



Article Experimental Study and Simulation Calculation of the Chloride Resistance of Concrete under Multiple Factors

Yang Ding ^{1,†}, Tong-Lin Yang ^{2,†}, Hui Liu ^{3,*}, Zhen Han ⁴, Shuang-Xi Zhou ⁴, Zhong-Ping Wang ⁵, An-Ming She ⁵, Yong-Qi Wei ⁵ and Jing-Liang Dong ^{4,*}

- ¹ Department of Civil Engineering, Zhejiang University, Hangzhou 310058, China; ceyangding@zju.edu.cn
- ² College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China; ytl181431@hnu.edu.cn
- ³ Yellow River Institute of Hydrautic Research, Zhengzhou 450003, China
- ⁴ School of Civil Engineering and Architecture, East China Jiao Tong University, Nanchang 330013, China; 2015018085213021@ecjtu.edu.cn (Z.H.); green.55@163.com (S.-X.Z.)
- ⁵ School of Materials Science and Engineering, Tongji University, Shanghai 201804, China; wangzpk@tongji.edu.cn (Z.-P.W.); sheanming@tongji.edu.cn (A.-M.S.); wei_yongqi@tongji.edu.cn (Y.-Q.W.)
- * Correspondence: liuhui@hky.yrcc.ogv.cn (H.L.); 2956@ecjtu.edu.cn (J.-L.D.)
- + These authors contributed equally to this work.

Abstract: Cement is widely used in marine concrete, and its resistance to chloride ion corrosion has been widely considered. In this paper, based on a laboratory test, the influence of different hydrostatic pressures, coarse aggregate contents and w/c ratios on the chloride resistance performance is analyzed. Based on COMSOL finite element software, a two-dimensional cementitious materials model is established, and the simulation results are compared with the experimental results. The results show that the penetration depth of chloride ions in cement increases with the increase of the w/c ratio. Under the hydrostatic pressure of 0 MPa, when the w/c ratio is 0.35, the penetration depth of chloride ions is 7.4 mm, and the simulation result is 8.0 mm. When the w/c ratio is 0.45, the penetration depth of chloride ions is 12.9 mm, and the simulation result is 12.1 mm. Under different hydrostatic pressure, the penetration depth of chloride ions obviously changes, and with the increase in hydrostatic pressure, the penetration depth of chloride ions deepens. Under the w/c ratio of 0.35, when the hydrostatic pressure is 0.5 MPa, the penetration depth of chloride ions is 11.3 mm, and the simulation result is 12.1 mm. When the hydrostatic pressure is 16.2 mm, and the simulation result is 17.5 mm.

Keywords: concrete; chloride transport; hydrostatic pressure; aggregate content; w/c ratio; COM-SOL software

1. Introduction

The durability life of a cement structure refers to the whole process from the construction of a cement structure to the destruction of a cement structure [1–4]. Cement is a kind of heterogeneous material which contains particles with different sizes and types of pores [5–8]. As a result, seawater containing chloride ions and other harmful substances can invade the cement, accelerate steel corrosion and cause durability damage to the structure of the cement. The transmission process of chloride ions in cement is mainly through the connected pores of the cement [9–13]. This process is not only restricted by the changes of the cement's own composition, structure and performance, but it is also affected by the external service environment of the cement, which makes the transmission mechanism of chloride ions in cement extremely complex [13–16]. The external service environment of cement is complex and changeable, in which a variety of soluble salts interact to form a multi-salt concentration field, which has been proven to be able to change or even significantly change the diffusion coefficient of chloride ions and is in the seabed



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). structure [17–22]. The cement of buildings is affected by the hydrostatic pressure field at the same time, thus forming a multi-field coupling environment, which makes the chloride ion transport mechanism in this environment worthy of further discussion [23–27].

Many scholars have conducted systematic research on the influence of cement on chloride ion transport which is worthy of reference. For example, Guimaraes et al. [28] conducted a chloride corrosion test on a marine concrete structure for 22 years, and the results showed that the degree of water saturation had a great influence on the diffusion of chloride ions in concrete. Roy and Chye [29] conducted a 560-day exposure experiment on concrete blocks in a tidal zone. The test results showed that the chloride diffusion coefficient of the concrete in a tidal zone had good correlation with the chloride diffusion mechanism established earlier, and the diffusion coefficient changed obviously with the w/c ratio of the concrete. Hong and Hooton [30] studied the effect of chloride entry into HPC under dry–wet cycles. Their test results showed that longer drying times led to higher chloride diffusion coefficients in cement-based materials. Field tests of cement structures in a marine environment showed that the structures exposed to tides and experiencing dry-wet cycles were more vulnerable to chloride corrosion damage than other parts in the immersion zone and atmospheric zone. S. L. Lee [31] measured the distribution of chloride ions in 0.6 w/c ratio concrete under the action of the water head pressure and concentration gradient, but the experiment only measured the depth of the chloride ions in the concrete under different pressure heads and action times with the AgNO₃ spraying method, and the distribution of chloride ion concentrations in the concrete along the direction of chloride ion invasion was not given.

This paper studied the chloride diffusion performance of concrete with different w/c ratios and different aggregate contents under different hydrostatic pressures based on COMSOL finite element software and compared the simulation results with the experimental results to verify the effectiveness of the simulation method. Specifically, this paper is mainly divided into four parts. The first part introduces the research status of the chloride model for cement. The second part introduces the basic conditions and experimental methods of the raw materials which were used in the experiment. The third part introduces the chloride ion transport model and its solution. The fourth part discusses the influence of different hydrostatic pressures, coarse aggregate contents and w/c ratios on chloride ion transport. The main content and conclusions of this paper will be elaborated upon in the fifth part.

2. Experimental Method

2.1. Materials

The cement was PII 52.5 Portland cement with a density of 3.0 g/cm^3 , which was produced by Anhui Tongling Conch Cement Co., Ltd., Anhui, China. Its oxide composition is shown in Table 1, and its chloride ion content is shown in Table 2.

Table 1. Chemical composition of the cement.

Sample		Oxide Composition (Mass Ratio, %)									
	Na ₂ O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	MnO	Fe ₂ O ₃	LOI
Cement	0.61	0.72	5.71	22.2	0.07	1.55	0.83	64.1	0.03	3.15	1.03

Table 2. Chloride ion components of the cement.

Samula	Chloride Ion Content (Mass Ratio, %)				
Sample	Total Chloride Ions	Water-Soluble Chloride Ions			
Cement	0.1578	0.0625			

Deionized water was used in the whole process. The fine aggregate's medium sand density was 1.4 g/cm^3 , and its modulus of fineness was 2.6, while the coarse aggregate's

crushed stone density was 2.5 g/cm³, and its particle size was 5–16 mm. The waterreducing agent (polycarboxylate super plasticizer) was produced by Shanghai Meister construction engineering high-tech Construction Chemical Co., Ltd., Shanghai.

Based on the requirements of test code DL/T5150-2001 for hydraulic concrete, corresponding matching was designed, which can be seen in Table 3.

Number	W/C	Cement	Water	Sand	Stone	Stone Volume
S-0.35	0.35	450	158	1350	-	-
S-0.45	0.45	450	203	1350	-	-
S-0.55	0.55	450	248	1350	-	-
C-0%	0.50	672	336	1350	0	0%
C-20%	0.50	563	282	1125	530	20%
C-30%	0.50	450	250	900	1060	40%
C-40%	0.50	338	169	675	1590	60%

Table 3. Mix proportion design of mortar concrete (kg/m^3) .

Note: W/C is the w/c ratio, and C-x% is the content of stone volume in concrete. For example, C-40% means the stone volume is 40%.

2.2. Experimental Equipment

2.2.1. Determination of Open Porosity

The open porosity in cementitious materials is the main means of chloride ion and water transmission. Therefore, the measurement of the open porosity of cementitious materials can effectively lead to understanding the transmission process of chloride ions and water in the pores of cementitious materials. Based on the mix proportion, the concrete and cement's size was 80 mm \times 80 mm, and this was cured in a fog chamber with a relative humidity of 95% at 20 \pm 5 °C for 28 days based on the GB/T50082-2009 standard for testing methods of the long-term performance and durability of ordinary concrete. The high-precision electronic scale and vacuum saturator are shown in Figure 1.

According to Equation (1), the open porosity of the cementitious materials was calculated, which can be seen in Table 4:

$$P_V = \frac{(M_C - M_0)}{V_C \rho_w} \tag{1}$$

where P_V is the open porosity (%); M_C is the average mass of the sample after vacuum filling (g); M_0 is the average mass of the sample after drying (g); V_C is the volume of the test piece after being full of water (mL); and ρ_w is the water density (g/mL).

 M_C/g M_0/g Number V_C/mL^3 P_V /% S-0.35 123.782 112.349 58.1 19.67 S-0.45 127.331 113.864 58.6 22.98 S-0.55 132.574 114.352 59.4 30.67 59.6 C-0% 128.163 114.324 23.21 59.2 C-20% 127.212 114.404 21.6419.59 C-40% 114.196 59.0 125.759 59.9 C-60% 129.954 116.163 23.02

Table 4. Open porosities of cementitious materials.



(a) Vacuum saturator (b) High-precision electronic scale

Figure 1. Test instrument.

2.2.2. Determination of the Chloride Diffusion Coefficient

According to GB/T50082-2009, the chloride ion diffusion coefficient can be calculated based on Equation (2), and the RCM rapid chloride analyzer is shown in Figure 2:

$$D_{RCM} = \frac{0.0239 \times (273 + T)L}{(U-2)t} \left(X_d - 0.0238 \sqrt{\frac{(273 + T)LX_d}{U-2}} \right)$$
(2)

where D_{RCM} is the unsteady ion transfer of specimens (m²/s); *U* is the absolute voltage used; *T* is the temperature (°C); *L* is the thickness of the specimen (mm); *X*_d is the depth (mm); and *t* is the test time (h). The results can be seen in Table 5.



Figure 2. Rapid chloride analyzer (RCM).

Number	Chloride Diffusion Coefficient/m ² /s
S-0.35	$9.8 imes10^{-12}$
S-0.45	$15.1 imes 10^{-12}$
S-0.55	$19.3 imes 10^{-12}$
C-0%	$14.2 imes 10^{-12}$
C-20%	$9.66 imes 10^{-12}$
C-40%	$7.13 imes 10^{-12}$
C-60%	$6.38 imes10^{-12}$

Table 5. Measured values of the chloride diffusion coefficients of cement-based materials.

3. Chloride Transport Theory

3.1. Solution of the Concentration Term in the Convection Diffusion Equation

In the one-dimensional model, the concentration C(x, t) is a function of the crosssection position x and the diffusion time t, such that [32]

$$\frac{\partial C(x,t)}{\partial t} = D_i \frac{\partial^2 C(x,t)}{\partial x^2}$$
(3)

For the above solution, the variable $u = x/\sqrt{t}$ is introduced so that C(x, t) can be transformed into a function about the single variable U, and the above formula can be rewritten as

$$\frac{\partial C}{\partial t} = \frac{dC}{du} \cdot \frac{\partial u}{\partial t} = -\frac{dC}{du} \cdot \frac{x}{2t^{\frac{3}{2}}} = -\frac{dC}{du} \cdot \frac{u}{2t} \frac{\partial^2 C}{\partial x^2} = \frac{\partial^2 C}{\partial u^2} \cdot \left(\frac{\partial u}{\partial x}\right)^2 = \frac{d^2 C}{du^2} \cdot \frac{1}{t}$$
(4)

By taking the above two formulas into Equation (3) and simplifying them, an ordinary differential equation is obtained:

$$2D_i\frac{d^2C}{du^2} + u\frac{dC}{du} = 0\tag{5}$$

After solving the ordinary differential equation, we can get

$$C(x,t) = A \int_0^u e^{(-\frac{u^2}{4D})} du + B$$
(6)

From Equation (6), the following can be derived:

$$C(x,t) = 2A\sqrt{D_i} \int_0^\beta e^{(-\beta^2)} d\beta + B\beta = \frac{u}{2\sqrt{D_i}} = \frac{x}{2\sqrt{D_i t}}$$
(7)

Finally, the solution of Equation (3) can be obtained:

$$C(x,t) = C_0 + (C_s - C_0)[1 - \operatorname{erf}(\frac{x}{2\sqrt{D_i t}})]$$
(8)

where C_0 is the initial chloride concentration in the porous media, C_s is the concentration of the chloride solution on the surface of the porous material, and the boundary conditions and initial conditions can be expressed as [33]

$$t > 0, x = 0, C(t,0) = C_s, \beta = 0$$

$$t = 0, x > 0, C(0,x) = C_0, \beta = \infty$$
(9)

3.2. Simulation of the Chloride Ion Transport Process Based on COMSOL

COMSOL multiphasic is high-level numerical simulation software which solves PDE based on the finite element method. It can not only solve the complex differential equation hidden behind the multi-physical field but also easily realize the coupling process between

multiple fields. In addition, it does not need to spend a lot of time on the complicated process of programming and solving problems. This feature makes the software a very convenient tool for theoretical realization in scientific research, rather than black box software which can only input the parameters for a solution [34,35].

When the eroded surface of cementitious materials makes contacts with the chloride solution, the water and chloride ions in the solution can enter the interior of the cementitious materials under the drive of a concentration field and hydrostatic pressure field. At this time, the water concentration in the solution was considered to be 1. The concentration of the solution remained unchanged. The specific boundary conditions were as follows [36]:

$$\theta(x = 0, t) = 1C(x = 0, t) = C_S \tag{10}$$

where θ is the surface saturation; *C* and *Cs* are the chloride concentration chloride concentration of the external solution, respectively; *x* is the distance from the outside bed surface of the cementitious materials; and *t* is the duration of erosion.

The initial conditions were the moisture content and chloride ion content of the cement-based materials. Therefore, it was necessary to avoid the effect of the initial conditions, strictly control the chloride ion content of the corresponding materials during the molding time and dry the specimens before the experiment. The initial conditions were as follows [37,38]:

$$\theta(x, t = 0) = 0C(x, t = 0) = 0 \tag{11}$$

The model parameters of the cement mortar test block are shown in Table 6.

Number	w/c Ratio	Porosity (%)	Permeability Coefficient ($\times 10^{-13}$ m/s)	Diffusion Coefficient $(\times 10^{-12} \text{ m}^2/\text{s})$	Volume Fraction of Fine Aggregate (%)
S-0.3	0.3	19.67	2.47	0.98	28.2
S-0.4	0.4	22.98	5.90	1.71	27.9
S-0.5	0.5	30.67	14.7	2.53	27.5

Table 6. Model parameters of the cement mortar block.

The external environment parameters of the cementitious materials in the simulation process are shown in Table 7.

Number	w/c Ratio	Hydrostatic Pressure (MPa)	Duration (d)	Chloride Concentration (%)
S-0.35/S-0.45/S-0.55	0.35/0.45/0.55	0 0.5 1.0	30	5%

Table 7. External environment parameters of the simulation.

4. Results and Discussion

4.1. Effect of Hydrostatic Pressure

4.1.1. Experimental Results

It can be seen from Figure 3 that when the hydrostatic pressure was 0.5 MPa, the depth of chloride ion diffusion in the concrete changed with different w/c ratios. Specifically, when the w/c ratio was 0.35, the chloride ion diffusion depth was 11.3 mm; when the w/c ratio was 0.45, the chloride ion diffusion depth was 16.7 mm; and when the w/c ratio was 0.55, the chloride ion diffusion depth was 19.4 mm. In addition, the chloride ion diffusion depths of the concrete with different w/c ratios under different hydrostatic pressures are shown in Table 8.

4.1.2. Numerical Results and Comparative Analysis

It can be seen from Figure 4 that when the hydrostatic pressure was 0.5 MPa, the calculated depth of chloride ion diffusion in the concrete changed with different w/c ratios. Specifically, when the w/c ratio was 0.35, the chloride ion diffusion depth was 12.1 mm; when the w/c ratio was 0.45, the chloride ion diffusion depth was 15.5 mm; and when the w/c ratio was 0.55, the chloride ion diffusion depth was 18.5 mm. In addition, the calculated depths of chloride ion diffusion of the concrete with different w/c ratios and different hydrostatic pressures are shown in Table 8. Obviously, with the increase of the water-to-cement ratio—that is, the diffusion coefficient of chloride increased—the diffusion depth of the chloride increased with the same chloride concentration and the same erosion time. Furthermore, it can be concluded that the multi-physical field calculation method based on COMSOL software had higher accuracy by comparing the experimental results with the calculated results.



(a) W/C = 0.35

(**b**) W/C = 0.45



Figure 3. Test results of chloride ion diffusion under different w/c ratios while under hydrostatic pressure of 0.5 MPa.



Figure 4. Simulation results of chloride ion diffusion under different w/c ratios and under a hydrostatic pressure of 0.5 MPa.

	Hydrostatic Pressure: 0 MPA								
Number	First Group	Second Group	Third Group	Experimental Value	Simulation Value	Error			
			(mr	n)		(/0)			
S-0.35	7.2	8.1	7.0	7.4	8.0	7.6			
S-0.45	8.9	9.4	9.6	9.3	9.9	6.4			
S-0.55	12.3	12.7	13.7	12.9	12.1	6.2			
		I	Hydrostatic Press	ure: 0.5 MPA					
Number	First Group	Second Group	Third Group	Experimental Value	Simulation Value	Error			
	(mm)								
S-0.35	10.3	12.1	11.6	11.3	12.1	6.7			
S-0.45	15.9	16.3	17.9	16.7	15.5	7.1			
S-0.55	19.1	18.4	20.7	19.4	18.5	4.6			
			Hydrostatic Pres	sure: 1 MPA					
Number	First Group	Second Group	Third Group	Experimental Value	Simulation Value	Error			
			(mr	n)		(/0)			
S-0.35	16.1	15.3	17.3	16.2	17.5	7.8			
S-0.45	18.9	19.1	20.6	19.5	20.8	6.5			
S-0.55	26.7	26.3	23.7	25.6	24.1	5.7			

Table 8. Test and simulation results for the cement mortar.

4.2. Effect of Coarse Aggregate Content

4.2.1. Experimental Results

The depth of chloride ion diffusion in the concrete with different aggregate volume fractions when the hydrostatic pressure was 0.5 MPa can be seen in Figure 5. Specifically, when the volume fraction of the aggregate was 0%, the chloride ion diffusion depth was 20.9 mm; when the volume fraction of the aggregate was 20%, the chloride ion diffusion depth was 15.3 mm; when the volume fraction of the aggregate was 40%, the chloride ion diffusion depth was 13.5 mm; and when the volume fraction of the aggregate was 60%, the chloride ion diffusion depth was 12.6 mm. In addition, the chloride ion diffusion depths of the concrete with different aggregate volume fractions under different hydrostatic pressures are shown in Table 9.



Figure 5. Test results of chloride ion diffusion under different volume fractions of the aggregate under a hydrostatic pressure of 0.5 MPa.

Hydrostatic Pressure: 0.5 MPA								
Number	First Group	Second Group	Third Group	Experimental Value	Simulation Value	Error		
			(mr	n)		(70)		
C-0%	20.3	20.9	21.5	20.9	20.1	3.83		
C-20%	15.8	15.6	14.5	15.3	17.3	13.1		
C-40%	12.6	12.9	15.1	13.5	15.0	10.8		
C-60%	11.9	11.4	14.6	12.6	13.2	4.48		
			Hydrostatic Pres	sure:1 MPA				
Number	First Group	Second Group	Third Group	Experimental Value	Simulation Value	Error		
			(mr	n)		(70)		
C-0%	31.6	31.0	32.9	31.8	32.2	1.15		
C-20%	22.4	20.7	24.1	22.4	25.5	13.8		
C-40%	15.3	19.5	20.1	18.3	20.5	12.0		
C-60%	13.2	18.5	20.41	17.37	15.2	12.5		

Table 9. Chloride ion penetration test and simulation results of the concrete.

4.2.2. Numerical Results and Comparative Analysis

The calculated depths of chloride ion diffusion in the concrete with different aggregate volume fractions when the hydrostatic pressure was 0.5MPa can be seen in Figure 6. Specifically, when the volume fraction of the aggregate was 0%, the chloride ion diffusion depth was 20.9 mm; when the volume fraction of the aggregate was 20%, the chloride ion diffusion depth was 15.3 mm; when the volume fraction of the aggregate was 40%, the chloride ion diffusion depth was 13.5 mm; and when the volume fraction of the aggregate was 60%, the chloride ion diffusion depth was 12.6 mm. In addition, the chloride ion diffusion depths of the concrete with different aggregate volume fractions under different hydrostatic pressure values are shown in Table 9. Obviously, with the increase of the concrete's aggregate volume, the diffusion path of the chloride ions became more and more tortuous, and the diffusion depth of the chloride ions also increased under the same chloride ion concentration and the same erosion time. This is because the aggregate can inhibit chloride ion diffusion in concrete, and it becomes more obvious with the increase in the aggregate content. The inhibition mechanism was due to the tortuous effect of the aggregate, and the increase in the chloride ion diffusion depth required longer time and more energy.



Figure 6. Simulation results of chloride ion diffusion under different volume fractions of the aggregate under a hydrostatic pressure of 0.5 MPa.

The deviation value of the data in Table 8 shows that the error of the physical test results and simulation results increased after the introduction of a coarse aggregate into the cementitious materials. The maximum error of the mortar test block comparison results

was only 7.8%, while the maximum error of the concrete test block comparison results was 13.8%. This is a sharp increase, and the dispersion of the concrete contrast error was large. At the same time, the average contrast error of the mortar test block was 6.54%, and the average error of the concrete test block was 8.97%. This phenomenon shows that the model in this paper had some deviation in the study of the concrete model, and it needs further improvement. Furthermore, it was proven that the cement would produce a large dispersion of the whole structure after the introduction of a coarse aggregate, and this needs to be paid attention to in future research.

4.3. Effect of the w/c Ratio

As is shown in Figure 7, the change of the w/c ratio of the mortar block had a great influence on the chloride penetration depth under hydrostatic pressure. The internal reason can be explained by the variation diagram of the porosity and diffusion coefficient of the mortar in Figure 8. With the increase of the w/c ratio, the porosity of the mortar increased, and the chloride diffusion coefficient of the mortar increased, indicating a high correlation. When the w/c ratio was large, the mortar sample was not dense enough, and there were many pores with large pore diameters. When the w/c ratio was large, the amount of cement was lower, and cement hydration formed. The hydration products of the chloride ions were relatively lower, and the chloride ions could be adsorbed and combined with fewer attachments.



Figure 7. Chloride ion transport depth at 1.0 MPa.



Figure 8. Variation diagram of the porosity and diffusion coefficient of the mortar.

5. Conclusions

This paper studied the chloride diffusion performance of concrete with different w/c ratios and different aggregate contents under different hydrostatic pressures based on COMSOL finite element software, and it compared the simulation results with the experimental results to verify the effectiveness of the simulation method. The main conclusions drawn from this study are summarized as follows:

- (1) Under the same w/c ratio and different hydrostatic pressures, the penetration depth of chloride ions in mortar had a very obvious change. When the w/c ratio of the mortar was 0.35, the final penetration depth of the chloride ions increased by 43.1% and 123.6% with the increase in hydrostatic pressure from 0 MPa to 1.0 MPa, respectively.
- (2) The chloride diffusion depth decreased linearly with the increase in the aggregate content, and this linear relationship did not change with the diffusion time. Further analysis showed that the final diffusion depth of the chloride ions decreased by 18.9%, 32.8% and 55.6% when the volume fraction of the concrete aggregate increased from 0 to 20%, 40% and 60% after 120 days of concrete infiltration under hydrostatic pressure, respectively.
- (3) Under hydrostatic pressure, the depth of chloride ion transport was greatly affected by the change in the w/c ratio and increased rapidly with the increase in the w/c ratio of the cementitious materials.

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