Cement and Concrete Composites 106 (2020) 103465

Contents lists available at ScienceDirect

Cement and Concrete Composites

journal homepage: http://www.elsevier.com/locate/cemconcomp

Changes of pore structure and chloride content in cement pastes after pore solution expression

Xiang Hu[a,b], Caijun Shi[a,*], Qiang Yuan[c,**], Jian Zhang[a], Geert De Schutter[b]

[a] Key Laboratory for Green & Advanced Civil Engineering Materials and Application Technology of Hunan Province, College of Civil Engineering, Hunan University, Changsha, 410082, PR China
[b] Magnel Laboratory for Concrete Research, Department of Structural Engineering, Ghent University, Ghent, B-9052, Belgium
[c] School of Civil Engineering, National Engineering Laboratory for High Speed Railway Construction, Central South University, Changsha, 410075, China

ARTICLE INFO

Keywords:
Pore solution expression
Chloride concentration index
Chloride ion
Pore structure

ABSTRACT

Pore solution expression is a widely accepted approach to extract pore solution of cement-based materials by appllying high pressure. In this study, the variations of pore solution distribution and chloride content in cement pastes before and after pore solution expression were examined. The results showed that the value of chloride concentration index N_c were mostly higher than 1.0 for cement pastes immersed in NaCl solution, and decreased with the chloride concentration of soaking solution and water-to-binder (w/b) ratio. During the pore solution expression, the pores larger than 40 nm were totally removed and the porosity of smaller pore was decreased. Based on a proposed physical model on structure of cement paste, the value of N_c was calculated according to the variations of pore structure and chloride content during pore solution expression. The calculated results showed similar trend as the experimental results obtained by pore solution expression method.

1. Introduction

Chloride-induced corrosion of steel bar in reinforced concrete structures is the most important durability problem for infrastructures all around the world [1,2]. When chloride concentration of pore solution around the steel bar reaches a threshold value to break the passivation film, the corrosion can initiate [3–5]. The formation of corrosion products generally leads to the volume expansion of steel bar which may result into the cracking of concrete cover around the steel bars and thus accelerate the penetration of aggressive substances in return. Chloride ions may either be chemically bound in compounds like Friedel's salt, be physically adsorbed onto, for instance, the amorphous calcium silicate hydrate (C–S–H) gel, or just exist in free state in the pore solution of cement pastes [6–8]. Among these three types of chloride, the free chloride ions in pore solutions were generally considered to be responsible for the corrosion of reinforcement steel [9]. However, under some conditions such as the decrease of free chloride concentration in pore solution and variations of pore solution chemistry [10], the bound chloride ions can be released into pore solution and take part in the chloride migration process.

In 1993, Nagataki et al. [11] studied the free chloride concentration of 3 mm thickness cement paste slices immersed in NaCl solution with the same chloride concentration as sea water (0.547 mol/L). The pore solutions of the paste samples were extracted by pore solution expression method and the chloride concentration of the expressed pore solution was determined. The results showed that the chloride concentration in the expressed pore solution gradually increased with the soaking time, and was almost equal to that of NaCl soaking solution after 28 d. As the soaking time sequentially increased to 180 d, the chloride concentration in the expressed pore solution almost doubled to that in the NaCl soaking solution. This phenomenon was defined as "chloride condensation" in this paper [11] and "chloride concentrate" in the subsequent studies [12,13]. Chloride concentration index (N_c) was the ratio of chloride concentration in the expressed pore solution to that in the chloride soaking solution. Electrical double layer (EDL) formed at solid-liquid interface was considered as the main reason for this phenomenon [11,14], where chloride ions may be concentrated to higher concentration than that of bulk solution.

Water extraction and pore solution expression methods have been widely applied for determining the free chloride concentration of cement-based materials. However, the results obtained by using water extraction method, which are considered as water-soluble chloride, are

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* Corresponding author.
** Corresponding author.
E-mail addresses: cshi@hnu.edu.cn (C. Shi), yuanqiang@csu.edu.cn (Q. Yuan).

https://doi.org/10.1016/j.cemconcomp.2019.103465
Received 13 January 2019; Received in revised form 27 October 2019; Accepted 15 November 2019

Table 1
Chemical composition of Portland cement (%).

Raw Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3
PC	22.51	5.31	3.78	63.11	2.56	0.71	2.02

affected by many factors including fineness of particle samples, extraction temperature, mixing time and water-solid ratio. The obtained water-soluble chloride content may be increased with water-solid ratio and extraction time [15]. Nevertheless, the pore solution expression is regarded as the most reliable method to obtain pore solution and study the free chloride concentration of cement-based materials. The validity of pore solution expression method has been evaluated in study [16], and it was shown that the level of applied pressure didn't impact the ion concentration in the expressed pore solution. However, when high pressure (around 500 MPa during pore solution expression) is applied to cement-based material, not only the bulk pore solution, but the solution in EDL will also be extracted out [11,17], consequently, the chloride concentration of the expressed pore solution can be increased. He et al. [17] calculated the chloride ion concentration in the expressed pore solution of cement paste based on an EDL model. They found that the porosity of cement paste was decreased from 20% to 10% after pore solution expression.

Due to the superiority in the acquisition of pore solution in cement-based materials compared to other methods, the pore solution expression method has been widely accepted and applied to analyze the pore solution chemistry [11,17–19]. However, the standardization of this method still has some issues needed to be clarified and solved. In order to obtain enough amount of pore solution, special expression apparatus with high pressure and a dilution operation are always needed which may increase the labor consumption and affect the accuracy of the ion concentration analysis results. Most importantly, there are two key issues on this method remain unclear. First, what's the percentage of the pore solution within pores and EDL can be extracted? Secondly, how does the pore structure of cement paste look like after the process of pore solution expression?

The determination of different types of chloride content within cement-based materials is very important for studies on steel-related corrosion and durability characterization of concrete structure. The acid soluble method has been widely applied and standardized the total chloride content. However, due to the issues and problems shown above, a standardized method to analyze the free chloride concentration in pore solution, which is more important for steel corrosion, is not achieved yet. Aiming at the two key issues, a study was carried out on the pore solution expression method. Pore solution of cement pastes immersed in NaCl solution was obtained by pore solution expression method and the chloride concentration in the expressed pore solution was measured. The total chloride content, pore structure and moisture distribution within samples before and after pore solution expression were investigated. Based on the experimental results, a model was developed to calculate the chloride concentration of the expressed pore solution. The results of this study may provide theoretical foundation for the application of pore solution expression method in studying the pore solution of cement-based materials and explain the chloride concentrate phenomenon.

2. Experimental

2.1. Raw materials

P·I 52.5 Portland cement (PC) with a specific surface area of 336 m^2/kg was used in this study. Its chemical composition is given in Table 1, and standard mortar compression strength was 26.6 MPa at 3 d and 57.3 MPa at 28 d, based on GB/T 17671–2007 (water/cement ratio = 0.5, sand/cement ratio = 3). NaCl and $AgNO_3$ used for soaking solution preparation and chloride concentration analysis were analytical grade chemicals. Deionized water was used to prepare solution for chemical analysis.

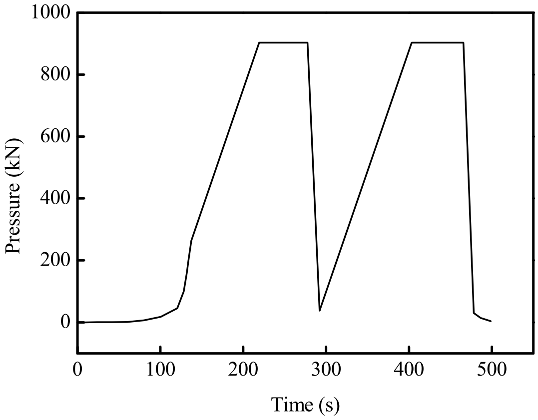


Fig. 1. Pore solution expression procedure.

2.2. Specimens preparation and immersion

Cement pastes with w/b ratios of 0.4 and 0.6 were prepared in this study. Polyvinyl chloride (PVC) pipe with a size of Φ50 × 200 mm was used as a mold. One end of the mold was sealed with PVC board. After cement paste was cast into the mold, the other end of the mold was sealed with plastic film immediately to avoid water evaporation, and then placed in an oscillator for 6 min of slow rotation to avoid segregation. Afterwards, the specimens with molds were left in a room at 20 ± 2 °C for 18 h, then demolded and cut into thin discs with 6 mm of thickness. The discs were cured in saturated limewater for another 6 d. On the last day of immersion, the discs were vacuum saturated with saturated limewater for 24 h prior to the immersion test to ensure the samples were fully saturated. Afterwards, the discs were immersed into the soaking solutions for 91 d before pore solution expression and chloride ion analysis. The soaking solutions were 0.1, 0.3, 0.5, 0.7 and 1.0 mol/L of NaCl solutions in this study. Cement paste discs were placed in plastic containers covered with plastic film at 20 °C. The volume ratio of NaCl solution to the specimens was kept above 40 and the NaCl solution was renewed every two weeks to ensure the relatively constant chloride ion concentration in the soaking solution.

2.3. Pore solution expression

After the immersion, the specimens were rubbed with a wet cloth to obtain saturated surface dry condition. Four cement paste discs were crushed into small pieces and put into the pore solution expression setup. The expression apparatus with specimens were loaded to 510 MPa (900 kN) at a rate of 1.5–2.5 MPa/s. The highest pressure was held for 1 min, then unloaded rapidly. The loading cycle was repeated once more. The loading procedure for pore solution expression is shown in Fig. 1 according to the procedure shown in Ref. [20]. The expressed pore solution was collected with an injection syringe whose pinhead was covered with a latex tube to prevent leaking [21]. The collected pore solution was injected into a plastic container and sealed immediately to avoid carbonation. The pore solution expression apparatus was cleaned with anhydrous ethanol after every expression test to avoid cross contamination. For each group, three pore solution expression tests were carried out to obtain the pore solution and for chloride concentration analysis.

2.4. Chloride concentration analysis

The collected pore solution was diluted by 20 times for chloride ion titration using an automatic potentiometric titrator with a silver electrode. AgCl solution of 0.01 mol/L was used as titration solution to determine the chloride concentration of expressed pore solution. At the end point of the titration, automatic potentiometric titrator can calculate the chloride concentration automatically. Three potentiometric titration tests were done for every expressed pore solution and average results were applied. The value of N_c was calculated by the following equation:

$$N_c = c_k / c_b \tag{1}$$

Where c_k is the chloride ion concentration in expressed pore solution, c_b is chloride ion concentration in the NaCl soaking solution (0.1, 0.3, 0.5, 0.7 or 1.0 mol/L). The reported results were the average value of three pore solution expression tests with chloride concentration analysis.

2.5. Total chloride content

The total chloride contents c_{total} of cement pastes before and after pore solution expression were measured. The specimens were oven dried at 105 ± 1 °C until constant mass. The acid-soluble method [22] was used to measure the total chloride content of cement paste. The samples were firstly ground by ball mill to particles with the size between 0.025 and 0.045 μm, and then these powders were placed in 60 °C vacuum drying oven for 24 h. When testing the total chloride content, about 2.0 g of powder samples and 120 mL of deionized water were mixed followed by addition of 7 mL of nitric acid solution (2.4 mol/L). The mixed solution was placed onto a heater to boiling. Another 5 mL of nitric acid solution was added after the mixed solution was cooled down. The chloride content of the prepared solution was then tested by chloride potentiometric titration.

2.6. ^{1}H NMR analysis

In this study, ^{1}H NMR test was conducted for samples before and after pore solution expression to investigate the variation of pore structure and pore solution distribution before and after expression. Small fragments with around 0.5 cm diameter were used for ^{1}H NMR test. After immersion in NaCl solution, ^{1}H NMR tests were conducted for samples before pore solution expression. After the pore solution expression test, samples were immediately collected and applied for ^{1}H NMR test. It has to state that only the free water filled in the remained pores (diameter smaller than 0.1 mm in this study) of samples can be detected by NMR test, but not the water on the surface of samples after pore solution expression. MicroMR12-025 produced by Niumag Corporation (Shanghai, China) was used for NMR relaxometry measurement. The resonance frequency was 11.845 MHz and the transversal relaxation time T_2 was measured at 20.0 ± 5.0 °C. Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was employed to measure NMR transverse relaxation time and the NMR results were transformed into pore size distribution according to the following equation proposed in Refs. [16,17]:

$$\frac{1}{T_2} \approx \frac{1}{T_{2,surf}} = \rho_2 \left(\frac{S}{V}\right)_{pore} = F_s \times \frac{\rho_2}{r} \tag{2}$$

where T2 is the transversal relaxation time of water; T2,surf is the transversal relaxation time due to surface relaxation; (S/V)pore is the specific surface area of pore; Fs is geometrical factor, Fs=2.0 for cylinder pore; ρ2 is surface relaxivity, 50 μm/s for cement pastes and mortars, r is the radius of the pore. Normally, the surface relaxivity relates with the "thickness" of surface layer, and the average value of ρ was adopted in literatures [23,24]. In this study, it is assumed that the average surface relaxivity (50 μm/s) of the testing samples are identical. The metallic element in samples may affect the stability of the magnetic field and the obtained relaxation time distribution, the cement paste without supplementary cementitious materials was prepared in this study.

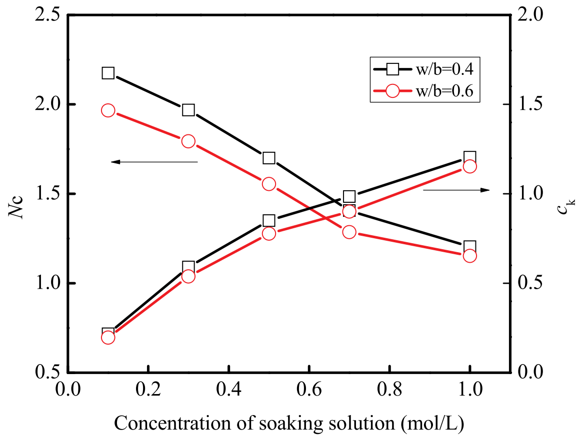


Fig. 2. Variation of N_c of cement pastes with different chloride concentrations of soaking solution and w/b ratios.

3. Results and discussion

3.1. Chloride concentration index

Fig. 2 shows the chloride concentration of the expressed pore solution (c_k) and chloride concentration index (N_c) of cement pastes with different soaking solution concentrations and w/c ratios. With the increase of concentration of NaCl soaking solution from 0.1 to 1.0 mol/L, more chloride contents were extracted out during pore solution expression test and the chloride concentration of the expressed pore solution (c_k) was proportionally increased. However, the increase of c_k was not proportional and lower than the increase of chloride concentration in soaking solution, therefore the value of N_c gradually decreased with the increase of chloride concentration of soaking solution as shown in Fig. 2. Lower value of c_k and N_c were presented for cement paste with w/b ratio 0.6 than that of the cement paste with w/b ratio 0.4.

3.2. Total chloride content

Fig. 3 shows the total chloride content c_{total} of cement pastes after 7 d of bath curing and 91 d of soaking in NaCl solution. The concentrations of soaking solution were 0.1, 0.3, 0.5, 0.7 and 1.0 mol/L. Total chloride content of pastes before and after pore solution expression along with the ratio of total chloride content to concentration of the NaCl soaking solution c_{total}/c_b were presented. With the increase of chloride concentration in NaCl soaking solution, total chloride content of cement pastes increased due to the increase of penetrated chloride ions, but the value of c_{total}/c_b gradually decreased as that the increase of the penetrated chloride was not as much as that in the soaking solution. The extent of total chloride increase was not as great as chloride concentration in NaCl soaking solution. The increase of chloride concentration in NaCl soaking solution enlarged the differences of total chloride content between samples before and after pore solution expression. The results showed that more chloride ions were extracted out during pore solution expression process for cement paste soaking in NaCl solution with higher chloride concentration. It can be also seen from Fig. 3 that for all samples, the total chloride content of cement pastes with w/b ratio 0.6 were higher than that of pastes with w/b = 0.4.

3.3. Pore solution distribution

From the ^{1}H NMR test, signal amplitude of water but not the water mass within samples is obtained. Thus, the relationship between water mass and signal amplitude has to be established. In this study, a series of ^{1}H NMR tests on a specimen with different water content were conducted. Firstly, a ^{1}H NMR test was conducted for the NaCl solution

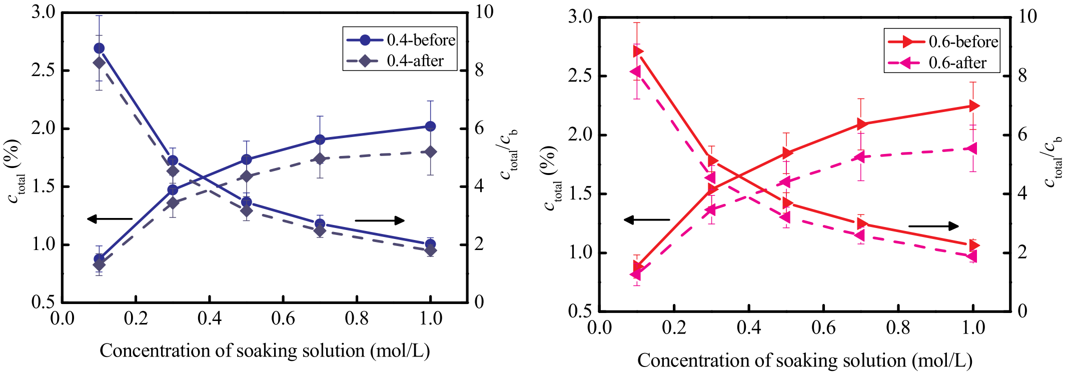


Fig. 3. Total chloride content and total chloride content ratio of cement pastes.

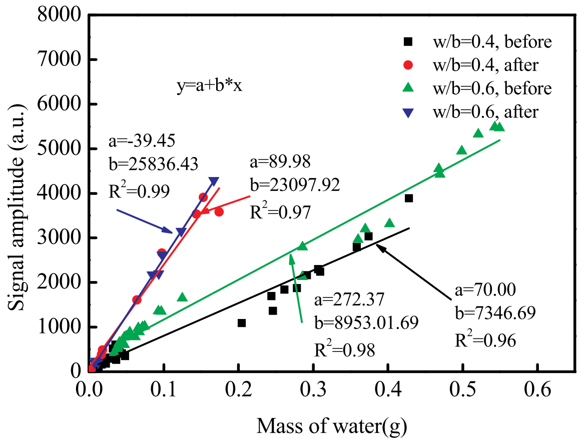


Fig. 4. Relationship between tested water mass and signal amplitude.

saturated specimens. After that, the specimens were placed in vacuum oven with 80 °C for 30 min and followed by another ^{1}H NMR test. NMR test and drying process were repeated three times and the mass of specimens were measured before every ^{1}H NMR test. After the NMR test, the decrease of mass and total signal amplitude of samples between samples after different times of drying process was correlated, by which the relationship between signal amplitude of NMR measurement and the mass of water within paste can be determined. For all of the cement pastes prepared in this study, the correlations between NMR signal amplitude and the mass of measured water within samples are shown in Fig. 4. It can be seen that the correlation between the signal amplitude and the mass of water is governed by w/b ratio and pore solution expression process. According to the slope of fitting line in Fig. 4 and the tested signal amplitude before and after pore solution expression without drying, the mass ratio of water within paste can be obtained.

Fig. 5 is T2 relaxation distribution plot of cement paste with different w/b ratios, and results of pastes before and after pore solution expression experiment are all presented. According to Equation (2), the T2 relaxation time was transformed to pore size shown in x axis (nm) below every plots in Fig. 5. Before pore solution expression, it can be seen clearly from the figures that the cement paste sample with w/b ratio 0.6 has a larger porosity than that of 0.4. With the decrease of w/b ratio, the amplitude of signal was reduced and the related T2 relaxation time or pore size of the peak shifted to left. The effects of w/b ratio on porosity and pore structure of cement paste obtained from NMR are in agreement with the results from MIP or other test methods shown in Refs. [25,26]. After the pore solution expression, it can be seen that samples with different w/b ratios showed less differences for water distribution or pore size distribution. The pores with diameter larger than 40 nm were almost removed from samples after the pore solution expression, and the porosity of smaller pores was decreased.

4. Discussions

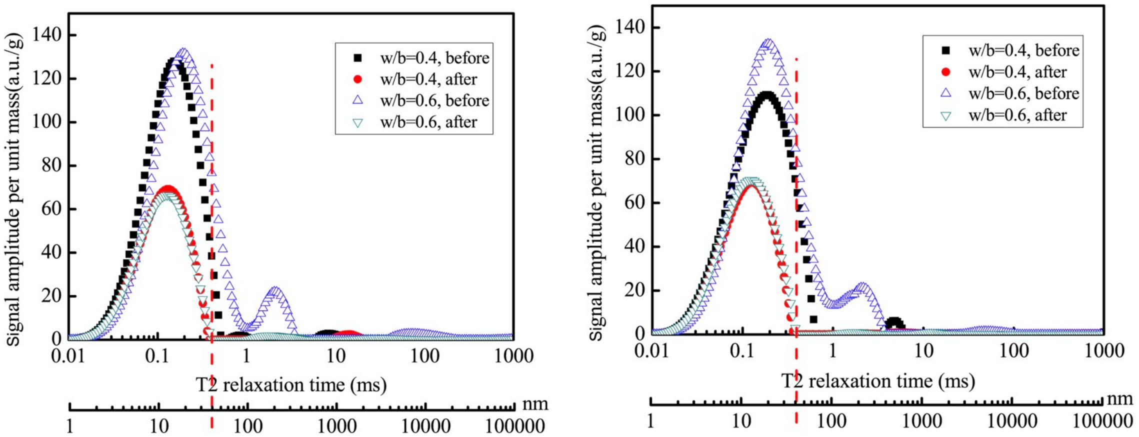
4.1. *Effects of chloride concentration on soaking solution and w/b ratio on N_c*

When immersed in solution, the EDL forms at the solid-liquid interface due to the ionization, ion exchange or binding and fraction contact. Fig. 6 shows the schematic diagram of EDL and potential distribution [27]. According to the Stern EDL model, the chloride ion distribution within EDL layer can be obtained from the potential distribution [14]. The descriptions on formation and ion concentration in EDL of cement-based materials have been reported in Refs. [12,14]. Within the diffuse layer, the chloride ions are diffusely distributed and the concentration gradually decreases into the same value of bulk pore solution with the increase of distance to solid phase. The solution in EDL was considered to be partly extracted out together with bulk solution and resulted into higher chloride concentration in the expressed pore solution. During the analysis on free chloride ion in pore solution by pore solution expression, pore solution expression method is generally applied and "free chlorides" is collectively referred to the chloride ions in the expressed pore solution. The phenomenon of "chloride concentrate" represents the higher chloride concentration in the expressed pore solution than that of external soaking solution and value of N_c higher than 1.0.

The chloride concentration of bulk solution and solution in EDL were gradually increased with the increase of concentration of NaCl soaking solution, which resulted into higher chloride concentration in the expressed pore solution. However, the value of N_c is decreased as shown in Fig. 2, which can be explained by the thickness of EDL and pore structure of cement paste. The thickness of EDL determines the amount of solution which can be expressed out by high pressure. The thickness of EDL can be calculated by Debye formula [27]:

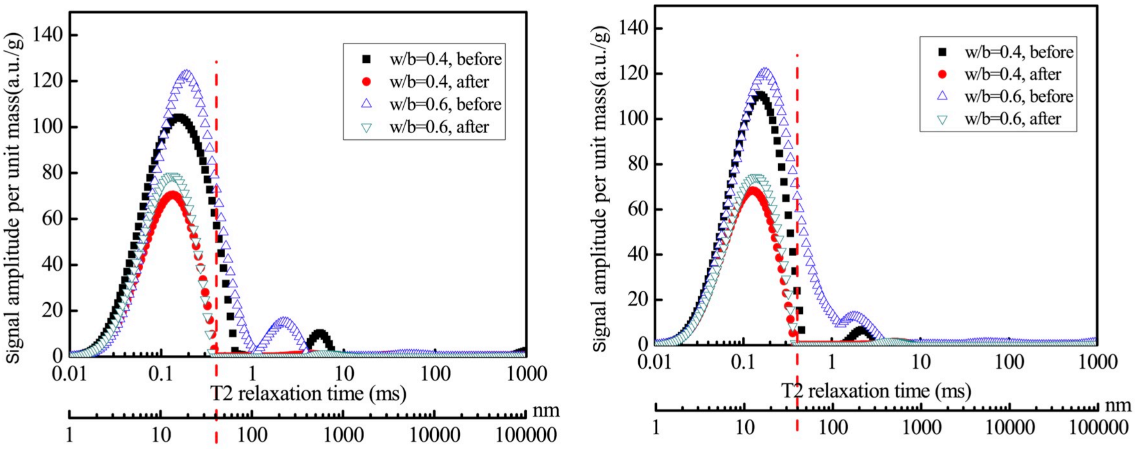
$$L = k^{-1} = \sqrt{\frac{RT\varepsilon}{2F^2 c_b}} \tag{3}$$

where k is Debye constant, c_b is the concentration of bulk solution or NaCl soaking solution in this study, ε is the dielectric constant. It can be seen from Equation (3) that the effect of soaking solution concentration on the thickness of EDL is significant. The lower the concentration of NaCl solution is, the larger the thickness of EDL of cement pastes is. Lower soaking solution concentration will result in larger amount of solution in the EDL which can be expressed out under high pressure. He [28] studied the thickness of EDL and found that the thickness of EDL decreased significantly with the chloride concentration in bulk pore solution, while the effects of chloride concentration in pore solution on EDL thickness became less obvious with the increase of the former. As the decrease of EDL thickness, the effect of EDL on chloride



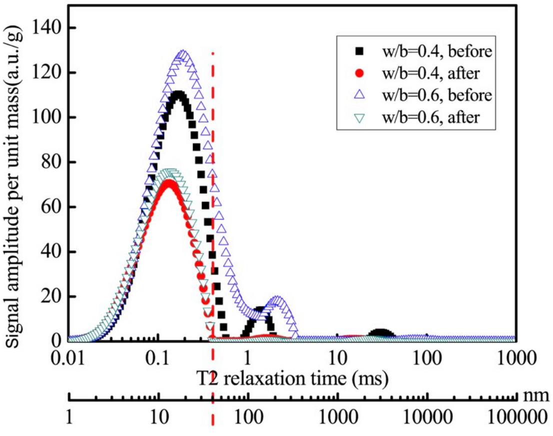
(a) 0.1 mol/L

(b) 0.3 mol/L



(c) 0.5 mol/L

(d) 0.7 mol/L



(e) 1.0 mol/L

Fig. 5. T_2 relaxation distribution of cement paste before and after pore solution expression.

concentration of the expressed pore solution was reduced. This explains that the value of N_c of paste specimens decreased and got close to 1.0 with the increase of soaking solution concentration to 1.0 mol/l.

The values of c_k and N_c of cement paste with higher w/b ratio was smaller than that of cement paste with lower w/b ratio due to the larger porosity and higher percentage of large size pores. The increase of w/b ratio can increase the porosity of cement paste and accelerate the chloride penetration, it can be seen from Fig. 3 that the total chloride

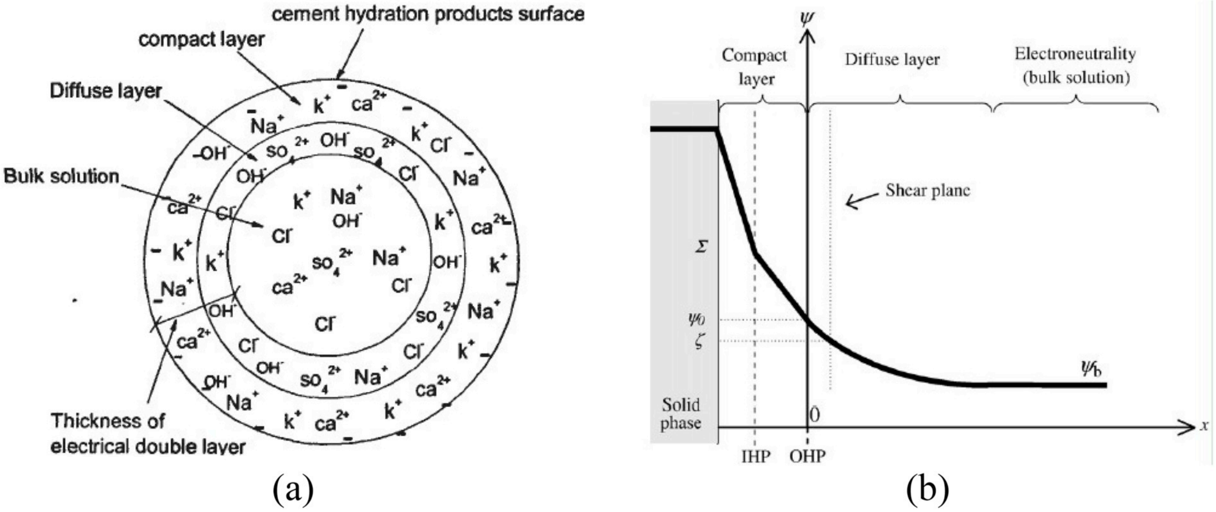


Fig. 6. Schematic diagram (a) and potential distribution (b) of the EDL [27].

content within cement paste with w/b ratio 0.6 was larger than that of 0.4. For a given EDL thickness and chloride content in EDL, the larger the pore is, the lower the percentage of chloride ion content in EDL over that in bulk pore solution is. Therefore, the incremental large pore percentage with w/b ratio may result in lower percentage of chloride ions in EDL to the total chloride content in the expressed pore solution, and thus the value of N_c may be decreased. Li [29] investigated the effects of w/b ratio on chloride concentration in the expressed pore solution and obtained similar results as this study.

4.2. Variations of chloride content during pore solution expression

As stated above, three types of chloride can be existed within cement-based materials, including free state, physically adsorbed and chemically bound chloride [6,7]. Total chloride content determined in this paper included all of these three types of chloride. With the increase of chloride concentration in NaCl soaking solution, the free chloride ions dissolved in pore solution may be also increased proportionally. Actually, it can be considered that the chloride concentration in bulk pore solution is equal to that in soaking solution when equilibrium state is reached. The increased chloride concentration in pore solution may also increase the content of chloride ions adsorbed onto the surface of solid phase or EDL and also react with alumina-phases in hydration products. The former effect results into higher physically adsorbed chloride within EDL, while the later increases the content of chemically bound chloride ions. Therefore, the total chloride content gradually increased with the soaking solution concentration. However, the increase of chloride concentration in EDL is not as much as that in soaking solution as described in Section 4.1, therefore the total chloride content was increased while the ratio of total chloride content to chloride concentration in soaking solution decreased. The thickness and zeta potential of EDL were decreased with the soaking solution concentration [14], which resulted into lower ratio of physically adsorbed chloride in EDL to chloride concentration in bulk pore solution. As discussed above, the value of N_c gradually decreased with the increase of chloride concentration in soaking solution. Moreover, solid phase can only provide limited binding sites for chemically bound chloride. Thus, the total chloride content increased while ratio of total chloride content to chloride concentration in NaCl soaking solution decreased with the increase of the latter. When immersed in higher concentration of NaCl solution, more chloride ions can be extracted and higher chloride concentration in the expressed pore solution (c_k) was obtained. This amplified the decrease of total chloride content during pore solution expression.

It is well known that the pore structure of cement-based materials can be improved with the decrease of w/b ratio [30,31]. The decrease of porosity and improvement of pore structure reduce the volume of pore solution, which results into the decrease of total chloride penetrated into cement pastes. Fig. 7 is the reduction of total chloride contents during pore solution expression process *vs.* the chloride concentration in soaking solution and with different w/b ratios. The reduction of total chloride content increased with the increase of chloride concentration of soaking solution. Due to the larger porosity of specimens with w/b ratio 0.6 than that of 0.4, the volume of pore solution which can be extracted out during pore solution expression process can be increased and also the content of chloride ions. It can be seen from Fig. 7 that the reduction of total chloride contents during pore solution expression for cement paste with w/b ratio 0.6 was larger than that of 0.4.

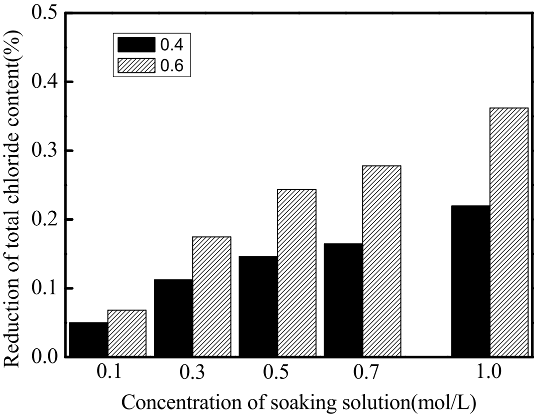


Fig. 7. Total chloride of cement paste reduced during pore solution expression.

4.3. Variations of pore solution distribution during pore solution expression

During the process of pore solution expression, the high external applied pressure compressed the cement paste and made the paste more compact. The increase of compactness extracted the pore solution inside and re-arranged the inner pore structure pf cement paste. He [17] investigated the variation of pore structure of cement paste during pore solution expression by MIP test, the results showed that the porosity of cement paste was decreased and the density was increased. Pore solution expression experiment compressed pores with large diameter (>150–200 nm) into pores with diameter smaller than 100 nm. In

Table 2
The mass of water per unit mass of cement paste (g/g).

Concentration of soaking solution (mol/L)	Mass of water			
	0.4		0.6	
	Before (ω_1)	After (ω_2)	Before (ω_1)	After (ω_2)
0.1	0.110	0.051	0.147	0.054
0.3	0.104	0.051	0.140	0.054
0.5	0.100	0.049	0.135	0.053
0.7	0.096	0.048	0.130	0.050
1.0	0.095	0.047	0.128	0.048

Table 3
Bulk density of cement paste (kg/m^3).

Concentration of soaking solution(mol/L)	Bulk density			
	0.4		0.6	
	Before (ρ_{s1})	After (ρ_{s2})	Before (ρ_{s1})	After (ρ_{s2})
0.1	1690.8	1890.5	1498.6	1753.4
0.3	1725.3	1853.4	1552.4	1764.9
0.5	1750.3	1855.9	1603.4	1789.6
0.7	1834.5	1903.4	1683.7	1784.9
1.0	1842.1	1953.4	1703.4	1804.9

Table 4
Porosity of cement pastes calculated from NMR results (%).

Concentration of soaking solution (mol/L)	Porosity			
	w/b = 0.4		w/b = 0.6	
	Before (P_1)	After (P_2)	Before (P_1)	After (P_2)
0.1	15.64	8.77	18.01	8.63
0.3	15.07	8.55	17.69	8.61
0.5	14.66	8.19	17.52	8.52
0.7	14.64	8.17	17.57	8.00
1.0	14.43	8.13	17.36	7.70

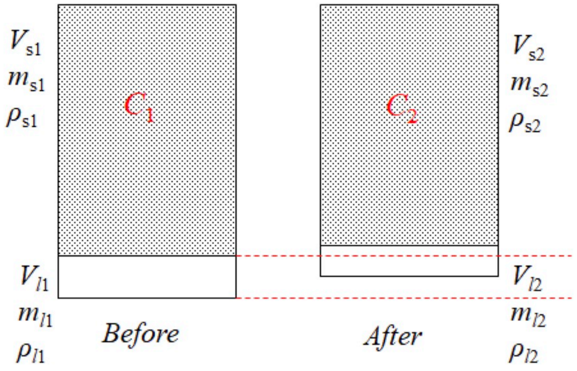


Fig. 8. Schematic diagram of sample before and after pore solution expression.

another study [25], it was also confirmed that pore solution expression affected large diameter pores more significantly than that on small pores. According to the NMR measurement results shown in Fig. 5, the peaks in NMR signal plots with the T_2 relaxation time larger than 0.4 ms (or pore size larger than 40 nm) were almost erased. Therefore, the pore solutions in pores with large diameter were totally extracted by pore solution expression. For pores with diameter smaller than 40 nm, the peak values of the NMR signal amplitude were significantly decreased after pore solution expression. It has been investigated in previous study [26] that the pore solution expression experiment decreased the total porosity and percentage of large pore volume in total porosity of cement pastes, which was confirmed in this study.

Table 2 summarizes the mass of inner water (ω) hosted by 1 g of cement paste with different chloride concentrations of NaCl soaking solution and w/b ratios, and results of pastes before and after pore solution expression are revealed. The results in Table 2 clearly show the reduction of water mass or total porosity within cement paste during the pore solution expression. The increase of chloride concentration in soaking solution and decrease of w/b ratio decreased the mass of water or pore volume within cement paste due to the decrease of porosity. After pore solution expression, the water mass within cement paste sample was similar with different chloride concentrations. Table 3 is the density of cement pastes before and after the pore solution obtained by true density measurement. It can be known from the table that the pore solution expression process compressed the cement paste and increased the density. Due to the higher porosity of cement paste with w/b ratio 0.6 and lower chloride concentration of soaking, the density is relatively lower for samples before pore solution expression. The results of density are in agreement with the water mass obtained by NMR measurement shown in Table 2.

If the sample is fully saturated, the obtained ratio of water to total paste mass can be transformed to volume porosity with the density of paste and pore solution. In this study, bath curing and water saturation process were taken to ensure the water saturation of pore solution within cement pastes. During the pore solution expression, the high pressure compressed the pores and extracted out the pore solution in these pores. Therefore, the state of pore solution saturation within samples after pore solution expression can be assumed. As a comparison, the porosity of sample was also calculated according to the ^{1}H NMR results. It has to be stated that the assumption on saturation of pore solution will not affect the calculation of N_c in this study (Section 4.4) because the weight of moist instead of porosity was used in the calculation.

Table 4 shows the volume porosity of cement pastes before and after pore solution expression. It can be seen that the porosity of cement paste gradually decreased with the increase of chloride concentration in soaking solution from the formation of Fridel's salt [32]. Porosities of pastes with w/b ratio 0.6 are higher than that of 0.4. For samples after pore solution expression, the chloride concentration and w/b ratio show little effects on the porosity of pastes. Generally, the porosity of samples after pore solution expression is more affected by the pressure and the loading history applied during pore solution expression test. It can be concluded that ^{1}H NMR is a reliable technique to characterize the porosity and pore size distribution of cement-based materials.

4.4. Calculation of chloride concentration index (N_c)

Fig. 8 is the schematic diagram of cement paste before and after pore solution expression experiment. During the pore solution expression, part of pore solution within cement paste can be extracted out, while the content of solid phase is unchanged. For the expressed pore solution, the amount of chloride ions n_{Cl} can be calculated as:

$$n_{\mathrm{Cl}} = (C_1 – C_2)*m_s/35.45 \tag{4}$$

Where, C_1 and C_2 is total chloride contents of pastes before and after pore solution expression, m_s is the mass of solid phase of cement paste. Then, the volume of pore solution (V_P) extracted out by pore solution expression is:

$$Vp = m_{l1}/\ \rho_{l1} - m_{l2}/\ \rho_{l2} = m_s\ \omega_1/[(1-\ \omega_1)\ \rho_{l1}] - m_s\ \omega_2/[(1-\ \omega_2)\ \rho_{l2}] \tag{5}$$

Where, m_{l1} and m_{l2}, ρ_{l1} and ρ_{l2} are mass and density of pore solution before and after pore solution expression. In this study, the density of immersed NaCl solution was used as the density of pore solution ρ_l. Then, the chloride concentration in the expressed pore solution can be calculated as:

Table 5
The value of N_c calculated from NMR results and total chloride content.

Chloride concentration (mol/L)	w/b = 0.4	w/b = 0.6
0.1	2.014	1.674
0.3	1.708	1.570
0.5	1.409	1.398
0.7	1.218	1.231
1.0	1.154	1.099

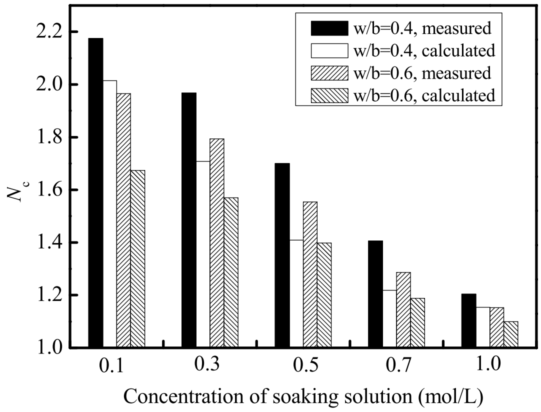


Fig. 9. Comparison of N_c between measured and calculated results.

$$N_c = n_{Cl}/V_p = (C_1 - C_2)/\{35.45*\omega_1/[(1-\omega_1)\rho_l]-\omega_2/[(1-\omega_2)\rho_l]\} \quad (6)$$

The total chloride content and mass of pore solution and solid phase has been determined previously by acid-soluble method and ^{1}H NMR test, respectively. The calculation results of N_c from these experimental data are shown in Table 5.

It can be seen from Table 5 that the chloride concentration in the expressed pore solution are higher than that in soaking solution since N_c of all pastes are larger than 1.0. With the increase of chloride concentration in soaking solution and w/b ratio, the value of N_c is obviously decreased, which is in agreement with the results from pore solution expression shown in Section 3.1. The comparison between measured and calculated N_c is shown in Fig. 9. It can be seen from the figure that similar trends of N_c with chloride concentration and w/b ratio are obtained between the measured and calculated results. However, the results from the calculation are lower than that of measured ones. Due to limited pore solution available for analysis, the calculation results are very sensitive to the data from NMR test and total chloride content. It can be imagined that part of chloride ions, which should be extracted out, may be remained on the surface of pastes after pore solution expression. However, during our experiment, the powder samples after pore solution were not washed or flushed to prevent the loss of water-soluble chloride. Therefore, this part of chloride was considered as the chloride ions remained within samples after pore solution expression. This may result into lower calculated amount of chloride in the expressed pore solution and thus lower N_c.

5. Conclusions

In this study, the variations of pore structure and chloride content within cement paste samples before and after pore solution expression test were studied. The reasons causing higher chloride concentration in the expressed pore solution than that in soaking solution were clarified, which may further improve the validity of this test. Based on the results and discussions above, the following conclusions can be drawn:

- The values of N_c of cement pastes are decreased with the increase of chloride concentration in soaking solution, the increase of w/b ratio decreases the N_c of cement pastes.
- The total chloride content of cement pastes are decreased after the process of pore solution expression, which is more significant for soaking solution with higher concentration; the higher w/b ratio also reduce more total chloride content after the process of expression.
- The results of ^{1}H NMR test provide useful information on pore solution distribution within cement paste, which can be transformed to pore size distribution of samples.
- During the pore solution expression, pores with diameter larger than 40 nm are totally removed and the porosity of smaller pores is decreased. After pore solution expression, chloride concentration in soaking solution and w/b ratio of cement paste do not show any effects on the change of pore structure of samples.
- A model is proposed to calculate the chloride concentration in the expressed pore solution. The value of N_c calculated in this study shows a similar trend in comparison to the experiment results, while relatively lower value of N_c is obtained due to the errors in the test process.

Extension of this study onto the blended cement and understanding the removability of chloride ions in EDL by external forces can be expected in future study.

Declaration of competing interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

Acknowledgements

The financial supports of the National Science Foundation of China under contract Nos. 51638008 and 51922109, the National Key Research and Development Program of China under contract Nos. 2018YFC0705400 are gratefully acknowledged.

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