of equivalent deterioration across the various types of deicing agent. On the other hand, there was a tendency for residual pieces of remaining specimens to have crumbling corners and thus exhibit a rounded appearance, and in this regard too, differences according to the type of deicing agent were observed. The test method proposed in this study can thus be said to be suitable for the observation of deformation due to scaling.

Evaluation of Freeze-Thaw Resistance with ASTM C672
Figure 3 shows the freeze-thaw test results obtained with the ASTM C672 method. These results match those obtained with the newly proposed test method, namely almost no scaling occurred in the case of distilled water, significant scaling occurred in the case of sodium salt, and scaling tended to be moderate in the case of calcium salt. On the other hand, the most important amount of scaling took place for sodium acetate, and in this regard the results differed from those of the new test method described above.

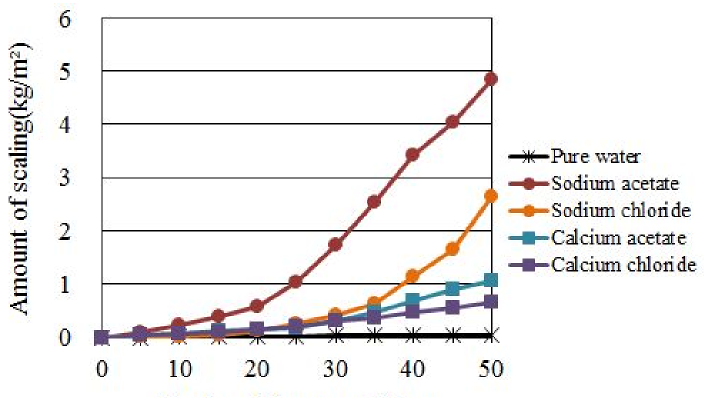


Figure 3
Freeze-thaw test results obtained with the ASTM C672 method.

Comparison of Assessments with Different Test Methods.
Figure 4 shows the relationship between the results of the new test method and the ASTM C 672 test method. Because discrepancies in assessment risk occurring for the results of the new test method depending on the freeze-thaw cycle under consideration, as shown in Figure 2, the extent of deterioration was quantified using the following equation.

$$SDI = P \times N/M \quad (1)$$

where is SDI = Scaling resistance index
P = Residual mass ratio when number of freeze-thaw cycles reaches N times
N = The smaller of either the number of cycles when P reaches 60% of the residual mass ratio, or the number of cycles at which the test is to end
M = Number of cycles at which the test is to end (in this study, M = 10)

The above equation, which adapts a previous equation for obtaining the resistance index in freeze-thaw testing by plugging in the results of this study, was adopted because it was considered that it allows quantification of the deterioration speed in Figure 1. Looking at

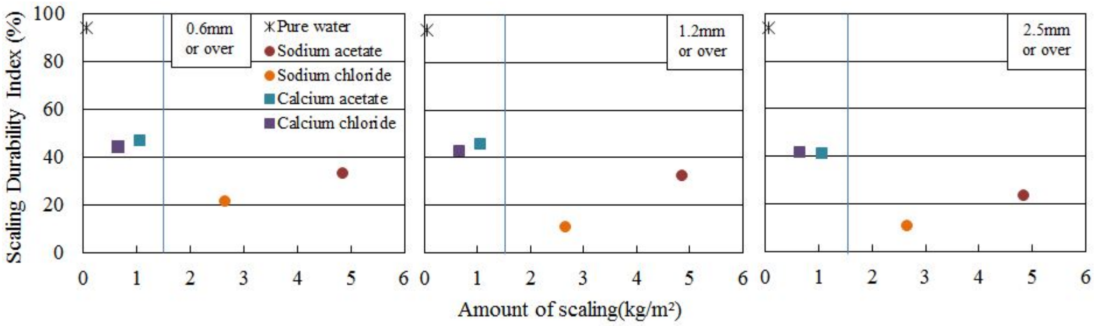


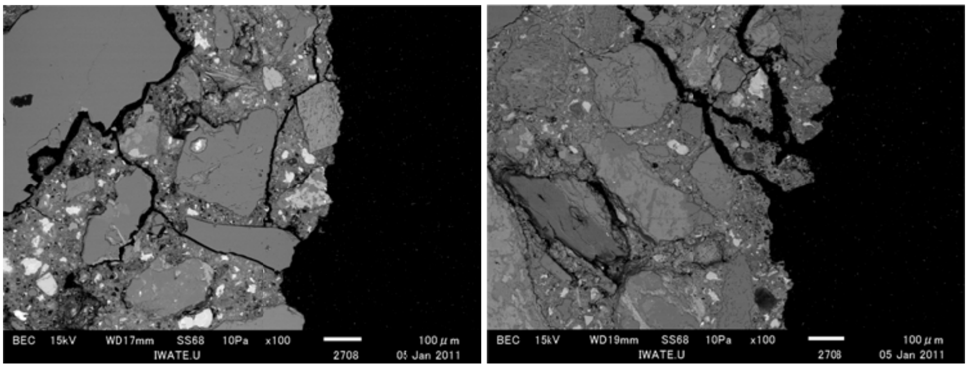
Figure 4 Relationship between the results of the new test method and the ASTM C 672 test method.

Figure 4, the new test method and the ASTM C 672 method can be seen to correlate overall for all mesh sizes. According to example (Tsukinaga 1997) comparing the scaling amount and visual rating of ASTM C 672, the cumulative scaling amount is 1.5kg/$m^{2,}$ which corresponds to moderate scaling where "some of the coarse aggregate is exposed." This scaling amount is indicated in the figure, and in the new test method, strong correlation with the ASTM C 672 method in the range up to this limit value is desirable. The results are well reflected in the cumulative scaling amount range up to 1.5kg/m^2 in the case of the mesh size of 2.5mm, and therefore it was decided to perform screening with the 2.5mm sieve size along with the test conditions described above in all subsequent tests.

Examination of Hardened Mortar.

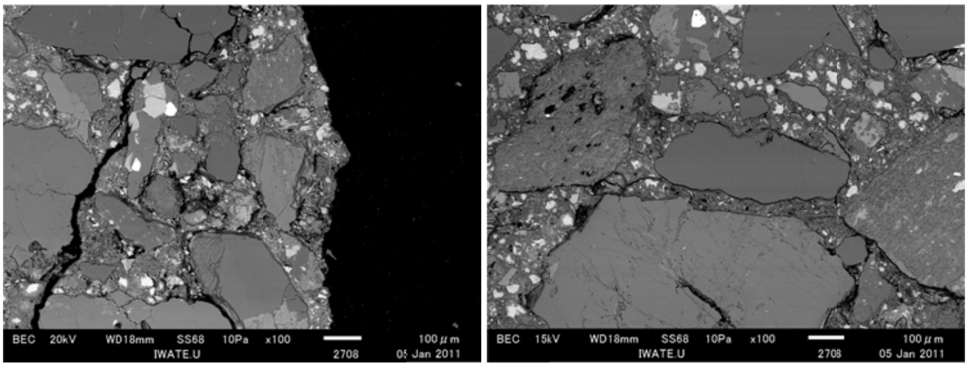
Observation of hardened mortar. One of the merits of the new test method proposed in this study is that, as previously mentioned, it employs small test pieces, which allows direct examination of the test pieces. Such examination makes it possible to verify not only the ease of deterioration but also the deterioration progress at the specimen level. As an example, Figure 5 shows the backscattered electron images(BEI) of polished surface of a test piece through the freeze-thaw test cycles. The images shown in this figure are those of a test piece subjected to freeze-thaw testing in a 3% solution of sodium chloride as the deicing agent, examined at 1 and 10 freeze-thaw cycles. The polished face of hardened mortar consisting of a residual piece of specimen was used for the examination. The figure, which presents the area around the surface of the specimen, shows that large cracks appeared under the action of even a single freeze-thaw cycle. Further, considerable delamination can be seen along the boundary between the aggregate and paste, and this condition became more widespread as the cycles progressed. Reversely, the presence of large amounts of left-over aggregate indicates that deterioration progresses from the paste part.

Figure 6 shows BEI images of the outside and inside of a specimen subjected to three freeze-thaw cycles using sodium chloride. When freezing-thawing is repeated in a deicing agent solution, the remaining specimen grows smaller as the cycles progress, but although large cracks can be seen in the outer edge, few cracks extend inside the structure. Moreover, at the surface of the outer edges, cracks tend to occur almost vertically, gradually penetrating inside the specimen and leading to crack progression to the boundary between the paste and aggregate. Figure 7 shows BEI images of specimens in the case of distilled water without deicing agent and after the third freeze-thaw cycle using sodium acetate. The results show that there is almost no surface deterioration in the case of distilled water. Moreover, a comparison of Figure 6 and Figure 7 shows that while there are differences in the extent of cracking depending on the type of deicing agent, no difference can be seen in the cracks themselves, and delamination is considered to occur under similar phenomena.



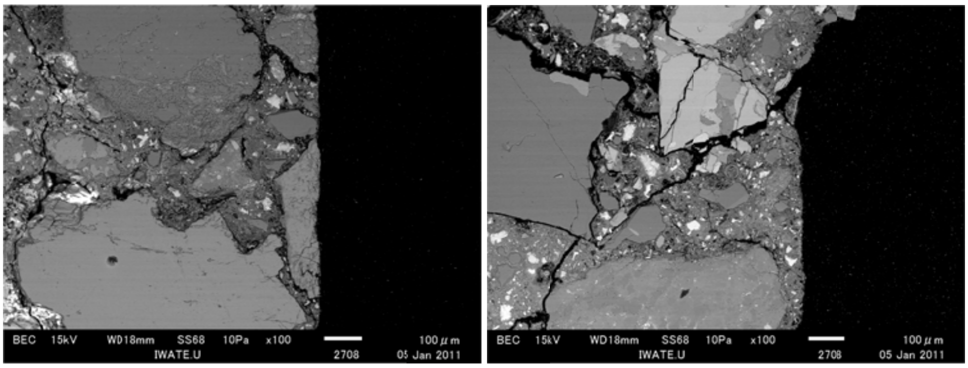
1 cycle (3%NaCl) 10cycles (3% NaCl)

Figure 5 Backscattered electron images(BEI) of polished surface of a test piece through the freeze-thaw test cycles



Outer edge Center

Figure 6 BEI images of the outer edge and center of a test piece subjected to three freeze-thaw cycles using sodium chloride.



Distilled water 3% CH_3COONa

Figure 7 BEI images of specimens in the case of distilled water without deicing agent and after the third freeze-thaw cycle using sodium acetate.

Pore structure in hardened mortar. Tests that use small test pieces have the merit of permitting direct measurement of the pore size distribution. Figure 8 shows the pore size distribution in specimens collected with a 2.5mm sieve following freeze-thaw testing using the new test method with a 1% solution of sodium chloride and sodium acetate. In the case of samples that have not been subjected to freezing-thawing (indicated as “0 cycles” in the figure) and samples that have undergone three freeze-thaw cycles in distilled water (indicated as “Distilled water, 3 cycles” in the figure), the amount of coarse capillary pores of 50nm or larger is the same, but if the samples are immersed in any of the deicing agent solutions and subjected to one freeze-thaw cycle, the amount of pores of 1μm or larger increases. As the number of freeze-thaw cycles increases, the number of pores of 1μm or larger decreases, as does the number of pores sized 50nm to 100nm and pores sized 100 nm to 1μm. The decrease in the number of pores of 1μm or larger is related to the fact that these pores have peeled off owing to the volume expansion of ice and passed through the sieve.

Comparing acetate and chloride salt, acetate is characterized by the fact that the number of pores sized 50nm to 100nm decreases as the number of freeze-thaw cycles increases. Judging from the pore size distribution, even if freezing-thawing is repeated in a solution of deicing agent, little change is seen in the number of pores smaller than 50nm, indicating that the change in the number of pores owing to delamination takes place among the pores sized 50nm or larger. Pores smaller than 50nm consist of gel pores present in the paste matrix and minute capillary pores. Pores 50nm or larger are present in the transition zone at the boundary between the aggregate and paste matrix. Scaling caused by deicing agent is thought to cause destruction of the transition zone between the aggregate and cement paste because of the large effect on capillary pores sized 50nm and larger. This result agrees with the polished face observation. The decrease of total porosity with cycles for each deicing agent is related with the measurement of specimens more than 2.5mm sieved. With the increase of freezing-thawing cycles, paste part of specimen passes through 2.5mm under.

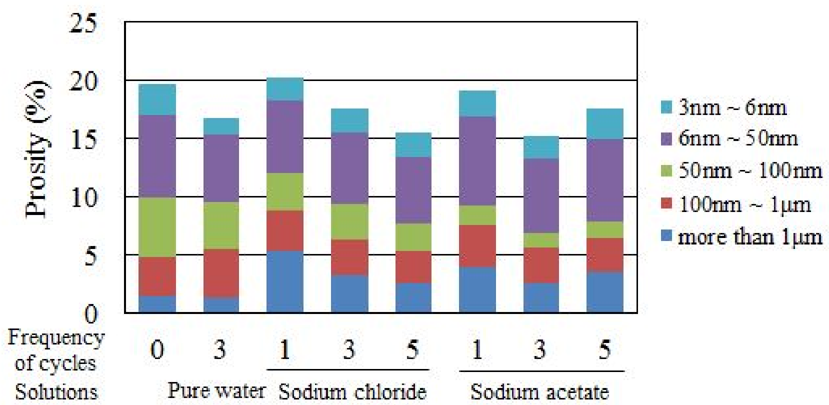


Figure 8 Pore size distribution in specimens collected by a 2.5mm sieve with a 1% solution of sodium chloride and sodium acetate

Effect of kind of deicing agents on salt scaling

The proposal method before mentioned shown in Table 1 was modified by using sand sieved smaller than 2.5mm. Sodium chloride, potassium chloride, magnesium chloride, calcium chloride, sodium acetate, potassium acetate, magnesium acetate and magnesium nitrate were used as deicing agents. Concentration of solutions of each deicing agent is 3%. The residue mass ratio obtained with the new freeze-thaw test is shown in Figure 9. In case of chloride salt, the residual mass ratio of mortar with sodium and potassium deceased remarkably after 3 freeze - thaw cycles and after 5 cycles, these ratios become to more than 50%. The residual mass ratio of mortar with calcium chloride kept about 100% was up to 7 cycles and became 40% after 10 freeze - thaw cycles. The residual mass ratio of mortar with magnesium chloride remained 100% after 10 cycles as same as that with pure water. Salt scaling by magnesium chloride was kindly observed. In case of chloride salt, the trend of the residual mass ratio is as follows

Na < K << Ca << Mg = water.

In case of acetate salt, the residual mass ratio of mortar with potassium and sodium also steeply deceased after one freeze - thaw cycle. The ratio with calcium acetate followed and the ratio with magnesium after 10 cycles did not vary. In case of acetate salt, the trend of the residual mass ratio is as follows

K < Na << Ca << Mg = water.

Using magnesium nitrate as deicing agent, that residual mass ratio kept as same as those with magnesium chloride and magnesium acetate. Salt scaling resistance with magnesium chloride, magnesium acetate and magnesium nitrate is proved be smaller than those with other deicers. Magnesium hydroxide were precipitated in those solutions. It was considered that precipitation of magnesium hydroxide on the surface of mortar could depress scaling of concrete using these magnesium salts.

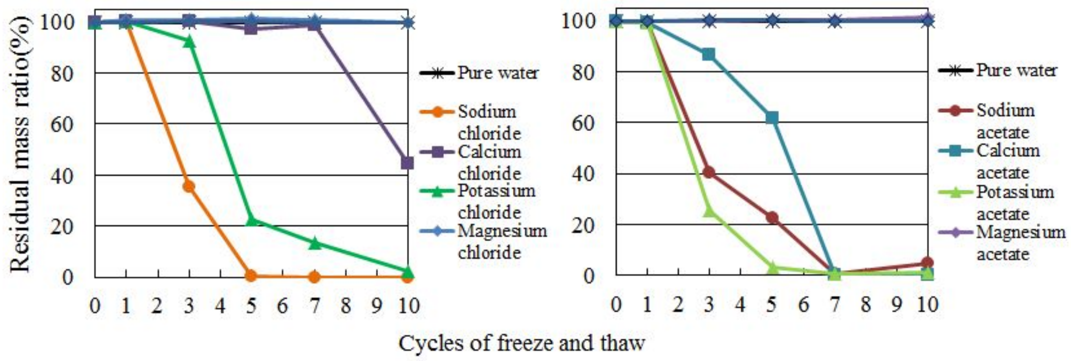


Figure 9 Residue mass ratio obtained with the new freeze-thaw test.

CONCLUSIONS

This study presents a test method to assess the scaling resistance of concrete by using mortar sectioned into cubic specimens of 7mm per side. Following immersion in water or a solution of deicing agent, the test specimens are then subjected to freeze-thaw cycles, and the scaling resistance is determined from the residual amount left over after sieving. The results obtained are as follows.

-The results of the proposed test method correspond to a certain extent with those of the ASTM C 672 method.

-The proposed test method, which uses small specimens and enables assessment of freeze-thaw resistance with about only ten freeze-thaw cycles, excels in terms of the simplicity and speed of the test procedure.

-Examination of hardened mortar with scaling deterioration showed that cracks do not start inside but rather in the surface layer and propagate from there. Further, based on the pore size distribution, the paste matrix part was found to be sound, and it is the transition zone at the boundary between the aggregate and paste that is considered to be the weak plane.

-There are differences in pore size distribution, which changes with freeze-thaw cycling, between acetate and chloride salt. Minute capillary pores 50nm to 100nm in size are particularly susceptible to destruction by the action of acetate.
- The trend of salt scaling resistance of chloride and acetate sult is as follows

Na = K << Ca << Mg = water.

Salt scaling resistance with magnesium chloride, magnesium acetate and magnesium nitrate is proved be smaller than those with other deicers.

REFERENCES

ASTM (1998). American Standard and Test method C672, Standard Test Method for Scaling Resistance of Concrete Surface Exposed to Deicing Chemicals, 1998,

JCI (2008). Japan Concrete Institute, Technical Committee Report on evaluation fore resistance of concrete to freezing and thawing, Chaired by H.Kawano, 2008.8

JIS (2010). Japan Industrial Standard A1148, Method of test for resistance of concrete to freezing and thawing", 2010

Oyamada (2009). T. Oyamada, T. Takahashi, S. Hanehara and T. Fujiwara, Effect of the Kinds of Cement and Deicing Agent on Scaling of Concrete, Cement Science and Concrete Technology, No.63, pp.450-457, 2009

Rilem (1996). Rilem Recommendation, CDF test-Test method for the freeze-thaw resistance of concrete test with sodium chloride solution, 1996

Tsukinga (1997). Y. Tsukinaga, M Shoya and Y.Kasai, A fundamental study on scaling resistance of concrete exposed to deicing chemicals, Concrete Research and Technology(JCI), Vol.8, No.1, pp.121-133, 1997