RESEARCH ARTICLE

Long-term durability of onshore coated concrete —chloride ion and carbonation effects

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ABSTRACT   Enhancing service life of reinforced concrete (RC) structures located in marine environments is an issue of great interest for design engineers. The present research addresses the effect of surface coatings on service life of onshore RC structures. Long-term performance of concrete samples up to 88 months of exposure at natural marine environment was investigated. Two onshore exposure conditions, including soil and atmosphere and different types of concrete coatings were studied. Carbonation rates of up to 0.5 and 1.5 mm/year were observed at the first 88 months of exposure for soil and atmospheric samples, respectively. Surface chloride ion build-up and variation in chloride ion diffusion were monitored with respect to time, and service life was estimated. Based on the obtained results it is proposed to use the aliphatic acrylic and polyurethane coatings for enhancing the service life of concrete structures in the investigated exposure conditions.

KEYWORDS   carbonation, chloride ion, corrosion, service life, surface coating

1   Introduction

Reinforcing bars embedded in concrete are covered by a thin oxide layer surrounded by an alkali environment. Formation of hydroxide ions as a result of cement hydration is the main source for this alkalinity and passive state of the oxide layer on the surface of steel rebar. However, this layer will be depassivated under two main circumstances: (1) drop in pH of the surrounding concrete to values lower than 9 [1]; (2) increase in chloride ion concentration on rebar surface to values higher than certain thresholds.

Reinforced concrete (RC) structures located in Persian Gulf region are experiencing serious risk of corrosion induced by synergic effect of carbonation and chloride ion ingress. This is due to the increasing concentration of atmospheric carbon dioxide as a result of petro-chemical activities [2] and high concentration of chloride ions available in the gulf water. Diffusion of carbon dioxide into concrete is one of the major causes of the aforementioned drop in pH. While diffused into concrete, CO_2 reacts with hydration products, and in particular with calcium hydroxide and C-S-H phases which results in a drastic drop in alkalinity [3]:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (1)$$

$$C\text{-}S\text{-}H + 2CO_2 \rightarrow SiO_2 + 2CaCO_3 + H_2O \qquad (2)$$
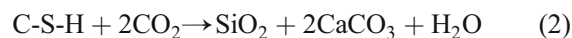
In addition, increase in chloride ion concentration around the reinforcing steel (typical of marine environments) is the other reason for destroying the passive film and corrosion initiation [3]:

$$Fe^{2+} + 2Cl^- \rightarrow FeCl_2 \qquad (3)$$

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2HCl \qquad (4)$$

Considerable research in the field of concrete durability is devoted to investigating the effect of carbonation or chloride ion penetration into concrete. However, few

projects are dealing with the simultaneous effects of these mechanisms. Even in the case of coupled effects, most of the research is based on accelerated test environments [3,4]. Given the micro-structural modifications caused by each of these phenomena, studying the behavior at natural test conditions is a necessity. This is of special interest in the case of methodologies that investigate durability of concrete, including surface treatments, etc.

Incorporation of surface coatings is an economic choice for increasing corrosion resistance in aggressive environments by reducing the rate of moisture, gas, and aggressive ions transfer into concrete [5,6]. However, given the fact that exposure conditions affect the life time and performance of various coating types, it is required to investigate the long-term performance of concrete surface coatings before employment in construction projects [7].

This paper addresses the long-term durability of coated and non-coated concrete samples at Persian Gulf region. Two different exposure conditions, including "soil" and "atmosphere" are investigated. RC structures are facing the risk of corrosion induced by chloride ions and carbonation at these exposures. Laboratory cast specimens were exposed to natural onshore marine environments up to 88 months. Sampling was conducted at various time intervals to monitor durability. Slices were extracted at each time step, transported back to the laboratory, and investigated for carbonation depth and chloride ion concentration.

2 Experimental program

The following section discusses materials, mixture proportions, curing and exposure conditions.

2.1 Mixture properties

Concrete mixture proportions are presented in Table 1. The reference concrete was proportioned with water-to-cement ratio (w/c) of 0.5. The same mixture was employed for casting the coated specimens. The relatively high w/c of 0.5 magnifies the effect of surface coatings on chloride ion and CO_2 penetration into concrete. A second concrete mixture was prepared with w/c of 0.4. The cement used in preparing the mixtures was portland cement equivalent to ASTM Type II qualifications. Both of the concrete mixtures were proportioned with 400 kg/m^3 of cement. The aggregates used were crushed limestone graded according to ASTM C33 [8]. Coarse aggregate had maximum size of 12.5 mm, absorption of 1.9%, and bulk specific gravity of 2.79. Fine aggregate had maximum size of 4.0 mm, absorption of 3.2%, bulk specific gravity of 2.59, and fineness modulus of 3.29.

Three concrete surface coatings, including polyurethane (PU), aliphatic acrylic (AA), and polymer modified cementitious coating (CPD) are compared in this study

Table 1 Concrete mixture proportions (kg/m^3)

mixture	water	cement	fine aggregate	coarse aggregate
Ref	200	400	778	956
w/c 0.4	160	400	836	1022

as described in Table 2. The selection was made in order to cover some of the most commonly used types of compounds commercially available in the area. Coating application procedures and dosages were based on manufacturer instructions and recommendations.

As the carbonation and chloride ion ingress may be affected by various factors such as the mixture properties, curing conditions, and consolidation, etc., coated specimens were prepared with the same mixture, consolidation method, and curing conditions. This way, it may be concluded that the differences in carbonation depth and chloride concentration may be traced in the performance of the coatings.

2.2 Casting and curing of specimens

Specimens were prepared at the CMI Laboratory, University of Tehran. The concrete mixtures were batched in a 0.1 m^3 pan mixer. The fresh mixtures were tested for air content according to ASTM C231 [9] together with controlling the slump according to ASTM C143 [10]. The unit weight of concrete was determined in accordance with ASTM C138 [11]. Cubes of 150 mm $\times$ 150 mm $\times$ 150 mm and prisms of 150 mm $\times$ 150 mm $\times$ 600 mm were cast in steel molds. A vibrating table was used to consolidate the fresh concrete in molds. The specimens were covered under wet burlap and plastic covering for 24 h. The specimens were then demolded and cured in lime-saturated water of 21 °C. The 150 mm cubes were used for determining the compressive strength in accordance with DIN 1048 after 7 and 28 days of curing [12]. Other specimens were cured for 28 days before transportation to the exposure site. Properties of the fresh and hardened concrete are reported in Table 3.

After the curing period, specimens were transported to the investigation site in Bandar-Abbas, northern coasts of the Persian Gulf. Prisms were sealed on four sides to ensure one-dimensional diffusion of chloride ion and CO_2. Because of its acceptable performance which was determined during previous studies [10], a thick layer of epoxy polyurethane coating was used for sealing the sides of specimens as shown in Fig. 1.

2.3 Exposure conditions

After sealing the four sides of the specimens, three types of coatings (that are going to be evaluated here) were used for covering the remaining top and bottom sides of the prisms. The first series of the specimens were placed on 1.5-m high racks exposed to the natural atmosphere. Specimens were

Table 2   Surface coatings investigated in the study

coating	code	description	average coverage rate (recommended by manufacturers)
no coating	Ref	reference specimen (without coating)	–
aliphatic acrylic	AA	primer: low viscosity silane/siloxane top coat: aliphatic acrylic (solvent based)	primer: 0.4 l/m^2 top coat: 0.175 l/m^2
modified cementitious type D	CPD	primer: without primer top coat: acrylic modified cementitious coating	2 coats each 1.8 kg/m
polyurethane	PU	primer: without primer top coat: epoxy polyurethane	2 coats each 0.45 l/m^2
no coating	w/c 0.4	without coating	–

Table 3   Fresh and hardened concrete properties

mixture	slump (mm)	air content (%)	fresh concrete density (kg/m^3)	compressive strength (MPa)	
				7 days	28 days
Ref	80	2.7	2370	25.9	33.9
w/c 0.4	50	2.9	2420	41.1	50.0
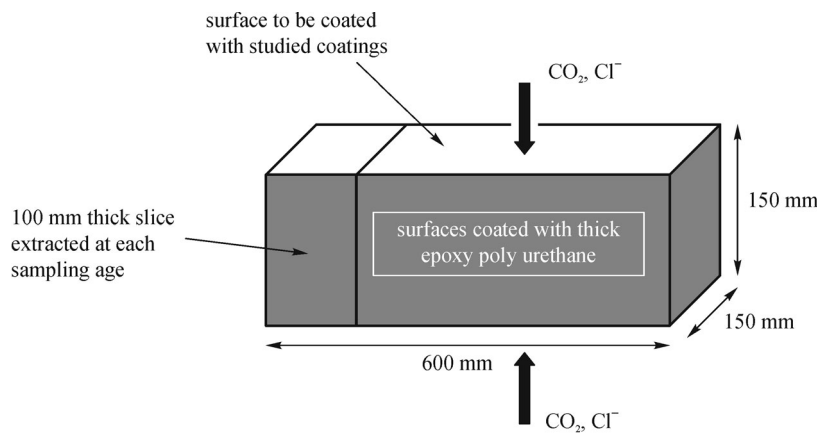
Fig. 1   Schematic of the concrete prism used for evaluating the surface coatings

resting on wooden supports to facilitate air circulation all around. Racks were placed at a minimum distance of 10 m from the sea water. The rest of the specimens were buried in the soil of the coast where chloride ions could penetrate into the specimens. An approximately 1-m deep hole was prepared close to the racks to make sure that the soil, in which the specimens were embedded, would not get saturated by the sea water. The average chloride ion concentration of the soil was 1.25% (by weight). Due to its enclosed condition and high rate of evaporation, the Persian Gulf's water is highly saline. The chemical analysis of the ions available in sea water in the region is presented in Table 4. As cited by Al-Amoudi et al. [13] the temperature fluctuation during a summer day can be up to 30 °C in this region. Relative humidity can also range from 40% to 100% during the same time. Figure 2 presents the mean variations in ambient temperature and relative humidity of the exposure site at Bandar Abbas, Persian

Gulf [14]. The mean relative humidity is usually within the critical range of 50% to 70% for high carbonation progress [14] as shown in Figure 2.

3   Sampling and testing procedures

3.1   Chloride ion concentration

With the aim of monitoring the chloride ion ingress into concrete, sampling was conducted at 9, 36, and 88 months, each time cutting a 100-mm thick slice from the prisms, coating the cut surface of prisms and returning the remaining part to the exposure conditions for future samplings. All of the slices were carried to the laboratory for testing purposes.

At laboratory, a nominal 45-mm diameter core was taken from each slice to provide chloride ion concentration
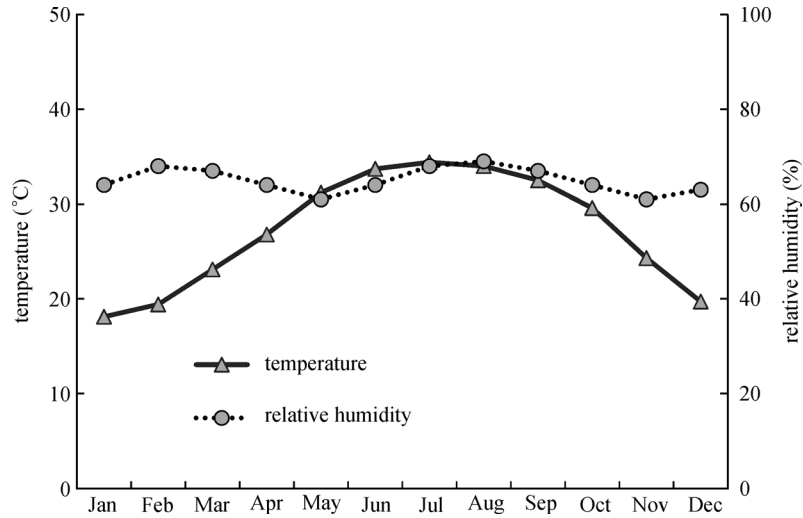
Fig. 2   Variations in mean ambient temperature and relative humidity of Bandar-Abbas

Table 4   Chemical analysis of the sea water

element	ion concentration (ppm)
Ca^{++}	480
Mg^+	1,600
Na^+	12,600
K^+	470
SO_4^-	3,300
Cl^-	23,400

profiles. It should be taken into account that the cross-section area of a 45-mm diameter core is large enough to represent the concrete properties, thus ensuring representative samples for each depth. Each core was grinded in eight depths from the finished surface to an estimated depth of chloride penetration. The method used for estimating the chloride ion penetration depth was based on the procedure described by Nord Test NT Build 492 [15]. This method is based on measuring the depth of color change of a freshly cut concrete surface in the direction of chloride penetration using 0.1 molar $AgNO_3$ aqueous solution. The powder samples for chloride analysis were collected using a profile grinder parallel to the exposed surface according to Nord Test NT Build 443 [16] with accuracy of 0.5 mm at eight increasing depths. The powder obtained from the first 1.0 mm was not included in calculations as it could be affected by such actions as washout, etc.

For each sample of concrete, the depth below the exposed surface was calculated as the average of six uniformly distributed measurements using a slide caliper after collecting the powder sample. The powder obtained from each layer was collected and passed through an 850 µm (No. 20) sieve. At each depth, a powder sample having a mass of approximately 10.0 gram was collected to the

nearest 0.01 gram and then analyzed for acid-soluble chloride content by the potentiometric titration of chloride with silver nitrate in accordance with ASTM C1152 [17], and ASTM C114 [18].

3.2   Carbonation depth

By the end of gathering powder for measuring the chloride content, a 30-mm thick slice was cut from the top surface of the specimens where carbon dioxide could diffuse into the specimens. These slices were split in planes perpendicular to the cut surface to determine the carbonation depth according to the RILEM CPC18 recommendations [19]. For determining the carbonation depth of specimens, a 1% phenolphthalein in ethyl alcohol solution was sprayed on the freshly broken surface of the specimens. Using a digital caliper, the thickness of the areas with no color change, i.e., the carbonated areas, was measured in several points. The average of these values was reported as the carbonation depth of specimens. Non-carbonated areas are differentiated with a purple color due to the chemical reaction between the solution and the alkali environment. Given the low rate of natural carbonation process, especially in the case of coated specimens and those embedded in soil, only the carbonation depths of the specimens at the 88 months are reported here.

4   Results and discussion

4.1   Carbonation depth

Carbonation depths of the specimens are reported in Fig. 3. The 88-month carbonation depths obtained for all the specimens were less than the typical reinforcement cover thickness recommended for harsh exposures. However, as

observed by Meijers et al. [20], even in the case of low carbonation depths, chloride ion profiles may be affected by the synergic effect of the two mechanisms of carbonation and chloride ion penetration.

Higher carbonation depth was observed for the specimens exposed to atmospheric exposure. This was expected, as the surrounding soil hinders the carbon dioxide diffusion into buried concrete samples. Decrease in carbonation depth was observed due to reducing the w/c from 0.5 to 0.4. This decrease was 15% and 13% for the specimens at soil and atmospheric exposures, respectively. At soil exposure, carbonation depth was determined to be 3.5 and 3.0 mm for the specimens made with w/c of 0.5 and 0.4, respectively. Negligible carbonation was observed for samples coated with AA and PU at soil exposure. The cementitious coating was also reducing the carbonation depth from 3.5 to 2.8 mm at soil. For atmospheric specimens, carbonation depths of 9.5 and 8.0 mm were observed for the specimens made with w/c of 0.5 and 0.4, respectively. The minimum carbonation depth of 1.5 mm was observed for the specimen coated with PU coating. Compared to the reference specimen, 50% reduction in carbonation depth was observed due to coating the sample with AA coating, limiting the carbonation depth to 5.0 mm. The CPD coating with carbonation depth of 11 mm was not effective in decreasing the carbonation depth in atmospheric condition. Assuming uniform carbonation propagation over time, slight carbonation rate of 0.5 mm/ year was observed for the non-coated specimens and the one coated with cementitious coating after 88 months at soil exposure. This rate was observed to be up to 1.5 mm/ year for similar samples at atmosphere.
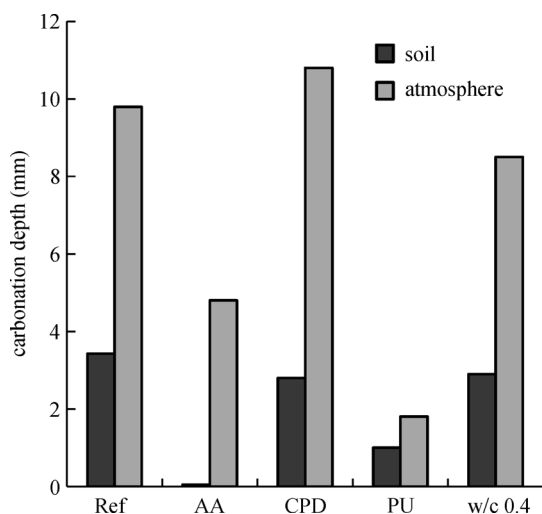

Fig. 3   Carbonation depths of the 88-month old specimens

4.2   Chloride ion profiles

Chloride ion profiles of the specimens obtained at different ages are plotted in Figs. 4–7. Given the low chloride ion concentration at early ages, the 9-month chloride ion profiles are not presented here. However, the corresponding surface chloride content and diffusion coefficient values are reported in following sections. It should be noted that a sharp decrease in chloride ion concentration at second point of the reference sample was observed at 36 month in soil exposure which is believed to be due to experimental errors. This point is omitted from calculations later on. The non-coated reference specimens had the highest amount of penetrated chloride ion in the same depths from the surface at 36 and 88 months. This reveals the fact that the effective life of the incorporated surface coatings should be further than 88 months in atmospheric and soil regions. However, the increasing concentration of chloride ion during the exposure period for coated specimens indicates that the surface coatings have a time-dependent performance and will lose their positive effects as the time passes. Similar observations were reported by Khanzadeh et al. [7]. Authors reported that surface coatings exhibit time-dependent performance at tidal zone of marine environment.
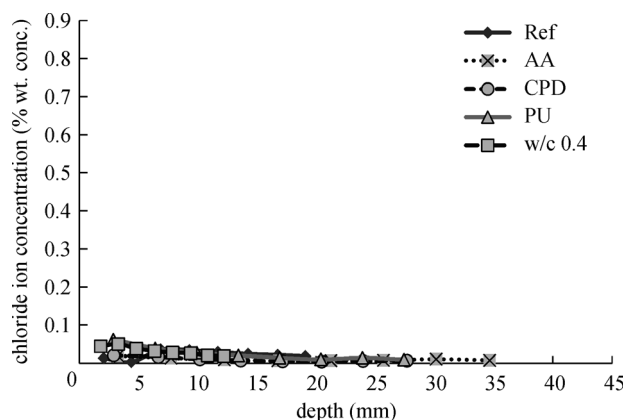

Fig. 4   Total chloride ion concentration at the age of 36 months at atmospheric exposure

Higher chloride concentration was observed at soil exposure. The chloride content and penetration depth increased with respect to the time for both exposures. Data obtained at 36 and 88 months reveal the fact that the chloride concentration in each certain depth was the lowest in the case of the samples coated with AA and PU coatings. The highest concentration was recorded for the reference specimens at these ages.

Polyurethanes are thermo-set polymers produced by the reaction of polyisocyanate and a polyol [21]. They have one pendant hydrogen molecule that can take part in hydrogen bounds. Such a bound allows for high hardness in low stress conditions and high flexibility and tensile strength in high stress conditions. This combination of hardness and flexibility is the main source of high toughness of polyurethanes as coatings. Moreover, high
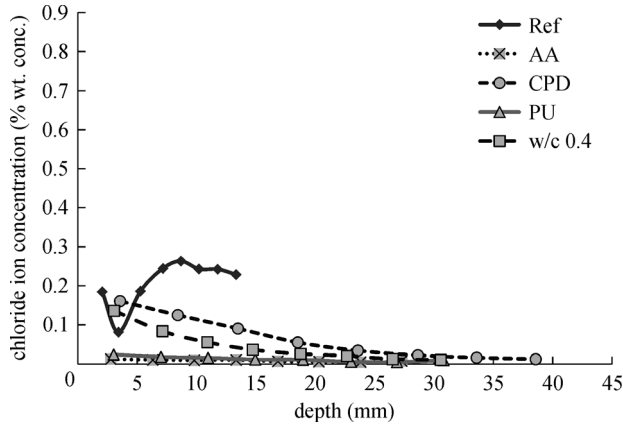
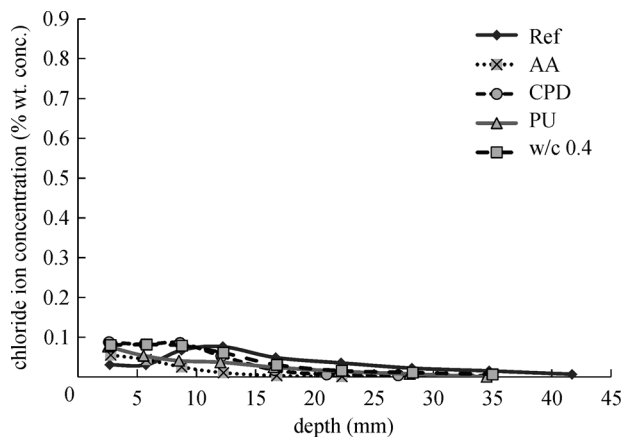**Fig. 5** Total chloride ion concentration at the age of 36 months at soil exposure

Fig. 6 Total chloride ion concentration at the age of 88 months at atmospheric exposure
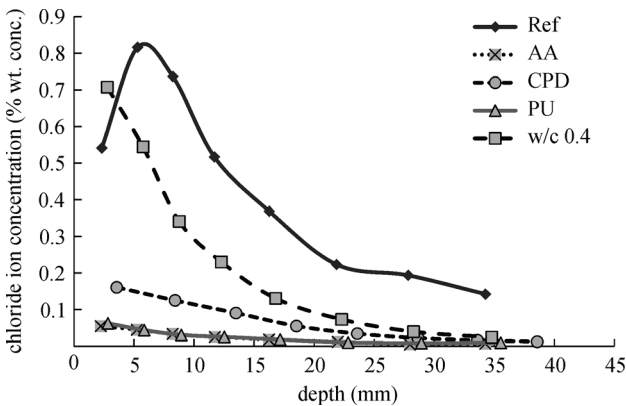

Fig. 7 Total chloride ion concentration at the age of 88 months at soil exposure

cross link density of polyurethane is another reason for high chemical resistance, rigidity, and tensile strength of

PU [21]. Therefore, PU was effective in reducing the chloride ion ingress significantly.

Similar improvements by AA may also be attributed to the dense microstructure. Acrylic coatings are typically produced from acrylic acid or methacrylic acids [22]. AA is a long lasting though coating with high weather and ultra violet (UV) exposure resistance that significantly reduces water and chloride ion penetration into concrete [22]. In the case of AA coating, a low viscosity primer was recommended, which is the typical practice of applying acrylic based coatings to enhance the adhesion between the base coat and substrate [14]. The final composite system of the coating ensures proper long-term performance against deteriorating agents' ingress into concrete.

Polymer modified cementitious coatings are featured by high flexibility, high water penetration resistance, and good breathability [22]. High breathability allows the water vapor to exit concrete, therefore reducing the risk of high pressures at concrete and coating interface. Such high pressures at interface may result in coating delamination and/or cracking [23].

Lowered chloride ion concentration close to the surface followed by formation of a maximum concentration was detected for the reference concrete after 36 months at atmosphere. Similar irregularities in chloride ion distribution were observed for the sample coated with cementitious coating and the specimen with w/c of 0.4 at the same exposure at 88 months. The reference concrete at soil exposure experienced the same distribution pattern at this age. Such chloride ion distribution pattern is believed to be due to carbonation effect that facilitates the migration of chloride ions to depth of carbonated concrete, usually resulting in formation of a peak in chloride concentration close to the carbonation front [1].

Chloride ions can take part in reaction with tricalcium aluminate (C_3A) which results in production of calcium chloroaluminate hydrate ($C_3A \cdot CaCl_2 \cdot 10H_2O$), usually regarded as Friedel's salt. This is reported to play the major role in chemical chloride binding [24]. Friedel's salt will no longer be stable in low pH environments such as the carbonated areas. Kobayashi et al. [25] and Suryavan- shi and Swamy [26] noted that carbonation of concrete results in dissolution of Friedel's salt. Anstice et al. [27] reported that the free chloride ion concentration is increasing in the case of specimens in 100% CO_2 environment compared to those in air. Kuosa et al. [4] reported that the chloride migration depth increases for the carbonated surface layer. Eto et al. [28] reported that the decrease in pH results in dissolution of Friedel's salt, which in turn causes the chloride ions to move to depth of concrete. This highlights the fact that not only the synergic effect of carbonation and chloride ion results in decrease in pH at the cover concrete, but also increased chloride concentrations should be expected close to reinforcement.

4.3 Chloride diffusion coefficient (D_c) and surface chloride contents (C_s)

Profiles obtained for the chloride ion concentrations were interpolated using the analytical solution of the Fick's second law of diffusion [29]:

$$\frac{\partial C}{\partial t} = D_c \frac{\partial^2 C}{\partial x^2}. \tag{5}$$

Simplifying assumptions were made in solving this equation, including assuming concrete as homogenous material, considering constant value for surface chloride content and coefficient of diffusion, ignoring bound between chloride ions and concrete, and so on. This equation also neglects the effect of other transport mechanisms including capillary absorption in atmospheric area, etc. However, given the fact that such restrictions apply for all samples and this study only aims at relative comparisons, such assumptions are considered to be valid [30]. The following initial and boundary conditions were considered for solving Eq. 5:

$$C_{x,0} = 0, \text{ for } x > 0.$$

$$C_{0,t} = C_s, \text{ for } t \geqslant 0.$$

Solving Eq. 5 with introduced conditions results in:

$$C_{x,t} = C_s \left(1 - erf \left(\frac{x}{2\sqrt{D_c \cdot t}} \right) \right), \tag{6}$$

where x is the depth from concrete surface (mm), t is the time (s), C_s is the chloride content at the surface (% weight of concrete), D_c is apparent chloride diffusion coefficient (mm^2/s), $C_{x,t}$ is chloride concentration at depth x and time t (% weight of concrete), and erf is the error function.

Values of D_c and C_s were calculated by iteration to produce the best fits. At the first step of curve fittings, all profile points were included in the process. But, in later steps, data points with a great diversion were omitted from the analysis with the aim of reaching to the best possible accuracy. In the case of the hump at profiles of the carbonated samples, the initial points with concentrations less than the normal distribution according to Fick's law of diffusion were eliminated from the curve fitting.

4.3.1 Chloride diffusion coefficients (D_c)

All coated samples were cast with the same concrete. So, one can conclude that the variations in D_c of the samples made with w/c of 0.5 can only be traced in performance of coatings. Therefore, the apparent diffusion coefficients obtained from Fick's second law of diffusion will represent the effect of coating on diffusion properties. In other words, comparing D_c obtained for different coated specimens actually compares penetration resistance of coatings.

Figures 8 and 9 depict the variations in chloride diffusion coefficient with respect to the exposure period. As expected, chloride diffusion coefficients show a descending trend during the exposure time for all specimens.
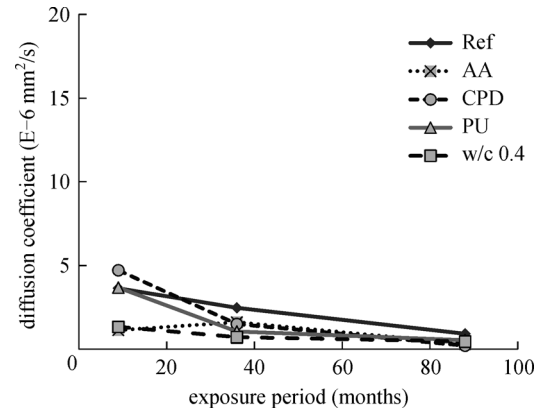

Fig. 8 Time dependent variation in chloride ion diffusion coefficient at atmospheric exposure
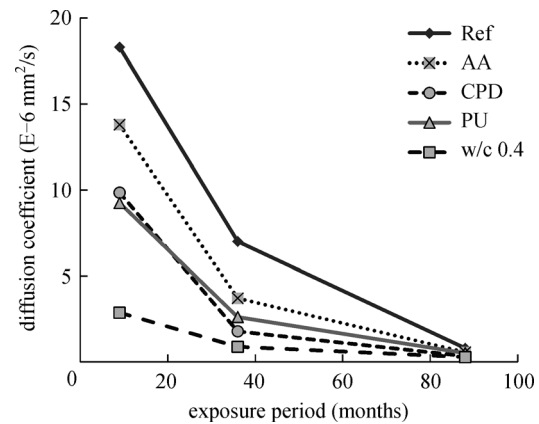

Fig. 9 Time dependent variation in chloride ion diffusion coefficient at soil exposure

Diffusion properties of concrete may change over time. In a situation that other chemical and physical processes do not damage the concrete, the measured D_c is expected to decrease with exposure time. The underlying reason is the dependence of diffusion process on distribution and connectivity of pores within concrete [31,32]. Variations in pore connectivity might in part be due to the modification of pore structure as a result of hydration in light of limited moisture content of the test environment. However, reactions between hydration products and advancing chloride ions which result in pore blocking may also be considered as one of the main reasons for such a decrease in rate of chloride ion diffusion [33,34].

Similar to what reported by Shekarchi et al. [35], it was observed that the diffusion coefficient is decreasing more rapidly at early ages. This was inferred by comparing the

rate of variation in D_c from 9 to 36 months with corresponding variations during the period between 36 and 88 months. Rate of decrease in D_c seems to be slower in the case of specimens made with w/c of 0.4 compared to the reference concrete made with w/c of 0.5.

Based on the data presented in Figs. 8 and 9, it was concluded that incorporation of coatings and reducing the w/c can effectively reduce the diffusion coefficient for both exposures. In the case of the 88-month measurements at soil exposure, it was observed that incorporation of AA, PU, and CPD coatings reduced the D_c by 29%, 36%, and 58% respectively. However, all D_c values were ranging from 0.338×10^{-6} to 0.796×10^{-6} mm²/s. The minimum diffusion coefficient was observed for the sample with w/c of 0.4 with up to 65% decrease in comparison with the reference sample with w/c of 0.5. For the atmospheric samples, it was again observed that incorporation of AA, PU, and CPD coatings will reduce the D_c by 67%, 43%, and 77% respectively. Reducing the w/c from 0.5 to 0.4 also reduced the 88-month D_c by 50%.

Considering the fact that rate of chloride ion ingress and accumulation in concrete is governed by the diffusion rate, reduction in D_c is expected to increase the time to corrosion initiation and service life. This pronounces the beneficial effect that surface coatings might have on durability. It is worth mentioning that most of these surface coatings were evaluated in another study in tidal zone of the same site [7]. Generally higher diffusion rates were observed at soil exposure at early ages. Values of diffusion coefficient obtained in soil and atmosphere are generally of the same order of magnitude, but less than those obtained for same type of coatings at tidal zone. More detail about performance in tidal zone is discussed by Khanzadeh et al. [7].

D_c for a given concrete sample varies with time. Considering the time dependent variation of chloride diffusion coefficient, following equation was employed to express the D_c as a function of exposure time [35]:

$$D_c = at^{-b}, \tag{7}$$

where D_c is the chloride ion diffusion coefficient (mm²/s), t is the exposure time (s), and a and b are the regression constants.

Table 5 summarizes the regression results. Good correlation between D_c and time is observed for all samples with regression coefficients varying from 0.82 to 0.99, except for the AA coated samples at atmospheric exposure. These results can be incorporated for estimating the variation of chloride diffusion coefficient of the reference and coated specimens at both exposures.

4.3.2 Surface chloride content (C_s)

Surface chloride content is considered to be the constant C_s

Table 5 Modeling the chloride ion diffusivity versus exposure time

specimen	soil			atmosphere		
	a	b	R^2	a	b	R^2
Ref	0.453	0.600	0.91	0.007	0.445	0.89
AA	5.242	0.760	0.96		NA*	
CPD	1.667	0.715	0.90	0.020	0.500	0.82
PU	1.933	0.725	0.95	11.8	0.883	0.99
w/c 0.4	23.81	0.939	0.99	0.004	0.465	0.99

*Regression was not possible

term of Fick's second law of diffusion introduced in Eq. 6. Figures 10 and 11 present the variation of surface chloride concentration with the exposure time. An increasing trend was observed in the case of the C_s values for all the coated specimens and the reference concrete.
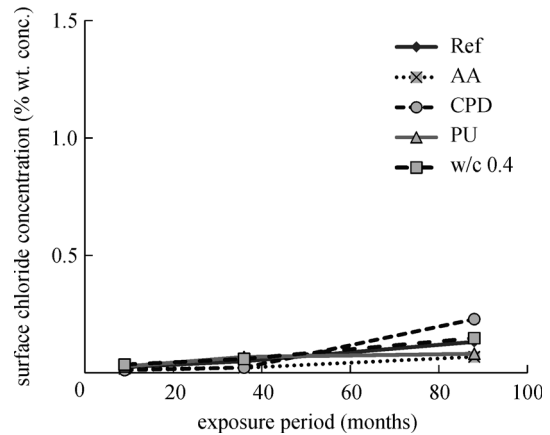

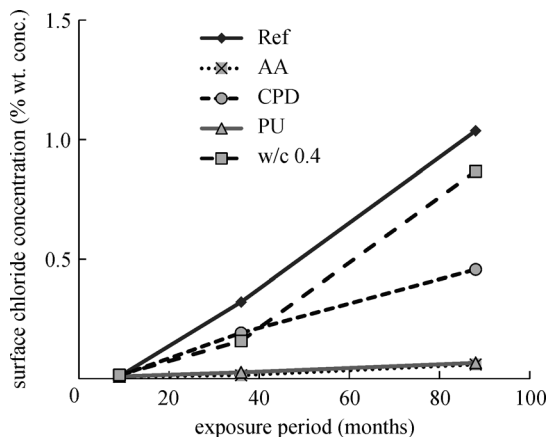**Fig. 10** Variation in the surface chloride concentration—atmospheric exposure

Fig. 11 Variation in the surface chloride concentration—soil exposure

C_s values are comparable at early age of nine months for both exposures. However, the exposure condition plays a more significant role in later ages. Surface chloride contents of the non-coated samples at soil exposure were significantly higher than those of the atmospheric samples. The C_s values of the non-coated samples made with w/c of 0.5 and 0.4 were 10 and 6 times higher in soil exposure, respectively. However, the magnitudes of the C_s of the corresponding coated samples in both exposures were comparable. In the case of the soil exposure, incorporation of AA, PU, and CPD coatings reduced the C_s value by 94%, 94%, and 56%, compared to the reference sample, respectively. Reducing the w/c from 0.5 to 0.4 on the other hand, reduced the C_s by 16% which is not as significant as the effect of coatings. AA and PU were also effective in reducing C_s at atmospheric exposure. The C_s was reduced by 48% and 39% due to the use of AA and PU, respectively. In comparison to the reference concrete, incorporation of CPD was not effective in reducing C_s in this exposure. No significant difference between the C_s of the non-coated samples made with w/c of 0.4 and 0.5 was observed at 88 months in this exposure.

Considering the effect of exposure period on surface chloride ion build-up, it is tried to express the surface chloride content as a function of time. According to Ann et al. [36] surface chloride build-up in concrete exposed to marine exposures can be expressed as a function of time. Such behavior is also suggested by Khanzadeh et al. [7] who argued that linear and square root build-up models can be considered to express the time dependant nature of the surface chloride content. Feasibility of using the four possible equations of linear and square root of time with and without the initial values was studied:

$$C_s = k \times t, \text{ (Linear build-up)}. \tag{8}$$

$$C_s = a + k \times t,$$
$$\text{(Linear build-up with initial value)}. \tag{9}$$

$$C_s = k \times \sqrt{t}, \text{ (Square root build-up)}. \tag{10}$$

$$C_s = a + k \times \sqrt{t},$$
$$\text{(Square root build-up with initial value)}, \tag{11}$$

where C_s is the surface chloride content (% weight of concrete), t is the time (s), k is the regression coefficient, and C_0 is the earliest available measurement for surface chloride content, i.e., C_s at nine months.

Tables 6 and 7 summarize the regression coefficients obtained for different scenarios. For the atmospheric samples, high scatter was observed for both the square root equations. It was observed that the linear regression with the initial value yields in good correlations with R^2 values ranging from 0.8 to 0.93. Therefore, this model was proposed as a good representative of the surface chloride ion build-up in atmospheric exposure. The linear regressions, both with and without the initial value have good correlations for soil exposure with R^2 values ranging from 0.78 to 0.99. This indicates that the proposed regression models are good representatives of the surface chloride ion build-up. High scatter was observed for the square root build-up models at this exposure as well. Based on the obtained regression results, it was finally proposed to employ the linear model with initial value (Eq. (9)) for simulating surface chloride ion build-up of both exposures for service life predictions.

Table 6   Time dependent surface chloride build-up at atmospheric exposure

coating	$C_s = k \times t$		$C_s = C_0 + k \times t$		$C_s = k \times \sqrt{t}$		$C_s = C_0 + k \times \sqrt{t}$	
	k	R^2	k	R^2	k	R^2	k	R^2
Ref	5.75E–10	0.90	4.40E–10	0.93	7.49E–06	0.84	5.43E–06	0.67
AA	2.92E–10	0.91	1.96E–10	0.84	3.81E–06	0.76	2.35E–06	0.55
CPD	8.90E–10	0.85	8.28E–10	0.81	1.08E–05	0.58	9.86E–06	0.53
PU	NA*		2.62E–10	0.80	5.80E–06	0.90	3.49E–06	0.79
w/c 0.4	6.54E–10	0.94	4.57E–10	0.92	8.63E–06	0.87	5.62E–06	0.66

Table 7   Time dependent surface chloride build-up at soil exposure

coating	$C_s = k \times t$		$C_s = C_0 + k \times t$		$C_s = k \times \sqrt{t}$		$C_s = C_0 + k \times \sqrt{t}$	
	k	R^2	k	R^2	k	R^2	k	R^2
Ref	4.35E–09	0.97	4.30E–09	0.96	5.46E–05	0.73	5.38E–05	0.72
AA	2.00E–09	0.99	1.99E–10	0.86	2.56E–05	0.79	2.40E–06	0.58
CPD	2.44E–10	0.94	1.94E–09	0.98	3.09E–06	0.71	2.46E–05	0.77
PU	1.47E–09	0.78	2.38E–10	0.96	1.98E–05	0.86	2.97E–06	0.71
w/c 0.4	3.48E–09	0.91	3.39E–09	0.90	4.27E–05	0.64	4.14E–05	0.62

4.4   Service life

Data obtained through analyzing the chloride ion concentration at different ages were employed to predict the service life of RC structures exposed to the investigated conditions. Given the uncertainties in calculating the corrosion propagation period [37], the corrosion initiation time was introduced as the service life as proposed by Tuutti [38]. The first approach was to determine the time required for chloride ion concentration to reach a certain threshold value at a certain cover depth. This hypothesis is true if enough oxygen is available in concrete to facilitate the corrosion reactions. The second approach was to calculate the service life based on the time required for carbonation front to reach the reinforcement.

The cover depth was assumed to be 50 mm in calculations. The chloride threshold was considered to be 0.07% by weight of concrete as recommended by [14]. Equations obtained for predicting the chloride ion diffusion and the linear regression with initial value suggested for surface chloride build-up were incorporated for calculating the corrosion initiation time based on Fick's second law of diffusion. The time required for chloride ions to reach the threshold value at rebar surface was introduced as the chloride governed service life t_{Cl^-}. Carbonation depth was also considered to be a function of squared root of exposure time according to Equation 12 [39]. Time required for the carbonation front to reach to the rebar surface was also considered as the carbonation governed service life (t_{carb}).

$$D_c = k\sqrt{t}, \tag{12}$$

where D_c is the carbonation depth (mm), k is the carbonation coefficient, and t is the exposure period (months).

Several uncertainties are involved in calculating the time to corrosion, including experimental errors during sampling, calculating the D_c and C_s, and back-calculating the time based on Fick's second law of diffusion. Moreover, the carbonation coefficient (k) calculated based on 88-month measurements is assumed to be constant in this study. Table 8 presents the predicted values for service life.

The presented values for service life are estimations to compare the relative behavior of the samples. Comparing the data obtained through laboratory investigation with the predicted time to corrosion initiation, it can be concluded that Table 8 might underestimate the time to corrosion initiation, especially for the reference mixture at soil exposure. It can be generally concluded that due to the slow rate of carbonation, the chloride induced corrosion can be considered as the main cause of deterioration in soil and atmospheric exposures. Shorter service life is generally predicted for samples in soil which is due to the considerably higher chloride ion concentration in this exposure. Decreasing the w/c from 0.5 to 0.4 is proved to be effective in enhancing the service life. It is also

Table 8   Predicted service life based on deterioration mechanism (year)

time to corrosion	soil		atmosphere	
	t_{Cl^-}	$t_{carb.}$	t_{Cl^-}	$t_{carb.}$
Ref	3		29	
AA	50		NA*	
CPD	12	≫100	22	>100
PU	54		>100	
w/c 0.4	NA*		66	

*Regression was not possible

observed that incorporation of proper type of surface coating can effectively enhance the durability and service life of onshore concrete. This effect is highlighted in the case of the AA and PU coatings in both exposures. Same results were also reported by Medeiros and Helene [40], Almusallam et al. [41], and Ibrahim et al. [42] who reported that polyurethane and acrylic based coatings exhibited the best protections against chloride ion ingress into concrete.

5   Conclusions

This study investigates the durability of concrete in atmospheric and soil exposure of the coasts of the Persian Gulf. Normal strength concrete with w/c of 0.5 and 0.4 were used for casting the specimens. The 28-day compressive strengths were 33.9 and 50.0 MPa, respectively. Beneficial effects of three types of concrete surface coatings were compared in two exposures. Specimens were cast at laboratory and cured for 28 days in lime-saturated water before transportation to the exposure site. Sampling was conducted up to 88 months. Carbonation depth and chloride ion concentration were determined at each sampling age. Based on the findings presented in this study, the following conclusions are warranted:

● Slight carbonation with approximate rate of 0.5 mm/year was observed for the reference concrete and specimens coated with cementitious based coating at soil exposure during the first 88 months. This rate was about 1.5 mm/year at atmosphere for the same period of time. Employment of suitable surface coating effective in hindering the diffusion of carbon dioxide into concrete. Negligible carbonation was observed for the specimens coated with aliphatic acrylic and polyurethane. Decrease in w/c from 0.5 to 0.4 resulted in decreasing the carbonation depth up to 15% and 13% for the specimens at soil and atmospheric exposures, respectively.

● Data obtained during this research was not enough to make quantitative evaluations on effect of carbonation on chloride ion distribution in concrete. Further investigation is required for this purpose. However, carbonation affected the chloride ion distribution pattern. A peak in chloride ion concentration was detected near

the carbonation front. This effect was more noticeable in atmosphere. Slight effects were also observed for the reference concrete in soil exposure.

- Variation in chloride ion diffusion coefficient was investigated with respect to exposure time. Diffusion coefficient decreased as a function of time. Penetration depth and chloride content increased as a function of time for both the coated and non-coated specimens.
- Based on the obtained experimental data, models were proposed for determining the surface chloride build-up at both exposures. Surface chloride content increased during the exposure time. The linear build-up model with initial value was a good representative for both exposures.
- Despite of the efficiency of all three surface coatings in preventing the chloride ingress into concrete, the aliphatic acrylic and the polyurethane coatings were the most effective ones in hindering the chloride ion diffusion into the concrete in both exposures.
- Increase in chloride ion concentration in coated specimens during the exposure time suggests that the performance of surface coatings against the chloride ion ingress is a time dependent phenomenon. However, all coated specimens had chloride ion concentrations less than the reference concrete, revealing the fact that the service life of the coatings is more than 88 months in investigated exposures.

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