

# Chloride Penetration Resistance of Cement Mortar Containing Different Contents of CNT

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**Abstract**—This study explored the effect of adding different concentrations of carbon nanotubes (CNTs) on the resistance to chloride ions penetration of cement mortars through natural penetration of chloride ions and Mercury Intrusion Porosimetry. The experimental results of natural penetration of chloride ions showed that, the chloride ions penetration depth of the samples which added with CNTs were deeper than the control group which was without the addition of CNTs in the case of 35 days, 45 days, 55 days, 65 days of natural penetration of chloride ions, and the penetration depth increased with the content of CNTs. However, Mercury Intrusion Porosimetry (MIP) experimental results indicated that the porosity of cement mortar incorporated CNTs instead decreased, so the speculation that adding CNTs makes the porosity of the cement mortar specimens increase resulting in the increase of the penetration depth can be excluded. Another assumption was proposed that there may be a water film on the surface of the CNTs, and this water film can accelerate the penetrating speed of chloride ions as a convenient channel.

**Keywords**- CNTs; cement mortar; chloride; penetrability

## I. INTRODUCTION

The most widely used cementitious composites in the construction sector are ordinary concrete consisting of Portland Cement, water, sand and stone. Concrete has always been an important and irreplaceable material in the field of construction. With the development of science and technology and the increasing demand of high-rise and super high-rise buildings in the construction industry, the importance of concrete durability is increasingly highlighted. For the durability of concrete, the corrosion of steel is one of the main problems, and among plenty of reasons for the corrosion of steel, the erosion of chloride ions is the most important reason. One of the main sources of chloride ions in concrete is the external penetration of chloride ions, which mainly occurs in the coastal areas. Salt spray environment causes chloride ions to invade the concrete through a series of chemical reactions. After years of exploration by scholars and engineering technicians in various countries, great progress has been made in the research on the resistance to chloride ions permeability of concrete. Halamickova et al [1] found that the coefficient of chloride ions diffusion varied linearly with the critical pore radius as determined by Mercury Intrusion Porosimetry while permeability was found to follow a power-law

relationship vs. this critical radius. Liu et al.[2] demonstrated that the carbonation of a cement paste increases with its water to cement ratio and with carbonation ages, but decrease with its amount of chloride ions, and it has also been found that increases of chloride ions of a cement paste refine its porous structures, decrease its porosity and eventually mitigate its carbonation rate. Concrete structures deteriorate prematurely under the influence of various factors, and the durability of the structure and the bearing capacity are greatly affected. With the development of society, concrete materials are gradually applied to more complicated structures and harsher environments, and the problems caused by material failure become increasingly serious [3]. In order to improve the bearing capacity and durability of the structure, the material has been developed towards high performance. Therefore, more and more researchers have been devoted to the research of cement-based composites in recent years, such as nano-reinforced cement-based composites and fiber reinforced cement-based composites, and have obtained a great deal of research achievements and experiences. However, only the fibers that prevent the cracking process can control the cracking of materials and enhance durability of concrete, so the CNTs provide the possibility for this.

CNTs are considered superior to other fibers. As a nano-material, CNTs are light in weight and perfectly connected in a hexagonal structure with superior mechanical, electrical and other properties. The mechanical properties of cement-based composites can be obviously enhanced due to the size effect of nanometer, filling effect, fiber connection between cracks and bridging effect between cement hydrates, and the incorporation of a small amount of CNTs[4,5]. Konsta et al.[6] indicated that MWCNTs improve the nano- and macro-mechanical properties of cement paste. Han et al.[7] found that CNTs can effectively improve the durability properties of cement-based composites. Li et al.[8] discovered that MWCNT could improve some mechanical properties and physical performances of cement-based composites under drying and freeze-thaw conditions from different degrees. Li et al.[9] found that NS may act as an ideal admixture for improving both the interactive behaviors between CNTs and cement matrix and the damping properties of cement composite. Although a series of research results show that the incorporation of CNTs not only improves the mechanical properties of cement-based composites, but also improves some of the durability

properties. However, there are few studies on the effect of CNTs on the resistance of cement mortar to chloride attack.

In view of the shortcomings and deficiencies of the above research status, the natural penetration experiment of chloride ions for cement mortar added with different content of CNTs has been conducted in this study. Furthermore, the influence of CNTs on the pore structure of cement mortar was investigated by Mercury Intrusion Porosimetry experiment. And the effect of different dosage of CNTs on cement mortar under the natural penetration of chloride ions was analyzed.

## II. EXPERIMENTAL DESIGN

The cement mortar with different adding amount of CNTs with a w/c ratio of 0.5 varied respectively from 0%(CT), 0.02%(C1), 0.04%(C2), 0.1%(C3) to 0.2%(C4). The specimen was a cylinder with a diameter of 100 mm and a height of 50 mm. The specimens which were cured in natural conditions after pouring and then removed from the mold after 24 hours cured in a standard curing room maintained at a constant temperature of  $22 \pm 3$  °C and a relative humidity of  $(95 \pm 3)\%$  for 28 days. And then, the specimens were transferred to a saturated calcium hydroxide solution at a temperature of about 23 °C for 14 days. For natural penetration of chloride ions (according to the European standard NT BUILD 443[10]), the upper surface

of the cement mortar was selected as the permeable surface and the other surfaces was sealed with paraffin.. Finally, the specimens were soaked for 35 days, 45 days, 55 days, 65 days in the sodium chloride solution (165g / L). For Mercury Intrusion Porosimetry test, the specimens cured for 28 days had a same mix with CT and C-CNTs, and took the central part as specimens for porosity testing under both low pressure and high pressure conditions.

## III. RESULTS AND ANALYSIS

### A. Results of Natural Penetration of Chloride Ions Test

The results are shown in Table 1 and Figure 1, in four different ages, the control group has the lowest penetration depth at the same age, except the chloride ions penetration depth of c2 for 55 days which was smaller than the control group (the chloride ions penetration depth of c2 for 55 days was caused by experimental error, but the overall trend hasn't been affect, so it was not as a reference.). The penetration depth of chloride ions showed an increasing trend with the concentration of CNTs, the increasing magnitude of samples with the age of 45 days, 55 days and 65 days kept basically at 4% -6%, while there was a significant decrease in the increase of penetration depth after adding CNTs to the specimens aged 35 days. In addition, the depth of chloride ions penetration increased with days.

TABLE I. THE NATURAL PENETRATION DEPTH OF CHLORIDE IONS OF DIFFERENT ADDING AMOUNT OF CNTS IN MORTARS AND THE RISING PERCENTAGE COMPARED TO THE LAST CONCENTRATION OF CT

Dosage	35 days		45 days		55 days		65 days	
	Depth (mm)	Rising percentage	Depth (mm)	Rising percentage	Depth (mm)	Rising percentage	Depth (mm)	Rising percentage
CT	13.2	-	17.99	-	20.56	-	22.11	-
C1	15.39	16.59%	18.72	4.06%	21.38	3.99%	23.43	5.97%
C2	16.51	7.28%	19.5	4.17%	18.58	-	24.48	4.48%
C3	17.28	4.66%	20.29	4.05%	22.58	5.61%	25.27	3.23%
C4	17.7	2.43%	21.03	3.65%	23.53	4.21%	26.85	6.25%

TABLE II. COMPARISON OF MIP EXPERIMENT RESULTS OF CEMENT MORTAR WITH AND WITHOUT INCORPORATING CNTS

Data of Mercury Intrusion Porosimetry								
Category	Total Intrusion Volume (ml/g)	Total Pore Area (mg)	Median Pore Diameter (Volume)	Median Pore Diameter (Area)	Average Pore Diameter (4V/A)	Apparent (skeletal) Density (g/ml)	Porosity	Stem Volume Used
CT	0.1328	13.1540	0.0842	0.0216	0.0404	2.4223	24.33%	18%
C-CNTs	0.1263	12.8260	0.0627	0.0278	0.0394	2.1971	21.71%	27%

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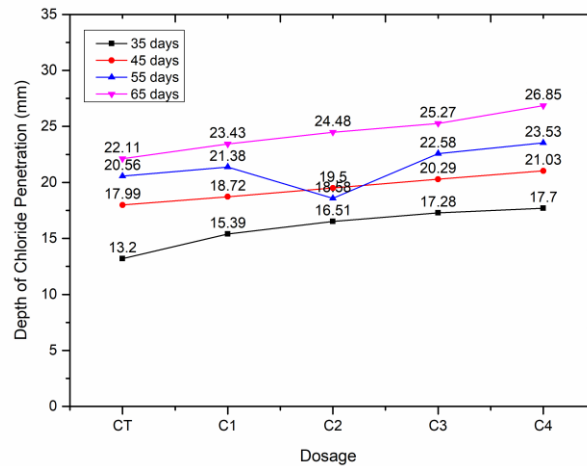


Figure 1. The line chart of the natural depth of chloride ions penetration.

### B. Results of Mercury Intrusion Porosimetry Test

Wu and Lian [11] divided the pores in the concrete structure into four grades which called harmless pores with a diameter of less than 20 nm, less harmful pores with diameters between 20 and 50 nm, harmful pores with a diameter between 50 and 200 nm, and more harmful hole with a diameter of greater than 200 nm. Therefore, this study also conducted data processing and analysis according to this classification method. The experimental results can be seen from Table 2 and Table 3, the porosity of C-CNTs which added CNTs have a certain reduction compared to CT. As Table 2 showed that, the total intrusion of mercury decreased from 0.1328mL/g to 0.1263mL/g. And the average pore diameter of cement mortar containing CNTs decreased from 0.0842 to 0.0627 with a reduction of 25.53%. It can be therefore concluded that CNTs can reduce the porosity of cement mortar effectively. As Table 3 showed that the number of harmful pores, fewer harmful pores and harmless pores of the specimens which added with CNTs respectively decreased significantly by 31.25%, increased by 26.86% and slightly reduced by 4.83%.

### C. Analysis and Discussion

The experimental results of natural penetration showed that the control group has the lowest infiltration depth at the same age, and the penetration depth of chloride ions showed an increasing trend with the concentration of CNTs. It can be inferred that the addition of CNTs will increase the penetration depth of chloride ions. However, results of Mercury Intrusion Porosimetry test indicated that CNTs can reduce the porosity of cement mortar effectively. Existing research [6,12] showed that, as a nano-material, CNTs can fill and block the pores through the effect of micro-filling in the cement-based composites, and play a role in reducing and refining the pores. Li et al [8] showed that the addition of MWCNT led to a reduction of lower water evaporation, indicating that there were less open pores in the specimens

of cement-based composites with CNTs. Thus, the cement-based composites with CNTs may have the better performance of water retention which can make unhydrated particles hydrate continuously compared with the cement mortar specimens which unincorporated CNTs, and make the structure more compact so that the distribution of pore diameter has a great improvement, and then the harmful pores and more harmful pores have a significant improvement. The results of this study are in accordance with the results of the previous studies. Therefore, the speculation that the addition of CNTs makes the porosity of the cement mortar specimens increase resulting in the increase of the penetration depth can be excluded.

There is another speculation according to the above experimental results: The functionalized MWCNTs (MWCNTs-COOH) were dispersed by applying ultrasonic energy with a combination of surfactant. Therefore, CNTs became more hydrophilic which can improve dispensability in water. What's more, the diameter of the water molecule is 0.4 nm and the CNTs used in this study are 10 to 20 nm. Thus, the cement mortar with CNTs may have the better performance of water retention. Natural penetration of chloride ions must use water as a carrier to penetrate into the interior of cement mortar, and the movement which made chloride ions move is actually the osmotic pressure. Thus, an assumption was proposed that there may be a water film on the surface of the CNTs, and this water film can accelerate the penetrating speed of chloride as a convenient channel. Ultimately, the penetration depth of chloride ions in the cement mortar specimens added with CNTs is deeper. Based on the above speculation, further researches and exploration are needed to explain the above experimental results more accurately in order to establish a certain model.

### IV. CONCLUSION

This study investigated that the penetration depth of chloride ions under natural infiltration with different adding

amount of CNTs and the porosity of cement mortar with and without CNTs under Mercury Intrusion Porosimetry test. The conclusions are as follows:

- The control group has the lowest infiltration depth at the same age and osmotic pressure, and the penetration depth of chloride ions showed an increasing trend with concentration of CNTs. It can be inferred that the addition of CNTs will increase the penetration depth of chloride ions.
- The results of Mercury Intrusion Porosimetry test indicated that CNTs can reduce the porosity of cement mortar effectively. Therefore, the speculation that the addition of CNTs makes the porosity of the cement mortar specimens increase resulting in the increase of the penetration depth can be excluded. Another assumption was proposed that there may be a water film on the surface of the CNTs, and this water film will accelerate the penetrating speed of chloride as a convenient channel.

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