



Risk of chloride-induced corrosion of steel in SF concrete exposed to a chloride-bearing environment

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HIGHLIGHTS

- SF concrete had a lower resistance to chloride-induced corrosion, compared to OPC.
- Due to a lower binding capacity, the surface chloride for SF concrete was lower.
- The dense pore structure could produce a lower diffusion of chloride in SF concrete.
- SF concrete benefits substantially in increasing the corrosion-free life against OPC.

ARTICLE INFO

Article history:

Received 11 July 2017

Received in revised form 27 November 2017

Accepted 28 January 2018

Available online 22 February 2018

Keywords:

Silica fume

Chloride

Corrosion

Diffusion

Sensitivity

ABSTRACT

The present study concerns the resistance of silica fume (SF) concrete against chloride-induced corrosion, when SF concrete is built in a chloride-bearing environment. Chloride transport and critical chloride threshold level were experimentally obtained, which were subsequently used for the Fick's 2nd law to calculate the corrosion-free life. As a result, it was found that SF concrete had lower chloride transport in terms of the apparent diffusion coefficient, due to a refinement of the pore structure, resulting from a further formation of C-S-H gel in the cement matrix. Simultaneously, the surface chloride for SF concrete had a slightly lower range, arising from the lower capacity to bind chlorides. However, SF mortar imposed the increased corrosion risk. The chloride threshold for SF mortar accounted for 0.45% by weight of binder, while OPC produced 0.96%. Despite the increased corrosiveness in SF concrete, SF concrete produced the longer corrosion-free life, compared to OPC. From the sensitivity analysis, a reduction of the parametric values on chloride transport in SF concrete could significantly increase the corrosion-free life. For example, the apparent diffusion coefficient for SF concrete was about 74% reduced compared to OPC concrete, and thus the time to corrosion was 270% increased.

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1. Introduction

Silica fume (SF) has been preferred to admix in concrete mix, arising from its benefits of high early strength and low permeability. As the pozzolanic reaction of SF is very active to form the C-S-H gel, incorporating with precipitated $\text{Ca}(\text{OH})_2$, the distribution of pores is often shifted to smaller ones with the increased porosity more or less then to be resistive against permeation of external ions and molecules. Moreover, particles of SF are usually located at the interface between cement paste and aggregate [1], where is regarded as a source of weakness in concrete, leading to a further development of the concrete strength at an early age. These peculiarities of SF concrete could enhance the durability, in particular, increased resistance to sulfate attack [2], and to chloride-induced

corrosion, although the alkalinity of the pore solution is reduced. Thus, SF seems to be an essential material to fabricate high durable concrete in a severe and harsh environment, despite its economic limitation. In particular, the high resistance to chloride-induced corrosion made it possible to use SF in concrete mix in a marine environment, arising from low permeability of chloride ions.

The resistance of SF concrete to chloride-induced corrosion may result from delayed chloride transport, which has been confirmed by a number of studies from laboratories [3] and in situ [4,5]. SF concrete has basically pores distributed to smaller ones (i.e. mainly gel pores), which would be otherwise governed by capillary pores. Thus, ionic transport could be lowered in SF concrete. Moreover, the C-S-H gel overwhelmingly formed in the cement matrix may increase the surface area of hydrated fractions, which could physically adsorb chloride ions then to remove from the pore solution. Substantially, the mobility of chlorides would be reduced in SF

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matrix, thereby increasing the lifespan against the onset of corrosion.

To date, the corrosiveness of steel in SF concrete is not well established: due to the very high resistance to chloride transport, SF concrete is often expected to protect the embedded steel from corrosion. In fact, the SF concrete could be susceptible to depassivation on the steel surface, presumably due to low alkalinity of the pore solution and chloride binding capacity [6]. However, the pore solution in SF concrete could keep 12.5 or above in the pH at any replacement ratio [7], at which the pH value the embedded steel would be adequately protected by the passivation from corrosion. For chloride binding, SF paste imposed the lower capacity to chemically bind free chlorides in a previous study [8]. As the onset of corrosion accompanies a pH fall in the vicinity of the steel then to acidify the pore solution, all bound chlorides would be decomposed to free and participate in the corrosion process [9]. Thus, the chloride binding capacity itself may not reflect the corrosion resistance. Notwithstanding, the increased corrosiveness of SF concrete was previously reported with the half-cell potential [10] and corrosion rate [11] measured by the anodic polarisation or AC impedance techniques.

However, the increased corrosiveness was not usually taken in determining the serviceability of SF concrete structures (i.e. corrosion-free life or/and the time to corrosion) into account. To reflect the variation in concrete mixes in predicting the time to corrosion, the corrosiveness of embedded steel and chloride transport must be simultaneously considered. For SF concrete, the rate of chloride transport has been extensively investigated and well established, whereas information on the corrosiveness of steel in SF concrete is rarely addressed. Thus, in determining the serviceability of SF concrete, the rate of chloride transport obtained from either the experiment or computer-aided mathematical calculation is usually used as a parametric value to the risk of corrosion. For the corrosiveness, constant values such as 0.4% in normal concrete [12] and 0.2% in prestressed concrete [13] are instead used as the critical chloride threshold level to determine the time to corrosion, although these values are guided for OPC concrete rather than for other mixes containing supplementary cementitious materials. With this calculation, the corrosion-free life for SF concrete would be erroneously determined.

In the present study, the rate of chloride transport and the corrosion behaviour for SF concrete were simultaneously obtained from experiments. Chloride transport was determined by an exposure of the SF concrete specimens to salt solution for a given duration, which was expressed by the apparent diffusion coefficient and surface chloride concentration. To evaluate the corrosion behaviour, the corrosion potential and rate of steel in SF mortar were monitored. Then, the critical chloride threshold was obtained. With information of the corrosiveness and chloride transport, the serviceability of SF concrete was predicted by the sensitivity analysis against OPC concrete.

2. Experiments

To assess the resistance of SF concrete to chloride-induced corrosion, corrosion behaviour of steel, chloride transport and chemistry at chlorides were examined. The mix proportion for SF concrete of binder, water, sand (Grade M) and gravel by mass was 1.00: 0.45: 2.45: 3.25, which was modified by removing sand and gravel from the mixes depending on types of specimen. As binder, a mixture of SF and ordinary Portland cement (OPC) was used and the replacement ratio of SF to total binder was set 10% by mass. The oxide composition of SF and OPC and their physical properties are given in Table 1. The specific gravity of sand and gravel was 2.60 and 2.65 respectively, and the $G_{\max}$ of gravel was

in the lowest range (10 mm) to minimise the influence of gravel on chloride profiles.

For corrosion resistance, the SF mortar specimens were used to quantify the chloride threshold level for the onset of corrosion, which were again used to evaluate the pore distribution by the mercury intrusion porosimetry. The rate of chloride transport was determined by the apparent diffusion coefficient of chlorides in SF concrete immersed in a salt solution. The chemistry of chlorides in SF paste was assessed by determination of chloride binding capacity and buffering to a pH fall, assuming that aggregates have no influence on chemical reaction between paste and chloride ions.

2.1. Measurement of corrosion behaviour

To monitor the corrosiveness of steel, the SF mortar specimen ($\varnothing 50 \times 80$ mm) was fabricated, containing a centrally located steel rebar with 10.0 mm in the diameter then to produce 20 mm of the cover depth. To determine the corrosion resistance to chloride ions in variation, chlorides were admixed in mixing water by NaCl at 0.2, 0.4, 0.6, 1.0, 1.5, 2.0, 2.5 and 3.0% by weight of binder. The mortar specimen was cured by wrapping in a polythene film at 20 ± 2 °C for 28 days to avoid leaching-out of chlorides in liquid media, which would often occur in the process of a wet curing. Then, the specimen was subjected to a wet and dry cyclic condition (3 days wet and 4 days dry) in a moisture-control chamber to accelerate the corrosion process. After the completion of 20 cycles, the corrosion rate of steel in SF mortar was measured by the linear polarisation method.

Prior to measurements, the specimen was immersed in 0.5 M NaCl solution for 30 min to enhance the electric connectivity in the process of polarisation. The standard calomel electrode was used for reference and titanium mesh in the electrolyte for counter electrode, respectively. The corrosion potential was preliminarily measured in at half-cell potential. Then, the potential of steel rebar was swept at a low scan rate of about 0.1 mV/s to 25.0 mV above the corrosion potential to achieve the polarisation resistance. The electrical resistance of mortar (i.e. IR drop) was automatically compensated by using a current interruption technique. The schematic of the measurement set-up is given in Fig. 1. Once the polarisation resistance was obtained, the corrosion rate was calculated by the Ohm's law as given in Eq. (1).

$$I_{\text{CORR}} = \frac{B}{R_p} \quad (1)$$

where I_{CORR} is the corrosion rate (mA/m²); B is a constant for the potential (mV); and R_p is the polarisation resistance (Ωm^2). In this study, B was taken 26 mV at all measurements, assuming that corrosion always occurred.

2.2. Chloride transport

The apparent diffusion coefficient of chlorides in SF concrete was determined by chloride profiles of the specimen immersed in a chloride solution for 150 days. A 150 mm cube concrete specimen was manufactured and cured for 28 days in a damp chamber, which was subsequently cut by a diamond saw in the middle to produce the dimension of $150 \times 150 \times 75$ mm. After an 1 day drying process in the atmosphere, all surfaces of the specimen were coated by epoxy resin except for one surface, to lead one-dimension permeation of chloride ions. Then, the coated specimen was further cured in water for 7 days to saturate with water, followed by being immersed in 4 M NaCl solution. The chloride profiles were obtained from dust samples by grinding the surface of concrete specimen with an increment of 5.0 mm depth. The concentration of acid-soluble chloride in each dust sample was determined by titration, after the dust sample was diluted in a

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