



# Influence of polycarboxylate superplasticizer on chloride binding in cement paste



Wei Feng, Jinxia Xu\*, Ping Chen, Linhua Jiang, Yingbin Song, Yalong Cao

College of Mechanics and Materials, Hohai University, Nanjing 210098, PR China

## HIGHLIGHTS

- The influence of polycarboxylate superplasticizer on chloride binding in cement paste has been investigated.
- Equilibrium isotherms, kinetics and thermodynamics were thoroughly examined.
- A modified electrical double layer model has been proposed.

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## ABSTRACT

This paper aims to study the influence of polycarboxylate superplasticizer on chloride binding in cement paste. The equilibrium isotherms, kinetics and thermodynamics of chloride ions binding in cement with different contents of polycarboxylate superplasticizer were thoroughly examined. It has been found that all of the equilibrium isotherms data can be well fitted by the Langmuir isotherm and Freundlich isotherm. However, the amount of chloride equilibrium binding is decreased with the increase of polycarboxylate superplasticizer content. The kinetic data in the initial 24 h is well described by pseudo-first-order kinetic model and pseudo-second-order model is well suitable to describe the long-period adsorption kinetics data. The rate of chloride binding within 24 h is decreased with the increase of polycarboxylate superplasticizer content. The negative value of free energy, enthalpy and entropy of chloride binding are increased with the content of polycarboxylate superplasticizer, and the process of chloride binding in cement paste is spontaneous and exothermic. Based on the above results, the 'electrical double layer' model is used to describe the influence of polycarboxylate superplasticizer on chloride binding in cement paste.

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## 1. Introduction

When reinforced concrete structures exposure to chloride laden environment at a long time, chloride ions can penetrate from the environment into concrete [1,2]. During the process of chloride ions penetrate into concrete, some of them are bound in cement hydrates by physical adsorption or chemical combination and another part of the chloride ions are free in concrete pore solution. These free chloride ions can potentially destroy the protective layer of steel and induce steel corrosion [3]. Therefore, chloride binding is very important for the durability of reinforced concrete because it can reduce the free chloride ions concentration in the pore solution of concrete.

In general, there is a complicated process in chloride binding, which can be affected by many factors. For example, a higher external chloride ions concentration makes for a higher chloride binding capacity [4,5]. The different cations of chloride salts have different effects on the chloride binding [6,7]. In addition, the ability of chloride binding is decreased with the increase of temperature [8]. Besides, carbonation and sulphate attacks may decrease the chloride binding [9]. What is more, supplementary cementations materials such as silica fume, slag and fly ash are widely used to prepare the concrete with high resistance, which can affect the ability to bind chloride of concrete. The additions of fly ash and ground granulated blast furnace slag can increase the chloride binding. However, the addition of silica fume can decrease the chloride binding [10–12]. However, the influence of water reducing admixtures on chloride binding is not still clear until now.

In our previous study [13], it has been found that surfactants have a significant effect on the chloride binding in cement paste.

\* Corresponding author.

E-mail address: [xujinxia@hhu.edu.cn](mailto:xujinxia@hhu.edu.cn) (J. Xu).

The reason is due to the fact that the surfactants can be adsorbed on the surface of cement clinker and hydrates and change the properties of cement paste surface, especially surface charge [14]. The cationic surfactant can increase the chloride adsorption, because of the zeta potential of cement surface from negative to positive. In contrast, the anionic surfactant can reduce the chloride binding because the negative zeta potential of cement surface is increased [13]. Polycarboxylate superplasticizer (PCS), one of the most widely used water reducing admixtures usually is an anionic surfactant, which can potentially affect the chloride adsorption. It is significant for us to investigate the influence of polycarboxylate superplasticizer on chloride binding in cement.

The objective of this investigation is to study the influence of polycarboxylate superplasticizer on chloride binding in cement paste. The equilibrium isotherms, kinetics and thermodynamics of chloride binding in cement paste with different contents of polycarboxylate superplasticizer were thoroughly examined. In the experiment, polycarboxylate superplasticizer is directly added in mixing water to prepare the cement paste specimens, which represents its practical application. However, according to our previous investigation [13], the effect of surfactants on the chloride binding is irrelevant to the addition methods of the surfactants (added in mixing water or later added with paste powers in water).

## 2. Experiment

### 2.1. Materials and specimen preparations

In the experiment, No. 42.5 ordinary Portland cement was used. Its oxide composition was shown in Table 1. A kind of polycarboxylate superplasticizer was used as water reducing admixture. Its monomer was acrylic polyoxyethylene glycols (APEGS50) and technical properties were shown in Table 2. The aggressive chloride ions were provided by analytically pure sodium chloride. All of the solutions were prepared by the distilled water.

Cement pastes with water-to-binder ratios (W/C) of 0.2 and 0.3 were prepared. The different contents of polycarboxylate superplasticizer (0%, 0.5% and 1.0% by mass of cement) were directly added into the mixing water. The cement paste was cast in the mould with size of 40 mm × 40 mm × 160 mm. All the paste samples were demolded after 24 h. And then, paste samples for standard maintenance were sent to the standard curing box immediately. After waiting for 28 days, the paste samples were dried and were crushed to sieve into 0.3–2.3 mm particles. The powder specimens were dried in a vacuum oven and used for the experimental.

### 2.2. Experimental procedures

Equilibrium isotherms were obtained by isothermal adsorption testing method at 293 K. 20 g dried powder specimens were stored in 60 ml sealed containers with 0.004, 0.012, 0.08, 0.2, 0.6 and 1 M NaCl solutions saturated with Ca(OH)<sub>2</sub>, respectively. After this, the containers were stored at 20 ± 0.5 °C for 14 days in order to achieve equilibrium. And then, these solutions were collected to analyse chloride ions concentration.

Kinetics of chloride binding was investigated according to the following procedure. Firstly, 20 g powder specimen was added to 60 mL saturated Ca(OH)<sub>2</sub> solution with 0.2 mol/L NaCl. After waiting for different periods, the solutions were collected for chloride ions analysis. The experiment was carried out at constant temperature of 293 K.

Thermodynamics of chloride binding was investigated according to the procedure similar to that for equilibrium isotherms. The experiment was carried out at three temperatures of 293, 313 and 333 K, respectively.

The free chloride ions concentration in the solution was analysed by automatic potentiometric titrations using the 0.01 M AgNO<sub>3</sub> solution. Then, the amount of bound chloride ions is obtained from Eq. (1):

$$q_t = 35.453 * V * (C_i - C_t) / W \quad (1)$$

where  $q_t$  is the content of bound chloride ions, mg/g of the specimen;  $V$  is the volume of solution, mL;  $C_i$  is the initial chloride ions concentration of the solution, mol/L;  $C_t$  is the free chloride ions concentration of the solution at time  $t$ , mol/L;  $W$  is the mass of the dry specimen, g.

**Table 1**  
Chemical composition of cement (w.t%).

Oxide	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	Ignition loss
Composition	57.27	24.99	9.32	3.11	0.86	0.83	0.28	1.13	2.16

X-ray diffraction (XRD) measurement was carried out using D/Max-RB diffractometer with Cu K $\alpha$  radiation. The diffraction angle ( $2\theta$ ) was ranged from 5° to 60° and the scanning rate was kept at 2 (°/min).

## 3. Results and discussion

### 3.1. Equilibrium isotherms

The equilibrium isotherm is usually to describe the relationship between free and bound chloride ions over a range of chloride concentrations at a given temperature. It is obvious that the relationship between free and bound chloride ions is a not linear in this research (see Fig.1(a) and (b)). Two non-linear equations (Langmuir isotherm and Freundlich isotherm) can be applied to fit the experimental data.

The Langmuir isotherm is described as [15]:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (2)$$

where  $q_m$  is the saturated adsorption amount (mg·g<sup>-1</sup>) and  $K_L$  is the Langmuir constant.

The Freundlich isotherm is expressed as:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

where  $K_F$  and  $n$  are constants for Freundlich isotherm related to binding capacity [16].

The Langmuir isotherm and Freundlich isotherm are shown in Fig. 1(a) and (b), respectively.  $K_L$ ,  $q_m$ ,  $K_F$  and  $n$  can be determined from the two isotherms and their parameters are presented in Table 3. The  $R^2$  for the two isotherms are very close to 1, indicating Langmuir isotherm and Freundlich isotherm represent good fit of experimental data. The applicability of the two equilibrium isotherms does not changed by the addition of polycarboxylate superplasticizer. From the Table 3,  $q_m$  and  $K_F$  both are decreased with the increase of polycarboxylate superplasticizer content. The result reveals that the addition of polycarboxylate superplasticizer reduces the chloride binding. Furthermore, the saturated quantity of chloride binding is increased with the W/C at the same content of polycarboxylate superplasticizer. These results are good agreement with the previous literature [13].

### 3.2. Kinetics

The amount of bound chloride ions is shown as a function of time in Fig. 2. It is observed that the amount of bound chloride ions,  $q_t$  (mg/g) increases with time at different contents of polycarboxylate superplasticizer. Further,  $q_t$  is decreased with the increase of polycarboxylate superplasticizer content. As shown in Fig. 2, there are two separate stages for the process of chloride binding. Within the first 24 h, the chloride binding happens rapidly (the first stage). Subsequent to this, it proceeds at a slower rate (the second stage) until saturation. About 14 days were required for the binding equilibrium. The influence of polycarboxylate superplasticizer content on the equilibrium time is not obvious.

From the experimental results, it is suitable to describe two stages of chloride binding in cement paste by pseudo-first-order and pseudo-second-order kinetic models, respectively. In the initial stage, the physical adsorption process plays a leading role, so the pseudo-first-order is well used. In contrast, the pseudo-second-order kinetic equation is very suitable to describe the chlo-

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