

Evaluation of the chloride ions penetration into concrete structure with the surface penetrants served in cold marine environment for 20 years

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ABSTRACT

The intrusion of chloride ions in concrete served in the marine environment is the leading cause of corrosion of steel bars. This paper examined the result of a long-term survey on the actual structure (the Tomakomai breakwater) treated with a set of penetrants partly. The survey was conducted twice, in the 12th and 20th years after construction. The results showed that the penetrants could effectively reduce the penetration of chloride ions into concrete. After using the penetrants, the calculated surface chloride ion concentration was decreased by 5.04%/72.18% (the 12th year/the 20th year). As the service years increase, surface chloride ion concentrations between treated and untreated concrete parts vary significantly. It was observed that the effect of the penetrants continued even after 20-years served in the actual severe environment. In the 12th year, the theoretical surface chloride ion concentration of all the concrete has exceeded 13 kg/m^3 , which is the value for durability design. Therefore, in the process of durability design for the marine structures, it is proposed to take a higher surface chloride ion concentration as a design value or take some powerful measures to improve concrete durability. After 12 years of use, the chloride ion diffusion coefficient tends to stabilize for untreated concrete. It is about $0.1 \text{ cm}^2/\text{year}$. While, for the treated, at the 12th year, the chloride ion diffusion rate was about half that of the untreated group. However, as the protective effect of the penetrant layer gradually weakened, at the 20th year, the chloride ion diffusion rate was about twice that of the untreated group, and the turning point was about 15.11 years. It means that If the impregnating agent is used for maintaining the concrete surface when construction, it is necessary to maintain it again in nearly 15 years.

Keywords: marine environment, penetrants, chloride ion concentration, diffusion coefficient, durability

1. INTRODUCTION AND BACKGROUND

As more and more concrete infrastructure facilities are "ageing" year by year [1], engineers started to pay much more attention to the durability of concrete in severe service environments. Concrete in the cold winter marine environment experiences harsh weather and saltwater erosion. Accordingly, various materials have been developed for improving the surface quality of concrete. Many laboratory experiments have shown [2, 3] that sodium silicate and silane can significantly improve the salt-freezing-thawing resistance of concrete surfaces than many other materials. However, there is not much data about its protective effect on concrete in a severe natural environment. The scholars of the Japanese Cold Land Institute of Civil Engineering

and some universities scholars of have conducted follow-up investigations in this area for many years: the exposure time after applied the penetrants was from 4 years [4], 5-10 years [5] to more than 10 years [6]. These studies confirmed that the impregnants still has good salt-freezing-thawing resistance for concrete after serving for more than 10 years in bridges and ports located in a cold environment with salt erosion. This paper is a continuation of the previous research, which studies the concrete surface state after being treated with impregnants for 12 and 20 years of service in the cold marine environment. The objective of this study is to dynamically follow up the changes in the protective effect of impregnation on the concrete surface, revealing the influence of the impregnant protection on the chloride ion concentration and chloride ion

Table 1 Concrete mix ratio of F part of the Tomakomai Port breakwater

W / C	s/a	Unit weight [kg/m ³]					S l u m p	A i r	
		W	C	S	G				A d.
					5-20m m	20-40m m			
[%]	[%]						cm	[%]	
51.9	39.9	144	277	755	588	585	0.069	5	4.5



Fig. 1 On-site situation —the effect durability of surface water repellency (watering test) (the 12th year)

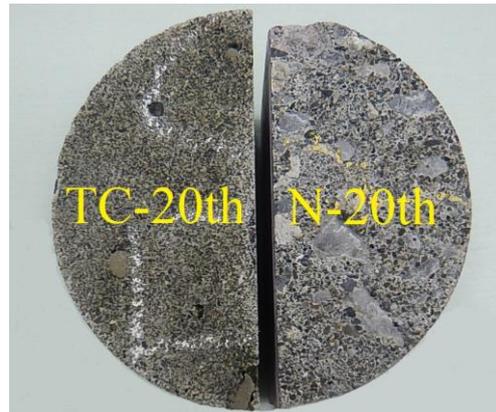


Fig. 2 Concrete surface morphology (the 20th year)
Notes: TC: Treated part; N: Un-treated part.

diffusion coefficient of the concrete surface.

2. OUTLINE OF INVESTIGATION

2.1 Target structure

The target structure is the chest wall of the F part of the Tomakomai Port breakwater. Tomakomai belongs to Hokkaido, Japan, with severely cold winters. There is snow for half a year in the whole year, and the days that weather meets freeze-thaw conditions is up to four months. Statistics show the freezing and thawing times are 99 per year, and the accumulated cold degree is 415°C·day. The main construction was built from May 11 to November 20, 2000, and composite penetrants were coated on the part of the chest for anti-corrosion in October of the same year. The cement used is normal Portland cement. The concrete mix ratio lists in **Table 1**.

The application of maintenance materials of compound penetrants: Sodium silicate solution (type-A) was brushed on the concrete surface of Tomakomai Port breakwater as the undercoat; then the silane solution (type-B) was applied as the top-coat and showered for curing following the product instructions. The coating dosages adopted the recommended amount for type-A and type-B.

Fig. 1 shows the state of the concrete surface after being splashed with water in the 12th year. After splashing on the treated part, water quickly flowed to the bottom. In contrast, the downstream length of water is significantly shortened for the untreated part. The reason is that the impregnant sodium silicate solution can make the concrete surface dense, and the silane solution can form a hydrophobic film on the concrete surface, which makes water challenging to penetrate. It can be seen that this effect is still significant after 12 years of service in a cold marine environment.

It can be seen from **Fig. 2** that in the 20th year, the concrete surface of the treatment part remained intact, with only a small amount of coarse aggregate leaking out. Still, the surface smoothness and flatness were not as good as in the 12th year (compared with the left part of **Fig. 1**). Uniform and slight spalling erosion occurred. For the untreated group, the concrete surface mortar layer had almost spalled. A large amount of coarse aggregate leaked out. It can be seen that the application of impregnant has an excellent protective effect on the concrete surface and can delay the spalling of the concrete surface.

2.2 The procedure of investigation and calculation method

In the 12th and 20th years after the construction,

several core samples were taken from Tomakoma's chest wall where penetrants were applied (left part of Fig. 1 and Fig. 2) and unpainted parts (right part Fig. 1 and Fig. 2). The sampling size is $\Phi 150 \times$ about 200 mm, and they were brought back to the laboratory for performance tests.

The test items of the total chloride ion concentration distribution test are briefly described as follows:

Take 10 mm as one layer from the concrete surface to the inner and sample layer by layer. The test depth range was 0-60 mm.

The experiment was conducted following the standard test method (precision analysis) of the Civil Engineering Research Institute-JCI-SC5 Simple analysis method for total salt in hardened concrete.

The transmission behavior of chloride ions in concrete complies with Fick's second law, **Formula 1**. Therefore, Fick's second law can be used to fit the chloride ion concentration of concrete obtained from the experiment from the surface to the inside. After fitting, the chloride ion diffusion coefficient D_{aps} and the concrete surface chloride ion content C_{0s} are obtained simultaneously.

$$C(x,t) - C_i = C_{0s} \left\{ 1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_{aps} \cdot t}} \right) \right\}$$

Formula 1

$C(x,t)$: chloride ion concentration were determined by the experiment;

C_i : The Initial chloride ion concentration on the concrete surface take the mean value of the innermost layer, which is 0.68 kg/m^2 ;

X : the depth from the concrete surface, $x=0.5, 1.5, 2.5, 3.5, 4.5, \text{ or } 5.5 \text{ cm}$,
 $t=12 \text{ or } 20, \text{ year}$.

3. RESULTS AND DISCUSSIONS

3.1 Total chloride ion concentration distribution

The experimental data of chloride ion concentration and fitting curves are shown in Fig. 3. It shows that at the same test depth: (a) In the same year, the chloride ion concentration of the treated part was lower than the untreated part. The penetrants can effectively resist the water and corrosive substances into the concrete. (b) For the same part, the concentration of the 12th year is lower than the 20th year's because the chloride ions were cumulated over time. Along the depth direction: (a) in the 12th year, chloride ion concentration decreases gradually from surface to inside. The chloride ion development frontier is roughly 35mm. (b) in the 20th year, the first layer chloride ion concentration is lower than the second layer; there is a gradual downward trend from the surface to the inside from the second layer. The chloride ion front reaches a depth of 45mm. The reason is that the concrete surface layer is a convective zone [7, 8]. The chloride ions

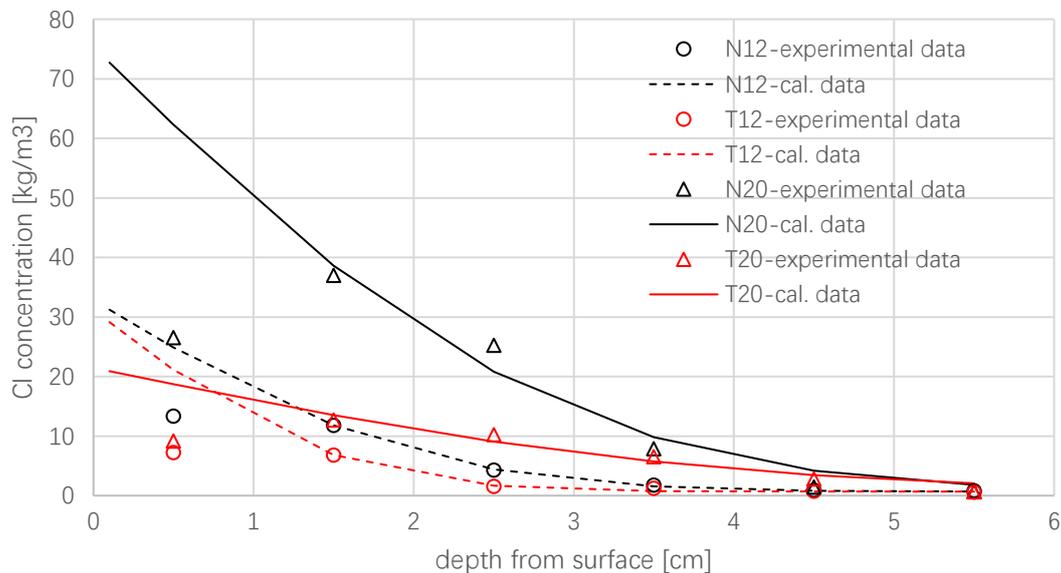


Fig. 3 Total chloride ion distribution (kg/m^3)

Where:

concentration of this layer is affected by rain, tides

and waves erosion and carbonization. When the surface chloride ions increase to a specific value, it is not easy to continue to grow. In this convective zone, the surface chloride ions concentration tends to deviate from Fick's second law [9]; therefore, the calculations related to chloride ion concentration should select the surface chloride ion concentration obtained by curve fitting regression. The concrete interior is dominated by diffusion, conforming to Fick's second law.

Fig. 3 also shows that the chloride ion concentration in each layer of the untreated concrete part increases synchronously with the year, showing no intersection of the fitting curves. For the untreated part, the chloride ion concentration of the inner layers (depth \leq 10mm) has a changing trend consistent with the treated part. In contrast, in the first layer, there is an intersection. It is because, in the 12th year, the chloride ion concentration of the first layer and the sub-layer differed significantly. By the 20th year, the concentration difference between the first layer and the sub-layer became smaller. It indicates that the first layer's penetration barrier function gradually weakened along the service year.

3.2 Surface Total chloride ion concentration C_0

Fig. 4 shows that the chloride ion concentration on the concrete surface is time-varying and is affected by the surface treatment. In the 12th year, the chloride ion concentration on the concrete surface of the treated part and the untreated part was almost equal. Still, as the service life increased, by the 20th year, the untreated concrete surface had a faster accumulation of chloride ion concentration than the concrete treated with impregnating agents, increasing from 32.16kg/m³ in the 12th year to 74.68kg/m³ of the 20th. In contrast, the treatment group has decreased from 30.54kg/m³ to 20.78kg/m³. The 20th year's chloride ion concentration on the concrete surface of the untreated part is about 2.32 times that of the 12th year of itself and 3.59 times that of the treatment part of the 20th year. And the treatment part, compared with itself 12th year, even decreased by 31.97%. After being coated with penetrants, the calculated surface chloride ion concentration was reduced by 5.04%/72.18% (the 12th year/the 20th year). The longer the time, the greater the difference between the surface chloride ions concentration of the two parts concrete. It is mainly because sodium silicate continuously reacts with the calcium hydroxide inside in water conditions during the concrete service. At the

same time, the surface carbonization of the concrete is faster than that of the untreated group. All of these can make the concrete surface dense. So, the water and chloride ions are not easy to enter. The existing chloride ions in the inner part will diffuse deeper into the concrete under the difference of chloride ion concentration, thereby reducing the surface chloride ion concentration of the treatment part. It can be seen that the concrete surface penetrants can effectively reduce the growth rate of the chloride ion concentration on the concrete surface.

In the durability design, the chloride ion concentration on the concrete surface is generally set to 13 kg/m³ proposed by the Civil Engineering Society [10].

For all the groups, the calculations show that the theoretical chloride ion concentration on the concrete surface have exceeded 13 kg/m³ at the service of 12, let alone the nearly 80 of the 20th year of the untreated part. Suppose the target service year is 100 and the concrete surface is without additional treatment. In that case, the theoretical chloride ion concentration of the concrete surface is obviously far more than 13 during 90% of the service time. Further, the measured chloride ion concentration has far exceeded 13kg/m³ in the 20th year.

In the concrete durability design, if the design value of 13 kg/m³ is taken and the mix ratio are designed as this project, it is far from achieving the 100-year service goal. Other concrete durability maintenance measures, such as covering the concrete surface with effective penetrants used in this project, should be used. But it is not a one-time fix. The service process still needs to be maintained in stages.

Another suggestion is to increase the surface chloride ion concentration for concrete durability design depending on the concrete service environment.

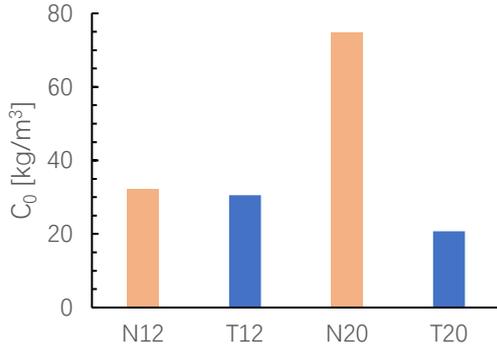


Fig. 4 The surface total chloride ion concentration (kg/m³)

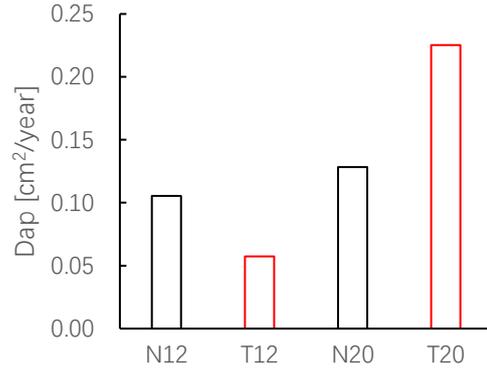


Fig. 5 Chloride diffusion coefficient D_{aps}

Table 2 The change index m

Groups	D_{aps-12} (cm²/year)	D_{aps-20}	Decay index m
No-treatment	0.11	0.13	-0.33
Treatment	0.06	0.23	-2.63

3.3 The chloride diffusion coefficient D_{aps}

Fig. 5 shows that the chloride ion diffusion coefficient of the treated part concrete has almost no change from the 12th year to the 20th year, indicating that the chloride ion diffusion rate in ordinary concrete tends to be stable after 12 years. However, the diffusion coefficient of the treated part has grown from about half of the untreated group's diffusion coefficient in the 12th year to twice that in the 20th year, which is a considerable change. It also means that, in the 20th year, the protective effect of the penetrants on the concrete surface was partially or wholly lost, leading to the chloride ion diffusion coefficient on the concrete surface increasing sharply. Although the chloride ion diffusion coefficient has become much larger, it can be known from section 2.2 that the chloride ion concentration on the surface of the treated group is about 27.82% of that of the untreated group, so the amount of chloride ions that can eventually be transmitted into the inner concrete is much smaller than that of the untreated group.

Fig. 6 shows the relationship between the treatment and the untreated groups' chloride ion diffusion coefficient. The treatment group's diffusion coefficient was lower than that of the untreated group in the 12th year, and a reversal

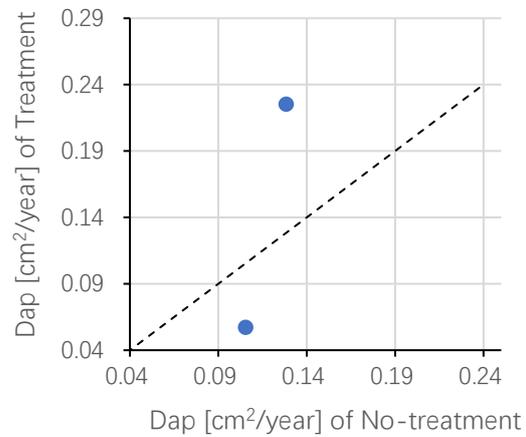


Fig. 6 The relationship of the Chloride diffusion coefficient D_{aps} between the treatment part and no-treatment part

occurred in the 20th year. The reversal time point can be regarded as the time when the protective effect of the impregnant on the concrete surface begins to lose. The reversal point is the intersection point of the two straight lines. This intersection's chloride ion diffusion coefficient can be obtained at 0.11 cm²/year.

The change index m is calculated by Formula 2.

$$D(t) = D_{ref} \left(\frac{t_{ref}}{t} \right)^m \quad \text{Formula 2}$$

Table 2 lists the change index m of the Chloride diffusion coefficient D_{aps} . For the treatment group, D_{aps-12} is still used as D_{ref} , and 0.11 cm²/year in Section 2.3.1 is used as $D(t)$ into the above formula 2. The value of m is -2.90, and the t_{ref} is 12, then the t can be calculated. It is 15.11. The time for the protective effect of the impregnant on the concrete surface to significantly reduce the inflexion point is about 15 years. After this year,

the chloride ion diffusion effect was greater than that of the untreated group. This conclusion suggests that the secondary maintenance of the concrete in the treatment group should be less than 15 years.

4. CONCLUSIONS

The data collected from the concrete service in the natural environment is extremely precious and can be fed back to the design stage to guide much longer-life concrete. This article focuses on the Tomakomai breakwater project, discusses the changing state of chloride ions on the surface of the concrete (0-60 mm) during 20 years of service in a cold marine environment, and provides valuable suggestions from a design and maintenance perspective.

- (a) The coating of impregnants can effectively slow down the penetration rate of chloride ions into the concrete with water. The chloride ion concentration of the treated groups was lower than the untreated groups. For the existence of the concrete surface convective zone, the chloride ions concentration of the surface layer tends to deviate from Fick's second law, they are lower than the second layer in the 20th year after construction, and the impact is not noticeable enough at the 12th year.
- (b) From the 12th year to the 20th year, the surface chloride ion concentration of the treated concrete didn't increase. Still, the chloride ion diffusion coefficient increased significantly, about twice that of the untreated group. While, for the untreated concrete, the chloride ion diffusion coefficient stabilized after 12 years, but its calculated surface chloride ion concentration was about three times that of the treated part at the 20th year.
- (c) In concrete durability design, if chloride ion concentration on the surface of the concrete is set to 13 kg/m³, the surface should be supplemented with other durability protection measures. Or the design value of chloride ion concentration on the surface of the concrete should be appropriately increased according to the service environment of the concrete.
- (d) For the treatment concrete, after 15 years of service, the diffusion coefficients of chloride ion are over the un-treatment part. It indicates that the protective effect of the surface impregnant begins to weaken at 15.11 years, and the migration of chloride ions inside the concrete becomes faster. In this case, it should be combined with other

test data and the target life to determine whether it is necessary to take further re-maintenance to prevent the accelerated penetration of chloride ions.

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