

## Prediction of RC structure service life from field long term chloride diffusion

Majid Safehian<sup>a</sup> and Ali Akbar Ramezaniapour\*

Concrete Technology and Durability Research Center, Department of Civil and Environment Engineering,  
Amirkabir University of Technology, Tehran, Iran

(Received July 21, 2014, Revised October 4, 2014, Accepted November 15, 2015)

**Abstract.** It is well-documented that the major deterioration of coastal RC structures is chloride-induced corrosion. Therefore, regional investigations are necessary for durability based design and evaluation of the proposed service life prediction models. In this paper, four reinforced concrete jetties exposed to severe marine environment were monitored to assess the long term chloride penetration at 6 months to 96 months. Also, some accelerated durability tests were performed on standard samples in laboratory. As a result, two time-dependent equations are proposed for basic parameters of chloride diffusion into concrete and then the corrosion initiation time is estimated by a developed probabilistic service life model. Also, two famous service life prediction models are compared using chloride profiles obtained from structures after about 40 years in the tidal exposure conditions. The results confirm that the influence of concrete quality on diffusion coefficients is related to the concrete pore structure and the time dependence is due to chemical reactions of sea water ions with hydration products which lead a reduction in pore structure. Also, proper attention to the durability properties of concrete may extend the service life of marine structures greater than fifty years, even in harsh environments.

**Keywords:** durability; chloride penetration; service life prediction models; silica fume; tidal zone

### 1. Introduction

Chloride-induced corrosion of steel reinforcement has been identified as one of the main causes of deterioration of marine reinforced concrete (RC) structures which can significantly affect the structural service life (Zhang *et al.* 2011). It has been extensively studied for decades, particularly, as a result of the high costs of repair in North America, Europe and Persian Gulf from the effects of seawater exposure of coastal structures (Shin *et al.* 2011).

Several studies have indicated that lowering the w/b ratio and adding different types of pozzolanic materials to the mix can improve the compressive strength, durability and permeability of concrete. Lowering the w/b ratio reduces the porosity, which thereby reduces chloride ingress during the exposure period by as much as 25% (Moodi *et al.* 2014). Among the mineral admixtures used for this purpose, silica fume (SF) has been observed to noticeably reduce chloride ingress into concrete in marine environments (Safehian and Ramezaniapour 2014). The effect of SF on concrete microstructure is well reported in the literature. SF is an artificial pozzolan that

---

\*Corresponding author, Professor, E-mail: [aramce@aut.ac.ir](mailto:aramce@aut.ac.ir)

<sup>a</sup>Ph.D., E-mail: [majidsafehian@aut.ac.ir](mailto:majidsafehian@aut.ac.ir)

increases the compressive strength of concrete by strengthening the transition zone and increasing the rate of hydration early in the life of the concrete (Wang *et al.* 2012).

The effect of chloride diffusivity on multi-zone concrete structures in marine environments differs from one exposure condition to another. Among all the exposure conditions, tidal and splash zones have been reported to be the most severe conditions in terms of durability. Due to the wetting and drying cycles and subsequent evaporation, splash and tidal zones tend to have the highest chloride content, while atmospheric zones undergo the least deterioration due to the low chloride penetration (Safehian and Ramezaniapour 2013).

Costa and Appleton (1999) exposed 54 concrete panels to marine environments for 3–5 years, and the study examined three concrete mixes and five exposure conditions (from tidal to atmospheric zone). They concluded that both the chloride diffusion coefficient and the surface chloride concentration were time-dependent, which has considerable implications in predicting chloride ingress into concrete and risk of rebar corrosion in concrete. Therefore, challenges are inherent in assessing concrete durability from its chloride diffusivity.

Depending on the exposure condition as well as on the moisture content of the concrete element, the ingress of chlorides into concrete is through coupled multiple transport mechanisms. However, most models for chloride ingress in concrete are still based on the assumption of a Fickian process of diffusion as the main transport mechanism. Moreover, diffusion-based models have been found acceptable for long-term monitoring of chloride ingress in concrete structures [Bamforth & Price 1997; Tang and Gulikers 2007]. The main differences between different diffusion-based models were summarized by Andrade *et al.* (2006) and possible approaches for improving the prediction of chloride ingress were suggested by Nilsson (2006).

Most of the studies found in the literature have focused on the investigation of the mechanisms of chloride transport in concrete and reinforcing steel corrosion, as well as development of corrosion protection, repair strategies and detection techniques; however, there are few studies on the development of reliable and practical design approaches for durability design and corrosion protection of concrete structures. In order to achieve a specified design life for concrete structures, it is imperative to develop mechanistic and practical models (deterministic or probabilistic) that can be used for the design of durable concrete structures, as well as for predicting the deterioration and maintenance optimization of existing concrete structures (Andrade *et al.* (2013).

In this paper, the emphasis is on the long term monitoring of chloride penetration in more than thirty new and repaired concrete piles in four coastal RC structures, depending on exposure duration at 6 months to 96 months in severe marine environment. Additionally, some accelerated durability tests were performed on samples which were made with local materials similar to concrete mixtures of real structures in the laboratory. It should be noted this study is an extension of previous research (Safehian and Ramezaniapour, 2013) which was focused on two parameters: (a) construction method: in situ and precast, (b) exposure conditions: atmospheric, splash and tidal zones.

## 2. Description of structures and materials

### 2.1 Environmental conditions

In this study, under investigated jetties are constructed in the latitude 30°, 25' N and longitude 49°, 4' E at a distance of 65 km from the mouth of Persian Gulf that is called BIK (Bandar Imam Khomeini) zone. Fig. 1 shows some pictures of location and present condition of investigated marine structures. The climatic conditions of Persian Gulf region are characterized by high temperature with salt-laden humidity and large fluctuation in the diurnal and seasonal temperature and humidity.

Table 1 Main aggressive ions of various seawaters

Location	Average ion content (mg/l)		Reference
	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	
Gulf of Thailand	2400	17000	Cheewaket <i>et al.</i> 2013
Panama City, FL	---	24560	Lau <i>et al.</i> 2006
Setubal Peninsula, Portugal	2500	18500	Costa and Appleton,
BRE marine site, England	2600	18200	Petcherdchoo 2013
Bandarabbas, Persian Gulf	3300	23400	Moradillo <i>et al.</i> 2012
BIK zone, Persian Gulf	3460	26700	Shekarchi <i>et al.</i> 2011
Average of Persian Gulf	2720	21450	Shekarchi <i>et al.</i> 2011
Average of world	2700	19800	Mehta, 1988



Fig. 1 Location and present conditions of under investigated coastal structures in BIK zone

In addition to severity of climatic conditions, the amounts of chloride and sulfate ions are higher than that found as the average of the world seawater (see Table 1). Semi-closed nature of the region, high level of evaporation, low rainfall, little freshwater inflow of rivers and existence of huge petroleum industries may be the main reasons for high concentration of aggressive ions in BIK zone, especially Cl<sup>-</sup> ion (Shekarchi *et al.* 2011). This fact makes the seawater more aggressive to portland-cement concrete. Therefore, assessment of long term chloride penetration in one of the most severe marine environment is valuable for enhancing durability in reinforced concrete structures, although there are other infield chloride ingress data in the literature. This is the key point of this study.

## 2.2 Description of marine structures

The under investigated structures (No.1 & 2 in Fig. 1), were constructed in 1940. After more than 65 years, these structures were decided to be repaired and rehabilitated due to physical development concepts of the port. Accordingly, old structures were totally repaired in 2004-2007 with proper attention to long term durability issues. Also, two other reinforced concrete structures,

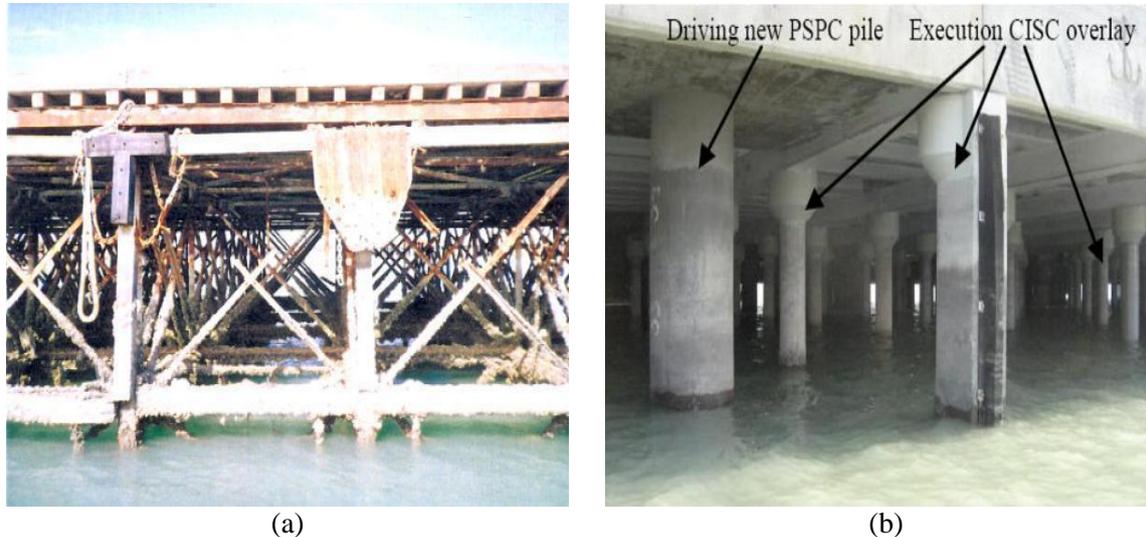


Fig. 2 Pictures from field structures in BIK zone, (a) before repair and (b) after repair

No. 3 & 4 in Fig. 1, were constructed in 1974 & 1980, respectively. Fortunately, all project technical specifications and methods of repair work were carefully recorded for future reference. Based on available documents, structural properties, raw material characteristics and concrete mix features are reported in the next section.

The strengthening of very old structures (No. 1 & 2) was carried out at two stages. Firstly, driving new piles manufactured in the factory which are called prestressed spun precast concrete piles (PSPC piles). Secondly, the execution of a 15 cm thick cast in-situ concrete overlay (CISC overlay) on old steel piles which are suffered from extensive corrosion. In this case, fresh concrete was cast in watertight formworks and moist cured for 7 days. Fig. 2 shows some pictures of marine structures before and after repair works.

### 2.3 Materials

According to the project documents, cement was type I(PM) blended cement, which would conform to the ASTM C595 standard. In addition to blended cement, silica fume was used containing 89%  $\text{SiO}_2$  with pozzolanic activity index of 103%. The chemical compositions of cement and silica fume are shown in Table 2. Blended (or pozzolanic) cements are being used worldwide to produce dense and impermeable concrete. Use of pozzolanic materials in concrete considerably reduces its permeability and the rate of diffusion of moisture and aggressive ions into the steel-concrete interface. The addition of a wide range of blending materials of differing chemical composition, also introduces significant diversity into the cementing system. The wide variation in the performance of the blending materials may be attributed to the variation in their physical, chemical, and mineralogical composition resulting from the industrial processes related to their production and the properties of the raw materials used. On the other hand, several studies have been carried out in the case of internal chloride to study the influence of  $\text{C}_3\text{A}$  on binding. All the results indicate that higher  $\text{C}_3\text{A}$  content in cement results in higher binding capacity. Due to the reactions between chloride ion and  $\text{C}_3\text{A}$ , resulting in the formation of Friedel's salt and its

Table 2 Chemical composition of cement and silica fume

Chemical compositions (%)	Materials	
	Cement type I(PM)	Silica fume
Silicon Dioxide (SiO <sub>2</sub> )	24.6	89
Calcium Oxide (CaO)	57.9	0.89
Magnesium Oxide (MgO)	3.25	1.6
Sulfur Trioxide (SO <sub>3</sub> )	1.9	0.43
Aluminum Oxide (Al <sub>2</sub> O <sub>3</sub> )	6.1	0.47
Ferric Oxide (Fe <sub>2</sub> O <sub>3</sub> )	3.57	1.53
Sodium Oxide (Na <sub>2</sub> O)	0.41	0.22
Potassium Oxide (K <sub>2</sub> O)	0.66	1.11
Loss on Ignition (LOI)	1.6	4.88

Table 3 Concrete mixture proportion

Repair solution	Cement (kg/m <sup>3</sup> )	Silica fume (kg/m <sup>3</sup> )	Fine agg. (kg/m <sup>3</sup> )	Coarse agg. (kg/m <sup>3</sup> )	Water (kg/m <sup>3</sup> )	HRWRA (kg/m <sup>3</sup> )	Water to binder	Slump (cm)
PSPC pile	520	36.4	1370	445	166	8.3	0.30	6-8
CISC overlay	450	32	1232	410	169	7	0.35	10-12

analogues, the C<sub>3</sub>A content in cement dominates chemical binding. Thus the threshold chloride value shifts to higher side with an increase in the C<sub>3</sub>A content of cement (Yuan *et al.* 2009).

Coarse aggregates were crushed calcareous stone with a maximum size of 25 mm and fine aggregates were natural river sand. The coarse aggregates have a density and water absorption of 2593 kg/m<sup>3</sup> and 0.52%, respectively, and the fine aggregates have water absorption of 0.75% and a density of 2585 kg/m<sup>3</sup>. The aggressive components of aggregates and mix water for casting and curing all concrete members were in authorized limits for construction in marine environment. Moreover, a polycarboxylate-ether type High-Range Water Reducer Admixture (HRWRA) had met the requirements for type-F of ASTM C494 standard. A more detailed description of the raw materials is presented in previous study (Safehian and Ramezani-pour 2013).

## 2.4 Concrete mixture

It is well known that durability issues are main concern for marine structures. Thus, concrete mixture for such structures exposed to marine environment should preferably be rich in cementitious materials. Also, the water to binder (w/b) ratio should be as low as possible. These precautions are vital for production of low permeability concrete which is the main key to durability. Based on the mentioned considerations, a summary of main proportions of concrete mixtures is shown in Table 3.

## 3. Experimental program and results

There are a number of mechanisms by which chloride ions can transport in concrete. These include diffusion under the influence of a concentration gradient, adsorption due to a capillary

Table 4 Laboratory test results at 28 days

Type	Compressive strength (MPa)	Rapid Chloride Migration (mm <sup>2</sup> /year)	Rapid Chloride Penetration (coulomb)	water penetration test (mm)	Water absorption (%)
	BS-1881:part116	NT Build-492	ASTM C1202	BS EN-12390-8	BS 1881:part12 2
PSPC pile	85.2	2.87	317	5	1.15
CISC overlay	63.8	4.89	767	≈10	1.55

action, migration in an electrical field, a pressure-induced flow and wick action. According to previous studies (Saassouh and Lounis 2012; Kropp 1995), the main transport mechanism of chloride ions into concrete are diffusion and adsorption. However, adsorption occurs in concrete surface layers that are subjected to wetting and drying cycles, and it only affects the exposed concrete surface down to 5-10 mm in concrete with low permeability, so beyond this adsorption zone, the diffusion process will dominate (Tuutti 1996). As a result, diffusion is the primary mechanism of chloride transport in concrete where there is no applied electrical field and the moisture condition of the concrete pore structure is stable such as saturated concrete in the tidal exposure condition of humid areas. There are two approaches to predicting chloride penetration or diffusion in concrete. The first is the conventional diffusion theory at the macroscopic level which is based on Fick's law. The second is based on electro-chemistry theory at the microscopic level. In this investigation the diffusion model which is based on Fick's second law, is adopted. This diffusion model can be used to model the time for chloride to reach and initiate corrosion at reinforcing steel depth.

For one dimensional diffusion into a semi-infinite medium, an error function solution to Fick's second law (Crank 1975) is usually used as follows:

$$C(x, t) = C_0 + (C_s - C_0) \left[ 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right] \quad (1)$$

where  $D$  = diffusion coefficient (m<sup>2</sup>/s);  $t$  = time of exposure (s);  $C(x, t)$  = chloride concentration at depth  $x$  after time  $t$  (%wt of concrete);  $C_s$  = surface chloride content (%wt of concrete);  $C_0$  = initial chloride content (%wt of concrete) and  $\operatorname{erf}$  is the error function. It should be noted that the initial chloride content, that is the chloride in the original mix ingredients, is determined 0.008% and 0.013% by weight of concrete in PSPC piles and CISC overlays, respectively.

In order to analyze long term chloride penetration into concrete and to assess durability performance of field structures, two series of experiments were performed. The first series were on standard samples with similar concrete mixture of field structures in the laboratory and the second series of tests were performed on the marine structures with PSPC piles and CISC overlays in BIK.

### 3.1 Laboratory test program

Based on section 2, the concrete mixtures and also raw materials which are used in the lab were similar to those of real investigated structures. For laboratory studies, the cylindrical concrete specimens of 100 mm diameter and 200 mm height were used to evaluate durability properties of concrete mixture. After removal of the mold, specimens were stored for 28 days in saturated limewater at a temperature of 20±3 °C. The obtained experimental results are shown in Table 4.

### 3.2 Field investigation program

The performed experiments on real structures included extracting concrete powder samples to assess chloride penetration and measuring carbonation depth by spraying a 1% phenolphthalein solution on internal surface of hole. Drilling was made to depth of 65 mm or upon reaching reinforcement. It should be mentioned, although dry drilling method for concrete has some uncertainty, but all recommendations of RILEM TC 178-TMC (Vennesland *et al.* 2013) was considered for reducing errors. For example, the number of drill holes for collecting concrete dust samples for all steps was five and diameter of each hole was 20 mm. Also, for appropriate collection of concrete dust samples during drilling, vacuum attachment is used and the geometry of the drilled hole is taken into account for calculation of the depth of each sample.

The first 2 mm concrete powder was not included in calculations as it might be affected by actions such as washout, etc. Also, surface electrical resistivity of existing members was measured by Wenner test method as a nondestructive test. Previous study (Moodi *et al.* 2014) showed the amount of surface electrical resistivity can represent the concrete surface permeability that is useful for evaluation of concrete durability in marine environment. Fig. 3 shows general tidal levels and the exact distance between extracted concrete powder and top deck of structure.

In the laboratory, the fine concrete particles were pulverized so that all the material passed a 150- $\mu\text{m}$  (No.100) sieve. At each depth, a sample having a mass of approximately 10gr was

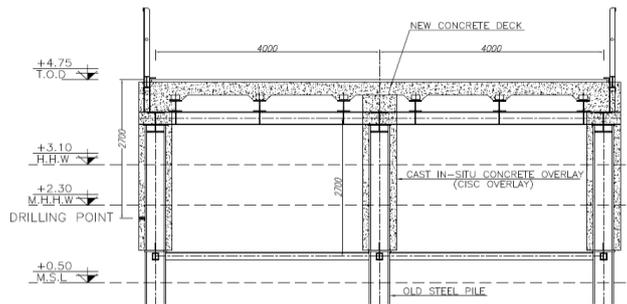


Fig. 3 General tidal levels and location of extracted concrete powder in real marine structures

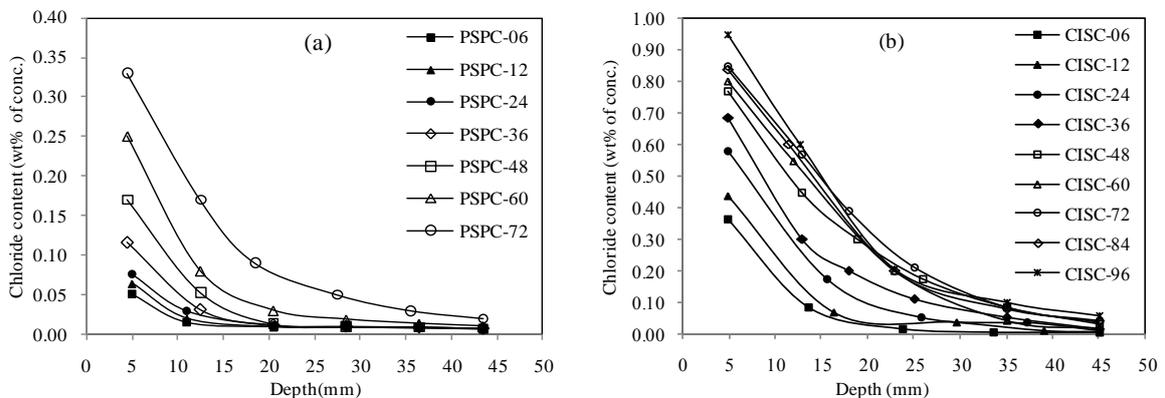


Fig. 4 Chloride penetration profiles at the tidal exposure conditions for (a) PSC piles, (b) CISC overlays

selected to the nearest 0.01gr. Subsequently, the samples were put through a nitric acid digestion process, and then filtered to remove excess solids. The total chloride content at different depths was determined using automatic potentiometric silver nitrate titration of the remaining liquid solutions according to ASTM C1152, and ASTM C114, part 19 test methods. Besides, for each sample, chloride measurement was repeated three times for eliminating test errors. The obtained chloride ion profiles for investigated structural members which were placed in the tidal zone at different exposure time of 6 to 96 months are presented in Fig. 4. It is noted, the number after dash line in sample codes indicates the exposure time in months.

The apparent diffusion coefficient ( $D_{app}$ ) and the surface chloride content ( $C_s$ ) as independent variables can be determined by fitting the field data to error function solution of Fick's second law, given by Eq. (1). In the analysis of the chloride profile by using a computer statistical program, sum of squared differences between fitted (theoretical) and actual data for the chloride content of each sample must be minimized by adjusting the nonlinear regression variable. This is obtained by minimizing the sum given in Eq. (2).

$$S = \sum_{n=2}^N \Delta C^2(n) = \sum_{n=2}^N (C_m(n) - C_c(n))^2 \quad (2)$$

Table 5 Main parameters of chloride ion penetration and field investigation results for PSPC piles

Sample code	$D_{app}$ ( $10^{-12}$ m <sup>2</sup> /s)	$C_s$ (wt% of conc)	$R^2$	Carbonation depth, (mm)	Resistivity (k $\Omega$ .cm)	Concrete cover, (mm)
PSPC-06	0.722	0.101	0.965	~0	47	52.1
PSPC-12	0.493	0.122	0.987	~0	49	49.5
PSPC-24	0.420	0.147	0.997	~0	47	56.5
PSPC-36	0.366	0.192	0.990	~0.5	45	51.5
PSPC-48	0.340	0.267	0.996	~0.5	36	51.1
PSPC-60	0.289	0.294	0.988	~1.0	26	50.6
PSPC-72	0.355	0.408	0.932	1.5	23	55.5

Table 6 Main parameters of chloride ion penetration and field investigation results for CISC overlays

Sample code	$D_{app}$ ( $10^{-12}$ m <sup>2</sup> /s)	$C_s$ (wt% of conc)	$R^2$	Carbonation depth, (mm)	Resistivity (k $\Omega$ .cm)	Concrete cover, (mm)
CISC-06	2.650	0.459	0.992	~0	10.8	77.6
CISC-12	1.262	0.635	0.996	~0	13.5	75.3
CISC-24	0.940	0.911	0.987	~0.5	15.3	78.2
CISC-36	1.080	0.863	0.965	~0.5	22	71.5
CISC-48	1.038	1.045	0.981	~1.0	17.7	74.2
CISC-60	0.875	1.034	0.980	2.0	15.3	75.1
CISC-72	0.945	1.093	0.955	3.5	16	70.9
CISC-84	0.900	1.035	0.930	3.5	14.4	65.6
CISC-96	0.845	1.083	0.930	4.0	15.0	63.3

Table 7 Durability requirements for reinforced concrete structures exposed to severe marine environment

Durability issue	Allowable limit	Laboratory and site results		Control
		PSPC pile	CISC overlay	
28-day compressive strength (MPa)	Min=40	85.2	63.8	O.K.
Water to binder ratio	Max=0.4	0.30	0.35	O.K.
Minimum cement content (kg)	Min=350	520	450	O.K.
Concrete cover on reinforcement (mm)	Min=50	52.4	74.7	O.K.
Water absorption (%)	Max=2	1.15	1.55	O.K.
Water penetration depth (mm)	Max=10	5	~10	O.K.
Rapid chloride penetration (coulomb)	Max=2000	317	767	O.K.

collection of concrete dust samples during drilling, vacuum attachment is used and the geometry of the drilled hole is taken into account for calculation of the depth of each sample.

The first 2 mm concrete powder was not included in calculations as it might be affected by actions such as washout, etc. Also, surface electrical resistivity of existing members was measured by Wenner test method as a nondestructive test. Previous study (Moodi *et al.* 2014) showed the amount of surface electrical resistivity can represent the concrete surface permeability that is useful for evaluation of concrete durability in marine environment. Fig. 3 shows general tidal levels and the exact distance between extracted concrete powder and top deck of structure.

In the laboratory, the fine concrete particles were pulverized so that all the material passed a 150- $\mu$ m (No.100) sieve. At each depth, a sample having a mass of approximately 10gr was

## 4. Discussion

### 4.1 Durability provisions in harsh marine conditions

Although most codes for concrete durability have been upgraded a number of times during the past 30 years, current code specifications are still based almost exclusively on prescriptive requirements to achieve the desired design service life according to the avoidance of deterioration approach. It means that the durability requirements for concrete structures are mostly based on the deemed-to-satisfy approach of specifying certain limiting values such as minimum specified concrete strength, maximum water to binder ratio, minimum cover thickness, maximum structural crack width and etc.

As explained in Section 2.1, the exposure conditions of tidal zone in BIK zone, are categorized at exposure class C2 & XS3 according to ACI 318-08 (2008) and EN 206-1 (2001), respectively. Therefore, certain limiting values shall be satisfied in concrete. Results of experiments in the laboratory on the concrete being very similar to the real structural members are evidences for considering durable concrete against chloride attack. According to Table 7, all results are complying with relevant minimum requirements.

Based on results in Table 7, conventional approach just ensures that the target reliability for not passing relevant limit state is not exceeded, during service life of structures. However, these approaches give no guidance on how long a structure may remain in service. Subsequently, in

advanced model codes like fib MC2010 (2011), the requirements related to exposure classes have been established by using performance-related design methods for durability and specified in terms of performance-related parameters.

#### 4.2 Chloride penetration profiles during exposure time

The chloride concentration profile in concrete from the exposed surface inwards is a valuable tool for assessing the risk of reinforcement corrosion in concrete structures exposed to marine environments. From the knowledge of the chloride profile of a structure at a given age, one can get some qualitative information about the rate of ingress of such ions into the structure, and then predictions about the initiation time of reinforcement corrosion can be formulated. These assessments are highly improved when several chloride profiles are obtained at different times for the same structure.

According to Tables 5 & 6, in the regression analysis of Eq. (1), correlation coefficients between 0.93 and 1 were obtained. This reveals that Eq. (1) can estimate quite well the chloride penetration in concrete for a certain time interval. Additionally, it is obvious from chloride profiles in Fig. 4 that the chloride penetration was much lower in PSPC pile than for CISC overlay at the same age, which may be due to the following major effects. Firstly, the formation of better pore structure in concrete with lower  $w/b$  ratio and secondly, the construction conditions which lead to enhancement of concrete quality and reduction of concrete porosity in precast structural members. Also, in comparison to other work on concrete with no addition of pozzolanic materials at the same exposure condition (Ramezaniapour and Pourkhorshid 2012), the chloride content is decreased significantly. This behavior is due to the silica fume effect on the pore structure and reducing concrete permeability. That could be attributed to its ultra-fineness and activity (higher values of amorphous components) which lead to the formation of intense pozzolanic reaction products within the capillary pore spaces and as a consequence, finer and more segmented pore system is produced as found in several previous studies (Safehian and Ramezaniapour 2013; Nokken *et al.* 2006).

#### 4.3 Time dependence of apparent diffusion coefficient

Diffusion coefficient is one of the important parameters in concrete behavior under chloride ion transport. Some researchers (Kassir and Ghosn 2002; Hooton *et al.* 2002) consider Eq. (1) as constant diffusion coefficient that is called apparent diffusion coefficient ( $D_{app}$ ). Some others use the crank solution method but consider apparent diffusion coefficient as a factor that varies as time changes. They suggest that apparent diffusion coefficient does not essentially represent the absolute diffusion coefficient rather indicates average of what has happened to concrete which is suitable for estimation of the behavior of concrete against chloride ion transfer (Ramezaniapour *et al.* 2012). Hence, the apparent diffusion coefficient is considered in this study. It should be noted some of the chloride ions bound to the cement paste system may be released when parameters of capillary water change, as pH value, temperature and pressure. Therefore, it is most convenient to determine the chloride of the concrete as acid-soluble chloride (Petcherdchoo 2013; Nokken *et al.* 2006).

In addition to several accelerated techniques for determination of the chloride diffusion in laboratory conditions, the time dependence of this coefficient has to be studied for each particular

concrete construction method and exposure condition, especially in harsh marine environments. Time dependent diffusion through concrete has been observed to be a power function (Mangat and Molloy, 1994; Tang and Gulikers 2007) as in Eq. (3).

$$D_{app}(t) = D_{ref} \left( \frac{t}{t_{ref}} \right)^{-m} \tag{3}$$

where  $D_{app}(t)$ ,  $D_{ref}$  are defined as the diffusion coefficient after exposure time  $t$  and  $t_{ref}$ , respectively. Also,  $t$  is expressed in years and reference time ( $t_{ref}$ ) is considered as one year ( $t_{ref} = 1$ ). The  $m$  coefficient in Eq. (3) is a constant. It is dependent on variables such as the type of cementitious materials used and the mixture proportions, and has been developed to account for the rate of reduction of diffusivity with time.

The  $m$  values for different concretes have yet to be well established, although some values have been published (Mangat and Molloy, 1994; Nokken *et al.* 2006). Further research to properly quantify this parameter, especially in one of the most severe marine environment (see Table 1), would help to improve the accuracy of service life predictions. Prediction of the time when a critical chloride concentration is reached at the depth of the steel reinforcement would be more accurate if the changes in diffusion properties of a concrete with time were better taken into account. Also, it should be noted that the diffusion coefficient for each exposure period in fact lies somewhere between the instantaneous values one would find if the specimen was tested at the beginning of the exposure period and at the end. Accordingly, Nokken *et al.* (2006) showed that the calculated time-dependant reduction coefficient is highly dependent on the time value used: total, average, or effective time. There are few, if any, published values of the time-dependant reduction coefficient using the average age method,  $m_{ave}$ , or the effective age method,  $m_{eff}$  (Stanish and Thomas, 2003). The majority of published data uses the maturity of the specimen at the end of the exposure period as the time basis used to calculate the reduction coefficient ( $m_{total}$ ). Therefore, the values presented in this paper are on the base of total time method.

The parameters  $D_{ref}$  and  $m$  were obtained by applying Eq. (3) to the field investigation results presented in Tables 5 & 6. This equation was written in a linear form and a linear regression analysis was applied until minimizing the sum of squares of errors. The values obtained for PSPC piles and CISC overlays are presented in Fig.5.

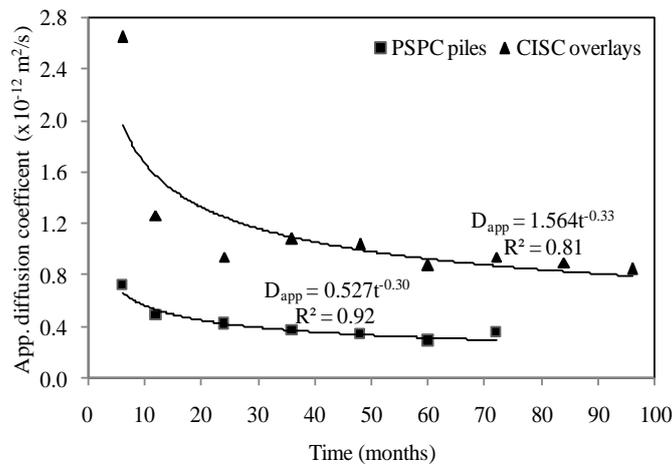


Fig. 5 Time-dependent variation of apparent diffusion coefficient

As shown in Fig. 5, a reduction trend is observed in the diffusion coefficient over time. The reduction coefficient,  $m$ , for PSPC piles is lower than for CISC overlays with increasing  $w/b$  ratio from 0.30 to 0.35, but the reference diffusion coefficient,  $D_{ref}$ , is much lower. This behavior may be due to the following major effects:

- Hydration of cement, which leads to a reduction of concrete porosity and hence the diffusion coefficient. This effect has particular influence in the first ages of concrete.
- Formation of a layer of aragonite and brucite on the concrete surface which reduces the chloride penetration. This effect is particularly relevant in the tidal zone where the concrete is in contact with sea water. The formation of this protective layer and its effect on the reduction of concrete permeability has been reported by others (Costa and Appleton, 1999; Amey *et al.* 1998).
- Reaction of the cement hydrated products with ions contained in sea water. Chloride ions react with tri-calcium aluminate to form chloroaluminates; magnesium and sulfate ions react with the cement compounds to form brucite and ettringite.

#### 4.4 Time dependence of surface chloride content

Surface chloride ion content ( $C_s$ ) is another important parameter for estimation of chloride ion transfer obtaining from fitting the equation of the Fick's second law. Extended researches (Safehian and Ramezaniapour 2013; Costa and Appleton 1999; Pack *et al.* 2010) for the estimation of this value indicate that amount of surface chloride ion not only depends on exposure conditions, but also depends on the concrete type and atmospheric and geometric conditions of the concrete. In addition, the surface chloride concentration depends on the chloride binding capacity of concrete and its porosity at the surface. The value of the bound chloride concentration may be estimated from the existing information on the relationship between bound and free chloride ions (Dousti *et al.* 2011).

Although a previous study suggested that the  $C_s$  could increase with time (Amey *et al.* 1998), a constant value of the  $C_s$  has been often used to model a chloride profile at tidal or splash zone, because of intuitive support that chemical equilibrium at the concrete surface sustain a certain concentration of chloride, when a concrete is subjected to a direct contact with seawater. In order to take this effect into account in a model for prediction of the chloride penetration, the relation between the surface chloride content and time can be expressed, as proposed by Costa and Appleton (1999), by a power function as in Eq. (4).

$$C_s(t) = C_{ref} \left( \frac{t}{t_{ref}} \right)^n \quad (4)$$

where  $C_s(t)$ ,  $C_{ref}$  are defined as the surface chloride content after exposure time  $t$  and  $t_{ref}$ , respectively. Also,  $t$  is expressed in years and reference time ( $t_{ref}$ ) is considered as one year ( $t_{ref}=1$ ). The  $n$  is an empirical constant parameter. The parameters  $C_{ref}$  and  $n$  were obtained by applying Eq. (4) to the field investigation results presented in Tables 5 & 6. In the regression analysis of Eq. (4), correlation coefficients are more than 0.90. This shows that in fact this equation expresses quite well variation of  $C_s$  over time. The obtained values for PSPC piles and CISC overlays are presented in Fig. 6.

The differences of  $C_s$  build-up for PSPC piles and CISC overlays, generally indicate how concrete quality ( $w/b$  ratio) and its permeability in the surface can significantly affect the chloride penetration at initial depths. Also, according to Tables 5 & 6, PSPC piles exhibited relatively higher surface electrical resistivity than CISC overlays. That could be attributed to their surface permeability which leads to lower surface chloride content in PSPC piles.

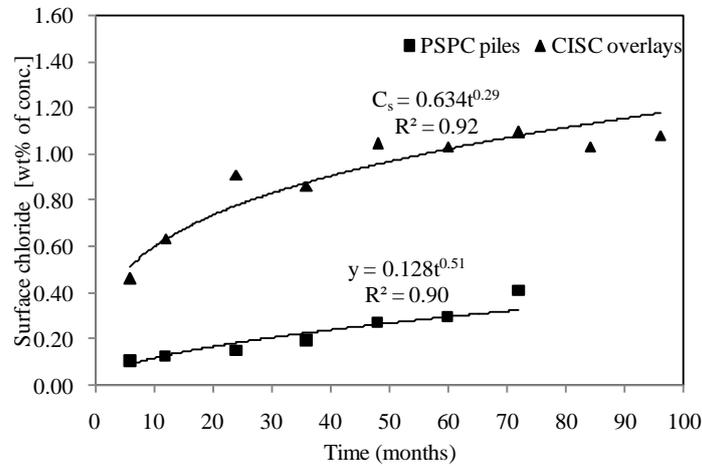


Fig. 6 Time-dependent variation of surface chloride content

As clearly mentioned in previous studies (Costa and Appleton 1999; Pack *et al.* 2010), in tidal zone near high water level, the wet and dry cycles result in a successive supply of chlorides by wetting with sea water, and evaporation and salt crystallization by drying. Water absorption may lead to a very rapid penetration of chloride ions dissolved in sea water. This mechanism may lead to an accumulation of chlorides in the surface zone and may also give rise to concentration peaks inside the concrete which tends to progress to the interior over time.

Also, the obtained surface chloride content is higher than reported values from the tidal zone of other marine environments (Costa and Appleton 1999; Moradillo *et al.* 2012). This finding confirms the high concentration of chloride ions in sea water of BIK zone, compared to other marine environments, as shown in Table 1.

#### 4.5 Prediction of long term chloride penetration

It is clear from previous sections that both the apparent diffusion coefficient and the surface chloride content show significant time dependence. Thus, such dependence should be considered in the prediction of long term chloride penetration. This can be done by substituting Eq. (3) and Eq. (4) in Eq. (1). Also, it should be noted, as proposed by other famous models such as Life-365™ (Thomas and Bentz 2001) and Fib2012-M (Ramezani-pour *et al.* 2012), in order to prevent the apparent diffusion coefficient decreasing with time indefinitely, Eq. (3) is assumed only valid up to 20 years and beyond this time,  $D_{app}(t)$  stays constant at  $D_{app}(t=20)$  value. Also,  $C_s(t)$  in Eq. (4) should be limited up to 1.4% by weight of concrete that is related to chemical equilibrium at the concrete surface which is subjected to a direct contact with seawater in the tidal exposure conditions of BIK zone.

To evaluate the validation of above method, four in field chloride profiles from other RC marine structures (No. 3 & 4 in Fig. 1) and predicted chloride profiles are presented in Figs. 7 & 8. These old structures have approximately similar PSPC piles and CISC overlays to under investigated structures in previous sections. As a result, comparison of chloride profiles in Figs. 7 & 8 shows that for both of PSPC piles and CISC overlays, the proposed equations could quite well predict chloride penetration after 33 & 39 years of exposure to tidal zone.

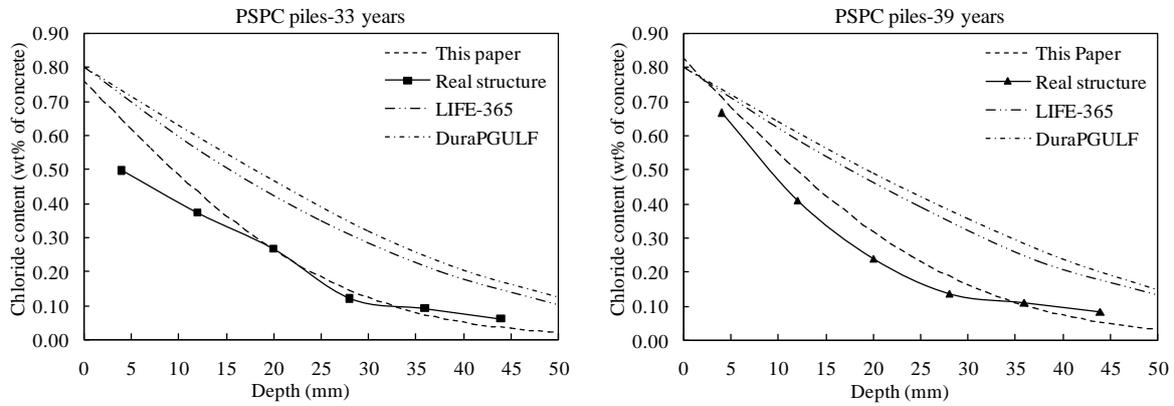


Fig. 7 Comparison between real and predicted chloride profiles in PSC piles

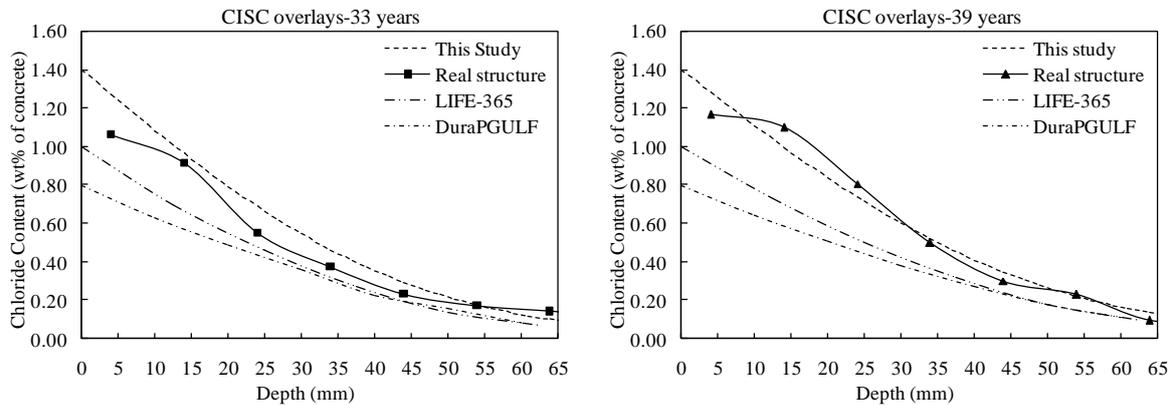


Fig. 8 Comparison between real and predicted chloride profiles in CISC overlays

On the other hand, There are software packages available to aid in concrete deterioration modeling and prediction of long term chloride penetration, such as DuraPGulf from Building Materials Institute of Tehran University (Shekarchi *et al.* 2008) and Life-365<sup>TM</sup> (Thomas and Bentz, 2001) service life predication model by the consortium consisting of the Slag Cement Association (SCA), the Concrete Corrosion Inhibitors Association (CCIA), National Ready Mixed Concrete Association (NRMCA) and the Silica Fume Association (SFA). The predicted chloride penetration profiles after 33 & 39 years of exposure in the same site conditions similar to BIK zone are presented in Figs. 7 & 8, using mentioned service life models. As could be seen in Figs. 7 & 8, the long term chloride penetration in the real marine environment can be very difficult to predict or even model, as it depends on not only the exposure conditions (see Table 1) but also on the heterogeneous nature of the concrete matrix, the difficulty in fabricating concrete in a reproducible manner, and the inherently probabilistic nature of species transport in concrete and of chloride-induced corrosion of rebar in concrete. Therefore, for applying the service life models in a specific location, it is important to calibrate the model by long term field investigations in a specific environmental condition.

It should be noted that proposed values for basic parameters in Eq. (3) and Eq. (4) are only

obtained for each particular concrete construction method and environmental conditions of BIK zone. Also, they are dependent on variables such as type of cementitious materials and mixture proportions. Therefore, it highly recommended that basic parameters of long term chloride penetration shall be calibrated by increasing number of tests performed on in-site RC structures in the real conditions, especially in severe marine environments.

#### 4.6 Prediction of corrosion initiation time

The corrosion of concrete structures can be described as two stages: (i) corrosion initiation; and (ii) corrosion propagation. The corrosion initiation stage corresponds to the process of chloride ions (chlorides) ingress into concrete (and/or carbonation, which is outside the scope of this paper) while the steel remains passive. The corrosion propagation stage starts after the initiation of active corrosion, and it often occurs after the chloride concentration on the steel surface reaches a certain critical value ( $C_{crit}$ ) and steel is depassivated. Therefore, the duration of the initial stage, which is often used as a quantitative indicator of service life or durability of concrete structures, depends on the rate of chloride penetration in concrete. The needs to predict the service life of existing structures and to design more durable structures, as well as to extend their service life through effective maintenance strategies, are the objectives of the extensive efforts for modeling chloride ingress, corrosion initiation, and corrosion propagation in concrete structures in the last three decades (Rilem report 14).

However, it should be mentioned that the service life is not a fixed value as calculated by a deterministic model, but instead it is a stochastic value determined by material characteristics, cover depth, and severity of marine environments. Therefore, the probabilistic approach for estimating service life of RC structures is more reliable than the deterministic approach. One common modern statistical technique is the application of modified Monte Carlo simulations that authors and their colleagues in CTDRC have used it in modifying the fib 2006 model for predicting the service life of under investigated RC structures in the tidal zone of BIK zone (Ramezani pour *et al.* 2012). According to this probabilistic model, the time of corrosion initiation for PSPC piles and CISC overlays (with minimum concrete cover in Tables 5 & 6) are predicted 58 & 40 years, respectively. It should be noted, the concrete cover on reinforcement is decreased to 50 mm in PSPC piles, but the predicted time of corrosion initiation is greater than CISC overlays due to high performance concrete (HPC) in PSPC piles. In contrast, a same increase in the concrete cover of PSPC piles to 70 mm, prolongs the time of corrosion initiation from 58 to 93 years.

## 5. Conclusions

This study was conducted to assess the effect of tidal exposure conditions on the long term chloride penetration into onshore RC structures. The exposure duration of investigated structures was 6 months to 96 months. The following conclusions can be drawn based on the test results:

(1) Both field investigations and accelerated durability tests have shown that used concrete in repair work is appropriately durable, even under the most severe exposure conditions like the one in the Persian Gulf region.

(2) The achieved excellent durability properties of PSPC piles in field investigations and accelerated durability tests, suggest that PSPC piles may reduce maintenance costs and help extend

the service life of marine structures, particularly those in harsh environments, greater than fifty years.

(3) The apparent diffusion coefficient ( $D_{app}$ ) and the surface chloride content ( $C_s$ ) are time dependent in the form of power functions. These relations could be used to predict long term chloride penetration into concrete structures exposed to the tidal zone.

(4) The influence of concrete quality on diffusion coefficients is related to the concrete pore structure and the time dependence is due to the cement particles hydration and to chemical reactions of sea water ions with hydration products which lead a reduction in the pore structure.

(5) Finally, it seems that making quantitative parameters out of qualitative parameters of durability is one of the most complicated stages of the modeling that generally has confronted strong uncertainties. Increasing number of tests performed on in-site structures in the real conditions and using probabilistic approach in estimations can be mentioned as guidelines to reduce uncertainties.

Further studies are going on at the Concrete Technology and Durability Research Center (CTDRC) to evaluate other factors affecting the chloride penetration into concrete in order to develop more reliable service life prediction models for improving concrete durability at severe marine environments.

## References

- ACI (American Concrete Institute) (2008), *ACI 318-08: Building Code Requirements for Structural Concrete*, ACI, Farmington Hills, MI, USA.
- Amey, S.L., Johnson, D.A., Miltenberger, M.A. and Farzam, H. (1998), "Predicting the service life of concrete marine structures: an environment methodology", *ACI Struct. J.*, **95**(2), 205–214.
- Andrade, C., Tavares, F., Castellote, M., Petre-Lazars, I., Climent, M.A. and Vera, G. (2006), "Comparison of chloride models: the importance of surface condition", *In: Second international symposium on advances in concrete through science and engineering*, Quebec City, Canada.
- Andrade, C., Prieto, M., Tanner, P., Tavares, F. and Andrea, R. (2013), "Testing and modelling chloride penetration into concrete", *Constr. Build. Mater.*, **39**, 9-18.
- Bamforth, P.B. and Price, W.F. (1997), *An international Review of Chloride Ingress into Structural Concrete*, Transport Research Laboratory report 359, Scotland.
- Cheewaket, T., Jaturapitakkul, C. and Chalee, W. (2013), "Concrete durability presented by acceptable chloride level and chloride diffusion coefficient in concrete: 10-year results in marine site", *Mater. Struct.*, DOI 10.1617/s11527-013-0131-4.
- Costa, A. and Appleton, J. (1999), "Chloride penetration into concrete in marine environment-Part II: Prediction of long term chloride penetration", *Mater. Struct.*, **32**, 354-359.
- Crank, J. (1975), *The Mathematics of Diffusion*, 2nd ed, London, Oxford.
- Dousti, A., Shekarchi, M., Alizadeh, R. and Taheri, A. (2011), "Binding of externally supplied chlorides in micro silica concrete under field exposure conditions", *Constr. Build. Mater.*, **33**, 1071-1079.
- EN 206-1, (2001), *Concrete-Part 1: Specification, Performance, Production and Conformity*, European standard, Berlin, Germany.
- Hooton, R.D., Geiker, M.R. and Bentz, E.C. (2002), "Effects of curing on chloride ingress and implications on service life", *ACI Mater. J.*, **99**, 201–206.
- Kassir, M.K. and Ghosn, M. (2002), "Chloride-induced corrosion of reinforced concrete bridge decks", *Cement Concrete Res.*, **32**, 139–143.
- Kropp, J. (1995), "Chlorides in concrete. In: Performance criteria for concrete durability", *RILEM Report 12*, E& FN SPON, 138–164.
- Lau, K., Powers, R.G. and Sagues, A.A. (2006), "Corrosion performance of concrete cylinder piles", *In:*

- 61th NACE conference on corrosion, Houston, USA.
- Mangat, P.S. and Molloy, B.T. (1994), "Prediction of long-term chloride concentration in concrete", *Mater. Struct.*, **27**, 338–346.
- Mehta, P.K. (1988), "Durability of concrete exposed to marine environment- fresh look", *ACI SP 109*, 1-29.
- Model code-fib, (2011), fib Special Activity Group 5.
- Moodi, F., Ramezani-pour, A.A. and Jahangiri, E. (2014), "Assessment of some parameters of corrosion initiation prediction of reinforced concrete in marine environments", *Comput. Concr.*, **13**(1).
- Moradillo, M., Shekarchi, M. and Hoseini, M. (2012), "Time-dependent performance of concrete surface coatings in tidal zone of marine environment", *Constr. Build. Mater.*, **30**(1), 198-205.
- Nilsson, L.O. (2006), "Present limitations of models for predicting chloride ingress into reinforced concrete structures", *J. Phys. IV France*, **136**, 123–130.
- Nokken, M., Boddy, A., Hooton, R.D. and Thomas, M.D.A. (2006), "Time dependent diffusion in concrete-three laboratory studies", *Cement Concrete Res.*, **36**, 200-207.
- Pack, S., Jung, M., Song, H., Kim, S. and Ann, K.Y. (2010), "Prediction of time dependent chloride transport in concrete structures exposed to a marine environment", *Cement Concrete Res.*, **40**, 302-312.
- Petcherdchoo, A. (2013), "Time dependent models of apparent diffusion coefficient and surface chloride for chloride transport in fly ash concrete", *Constr. Build. Mater.*, **38**, 497-507.
- Ramezani-pour, A.A., Jahangiri, E., Ahmadi, B. and Moodi, F. (2012), "Evaluation and modification of the fib service-Life design model for the Persian Gulf region", In: fib symposium: concrete structures for sustainable community, Stockholm, Sweden.
- Ramezani-pour, A.A. and Pourkhorshid, A.R. (2012), "Durable concretes for hot and severe environments", In: International congress on durability of concrete, Trondheim, Norway.
- Rilem report 14, (1996), "Durability design of concrete structures", In: *Sarja A, Vesikari E, Editors*, E&FN Spon.
- Saassouh, B. and Lounis, Z. (2012), "Probabilistic modeling of chloride-induced corrosion in concrete structures using first and second-order reliability methods", *Cement Concrete Compos.*, **34**, 1082–1093.
- Safehian, M. and Ramezani-pour, A.A. (2013), "Assessment of service life models for determination of chloride penetration into silica fume concrete in the severe marine environmental condition", *Constr. Build. Mater.*, **48**(1), 287-294.
- Safehian, M. and Ramezani-pour, A.A. (2014), "Assessment of long term chloride diffusion in real RC structures in marine environment", *European J.Sci. Res.*, **120**(3), 332-345.
- Shekarchi, M., Alizadeh, R., Ghods, P., Chini, M. and Hosseini, M. (2008), "Durability based design of RC structures in south of Iran using DuraPGulf model", *AJSE, Arabian J.Sci. Eng.*, **33**(1), 77–88.
- Shekarchi, M., Moradi, F. and Pargar, F. (2011), "Study on corrosion damage of a reinforced concrete jetty structure in coastal region of Persian Gulf, a case Study", *Struct. Infrastr. Eng.*, **7**(9), 701-713.
- Shin, K.J., Kim, J.S. and Lee, K.M., (2011), "Probability-based durability design software for concrete structures subjected to chloride exposed environments", *Comput. Concr.*, **8**(5).
- Stanish, K. and Thomas, M.D.A., (2003), "The use of bulk diffusion tests to establish time-dependent concrete chloride diffusion coefficients", *Cement Concrete Res.*, **33**, 55-62.
- Tang, L. and Gulikers, J. (2007), "On the mathematics of time-dependent apparent chloride diffusion coefficient in concrete", *Cement Concrete Res.*, **37**, 589–595.
- Thomas, M.D.A. and Bentz, E.C. (2001), "Life 365: Computer program for predicting the service life and life-cycle costs of reinforced concrete exposed to chlorides", *Am. Concrete Inst.*, Committee 365, Service life prediction, Detroit, Michigan.
- Tuutti, K. (1996), "Chloride induced corrosion in marine concrete structures", In: *Durability of concrete on saline environment*, Uppsala; 81–93.
- Vennesland, Q., Climent, M.A. and Andrade, C. (2013), "Recommendation of RILEM TC 178-TMC: Testing and modelling chloride penetration in concrete", *Mater. Struct.*, **46**, 337-344.
- Wang, X.Y., Park, K.B. and Lee, H.S. (2012), "Modeling of chloride diffusion in a hydrating concrete incorporating silica fume", *Comput. Concr.*, **10**(5).

- Yuan, Q., Shi, C., Schutter, G.D., Audenaert, K. and Deng, D. (2009), "Chloride binding of cement-based materials subjected to external chloride environment-A review", *Constr. Build. Mater.*, **23**(1), 1-13.
- Zhang, S., Lu, C. and Liu, R. (2011), "Experimental determination of chloride penetration in cracked concrete beams", *Procedia Eng.*, **24**, 380-384.

CC