### Degradation mechanisms of concrete subjected to combined environmental and mechanical actions: a review and perspective

Hailong Ye<sup>\*1</sup> and Nanguo Jin<sup>2a</sup>

<sup>1</sup>Department of Civil Engineering, The University of Hong Kong, Pokfulam, Hong Kong, SAR China <sup>2</sup>Department of Civil and Architectural Engineering, Zhejiang University, Hangzhou, PR China

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**Abstract.** In-service reinforced concrete structures are simultaneously subjected to a combination of multi-deterioration environmental actions and mechanical loads. The combination of two or more deteriorative actions in environments can potentially accelerate the degradation and aging of concrete materials and structures. This paper reviews the coupling and synergistic mechanisms among various deteriorative driving forces (e.g. chloride salts- and carbonation-induced reinforcement corrosion, cyclic freeze-thaw action, alkali-silica reaction, and sulfate attack). In addition, the effects of mechanical loads on detrimental environmental factors are discussed, focusing on the transport properties and damage evolution in concrete. Recommendations for advancing current testing methods and predictive modeling on assessing the long-term durability of concrete with consideration of the coupling effects are provided.

Keywords: concrete; multi-deterioration mechanisms; environmental factors; mechanical loading; durability design

### 1. Introduction

The research on durability of reinforced concrete (RC) structures can be hierarchically categorized into three levels, namely, concrete materials (Mehta 1986, Papadakis et al. 1991, Clifton 1993), structural members (e.g., columns and beams) (Al-Sulaimani et al. 1990, Rodriguez et al. 1996), and structural systems (Mori and Ellingwood 1993, Stewart and Rosowsky 1998, Vu and Stewart 2000). Understanding the deterioration mechanisms and processes of concrete materials is the initial step towards comprehensive assessment and accurate prediction of the service-life performance of RC structures. Although the degraded materials may not induce immediate safety issues, it will result in a progressive failure of structural members and finally jeopardize structural safety. The assessment of concrete durability is traditionally based on its performance under a single main deteriorative action alone, e.g., the rebar corrosion-induced concrete cover cracking (Broomfield 2002, Ahmad 2003, Guzmán et al. 2011), or deleterious volume change due to alkali-silica reaction (ASR) (Monette et al. 2002, Swamy 2002, Chen et al. 2018). However, realistic in-service RC structures are simultaneously subjected to multiple deterioration mechanisms (e.g., combined chloride salts attack, carbonation, and cyclic freeze-thaw action) (Mu et al. 2002, Kuosa et al. 2014, Maes and De Belie 2014, Vorechovska et al. 2017). These multiple environmental factors could

\*Corresponding author, Assistant Professor E-mail: hlye@hku.hk

E-mail: jinng@zju.edu.cn

Copyright © 2019 Techno-Press, Ltd. http://www.techno-press.org/?journal=cac&subpage=8 have synergetic and coupled impacts on the performance of concrete materials, resulting in accelerated degradation and aging of material properties (Kuosa *et al.* 2014, Wittmann *et al.* 2014, Tang *et al.* 2015). Furthermore, two or more deterioration symptoms, e.g., ASR and sulfate attack, are sometimes simultaneously detected in concrete in the fields (Skalny and Brown 2002). As such, it is crucial to understand the basic physical-chemical interaction mechanisms among various deteriorative driving forces from environments, as well as their coupled impacts on accelerating the aging of concrete materials. The first subject of this paper is to review the state-of-the-art research on concrete degradation exposed to combined deteriorative environmental factors and to highlight some needs for future research.

On the other hand, the mechanical loads externallyapplied on concrete can work jointly with the environmental factors to exacerbate concrete degradation. The mechanical load-induced stress can modify the deterioration kinetics and process of concrete, as both external loads- and physiochemical environments-induced stresses impose on the same receptor. Although a significant amount of work has been done on characterizing the effects of external mechanical loading on transport properties (e.g., water permeability and chloride diffusivity) of concrete materials (Saito and Ishimori 1995, Aldea et al. 1999b, Castel et al. 1999, Gontar et al. 2000, Lim et al. 2000, Hoseini et al. 2009, Fu et al. 2015a, Ye et al. 2015), insufficient attention was paid to the effects of external loads on the thermodynamics and kinetics of other deterioration mechanisms, e.g., ASR-, cyclic freeze-thaw (F-T) action-, and sulfate attack-induced cracking development. This is the second subject of this paper.

In order to provide reliable guidance for designing concrete materials to meet the targeted performance in the

<sup>&</sup>lt;sup>a</sup>Professor

fields, accelerated laboratory testing methods are typically used. However, most existing testing standards or protocols basically assess the performance of concrete under a single deterioration mechanism. Depending on the geographic location and exposed conditions, the RC structure would be subjected to numerous and sometimes simultaneous forms of detrimental environmental factors and mechanical loads. As such, the laboratory testing which incomprehensively characterizes the exposure condition would provide inconclusive or even contradictory information regarding long-term durability of concrete. In this paper, some recommendations for developing new laboratory methods for assessing the durability of concrete with considering the combinational effects of selected various deterioration mechanisms are provided.

### 2. Interactions among various environmental factors

The detrimental environmental factors considered in this paper include chloride salt attack, carbonation, cyclic freeze-thaw (F-T) action, alkali-silica reaction (ASR), and sulfate attack. The mechanism for each individual deteriorative action can be found in numerous literature and thus merely mentioned briefly here. The main focus of this paper is to outline the coupling effects of various deteriorative actions. For all the deteriorative actions considered here, any combination of two or more has a synergetic impact on the deterioration of concrete.

### 2.1 Combined chloride salts attack and carbonation

Chloride- and carbonation-induced depassivation of reinforcement bars in RC structures are the two main driving forces for corrosion initiation. The expansive rusts due to corrosion of rebar can generate longitudinal cracks in concrete cover, degrade the bonding between reinforcement and concrete, and finally result in a reduction of the carrying capacity of structural members and failure of structural systems (Broomfield 2002, Ahmad 2003, Guzmán et al. 2011, Fu et al. 2017, Ye et al. 2017a, Ye et al. 2018). The depassivation of steel starts either when the chloride concentration in pore solution (i.e., free chloride concentration) around rebar reaches a threshold value or as the pH drops below a critical value due to carbonation (Angst et al. 2009, Kulakowski et al. 2009). The chlorideinduced corrosion is particularly concerned for RC structures in marine environments or exposed to deicing salts, while carbonation-induced corrosion affects a wider range of RC structures. Nevertheless, chloride-induced corrosion is typically more pernicious and expansive to repair than that induced by carbonation (Broomfield 2002). A significant amount of investigation has been done over decades on illuminating the transport mechanisms and kinetics of chloride and carbon dioxide (CO2) ingress (Collepardi et al. 1972, Thomas and Bamforth 1999), as well as the physical-chemical interaction of chloride ions and carbonation with the microstructure (e.g., hydrated phase assemblage, pore structure, pore solution chemistry) of hardened cement and concrete (Andrade and Page 1986,

Ngala and Page 1997, Balonis *et al.* 2010). Few studies have been reported regarding the steel corrosion in concrete exposed to a combined effect of chloride attack and carbonation.

In marine environments, the structural members can be either exposed to a submerged zone, tidal and splash zone, or atmospheric zone (Song et al. 2008). The steel corrosion is most accelerated for RC members exposed to tidal and splash zones since the cyclic drying-wetting action accelerates chloride ingress and supplies sufficient oxygen (O<sub>2</sub>) and water for corrosion propagation (Ann et al. 2009, Ye et al. 2012). The atmospheric zone can also provide a cyclic drying-wetting effect due to seasonal variation in ambient relative humidity, temperature, and adsorbed surface chloride concentration (Cheung et al. 2009, Ye et al. 2016a). Depending on the wetting-to-drying duration ratio, CO<sub>2</sub> concentration, and properties of concrete, the coupled effects of chloride attack and carbonation may not be negligible. The physical-chemical interaction between chloride-bearing salts attack and carbonation in concrete can primary originate from (i) de-bonding of chloride ions; (ii) modification of pore structure; (iii) decrease in chloride threshold level for corrosion initiation; (iv) accelerated carbonation kinetics.

Given that chloride bound on hydrated phases (e.g., AFm, hydrotalcite-like layered double hydroxide, and calcium-silicate-hydrate) of cement does not contribute to the depassivation of steel, cement with a strong chloride binding capability is preferred in term of chloride resistance. However, these chloride binding phases are susceptible to carbonation and exhibit declined binding capabilities as carbonation progresses (Backus et al. 2013, Lee et al. 2013, Saillio et al. 2014, Ye et al. 2016b, Ye et al. 2016c). More specifically, the chloride ions in the chloridebearing AFm (e.g., Friedel's salts) can be considerably replaced by the carbonate ions (e.g.,  $CO_3^{2-}$ ) forming  $CO_3^{-}$ AFm (Suryavanshi and Swamy 1996; Birnin-Yauri and Glasser 1998). Analogous ionic exchange mechanism also occurs between chloride ions and CO<sub>3</sub><sup>2-</sup> in the interlayer of double hydroxides (LDHs), although the layered transformation may not be significantly favored or kinetically slow (Khan et al.). The released chloride ions then become mobile and increase the free chloride concentration in the pore solution. Additionally, the carbonation of calcium-silica-hydrates (C-S-H) can potentially release physically-bound chloride ions by changing the surface adsorption properties and morphology (Saillio et al. 2014).

Both carbonation-induced precipitates and dryinginduced salt crystallization can modify the pore structure of concrete, which further affect the kinetics of moisture, chloride ions, and CO<sub>2</sub> ingress simultaneously (Puatatsananon and Saouma 2005). For instance, the salts precipitates and the hygroscopic moisture-adsorbing properties of free chloride can physically block the pores, reducing carbonation depth. In return, carbonation of concrete results in pore coarsening and reduction in porosity (Ngala and Page 1997, Fu et al. 2015b), which retards the chloride uptake and penetration forward as well (Malheiro et al. 2014). As such, for unsaturated concrete exposed to



Fig. 1 Illustration of the interaction of carbonation and chloride (a) The chloride profiles of concrete with and without carbonation, which shows that carbonation increases the depth of convective zone (after Ye *et al.* 2016c); (b) the relation between the depth where maximum chloride concentration occurs and the depth where pH is less than 12.5 (after Chang *et al.* 2018)

drying-wetting cycles, the competition between carbonation-induced chloride release and depth-sensitive pore characteristics could result in complicated free chloride profiles (Ye *et al.* 2016c). Fig. 1 clearly shows the carbonation of concrete considerably affects the chloride profiles and could be the primary reason for the maximum free chloride concentration phenomenon at the skin layer of concrete.

The concomitant presence of  $CO_3^{2-}$  and free chloride ions in the pore solution can decrease the chloride threshold level and shorten the initiation time to steel corrosion (Liu *et al.* 2016). It may indicate that the  $CO_3^{2-}$  and chloride ions can work jointly to initiate the rebar corrosion and affect the kinetics of de-passivation process. Nevertheless, further investigation regarding the rebar corrosion development characteristics in concrete exposed to combined action of chloride attack and carbonation is needed.

For concrete seasonally-exposed to the deicing salts (e.g., sodium chloride), the salts penetrated or contaminated in concrete can accelerate its carbonation, increasing the carbonation depth and potentially shorten corrosion



Fig. 2 Illustration of the effect of salt contamination and alkali contents on the carbonation resistance of cementitious materials (a) effect of chloride and sulfate contamination in Type I and Type V cement mortars on the carbonation depth (after Kobayashi and Uno 1990); (b) effect of equivalent alkalis content ( $R_2O$ ) in cement composition on the carbonation depth of cement pastes with various *w/c* ratios (after Maslehuddin *et al.* 1996)

initiation time (Maslehuddin *et al.* 1996). The presence of salts can increase the alkalinity of pore solution, which would increase the carbonation rate of cement (see Fig. 2) (Kobayashi and Uno 1990, Ye *et al.* 2017b). As Friedel's salt forms due to anion-exchange between Cl<sup>-</sup> and OH<sup>-</sup> in AFm phases, the OH<sup>-</sup> ions can be released to maintain the charge neutrality of pore solution (Suryavanshi *et al.* 1996); thus carbonation of pore solution is enhanced. Furthermore, the presence of alkali salts can potentially affect the precipitation process of calcium carbonate (CaCO<sub>3</sub>) in concrete (Dow and Glasser 2003).

### 2.2 Combined chloride salts attack, carbonation, and freeze-thaw action

In cold environment, premature damage in RC structures due to F-T action has been reported, despite the use of air-entraining admixtures (Stutzman 1999, Sutter *et al.* 2006, Li *et al.* 2011a). Although the deterioration mechanism of cyclic F-T action on concrete is still



Fig. 3 (a) The effect of NaCl concentration on the degree of saturation in concrete (after Yuan *et al.* 2017); (b) The increase of freeze-thaw damage rate in concrete with the increase of degree of saturation. The critical degree of saturation in the range of 86%~88%, above which the F-T damage will occur (after Li *et al.* 2011a)

controversial, it is associated with the generation and accumulation of internal and surficial damage in concrete due to ice formation in pores (Pigeon and Pleau 2010). For urban infrastructure, deicing salts are widely used to lower the melting temperature of ice, which however exacerbates the damage and complicates the mechanisms of F-T action (e.g., salt scaling problem) (Mu *et al.* 2002, Wang *et al.* 2006, Pigeon and Pleau 2010). For harbor and offshore infrastructures, the F-T action and chloride salts attack (even further combined with carbonation) can jointly accelerate the rebar corrosion and concrete degradation (Chung *et al.* 2010, Kuosa *et al.* 2014, Wang *et al.* 2014, Zhao *et al.* 2014). The physical-chemical interaction between salt-enriched pore solution and F-T action in concrete can be summarized as follows:

Thermodynamically, the presence of salts in pore solution can decrease its freezing point and water activity (Adamson and Gast 1967); hence increase the degree of saturation by preventing drying (see Fig. 2) (Villani *et al.* 2014, Ye and Radlińska 2016). The significance of degree of saturation in freezing concrete has been widely reported in the field observation and emphasized in several phenomenological explanations of F-T behaviors in



Fig. 4 Illustration of the combined effect of chloride salts and cyclic freeze-thaw action on the damage of concrete (after Sun *et al.* 2002)

concrete (Fagerlund 1977, Penttala and Al-Neshawy 2002, Li *et al.* 2011a, Spragg *et al.* 2011). It was proposed that concrete will be damaged by F-T action when the degree of saturation reaches a critical value (in the range of 86%~88% (Li *et al.* 2011a)), irrespective of F-T cycles and air-entrainment (see Fig. 3) (Fagerlund 1977, Li *et al.* 2011a). In addition, it is observed that the degree of saturation in concrete increases gradually with increasing F-T cycles, which exacerbates the freezing damage for the openly-exposed concrete (Kaufmann 2004).

Laboratory studies showed that the concrete is scaled severely in a NaCl solution than in water when subjected to cyclic F-T (Sun et al. 2002), as demonstrated in Fig. 4. Powers and Helmuth suggested that deicing salts can amplify the generated osmotic pressure during freezing (Powers and Helmuth 1953). The osmotic pressure is triggered by the movement of unfrozen water (less concentrated alkaline solution) towards the frozen sits (more concentrated solution) due to salt concentration gradient (Powers and Helmuth 1953, Scherer 1993, Penttala 1998). In addition to exacerbating physical distresses, the deicing salts can chemically react with the species in pore solution and hydrates of cement, forming new phases in pore and cracks (Shi et al. 2010). For highly-concentrated salts solution, these trigged phases can be volumetric expansive and result in premature damage during F-T, even as the freezing of pore solution is not yet occurring (Farnam et al. 2014). Although the deleterious effects of deicing salts on F-T durability have been recognized, there is no strong correlation between salt concentration and the level of F-T damage (Pigeon and Pleau 2010).

The accumulated F-T damage in concrete can potentially accelerate the penetration of chloride salts and  $CO_2$  (see Fig. 5) (Kuosa *et al.* 2014). However, the progressive augmentation of ice and accumulation of salts precipitates during freezing can also physically block the pores and cracks, which restrict the penetration of aggressive agents. The decreasing temperature can also lower the activity of ionic diffusion and depress the corrosion potential of rebar. As such, the steel in concrete can remain passive, although serious damage may occur in



Fig. 5 Illustration the effects of F-T induced internal damage of concrete presented as the relative dynamic modulus of elasticity on the chloride migration coefficient (after Kuosa *et al.* 2014)

concrete (Wang et al. 2014).

### 2.3 Combined chloride salts attack, carbonation, and alkali-silica reaction

Alkalis-silica reaction (ASR) refers to the chemical reactions between reactive siliceous aggregates and alkalis in pore solution of concrete, forming deleterious alkali-silica gels. The alkali-silica gels can swell upon moisture adsorption, generating expansive stress that causes damage in concrete. The four prerequisites for ASR damage occurring in concrete are: (i) reactive aggregates that provide silica, (ii) high alkalinity of pore solution to attack silica, (iii) a source of soluble calcium (e.g., portlandite) to form deleterious ASR gel, and (iv) sufficient moisture to allow gel expansion (Hobbs 1988, Rajabipour *et al.* 2015). As such, the effects of chloride salts and carbonation on ASR damage can be magnified by affecting at least one of these four prerequisites.

The alkalis contribution in ASR can from the ingress of salts from seawater and deicers, besides that from compositions of clinker, SCMs, and aggregates (Ye and Radlińska 2017). As aforementioned, the addition of alkali salts (e.g., NaCl) can potentially elevate the hydroxyl ion concentration in pore solution as a result of anion-exchange mechanism. The increased alkalinity can enhance the dissolution of siliceous aggregate and exacerbate ASR expansion (i.e., affect prerequisite (i) and (ii)) (Nixon et al. 1988, Kawamura et al. 1994). In addition, as mentioned in Section 2.2, the salts enrichment in pore solution reduces the water activity. To reach equilibrium with ambient relative humidity, the pore solution of concrete with alkalis enrichments is more hygrophilous and tends to absorb a higher amount of moisture (Adamson and Gast 1967, Ye and Radlińska 2016). Alternatively, the alkali addition makes the concrete more 'thirsty'; thus the formed ASR can absorb a higher amount of moisture that may lead to higher swelling stress, in comparison to the plain system (i.e., affect prerequisite (iv)).

The decalcification of hydrates in cement by carbonation may provide less amount of available calcium



Fig. 6 Time-dependent evolution of weight percentage of ettringite (AFt), Friedel's salts, and calcium hydroxide (CH) in cement paste samples exposed to sodium sulfate solutions (after Geng *et al.* 2015)

for calcium-enriched ASR gels formation (i.e., affect prerequisite (iii)) (Chatterji 1979). Nevertheless, the ASR is thermodynamically unstable in the presence of calcium and gradually transforms to C-S-H through cation exchange between  $Ca^{2+}$  in pore solution and alkali cation (i.e.,  $Na^+$ ,  $K^+$ ) in ASR gels (Thomas 2001, Hou *et al.* 2004). The driving force for this conversion is attributed to the higher affinity of  $Ca^{2+}$  to the silicate structure than that of alkali cation. However, carbonation is primarily a diffusioncontrolled process which mainly affects the exposed surfaces, while ASR can occur through the entire matrix. The differences in kinetics of carbonation and ASR in concrete may also make the effects of carbonation on ASR complicated. More investigation is needed to shed some lights on this problem.

The ASR-induced cracking allows the faster penetration of moisture and other aggressive agents e.g., deicer, which can lead to enhanced or secondary deterioration, e.g., corrosion of steel reinforcement, in the RC structures. However, as will be elaborated in Section 3.2, the quantitative impacts of ASR damage on permeability or other transport properties of concrete remains unclear.

# 2.4 Combined chloride salts attack, carbonation, and sulfate attack

Sulfate attack involves the chemical reactions between sulfate ions and the hydrates (e.g., portlandite and AFm) in hardened cement, forming secondary expansive crystals (e.g., ettringite and gypsum) that generate damage and disintegration in concrete. The mechanism of sulfate attack in concrete is complicated and still controversial (Skalny and Brown 2002, Neville 2004). The source of sulfate can either be internally (e.g., oxidation of sulfide minerals like pyrrhotite, or delayed ettringite formation) or externally. For external sulfate attack (commonly in a form of Na<sub>2</sub>SO<sub>4</sub> or MgSO<sub>4</sub>), its penetration into concrete is typically accompanied by chloride ions, in the case of RC structures exposed to marine and saline environments.

The synergistic effect of sulfate on chloride ingress is different at an early exposure period from that at latter



Fig. 7 The compressive strength of concrete specimens after 18-month exposure in water, chloride and sulfate composite solution, or sulfate solution. It shows that the presence of chloride delays the sulfate attack in concrete (after Sotiriadis *et al.* 2012)

exposure period (Zuquan et al. 2007). At early ages, the penetration of chloride ions is hindered, which is attributed to the ettringite crystals formation that blocks the pores, as well as the inhibition during multicomponent diffusion (Zuquan et al. 2007). However, the presence of sulfate in the composite solution increases chloride ingress at a later stage. In fact, as shown in Fig. 6, the chloride ions bound in hydrates of cement can be destabilized by the  $SO_4^{2-}$  in pore solution, resulting in increased free chloride concentration and AFm to AFt transformation. Under MgSO<sub>4</sub> attack, the bound chloride at C-S-H surface can also be released due to the transformation of C-S-H to magnesium-silicate-hydrate (M-S-H) (Geng et al. 2015). The increased free chloride concentration can accelerate the corrosion initiation of rebar. Sulfate attack-induced cracks can also accelerate the chloride penetration in concrete (Zuquan et al. 2007). On the other hand, when  $SO_4^{2-}$  is competed with Cl<sup>-</sup> on reacting with the AFm phases, the initial formed Friedel's salts can postpone the generation of sulfate-bearing phases. In other words, the presence of chlorides can mitigate the sulfate attack at an early stage, as demonstrated in Fig. 7 (Al-Amoudi et al. 1995, Sotiriadis et al. 2012, Maes and De Belie 2014). In addition, it was reported that the concomitant presence of chloride and sulfate ions can decrease the chloride threshold level, while the time-toinitiation for reinforcement corrosion is not affected (Liu et al. 2016).

The effect of carbonation on sulfate attack in concrete is multi-fold. First, the dissolution of  $CO_2$  in pore solution leads to the removal of  $Ca^{2+}$  and OH ions from the liquid phase, forming calcium carbonate precipitates and decreasing pH. As the pH of pore solution falls below about 11.5, ettringite becomes unstable and decomposes into gypsum (Skalny and Brown 2002, Neville 2004). Furthermore, when the supply of sulfate and carbonate ions is adequate and at low enough temperature and pH levels above 10.5, thaumasite may be formed in concrete (Skalny and Brown 2002). The formation of thaumasite results from the decomposition of C-S-H, leading to severe degradation of concrete. The enhanced decalcification of the



Fig. 8 Illustration of the combined effect of sulfate salts and cyclic freeze-thaw action on the damage of concrete. It shows that the presence of sulfate ions in the solution mitigate the damage of concrete exposed to F-T actions (after Miao *et al.* 2002)

cementitious system due to combined carbonation and sulfonation can result in the formation of soft silica gel which shows little cohesion strength and causes disintegration. The occurrence of sulfate attack-induced expansive and decalcification shrinkage could result in extensive cracks that accelerate the penetration of sulfate and  $CO_2$ .

### 2.5 Combined freeze-thaw action and sulfate attack

The combined action of cyclic F-T and sulfate attack can result in complicated deterioration phenomenon in concrete a result of coupling physical-chemical process. First, it is well acknowledged that the solubility of ettringite or other expansive detrimental crystals is temperaturedependent. This temperature-dependent solubility of ettringite is commonly regarded as the main cause for the delayed ettringite formation (DEF) (a type of internal sulfate attack) (Taylor et al. 2001). As such, the cyclic F-T can potentially result in a physical volumetric expansioncontraction in the porous body of concrete, due to repeated precipitation-dissolution of salts. This triggered cyclic volumetric variation leads to internal fatigue stress within the matrix of concrete, which can exacerbate the damage merely due to chemical reactions between sulfate and hydrates.

The salt crystals, either by chemical reaction or reprecipitation due to temperature variation during cyclic F-T, can deposit in the entrained air voids of concrete. The crystallization pressure of precipitates in entrained air void does not appear to be deleterious due to the relatively large size of entrained voids. Nevertheless, the blocking of air entrained voids may prevent the water from escaping to the entrained air voids to freeze, triggering the generation of extensive internal hydraulic pressure in the matrix (Powers 1975). As mentioned in Section 2.2, the enrichment of salt in pore solution can increase the degree of saturation, although the freezing point of salt solution declines. All these effects can enhance the damage accumulation in concrete and accelerate the penetration of external sulfate. However, the decreasing temperature in cold weather may also have a positive effect on reducing the kinetics of ionic diffusion and associated sulfate-involved deleterious reactions, as demonstrated in Fig. 8 (Miao *et al.* 2002).

#### 2.6 Combined alkali-silica reaction and sulfate attack

In the fields, the frequent observation of the cooccurrence of ettringite formation and ASR gels at least circumstantially suggests that sulfate attack and ASR may be connected (Pettifer and Nixon 1980). First, as sulfate reacts with the Ca<sup>2+</sup> in pore solution to form precipitates, the dissolution of calcium hydroxide is triggered to preserve the solution equilibrium of a saturated solution of calcium hydroxide. As such, the OH<sup>-</sup> concentration in the pore solution would increase with the simultaneous precipitation of calcium sulfate-bearing phases (Chatterji 1978). In addition, the reaction of sulfate with the AFm phases may release  $OH^{-}$  due to the anion exchange between  $SO_4^{2-}$  and OH<sup>-</sup>, which is analogous to the effects of chloride-bearing salts as mentioned in Section 2.3. As a consequence, the increased pH can enhance the dissolution of siliceous aggregates and therefore exacerbate ASR (i.e., affect prerequisite (i) and (ii)). It was reported in laboratories that mortar bars containing reactive aggregate show increased ASR expansion when alkali sulfates and chlorides are added. A solution of Na<sub>2</sub>SO<sub>4</sub> may cause both sulfate attack and enhanced ASR damage.

The formation of ettringite is inhibited by the presence of alkalis (Brown and Bothe Jr. 1993). Therefore, the progressive consumption of alkalis during ASR gel formation can potentially lower the alkali concentration in the pore solution. Correspondingly, the stability of ettringite is enhanced and formation of ettringite may be preferred with continuous formation of ASR gels (Hobbs 1988, Brown and Bothe Jr. 1993). However, the alkali in ASR gel can be recycled back to solution through cation exchange with  $Ca^{2+}$ , transforming into C-S-H (Hou *et al.* 2004), as mentioned in Section 2.3. The alkali cations can also be adsorbed onto the surface or incorporated into the nanostructure of C-S-H (Lodeiro et al. 2009). More investigation is needed to better understand the mechanisms of coupling effects of ASR and external or internal sulfate attacks in concrete.

# 2.7 Combined freeze-thaw action and alkali-silica reaction

ASR results in a network of surface and internal cracks, as well as splitting of aggregate. The formation of ASR cracking allows increased water adsorption during soaking. The presence of water in ASR cracks can freeze at low temperature, which may exacerbate the existing ASR cracks. Therefore, even when the ASR is complete, the F-T action in humid air greatly promotes ASR expansion and cracking in concrete (Bérubé *et al.* 2002). In addition, during freezing, the expansion of ASR is reduced but the surface cracking is enhanced (Bérubé *et al.* 2002). It may be attributed to the competition effects between ASR expansion and physical contraction at decreasing

temperature, generating high mismatch stress that promotes map cracks. Although the decreasing temperature during F-T can lower the reactivity of ASR, the freezing of pore solution can increase the alkali concentration in the liquid phase, enabling a further attack on siliceous aggregates. It will be informative to monitor the evolution of pore fluid composition during the F-T action.

The alternation of aggregate integration and formation of ASR cracks in the concrete can impair the frost resistance of concrete. As mentioned in Section 2.2, the degree of saturation is critically important in controlling the F-T behavior of concrete. The degree of saturation in a certain type of concrete at a particular relative humidity is related to the pore structures (including micro-cracks) in both cement paste and aggregates. The network of ASR cracks and cracks in aggregates may be able to entrap water (e.g., due to 'ink-bottle' effects) and increase the degree of saturation.

# 3. Combined mechanical loads and environmental factors

# 3.1 Effects of mechanical loads on transport properties

Depending on the magnitude and nature of external mechanical loads, the stressed concrete can undergo either elastic deformation (Gerard et al. 1998, Fu et al. 2015a), permanent damage (micro-cracks) (Konin et al. 1998, Gowripalan et al. 2000), or macro-cracks formation (Aldea et al. 1999b, Ye et al. 2012, Ye et al. 2013, Yang et al. 2017), all of which can affect the transport properties (e.g., permeability, ionic diffusivity, and capillary adsorption) of concrete. Based on the form of external loads (e.g., uniaxial sustained loads, pure shear, flexural loads, cyclic loads including fatigue, and multi-axial loads), the microstructural alternation in concrete can be different; therefore, their influence on the transport properties of concrete can also be different (Hoseini et al. 2009, Huang et al. 2017). In literature, a significant amount of work has been done on characterizing the effects of mechanical loads on water and chloride permeability in concrete subjected to either static uniaxial compression (Lim et al. 2000, Guoping et al. 2011), or tension (Guoping et al. 2011), or flexural loads (Gowripalan et al. 2000, Mien et al. 2009, Ye et al. 2015, Ye et al. 2016c), or cyclic compression loads (Saito and Ishimori 1995, Nakhi et al. 2000).

According to the outcomes of the previous studies, cyclic compression loading has been shown to cause severe damage and significantly enhance the chloride ingress and rebar corrosion in concrete, in comparison to static loads (Saito and Ishimori 1995, Gontar *et al.* 2000, Ahn and Reddy 2001, Hoseini *et al.* 2009). As shown in Fig. 9, there exists a threshold value for the magnitude of applied stress or crack width (about 0.5-1.0 mm), below which the permeability and chloride diffusivity change little or slightly decrease. However, above that threshold value, a dramatic increase in permeability or diffusivity is observed. The threshold value varies depending on the type of



Fig. 9 Normalized water permeability of concrete as a function of cracked width (after Wang *et al.* (1997), Aldea *et al.* (2000))

transport agent (e.g., gas or liquid) and properties of concrete (Hoseini *et al.* 2009). However, the distribution of stress in concrete is typically not uniform and the crack characteristics (e.g., crack width, crack surface roughness, tortuosity, and pores at crack surface) varies along the length (Ye *et al.* 2012); more research is demanded on quantifying the effects of realistic patterns of stress or cracks on the permeability or diffusivity of concrete.

Assessing the combined effects of external mechanical loads and environmental actions on transport properties of concrete is more challenging. Besides from direct mechanical loadings, the damage and cracks in concrete can result from environmental actions, including early-age drying shrinkage, F-T action, ASR expansion, and sulfate attack. In other words, concrete itself is exposed to a combination of external loads and internal stress, which may result in complicated evolution and propagation of damage, as compared to merely external loads. For example, when concrete is subjected to F-T action and fatigue loads, two damage sources (pore for F-T action, and interfacial zones for fatigue loads) can potentially be connected, enhancing degradation (Li et al. 2011b). Although there are some published equations available to estimate the effects of mechanical loads, stress, or damage on chloride diffusivity or permeability (Lim et al. 2000; Guoping et al. 2011, Fu et al. 2015a, Ye et al. 2015), they may not be directly applicable to concrete exposed to merely environmental actions or combined mechanical loads and environmental actions.

Besides affecting the pore structure, it remains unclear whether the mechanical stress has any long-term impacts on chloride binding behaviors of hydrates, as well as the reaction mechanisms of sulfate and  $CO_2$  with cement matrix. The mechanical loads can apparently induce creep phenomena in concrete, which may be related to the reorganization and redistribution of the microstructure (e.g., via dissolution- diffusion- reprecipitation), as well as chemical reactions (e.g., C-S-H polymerization, hydrates dissolution) (Ye 2015). The load-induced alternation of microstructure and phase assemblage may have a long-term impact on the thermodynamics and kinetics of deleterious reactions. It is also appealing to mention that the internal stress may also generate creep or relaxation phenomena, according to the state of stresses and strains.

### 3.2 Effects of mechanical loads on damage evolution in concrete

The ASR, F-T action, corrosion of rebar, and sulfate attack can all induce internal expansive stress in concrete, due to the formation of swelling ASR gels, ice, expansive and sulfate-bearing crystals (e.g., ettringite), rusts, respectively. However, as concrete is subjected to external loads, the external loads or restrains can alter the distribution and development of internal damage in concrete. For instance, the external loads can affect the kinetics of ASR expansion, alter the orientation of the micro-cracks at the microstructural level, and accelerate the splitting of aggregates (Multon and Toutlemonde 2006). For concrete under sulfate attack, the restrains provided by external compressive loads can prevent the existing microcracks from significant propagation and new cracks from initiation, depressing the ettringite formation (Bary et al. 2014). As such, further modeling of the damage evolution in concrete due to environmental factors (e.g., F-T action and sulfate attack) should consider the presence of external loads or restrains (Yin et al. 2017).

In addition, the viscous nature of concrete, regardless of being exposed to external or internal loads, can also affect the development and evolution of damage. The origin of viscous nature of concrete can either from the reorganization of semi-amorphous C-S-H (Ye 2015), dissolution of restrained crystals (e.g., ettringite) (Bentz et al.), or other mechanisms. For concrete under sulfate attack. the creep phenomena associated with a more progressive generation of internal pressures are likely to significantly lessen the crack formation (Bary et al. 2014). For concrete undergoing ASR, the creep phenomenon affects the damage distribution in the microstructure of concrete; At a low degree of ASR, creep can explain the low level of damage in the paste, while as the rate of ASR increases, creep increases the amount of damage in the aggregates (Giorla et al. 2015). Taking account of the creep effects may be essential for assessing the long-term performance of concrete. Considering the coupling effects of environmental and mechanical actions on concrete is important but were unfortunately overlooked in the past studies.

### 4. Laboratory testing methods for evaluating concrete durability

Most of the current laboratory testing standards and protocols assesses the performance of concrete materials subjected to a single type of environmental action (e.g., chloride resistance, F-T resistance, ASR reactivity), and without considering the effects of mechanical loading. It is undoubted that most of the current methods have more or fewer drawbacks that need future attention and improvement. Nonetheless, the most urgent issue in current laboratory testing method is their inconsistency with the performance in the fields. One potential cause (clearly not the only one) of the inconsistency between laboratory testing with filed performance is the ignorance of coupling effects among multi-deterioration mechanisms.

Regarding the investigation of mechanical effects on deterioration mechanisms of concrete, several apparatus were designed in literature (Saito and Ishimori 1995, Gowripalan et al. 2000, Lim et al. 2000, Nakhi et al. 2000, Banthia et al. 2005, Mien et al. 2009, Guoping et al. 2011, Ye et al. 2015, Fu et al. 2016, Ye et al. 2016c). Some of the apparatus is easily portable and can be placed in environmental chambers or containers to allow the simulating of environmental action attacks while the specimen is loaded (Yoon et al. 2000, Ballim and Reid 2003, Wang et al. 2011, Fu et al. 2015a, Ye et al. 2015). However, some apparatus only allow the degradation tests on specimens that is after unloading (Sugiyama 1994, Aldea et al. 1999a). In the former case, loading system should be capable of exerting relatively constant magnitude of loads over time, as some of the previous studies ignore the prestress losses (Wang et al. 2011).

For simulating the combined effects of chloride and sulfate attack, the composite solution is typically adopted; but the type and dosage of chloride- and sulfate-bearing salts in liquid are different among various researchers (Al-Amoudi et al. 1995, Zuquan et al. 2007). For simulating the combined effects of other diffusion-controlled deterioration action (e.g., sulfate attack) and ASR, composite solution may also be a useful candidate. However, the measurement of length or weight loss (as per most current testing methods) may be inconclusive and misleading. The coupling effects of carbonation on chloride penetration, sulfate attack, or ASR can be illuminated by adopting cyclic drying-wetting condition. In the drying period, concentrated CO2 gas, rather than air, can be used to accelerate the carbonation. However, the concentrated CO2 may not represent the realistic circumstance, as the thermodynamics of aqueous systems may be substantially changed depending on the CO<sub>2</sub> concentration. In addition, the duration ratio of drying-to-wetting plays an important role in affecting the coupling effects of various deterioration actions on concrete. Current F-T resistant testing methods are typically conducted on a specimen that is soaked in water or NaCl solution. Replacing the type of solution around the specimens may be intuitively interesting to study the combined effects of other deterioration actions with F-T action. However, finding the simple, informative, and reliable criteria for evaluating the performance of concrete under combined deterioration actions is lacking.

### 5. Conclusions

In-service RC structures are typically exposed to combined multi-deterioration environmental actions and mechanical loads. Understanding the coupling effects among various deteriorative driving forces is fundamentally important. It provides the elementary and important knowledge towards accurate modeling and simulation of service-life performance of RC structures, as well as meaningful guidance to laboratory-scale measurements and evaluation.

As reviewed in this paper, any of the two deterioration

mechanisms can potentially have a synergistic effect on accelerating degradation of concrete materials. One deteriorative action can have either positive or negative (inhibition or exacerbation) impacts on another action. The competition between these positive and negative effects can be controlled by the properties of concrete itself. For instance, the carbonation can marginally affect the chloride profiles in ordinary portland cement concrete, but significantly affect that in concrete with a considerable amount of slag and fly ash (Lee et al. 2013, Ye et al. 2016a, Ye et al. 2016c). Furthermore, the environmental condition, such as the duration ratios of carbonation to chloride immersion, can also considerably impact the chloride profiles in concrete (Ye et al. 2016c). In other words, although the coupling effects among various deterioration mechanisms can be multi-fold, the dominant mechanism(s) may be dependent on the properties of concrete (e.g., hydrated phase assemblage, composition, pore structure) and exposure environments. As such, abstracting the field condition by a simple but representative simulating condition (after a careful examination of the field exposures) and identifying the dominant coupling effects among various deterioration actions are crucial. Take the concrete exposed to combined chloride attack, carbonation, and F-T action as an example, it was recommended that if frost attack is rapid, the reinforcement corrosion issue can be relegated; while if frost attack proceeds slowly, reinforcement corrosion becomes dominate and the coupling effects should be considered in the service-life design (HOLT et al. 2015).

There are few studies on illuminating the long-term effects of mechanical loading on the microstructural evolution of cement and concrete. It remains unclear whether the mechanical loads can significantly modify the thermodynamics and kinetics of interactions between environments and concrete materials. The creep or stress relaxation phenomena of concrete should be considered for modeling and simulation of the long-term performance of concrete.

Current laboratory testing methods do not comprehensively consider the complexity of exposed conditions in the fields, as well as the coupling effects among various deterioration mechanisms. Continued research is demanded to establish rapid but reliable testing methods for evaluating the durability of concrete exposed to more complex conditions. The transition from prescriptive specifications to more performance-based specification is needed. It provides more pertinent and flexible material selection and mixture design of concrete to meet the specific requirement in the fields.

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