Effect of Carbon Nanotubes on the Chloride Penetration in Ultra-High-Performance Concrete

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Abstract. The improvement of Carbon Nanotubes (CNTs) addition on the properties of concrete has been recently investigated, e.g. mechanical properties and durability, but is rarely reported for Ultra-High-Performance Concrete (UHPC) with a very low water to binder ratio. This study evaluates the effect of CNTs on chloride penetration in UHPC and some mechanical properties of this material. The results of experimental tests show that the addition of CNTs in UHPC with contents from 0% to 0.5% by weight of binder in UHPC will reduce the workability of the concrete mixture, and not significantly improve the compressive strength of UHPC under both standard curing and heat curing conditions. However, the results showed that the addition of CNTs improves the dense microstructure of both the UHPC matrix and interfacial transition zone, and resulting in reducing the chloride penetration in UHPC. This is very important in cases of using UHPC for the constructions working under extreme conditions such as on a coastal, island, or underground structures with water erosion.

Keywords: UHPC · Carbon Nanotubes · Chloride penetration · Compressive strength · Microstructure

1 Introduction

Ultra-high-performance concrete (UHPC) is a concrete made from a mixture of quartz sand with a size of about 100–600 μm, cement, mineral admixture, superplasticizer, and water, in which the water to binder ratio (W/B) is very low (less than 0.25) [1–3]. This material has superior properties compared to conventional concrete, such as high workability, very high mechanical properties, i.e., the compressive strength of usually

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over 150 MPa, low permeability, and superior durability. Due to these advantageous properties, UHPC is capable of opening the door for potential applications in the future, such as in the construction of thin, large structures, large-span bridge structures, highway roads, skyscrapers, corrosion-resistant structures, etc. [2, 4, 5]. In fact, the production of UHPC is based on the essential principles, including (i) Improving microstructure of concrete, (ii) Enhancing homogeneity, (iii) Optimizing the packing density, (iv) Promoting hydrate reaction, and (v) Bettering the toughness [6, 7]. Under special conditions of materials and manufacturing technology, the compressive strength of UHPC can be achieved over 800 MPa [1]. The application of the above principles will increase mechanical properties and especially the durability of UHPC, and this will contribute to improving the possibility of resisting the impact of aggressive erosion agents and deterioration of structures.

For concrete structures when exposed to aggressive environmental conditions such as physical, chemical, or mechanical factors will lead to deterioration of concrete quality, these impacts often influence simultaneously, and accelerate the quality degradation of concrete [8, 9]. One of the reasons leading to corrosion on reinforcement and damage to construction works is the chloride ion penetration. When the concentration of that in concrete exceeds the safety threshold, it will break the passive protective layer of steel bar and causing corrosion [10–12]. Until now, many studies have been conducted to consider the effects of mineral admixtures, curing regime, W/B, corrosive environment, etc., on the extent of chloride ion diffusion into concrete [12–14]. Of those, the use of nanomaterials to improve the durability of concrete is also a topic of concern and research. Among materials in nanoscale, carbon nanotubes (CNTs) are relatively new materials with unique properties. The size of CNTs at the nanoscale, as well as the high specific surface area, allow this material to become an ideal reinforcing agent at the micro-level. It can improve the quality of concrete even at low contents by the ability to fill voids [15, 16], combine with hydration products, and bridge effect for micro-cracks to prevent the crack expansion propagation of concrete [17, 18]. With minimal content added, CNTs show an excellent interaction with binder paste to make a denser microstructure and resulting in better resistance to the penetration of corrosive agents compared to the reference without CNTs [16].

Studying the effect of CNTs on its possibility to resist the chloride ions penetration into UHPC and improvement of some other properties of concrete is an excellent approach to confirm the role of this material for concrete, especially UHPC intended for use in particularly harsh conditions, such as underground structures, structures on the coast or islands.

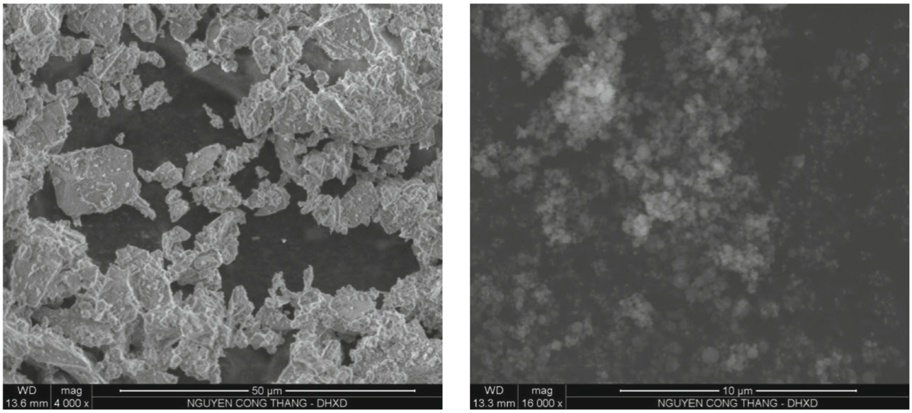
2 Materials and Methods

2.1 Materials

In this study, some materials were used including quartz sand (S) with a mean particle size of 300 μm; Portland cement (C) PC40 with the properties meeting the requirements of Vietnamese standard TCVN 2682: 2009 (Table 1); Condensed Silica fume (SF) having a mean particle size of 0.15 μm; Fly ash (FA) with the particle size in the range of 0.05–50 nm; Polycarboxylate-based Superplasticizer (SP) with 30% solid content by weight; CNTs, used in concrete mixtures are long multi-wall carbon nanotubes, the inner diameter of those is from 5 to 10 nm and outer diameter from 10 to 30 nm, the density of 0.14 g/cm^3, and some physical properties of CNTs are given in Table 2. To increase the dispersion and reactivity of CNTs in concrete, CNTs were dispersed into the SP solution. The SEM images of cement and SF used in these experiments are shown in Fig. 1. The mixture of CNTs and SP solution was then dispersed for 30 min in an ultrasonic bath before using (Fig. 2).

Table 1. Physical properties of Portland cement.

Properties	Unit	Value	Specification	Test methods (Vietnamese standard)
Retained on 0.09 mm sieve	%	0.6	≤ 10	
Fineness (Blaine)	cm^2/g	3870	≥ 2800	TCVN 4030-2003
Standard consistency	%	29.5	-	TCVN 6017-2015
Compressive strength				TCVN 6016-2011
- 3 days	MPa	29.8	≥ 21.0	
- 28 days		52.2	≥ 40.0	



(a) (b)

Fig. 1. SEM images of (a) cement, (b) SF

Table 2. Physical properties of CNTs

No	Properties	Unit	Value
1	Color		Black
2	Average Inside Diameter	nm	5–10
3	Average Outside Diameter	nm	10–30
4	Length	µm	10–30
5	Specific Surface Area	m^2/g	>140
6	Density	g/cm^3	0.14

(a) (b)

Fig. 2. CNTs dispersing (a) in SP solution and (b) in an ultrasonic bath

2.2 Experimental Methods

The determination of the influence of CNTs on the workability of UHPC was conducted by measuring the flow of the concrete mixture. The flow diameter of UHPC mixtures was controlled from 200 to 250 mm under the test method ASTM C1437.

The compressive strength of concrete was determined at 28 days using cube samples with a size of 100 × 100 × 100 mm.

The apparent chloride diffusion coefficient of UHPC was determined according to ASTM C1556 based on the cylinder samples of 100 mm diameter and 200 mm height. The evident chloride diffusion coefficient of UHPC was tested with variable CNTs contents from 0% to 0.5% by weight of the binder (the binder used here is a mixture of cement, FA and SF). At the same time, the other material components are kept the same.

The principle of the method for determining the chloride ion diffusion coefficient is described as follows: before being immersed in a solution containing chloride ions, the UHPC sample is separated into two sub-samples, one for the test sample and the other for determining the initial chloride-ion content (C_i). The initial chloride-ion content sample was cruised, and then the initial chloride-ion content in the acid-soluble fluid is specified. All surfaces of the test sample, except the finished surface, were sealed with a suitable coating. The sealed sample was then soaked to saturation in a calcium hydroxide solution with a concentration of 165 g per liter at 23 °C for 60 days, then rinsed with tap water and placed in sodium chloride solution. After a defined exposure time, i.e., 35 days, the test sample was removed from the sodium chloride solution and cut into thin layers parallel to the contact surface of the sample. The acid-soluble chloride content of each sample layer is determined. Finally, the apparent chloride diffusion coefficient (D_a) and the expected surface chloride-ion concentration (C_s) were calculated based on the initial chloride ion content. At least six values of chloride-ion content and related depth from the exposed surface are determined.

2.3 Concrete Mix Proportions

In this study, the influence of CNTs on some mechanical properties and chloride ion diffusion coefficients of UHPC was determined. The ratio of sand to the binder (S/B) was fixed at 1/1 by weight. The superplasticizer dosage was adjusted to keep the flow of UHPC mixtures from 200 to 250 mm; the ratio of water to binder (W/B) was fixed at 0.16. The concrete mixture proportion is given in Table 3.

Table 3. Mixture proportions of UHPC

No	W/B	S/B	SF, %	FA, %	CNTs, %	SP, %
1	0.16	1	10	20	0	0.52
2	0.16	1	10	20	0.05	0.51
3	0.16	1	10	20	0.1	0.53
4	0.16	1	10	20	0.3	0.64
5	0.16	1	10	20	0.5	0.85

2.4 Mixing Procedure, Curing Conditions

In this study, concrete mixtures were mixed in a 20 liter-Hobart mixer, and the mixing procedure is provided in Fig. 3.

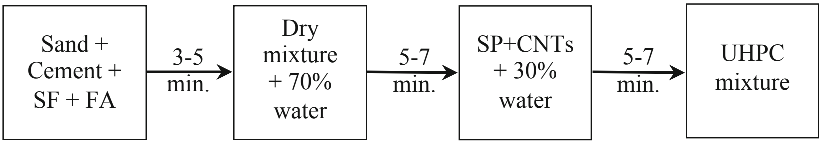


Fig. 3. Mixing procedure of UHPC mixtures

The test samples were cured under the standard curing condition (27 ± 2 °C, RH $\geq$ 98%), and then de-molded after a cast of 24 h. After that, the samples were continuously cured under two different curing conditions:

- Standard curing condition: (27 ± 2 °C, RH $\geq$ 98%) until defined testing ages;
- Heat curing condition: in hot water (90 ± 5 °C) for 48 h, followed by standard curing conditions until defined testing ages.

The samples were tested for compressive strength at the ages of the 3rd, 7th, and 28th days.

3 Experimental Results and Discussion

3.1 Flow of Freshly Mixed UHPC

Experimental results on the effect of the CNTs' content on the workability of fresh UHPC mixtures are shown in Fig. 4, in which the flow evaluated the practicability indicated in Sect. 2.2. It can be seen that when the amount of CNTs increases up to 0.1%, the flow of the UHPC mixture is similar to that of the reference mixture without CNTs. However, when increasing the CNTs' content of over 0.1%, the flow of the concrete mixture is decreased, e.g., with the CNTs content of 0.3%, the dosage of SP is increased by 23% compared to that of the reference sample. It is clear that when the CNTs' content is increased to 0.5%, the SP dosage is increased significantly, up to 73% compared to that of the reference sample to attain the flow ranging from 200 to 250 mm.

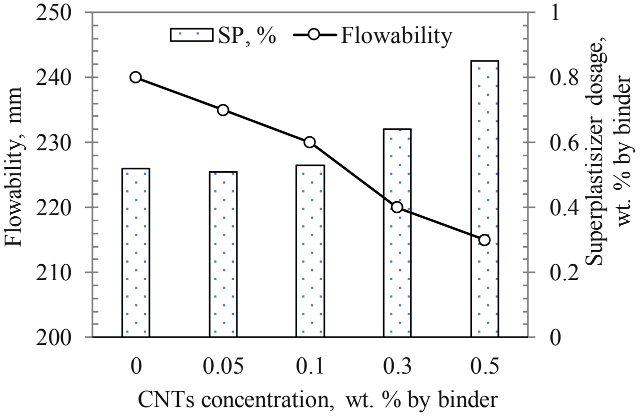


Fig. 4. Relationship between the CNTs content with the SP dosage and the flow of UHPC mixtures

CNTs can explain the effect of the CNTs content on the flow of fresh UHPC mixtures with a fibrous type, but in nanostructures, when added in concrete with a reasonable content, CNTs will fill in the voids between cement, SF and FA particles releasing a certain amount of water, as a consequence, the amount of free water may be increased, and this will improve the flow of the concrete mixture. However, as the content of CNTs is increased, the amount of water needed to wet the nanoparticles increases, and the dispersion of nanoparticles in the mixture will be more difficult, easy to create agglomerations, and forming more massive particles. Therefore, a certain amount of water is retained inside these agglomerations, thereby reducing the flow of the concrete mixture.

3.2 Compressive Strength

The influence of the CNTs' content on the compressive strength of UHPC samples is shown in Fig. 5. The experimental results show that the addition of CNTs does not improve the compressive strength of samples under both standard curing and heat curing conditions. It should be noted that the curing state influences the development of the compressive strength of specimens. The compressive strength of samples is enhanced significantly at the age of 7 days under the heat curing condition and much higher than that of samples curing under the standard condition. However, the compressive strength of samples at 28 days is not shown a significant difference for both curing conditions.

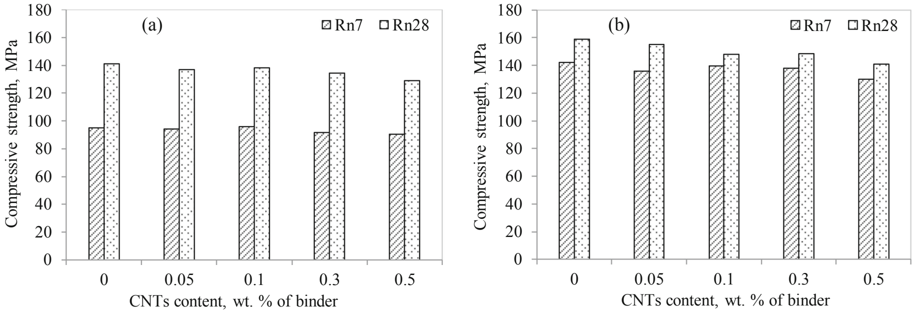


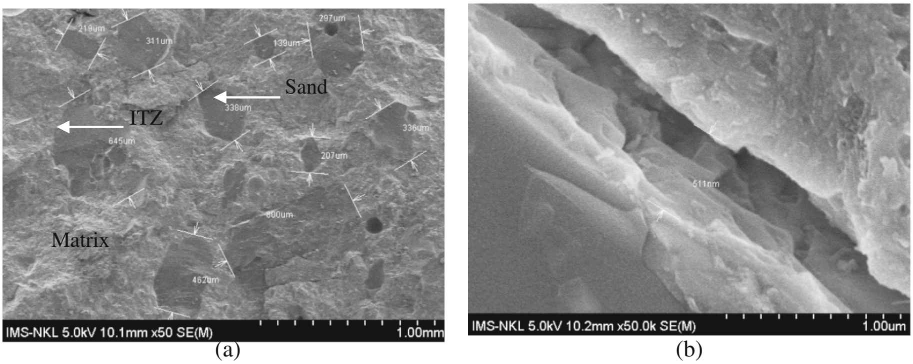
Fig. 5. Effect of CNTs content on compressive strength of UHPC under (a) standard curing (27 ± 2 °C), (b) heat curing (90 ± 5 °C)

3.3 The Microstructure of UHPC Using CNTs

UHPC, with a meager W/B ratio, using large amounts of cement and mineral admixtures, applying heat curing condition, will fully promote the pozzolanic reaction and leading to minimize pore size, very low porosity and CH content [19–21]. In this study, the characterization of the microstructure of UHPC will be evaluated in the hardened cement paste and the interfacial transition zone (ITZ).

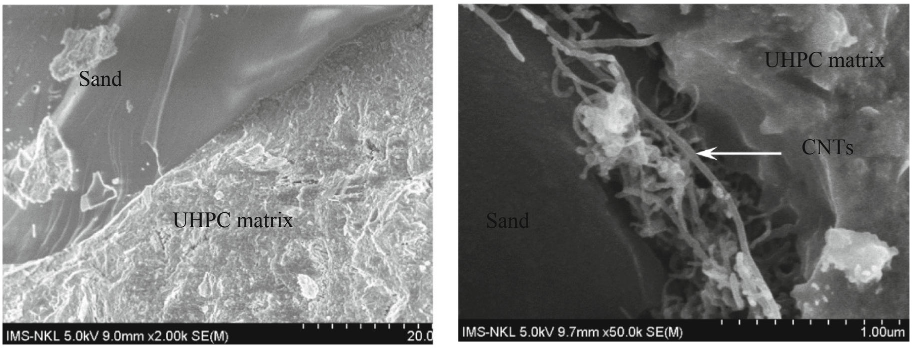
It can be observed from SEM images that for the reference samples (Figs. 6 and 7), the hardened cement paste area exhibits a dense structure and the ITZ with a vast improvement compared to normal and high strength concrete, i.e., the width of the ITZ of about 40–500 nm. However, when adding CNTs, especially with heat curing conditions, it is possible to observe that the microstructure of concrete is improved both in the hardened cement paste and the ITZ to make a denser microstructure. As a consequence, the compressive strength of UHPC is enhanced.

UHPC with a meager W/B ratio shows a very dense microstructure, and a resulting very low porosity when compared to normal and high strength concrete. Therefore, the space for the development of hydration products is limited, leading to a denser C-S-H and CH structure. The compact C-S-H structure and low CH content significantly improve the ITZ between aggregates and cement. In UHPC, the thickness of the ITZ between cement and sand is minimal compared to that of standard concrete. This is because the elimination of large aggregate particles results in a decrease in the natural retaining wall effect that appears around the surface of large aggregates. The use of CNTs has been shown to solidify both of the hardened cement paste and the ITZ of UHPC, especially



(a) (b)

Fig. 6. SEM images of microstructure of UHPC reference sample without CNTs with a magnification of (a) ×50, and (b) ×50.000



(a) (b)

Fig. 7. SEM images of microstructure of UHPC using CNTs with a magnification of (a) ×2.000, and (b) ×50.000

under the heat curing condition. The thickness of this ITZ of UHPC is observed from 40 to 500 nm, while for standard concrete and high strength concrete, this thickness is about 20–50 μm [22], 100 times and 40 times higher than that of UHPC with CNTs, respectively.

3.4 Chloride ion Concentration and Chloride ion Diffusion in Concrete

The diffusion of chloride ion in concrete occurs within the void spaces, fluid-filled pores, and cracks. Also, the mixture composition, curing, finishing, the environment, age, and artistry influences the resistance to chloride penetration of concrete. Besides, the rate of chloride diffusion is also influenced by the valence and concentration of other chloride ions in the pore fluid. Therefore, the apparent diffusion coefficient as determined by the same test procedure. According to Fick's second law of diffusion, this diffusion coefficient is used to evaluate chloride penetration into mortar or cement concrete under saturated conditions.

In this study, the chloride ion concentration in UHPC samples at different depths and with different content of CNTs are determined and shown in Fig. 8. It should be noted that the reference sample without CNTs before exposure to chloride ion has a chloride ion concentration of 0.0532%, and this value is considered as the initial chloride ion concentration of all samples. The experimental results show that for the reference sample (0% CNTs), when exposure to chloride ion, the largest concentration of chloride ion of 0.0859% can be reached with a depth of 1 mm. However, at a depth of 2 mm, the value of chloride ion concentration shows a massive reduction of about 38.4%. At a depth of 4 mm, no chloride ion penetration can be observed.

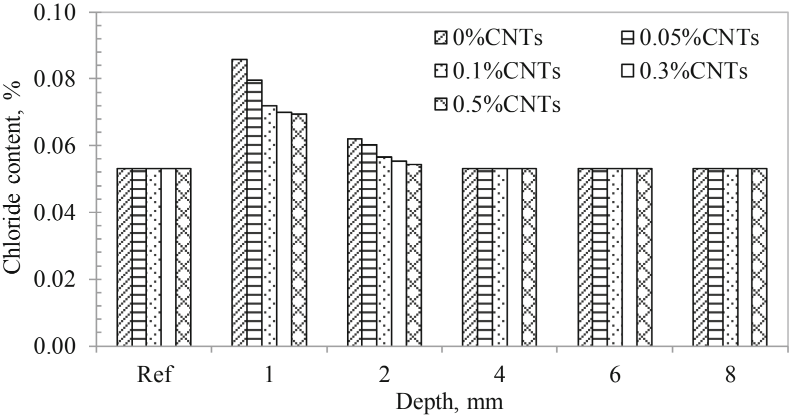


Fig. 8. The chloride content in UHPC at different depths

The addition of CNTs significantly reduces the concentration of chloride ion in UHPC samples. It can be observed that with the CNTs content of 0.05%, the chloride ion concentration in the UHPC samples is decreased at different depths, but not significant compared with the samples using 0% CNTs. However, when adding 0.1% CNTs, the concentration of chloride ions in the UHPC sample at the depths from 1 mm to 2 mm is decreased sharply compared to the samples using 0% CNTs, for example, at a depth of 1 mm, the reduction of chloride ion concentration can be reached up to 35%. As the content of CNTs increases to 0.3% and 0.5%, the chloride ion concentration in the UHPC sample is decreased significantly compared to the sample using 0.1% CNTs. It should be noted that no increase in chloride ion concentration can be seen with different CNTs' contents at a depth of the 4 mm. These results demonstrate that the dense microstructure of UHPC with CNTs gives perfect prevention of chloride ion penetration. In this study, it is almost impossible to see the penetration of chloride into the concrete at a depth of 2 mm.

According to ASTM C1556, a regression analysis of a function expressed as chloride concentration was measured at different depths for 60 days, and the apparent diffusion coefficient of chloride (Da) was determined. Through the analysis of experimental results, the chloride ion diffusion coefficient was identified (Fig. 9). The results show that when adding CNTs in concrete, the chloride ion diffusion coefficient is significantly reduced compared to the sample using 0% CNTs. However, when CNTs content increased above 0.3%, chloride ion diffusion coefficient tended to increase slightly. This value indicates the need for further study of chloride ion diffusion coefficients in UHPC at later ages.

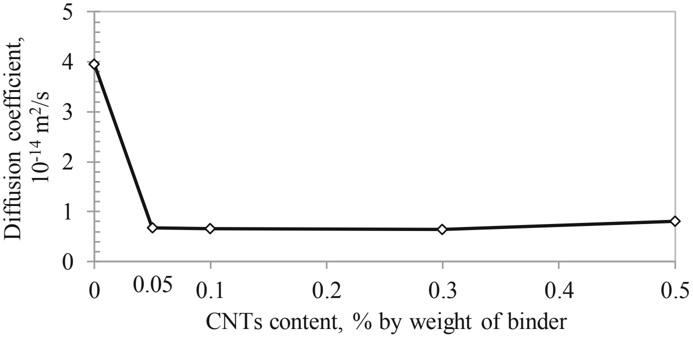


Fig. 9. The apparent chloride diffusion coefficient of UHPC with different CNTs contents

The addition of CNTs above 0.3% increasing the Da coefficient can be explained that CNTs with a fibrous type but in nanostructures, when added in concrete with a reasonable content, it will be filled in the voids in the matrix and ITZ region, improving the dense structure of concrete. However, when more CNTs are added, the dispersion of nanoparticles in the mixture will be more difficult, the CNTs will easily be agglomerated and form larger particles, which affects the consistency of concrete.

4 Conclusions

Based on the experimental results of the effect of CNTs concentration on some mechanical properties and the calculated apparent chloride diffusion coefficient of UHPC, some conclusions can be drawn as follows:

- The addition of CNTs influences the flow of the UHPC mixture when the CNTs content is less than 0.1% by weight of the binder, the flow of the UHPC mixture is similar to that of the reference sample, but above this content, the flow of the UHPC mixture is decreased.
- The addition of CNTs does not significantly improve the compressive strength of UHPC under both standard curing and heat curing conditions. When the CNTs content is higher than 0.3% by weight of the binder, the compressive strength of concrete tends to decrease.
- The addition of CNTs improves both in the hardened cement paste and the ITZ of UHPC. The thickness of ITZ of UHPC observed from SEM images is from 40 to 500 nm, i.e., much improved in comparison with that of standard concrete and high strength concrete, the ITZ of those are about 20–50 μm.

- The addition of CNTs reduces the chloride ion penetration in UHPC. The chloride ion concentration in the UHPC sample using 0.1% CNTs is decreased sharply compared to the sample using 0% CNTs at the depth from 1 mm to 2 mm, i.e., up to 35% at 1 mm depth. No chloride ion penetration can be observed at a depth of 4 mm.

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