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Influence of HCl corrosion on the mechanical properties of concrete

Pengfei Huang*, Yiwang Bao, Yan Yao

China Building Materials Academy, Guanzhuang, Beijing, 100024, PR China

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Abstract

Corrosion damage in three types of concrete (C25, C45, and C55), resulting from HCl with various contents, was investigated by comparing the mechanical properties of different types of concrete and their corrosion damage. The test samples that were cured for 360 days were exposed in an aggressive environment (with 5%, 10%, 15%, and 20% HCl content, respectively) for 24 h. The mass loss, the dynamic modulus loss, the flexural strength, and the compressive strength were measured using a series of the etched samples. The results indicate that the mechanical properties of concrete were degraded with the increasing HCl content of the corrosion medium. The etched samples of both the high- (C55) and normal-strength concretes (C25) exhibited the similar degradation of compressive strength. On the other hand, due to its greater sensitivity to defects when bending load is applied, bending strength showed greater decline in the high- than in the normal-strength concrete, which has greater loss of mass and elastic modulus.

Keywords: Mechanical properties; Corrosion; Concrete; Strength degradation

1. Introduction

One of the main causes for deterioration in concrete structures is the corrosion of concrete due to its exposure to harmful chemicals that may be found in nature, such as in some ground waters, industrial effluents, acid rain, acid mist, and seawater [1]. The chlorides and sulfates belong to the most aggressive chemicals that affect the long-term durability of concrete structures. The degradation of a porous medium depends on two consecutive phenomena: (1) material transport by diffusion, resulting from concentration gradients between the solid interstitial solution and the aggressive solution, and (2) dissolution-precipitation chemical reactions, induced by the concentration variations reached in the diffusion process. In the presence of waters containing chlorides, cement mass is chemically exposed to the pH of the incoming water that produces a progressive neutralization of the alkaline nature of the cement paste, removing alkalies and dissolving portlandite and CSH gel (dissolution produces the increase in porosity and permeability). In the presence of Cl^-, the release of calcium from $Ca(OH)_2$ and CSH could be controlled by the precipitation of alteration solid phases. The chloride dissolved in waters speeds up the rate of the leaching of portlandite and thus increases the porosity of concrete, and then leads to the loss of stiffness and strength. The degradation rate of the concrete exposing in harmful chemicals depends mainly on the fraction of the chemicals in water, the exposure time, and the chemical resistance of concrete. The damage mechanism and retained strength of concrete structures in chemical environment therefore has drawn increasing attention from material scientists and structural engineers [1–9]. Delpak et al. [2] found that the strength of RC beam element exposed to an acidic environment was decreased by 20% of initial level, compared with the control element. Corrosion caused by H_2SO_4 has been widely investigated during the past decades [1,3,7,10–17]. Hidalgo et al. [7] revealed that the resistance of hardened cement pastes to chemical attack and physical degradation was due to a combination of chemical composition and microstructural factors. Wada and Kawano [3] studied the effect of rice husk

* Corresponding author. Tel.: +86 10 51167676; fax: +86 10 65761715.

E-mail address: hpf111cn@yahoo.com.cn (P. Huang).

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ash (RHA) addition on the durability of mortar and concrete, their results revealed that the mass loss of the mortar immersed in 2 vol.% HCl and 1 vol.% H_2SO_4 solutions decreased markedly with increasing RHA content in the mortar. The corrosion damage in concrete was also evaluated by ultrasound [18], acoustic [19], Koch-Steinegger test method [20].

Because failures of concrete structures are mostly caused by bending stress, understanding the degradation of flexural strength and stiffness is of importance for safe application and lifetime prediction. However, the influence of HCl corrosion on the stiffness is seldom reported. As two main factors that control the stiffness of concrete, dynamic modulus and mass loss, as well as their variation with HCl content, are investigated in the present work.

This work focuses on exploring the influence of HCl corrosion on the strength and stiffness of concrete with various strength grades and the damage degree varying as a function of the HCl contents. The flexural strength, the compressive strength, the dynamic modulus of elasticity, and the mass loss were measured using the etched and nonetched samples to understand the corrosion resistance of various types of concrete.

2. Experimental materials and test procedure

2.1. Specimen preparation

Specimens with sizes of 100×100×400 and 100×100×100 mm^3 were prepared to investigate the degradation of the mechanical properties of the concrete (curing ages=360 days, curing in tap water refreshed every week) corroded in various HCl contents for 24 h. The 360-day cured samples were used in the corrosion test because the concrete samples would nearly finish hydration at the age of 360 days, and then, the strength would be stable. As a result, HCl corrosion tests are not influenced by strength change with age. Type I portland cement was used as cementitious materials. The strength properties are shown in Fig. 1, and the chemical compositions are displayed in Table 1. Washed

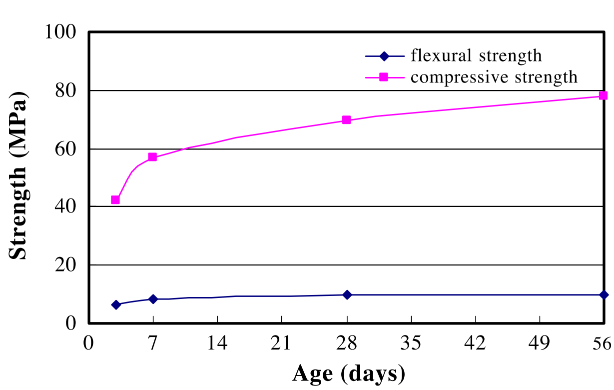

Fig. 1. Measured flexural strength and compressive strength of cement paste, varying with the curing age.

Table 1
Chemical compositions of Portland cement

Chemical compositions	Weight ratio to total Portland cement [%]
SiO_2	21.06
Al_2O_3	6.04
Fe_2O_3	3.63
CaO	63.98
MgO	2.67
SO_3	0.23
K_2O	0.67
Na_2O	0.25
TiO_2	0.32
Loss	1.06
SUM	99.91

river sand with a specific gravity of 2.7 and water absorption of 1.46% and crushed granite with a nominal maximum size of 25 mm and a specific gravity of 2.61 were used as the fine and coarse aggregates, respectively.

Table 2 shows the mixture proportions of the three types of concrete used in this study. The ratios of water to cementitious materials, w/cm, were 0.44, 0.52, and 0.7, respectively. A naphthalene sulfonate-based, high-range water-reducing agent (HRWR) was used to improve the workability of all mixtures.

2.2. Test device and procedure

The concrete ingredients were mixed in a forced mixer with smooth inner surface and blades moisture-conditioned to avoid adsorption of mixing water. The fresh concrete in the cuboid molds was compacted using a vibrator to ensure the uniform distribution of concrete and to reduce the amount of entrapped air. All molds were stored for 24 h at a controlled temperature of 20 °C and a relative humidity of 65% before the specimens were taken out from the molds. The specimens were then cured in a bath and maintained at 20 °C in the curing process until they were removed for testing at the curing age of 360 days. The cured samples were divided into many groups and then respectively placed in corrosion solution with various HCl contents (5%, 10%, 15%, and 20%) to prepare the samples with different corrosion damage. The flexural strength was measured using four-point bending tests with an inner span of 100 mm and outer span of 300 mm. The compressive strength was measured using uniaxial compression test with the specimen dimension of 100×100×100 mm^3. The compressive strength, dynamic modulus of elasticity, and mass of the etched and nonetched samples were measured by means of the universal test machine, the apparatus of dynamic modulus of elasticity, and the balance, respectively. The dynamic modulus of elasticity of the concrete (100×100×400 mm^3) was measured according to a national standard of China GBJ82-85 [21]. The basic principle for this test is to determine the elastic modulus through measuring the basal frequency of the concrete

Table 2
Concrete mixture proportions per m^3

Concrete type.	w/c [%]	S/A (%)	Water [kg]	Cement [kg]	Fine aggregate [kg]	Coarse aggregate [kg]	HRWR[a]	
							[%][b]	[kg]
C25	70	42	175	250	835	1153	0.5	1.25
C45	52	40	172	330	748	1123	0.5	1.65
C55	44	39	167	380	713	1117	0.5	1.90

S/A Weight ratio of fine aggregate to total aggregate.
[a] High-range water-reducing admixture.
[b] Weight ratio of $HRWR^+$ to cement.

sample. The etched samples by different HCl contents were observed using optical microscope with a camera.

3. Results and discussion

3.1. Permeability

Under the impact of HCl, damage induced by surface denudation, neutralization, and intensive dissolution of cement stone would occur in the concrete structure. The permeability of concrete is mainly attributed to the diffusivities of aggressive ions in concrete, which depends on material microstructure and fluid properties. However, in general, chemical reactions are much faster than the diffusion rate, and thus, the overall rate of the degradation processes will be governed by the slower diffusion of one of the species (reactant or product). The diffusivities of chloride ion have significant effect on the corrosion resistance of concrete to HCl. As a result, the Nernst–Einstein–Lu method [22] was used to measure the diffusion coefficients of chloride ion in the three types of concrete in this study. The results shown in Table 3 suggested that the diffusion coefficient of chloride ion decrease with increasing strength grade of the concrete and implied that the normal-strength concrete (C25) showed greater mass loss caused by HCl corrosion.

3.2. Mechanical properties

3.2.1. Original flexural and compressive strengths

Fig. 2 shows the flexural strength measured from three types of concrete (C25, C45, and C55) and their variation with the curing ages. It was noticed that the flexural strength of the three types of concrete was greatly enhanced during the curing period of 28 days and then kept very slight enhancement up to 360 days.

Table 3
Diffusion coefficients of chloride in three types of concrete measured by the modified Nernst–Einstein method

Concrete type	C25	C45	C55
Diffusion coefficients of chloride [10^{-8} cm^2/s]	5.60	3.84	2.71

The relationship between the measured compressive strength and curing ages for the three types of concrete is shown in Fig. 3. It indicated that the measured compressive strength of the concrete approximately keeps a linear increase from 7 to 360 days.

3.2.2. Flexural and compressive strengths after HCl corrosion

Figs. 4 and 5 show the influence of corrosion with various HCl contents on the flexural and compressive strengths, respectively. It was noticed that the law of the strength degradation depended on both the strength grades of the concrete and the HCl content of corrosion. The loss of the flexural strength as a function of HCl contents for the three types of concrete is shown in Fig. 6. On the basis of the data fitting, the strength variation with the HCl content of the corrosion resolution was approximately described by an exponential function,

$$f = Ae^{Bx} \quad (1)$$

where A and B are constants related to strength grades of the concrete, f is the measured strength, and x is HCl contents (5%, 10%, 15%, and 20% were used in this study).

It is obvious that the measured strength loss increased with increasing HCl content from 0% to 20% in this study. Based on the experimental data, the parameters A and B were estimated so that the flexural and compressive

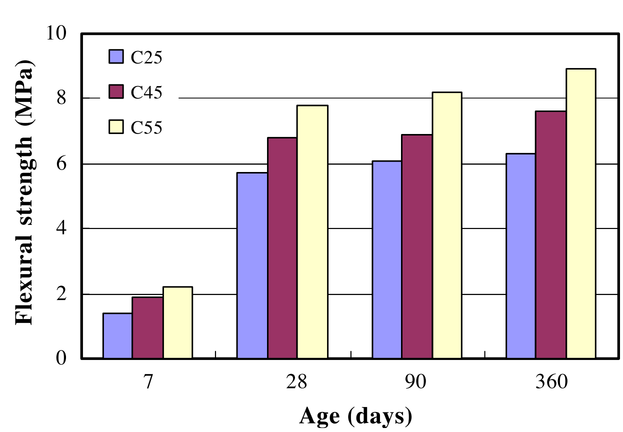

Fig. 2. Measured flexural strength of three types of concrete (C25, C45, and C55) vs. the curing age.

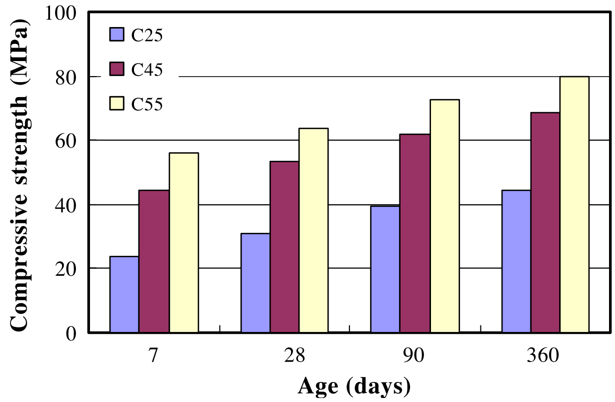

Fig. 3. Measured compressive strength of three types of concrete (C25, C45, and C55) vs. the curing age.

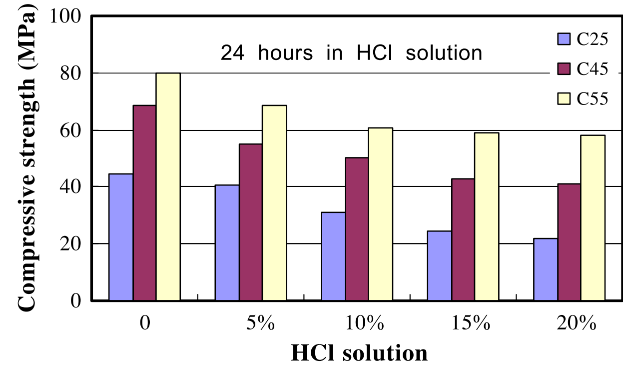

Fig. 5. Measured compressive strength of three types of concrete (after corrosion of 24 h), showing the strength degradation with increasing HCl contents.

strengths for three types of concrete were described approximately as follows:

$$f_f = 6.3694e^{-0.04x} \quad R^2 = .8804 \quad \text{for C25} \quad (2-a)$$

$$f_f = 8.1765e^{-0.0802x} \quad R^2 = .9954 \quad \text{for C45} \quad (2-b)$$

$$f_f = 9.5024e^{-0.1043x} \quad R^2 = .9644 \quad \text{for C55} \quad (2-c)$$

$$f_c = 55.871e^{-0.1939x} \quad R^2 = .9779 \quad \text{for C25} \quad (3-a)$$

$$f_c = 74.14e^{-0.1266x} \quad R^2 = .9549 \quad \text{for C45} \quad (3-b)$$

$$f_c = 81.867e^{-0.0783x} \quad R^2 = .8607 \quad \text{for C55} \quad (3-c)$$

where f_f is the measured flexural strength, f_c is the measured compressive strength, and x is the HCl content. It can be seen from the above functions that the correlation coefficients, R^2, are all higher than 85%, which indicate that the formula listed above coincide with the experimental data. The remarkable degradation of flexural strength in C55 samples and relatively less strength loss in C25 samples indicate that the high-strength concrete is more sensitive to the HCl corrosion than the normal-strength concrete is. It was noticed that, after the corrosion in 20% HCl for 24 h, the measured flexural strength of the three types of concrete were almost at the same level.

On the other hand, the degradation of the measured compressive strength with increasing HCl contents shows similar law for the three types of concrete. The different influences upon the flexural and compressive strengths implied that the damage result from HCl corrosion is more dangerous for concrete structure subjected to tensile load than that subjected to compressive load.

3.2.3. Relative dynamic modulus of elasticity

The measured dynamic modulus of elasticity as a function of HCl contents is shown in Fig. 7. It is interesting that, with the increase of the HCl content, the degradation of the measured dynamic modulus of the high-strength concrete is lower than that of the normal-strength concrete, although the measured flexural strength of C55 concrete degraded faster than that of the C25 concrete. This is probably due to deeper corrosion in C25 concrete, which has high permeability, which leads to greater loss of the dynamic modulus and mass, while the higher defect sensitivity of the high-strength concrete results in the fact that the flexural strength degraded faster in C55 concrete than in C25 concrete after the same corrosion. In some cases, the flexural strength was not considered [20] as a

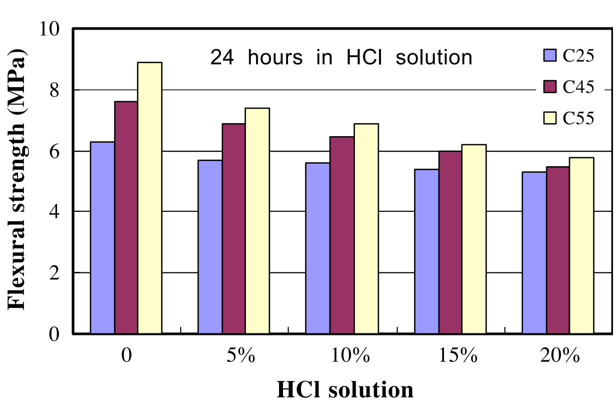

Fig. 4. Measured flexural strength of three types of concrete (C25, C45, and C55) etched for 24 h, showing the strength degradation with increasing HCl contents.

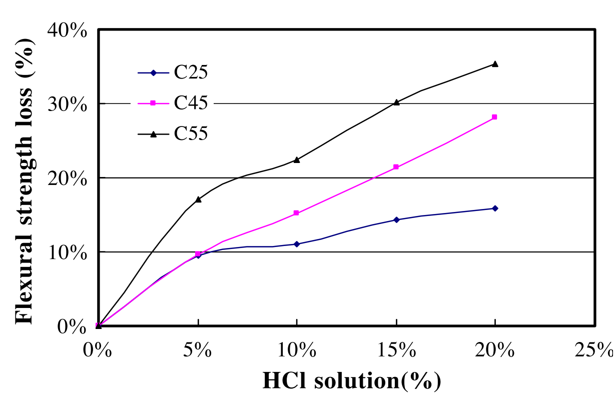

Fig. 6. Flexural strength loss of three types of concrete corroded for 24 h, varying with various HCl contents.

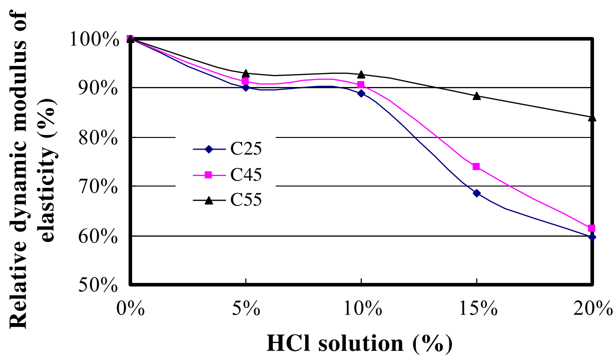

Fig. 7. Measured dynamic modulus of elasticity of three types of concrete (C25, C45, and C55) corroded for 24 h and their variation with HCl contents.

good parameter to evaluate the degradation degree of cement paste in acid medium due to two effects were supposed to take place, with opposite consequences on the measured flexural strength as a result of acid attack: the densification of the cement paste in the specimen core and a degradation of the outer surface with loss of resistance. Experimental results drawn from this study, however, did not confirm the densification of the cement paste in the specimen core. Meanwhile, as shown in Fig. 7, the influence of HCl corrosion on the stiffness of concrete can be characterized by the loss of the dynamic modulus of elasticity. Elements in the cement, with the exception of the alkaline salts, generally remain in the form of sparingly soluble hydroxides. These hydroxides, in some cases together with nonsoluble Ca salts, form a loose slime coating on top of the unreacted concrete. This coating provides a certain protection against continued destruction because the aggressive acid must first diffuse through the hydroxide layer before it can reach and attack the undamaged concrete. In other words, the layer delays the attack.

3.2.4. Surface damage and mass loss

The samples from the three types of concrete subjected to HCl corrosion for 24 h were examined by optical microscope, and the surface damage is shown in Fig. 8. The

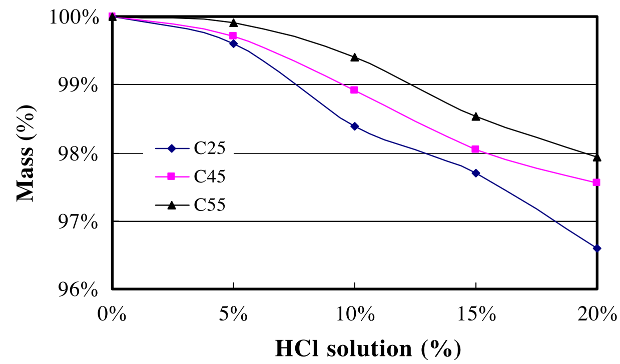

Fig. 9. Measured mass loss of three types of concrete (C25, C45, and C55) after corrosion in various HCl contents for 24 h.

surface cavity caused by the HCl corrosion in C25 concrete was obviously larger than that in C55 concrete. This phenomenon confirmed that the mass loss of the normal-strength concrete is more serious than that of the high-strength concrete. It was found that the degree of the corrosion damage decreases with increasing depth. A deteriorating effect of HCl corrosion is highest at the surface of the samples. The mass loss versus HCl content is shown in Fig. 9, which indicates that the measured mass loss is in converse proportion to the strength grade of concrete. A main reason for the fact abovementioned is that the normal-strength concrete has higher permeability of chloride than the high-strength concrete does. Our experiments using modified Nernst–Einstein method [22] provided evidences that the diffusion coefficients of chloride increased with decreasing strength grade of concrete, and the results are listed in Table 3.

4. Conclusion

The damage resulted from HCl corrosion is dangerous for safe application of concrete structure, especially when the structure is subjected to tensile or bending load. After HCl corrosion, the flexural strength loss of the high-strength concrete is larger than that of the normal-strength concrete, which indicates that the sensitivity to HCl corrosion

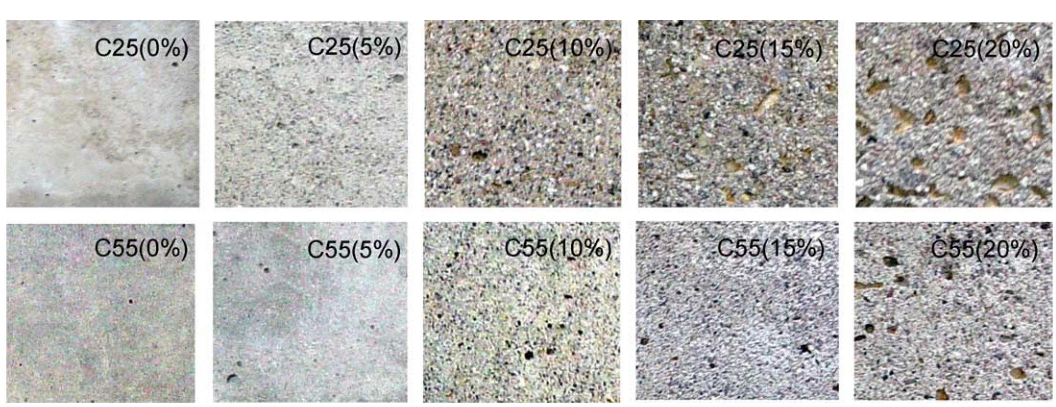

Fig. 8. The profiles of C25 and C55 concrete after corrosion in various HCl contents (from 0% to 20%) for 24 h, showing different surface damages.

increases with increasing strength grade of concrete. The measured compressive strength of the three types of concrete (C25, C45, and C55) exhibited similar degradation trend with growing HCl content. The strength degradation was approximately described as an exponential function of HCl content. The experiments demonstrated that surface corrosion caused by HCl solution strongly affects the flexural and compressive strengths and the elastic modulus of concrete, and that the effect degree is an increasing function of the HCl content. The study revealed that the degradation of the flexural strength was more remarkable for the high-strength concrete than for the normal-strength concrete due to higher defect sensitivity in the high-strength concrete than in the normal-strength concrete. On the other hand, the loss of both the mass and the elastic modulus, caused by HCl corrosion, was in reverse proportion to the strength grade of concrete. The tests of the diffusion coefficient of chloride by using modified Nernst–Einstein method demonstrated that the greater mass loss occurred in the normal-strength concrete was due to higher chloride permeability in C25 concrete.

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References

[1] M.J. Shannand, H.A. Shaia, Sulfate resistance of high-performance concrete, Cem. Concr. Compos. 25 (3) (2003) 363–370.
[2] R. Delpak, D.B. Tann, E. Andreou, M. Abuwarda, D.K. Pugh, Behaviour of FRP strengthened flexural RC elements subjected to degradation influences, First International Conference on Advanced Polymer Composites for Structural Applications in Construction, Apr 15–17, 2002, Southampton University, UK, Thomas Telford, London, 2002, pp. 143–151.
[3] I. Wada, T. Kawano, Influence of rice husk ash addition on the durability of mortar and concrete, Cem. Concr. 53 (1999) 340–346.
[4] K.K. Tseng, Health monitoring of concrete structures subjected to environmental attacks, Conference on Smart Structures and Materials 2002: Smart Systems for Bridges, Structures, and Highways, Mar 18–20, 2002, SPIE—The International Society for Optical Engineering, San Diego, USA, 2002, pp. 168–175.
[5] C.J. Mc. N. Thomas, D. Perry Manfred, Zinn Margaret Breuker RalphMitchell, Biodeterioration of concrete and Stone, 2002 National Association of Corrosion Engineers—International Research Topical Symposium (RTS) (CORROSION/2002), NACE International, 2002, pp.113–121.
[6] P. Waldron, E.A. Byars, Valter Dejke, Durability of FRP in concrete/A State of the Art, COMPOSITES IN CONSTRUCTION: A REALITY, Capri, Italy, 2002, pp.92–101.
[7] A. Hidalgo, C. Andrade, C. Alonso, Role of alkaline reserve in the acidic resistance of cement pastes, Workshop on the Role of Calcium Hydroxide in concrete, AnnaMaria Island, Florida, The American Ceramic Society, Nov. 1–3, American Ceramic Society, Westerville, OH, 2001, pp. 93–112.
[8] N. Milestone, Concrete durability how to make a reactive material last a lifetime, J. Eur. Ceram. Soc. 35 (1/2) (1999) 87–95.
[9] Y. Matsufuji, T. Koyama, S. Harada, Service life predictive method of building materials, Proceedings of “Durability of Building Materials and Components 7”, E & FN Spon, London, 1996.
[10] A. Çolak, Adhesion and durability characteristics of concrete prisms repaired by methyl methacrylate resin injection, ACI Mater. J. 100 (5) (2003) 413–418.
[11] F. Puertas, S. Martinez-Ramirez, Alkali-activated fly ash/slag cement Strength behavior and hydration products, Cem. Concr. Res. 30 (10) (2000) 1625–1632.
[12] T. Yamato, Y. Emoto, Chemical resistance of concrete containing condensed silica fume (SP-114), ACI Mater. J. 114 (5) (1989) 897–914 (Special Publication).
[13] N. De Belie, R. Verschoore, D. Van Nieuwenburg, Resistance of concrete with limestone sand or polymer additions to feed acids, J. Electron. Packag. 41 (1) (1998) 227–233.
[14] T. Novinson, Thermochemical concrete pavement scaling mechanism: Navy F/A-18 Jet Aircraft Parking Apron Problem. FY94-FY98, 1998.
[15] P. Luca, Environmental degradation of fiber-reinforced plastics. Dissertation Abstracts International, The Catholic University of America. Washington, DC, 1998.
[16] G. Sergi, G.K. Glass, A method of ranking the aggressive nature of chloride contaminated concrete, Corros. Sci. 42 (12) (2000) 2043–2049.
[17] S. Sugita, Q. Yu, M. Shoya, Y. Tsukinaga, Y. lsojima, The resistance of rice husk ash concrete to carbonation, acid attack and chloride ion penetration, ACI Mater. J. 172 (12) (1999) 29–44 (Special Publication).
[18] N.S. Goueygou, M. Piwakowski, B. Buyle-Bodin, F. detection of chemical damage in concrete using ultrasound, Ultrasonics 40 (8) (2002) 247–251.
[19] C. Chiang, Y. Kan, C. Tang, C. Su, Acoustic inspection of bond strength between mortar and reinforcement, The 23rd Annual Symposium on Progress in Quantitative Nondestructive Evaluation, San Diego, 1997, pp. 1551–1556 http://www.NDT.net.
[20] A. Macias, J. Madrid, Limitations of Koch-Steinegger test to evaluate the durability of cement pastes in acid medium, Cem. Concr. Res. 29 (12) (1999) 2005–2009.
[21] Chinese Standard GBJ82-85, Test Methods for Long Term Properties and Durability of Ordinary Concrete, China Architecture and Building Press, Beijing, China, 1985.
[22] X. Lu, Application of the Nernst–Einstein equation to concrete, Cem. Concr. Res. 27 (2) (1997) 293–302.