

## Influences of chloride immersion on zeta potential and chloride in concentration of cement-based materials

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### Abstract

*In this paper, the zeta potential of freshly mixed cement paste and hardened cement pastes, as well as the concentration index, was measured. The influences of chloride concentration in mixing water and slag content on zeta potential of freshly mixed pastes were studied. A proposed model was expressed to explain the relationship of zeta potential and concentration index of hardened cement pastes immersed in chloride solution. The results showed that the increase of chloride concentration in mixing water and slag replacement improved the zeta potential of freshly mixed cement, the hydration rate and concentration of ions in mixed water affects the zeta potential. With the increase of chloride concentration in soaking solution, the chloride concentration index and zeta potential of hardened cement paste all gradually decreased. The addition of slag gave some changes on chloride in concentration and zeta potential. The relationship among chloride concentration index, chloride concentration in soaking solution and slag replacement revealed by Gouy-Chapman model was in good agreement with the measured results.*

**Keywords:** Chloride; Concentration index; Early hydration; Zeta potential; Gouy-Chapman model;

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## 1. Introduction

Corrosion of steel in concrete is one of the major causes for deterioration of reinforcement steel concrete, especially in the presence of chloride ions and carbon dioxide (Maekawa K., 2003). For concrete structure exposed to extreme condition, such as marine exposition or highway structure where de-icing salt is used, the damage caused by chloride ingress do great harm to the durability of reinforcement concrete structure and give rise to much high repairing and reconstruction cost (Mangat P.S., 1992, Neville A., 1995, Federal Highway Administration, 2002, Johnson J.T., 2007). The high alkaline condition in cement-based materials forms a passivation membrane at the rebar surface to protect it from being corroded. However, the corrosion initiated when the threshold chloride content is reached at the surface of steel and the passivation film breaks.

In concrete, chlorides can be existed in three forms: physical adsorption chloride, chemical binding chloride and free chloride (Berman H A., 1972). The physically adsorbed chlorides and chemically bound chlorides are collectively called binding chlorides. However, according to the former studies on chloride-related issues, it was reported that it is free chloride in pore solution that affected and resulted in steel corrosion (Kayali O A., 1995). However, when it concerns to the study of chloride-induced corrosion, binding chloride will bring significant influences. Chloride binding decreases the content of free chloride in pore solution and reduces the chloride flux into concrete. Meanwhile, the formation of Friedel's salt due to the chemical binding of chloride decreases the porosity and improves the impermeability of pastes/mortars/concrete (Glass G K., 2000, Reddy B., 2002).

Chlorides may derive from aggregates/mixing water (internal chloride), or penetrate into concrete during exposure to chloride-bearing environments (intruded chloride) (Wang S D., 2000). Chloride ions added or penetrated into concrete will react with some of the cement constituent or hydration products. Due to the differences in hydration degree when chlorides appeared, internal and intruded chloride shows different influences on properties and performance of cement-based materials.

The internal chlorides may participate in the hydration process of cementitious materials and affects hydration rate and the morphology and properties of hydration products. A. Traetteberg et al (Traetteberg A., 1974) found that calcium chloride accelerated the hydration of C<sub>3</sub>S and chloride appears to promote the formation of a higher Ca/Si hydrated product, especially at a lower w/s ratio. It was also reported in their paper that the presence of CaCl influenced the morphological features, especially in the early stages of hydration. Both C<sub>3</sub>A and C<sub>4</sub>FA in cementitious materials form Friedel's salt (C<sub>3</sub>A·CaCl<sub>2</sub>·10H<sub>2</sub>O) or its analogues with Cl<sup>-</sup> (Diamond S., 1986), which may decrease the porosity of concrete. Meanwhile, the binding of chloride ions by cement particles and hydration products changes the charge density and distribution at the surface of hydration products, affects the formation of electric double layer at the solid-liquid interface (Yuan Q., 2009a).

After a period of hydration, the intruded chloride gives rise to some changes in structure and morphological features through the physical chemistry reaction to hydration products. Different from the internal chloride, the chemical binding of intrude chloride ion is mainly occurred between chloride and aluminate. The Kuzel's salts form firstly and transform to Friedel's salts with the increase of chloride concentration in pore solution (Balonis M., 2010). In cement-based materials, chloride ions can also be physically absorbed by solid, and the electric double layer (EDL) formed at the interface of solid and liquid was regarded as the reason cause the physical adsorption.

In 1993, Japanese researchers Nagataki et al (Nagataki S., 1993) immersed the cement paste discs in the sodium chloride solution whose concentration equals to seawater and measured the free chloride content of samples by pore solution expression. They found that after 91d of immersion, the concentration of free chloride in pore solution almost upped to twice of that in soaking solution. They called this phenomenon as chloride condensation, the ratio of chloride concentration in expressed pore solution to that in soaking solution was defined as concentration index. Li et al (Li Q L., 2013) investigated the influences of concentration of soaking solution, soaking time, curing age, soaking temperature and pore solution expression pressure on free chloride content of cement-based materials. The concentration index decreased with the concentration of soaking solution, and it increased with soaking time before the 63d of immersion, then decreased. The chloride ion concentration in pore solution decreased as the curing time increased. Soaking temperature and pressure did not affect free

chloride ion concentration. The definition of chloride condensation has been proposed for about 20 years and a lot of studies have used and studied chloride condensation. Although in this paper the definition of chloride condensation is also used, it has to emphasize that what we talk about here is deviated from the meaning of condensation in chemistry. The phenomenon of chloride condensation may be much more close to a kind of unstable physical adsorption. Therefore, author of this paper redefined this phenomenon as chloride in concentration, replaced the concentration index as condensation index applied before

Nagataki et al(Nagataki S., 1993) tried to interpret the chloride in concentration in pore solution of cement-based materials by using the theory of electric double layer firstly. After that, Yuan(Yuan Q., 2009b) calculated the length of electric double layer based on Debye equation, and gained the conclusion that the higher concentration of soaking solution, the thinner thickness of electric double layer and the smaller concentration index. Based on the results of Yuan, He(He F Q., 2010) assumed the average concentration of chloride ion in diffusion layer and proposed a computational formula to calculate chloride concentration index caused by electric double layer formed within pore structure of cement-based materials.

The electrical double layer forms at the interface between pore walls and pore solution. The electric double layer consists of two layers: compact layer and diffusion layer. In compact layer, ions are tightly adsorbed on the solid surface, while ions diffusely distribute in diffusion layer due to the interactions between attraction of solid phase and thermal motion. Most of the ions in diffusion layer may move with pore solution, electrokinetic potential formed at shear plane is defined as zeta potential. Zeta potential of clinker and cement have provided a lot of useful information on early hydration of C<sub>3</sub>S and other calcium silicate compounds and rheological property of freshly mixed pastes(Traetteberg A., 1974). However, the studies on zeta potential were mainly concentrated on mechanism of water reducing agent on cement hydration(Plank J., 2007a). The research on influences of chloride ion on cement hydration and ion binding is limited. Besides, limited by testing technology, most of the existed studies on zeta potential need to dilute the sample during the measurement, which restricted the researches.

This paper studies the influences of chloride ions on early hydration by measuring the zeta potential of original suspension, and effects on concentration index based on zeta potential of an simplified artificial cement pastes. A model was established to investigate the relationship between zeta potential and chloride concentration index.

## 2.Theory on electroacoustic measurement of zeta potential

Particles with diameter between 10<sup>-6</sup> and 10<sup>-9</sup> meters suspended in a continuous phase of another component, neither precipitation nor dissolution, is called as colloidal suspension. Zeta potential at the surface of colloid particle reveals the surface potential storage and had close relationship with the stability of colloid system. According to the theory of DLVO(Derjaguin LandanVerwey Overbeek), zeta potential is an important factor representing the stability of colloidal suspension system.

When placed in a sound field, the stability of electric double layer may be broken down. The surplus ions are removed and a new polarized state reoccurs, which results to the rearrangement of electric charge at the surface of particles. The polarization effects induce dipole moment and produce a colloid vibration current within the suspension system.

The colloid vibration current(CVI, I<sub>CV</sub>) is a kind of current at macrolevel for suspension system. For thin electric double layer of monodisperse suspension and low conductivity, the macroscopic current and field intensity can be calculated based on Shilov Zharkikh cell model:

$$\langle I \rangle = I_r / \cos \theta_{r=b} \quad \langle E \rangle = \phi / (b \cos \theta_{r=b}) \quad (1)$$

Where,  $r$  is polar coordinate,  $\theta$  is polar angel,  $b$  is the cell diameter in cell model,  $\phi$  is potential (V),  $\langle E \rangle$  and  $\langle I \rangle$  is macroscopic field intensity (N/C) and current (A).

Based on equation (1), I<sub>CV</sub> can be calculated as

$$I_{CV} = (-K_m / \cos \theta) (\partial \phi / \partial r_{r=b}) \quad (2)$$

Where,  $K_m$  is conductivity of medium (S/m). Introducing the Kuwabara cell model and considering the overlap of electric double layer:

$$I_{cv} = \zeta G Q (1 + F) \nabla p \quad (3)$$

$$G = (9j / 2s) h(s) / \{3H + 2S / [1 - \rho_p(1 - \varphi) / \rho_s]\}$$

$$Q = 2\varepsilon_0 \varepsilon_m \varphi (\rho_p - \rho_s) / (3\eta \rho_s), F = (1 - \varphi) / (2 + \varphi), \nabla p$$

Where  $\zeta$  is zeta potential (V),  $\nabla p$  is pressure gradient (Pa/m),  $j$  is imaginary unit,  $s = a[\omega / (2\nu)]^{1/2}$ ,  $a$  is fineness of dispersion phase (m),  $\omega$  is ultrasonic frequency (rad/s),  $\nu$  is kinematic viscosity ( $m^2/s$ ),  $h, H, S$  is special function proposed in Kuwabara cell model,  $\rho_p, \rho_s$  is density of dispersion phase and colloid respectively ( $kg/m^3$ ),  $\varphi$  is volume concentration,  $\varepsilon_0$  and  $\varepsilon_m$  is vacuum dielectric constant and relative dielectric constant of dispersion medium (F/s),  $\eta$  is viscosity (Pa•s).

Comparing to other methods, such as electrophoretic and electroosmosis technique, electroacoustic technique shows superior in zeta potential measurement of aqueous colloids. Acoustic wave is appropriate for system with complicate and high concentrate. Electroacoustic method has the advantages in measuring the zeta potential of samples with higher concentrate, larger particle size range and fewer samples consumption and has been used to investigate the electrochemical properties at the interface within various materials. In this paper, a DT-300 instrument from Dispersion Technology was used for zeta potential measurement without dilution of samples, which to some extent avoided the differences in hydration and surface properties between diluted and original samples.

### 3. Experimental

#### 3.1. Raw Materials

P-I 52.5 Portland cement (PC) and Grade 95 slag powder were used in this study. The chemical compositions of the cement and slag are given in table 1. NaCl, Ca(OH)<sub>2</sub> and AgNO<sub>3</sub> were analytical grade chemicals. De-ioned water was used to prepare solution for chemical analysis.

Tab. 1 Chemical composition of raw materials /%

| Raw Material | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO   | MgO   | K <sub>2</sub> O | SO <sub>3</sub> | C | LOSS |
|--------------|------------------|--------------------------------|--------------------------------|-------|-------|------------------|-----------------|---|------|
| Cement       | 21.09            | 4.34                           | 2.81                           | 62.50 | 1.81  | 0.62             | 2.87            | — | —    |
| Slag         | 33.00            | 13.91                          | 0.82                           | 39.11 | 10.04 | 1.91             | 0.16            | — | 0.08 |

#### 3.2 Specimen preparation and curing

Water to binder ratio of cement pastes is 0.4. PVC pipe with a size of  $\Phi 50 \times 200$  mm was used as a mould. One end of the mold was sealed with polyvinyl chloride board. After cement paste was cast into the mold, the other end of the mold was sealed with plastic film immediately, then placed in an oscillator for 6h of slow rotation to avoid segregation. After that, the specimens with mould were left in a room at 20°C for 24h, then demolded and cut into thin-disc about 5mm of thickness.

The cement paste disc specimens were cured in water for another 27 days before vacuum saturation with saturated limewater, then immersed into 0.1, 0.3, 0.5, 0.7 and 1.0 mol/L of NaCl solutions respectively in plastic containers covered with plastic film at 20°C. The volume ratio of soaking solution to specimens was kept above 40. The solution was replaced every two weeks so to ensure the relatively constant chloride ion concentration in the soaking solution.

#### 3.3 Zeta potential measurement of freshly mixed cement pastes

Mixing 20g Portland cement with different concentration of sodium chloride solution, that is 0, 0.1, 0.3, 0.5, 0.7 and 1.0 mol/L respectively in a beaker. The water to binder ratio is 0.4. Placed the beaker on a magnetic stirring apparatus with a magnetic stirring son, the beaker was sealed with plastic film in case of evaporation. After 20 minutes' stirring and 1 minute of standing, zeta potential of freshly mixed cement pastes was measured.

#### 3.4 Zeta potential measurement of hardened cement pastes

When the designed soaking time was reached, the samples were grounded by ball mill and placed in 60°C vacuum drying oven for 24h. The fraction of particles having diameter between 0.0025 to 0.0045 mm was separated by sieving and used for zeta potential measurement. The suspension was prepared by mixing 2g of powder samples with sodium chloride solution whose concentration equals to that of soaking solution the samples immersed. The mass ratio of solid to liquid was 1:1. The suspensions were kept for 6 h, and then dispersed by ultrasonic waves for one minute before the measurement. Zeta potential in the suspensions was measured with DT300 instrument.

### 3.5 Pore solution expression and chloride analysis

The specimens with three cement paste discs for every group were rubbed with cloth soaked in the chloride solution and twisted to obtain saturated surface dry condition after 56 and 91 days of soaking in NaCl solutions. Those specimens were crushed, placed in an expression apparatus and loaded to 510MPa at a rate of 1.5~2.5MPa/s. They were held at this pressure for 1 min, then unloaded rapidly and repeated once more. The expressed pore solution was collected with an injection syringe whose pinhead was covered with a latex tubing to prevent leaking, then was injected into a plastic container and sealed immediately to avoid carbonation. The pore solution expression apparatus was cleaned with anhydrous ethanol after a pore solution expression procedure to avoid cross contamination. For every batch the reported results are average of three concentration of expressed pore solution.

### 3.6 Chloride ion concentration index

Collected pore solution was diluted for 20 times for chloride ion titration using an automatic potentiometric titrator with a silver electrode. The titration solution was 0.01mol/L of AgCl solution. At the end point of the titration, automatic potentiometric titrator calculated the chloride concentrations automatically according to potential-volume curve. Chloride ion concentration index  $N_c$  was calculated by the following equation:

$$N_c = c_k / c_b \quad (4)$$

Where  $c_k$  is the chloride ion concentration determined by chloride ion titration,  $c_b$  is chloride ion concentration in exposure solution.

## 4. Results and Discussion

### 4.1 Influences of chloride concentration in mixing water on zeta potential of freshly mixed pastes

The development of zeta potential of freshly mixed cement pastes with chloride concentration in mixing water and slag replacement is plotted in figure 1. It can be seen that with the increase of chloride concentration in mixing water, zeta potential of 4 groups with different slag replacement all gradually increased. Meanwhile, the addition of slag had positive effects on higher zeta potential of paste samples.

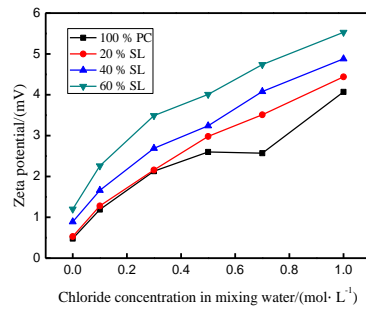
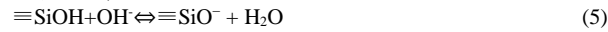


Figure 1 Zeta potential of freshly mixed cement pastes

The phenomenon of electrization is ubiquitous at the interface of solid and liquid. The contact of an overwhelming majority of dispersion particles with polar solution or polar media will create an electrical charge. The charged dispersion system will attract ions with opposite charges so that the system as a whole is electrically neutral, which results in the formation of electric double layer. Immersed in solution, the electric double layer formed at the interface of solid and liquid due to the ionization, ion exchange or binding and fraction contact. In electric double layer model established by

Stern, the electric double layer consists of two layers: internal layer and external layer. Internal layer refers to compact layer while external layer refers to the diffusion layer. In compact layer, ions opposite to solid surface potential are strongly bound due to electrical or non-electrical attraction. Out of the compact layer, ions diffusely distribute in diffusion layer, where the concentration of counter-ion is higher than that of ions who take same charge as compact layer. With the increase of distance to solid surface, the concentration of counter-ion decreases to that of bulk solution. In diffusion layer, there exists a shear plane, solution on the side of pore solution is flowable and moves with bulk solution. This movement generates a potential difference at the shear plane, which was defined as zeta potential.

The main hydration product of cement-based materials is calcium silicate hydrates (C-S-H) with a high specific surface area. In fully hydration Portland cement paste, C-S-H may reach up to 70% of total volume and 200 m<sup>2</sup>/g (Elakneswaran Y., 2009a). The surface of C-S-H is negative charged due to ionization of silanol sites in alkaline condition. The dissociation equilibrium of silanol sites due to pH increase is given by (Elakneswaran Y., 2009b):



The specimens were vacuum saturated with saturated limewater solution before soaking in chloride environment, saturated limewater solution might fill the pore of specimens. The hydration of cement may also produce calcium hydroxide. The adsorption of Ca<sup>2+</sup> on the silanol sites resulted in a positive charge:



The specimens were then immersed in a NaCl solution, chloride ion penetrated into pore solution, and adsorbed onto the silanol sites:



Therefore, due to the adsorption of hydration product C-S-H gel, electric double layer formed on the surface of cement pastes particles. The study (Elakneswaran Y., 2009a) also found that other hydration products, such as portlandite and Friedel's salt, can also adsorb chloride ions. The surface properties of solid and ion concentration in pore solution affect zeta potential of electric double layer, and zeta potential of freshly mixed paste can also represent the hydration characteristics of cement pastes.

Many researches have studied the reaction of chloride ions with component of cement during hydration and how that affected the hydration rate of cement. During the study on mechanism of coagulant and set retarding admixtures, Joisel (Joisel L., 1993) found that the dissolution of ion into pore solution has close relationship with hydration rate of cement. Monovalent anion or group in solution (such as Cl<sup>-</sup> or NO<sup>3-</sup>) can promote the dissolve of Ca<sup>2+</sup> and accelerate the hydration of cement, which have positive effects on the development of early strength (Mehta P K., 2006). The paper of A. Traetteberg (Traetteberg A., 1974) also revealed the acceleration effects of chloride ion on hydration of tricalcium silicate. Especially when part of cement is replaced by slag, the addition of chloride salt increases the pH of pore solution, the acceleration effects may be more significant. The development of hydration will promote the production of hydration products and boost the zeta potential of freshly cement pastes.

Koleva et al (Koleva D A., 2007) studied the influences of chloride ion on hydration products of cement-based materials and found that internal chloride had close relationship with C/S ratio of hydration products. The chloride in mixing water can increase the C/S ratio from 1.8 to 2.19~2.95. C/S ratio in hydration products decides the surface charge of C-S-H gel. For C-S-H gel with high C/S ratio, the gels are positively charged and attract the Cl<sup>-</sup>, OH<sup>-</sup> and other anion into the surface of C-S-H gels. Instead, the surface of C-S-H gels may be negative charged when the C/S ratio lower than 1.2~1.3 (Monteiro P., 1997). In some studies, negative zeta potential was obtained by other testing method and instrument, which need to dilute the samples to a very low solid-liquid ratio. The dilution process decreases the concentration of Ca<sup>2+</sup> in pore solution, and thus promotes the dissolve of calcium hydroxide, which may obviously affect the value of zeta potential. In this study, the values of zeta potential are all above zero. The formation of hydration products with high C/S ratio after the addition of sodium chloride in mixing water increased the zeta potential of freshly mixed cement pastes.

Meantime, zeta potential can also be used to represent the dispersion properties of suspension system. Generally speaking, the larger absolute value of zeta potential, the better dispersion properties of system. The electrification at the surface of cement particles is complicated, and the signal and density of charge at the surface of various mineral admixture particles and hydration products are totally different. Electrostatic repulsion is considered as one of the important reasons for particles keep the dispersed state, as well as the mechanism of superplasticizer on hydration properties of freshly mixed cement pastes (Yu Y H., 2012). Many researches (Plank J., 2007b, Ferrari L., 2010) on mechanism of superplasticizer found that the addition of it apparently increased the absolute value of zeta potential. It can be seen from our experimental results that chloride ions has a certain role in improving the flowing property of cement pastes and can to some degree be considered as a kind of inorganic superplasticizer.

Few studies (Zhang C., 2013) were conducted on the influences of slag on zeta potential of freshly mixed cement pastes. The ion concentration at the boundary layer of cementitious materials particles has close relationship with zeta potential, and even few added electrolyte brings prominent effects on value of zeta potential. During the hydration process, the dissolved mineral admixtures forms new electrolyte and affects the system's charge balance. At the same time, slag can break down the flocculation group formed around the cement particles and increase the adsorption group. The results that slag increases the absolute value of zeta potential and improve the flowing property of paste is consistent with the former study that mineral admixtures was able to promote the flowability of cement pastes (Chen L., 2010).

Among the mineral composition of cement,  $C_3A$  shows highest hydration activity and have significant influences of early hydration and rheological property of cement pastes. In this study, samples after only 20min of hydration was chosen for the measurement of zeta potential, thus at that stage  $C_3A$  was the main component that start to hydrate. Research on zeta potential of synthetic  $C_3A$  at early stage revealed that zeta potential sharply increased in the moment that water and  $C_3A$  was mixed and reached up to 20mV about only 2 minutes later. AFt and AFm are the main hydration products of  $C_3A$ , whose structural formula can be represented as  $\{[C_3A]_m n Al(OH)_4 \cdot [(n-x)/2 Ca^{2+}]\} \cdot x(OH)^-$ . With the development of hydration, concentration of  $Ca^{2+}$  on the surface of hydration products particle of  $C_3A$  gradually increases and improve the value of zeta potential. Content of  $Al_2O_3$  in ground granulated blast furnace slag (GGBFS) is much higher than cement, therefore the content of  $C_3A$  in large admixture slag cement may be higher than cement without slag, which promote the early hydration activity of samples and increase the zeta potential of freshly mixed cement paste.

#### ***4.2 Influences of chloride concentration in soaking solution on chloride concentration index of hardened cement paste***

Figure 2 and figure3 is chloride concentration index of samples with different content of slag after 28d of bath-curing and 56d and 91d of soaking in chloride solution. After 56d of soaking, chloride concentration index gradually decreased with the slag replacement, which was more apparent in low concentration of soaking solution. When the soaking reached up to 91d, the chloride ion concentration index of pastes with 20% slag showed no obvious differences from the PC samples, then decreased with the increase of slag content from 20% to 60%. The paste specimens with 40% and 60% slag showed lower concentration indices than the PC samples did over the entire soaking solution concentration range. It can be seen that the chloride concentration index of pastes changed from 40% to 60% replacement was not as notable as slag replacement increased from 20% to 40%.

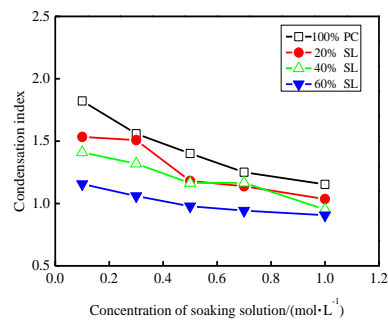


Figure 2 Chloride concentration index of cement paste after 56d of soaking

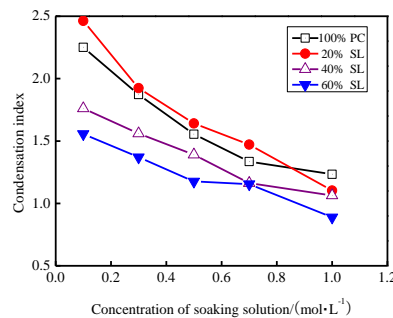


Figure 3 Chloride concentration index of cement paste after 91d of soaking

Slag is a kind of potentially hydration active supplementary cementitious material, and produces hydration products C-S-H gels react with the primary hydration products  $\text{Ca}(\text{OH})_2$  of cement. The reaction of slag falls behind of the hydration of cement(Wang C., 2000). The increase of slag replacement leads to a reduction of cement content, and decreases the content of primary hydration product  $\text{Ca}(\text{OH})_2$  significantly. These may have negative effects on the formation of C-S-H gel and adsorption of chloride ions(Yu H., 2007). Meanwhile, the reduction of  $\text{Ca}(\text{OH})_2$  content and adsorption of alkali metal ion to hydration products results in the decrease of pH of pore solution and affects the ionization of silanol sites. The addition of slag may also change the surface properties of hydration products and reduce surface potential of pastes(Elakneswaran Y., 2009c). These may all show negative effects on physical adsorption of chloride ions within hardened pastes.

Chemical binding is generally the result of reaction between chlorides and  $\text{C}_3\text{A}$  to form Frieda's salt or the reaction with  $\text{C}_4\text{AF}$  to form a Frieda's salt analogue. Sulfates react with  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$  and form ettringite or monosulphate. Thus,  $\text{SO}_3$  content in the cement has a negative influence on the binding capacity, especially in low chloride concentrations (such as 0.1 M). The content of  $\text{Al}_2\text{O}_3$  in slag was higher than that in the cement, while the content of sulfate was lower, which may enhance the chemical binding of cement pastes. Chemical binding and physical adsorption in cement pastes coexist in a competitive dynamic process(Luo R., 2001). The enhancement of chemical binding would decrease the chloride concentration in pore solution and inhibit the physical adsorption of chloride ions onto electrical double layer. The restriction of chemical binding on chloride in concentration may be much more obvious for samples soaking in lower concentration of chloride solutions, with the increase of concentration of soaking solution, the concentration of chloride in pore solution increased, which may weaken the influence of chemical binding on chloride in concentration.



In the meantime, the improvement of pore structure after the slag replacement may block the migration of chloride ions within pastes and a longer time is needed for the penetration of chloride into small pore. This may be another reason for the decrease of chloride concentration index with the replacement of slag.

#### 4.3 Influences of chloride concentration in soaking solution on zeta potential of hardened cement paste

In figure 4 and figure 5, zeta potential of hardened cement pastes for different slag content and soaking solution concentration is showed. After 56d of soaking, zeta potential of pastes gradually decreased as concentration of soaking solution increased. Cement pastes samples showed decreased zeta potential with the increase of slag content, which is weakened as chloride concentration increased. When soaking time reached to 91d, zeta potential of samples obviously increased than that of 56d soaking. However, the improvement of zeta potential was faster for sample with slag.

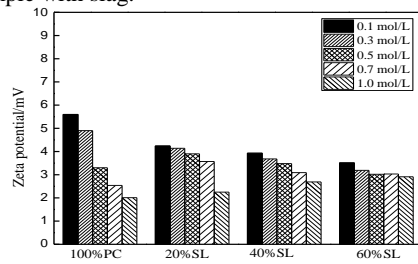


Figure 4 Zeta potential of cement paste after 56d of soaking

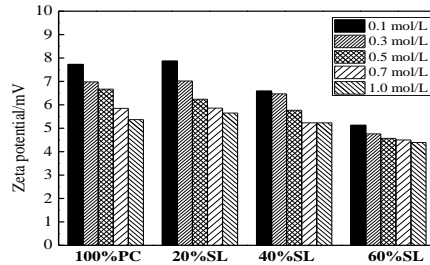


Figure 5 Zeta potential of cement paste after 91d of soaking

Electric double layer can be divided into several part according to the existential form of ions. Firstly is potential-determined layer, where ions are chemically bound at the surface of solid, the ions in this layer are desolvated. Then the ions adsorbed due to physical and electrostatic interaction form the Stern layer. The thickness of Stern layer equals to that of 1 or 2 molecule, and contains the solvated ions. The potential of electric double layer is decreased in Stern layer from  $\psi_0$  to  $\psi_d$ . Outside of the Stern layer is the diffusion layer. There exists a shear plane in diffusion layer, on the two side of shear plane, one is motionless while another is flowable layer. The potential at shear plane is defined as zeta potential related to electrokinetic phenomenon. Fig. 6 is the potential changes in electric double layer of Stern model as a function of distance from solid phase.

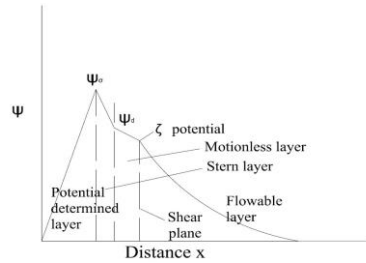
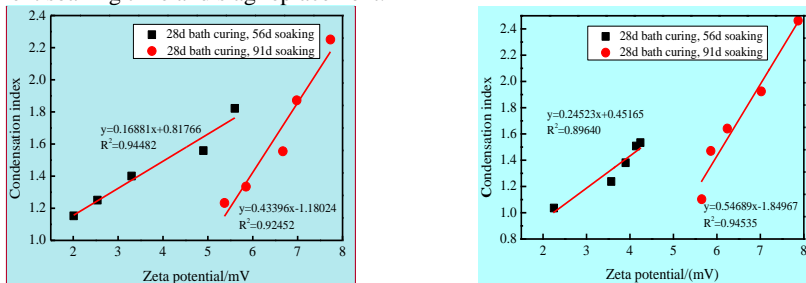


Figure 6 Potential changes in electric double layer

According to Stern electric double layer model, potential-determined ions in potential-determined layer and counter-ions in diffusion layer have close relationship with the zeta potential at shear plane. On one hand, the concentration of potential-determined ions affects the surface potential of hydration products and the signal and value of zeta potential. On the other hand, zeta potential changes with concentration of counter-ions in Stern layer. With the increase of electrolyte concentration in pore solution, the concentration of counter-ions in Stern layer will also increase, which may result into the more reduction of potential in Stern layer and zeta potential. Within cement-based materials, potential-determined layer forms due to the adsorption of calcium ions on the surface of hydration products, then the chloride ions attracted by potential-determined layer diffused distribute in diffusion layer. It can be known that the increase of chloride concentration in soaking solution to some extent increases the concentration of counter-ions ( $\text{Cl}^-$ ) and potential reduction in Stern layer. When the properties and quantity of hydration products and other factors are identical, the decrease of zeta potential in electric double layer is simultaneous with increase of soaking solution concentration. At the same time, the decrease of C/S ratio in hydration products and pH of pore solution caused by the slag replacement may reduce charge density in potential-determined layer. Thus, zeta potential of hardened cement pastes gradually decreased with content of slag. With the extend of soaking time, hydration of slag may increase hydration products, which is beneficial to development of zeta potential.

#### 4.4 Relationship of chloride concentration index and zeta potential

Figure 7 shows the relationship of measured chloride concentration index and zeta potential. A good linear relationship was obtained for our experimental results between concentration index and zeta potential. However, it is known that besides zeta potential, pore structure distribution, ion composition in pore solution and other factors also affects chloride concentration index. In this paper, different fitting equation was established for samples with different soaking time and slag replacement.



批注 [XH1]:

批注 [XH2]:

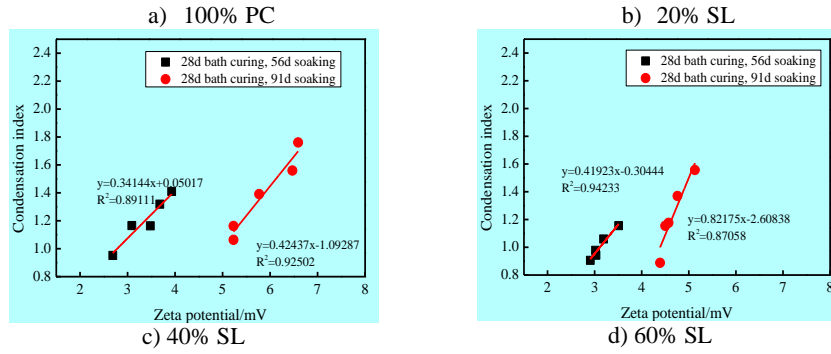


Figure 7 Relationship of measured chloride concentration index and zeta potential

The ions distribution in diffusion layer can be modeled by Gouy-Chapman model, based on the assumption in this model, the probability of ions in diffusion layer is in direct proportion to Boltzmann factor  $e^{-ze\psi/kT}$ . The ion concentration in diffusion layer can be showed as follow:

$$\begin{aligned} n_+ &= n_0 \exp\left(-\frac{ze\psi}{kT}\right) \\ n_- &= n_0 \exp\left(\frac{ze\psi}{kT}\right) \end{aligned} \quad (8)$$

Where,  $n^+$ 、 $n^-$ —the number of cation or anion per unit volume solution;

$n_0$ —the number of ions per unit volume solution at the distance where electric neutrality ( $\psi=0$ ) reaches;

$z$ —charge number of cation or anion;

$\psi$ —the potential at  $x$  distance from shear plane。

According to classical theory of electrostatics, the relationship of potential on the side of solution and the distance from solid surface (or shear plane) can be showed by Poisson equation.

$$\nabla^2\psi = -\frac{\rho}{\varepsilon_0\varepsilon_r} = -\frac{ze(n_+-n_-)}{\varepsilon_0\varepsilon_r} = \frac{2n_0ze}{\varepsilon_0\varepsilon_r} \sinh\left(\frac{ze\psi}{kT}\right) \quad (9)$$

Where,  $\varepsilon_0$ 、 $\varepsilon_r$ —vacuum permittivity of electric double layer and relative permittivity of solution media;

$\nabla^2$ —Laplace operator, which express the divergence of a function;

$\rho$ —the number of negative charge per unit volume minus that of positive

charge.

Solving the equation above with boundary conditions introduced, the following result obtained:

$$\kappa x = \ln \frac{(e^{y/2} + 1)(e^{y_0/2-1} - 1)}{(e^{y/2} - 1)(e^{y_0/2-1} + 1)} \quad (10)$$

Where,  $\kappa^2 = \frac{2n_0z^2e^2}{\varepsilon_0\varepsilon_r kT}$ ,  $\frac{1}{\kappa}$  is defined as effective thickness of diffused electric double layer;

$y=ze\psi/kT$ ,  $y_0$  equals to the value of  $y$  at  $x=0$ .

Considering the value of  $y$ , in this experiment, the maximum value of zeta potential equals to 7.87mV. Introduced into the equation above, the value of  $y$  is 0.3114. Therefore, in this study, the value of  $y$  calculated is all lower than 1.0, so series expanded  $e^{y/2}$  and leave the former two items:

$$e^{y/2} = 1 + \frac{y}{2} + \frac{(y/2)^2}{2!} + \frac{(y/2)^3}{3!} + \dots \approx 1 + y/2$$

Substitutes it into formula 10, then:

$$\kappa x = \ln \frac{(2 + y/2)y_0/2}{y/2(2 + y_0/2)} \approx \ln \frac{y_0}{y} = \ln \frac{\psi_0}{\psi} \quad (11)$$

or  $\psi = \psi_0 e^{-\kappa x}$

Substitutes formula 11 and effective thickness of electric double layer into formula 8:

$$n_{cl} = n_0 \exp\left(\frac{ze\psi_0 e^{-\kappa x}}{kT}\right) = n_0 \exp\left(\frac{ze\psi_0 e^{-x\left(\frac{2n_0 z^2 e^2}{\epsilon_0 \epsilon_r kT}\right)^{1/2}}}{kT}\right) \quad (12)$$

Do the integral for chloride concentration in diffusion layer, we can obtain the average concentration of chloride ions, that is:

$$n_{ave} = \kappa \int_0^L n_0 \exp\left(\frac{ze\psi_0 e^{-x\left(\frac{2n_0 z^2 e^2}{\epsilon_0 \epsilon_r kT}\right)^{1/2}}}{kT}\right) dx \quad (13)$$

It can be known more clearly from the formula above that, the increase of chloride concentration in soaking solution on one hand decreases the thickness of diffusion layer in electric double layer and probability of chloride ions exist in electric double layer. On the other hand, it results into the increase of counter-ions concentration in Stern layer and decreases zeta potential of electric double layer. He(He F., 2010) studied the thickness of electric double layer and found that it decreased significantly with concentration of bulk solution, which became less obvious when the concentration higher than 0.5mol/L. These can be used to interpret the decreased concentration index with the increase of chloride concentration in soaking solution.

Pore structure of cement-based materials has close relationship with chloride concentration index. Then, a formula for chloride concentration index calculation is obtained based on the assumption of cylindrical pore model (figure 8) and pore diameter distribution (table 2). The results are showed in figure 9. The vacuum permittivity of electric double layer is  $8.854 \times 10^{-12}$ F/m and relative permittivity of sodium chloride solution is calculated by the fitting formula proposed in references(Yang X Q., 2006).

$$N_{condensation\_index} = \int \frac{n_{ave} \times \pi[(R+L)^2 - R^2] + N_0 \times \pi R^2}{N_0 \times \pi(R+L)^2} d(R+L) \quad (14)$$

Tab. 2 Assumed pore diameter distribution

|              | 0~5nm | 5~10nm | 10~50nm | 50~1000nm |
|--------------|-------|--------|---------|-----------|
| Average/nm   | 2.5   | 7.5    | 30      | 500       |
| Percentage/% | 20    | 10     | 60      | 10        |

It can be seen from figure 9 and figure 10 that after 56d and 91d of soaking, the development of calculated concentration index with chloride concentration in soaking solution and slag replacement is in agreement with the measured results. However, the value of calculated concentration index is much lower than measured results. Two reasons may be responsible. The first is we assumed the pore shape as cylindrical model and a simple pore diameter distribution. However, the specific surface area of hydration products is much higher and there existed many capillary and gel pore within cement pastes, which may promote the chloride concentration significantly. Specially, for some small pore, the electrical double layer may overlap with each other and have positive effects on chloride concentration. Secondly, the method we used to measure the zeta potential has to grind the hardened cement pastes into powder and mix with same mass of corresponding soaking solution. These may change the

condition around the solid phase and affects the measured zeta potential. A new non-destructive testing method which can measure the zeta potential of hardened cement pastes may be helpful for further study.

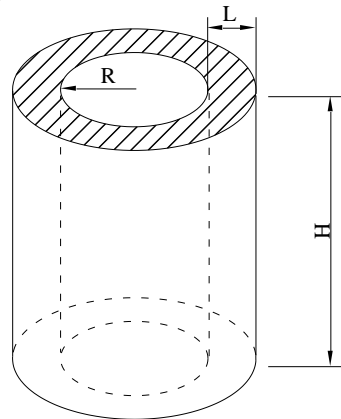


Figure 8 Pore structure model within cement-based materials

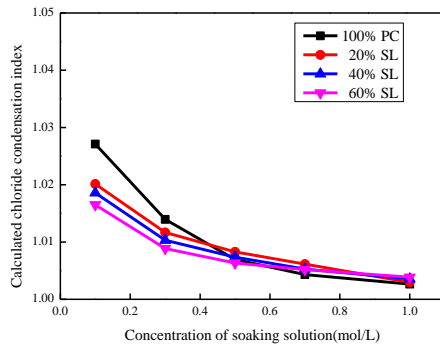


Figure 9 Calculated chloride concentration index after 56d of soaking

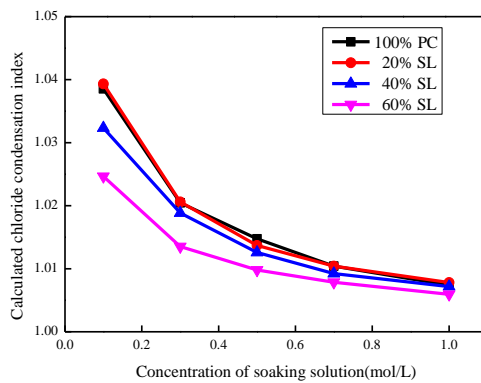


Figure 10 Calculated chloride concentration index after 91d of soaking

## 5. Conclusions

Based on the results and discussion above, the following conclusion can be made:

- (1) Zeta potential of freshly mixed cement pastes gradually increased with the sodium chloride concentration in mix ingwater. At the same time, slag also higher the zeta potential of samples.
- (2) With the increase of chloride concentration in soaking solution, the chloride concentration index of paste samples decreased significantly. After soaking 56d, chloride concentration index gradually decreased with the slag replacement. 91d of soaking, chloride concentration index of samples with 20% slag reached the same level as control group.
- (3) Zeta potential of hardened cement pastes was decreased with the increase of soaking solution concentration and slag content, while this effects was weakened as concentration of soaking solution increased.
- (4) Chloride concentration index can be calculated by Gouy-Chapman model based on provided zeta potential and pore diameter distribution.

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## References

- Maekawa K, Ishida T, Kishi T. Multi-scale modeling of concrete performance. *J Adv Concr Technol*. 2003,1(2):91–126
- Mangat PS, Molloy BT. Factors influencing chloride-induced corrosion of reinforcement in concrete. *Mater Struct*. 1992,25(151):404–411
- Neville A. Chloride attack of reinforced concrete: an overview. *Mater Struct*. 1995,28(176):63–70.
- Federal Highway Administration. Corrosion costs and preventative strategies in the United States. Publication No. FHWA-RD-01-156. 2002
- Johnson JT Corrosion costs of motor vehicles. <http://www.corrosioncost.com/pdf/transportation.pdf>. Accessed in July 2007
- Berman H A. Determination of chloride in hardened Portland cement paste, mortar, and concrete. 1972
- Kayyali O A, Haque M N. The  $\text{Cl}^-/\text{OH}^-$  ratio in chloride-contaminated concrete—a most important criterion. *Magazine of Concrete Research*. 1995, 47(172): 235-242
- Glass G K, Buenfeld N R. The influence of chloride binding on the chloride induced corrosion risk in reinforced concrete. *Corrosion Science*. 2000, 42(2): 329-344
- Reddy B, Glass G K, Lim P J, et al. On the corrosion risk presented by chloride bound in concrete. *Cement and Concrete Composites*. 2002, 24(1): 1-5
- Wang S, Huang Y. Concrete resistance to chloride ingress: effect of cement. *J Chin Ceram Soc*. 2000, 28(6): 570-574
- Traetteberg A, Ramachandran V S, Grattan-Bellew P E. A study of the microstructure and hydration characteristics of tricalcium silicate in the presence of calcium chloride[J]. *Cement and Concrete Research*, 1974, 4(2): 203-221.
- Diamond S. Chloride concentrations in concrete pore solutions resulting from calcium and sodium chloride admixtures [J]. *Cem Concr Aggregates*. 1986,8(2): 97–102.
- Yuan Q, Shi C J, Geert de S, et al. Chloride binding of cement-based materials subjected to external chloride environment—a review[J]. *Construct Build Mater*, 2009, 23(1): 1–13
- Balonis M, Lothenbach B, Le Saout G, et al. Impact of chloride on the mineralogy of hydrated Portland cement systems [J]. *Cem Concr Res*, 2010, 40(7): 1009–1022.
- Nagataki S, Otsuki N, Wee T, et al. Condensation of chloride ion in hardened cement matrix materials and on embedded steel bars. *ACI Materials Journal*. 1993, 90(4)
- Li Q, Shi C J, He F Q et al. Factors Influencing Free Chloride Ion Condensation in Cement-based Materials[J]. *J Chin Ceram Soc*. 2013, 41(003): 320-327
- Yuan Q. Fundamental study on test method of chloride transport in cementitious based materials[D]. Centre South University, 2009
- He F Q. Measurement of Chloride Migration in Cement-based Materials Using  $\text{AgNO}_3$  Colorimetric Method[D]. Centre South University, 2010
- Plank J, Hirsch C. Impact of zeta potential of early cement hydration phases on superplasticizer adsorption[J].

Cement and Concrete Research, 2007, 37(4): 537-542.

- Elakneswaran Y, Nawa T, Kurumisawa K. Electrokinetic potential of hydrated cement in relation to adsorption of chlorides[J]. Cement and Concrete Research. 2009, 39(4): 340-344
- Elakneswaran Y, Nawa T, Kurumisawa K. Zeta potential study of paste blends with slag[J]. Cement and Concrete Composites. 2009, 31(1): 72-76
- Joisel L. Proceedings of the International Symposium on Chemistry of Cements. Stockholm. 1993, 26(7): 414-424
- Mehta P K, Monteiro P J. Concrete: microstructure, properties, and materials. Vol.3. New York: McGraw-Hill, 2006, 20-22
- Koleva D A, Hu J, Fraaij A, et al. Microstructural analysis of plain and reinforced mortars under chloride-induced deterioration[J]. Cement and concrete research. 2007, 37(4): 604-617
- Monteiro P, Wang K, Sposito G, et al. Influence of mineral admixtures on the alkali-aggregate reaction[J]. Cement and Concrete Research. 1997, 27(12): 1899-1909
- Yu Y, Ran Q, Qiao M, et al. Interfacial interaction between polycarboxylate-based superplasticizer and cement component minerals and its impact on the hydration behavior[J]. Bulletin Chin Ceram Soc. 2012, 31(006): 1503-1507
- Plank J, Hirsch C. Impact of zeta potential of early cement hydration phases on superplasticizer adsorption[J]. Cement and concrete research. 2007, 37(4): 537-542
- Ferrari L, Kaufmann J, Winnefeld F, et al. Interaction of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements[J]. Journal of colloid and interface science. 2010, 347(1): 15-24
- Zhang C, Wang Z, Wang L, et al. Study on  $\zeta$ -potential of cement paste system[J]. Bulletin Chin Ceram Soc. 2013, 32(7): 1260-1268
- Chen L, Pan R, Ye P, et al. Strength and hydration property of fly ash-slag-cement composite cementitious materials[J]. Journal of Building Materials. 2010, 13(3): 380-384
- Wang C, Chen X, Zhang Y et al. A Study on High-Performance Concrete with Ground Granulated Blast Slag[J]. Port & Waterway Engineering. 2000, 8: 12-18
- Yu H, Wen Z, Sun W et al. Influences of slag content on chloride ion binding capacity of concrete[J]. J Chin Ceram Soc. 2007, 35(6): 801-806
- Elakneswaran Y, Nawa T, Kurumisawa K. Influence of surface charge on ingress of chloride ion in hardened pastes[J]. Materials and Structures. 2009, 42(1): 83-93
- Luo R, Cai Y, Wang C. Binding capability of chloride ions in mortar and paste with ground granulated blast furnace slag[J]. JOURNAL OF BUILDING MATERIALS. 2001, 4(2): 148-153
- Yang X, Huang K. The new method to calculate the complex effective permittivity of mixed aqueous electrolyte solution at microwave frequency [J]. ACTA ELECTRONICA SINICA, 2006, 34(2): 356-360.