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Releases of bound chlorides from chloride-admixed plain and blended cement pastes subjected to sulfate attacks

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HIGHLIGHTS

- We examine the releases of bound chloride by binders due to sulphate attack.
- The released chlorides are affected by water–binder ratio, total chloride, etc.
- During the sulphate attack, Friedel's salt transforms to ettringite.
- We discuss influences of mineral admixtures and sulphate types on corrosion risk.

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ABSTRACT

This paper reports results of a study conducted to evaluate the releases of bound chlorides from pastes made of ordinary Portland cement alone and a mixture of ordinary Portland cement and the partial replacements of cement with 10% silica fume (SF), 30% pulverised fly ash(PFA) and 50% ground granulated blastfurnace (GGBS) subjected to Na_2SO_4, K_2SO_4 and $MgSO_4$ attacks. The pastes were prepared by mixing water, cementitious materials and sodium chloride considering three levels of water/cementitious material ratios and four levels of sodium chloride. Powder samples collected by triturating the cement paste specimens were immersed in 5.0% Na_2SO_4, K_2SO_4 and $MgSO_4$ solutions, respectively for allowing releases of bound chlorides. The chloride concentrations and pH values of the leachates obtained by filtering the solutions were measured, and the chemical phases of insoluble powders in the solutions were analysed by X-ray diffractometer (XRD). It has been found that the bound chlorides are partially released by sulphate attacks to form free chlorides. The released chlorides are affected by the water–binder ratio, total chloride content, mineral admixtures and sulphates with different associated cation type. After the sulphate attacks, Friedel's salt has transformed to ettringite, which contributes to the releases of bound chlorides. Besides, by means of the index of Cl^-/OH^-, the influences of various mineral admixtures and sulphate types on the corrosion risk of steel reinforcement have also been discussed.

1. Introduction

The steel reinforcement in concrete is normally in a passive state against corrosion due to a thin iron oxide layer that is formed on the steel surface and remains stable in the high alkaline environment of the concrete. However, a localised breakdown of the passive layer occurs when a sufficient amount of chloride ions penetrated from the external environment reaches the steel reinforcement. The corrosion is then initiated. The corrosion of steel reinforcement induced by chloride ion contamination is now recognised as a major problem in the maintenance of the structural integrity of structures [1,2].

When the chloride ions are penetrated into concrete, they react with the products of binder hydration. As a result, some chloride ions are physically absorbed and chemically combined by the hydration products, and the rest remain free in the pore solution of concrete. It is generally believed that only the free chloride ions are responsible for depassivating the steel reinforcement in concrete [3]. On one hand, the chloride binding can reduce the free chloride ion concentration in the pore solution of concrete, and hence the corrosion risk is decreased. On the other hand, the chloride binding can remove the chloride ions from the diffusion flux, and consequently retards the process of chloride penetration. So, the chloride binding is generally accepted to be beneficial for the durability of reinforced concrete structure opposed to chloride-bearing environment [4,5].

However, the bound chlorides by the hydration products seem not to be firmly fixed. Glass et al. have reported that the bound chlo-

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Table 1
Oxide compositions of OPC, SF, PFA and GGBS used in this study (%).

	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SO_3	Ignition loss
OPC	22.55	9.34	61.28	3.10	1.03	1.35	0.15	0.99	0.16
SF	93.32	–	–	0.41	0.45	0.60	0.37	–	1.50
PFA	53.93	31.31	2.99	3.56	0.29	0.58	1.82	0.94	2.82
GGBS	33.60	20.30	27.40	1.00	0.41	13.50	0.33	0.20	0.48

rides have the pH dependent dissolution characteristics in concrete [6,7]. When the pH value falls to 11.5, most of bound chlorides are released as a result of the dissolution of several hydration phases. Because the carbonation can lower the concrete alkalinity to as low value as about pH 8.5, a similar release of bound chlorides appears when the chloride contaminated concrete is subjected to the atmospheric carbonation [8,9]. Moreover, Page and Vennesland [10] have stated that the solubility of Friedel's salt is increased in Portland cements blended with silica fume due to the pozzolanic reaction of silica fume. As soon as the bound chlorides are released to form free chloride ions in the pore solution of concrete, they are to take part in the diffusion into concrete and present the corrosion risk similar to the aggressive free chloride ions. It is significant for us to investigate the releases of bound chlorides so as to evaluate more accurately the durability of reinforced concrete structure opposed to chloride-bearing environment.

In previous literatures, it has been indicated that the sulphate ions obviously decrease the chloride binding capacity of hydration products [4,11]. The reason has been attributed to the preferential reaction of sulphate ions with C3A to produce ettringite, which inhibits the formation of Friedel's salt. Accordingly, it seems to be that ettringite is more stable than Friedel's salt under a suitable condition. Such a conclusion has been confirmed by Brown and Badger [12], who found that Friedel's salt can convert to ettringite in Na_2SO_4 solution. During this process of the conversion, it is anticipated that chemically bound chlorides can be released to form aggressive free chlorides. Moreover, the sulphate ions may compete with the chloride ions to adsorb physically on the C–S–H phase, which lead to the release of physically bound chlorides. Therefore, the sulphate attack is a potential factor that results in the release of bound chlorides in concrete. Despite this, no special investigation on the influence of sulphate ions on the release of bound chlorides by the hydration products can be found.

The aim of this study is to evaluate the releases of bound chlorides by ordinary Portland cement (OPC) alone and a mixture of ordinary Portland cement and the partial replacements of cement with 10% silica fume (SF), 30% pulverised fly ash(PFA) and 50% ground granulated blastfurnace(GGBS) subjected to Na_2SO_4, K_2SO_4 and $MgSO_4$ attacks. The experiment has been carried out by adding preliminarily sodium chloride into the mixing water to prepare pastes. Besides, the powders collected by triturating the pastes were immersed in 5.0% Na_2SO_4, K_2SO_4 and $MgSO_4$ solutions, respectively. The chloride concentrations and pH values of the leachates obtained by filtering the solutions were measured, and the chemical phases of insoluble powders in the solutions were analysed by X-ray diffractometer (XRD).

2. Experiment

2.1. Materials

The cement used in this work was No. 42.5 ordinary Portland cement (OPC) made in China. The SF, the graded II PFA and GGBS in accordance with Chinese standard GB/T 21236-2007, GB1596-2005 and GB/T 203-2008 were applied to replace partially the OPC at 10%, 30% and 50% by weight of binder, respectively. The oxide compositions of OPC, SF, PFA and GGBS were listed in Table 1. Three water to cementitious material ratios (W/CM ratios) of 0.22, 0.32 and 0.42 were studied. Four levels of chloride ions supplied by sodium chloride were preliminarily added to the mixing water (tap water), ranging from 0.5% to 3.0% by mass of binder. Moreover, all the chemical reagents used were analytically pure.

2.2. Specimen preparation and measurement

All the paste specimens with a size of 40 mm × 40 mm × 160 mm were cast in plastic molds. Subsequently, the molds were sealed and stored in a 95% humidity chamber at 20 ± 2 °C. For ensuring full hydration of binders, a long curing period of 4 months was adopted. After the curing, all the paste specimens were demolded.

At the end of the curing period, the demolded paste specimen was triturated until it passed through the sieve of 0.16 mm. Then, the powder was dried at the temperature of 60 °C to attain constant weight in a vacuum of about 10^{-3} Pa. Subsequently, 20 g powder was added to 200 ml solution in a sealed container. The solution contained 5.0% sodium, potassium or magnesium sulphate. Moreover, for the purpose of comparison, a control suspension by adding 20 g powder to 200 ml distilled water was prepared. The mixture was vigorously stirred for a period to attain a steady state. The steady state was identified by monitoring the pH and chloride concentration of one suspension until no significant changes were observed. As soon as the steady state was achieved, the suspension was filtered and analysed with a potentiometric titration against silver nitrate to determine the chloride content. During this process, an excessive amount of barium nitrate was added to remove the sulphate ions in the leachate in order to exclude their effects on the end-point of titration.

The leaching technique, which consists of mixing crushed or ground paste or mortar with a solvent (such as distilled water and ethyl alcohol) and measuring the amount of chloride ion passing into solution, had been extensively applied as an alternative method to determine the free chloride content [13]. The experimental procedure in this investigation was attempted to follow this technique so as to determine the free chloride content in the control specimen and the specimens subjected to Na_2SO_4, K_2SO_4 and $MgSO_4$ attacks. At this time, the free chloride contents were considered to be equal to the chloride contents measured in the leachates.

In addition, the pH value of the leachate was measured using a pH-meter. The powder after filtration was collected and dried. Subsequently, the X-ray diffraction instrument (D/Max-RB diffractometer with Cu Ka radiation) was employed to investigate the chemical phases of the powder sample. The scan from 5° to 40° (2θ) was made using a step size of 0.02°(2θ) and at a count time of 1°(2θ) per minute.

3. Experimental results

3.1. Chloride binding

The changes of bound chloride with W/CM ratio and the total chloride content of OPC paste specimens are presented in Fig. 1. For four levels of total chloride, the increase of W/CM ratio from 0.22 to 0.42 raises linearly the bound chloride in the suspension. Accordingly, the increase of W/CM ratio gives rise to the chloride binding. Moreover, the higher the content of total chloride is, the more obviously the chloride binding is increased.