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Carbonation Induced Corrosion in Reinforced Concrete Structures - A Review

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Abstract: Carbonation a major reason for corrosion is one of the most critical problems that impair the durability of RC structures and is caused due to decrease in P^H of concrete, relative humidity, temperature and carbon dioxide percentage. The cracking and spalling in concrete due to expanding corrosion products and the reduction in the cross-sectional area of rebar jeopardize the safety and serviceability of RC structures.

Keywords: corrosion, reinforced concrete

I. INTRODUCTION

Corrosion termed as a chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material in carbonated concrete was a major concern of research and practice in the years from 1950 to 1980. The research findings lead to the requirement of dense concrete (lower w/c ratio), the control of concrete properties and to a marked increase in the cover depth (from 20 mm to 35 mm) in the codes of practice. The European standard on concrete EN 206-1 published in the year 2000 classified the risk of carbonation-induced corrosion depending on the severity of the environment (XC1 to XC4). With the minimum requirements given in the recommendations (maximum w/c ratio, minimum cement content, minimum cover depth) the codes of practice since then gave guidance for reinforced concrete made with Portland cement (CEM I) on how to avoid carbonation induced corrosion for structures with expected service life of 50 or 100 years.

Carbonation of concrete has started to attract more attention recently as a result of climate change (Yoon et al. 2007). Evans (1960) defined the corrosion types as general corrosion, localized corrosion, and pitting. Either or both of the microcell and macrocell corrosion mechanisms may exist in RC structures. Microcell corrosion occurs when anodic and cathodic half-cell reactions take place at adjacent parts of the same metal. On the contrary, macrocell corrosion takes place when the actively corroding rebar is coupled to another rebar, which is passive, either because of its different composition or because of different environment. Hansson et al. (2006) concluded that microcell corrosion is the major mechanism of corrosion in RC.

The role of carbonation as a factor that contributes to the degradation of reinforced concrete is becoming increasingly important again for two reasons. First, many old reinforced concrete structures that were built before modern standards were applied are ageing and have to be maintained. Secondly, the need to reduce CO_2 emissions and to obtain materials having a reduced environmental footprint, is leading to a reduction of the clinker content in the cements. Clinker (CEM I) is substituted with supplementary cementitious materials (SCM) such as limestone, fly-ash, geopolymers etc. In the future blended cements with increasingly lower clinker content and a huge variety of supplementary cementitious materials (SCM) will be used. The introduction of non-Portlandite binders has strongly reduced the pH buffer capacity as a result of the reduction (or elimination) of the calcium hydroxide reserve considered one of the main reasons for the corrosion inhibiting nature of Portland cement systems. The carbonation rate of such modern blended cements is a factor of 2-4 higher than for Portland cement, thus the recommendations based on the experience with Portland cement do no more guarantee the required service life.

The service life of reinforced concrete structures is a major concern for building owners as it is related to safety, economy and sustainability. In recent years the number of reinforced concrete structures with anomalies associated with reinforcement corrosion problems has significantly increased and made it necessary to invest large amounts in repairing and strengthening structures. The long-term performance of a concrete structure is largely a function of its deterioration level. The common protection measures against corrosion of the reinforcing steel include the use of corrosion resistant steel, cathodic protection, surface treatment of the reinforcing steels (e.g., epoxy coating) and the use of inhibitors in the concretes. Inhibitors are chemical substances which can prevent or slow corrosion of the steel in concretes. They work by being mixed in the concretes or coated on the concrete surface. The use of inhibitors is particularly attractive due to its simplicity and relatively low cost. The urban and industrial areas are characterized by the presence of SO_2 and NO_2 in the forms of atmospheric contaminants, which can react with water from the atmosphere and form sulfuric and nitric acids. Sulfuric acid attacks the calcium hydroxide and hydrated calcium silicates which constitute hydrated concrete, and the formation of the products with greater volumes can introduce stresses and produce cracks in concretes. The penetration of nitric acid into concrete causes the pH of the pore solution to decrease and results in hydrated calcium nitrate, which is highly soluble and leaches from the concrete. As the result the porous matrix would be susceptible to other types of attack. With the pH decrease of the pore solution the surface of the reinforcing steel depassivates and the corrosion begins

Reinforcement corrosion is the most common type of deterioration. Zhou et al(2014) revealed that a variety of interrelated factors influence the carbonation depth in concrete, including cover thickness, carbonation resistivity, effective CO2 diffusion coefficient, binding capacity for CO2, curing condition, age, cement type, cement composition, calcium oxide (CaO) content in cement, surface concentration of carbon dioxide, time of wetness, ambient temperature, and relative humidity. Environmental conditions, such as sheltered versus exposed and underground versus atmospheric, also have an important impact on concrete carbonation process

II. CARBONATION-INDUCED CORROSION

Leber and Blakey (1956) and Papadakis et al. (1989) reported carbonation induced corrosion occurring naturally in RC structures in the following forms by:

A. $Ca(OH)_2 \rightarrow Ca2(aq)+2OH^{-}(aq)$
B. $Ca^{2}+(aq)+2OH^{-}(aq)+CO_2 \rightarrow CaCO3 +H_2$
C. $3CaO \cdot 2SiO_2 \cdot 3H_2O+3CO_2 \rightarrow 3CaCO3 \cdot 2SiO2 \cdot 3H_2O$
D. $3CaO \cdot SiO2 +\mu H_2O+3CO_2 \rightarrow 3CaCO3 +SiO_2 \cdot \mu H_2O$
E. $2CaO \cdot SiO_2+\mu H_2O+3CO_2 \rightarrow 2CaCO3 +SiO_2 \cdot \mu H_2O$

Equations 1-5 reveal that carbonation of concrete is the chemical reaction of portlandite, $Ca(OH)_2$, in the cement matrix with carbon dioxide (CO_2) gas leading to calcite ($CaCO_3$). Interaction of carbon dioxide with the calcium hydroxide in concrete leads to formation of Carbonation. Carbonic acid (H_2CO_3), that results from dissolution of the carbon dioxide gas in water reacts with calcium hydroxide and precipitates mainly as calcium carbonate (CaCO3), which lines the pores. Pore water pH is lowered from above 12.5 to below 9.0 on account of depletion of hydroxyl ions (OH−1) where the passive layer becomes unstable, allowing general corrosion to occur if sufficient oxygen and water are present (Heiyantuduwa et al. 2006).

Suba et al.(2016) revealed that two major causes which leads to the deterioration are carbonation induced corrosion and chloride induced corrosion. Carbonation is due to the fact that in the presence of carbonate ions, the calcium ions in the pore solution precipitate and form calcium carbonate. The atmosphere contains substantial amounts of carbon dioxide. Gaseous CO_2 cannot, however, react directly with the hydrates of the cement paste. Thus the CO_2 gas must first dissolve in water and form carbonate ions that in turn will react with the Ca ions of the pore water. The type of carbonate ions depends on the pH. When CO_2 comes into contact with water at neutrality it forms bicarbonate. Inside concrete, the pH is high and as a result the bicarbonate dissociates and forms carbonate ions. Thus in the carbonated layer bicarbonate forms but closer to the uncarbonated cement paste this carbonate ions form (due to higher pH) and precipitate calcium carbonate crystals (CC). Calcium carbonate exists in three crystallographic forms, aragonite, vaterite and calcite. Calcite and vaterite are commonly found in carbonated concrete. Presumably the metastable vaterite will transform into stable calcite over time.

The carbonation process can be described by the following chemical equations;
CO_2 (g) + H_2O = HCO3- (bicarbonate ion) + H^+
HCO_3^- = CO_3^{2}-(carbonate ion) + H^+
The carbonate ion will react with Ca ions in the pore solution. $Ca^{2+} + CO_3^{2-} = CaCO_3$
This will lead to lower concentration of Ca^{2+} which in turn will lead to dissolution of primarily calcium hydroxide (CH). The solubility of CC is much lower than that of CH.
$Ca\ (OH)_2 = Ca^{2+} + 2\ OH^-$
$Ca^{2+} + CO_3^{2-} = CaCO_3$
Thus Ca $(OH)_2$ (CH) will dissolve and $CaCO_3$ (CC) will precipitate and the process will continue until all of the CH is consumed. Apart from CH, the cement paste contains calcium silicate hydrate (C-S-H) and ettringite/monosulphate (AFt/AFm). These components are in equilibrium with and stabilized by high pH and Ca ions in the pore solution. Thus when the CH is consumed the pH and the Ca ion concentration drops and the C-S-H will dissolve congruently. Monosulphate (AFm) will decompose at a pH of around 11.6 and later the ettringite (Aft) will decompose at a pH of around 10.6. At pH < 9.2 (when the phenolphthalein change colour) none of the original Ca containing phases remain. Most of the Ca from the C-S-H will be bound to calcium carbonate but

some Ca will always remain in silica gel. The following equation tells us that, during the chemical reaction, the C-S-H releases CH which is carbonated and that this process gives a C-S-H with lower contents of CaO.

Tommaselli et al. (2009) studied the inhibitive effects of sodium molybdate and sodium nitrite on carbon steel at low concentrations (less than 0.040 wt.%) in acid atmosphere and pointed out that a small amount of sodium molybdate shows high efficiency in preventing rebar corrosion. Sodium tungstate and sodium molybdate are two kinds of environmental friendly inorganic inhibitors, which have been widely used for many applications, including engine coolants, paints and coatings, metalworking and hydraulic fluids, and cooling waters. However, these inhibitors are rarely used in acid polluted concrete environments. It is also reported that sodium phytate, an organic inhibitor, shows inhibitive effect for carbon steel in simulated pore solutions, and its strong chelate ability is available in a large pH range.Das et al. (2012) showed that the carbonation potential of concrete decreases with an increase in the compressive strength of the concrete. The results indicated that using a decrease in the charge passed through concrete as a measure of carbonation could lead to misleading results in evaluation of the service life of concrete structures. It was also observed that a low water-to-cement ratio concrete with portland pozzolana cement has higher resistance to carbonation and rapid chloride ion permeability compared with ordinary portland cement. Moreno et al.(2004) studied carbonation induced corrosion in urban concrete structures and concluded that carbonation front has reached the depth of the rebars in buildings that are 18 to 25 years old in. The observed corrosion was attributed to carbonation. A wide variability in the concrete quality was observed.The higher carbonation depths were observed in the low-quality concrete elements. Premature damage was observed in beams with concrete cover less than specified.

Bakharev (2001), Cengiz Duran atis (2003), Khunthongkeaw et al. (2006), Talukdar et al.(2012), Jian Geng & Jiaying Sun (2013), Salvoldi et al.(2015), Chandrasekaraiah et al.(2014) studied impact of CO_2 concentration, relative humidity and temperature on carbonation induced corrosion. Bakharev et al. (2001) concluded that the Alkali Activated Slag concrete of Grade 40 has lower resistance to carbonation than that of OPC concrete. According to Cengiz Duran atis (2003) Fly ash concrete made with 70% replacement ratio showed higher carbonation than that of 50% FA replacement concrete and NPC concrete for both moist and dry curing conditions. Khunthongkeaw et al. (2006) arrived at a result, that the carbonation depth of concrete and mortar specimens measured until 24 months were equivalent to the cement-only samples. The increment was drastic when the fly ash content was higher than 30%. Jian Geng & Jiaying Sun (2013) analyzed the effect of the cement replacement ratio by fly ash on the carbonation depth and it was revealed that the carbonation depth initially decreased and then increased with increased replacement ratio from 10% to 30%, and then reached the minimum at 20%. Also, they found that the workability of Recycled Fine Aggregate concrete was improved well at low w/b ratio, because the use of fly ash helped (Recycled Fine Aggregate concrete) RFCA to obtain a more compact structure. The resistance to carbonation of RFAC was improved by adding fly ash because the Fly ash addition enhanced the microstructure of RFAC.

III. COMMON CORROSIVE AGENTS

Acids (Sulfuric acid :battery acid, halogen acids:hydrochloric,hydrofluoric, and hydrobromic, nitrous oxide compounds, and organic acids found in the wastes of humans and animals), alkalies, (washing soda, potash :wood ashes, and lime :cement dust),salts, atmosphere (oxygen and airborne moisture, industrial atmosphere(contaminants: oxidized sulfur compounds), marine atmosphere (chlorides in the form of salt particles or droplets of salt saturated water), water (water temperature and velocity) and microorganisms(bacteria: aerobic or anaerobic, fungi: Organic acids, alcohols, and esters are produced by growth of the fungus, or molds) are the common corrosive agents.

IV. CORROSION AND MECHANICAL FACTORS

Corrosive attack is often aggravated by mechanical factors that are either within the part (residual) or applied to the part (cyclic service loads). Erosion by sand and/or rain and mechanical wear will remove surface protective films and contribute to corrosive attack of underlying metal surfaces. Corrosive attack that is aided by some mechanical factor usually causes the part to degenerate at an accelerated rate compared to the rate at which the same part would deteriorate if it were subjected solely to corrosive attack. Environmental conditions and the composition of the alloy also influence the extent of attack. Examples of this kind of alliance are i)stress corrosion cracking(inter granular cracking of the metal produced by non uniform deformation during cold working, by unequal cooling from high temperatures, and by internal structural rearrangement involving volume changes. Specific environments have been identified which cause stress corrosion cracking of certain alloys. Salt solutions and seawater may cause stress corrosion cracking of high strength heat treated steel and aluminum alloys. Methyl alcohol hydrochloric acid solutions will cause stress corrosion cracking of some titanium alloys. Magnesium alloys may stress corrode in moist air. Stress corrosion may be reduced by applying protective coatings, stress relief heat treatment, using corrosion inhibitors, or controlling the environment. Shot peening a metal surface increases resistance to stress corrosion cracking by creating compressive stresses on the surface which should be overcome by applied tensile stress before the surface sees any tension load. Therefore, the threshold stress level is increased),ii)corrosion fatigue (Corrosion fatigue is caused by the combined effects of cyclic stress and corrosion. Fracture of a metal part, due to fatigue corrosion, generally occurs at a stress level far below the fatigue limit in laboratory air, even though the amount of corrosion is relatively small. For this reason, protection of all parts subject to alternating stress is particularly important, even in environments that are only mildly corrosive) and iii)fretting corrosion(Damage can occur at the interface of two highly loaded surfaces which are not supposed to move against each other. Fretting can cause severe pitting. Dampening of vibration, tightening of joints, application of a lubricant, or installation of a fretting resistant material between the two surfaces can reduce fretting corrosion).

V. EFFECTS OF MECHANICAL DEGRADATION

Stanish(1977) revealed that corrosion damage was not found to significantly impact ductility of RC members, it results in concrete spalling and cracking ,reduction in reber properties and interfacial loss. Cracks reduce the load-bearing capacity, shorten the service life, and increase the rate of ingress of aggressive elements (Alonso et al. 1998). Castel et al. (2000) noted that rebar area reduction and bond strength loss are coupled. Webster (2000) reported that the amount of corrosion observed to cause cracking is typically an order of magnitude greater than the amount of radial expansion theoretically required to induce cracking. Tension stiffening in RC is also sensitive to the degree of reinforcement corrosion (Shayanfar et al. 2007).

Webster 2000 and Zhang et al.2006 revealed that the yield and ultimate stress and strain at ultimate stress of rebar deteriorated, and the yield plateau became narrower or even disappeared with the development of corrosion.These reductions could lead to a premature fracture of the rebar before yielding is observed. Kashani et al. (2013) found that a corrosion level above 15% mass loss significantly affected the ductility and plastic deformation of rebar in tension. Al-Sulaimani et al. (1990) observed a sharp jump in the value of the free-end slip with the opening of a longitudinal crack indicating a sudden loss of rebar confinement in the rebar pullout tests. It was found by Almusallam et al. (1996) that in the precracking stage (0–4% corrosion, measured as gravimetric loss in weight of rebar) the ultimate bond stress increases, whereas the slip at the ultimate bond stress decreases with increasing corrosion level. The degradation of bond results from the crushing of the concrete near the lugs of the rebar. When reinforcement corrosion is in the range of 4–6%, the bond failure occurs suddenly at a very low free-end slip. Bajaj (2012) confirmed that the bond strength increases with an increase in the corrosion level up to a critical percentage (2% for plain concrete

VI. FORMS OF CORROSION

There are many different types of corrosive attack and these will vary with the metal concerned, corrosive media location, and time exposure. Direct chemical attack on a metal surface results in Uniform Etch Corrosion. Discoloration or general dulling of metal created by exposure to elevated temperatures should not be confused with Uniform Etch Corrosion. Pitting Corrosion effects on aluminium and magnesium alloys is noticeable as white or gray powdery deposit, similar to dust, which blotches the surface. When the deposit is cleaned away, tiny pits or holes can be seen in the surface. When two dissimilar metals make electrical contact in the presence of an electrolyte, they cause Galvanic corrosion. For example, magnesium would corrode very quickly when coupled with gold in a humid atmosphere, but aluminum would corrode very slowly in contact with cadmium. Corrosion is crevice corrosion occurs at the edge of a joint even though joined metals are identical. Exfoliation corrosion (advanced form of intergranular corrosion where the surface grains of a metal are lifted up by the force of expanding corrosion products occurring at the grain boundaries just below the surface) is most prone to occur in wrought products such as extrusions, thick sheet, thin plate and certain die forged shapes which have a thin, highly elongated platelet type grain structure. Oxygen concentration cell corrosion or crevice corrosion which occurs on metal surfaces having an organic coating system is termed as Filiform Corrosion. Filiform occurs when the relative humidity of the air is between 78 and 90 percent and the surface is slightly acidic and can be removed using glass bead blasting material with portable abrasive blasting equipment and/or mechanical means such as buffing or sanding.

VII.CONCLUSION

Corrosion results in deteriorating rebar area, yield strength, ultimate strength, and ultimate strain. Concrete crack width increases with an increase in corrosion level.

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