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Influence of elevated temperature on release of bound chlorides from chloride-admixed plain and blended cement pastes

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HIGHLIGHTS

- We examine the release of bound chloride due to the elevated temperature.
- The amount of released chloride ions is affected by W/B ratio, total chloride, etc.
- We discuss influences of SF and GGBS on corrosion risk at different temperatures.

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ABSTRACT

This paper is aimed to evaluate the influence of elevated temperature on the release of bound chloride ions 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) and 50% ground granulated blast furnace slag (GGBS). Three ratios of water to binder (W/B) and four levels of total chloride ions were applied. The contents of free chloride ions and pH values in the pastes at different temperatures (0 °C, 20 °C, 40 °C and 60 °C) were determined by the measurements in the suspensions with 1:10 mass ratio of triturated paste powders to water. The results indicate that the increase of temperature can release partially the bound chloride ions. The amount of released chloride ion is dependent on the W/B ratio, content of total chloride ions and temperature range. Besides, the released chloride ions for the partial replacements of cement with 10% SF and 50% GGBS exhibits different trends with the temperature range. Furthermore, the influences of 10% SF and 50% GGBS on the corrosion risk of reinforcing steel at different temperatures are discussed by means of the index of Cl^-/OH^-.

1. Introduction

The chloride-induced corrosion of reinforcing steel is one of the most important factors governing durability of reinforced concrete structures. The products due to the steel corrosion have a larger volume than the steel, which will increase the tensile stress in concrete. Accordingly, the cracking and spalling of the concrete cover may be incurred. Meanwhile, the corrosion reduces the cross-sectional area of reinforcing steel. These results may lead to the loss of serviceability often much earlier than the designed service life of the structure [1–3].

The chloride ions can be introduced at the time of mixing or later penetrated into concrete. Anyway, the intruded chloride ions will react with the products of binder hydration in concrete. Some chloride ions are bound to the hydration products by physical absorption or chemical combination. The others remain free in the pore solution of concrete. Only the free chloride ions can be moved, and generally considered to be responsible for the corrosion of the reinforcing steel in concrete [4,5]. The chloride binding in the hydration products can lower the chloride concentration in the pore solution. Hence, it can retard the process of chloride ingress, and decrease the corrosion risk of reinforcing steel. A great effort has been made to produce the concrete with better capacity of chloride binding to extend the service life of concrete structure exposed to chloride-bearing environment [6–8].

Despite this, the bound chloride ions by the hydration products seem not to be firmly fixed. Under suitable conditions, the bound chloride ions can be released to form free chloride ions in the pore solution of concrete. Some factors may result in the release of bound chloride ions. For example, most of bound chloride ions can be released by acidification attacks [9,10]. When the chloride contaminated concrete is subjected to the atmospheric carbonation, a similar release of bound chloride ions can be found

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[11,12]. Besides, sulphate attacks can release partially the bound chloride ions [13,14]. The amounts of released chloride ions are affected by the water–binder ratio, total chloride content, mineral admixtures and sulphates with different associated cation type. Once the bound chloride ions are released, they will diffuse into concrete and present the corrosion risk similar to the aggressive free chloride ions. Therefore, the concrete with better capacity of chloride binding does not mean higher corrosion resistance, especially when the aforementioned factors are fulfilled. The durability of reinforced concrete structures opposed to chloride-bearing environment is greatly affected by the release of bound chloride ions, mainly leading to the increase in the amount and accelerating the transport of aggressive free chloride ions [15], and even altering the expression of critical chloride threshold level [10]. It is significant for us to explore the other potential factors resulting in the release of bound chloride ions so as to evaluate more accurately the durability of concrete structure opposed to chloride-bearing environment.

One of the possible factors is the increase of temperature. In early literatures [8,16], the increase of temperature has been found to reduce the chloride binding capacity of concrete. This phenomenon can be interpreted by analysing the influence of elevated temperature on the binding behaviour of chloride ions. For the physical adsorption, the increase of temperature gives rise to the thermal vibration of absorbed chloride ions. For the chemical combination, the elevated temperature may increase the solubility of the chemically combined products (Friedel's salt). In a similar way, it is naturally anticipated that the bound chloride ions in concrete may be released by the increase of temperature. However, there is still a lack of knowledge about the release of bound chloride ions due to the elevated temperature.

This paper is aimed to evaluate the influence of elevated temperature on the release of bound chloride ions 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) and 50% ground granulated blast furnace slag (GGBS). Three ratios of water to binder (W/B) and four levels of total chloride ions were applied. The contents of free chlorides and pH values in the pastes at different temperatures (0 °C, 20 °C, 40 °C and 60 °C) were determined by the measurements in the suspensions with 1:10 mass ratio of triturated paste powders to water. Furthermore, the influences of 10% SF and 50% GGBS on the corrosion risk of reinforcing steel at different temperatures are discussed by means of the index of Cl^-/OH^-.

2. Experiment

2.1. Materials and specimen preparation

The cement was No. 42.5 ordinary Portland cement (OPC) in accordance with Chinese standard GB175-2007. The SF and GGBS with the replacement levels of 10% and 50% by weight of total binder were in accordance with Chinese standard GB/T 21236-2007 and GB/T 203-2008, respectively. The oxide compositions of OPC, SF and GGBS are listed in Table 1. Tap water was used to prepare the paste and deionized water was adopted in the subsequent measurement of free chloride ions. All the chemical reagents used were analytically pure.

Three ratios of water to binder (*W*/*B*) (0.22, 0.32 and 0.42) were used. The detailed mixing proportions were indicated in Table 2. For the aim of saving the time and achieving representative results, the chloride ions supplied by sodium chloride were preliminarily added to the mixing water. The added amounts of chloride ions were 0.5%, 1.0%, 2.0% and 3.0% by mass of binder, respectively. The paste mixture was prepared using a planetary mixer in accordance with Chinese standard JC/T 729-2005. The mixing process was consisted of initially mixing with slow speed (rotation speed: 140 ± 5 rpm) for 120 s, then stopping for 15 s and eventually mixing with high speed (rotation speed: 285 ± 10 rpm) for 120 s.

Table 2
Mixing proportions of fabricated paste specimens.

W/*B* ratio	Quantity for 1L paste			
	Cement (g)	Water (g)	SF(g)	GGBS (g)
0.22	1807.20	397.60	–	–
	1626.50	397.60	180.70	–
	903.60	397.60	–	903.60
0.32	1530.60	489.80	–	–
	1377.60	489.80	153.00	–
	765.30	489.80	–	765.30
0.42	1327.40	557.50	–	–
	1194.70	557.50	132.70	–
	663.70	557.50	–	663.70

The size of paste specimens was 40 mm × 40 mm × 160 mm. Six paste specimens for each *W*/*B* ratio, total chloride ion content and binder type were fabricated. After one day of casting in plastic molds, they were demolded and cured in a 95% humidity chamber at 20 ± 2 °C. For ensuring full hydration of binders, a long curing period of 4 months was adopted.

2.2. Measurement

After the curing, the paste specimen was triturated until it passed through the sieve of 0.16 mm. Subsequently, the powder was dried at the temperature of 60 °C to attain constant weight in a vacuum of about 10^{-3} Pa. Then, 20 g powder was added to 200 ml deionized water in a sealed container. This mixture was controlled at a constant temperature. After vigorously stirred for a period to attain a steady state, the suspension was filtered and analysed with a potentiometric titration against silver nitrate to determine the chloride content. At the same time, the pH value of leachate was measured by a pH metre with accuracy of 0.01. It should be pointed out that different temperatures such as 0 °C, 20 °C, 40 °C and 60 °C were adopted in order to compare the results. Moreover, all the experiments were repeated three times.

Similar to our previous investigation [13], the above experimental procedure in this work was attempted to follow the leaching technique so as to determine the free chloride content. The leaching technique as an alternative method had been extensively applied, which consisted of mixing crushed or ground paste or mortar with a solvent (such as distilled water and ethyl alcohol) and measuring the amount of chloride ions passing into solution [17]. In this technique, the measured chloride content of leachate was considered to be the content of free chloride ions in the paste or mortar.

3. Results and discussion

Fig. 1 indicates the changes of bound chloride with *W*/*B* ratio and the total chloride content of OPC paste specimens at the temperature of 0 °C. With the increase of total chloride content, the amount of bound chloride ions is increased for the paste specimens with different *W*/*B* ratios. At relatively higher total chloride content (more than 1.0% by mass of binder), the amount of bound chloride ions is increased with the increase of *W*/*B* ratio. However, at lower total chloride content (1.0% by mass of binder or less), an initial increase and then decrease of bound chloride with the increase of *W*/*B* ratio can be obtained. There are similar changes of bound chloride with *W*/*B* ratio for the paste specimens at the other temperatures. This result is different from that in our previous investigation [13]. However, it is acceptable since the amount of bound

Table 1
Oxide compositions of OPC, SF 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	23.14	6.58	55.30	2.89	0.70	1.52	0.21	2.56	0.46
SF	93.32	–	–	0.41	0.45	0.60	0.37	–	1.50
GGBS	33.60	20.30	27.40	1.00	0.41	13.50	0.33	0.20	0.48