Pergamon

Cement and Concrete Research, Vol. 28, No. 2, pp. 209–219, 1998
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0008-8846/98 $19.00 + .00

PII S0008-8846(97)00270-6

CHLORIDE CONTAMINATION OF CONCRETE BY INTERACTION WITH PVC COMBUSTION GASES

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(Received January 14, 1997; in final form December 17, 1997)

ABSTRACT

Chloride contamination of concrete by interaction with PVC combustion gases has been studied in a small-scale testing chamber, which allows simulating the conditions probably prevailing in PVC fires of different magnitude through variation of the quotient between mass of burnt PVC and exposed concrete surface (PVC/S). In all cases, a steep gradient of chloride concentration with depth is found after the fire: most chloride is detected in the outermost layer at depths below 5 mm. Surface chloride contents (within 5 mm) for prestressed and reinforced concretes, tested with a high (PVC/S) ratio, are as high as 2.5 and 5% by weight of cement, respectively. Chloride concentrations in concrete near the steels are below the corrosion thresholds after the fire, but they can rise by diffusion to values able to induce rebar corrosion, especially if concrete is exposed to a humid atmosphere. *© 1998 Elsevier Science Ltd*

Introduction

Reinforced or prestressed concrete structural elements of a building may be damaged in fires, especially if they suffer the direct action of flames. When halogenated plastic materials are involved in the fire, there is an additional risk for mixed concrete-steel structures due to the generation of acid gases. These products can react directly with concrete, partially neutralizing its alkaline reserve and contaminating it with halide ions, whose depassivating and corrosive character for iron and its alloys is well-known. This contamination may be produced in locations far away from the ignition point. The corrosion of steel reinforcements is one of the factors that most seriously affect the durability of constructions, this being the cause of expensive repairs to maintain the functionality and safety of structures.

PVC is a thermoplastic material product of the polymerization of vinyl chloride. Its chlorine content is 56.7% in weight. As a consequence of its low price and varied properties, it has a wide range of applications (1): pipes, cables, furniture, shutters, floor and wall

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coatings, containers, packing materials, etc. The PVC resin content of manufactured products ranges from 50% for cable covers to more than 90% for pressure pipes.

Main products of the combustion of PVC in air are HCl, CO_2, CO, H_2O, and a great variety of organic compounds (2,3). Dehydrochloration of PVC, i.e., HCl liberation, is a rapid and practically quantitative reaction for temperatures between 250 and 300°C, both in air and nitrogen atmospheres (4). This process needs no flame, but is essentially a thermal decomposition. The corrosivity of the combustion products of PVC is due to HCl (5–9).

A number of papers (10–15) have shown that HCl(g) concentration is not constant in the atmospheres of enclosures where PVC has been burnt: it rises during the combustion to a peak value corresponding to less than half of the total chlorine in the sample, and afterwards this concentration decays progressively due to adsorption onto solid surfaces (gypsum, ceiling tiles, concrete, etc.), followed by a mixture of reaction and diffusion (10). Some experiments in which the effects of the most common construction materials were studied (14), showed that HCl decay is very fast on cement block or unpainted gypsum board (almost impossible to saturate with HCl) and almost as fast on ceiling tile and calcium silicate board. Saturation of HCl can be reached on painted gypsum board. An increase of the atmospheric humidity enhances the sorptivity of surfaces. Part of the generated HCl may be fixed as well by $CaCO_3$ used as a load in some PVC formulations (10), by metals at high temperature, such as copper of wires (12), and by smoke particulates (15).

Locher and Sprung (16) studied the chloride contamination of concrete specimens exposed, for 24 h, to a flowing atmosphere of constant and high HCl content (approximately 1.25×10^5 ppm). These authors demonstrated that chloride penetration into the specimens was deeper the lesser the cement content of concrete and the higher its porosity. Chloride ions diffused towards the interior of concrete when the specimens were maintained in humid atmospheres after the HCl exposure. Briesemann and Greger (17) and Martin (18) analysed samples taken from the prestressed concrete beams of a factory that suffered a fire with thermal decomposition of 500 Kg of PVC. The first samples were taken 7 months after the fire and the chloride concentrations found at the outermost layers of the beams were as high as 1.6% refered to cement weight at a depth of 5 mm and 0.6% at 20 mm. A progressive transport of chloride due to the concentration gradient was also observed.

Morris and Hopkinson (19) performed PVC combustion tests (59 Kg in a precinct of 34 m^3 of capacity) with exposure of different types of concrete. Chloride contents found at the surface of prestressed concrete specimens tested were up to 1.5% by weight of cement, nevertheless, the concentrations in the vicinity of reinforcement was less than 0.4% and did not increase after 12 months of storage.

The main objective of this work is to study the chloride contamination of samples of different commercial concretes in small-scale exposure tests to the combustion gases of PVC without direct action of fire. The number of variables that must be taken into account in tests aimed to evaluate the risk of corrosion of reinforcement in concrete due to combustion of PVC is high: mass of burnt PVC, absorbent surface exposed, concentration of HCl(g), temperature, ventilation effects, concrete properties, etc. Some of these parameters are difficult to be quantified and others may vary in the course of a real fire. The study parameter chosen in this work as the most relevant from the point of view of chloride contamination of concrete has been the quotient between the mass of burnt PVC and the area of absorbent surfaces exposed (PVC/S). An estimation of the order of magnitude of this ratio in household and commercial or industrial enclosures would allow us to simulate, in small-scale tests, the conditions probably prevailing in real PVC fires in such precincts.

Estimation of the Ratio (PVC/S)

An evaluation of the ratio (PVC/S) in lodgings is difficult because PVC is used in a wide range of applications. Nevertheless, its order of magnitude may be estimated taking into account the most likely indoor applications of PVC in dwelling houses: pipes, covers, and conduit protections of electric cables. The overall absorbent surface may be calculated as the sum of areas of ceilings, walls, and floors, considering, in a first approximation, that all porous materials present (painted or unpainted gypsum, concrete, etc.) have the same HCl absorption properties.

The estimations mentioned in the precedent paragraph have been performed for several houses of an approximately 90 m^2 dwelling area, leading to a total mass of 25 Kg of PVC per house and to a (PVC/S) ratio of approximately 5.4 mg PVC/cm^2. So, the values adopted for this ratio in the experiments performed in this work have been 5.4, 54, and 270 mg PVC/cm^2. The first figure (5.4 mg/cm^2) would be representative of a fire in a house, while the others (10 or 50 times higher) would correspond to fires in commercial or industrial enclosures where PVC is stored or produced.

For the sake of comparison, the calculated (PVC/S) ratio in the tests performed by Beitel et al. (10) with thermal decomposition of 9 m of PVC cable by electric overload in a 10 m^3 simulated plenum of a house is 0.7 mg PVC/cm^2. A rough estimation of this ratio in the experiments by Morris and Hopkinson (19) leads to a value of 45 mg PVC/cm^2, taking into account only the absorbent surface due to the ceiling, floor, and concrete block walls (the area of the concrete specimens exposed was not reported) and supposing a PVC resin content of 75% in weight of the PVC fire load (corrugated profile sheet attached to the walls).

It is worth noting that, in the case of houses, some PVC objects are not likely to be involved in a fire, for example pipes. On the other hand, the PVC load present may be eventually high due to other applications: floor and wall coatings, containers, furniture, etc. Anyway, it is unlikely that a high HCl(g) concentration be reached in a house fire, due to the non-localized disposition of the PVC load, and so, severe chloride contamination of concrete is not expected to be produced. In this sense, the (PVC/S) value adopted in this work for lodging fires (5.4 mg/cm^2) may be considered as a conservative value.

Experimental

Polyvinyl Chloride

Pure PVC resin (Solvic 264 GC, Hispavic Industrial, Solvay) was used throughout this work.

Combustion Chamber and Thermal Decomposition System

The combustion chamber, with dimensions of 40 × 40 (height) × 80 cm, was constructed in a polymethylmethacrylate (PMMA) sheet of 14 mm in thickness (Fig. 1). It had a lid with a neoprene gasket and screws to ensure its airtightness, and was provided with two PMMA tubes, 8 mm in diameter, that allowed the ingress and purge of liquid water.

A vitrified ceramic hot-plate, with dimensions of 22 × 22 cm, was used for the thermal decomposition of PVC resin samples. All external metallic parts were removed from the plate and the electronic power controls located outside the chamber. This procedure had the

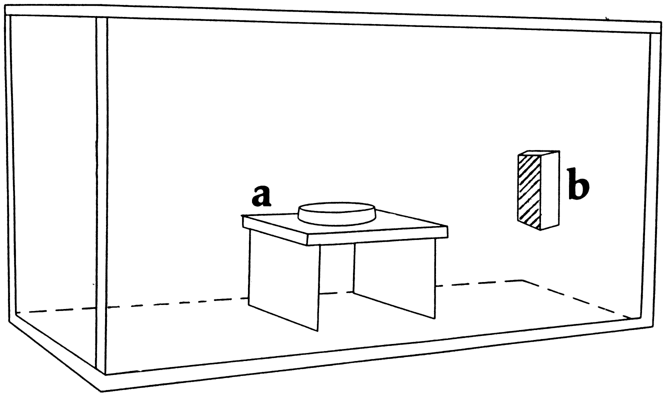

FIG. 1.
Combustion chamber sketch. **a**: Hot plate. **b**: Typical position of a concrete specimen, showing the exposed surface (shaded).

advantages of providing a wide heating area, minimum metallic hot surfaces that could react with HCl(g) (12) and enough heating power. Several calibration tests were performed to know the maximum weight of PVC resin that could be completely decomposed, which was found to be about 15 g; and the heating power and times needed for a total sample decomposition without danger for the PMMA chamber. PVC samples were located on a Pyrex Petri dish over the hot-plate.

Concrete Specimens

The prismatic specimens tested (4 × 4 × 15 cm) were obtained from some commercial concretes whose characteristics are summarised in Table 1. Compressive strengths and mix proportions were provided by the manufacturers except for the bulk concrete, whose proportions were determined by analysis in a control laboratory. Porosities were measured through the hydrostatic balance method.

The surfaces exposed to the combustion gases of PVC were natural faces generated by contact with the moulds except for the bulk concrete specimens where cut surfaces were used. All concrete specimens were exposed to the laboratory atmospheric humidity (50–65%) for at least a month before testing them.

TABLE 1
Characteristics of the concretes tested.

Material	Cement content (Kg/m^3)	Aggregate content (Kg/m^3)	Water content (L/m^3)	Compressive strength (MPa)	Porosity (%)
Prestressed beam	368	1759	99	44	13.6
Reinforced beam	312	1679	224	19	17.7
Bulk concrete	268	1740	226	20	15.9

TABLE 2
Data relative to the exposure tests of concrete specimens to the combustion gases of PVC (mean values).

(PVC/S) (mg/cm^2)	Mass of burnt PVC (g)	Concrete area exposed (cm^2)	Theoretical max. HC1(g) concent. (ppm)
5.4	2.075	384.3	6950
54	12.926	239.4	43300
270	12.900	47.8	43210

Exposure Conditions

The amounts of PVC resin decomposed and the exposed concrete areas were adjusted so as to give the (PVC/S) values selected, see precedent paragraphs. Normally, a single face of each specimen (between 45 and 65 cm^2) was exposed, the remaining faces being protected with insulating tape.

Some previous tests were performed with a single type of concrete to decide the most appropriate disposition of the specimens within the chamber. The chloride contamination of the samples located at ceiling or medium height was found to be similar, except for the singular point situated just above the hot-plate; while the floor positions induced a substantially lower chloride contamination. So, the concrete specimens were always located at equidistant distances from the center of the heating plate (25 cm) and at a medium height (12 cm from the floor, see Fig. 1). Due to this experimental disposition the exposed concrete surfaces did not receive much radiation from the plate during the combustions and their surface temperature, although not measured, may have reached values similar or slightly higher than those of the internal atmosphere of the chamber (30–35°C).

Table 2 summarises the conditions of the exposure tests performed in this work. The theoretical maximum HCl(g) concentrations correspond to the values that would have been reached after completion of dehydrochloration without HCl decay, i.e., if all HCl had remained in the gaseous phase. The calculated value corresponding to the (PVC/S) ratio of 5.4, i.e., 6950 ppm, is comparable to the figure of 7900 calculated for the tests performed by Beitel et al. (10) with thermal decomposition of PVC cable in a plenum of a house.

The relative atmospheric humidity in the chamber before testing was always between 50 and 65%, but the releasing of $H_2O(g)$ during thermal decomposition of PVC and the dew point raising due to the presence of HCl(g) (16) led to water steam saturation of the chamber atmosphere during the tests. This fact could be appreciated by the condensation of liquid on the chamber walls.

The exposure tests lasted 30 min., after which the floor of the chamber was flooded with water without touching the concrete specimens. The chamber was opened 24 h later. The aim of this experimental program is to simulate the conditions of a fire without direct action of flames on concrete and quenching with water that produces a humid atmosphere after the fire.

The increase of pressure in the chamber during combustions by HCl(g) and $H_2O(g)$ production and by heating of gases was low, due to the high internal volume of the chamber (115 L), to the limited mass of the burnt PVC samples (see precedent paragraphs), and to the fact that high temperatures were not developed within the chamber in the course of these tests. In any case, some proofs with pH indicator paper in the surroundings of the neoprene gasket and the liquid ingress and purge tubes showed that no HCl(g) escaped from the chamber.

Chloride Diffusion Tests

Some reinforced beam specimens, tested with a (PVC/S) ratio of 54 mg PVC/cm^2, were kept in closed containers with 50 and 95% relative humidity atmospheres. After a storage of 16 months in these conditions, they were taken for sampling and analysis in order to study the diffusion of chloride towards the interior of concrete.

Sampling and Analytical Techniques

Concrete samples were obtained through dry drilling with a 12-mm bit at different depths from the exposed surface: 0 to 5 mm; 5 to 10 mm; 10 to 20 mm; and 20 to 30 mm. In all cases, concrete powder was obtained from several points (at least three) on the specimen tested. Special care was taken in order to avoid contamination of each sample with powder coming from another depth interval. Powdered samples were kept in plastic containers until total chloride analyses (extraction with nitric acid) were performed by potentiometric titration against a silver nitrate solution, with an ionic selective electrode. Control analyses were performed on specimens non-exposed to PVC combustion gases and all concrete analytical results were corrected with their corresponding initial chloride contents. After sampling, the specimens were broken with a flexural strength machine, and the new surface generated was tested with phenolphthalein in order to measure the penetration of the alkalinity reduction front.

Results and Discusion

Figure 2 shows the influence of the ratio (PVC/S) on the chloride contamination of the three types of concrete under study, just 24 h after exposure to the combustion gases of PVC, and at different depths from the exposed surface. For all values of the (PVC/S) ratio tested and all concretes there is a steep gradient of Cl^- concentration between the outermost layer and more internal concrete layers, in agreement with results reached by Morris and Hopkinson (19). The Cl^- contents found for the 5- to 10-mm samples are always less than 10% of those corresponding to the 0- to 5-mm ones.

Surface chloride concentrations (first 5 mm) are approximately 1% by weight of cement for all materials tested with a (PVC/S) of 5.4 mg/cm^2, typical of house fires. For (PVC/S) ratios of 54 and 270 mg/cm^2, representative of fires in commercial or industrial enclosures where PVC is stored or produced, the influence of the nature of each concrete is more notorious: reinforced beam specimens have the most absorbent surface against HCl(g) showing surface Cl^- contents of about 5% by weight of cement, while this concentration ranges from 2 to 2.6% for prestressed concrete and from 1.6 to 2.2% for bulk concrete. The HCl(g) absorption behaviour of reinforced concrete may be explained by its high porosity (see experimental section); but, surprisingly, bulk concrete shows a lower surface Cl^- contamination than prestressed concrete, contradicting the expected relationship between porosity and hydrogen chloride absorption capacity (16). Nevertheless, this experimental

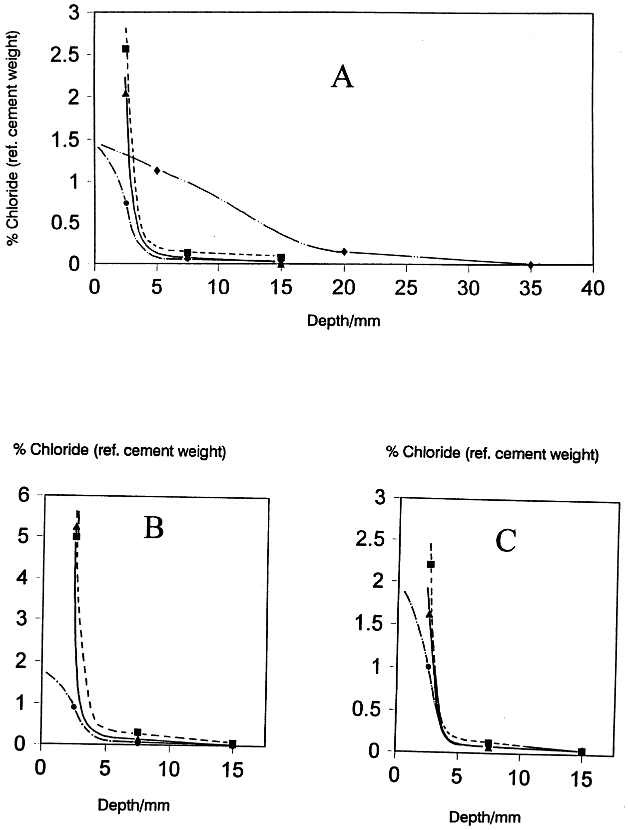

FIG. 2.

Chloride concentrations in concrete after exposure to PVC combustion gases. **A**: Prestressed beam specimens; **B**: reinforced beam; **C**: bulk concrete.
(PVC/S) ratios in mg/cm^2: (—·—●—·—):5.4; (——▲——):54; (— —■— —):270.
(—··—◆—··—): Data from ref. (17) corresponding to prestressed beams analysed 7 months after a real PVC fire (values corrected with its initial chloride content).

finding may be attributed to the different nature of the surfaces exposed to PVC combustion gases: natural faces generated by contact with the moulds for reinforced and prestressed beams and cut faces for bulk concrete. Natural surfaces have an outermost layer rich in cement paste, which probably acts as an effective sink for HCl(g) and is absent on cut surfaces, in addition to the superficial aggregate particles present in the latter. These considerations would help to explain the less absorbent and reactive character against hydrogen chloride shown by bulk concrete specimens.

Evaluation of risk of corrosion of reinforcement due to the presence of chloride implies the adoption of a critical Cl^- concentration threshold in the surroundings of embedded steels. In this work, the values of 0.4 and 0.2% refered to cement weight have been adopted for reinforced (20) and for prestressed concrete (21), respectively. The assumed rebar covers have been taken as the minima prescribed by Spanish normative: 8 to 10 mm for prestressed

TABLE 3
Percentage chloride absorption of concrete specimens referred to total chlorine released by the burnt PVC samples.

(PVC/S) (mg/cm^2)	Individual $C1^-$ absorption* (%)	Total Cl^- absorption (%)	Total concrete surface/PMMA surface (%)
5.4	5–9	54	2.5
54	1.5–8.3	15	1.5
270	2.3–6.2	2.3–6.2	0.3

*The exposed concrete surface of a single specimen is 0.3% of the internal PMMA surface in the chamber.

and 20 mm for reinforced concrete at indoor or slightly wet outdoor exposure conditions (20,21).

Chloride concentrations at the assumed depths of rebar steels are always lower than the corresponding corrosion thresholds as may be appreciated in Figure 2. Nevertheless, prestressed concrete tested with (PVC/S) ratios of 54 and 270 mg/cm^2 shows Cl^- contents at a depth of 7.5 mm of 0.09 and 0.13% by weight of cement, respectively. These values are relatively close to the arbitrary critical concentration of 0.2% taken for prestressed elements (21) and so, corrosion of the steel wires could eventually occur in the short term.

A comparison between the Cl^- contents found for the concretes under study and those obtained by Briesemann and Greger (17) for prestressed concrete beams contaminated by Cl^- due to a real PVC fire may be performed in Figure 2A. Data from both origins may be considered as consistent because the latter were obtained from samples taken 7 months after the fire, when Cl^- ions might have diffused to the interior of concrete to a certain extent. Surface Cl^- concentrations in prestressed concrete specimens submitted by Morris and Hopkinson (19) to a PVC fire experiment, ranging from 0.4 to 1.6% refered to cement weight, may also be considered as in agreement with the results obtained in this work, taking into account that the latter authors probably used a (PVC/S) ratio lower than 45 mg/cm^2 (see precedent sections) and the depth interval of sampling is not specified in their article. So, the small-scale testing system proposed in this work seems to be able to reproduce the distribution of Cl^- concentrations laden in concrete by a real PVC fire and even to match the real surface chloride contents by an appropriate modulation of the (PVC/S) parameter. The scarcity of data from real PVC fires prevents further assessments of the validity of this small-scale system, whose main advantages are its low cost and short testing times, which allows the acquisition of a large number of data.

All specimens exposed to PVC combustion gases were tested with phenolphthalein showing a negligible penetration of the alkalinity reduction front by comparison with the non-exposed control specimens. This experimental fact is in agreement with previously reported results (17–19).

It is worthwhile to study the collection efficiency of concrete for hydrogen chloride in these experiments. Table 3 shows the integrated amounts of Cl^- absorbed both by individual and by all specimens tested with a single PVC/S ratio, expressed as percentages refered to

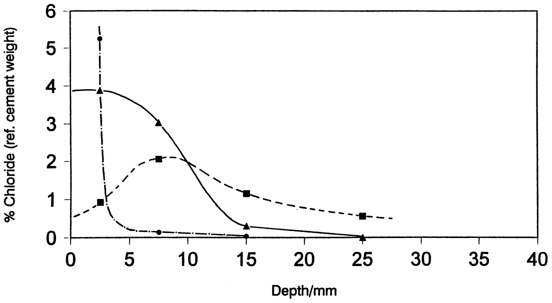

FIG. 3.

Chloride concentrations found in reinforced concrete specimens tested with a (PVC/S) ratio of 54 mg/cm^2. (—·— ● —·—): After the fire; (—— ▲ ——): 16-month storage in a 50% relative humidity atmosphere; (— — ■ — —): 16-month storage in a 95% relative humidity atmosphere.

total chlorine released by the burnt PVC samples. Total Cl^- absorptions are always an order of magnitude higher than the corresponding quotients between exposed concrete surface and total internal PMMA surface in the combustion chamber (fourth column in Table 3). This fact points to a scavenging action of gaseous hydrogen chloride by concrete. Note the high HCl collection efficiency of concrete for a low PVC/S ratio (5.4 mg/cm^2). In this case, 54% of the total available chlorine has been absorbed by concrete, whose surface represents only 2.5% of the total internal surface of the chamber. These results are in agreement with the great HCl absorption capacity of concrete and other porous materials found by Galloway et al. (14).

Figure 3 shows the Cl^- concentrations distribution in reinforced concrete specimens tested with a (PVC/S) ratio of 54 mg/cm^2 and stored for 16 months in containers with 50 and 95% relative humidity as well as the data obtained just after the exposure test. The net transport of Cl^- towards the interior of concrete with time and its strong enhancement by a high humidity environment may be clearly appreciated in Figure 3. Chloride contents at a depth of 20 mm (nominal cover of steel), which are practically negligible after the fire and after a 16-month storage in 50% relative humidity, rise to values of about 0.8% refered to cement weight in the case of a 95% relative humidity exposure.

The effect of some other variables that may have important influences in real PVC fires affecting concrete, such as humidity of concrete previous to test, ventilation effects, extensive heating or direct action of fire on concrete, etc. have not been studied in this work, but are currently under research. This prevents a direct extrapolation of these results to real fires. Nevertheless a distribution of chloride in concrete just after the fire with most Cl^- present in the outermost layers seems to be a common pattern in all cases studied in this work and in higher scale tests where ventilation of the combustion chamber was allowed (19). So, the convenience of an early undertaking of the concrete reparation works after a PVC fire must be stressed. A high pressure water cleaning or a sandblasting taking off a 5-mm superficial layer may remove most of the Cl^- present in concrete just after the PVC fire. On the other hand, a prolonged exposure to a humid atmosphere after the fire may bring Cl^- ions to the interior of concrete, leading to concentrations in the surroundings of steel able to unchain the corrosion of rebars.

Conclusions

A small-scale system for studying the chloride contamination of concrete by interaction with PVC combustion gases has been developed. By selecting the appropriate (PVC/S) ratio in these experiments, a simulation of the conditions probably prevailing in real PVC fires of different magnitude may be obtained.

Tests carried out with this system reproduce the distribution of Cl^- contents found in concrete after large-scale PVC fires. In all cases, an important gradient of Cl^- concentration with depth is observed: most of the chloride is detected in the outermost layer, at depths below 5 mm. Surface Cl^- contents, within the first 5 mm, for prestressed and reinforced concrete specimens tested with a high (PVC/S) ratio, representative of a large PVC load fire (commercial or industrial enclosures), are as high as 2.5 and 5% by weight of cement, respectively. Chloride concentrations found in the surroundings of steels are always lower than the corresponding thresholds considered to provoke corrosion. Only prestressed specimens tested with large (PVC/S) ratios show Cl^- concentrations near the steels that approach the arbitrary limit of 0.2% by weight of cement and that eventually could induce corrosion in the short term.

Cut surfaces of concrete are less sorptive and reactive against HCl(g) than natural concrete faces, probably due to the superficial cement-paste-rich layer present in the latter.

Chloride ions laden in concrete by a PVC fire may diffuse towards the interior of concrete, eventually leading to dangerous concentrations near the steels, especially if the concrete elements are exposed to a high humidity environment. For this reason, it is convenient to undertake the concrete reparation works, for instance cleaning through high pressure water or sandblasting, as soon as possible after the fire.

Acknowledgments

This work has been financially supported by a grant from Fundación Mapfre and by the Consellería d'Educació i Ciència de la Generalitat Valenciana through project GV-3224/95. We also thank Prof. Andrade for her advice and valuable comments, and Prof. Saval and the company Cerámica Saval for providing the concrete beams samples tested.

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