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Fire's effect on chloride ingress related durability of concrete structure*

JIN Wei-liang, ZHANG Yi†‡
(*Structural Engineering Institute, Zhejiang University, Hangzhou 310027, China*)
†E-mail: zhangyi.zju@gmail.com

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Abstract: This paper describes the effects of fire on durability of reinforced concrete structures, and points out that fire not only damages the chemical composition and physical structure of concrete by high temperature, but also leads to an additional risk due to the generation of polyvinyl chloride (PVC) combustion gases. A mathematical model is proposed to calculate chloride ingress profiles in fire damaged concrete, so as to explore the service life prediction of the structure. Rapid Chloride Migration (RCM) test was carried out to determine the chloride diffusion coefficients for the application of the mathematical model. Finally, the detected results of a reported case testified to the validity of the mathematical model.

Key words: Fire, High temperature, Polyvinyl chloride (PVC), Mathematical model, Rapid Chloride Migration (RCM)
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INTRODUCTION

When fire breaks out in a building, the maximum temperature of the center area of the structure in fire is always as high as 1000 °C. In this case, both high strength concrete (HSC) and normal strength concrete (NSC) would be structurally damaged, only 9%~21% of the original compressive strength is left. However, in the sub-center area of fire, a certain distance away from the center, the temperature drops to below 500 °C, and the damage to the micro-structure of the material becomes comparably not serious. A much higher proportion at 52%~100% of its original compressive strength may be retained after fire (Ulrich, 1986; Mirza *et al*., 1991; Chew, 1993). Therefore, the assessment of a post-fire building is accordingly around the center area of the fire. Consequently, the repair engineering based on the assessment pays little attention to the structures in sub-center areas. However, recent researches indicated that when exposed to a lower temperature (i.e. temperature of sub-center area of fire) the concrete especially HSC may be getting worse permeability-related durability in contrast to the marginally small loss of mechanical strength (Chan *et al*., 1999; 2000; Luo *et al*., 2000; Poon *et al*., 2001). In addition, the concrete in sub-center area is often contaminated by polyvinyl chloride (PVC) combustion gases generated in the fire (Briesemann and Greger, 1970; Martin, 1975; Climent *et al*., 1998). As a result, the concrete will gradually and sometimes significantly lose its durability after fire. Therefore, great attention should be paid on the assessment of chloride ingress related durability of fire-damaged buildings, especially when PVC combustion is involved. Unfortunately, there is very little work available on the remaining service life prediction of fire-damaged building.

In order to explore the service life prediction of fire-damaged concrete structure, a mathematical model is proposed to calculate chloride ingress profiles in fire damaged concrete and experimental work is carried out to determine the chloride diffusion coefficient of high

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‡ Corresponding author

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temperature affected concrete for the model.

MATHEMATICAL MODEL OF CHLORIDE INGRESS

A marine environment and acid chloride gases generated in combustion of PVC are the two main sources of chloride ions which can penetrate into concrete. In high humidity environment like coastal areas, diffusion is considered to be the main mechanism of chloride ingress. Other mechanisms, not considered in this work, such as the capillary absorption, may operate for structures exposed to the atmospheric marine environment or exposed to fires involving PVC combustion. Fick's 2nd Law was used to describe the diffusion behaviors in concrete, under the simplified assumptions: homogeneous, isotropic and inert.

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(D_{\mathrm{Cl},t}\frac{\partial C}{\partial x}\right), \tag{1}$$

where C is percentage mass ratio of chloride concentration to concrete, t is time (s), x is distance from the surface (mm), and $D_{\mathrm{Cl},t}$ is non-stationary diffusion coefficient (mm^2/s), which is closely related to the porosity of concrete and is a power function of time for fire affected concrete:

$$D_{\mathrm{Cl},t}=(t_0/t)^m D_{\mathrm{Cl},0}, \tag{2}$$

where $D_{\mathrm{Cl},0}$ is an initial chloride diffusion coefficient (mm^2/s), t_0 is an initial time (s), and m is the recovery coefficient caused by rehydration.

Chloride concentration from PVC combustion

A steep gradient of chloride concentration with depth has been found in a concrete structure after PVC combustion and most of the chloride was detected in the outermost layer of the structure at a depth below 5 mm (Climent *et al*., 1998). The diffusion model may be established based on simplifications and assumptions as follows:

(1) From surface to interior of the fire damaged structure, the concrete is divided into two different parts as shown in Fig.1: the surface layer (0~5 mm) and the interior part (>5 mm);

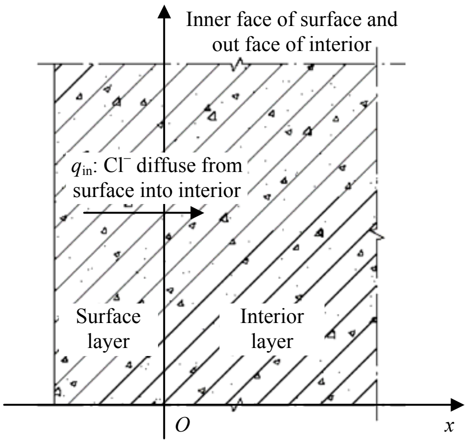

Fig.1 Model of the chloride ions diffusing from surface layer into interior layer of concrete after PVC combustion fire

(2) After PVC combustion involved fire, chloride ions are distributed averagely in the surface layer of concrete with the initial concentration of C_0. The initial condition can be represented by Eq.(3):

$$C_{\mathrm{s}}=C_0\ (t=0), \tag{3}$$

where C_{s} is concentration of chloride ion in the surface layer;

(3) There are no chloride ions distributed initially in the interior part of the concrete;

(4) As time elapses, the chloride ions in the surface layer will gradually penetrate into the interior part of the concrete with a steep gradient of concentration, and no additional chloride ions will penetrate into the surface layer from outside;

(5) The flux of chloride ions penetrating into the interior of the concrete q_{in} (1/s) is proportional to the concentration of chloride ions in the surface layer and can be expressed by Eq.(4):

$$q_{\mathrm{in}}=kC_{\mathrm{s}}=-\mathrm{d}C_{\mathrm{s}}/\mathrm{d}t\ (t>0), \tag{4}$$

where k is an inflow coefficient (1/s) (Yamada *et al*., 1999).

Combining Eq.(3) and Eq.(4) yields the concentration of chloride ions in the surface layer:

$$C_{\mathrm{s}}=C_0\mathrm{e}^{-kt}. \tag{5}$$

According to the principle of concentration continuity, the concentration $C_{x=0}$ of chloride at the interface between surface layer and interior part (Fig.1) is

$$C_{x=0}=C_{\mathrm{s}}=C_0\mathrm{e}^{-kt}. \tag{6}$$

Based on Fick's 2nd Law, the diffusion model of chloride ions in the interior layer can be derived from following conditions:

(1) Initial condition:

$$C=0\ (t=0). \tag{7}$$

(2) Boundary condition (semi-infinite medium):

$$C=\begin{cases} C_{\mathrm{s}}=C_0\mathrm{e}^{-kt}, & x=0; \\ 0, & x=\infty. \end{cases} \tag{8}$$

Finally, the diffusion model is derived based on the discrete method (Zhang, 2005):

$$\begin{aligned} &C_{\mathrm{in}}(x,t) \\ &=\sum_{n=1}^{\infty}\left\{\mathrm{e}^{-\gamma(n\pi)^2 t^{-m+1}}\frac{2kC_0}{n\pi}\left[\int \mathrm{e}^{-kt+\gamma(n\pi)^2 t^{-m+1}}\mathrm{d}t-\alpha\right]\sin(n\pi\chi)\right\} \\ &\quad +C_0\,\mathrm{e}^{-kt}(1-\chi), \end{aligned} \tag{9}$$

where n is the discrete parameter, m is recovery coefficient caused by rehydration, and l is the length of the semi-infinite medium, $l\rightarrow\infty$.

$$\chi=x/l,\ \alpha=\frac{D_0(n\pi/l)^2}{k(1-m)[-k+D_0(n\pi/l)^2]},\ \gamma=\frac{D_0t_0^m}{l^2(-m+1)}.$$

Chloride concentration from corrosive environment

Fire damaged concrete structures in a marine environment (ocean flat-forms, docks, ocean floor tunnels, etc.) and industry corrosion environment (industry factories) will lose part of their life-spans due to degraded resistance against invasion of chloride ions. The diffusion model may be written based on the following assumptions:

(1) The chloride in concrete structures before fire is distributed evenly in the cover depth with the concentration of C_0, which is equal to the total chloride mass of the concrete cover depth.

(2) When $x=0$ and $t>0$, the concentration C is equal to that in the surface of concrete, that is

$$C=C_{\mathrm{s}}. \tag{10}$$

The diffusion model of chloride ions, which come from marine environment into a fire affected concrete, can be derived from Fick's 2nd Law:

$$C_{x,t}=C_0+(C_{\mathrm{s}}-C_0)\left[1-erf\left(x\middle/\left(2\sqrt{\frac{1}{1-m}\left(\frac{t_0}{t}\right)^m D_{\mathrm{Cl,0}}t}\right)\right)\right], \tag{11}$$

where *erf* is the error function.

Eqs.(9) and (11) may be used as a base for service life prediction of fire-damaged concrete structures. The application of the models depends on their coefficients to be determined, among which C_0 can be detected in situ, k was studied (Yamada *et al.*, 1999), and the rest of $D_{\mathrm{Cl,0}}$ and m must be conducted by means of experiments.

EXPERIMENTAL DETAIL

Materials

Cylindrical samples 100 mm in diameter and 50 mm in height were prepared for three grades of concrete named NSC, HSC-1 and HSC-2 respectively, using ordinary Portland cement (OPC), 10~20 mm crushed granite, sand and super-plasticizer. The OPC complied with the requirements of BS12:1991. The mix proportions and the 28-day compressive strength are listed in Table 1.

Table 1 Mix proportion and compressive strength of three strength grade concretes

Type	w/c	Mix proportions (kg/m^3)				Compressive strength (MPa)
		Cement	Aggregate	Sand	Water	
NSC	0.51	398	1114	597	203	28.9
HSC-1	0.35	450	1080	608	158	50.5
HSC-2	0.28	520	998	624	145	72.9

Curing and heating regimes

The specimens were demolded 24 h after the casting and then transferred to an environmental chamber maintained at 20 °C and 90% RH. After 60 d ageing, the specimens were heated in an electric furnace up to 300, 500 and 700 °C in an electric furnace respectively, which were selected according to the typical values in the sub-center area of fires. Each temperature level was maintained for 2 h to achieve thermal steady state. The heating rate was set at 5 °C/min. The specimens then were allowed to cool down naturally to room temperature.

The heat treated samples were then placed in an environmental chamber at 20 °C and 75% RH representing typical climatic conditions in south China. Tests were done after 5, 25, 45 and 65 d of recurring respectively.

Test method

Conventional methods, such as diffusion-cell test or immersion test were adopted. In immersion test concrete samples are kept submerged in a chloride containing solution to measure the chloride ingress after certain testing period by chemical analysis of dust samples. The apparent diffusion coefficient can be derived by curve fitting technique based on Fick's 2nd Law of diffusion using obtained chloride profiles.

However, the chloride diffusion coefficient is highly dependent on the concrete porosity, and fire damaged concrete shows substantial porosity related recovery performance for the rehydration reaction. Therefore, the corresponding chloride diffusion coefficient is time-dependent and declines persistently in the test, so the test result had to be just a "mean value", while the derivation of recovery coefficient m in Eq.(2) calls for the "point value" versus time. Accordingly, a rapid chloride diffusion coefficient determination method is required.

The Rapid Chloride Migration (RCM) method of concrete test was proposed by DuraCrete (2000) and NT Build492 (1999). Earlier researches (Lay *et al.*, 2003) indicated that, for equal concrete compositions the chloride diffusion coefficient $D_{\mathrm{RCM},0}$ shows strong statistical correlation with effective diffusion coefficients (Although not considered in this work, the chloride diffusion coefficient also depends on the degree of water saturation of the concrete structure (Climent *et al.*, 2002)). Therefore, RCM test is proposed to determine the chloride diffusion coefficient of fire-damaged concrete here.

TEST RESULTS AND DISCUSSION

Compressive strength and chloride diffusion coefficient

The unstressed compressive strength and chloride diffusion coefficient of concrete before and after heating are listed in Table 2. Test results showed a distinct pattern of variation strength and chloride ingress resistance loss in each temperature range.

In temperature range of 20 °C to 300 °C, hydrated cement paste tends to shrink because of evaporation of planar water in the capillary. On the contrary, aggregates tend to expand under elevated temperature. The inharmony between the cement paste and aggregate leads to micro-cracks in the paste around the aggregates, which eventually lead to a loss of concrete compressive strength. However, as the free water evaporates from capillary, the dissolved calcium-hydroxide (CH) is separated out to form additional CH which contributes to the compressive strength of concrete. In addition, high temperature speeds up the process of hydration of unhydrated particles to form new gel in concrete. As a result, both NSC and HSC showed only a slight decrease of the original strength, which was 6%~18%. On the contrary, the appearance of micro-cracks in the paste cripples the resistance of concrete against the chloride ingress significantly, a sharp increase of chloride diffusion coefficient in concrete was observed at 648%~1651%.

Table 2 Compressive strength and chloride diffusion coefficients of concretes before and after elevated temperature

Type	f_c (MPa)				$D_{\mathrm{Cl},0}$ ($\times10^{-12}$ m^2/s)			
	20 °C	300 °C	500 °C	700 °C	20 °C	300 °C	500 °C	700 °C
NSC	28.9	23.70 (0.82)	15.03 (0.52)	8.09 (0.28)	3.52	22.80 (6.48)	25.00 (7.10)	63.51 (18.04)
HSC-1	50.5	46.46 (0.92)	37.37 (0.74)	18.18 (0.36)	1.69	22.21 (13.14)	22.41 (13.26)	51.74 (30.62)
HSC-2	72.9	68.52 (0.94)	54.68 (0.75)	22.60 (0.31)	1.26	20.81 (16.51)	21.07 (16.72)	34.56 (27.42)

In conclusion, concrete especially for HSC suffers great worsening of resistance against the chloride ingress in contrast to a marginally small loss of mechanical strength in the environment below 300 °C (a typical temperature in the sub-center area in the fire), which highlights the importance of the durability assessment of the concrete in the corresponding areas.

The temperature range of 300 °C to 500 °C corresponds to the decomposition of CH which is the important supporting material in the paste. Consequently, both NSC and HSC show significant losses of the compressive strength at 25%~48%. While the resistance against the chloride ingress decays at slower speed.

In the temperature range of 500 °C to 700 °C, calcium-silicate-hydrate (CSH) as the main supporting material in the paste decomposed gradually. Meanwhile, the quartz in concrete expands suddenly with the crystal structure transformation from *α* to *β* at 573 °C. The resulting high porosity and numerous micro-cracks in the paste degrade significantly both compressive strength and resistance against the chloride ingress. Test results showed that, for both NSC and HSC, only 28%~36% of original compressive strength remained after exposure to the elevated temperature of 700 °C. Furthermore, the corresponding chloride diffusion coefficients of concrete were 34.56~64.51 times larger than the original ones.

Recovery coefficients of chloride diffusivity

Test results of 5, 25, 45, 65 d after heating are plotted in Fig.2 showing that the chloride diffusion coefficients for high temperature affected concrete declined with time in every case. The test results were fitted into Eq.(2) to get the recovery coefficients. A higher recovery coefficient indicates better recovery performance of fire-damaged concrete in the resistance against the chloride ingress. The recovery coefficients of chloride diffusivity and the corresponding $\sqrt{R}$ are given in Table 3. The results indicated that though both HSC and NSC showed continuous decrease with temperature in the recovery performance; each temperature range also corresponds to a distinct pattern of recovery performance.

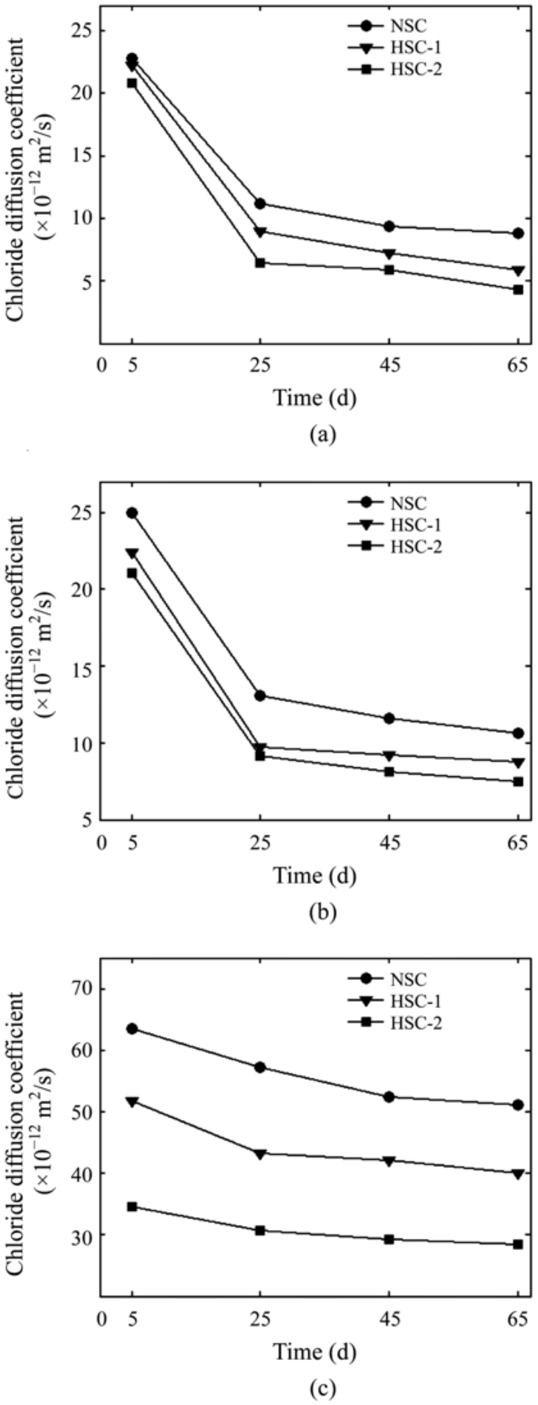

Fig.2 Chloride diffusion coefficient of different types of concrete decays with time after exposed to 300 °C (a), 500 °C (b) and 700 °C (c)

HSC has higher percentage of cement content than that of NSC. Accordingly, when exposed to a higher temperature (blow 500 °C) HSC tends to undergo more serious worsening of the resistance against chloride ingress than NSC due to the thermal instability of hardened cement paste (HCP).

Table 3 Recovering coefficients of diffusivity of concrete after elevated temperature

Type	m			$\sqrt{R}$		
	300 °C	500 °C	700 °C	300 °C	500 °C	700 °C
NSC	0.4041	0.3585	0.07913	0.9930	0.9902	0.9680
HSC-1	0.5294	0.4220	0.09985	0.9976	0.9680	0.9803
HSC-2	0.6422	0.4420	0.07517	0.9907	0.9850	0.9999

Correspondingly, when exposed to the occurring environment after fire, HSC shows better recovery performance than that of NSC for the partial restorability of the decomposition of CH and the evaporation of water. When exposed to temperature rises above 500 °C, the degraded resistance against chloride ingress of concrete can be hardly restored by post-fire curing due to the irrestorability of the decomposition of CSH and the transformation of crystal structure. Test results showed that after exposure to elevated temperatures of 300 °C and 500 °C, HSC always has higher recovery coefficient of diffusivity than that of NSC, while after exposure to 700 °C, both HSC and NSC showed poor recovery performance with very low recovery coefficients.

TEST EXAMPLE

The available samples were taken from the concrete beams of a factory which had a fire with thermal decomposition of 500 kg of PVC (Briesemann and Greger, 1970). The profile of detected chloride content vs depth in the interior layer of the beam 7 months after the PVC fire is shown in Fig.3. From data detected in situ and Tables 2 and 3, the calculated profiles based on Eq.(9) are also given in Fig.3 showing that the detected result is closer to the calculated profile with elevated temperature of 300 °C, which is in accord with the typical temperature range of the release of HCl gas from PVC thermal decomposition (240~351 °C) (Guo *et al*., 2000).

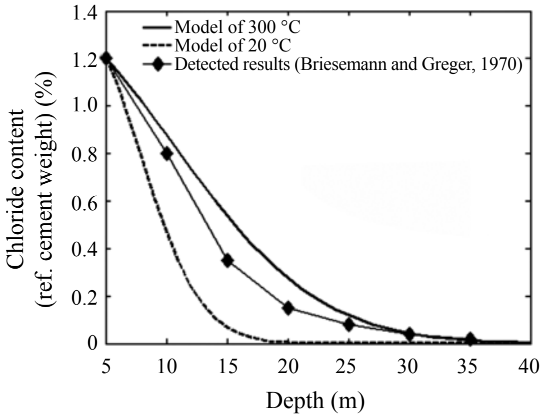

Fig.3 Detected and calculated profiles in the concrete 7 months after PVC combustion involved fire

CONCLUSION

(1) Fire affects the durability of concrete structures in many ways. Damages of micro-structures caused by high temperature disable the resistance of concrete against chloride ingress, and the HCl gas released by PVC combustion in fire would introduce additional chloride ions into concrete.

(2) Mathematical models are proposed to calculate the chloride ingress profiles in the concrete after fire. RCM test is used to determine the chloride diffusion coefficient of the fire-damaged concrete.

(3) Test results showed that concrete, especially for HSC suffers great worsening of resistance against chloride ingress in contrast to a marginally small loss of mechanical strength when exposed to a comparatively low temperature.

(4) Test results also indicated that fire-damaged concrete shows a substantial recovery performance in the resistance against the chloride ingress, and that the recovery performance degrades with the elevated temperature.

(5) Computed results based on the diffusion model Eq.(9) are rather close to the detected data from the concrete beams 7 months after a real PVC fire.

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