Second Conference on Smart Monitoring,
Assessment and Rehabilitation of Civil Structures

SMAR 2013

Assessment of long term chloride diffusion in real RC structures exposed to Persian Gulf region

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ABSTRACT: Reinforced concrete marine structures are widely constructed in the Persian Gulf region for infrastructures of ports and oil exploration. But these structures are increasingly being deteriorated, mainly due to the chloride-induced corrosion of embedded bars. Consequently, hundreds of million dollars are spent for repair and rehabilitation of structures every year.

In present study, two reinforced concrete jetties and their access bridges exposed to severe tidal zone of Persian Gulf marine environment were examined to assess the long term chloride penetration, depending on exposure duration at 7 months to 72 months. Also, some accelerated durability tests were performed on standard samples with same concrete mixture in laboratory.

As a result, the apparent diffusion coefficient (D_{app}) and the surface chloride concentration (C_s) are time dependent in the form of a negative and positive power function, respectively. Additionally, carbonation depth result shows that the influence of carbonation on corrosion of reinforcement is not significant in tidal zone.

1 INTRODUCTION

For reinforced concrete structures exposed to chloride-laden environments, the chloride permeability of concrete has been recognized as a critical intrinsic property of concrete [1]. Both the chloride ingress into concrete and the subsequent corrosion initiation of rebar in concrete are complex processes, which are influenced by numerous factors (e.g., temperature cycles and wet–dry cycles experienced by field concrete) [2]. Costa and Appleton [3] 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). It 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.

The application of Fick's law and a constant diffusivity of concrete assume the concrete to be fully saturated and free of time-dependent cover cracking. Castro et al. [4] studied chloride concentration profiles from field exposed concrete and revealed that "the environmental conditions of the tropical marine climate in cylindrical concrete specimens promoted the formation of two zones: one internal that is always dampened and one external that is always wetting and drying".

Through the use of concrete deterioration models, cost-effective decisions can be made concerning the appropriate time to repair or replace existing structures, and the most effective corrosion control strategies [2]. The effect of environmental conditions on the prediction of models is one of the most important issues. Hence, regional investigations are necessary. This is particularly important in harsh environment such as Persian Gulf region where structures have been characterized by short service life spans compared to their counter parts elsewhere [5]. Ramezanianpour et al. [6] proposed a modified fib service-life design model for predicting the service life of reinforced concrete structures in Persian Gulf environment.

In present study, two reinforced concrete jetties and their access bridges exposed to severe tidal region of Persian Gulf marine environment were examined to assess the long term chloride penetration, depending on exposure duration at 7 months to 72 months. 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. Finally, corrosion initiation time was estimated by four service life prediction models.

2 ENVIRONMENTAL CONDITIONS

The level of chloride transport may be varied to a large degree by the location of structure, the degree of exposure to chloride environment and weathering condition with regard to temperature and humidity. Uji et al. [7] showed from a long-term monitoring from 23 to 58 years that the order of C_S with regard to the degree of vicinity of seawater is tidal>splash>atmospheric zone. The climate is also a crucial impact to the rate of chloride transport. Song et al. [8] compared the chloride transport of concrete from three different latitudes: in the UK, Japan and Venezuela. Then they found that concrete structures exposed to a tropical environment are more susceptible to chloride attack, and concluded that the tropical climate is better for chloride ions to move into concrete due to high level of relative humidity, temperature and chloride concentration.

In this study, under investigated jetties are constructed in the latitude 30°, 25' N and longitude 49°, 4' E at a distance of 65km from the mouth of Persian Gulf that is called BIK (Bandar Imam Khomeini) zone. 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. Accordingly, BIK zone has a desert type climate that is described in table 1. The annual rainfall is less than 200mm on the average and also, the mean evaporation rate is estimated to be around 2000mm per year.

Table 1. Climatic features in BIK zone

Feature	amount	unit
Average maximum temperature	35	°C
Average minimum temperature	12	°C
Absolute maximum temperature	50	°C
Absolute minimum temperature	6	°C
Average relative humidity	46	%
Absolute maximum humidity	96	%
Absolute minimum humidity	8	%
Average of dusty days in year	87	day

Source: I.R. of Iran Meteorological Organization website (www.weather.ir)

In addition to the importance of climatic conditions, other factors, e.g. salinity of seawater, should be considered in the durability-based design of structures in marine environments. The measurement of the main aggressive elements of seawater values are given in Table 2. The amounts of chloride and sulfate ions are higher than the average of Persian Gulf water. Semi-close nature of region, type of ocean current system, high level of evaporation, not much of rainfall and not much freshwater inflow of rivers may be the main reasons for high salinity of the seawater in this region [9].

Table 2. Chemical analysis of seawater in BIK zone

Feature	ion K^+	ion Ca^{2+}	ion Mg^{2+}	ion Na^+	ion SO_4^{2-}	ion Cl^-	PH
Amount	450	430	1460	12400	4650	29370	8.03
Unit	mg/lit	mg/lit	mg/lit	mg/lit	mg/lit	mg/lit	---

3 DESCRIPTION OF STRUCTURES

With a history of 85 years, Imam Khomeini Port is considered to be one of the most important commercial ports of Iran which handles about half of all non-oil trades of the country.

The under investigated structures, eastern and western jetties and their access bridges, were constructed 1928 to 1940. After more than 65 years, these structures were decided to repair and rehabilitate according to physical development concepts for port. Repair work was undertaken six years ago with proper attention to long term durability issues. Fortunately, all project technical specifications and methods of repair work be carefully recorded and maintained for future reference. Based on the official documentary information, structural properties, raw material characteristic, concrete mix features and under construction pictures which are investigated in this study, are reported as follows. Figure 1 shows some pictures of western truck bridge before and after repair work.

Figure 1. Pictures from field structures in BIK zone, left: before repair (2002), right: after repair (2012)

According to documentary information, cement used was type I(PM) blended cement from the Bushehr company, which would conform to the ASTM C595. Chemical analysis of cement is shown in Table 3. In addition to blended cement, silica fume was used that contained 89% SiO_2 with pozzolanic activity index 103% and meets other requirements of ASTM C1240. Dolomite and quartzite were used as coarse aggregate, and fine aggregates were natural river sand. The results of tests showed that these aggregates were inactive according to ASTM C289. The aggressive components of aggregates and mix water were in authorized limits for construction in marine environment. Also, superplasticizer was used to achieve desired workability. High range water reducing agent had met the requirements for type-F of ASTM C494.

Table 3. Chemical and features of cement

Item	amount	ASTM C595	unit
Silicon Dioxide (SiO_2)	24.6	24±3	%
Calcium Oxide (CaO)	57.9	57±3	%
Magnesium Oxide (MgO)	3.25	6.0 max	%
Sulfur Trioxide (SO_3)	1.9	4.0 max	%
Aluminum Oxide (Al_2O_3)	6.1	6±2	%
Ferric Oxide (Fe_2O_3)	3.57	---	%
Loss on Ignition (LOI)	1.6	5.0 max	%
Equivalent Alkalies	0.84	---	%

It is well known that durability issues are of main concern for marine structures. Therefore, concrete mixes for such structures or at least the elements exposed to marine environment should preferably be rich in cementitious materials. Also, the water to binder materials (w/b) ratio should be as low as possible. These precautions are normal for production of low permeability concrete which is the main key to durability. Based on the mentioned considerations, a summary of the main features of designed concrete mixtures shown in table 4.

Table 4. Properties of concrete mixtures (in 1xm^3 fresh concrete)

Item	water	cement	Silica fume	Coarse aggregate	Fine aggregate	Super plasticizers	Density	Slump	Characteristic Strength	Water-to-binder ratio
Amount	169	450	32	410	1232	7	2300	10-12	45	0.35
Unit	kg	kg	kg	kg	kg	kg	kg	cm	MPa	---

In addition to regular quality control for raw materials in concrete, some other strength and accelerated durability tests are carried out in local laboratory during rehabilitation of structures. Table 5 represents some result of mentioned tests, briefly.

Table 5. Local test results during rehabilitation of structures

Experiment	Standard method	result	unit
Workability by Slump test	ASTM C143	10-13	cm
Rapid Chloride Penetration Test	ASTM C1202	1033-1291	coulomb
Water penetration test	EN-12390-8	6-16	mm
Water absorption test	BS-1881 part122	1.6-3.1	%
Compressive strength (28day)	BS-1881 part116	53-65	MPa

4 EXPRIMENTAL PROGRAM

In order to analyze chloride penetration into concrete and predict corrosion initiation time with available models, two series of experiments were performed. The first series was on standard samples with similar concrete mix design of field structures in laboratory and the second series of tests were performed on the real repaired piles with new concrete jacket in Bandar Imam Khomeini (BIK) zone.

4.1 Laboratory test methods

As mentioned before, the mix design of concrete made in the lab and the applied materials were similar to those of real investigated structures [10]. The experiments in lab included: RCPT (Rapid Chloride Penetration Test), SR (Surface Resistivity), RCMT (Rapid Chloride Migration Test) and compressive strength at the ages of 28 days. The results of these experiments are shown in table 6.

Table 6. Laboratory experimental results

Experiment	Standard method	result	unit
Rapid Chloride Penetration Test	ASTM C1202	1365	coulomb
Surface Resistivity	Wenner test	36	kΩ.cm
Rapid Chloride Migration Test	NT Build 492	169	mm^2/y
Compressive strength (28day)	BS-1881 part116	75	MPa

4.2 Field investigation methods

The performed experiments on real structures included surface resistivity (SR) by Wenner test method, extracting concrete core samples (50mm diameter) to assess chloride penetration and measuring carbonation depth by spraying a 1% phenolphthalein solution on internal surface of hole. Coring was made to depth of 65mm or upon reaching reinforcement. The assessment of in-site structures is fulfilled in 3 steps at October 2006, November 2010 and September 2012.

The core in each age of concrete was extracted from tidal exposure conditions. Figure 2 shows general tidal levels and the exact distance between extracted core and top deck of structure.

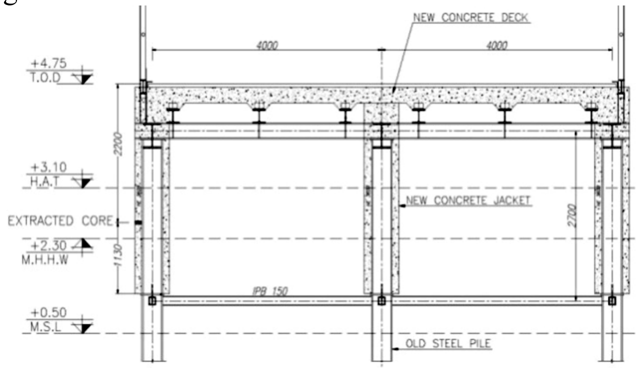

Figure 2. Location of extracting cores in transverse section of structure

In the laboratory, each core is grinded in six increments from finished surface to an estimated depth of chloride penetration. The first 2mm fine particles are not included in calculations as it might be affected by actions such as washout, etc. The fine particles from each layer is collected and pulverized so that all material will pass a 150-µm (No.100) sieve. At each depth, a sample having a mass of approximately 10gr is selected to the nearest 0.01gr and the analyzed for acid-soluble chloride content by the potentiometric titration of chloride with silver nitrate according with ASTM C1152, and ASTM C114, part 19. Chloride profiles of the concrete specimens which were placed in tidal zone at exposure time (7 to 72 months) are presented in figure 3.

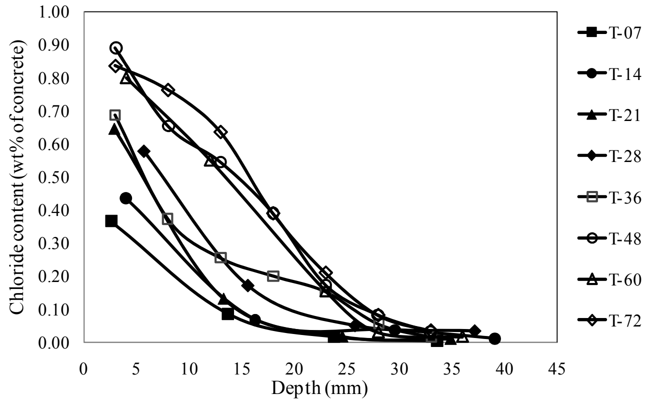

Figure 3. Obtained chloride profiles at tidal exposure conditions

Using a computer statistical analysis program, the nonlinear regression is carried out on the experimental data and by curve fitting of solutions of Fick's second law of diffusion, the values of D_{app} (apparent coefficient of diffusion) and C_s (surface chloride content) are determined as shown in table 7. Also, the results of surface electrical resistivity and carbonation depth are presented in the same table.

Table 7. Field investigation results

Sample code	Age (month)	D_{app} [i] (mm^2/year)	C_s [ii] (wt%/con)	R^2	Surface Resistivity (kΩ.cm)	Carbonation Depth (mm)
T-07	7	83.60	0.4587	0.99	10.8	~0
T-14	14	39.82	0.6349	0.99	N.D.	~0
T-21	21	23.29	0.8598	0.99	14.1	~0
T-24	24	N.D.[iii]	N.D.	N.D.	15.3	≤0.5
T-28	28	29.65	0.9107	0.99	N.D.	≤0.5
T-36	36	34.07	0.8634	0.96	22	≤0.5
T-48	48	32.73	1.045	0.98	14.7	~1.0
T-60	60	27.61	1.034	0.98	21.3	2.0
T-72	72	29.81	1.053	0.95	21	3.5

i Apparent coefficient of diffusion, ii Surface chloride content, iii No Data

5 DISCUSSION

5.1 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 for concrete durability are still based almost exclusively on prescriptive requirements for concrete composition and execution of concrete work [11]. It means that the durability requirements for concrete structures are mostly based on deemed-to-satisfy approach of specifying certain limiting values such as minimum specified concrete strength, maximum water-cement ratio, minimum cover thickness, maximum crack width and etc. But, these codes give no guidance on how long a structure may remain in service.

As explained in section 2, the exposure conditions of Persian Gulf, particularly BIK zone, is categorized at exposure class-C2 and class designation-XS3 according to ACI 318M-08 and EN206-1, respectively. So, certain limiting values shall be satisfied in concrete.

Results of experiments in laboratory on the concrete that is very similar to the real structures are evidences for considering durable concrete against corrosion induced by chlorides from sea water. As shown in table 8 all results are complying with relevant minimum requirements.

Table 8. durability requirements for structures in contact with sea water

feature	code	limit	result	unit
Specified strength (28day)	ACI318	min=35	45	MPa
Water to cement ratio	ACI318	max=0.4	0.35	---
Concrete cover on rebars	ACI318	min=50	70	mm
Rapid chloride penetration	EN206	max=20	1365	Culomb
Minimum cement content	EN206	min=350	450	kg/m^3

5.2 *Apparent diffusion coefficient*

Diffusion coefficient is one of the important parameters in estimation of concrete behavior under chloride ion transports. Researches indicate that the phenomenon of chloride ion transfer into concrete can be occurred due to mechanisms of diffusion, penetration, capillarity, migration and absorption [12]. Estimation of the behavior of concrete since 1970 has been mostly considered based on diffusion phenomenon and investigations on concrete also confirm above fact. Equations governing the diffusion are based on Fick's laws in the form of differential equation and can be solved in various forms. Some consider this equation as constant diffusion coefficient (Crank solution) that is called apparent diffusion coefficient used for estimations. Some other researchers 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 that is suitable for estimation of the behavior of concrete against chloride ion transfer into the concrete. Some others analyze the Fick's law with time variable diffusion coefficient and practically use the Fick's law of this parameter in the initial conditions of differential equation. Finally, it is not possible to judge about it via obtained chloride ion profile [12]. Hence, the apparent diffusion coefficient is considered in this study.

According to previous studies [13,14], it is shown that the D_{app} decreased with time, irrespective of binder, which may be related to a further hydration of cement, leading to a lower pore network. Increased hydration matrix may also repel the external aggressive ions from the cover concrete. Obtained results of chloride ion profiles in figure 4 represent this issue in a general case but by careful examination of the results it seems that this coefficient did not necessarily decrease under different conditions and sometimes even the apparent diffusion coefficient increases. This phenomenon can be investigated in unknown behavior of concrete in different conditions and assumptions about calculation of the apparent diffusion coefficient. However, determination of diffusion coefficient in different concrete ages by sampling from different parts of the structure, created at different time periods and consequently at different performance levels, leads to increased error that in return indicates inherent uncertainties of the problem. Calculated regression of power function with its correlation coefficient (R^2) is given in figure 4.

5.3 *Surface chloride content*

Surface chloride ion content is another important parameter in estimation of chloride ion transfer that is obtained after fitting of the equation of the Fick's second law. Extended researches related to estimation of this value indicate that amount of surface chloride ion in addition exposure conditions of the chloride ion is also dependent on concrete type, and atmospheric and geometric conditions of the concrete. This issue makes its estimation more complicated.

Although a previous study suggested that the C_s could increase with time [15], 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. It is, however, evident that a build-up of the C_s for concrete structures exposed to seawater was observed in previous surveys [13,14].

The amount of surface chloride at different ages of the samples extracted from real structures is shown in figure 4. According to results, amount of surface chloride ion increases during the time and its value is different in various durations. Calculated regression of power function with its respective correlation coefficient (R^2) is given in figure 4, too.

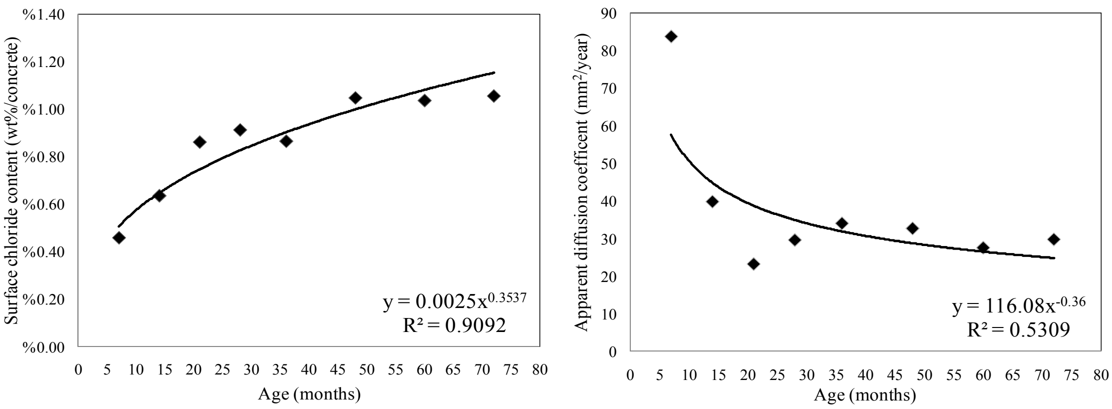

Figure 4.Time-dependent variation of surface chloride content (left), apparent diffusion coefficient (right)

5.4 *Surface electrical resistivity*

Theoretical and experimental studies indicate a correlation between concrete resistivity and chloride ingress [16]. In general, the chloride diffusion coefficient is inversely proportional to the concrete resistivity. One of the best methods to measure concrete resistivity is using four-point Wenner array probe resistivity meter. The non-destructive nature, speed, and ease of use, make the Wenner array probe resistivity technique a promising alternative test to characterize the chloride penetration resistance concrete, especially for marine in-situ assessments.

Figure 5 represents the results of this experiment at different ages of the real concrete structures. It is expected that concretes with higher age will show greater electrical resistivity. Because, when the age of concrete increases and rate of chloride ion penetration into concrete decreases (because of decreasing the permeability due to progress of hydration process), effect of increasing the age of concrete on electrical resistivity dominates comparing with effect of presence of chloride ions, and electrical resistivity increases as the age of concrete increases.

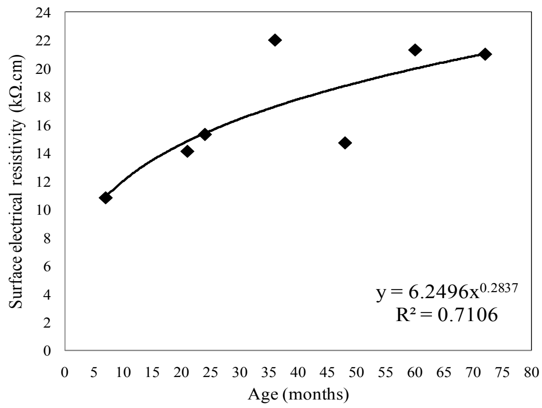

Figure 5. Time-dependent variation of surface electrical resistivity

6 CONCLUSIONS

This study was conducted to assess the effect of tidal exposure conditions on long term chloride diffusion into field RC structures. The following conclusions can be drawn based on test results:

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

(2) The apparent diffusion coefficient (D_{app}) and the surface chloride content (C_s) are time dependent in the form of a negative and positive power function, respectively. These relations could be used to predict long term chloride ingress in concrete structures exposed to tidal zone.

(3) Carbonation depth result shows that the influence of carbonation on the corrosion of reinforcement is not significant in tidal zone.

(4) According to the test results of the structure, it can be said that, considering the spent time and cost, surface electrical resistance test known as Wenner method provides relatively satisfactory results. However, application of this method depends on the user's experience and concrete moisture.

(5) Finally according to performed investigations 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.

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