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Chloride content and pH value in the pore solution of concrete under carbonation^{*}

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Abstract: Chloride content and the pH value of the pore solution in the neighborhood of steel reinforcement are decisive parameters for initiation and rate of corrosion. The pore solution of cement mortar and hardened cement paste has been expressed from the pore space by high pressure in the investigation. The influence of the water-cement ratio, age, and addition of chloride to the fresh mix on chloride content in the pore solution has been determined by ion chromatography. At the same time the pH value of the pore solution has been determined. The dissolved chloride content decreases with increase in the water-cement ratio. The amount of bound chloride increases with time, but it decreases with decreasing content of dissolved chloride in the pore solution. A significant influence of carbonation on the dissolved chloride content of the pore solution has been observed. With complete carbonation, the dissolved chloride content in cement mortar and hardened cement paste increases by a factor between 2 and 12. The bound chloride decreases by 27%–54%. As expected, the pH value decreases from around 13.2 to as low as 8.0 due to carbonation. It can be concluded that carbonation not only lowers the pH value but liberates bound chloride. This is one obvious reason why the combined action of chloride penetration and carbonation accelerates steel corrosion and shortens the service life of reinforced concrete structures.

Key words: Chloride, Pore solution, Carbonation, pH value doi:10.1631/jzus.A1200187 Document code: A

1 Introduction

The complex pore structure of hardened cement paste in concrete consists of nanopores with a maximum diameter of 2 nm, micropores with a maximum diameter between 0.1 and 1 μ m, and wider capillary pores with a diameter up to 1 mm. Under usual climatic conditions the pore space is partially filled with water, depending on the relative humidity of the environment. The aqueous solution in the pore space contains primarily such cations as Na⁺, K⁺, and Ca²⁺, such anions as OH⁻, Al(OH)₄⁻, and SO₄²⁻, and Si(OH)₄ (Page and Vennesland, 1991). The exact CLC number: TU528.01

chemical composition of the pore solution in the initial state varies with the type of cement, the watercement ratio, and the degree of hydration. At a later stage some ions may leave the pore space by leaching and other ions such as chloride, sulfate, and ammonium may penetrate. In addition, CO_2 may penetrate the pore space, either dissolved in water or as gas from the environment.

Chloride concentration and the pH value of the pore solution adjacent to the steel reinforcement are decisive parameters for initiation and rate of corrosion. The process of chloride penetration into the pore space of concrete is very complex and has not been fully understood (Geiker *et al.*, 2007; Conciatori *et al.*, 2008; 2010; Tang, 2008; Bermudez and Alaejos, 2010; Pack *et al.*, 2010). If the surface of concrete gets in contact with seawater or with water containing

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deicing salt, the aqueous solution is first taken up quickly by capillary action. When the rate of capillary absorption becomes negligible, chloride can be transported deeper into the concrete by a slow diffusion process. But this diffusion process is difficult to predict as it is counteracted by convective flow of chloride ions towards the surface during the prolonged drying process. In addition, chloride diffusion is a reactive diffusion process. Part of the ions will be chemically bound on the way towards the reinforcement, and the other part will be fixed by adsorption on the huge inner surface area of hardened cement paste.

During cement hydration in the presence of chloride, Friedel's salt $(3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O)$ and Kuzel's salt $(3CaO \cdot Al_2O_3 \cdot 0.5CaSO_4 \cdot 0.5CaCl_2 \cdot 10(11)$ $H_2O)$ can be formed in concrete. Both Friedel's salt and Kuzel's salt can be classified as AFm, which is a simple term of a family of hydrated calcium aluminate phases (Matschei *et al.*, 2007). Balonis *et al.* (2010) determined the solid solutions and interactions of Friedel's salt with other AFm phases. They also proposed an equilibrium model of the chloride binding by the AFm and elaborated the factors on the Aft/AFm mineralogy. The crystal structure of Kuzel's salt was investigated in detail by Mesbah *et al.* (2011). In addition, some chloride can be chemically bound by other hydration products of cement by substitution.

Theissing *et al.* (1978) studied the binding of chloride in different hardened cement pastes in the presence of NaCl and CaCl₂. Their results showed that there is a chemical equilibrium between the chloride concentration in hydration products and the chloride concentration in the pore solution. Hashimoto *et al.* (2012) found that binding chlorides in the presence of NaCl was accelerated compared with CaCl₂.

In the project described in this paper, the chloride content in the pore solution of cement mortar and hardened cement paste has been determined. The pore solution has been expressed under high pressure. The water-cement ratio (W/C) and the curing age were varied in the investigation and some samples were made with chloride added to the fresh mix. Finally, the

influence of carbonation on the dissolved chloride content was investigated. The dissolved chloride ions in the pore solution were determined by ion chromatography.

2 Experimental

2.1 Preparation of specimens

One mortar mix (M) and two cement paste mixes (HCP1 and HCP2) were selected for these investigations by using ordinary Portland cement P.O 42.5 produced by Dongyue Cement Ltd. (Qingdao, China) and distilled water. ISO standard sand was used for producing the mortar specimens. For some specimens, 0.5% or 1.0% sodium chloride relative to the mass of cement has been added. The chemical composition and some additional characteristics of the cement are given in Tables 1 and 2. The compositions of all the mixes of mortar and cement paste are given in Table 3.

Two types of cylinders with a diameter of 50 mm were cast for these experiments. One type of cylinder had a height of 50 mm. These cylinders were used to express the pore solution after 3 d and 7 d, respectively. The second type had a height of 10 mm. These thinner discs were exposed to accelerated carbonation before the pore solution was expressed.

Table 1 Chemical composition of the cement

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Chemical	Percentage	Chemical	Percentage
composition	(%)	composition	(%)
SiO ₂	22.69	SO ₃	1.91
Fe ₂ O ₃	4.21	K ₂ O	0.51
Al_2O_3	7.79	Na ₂ O	0.56
CaO	57.03	TiO ₂	0.41
MgO	4.54	P_2O_5	0.14

Item	Value
Free CaO (%)	1.26
Total chloride content (%)	0.1773
Specific surface area (m ² /kg)	338.92
Loss on ignition (%)	2.31

Table 3	Mix co	mposition	of the	specimens
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Mix	Cement (kg/m ³)	Sand (kg/m ³)	Water (kg/m ³)	W/C	NaCl
М	789	523	552	0.7	0, 0.5%, 1.0%
HCP1	1243	0	621	0.5	0, 0.5%, 1.0%
HCP2	1096	0	768	0.7	0, 0.5%, 1.0%

The molds of all specimens were removed after 24 h of casting, and the young specimens were further stored in water with a temperature of (20 ± 3) °C for 2 d or 6 d. At 3 d or 7 d the pore solution was expressed with a special device. Part of the thin discs was dried at 50 °C for 2 d and then put into an atmosphere with 20% carbon dioxide content at a relative humidity of 70% until the discs were completely carbonated. The progress of carbonation was checked by spraying a solution of phenolphthalein on freshly broken surfaces. After the carbonation was complete the discs were saturated again with distilled water in a container which is only slightly bigger than the discs, in order to minimize the risk of significant leaching during the saturation process. After saturation, five discs were stacked one above the other to form a cylinder having a height of approximately 50 mm. The pore solution of this composite cylinder was then also expressed.

2.2 Acquisition of pore solution

Barneyback and Diamond (1981) developed a method to squeeze out the pore solution from hardened mortar and concrete. It has been shown that the chemical composition of the liquid obtained by this method may be considered to be close to the composition of the real pore solution in mortar or concrete (Page and Vennesland, 1991; Duchesne and Berube, 1994; Lloyd et al., 2010). However, this method has its limitations. Specimens have to be specially prepared, the water-cement ratio cannot be below a certain limit, and the hydration of the specimens cannot be too advanced. Certainly, there is still a small amount of liquid, which can be pressed out of the cement-based materials. Therefore, alternative methods such as leaching have also been applied in the past (Arya and Newman, 1990; Hague and Kayyali, 1995).

In spite of the limitations, a direct expression is still the reasonable way to acquire pore solution from cementitious materials compared with other methods. Haque and Kayyali (1995) showed that the chloride concentration of the decanted solution from the ground powder of concrete was about twice those of the expressed solution in their 24 concrete tests. Furthermore, the factor of overestimation decreased with the increase in the strength grade of the concrete and added chloride concentration in concrete. In the tests on cement paste specimens, Arya and Newman (1990) concluded that the water soluble chloride test almost invariably overestimates the free chloride content of mixes containing internal and external chloride, sometimes as much as several hundred percent.

In the investigation, when the longer cylinders were cured as indicated above or the carbonation of the shorter cylinders was complete, the specimens were placed in the pore solution expression device, which was designed based on the concepts of Barneyback and Diamond (1981) (Fig. 1). The device was loaded in a testing machine at a constant rate. When the load level has attained a value between 1600 and 1800 kN, the load was kept constant for 3 to 5 min. Under the applied load the pore solution began to flow through the fluid drain and could be collected in a small glass beaker. From each specimen, 4 to 6 ml of pore solution could be obtained by this device for the following analysis.





2.3 Analysis of pore solution

The expressed pore solution was filtered through a 0.45 μ m filter membrane. Then the dissolved chloride content in the expressed pore solution was determined by ion chromatography (Dionex, ICS-1500).

The pH value of the pore solution was measured with a calibrated digital pH meter.

3 Results and discussion

3.1 Chloride content in the pore solution

The dissolved chloride content in the pore solution of mortar (M) and hardened cement paste with two different water-cement ratios W/C=0.5 (HCP1) and W/C=0.7 (HCP2) are shown in Table 4. Certain amounts of NaCl (0, 0.5%, and 1.0%) have been added to the fresh mix. This is marked in Table 4 by 0, 0.5, and 1.0 after the corresponding mix designation. The dissolved chloride content in the pore solution of the lower W/C (0.5) is higher than the one in the pore solution of the higher W/C (0.7). The obvious reason for this effect is the significant difference of water content in the pore system and hence the higher dilution of chloride in HCP2.

Table 4	Dissolved	chloride in	the	pore solution
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Type of mix	Dissolved chloride (mg/L)			
Type of mix	3 d	7 d	7 d-C	
M-0	130	106	1353	
M-0.5	2459	1023	7332	
M-1.0	6871	4262	12 746	
HCP1-0	485	444	1767	
HCP1-0.5	4866	2294	9063	
HCP1-1.0	9488	8894	24 384	
HCP2-0	292	233	983	
HCP2-0.5	3140	1175	6436	
HCP2-1.0	8372	3728	14 901	

In the first column, 0, 0.5, and 1.0 represent 0, 0.5%, and 1.0% NaCl added to the fresh mix after the corresponding mix designation, respectively

Table 4 shows that the concentration of the dissolved chloride decreases with ongoing hydration. This can be explained by the fact that more and more chloride is bound as hydration goes on. Part of it will be found in Friedel's salt and Kuzel's salt, while a second part will substitute other ions in other conventional hydration products. A third part will be adsorbed at the huge internal surface of the hydration products and in the nanopores. The chloride in the nanopores increases shrinkage significantly by increasing the disjoining pressure (Scovazzo and Todd, 2001; Wittmann *et al.*, 2009).

The addition of chloride will directly elevate the content of free chloride in the pore solution of cementitious materials. However, note that the increase of dissolved chloride in the pore solution is beyond a direct proportion to the addition of chloride. It is related with the capability of binding chloride of the hydration product. Furthermore, the free chloride content in the pore solution of mortar is lower than that of hardened cement paste.

Carbonation leads to an enormous increase of chloride concentration in the pore solution (Table 4). For all nine mixes, the contents of dissolved chloride in the pore solution subjected to accelerated carbonation are about 2–12 times those subjected to natural

atmosphere. Decrease of the total porosity of hardened cement paste and the content of dissolved water that enters into pores during saturation is one of the reasons for the increase of dissolved chloride content in the pore solution after carbonation. Nevertheless, in the carbonated state some compounds become unstable and then the bound chloride is freed back into the pore solution. Nagao and Ueda (2003) reported that the ratio of soluble chloride to total chloride near the exposed surface is larger than that in the case of non-carbonated specimens, and that soluble chloride occupies about 90% of total chloride at the closest area to the exposed surface. Goñi and Guerrero (2003), however, studied the stability of Friedel's salt with respect to carbonation in calcium aluminate cement pastes containing 3% chloride. They reported that the carbonation of Friedel's salt does not produce a significant increase of soluble chloride. Through the investigation it can be found that the dissolved chloride is indeed enhanced by carbonation.

The content of total chloride can be calculated as the sum of the initial chloride in the cement (Table 2) and the chloride added separately. In addition, the water content of a saturated specimen can be determined by drying. Then the amount of dissolved chloride in a saturated specimen can be obtained. The bound chloride content is calculated from the difference of total and dissolved chloride. The contents of total chloride, dissolved chloride, and bound chloride are given in Table 5 and Figs. 2–4.

The distribution of chloride in concrete depends on the total chloride content. It is indicated that the amount of bound chloride decreases with decreasing content of dissolved chloride in the pore solution. Compared with the specimen with no NaCl addition, the ratios of bound chloride to total chloride in the pore solution from the specimens with chloride addition of 0.5% and 1.0% decrease by 25% and 46%, respectively, at the age of 3 d. At the age of 7 d, the ratios of bound chloride to total chloride in the pore solution from the specimens with chloride addition of 0.5% and 1.0% decrease by 7% and 21%, respectively.

Figs. 2–4 show a significant influence of carbonation on the chloride content of the pore solution. The bound chloride decreases significantly (by 27%– 54%) due to carbonation. It is also indicated that the ratio of bound chloride to total chloride increases with the curing time.

Mire trans	Total chloride	Disso	Dissolved chloride (mg/g)		Bound chloride (mg/g)		
with type	(mg/g)	3 d	7 d	7 d-C	3 d	7 d	7 d-C
M-0	1.77	0.07	0.05	0.51	1.70	1.72	1.26
M-0.5	4.81	1.36	0.44	2.79	3.45	4.37	2.02
M-1	7.84	3.79	1.83	4.84	4.05	6.01	3.00
HCP1-0	1.77	0.12	0.07	0.25	1.65	1.70	1.52
HCP1-0.5	4.81	1.25	0.37	1.30	3.56	4.44	3.51
HCP1-1	7.84	2.43	1.44	3.50	5.41	6.40	4.34
HCP2-0	1.77	0.10	0.08	0.29	1.67	1.69	1.48
HCP2-0.5	4.81	1.09	0.40	1.92	3.72	4.41	2.89
HCP2-1	7.84	2.91	1.25	4.44	4.93	6.59	3.40

Table 5 Total, dissolved, and bound chloride contents

7 d-C: 7 d, carbonated



Fig. 2 Chloride distribution in mortar (M) as function of the total chloride content at different ages and after carbonation, mg/g of cement

(a) Bound chloride; (b) Chloride dissolved in the pore solution



Fig. 3 Chloride distribution in hardened cement paste with W/C=0.5 (HCP1) as function of the total chloride content at different ages and after carbonation, mg/g of cement

(a) Bound chloride; (b) Chloride dissolved in the pore solution



Fig. 4 Chloride distribution in hardened cement paste with W/C=0.7 (HCP2) as function of the total chloride content at different ages and after carbonation, mg/g of cement

(a) Bound chloride; (b) Chloride dissolved in the pore solution

3.2 pH value of pore solution

The pH value of young concrete is high and therefore steel is protected from corrosion when embedded in young concrete. After carbonation the pH value decreases. The measured pH values of the pore solution are shown in Table 6. Independent of the age the pH value of the hardened cement paste is slightly higher than 13, as expected. After carbonation, values around 8 have been measured.

Table 6 pH values of the pore solution before and aftercarbonation

Mix type	pH				
witz type -	3 d	7 d	14 d	7 d-C	
HCP1-0	13.35	13.39	-	8.10	
HCP1-0.5	13.37	13.47	-	7.92	
HCP1-1.0	13.42	13.47	-	7.67	
HCP2-0	-	13.29	13.23	8.00	
HCP2-0.5	-	13.40	13.36	7.70	
HCP2-1.0	-	13.19	13.39	7.68	

As the pH value of the pore solution decreases to below 9, some hydration products become unstable. The main form of chloride binding is generally reported as a chemical reaction with the aluminate, iron, and ettringite phase to produce Friedel's salt or Kuzel's salt and a physico-chemical reaction between chloride ions and C-S-H. For chloride adsorption by AFm (Friedel's salt or Kuzel's salt), dropping the pH value may decrease the degree of competition offered by hydroxyl ions, hence leading to an increase in the solubility of AFm. For chloride adsorption by C-S-H, the reduction in total porosity may provide fewer sites for ion exchange reaction and physical binding. The mechanisms are major reasons why chloride is liberated into the pore solution after carbonation. The increased chloride concentration after carbonation increases the difference between the concentrations in the outer layer and the deeper regions. Due to this increased difference of chloride concentration, the diffusion of chloride towards steel reinforcement is significantly accelerated. Yoon et al. (2012) studied the chloride ion adsorption and desorption in the pore solution with the pH value, and a large amount of adsorbed chloride ions were found at a high pH value. Anstice et al. (2005) found that only a small fraction of sodium and potassium ions present in the specimens were retained in the pore solution after carbonation. This can also somewhat explain the low alkalinity of the pore solution after carbonation.

Note that chloride concentration in the aqueous pore solution depends strongly on the degree of carbonation. It is obvious that chloride penetration into concrete cannot be described correctly by a simple diffusion process. If the carbonation front reaches the steel reinforcement, the increased chloride concentration after carbonation may lead to initiation of steel corrosion, even if the amount of chloride penetration from outside has not yet reached a critical value for an uncarbonated state. This is a typical example for combined actions aggravating the situation for durability and service life of reinforced concrete constructions.

4 Conclusions

Based on the results described in this investigation the following conclusions can be drawn:

1. The analysis of the expressed pore solution gives us new and interesting insight into the chloride distribution in concrete.

2. The distribution of chloride in concrete depends on the total chloride content. Both the bound chloride content and the concentration of the dissolved chloride increase with increasing total chloride content following a chemical equilibrium.

3. Carbonation not only lowers the pH value but at the same time liberates bound chloride. A considerable amount of bound chloride is freed into the pore solution by carbonation. A complete carbonation of cement mortar and of hardened cement paste with different water-cement ratios (0.5 < W/C < 0.7) and with different amounts of chloride added to the fresh mix (0<chloride added<1%) increases by a factor between 2 and 12. In parallel, the bound chloride decreases significantly (by 27%–54%) due to carbonation.

4. Under given circumstances this combined action of chloride penetration and carbonation can considerably reduce the service life of reinforced concrete structures due to initiation of steel corrosion.

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