

"Service Life Enhancement: Exploring the Effects of Supplementary Cementitious Materials on RC Structures in Marine and Urban Contexts"

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Abstract

Reinforced concrete (RC) structures stand as the cornerstone of modern construction due to their cost-effectiveness and widespread availability. The most predominant factor for the deterioration of RC structure is due to the corrosion of reinforcement. This review paper comprehensively explores the occurrence and degradation mechanism of reinforced concrete (RC) structures when exposed to adverse environmental conditions, i.e., marine, or urban environments. Corrosion of reinforcement takes place when RC structures are exposed to a marine environment (chloride ion penetration) or urban environment (carbonation). The study explores the mechanism of corrosion and corresponding corrosion products in detail. Furthermore, the review highlights the effects of supplementary cementitious materials such as ground granulated blast furnace slag, fly ash, and silica fume on the above adverse environmental conditions based on analysis of existing literature, including laboratory studies and real-world exposure data. The insights provided aim to enhance the understanding of service life prediction for RC structures and contribute to more durable construction practices.

Keywords: *Corrosion of reinforcement, Chloride ion penetration, Carbonation, Supplementary cementitious materials (SCMs), Service life prediction*

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1. INTRODUCTION

Over the past few decades, reinforced concrete has become one of the most popular building materials. When utilized appropriately, it is an efficient structural material with excellent durability performance. However, a lot of structures, particularly those exposed to adverse conditions, exhibit early decay (1). As concrete is good in compression and weak in tension, reinforcements are provided in the concretes. Structures and buildings can have many decades of service life when reinforced concrete is properly designed, built, and maintained. Excellent corrosion protection for reinforcing steel is provided by concrete because of its high alkalinity and low permeability when designed and constructed properly (2). A thin, stable, and firmly adhering protective iron oxide passive layer spontaneously forms on the steel reinforcement surface embedded in concrete due to its extremely alkaline environment, shielding the steel from corrosion. Furthermore, relatively high electrical resistivity and poor penetrability of concrete minimize the entry of harmful substances like chloride ions and carbon dioxide, that cause corrosion (3).

The time after installation—or, in the case of concrete, placement—during which all the attributes surpass the minimally acceptable values when properly maintained is known as the service life of a building component or material. Information about the current condition of the concrete, rates of degradation, historical and future loading, and the definition of the end-of-life are needed to predict the service life for present concrete structures. Economic decisions on whether to repair, rehabilitate, or replace a structure can be made based on remaining life forecasts (4).

It is certain that "Service Life Design" necessitates "Service Life Models" that are sufficiently predictive. As a result, Service Life Prediction (SLP) involves Service Life Modelling (SLM) and vice versa. To use SLP and SLM approaches, a shift in design approaches from prescriptive to performance is important. The prescriptive approach in construction involves specifying specific limits for elements like material mix and proportions, along with the construction processes such as curing. It operates on a 'deemed-to-satisfy' principle. However, this method has notable drawbacks: it doesn't allow for on-site verification, quality assurance, service life prediction, economic analysis, or encouraging innovation. In construction, performance approaches can be partial (called 'hybrid') or full performance-based methods. Both involve defining desired performance through tests, setting acceptable performance limits, and integrating durability requirements using service life models for reinforced concrete structures. Performance-based standards that specify the requirements for the finished product are currently being developed (5). In a full performance approach, concrete properties are measured on-site to ensure they meet specifications, which raises questions about performance testing and specifications (6).

When estimating service life models, the two main periods that are typically estimated are the initiation period and the propagation period. The time required for the chlorides to penetrate the concrete cover and accumulate at the rebar's surface in a quantity (threshold amount) large enough to disintegrate the passive protective layer and initiate corrosion is known as the initiation period. The propagation period begins with the onset of corrosion and continues until the RC structure's cracking, spalling, and collapse (7).

When the reinforced concrete (RC) structure is exposed to an aggressive environment, it undergoes rapid deterioration and hence leads to a reduction in the durability and service life of the structure. The carbonation induced corrosion is slower (up to 30 $\mu\text{m}/\text{year}$) compared to chloride induced corrosion (up to 1mm/year). So, the most common causes of deterioration of RC structure are due to chloride attack than by carbonation attack (8)(9). In this study, we will discuss their occurrence, mechanism, role in the corrosion of reinforcement, and their service life. Furthermore, role of supplementary cementitious materials (SCMs) regarding chloride ions penetration and carbonation is reviewed.

2. SIGNIFICANT DEGRADATION PROCESSES FOR RC STRUCTURES

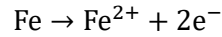
Concrete is a porous material when subjected to adverse environmental conditions like exposure to urban or marine environment, ingress of carbon dioxide or chloride ions takes place (10). When sufficient amount of chloride ions (threshold quantity) or carbonation front reaches the surface of the reinforcement it will initiate corrosion and is the major cause of deterioration of the RC structures (11). **2.1 Mechanism of Corrosion of Reinforcement**

Concrete acts as a barrier to the corrosion of steel reinforcement physically, as well as chemically due to its high alkalinity. Concrete that has not been influenced by outside factors has a pH between 12.5 and 13.5 (8). This high alkalinity is due to the sodium and potassium hydroxides in the pore solutions form, and due to calcium silicate hydrate (CSH) gel and calcium hydroxides in solid form. Rebar and water in the concrete combine to generate a thin layer of rust that serves as a passive protective layer and is composed of $\gamma - \text{Fe}_2\text{O}_3$ (maghemite) (12). The thickness of this protective layer is <10 nm (13). However, active corrosion of steel bars results from the partial or total loss of the passive layer, known as depassivation. As a result, concrete can crack and continue to deteriorate due to the expanding nature of the corrosive products of iron. Carbon dioxide from the environment and chloride ions, which are primarily found in deicing salts or seawater, are the two main causes that can damage the passive film on the surface of the steel and start corrosion. Other elements that could contribute to active corrosion in reinforced steel structures include a lack of oxygen to maintain the passive film, the creation of galvanic cells from metal-to-metal contact, hydrogen embrittlement, and stray currents (14).

The corrosion of reinforcement in concrete is the electrochemical process (9). The process involved in the corrosion of reinforcement is presented in Fig.1 and is explained as follows:

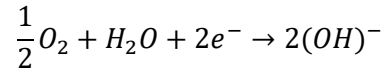
Anodic process (oxidation of iron)

In this process electrons are liberated from metallic phase and iron ions are formed.



Cathodic process (reduction of oxygen)

Alkalinity is formed by the consumption of electrons liberated.



Transport of electrons (anode to cathode)

As electrons are negatively charged particles, the movement of electrons from anode to cathode produces a nominal electric current which flows in the opposite direction.

Flow of current (inside concrete)

To complete the circuit, the current flows from anode to cathode by transporting hydroxyl ions from cathode to anode through the pore solution of concrete.

The rust product $\text{Fe}(\text{OH})_2$ (Ferrous hydroxide) gets precipitated into the surface of the reinforcement because of diffusion of Fe^{2+} and $(\text{OH})^{-}$ ions. In oxygen rich environments $\text{Fe}(\text{OH})_2$ gets oxidized to $\text{Fe}(\text{OH})_3$ gradually.

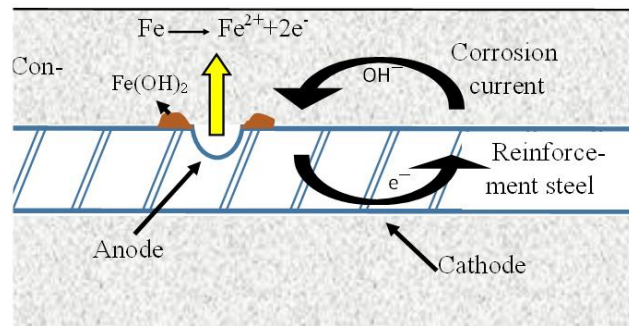


Fig.1: Reaction Involved in Corrosion of Reinforcement (15).

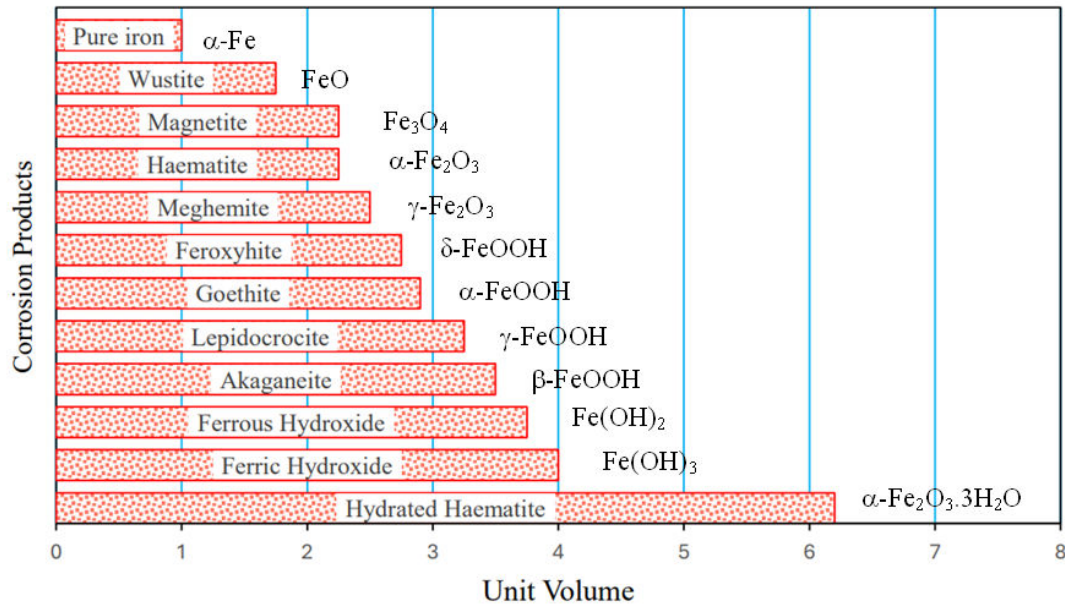
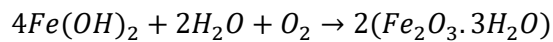
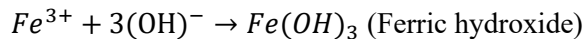


Fig.2: Corrosion Products and Their Respective Volume (16)

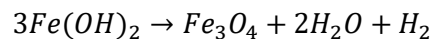
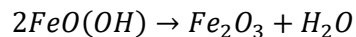
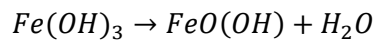
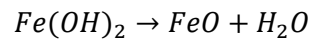
2.2 Corrosion Products

The various corrosion products and their respective volume is shown in Fig.2.

The reaction sequence for the formation of rust are as follows:



Dehydration reaction that occurs and results in formation of rust compounds are:



These equations also show that the availability of oxygen and water controls the corrosion products. With limited supply of oxygen, black or green rust is formed, while red-brown rust is formed when the supply of oxygen is sufficient. The dominant phase of black as well as red-brown rust are Goethite, Magnetite, and Akaganeite. The transition from anoxic to oxic conditions caused the green rust products seen for some reinforcing bars to rapidly become black and finally red-brown in a matter of hours (17).

The rust products hydrated haematite ($\alpha - \text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, (red rust)) exerts nearly six times more volume as shown in Fig.2, when compared to Fe and thus formation of rust products leads to the increase in volume and hence exerts stress on the concrete. If the stress is greater than tensile strength of concrete, then concrete cracks and further goes for spalling of concrete and exposure of the reinforcement to the aggressive environment and leads for the end of service life of the structure.

3. Exposure of RC structures to marine Environment

For structures exposed to marine environment, deterioration of RC structures takes place mainly due to corrosion of reinforcement by chloride ions penetration.

3.1 Chloride-induced corrosion

Chloride ions can be present in the concrete from internal as well as external sources as listed in Fig.3. The internal sources include the materials used in the manufacturing of concrete and the external sources are related to the exposure conditions.

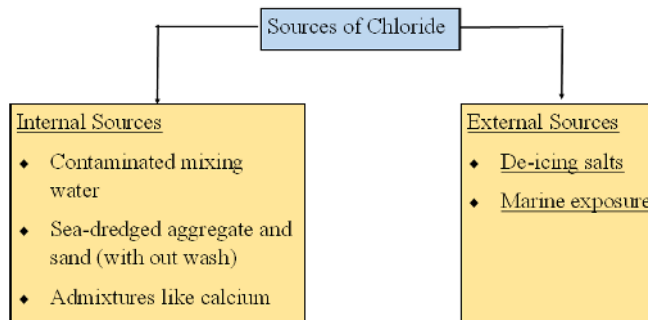


Fig.3: Sources of Chloride Ions

RC structures in marine environment are classified into three zones, i.e. submerged, tidal/splash, and atmospheric zone (18). The major mechanisms of transport of chloride ions in marine environments are capillary absorption, ionic diffusion, permeation, and wick action as illustrated in Fig.4.

Absorption: It is the mass uptake of water into a porous substance, like concrete. It generally takes place in partially or fully saturated concrete that is submerged completely or partially.

Capillary absorption: It is the intake of water, usually unidirectionally, because of capillary action. This illustrates scenarios in which the concrete comes into touch with water on a single surface.

Permeability: This mechanism functions in the classic permeability scenario, in which saturated liquid transfer across the concrete is controlled by a pressure gradient. It is increased when defects or cracks are present in the concrete.

Ionic diffusion: This is the flow of dissolved ionic species in water caused by a concentration gradient, i.e., the flow of ionic species from zones of higher concentration to zones of lower concentration.

Wick action: Wick action is the movement of water, together with any associated species, from a wet face to a dry face through a concrete element. Wick action takes place due to the combination of water vapor diffusion and capillary absorption, with evaporation acting as the connecting mechanism (19).

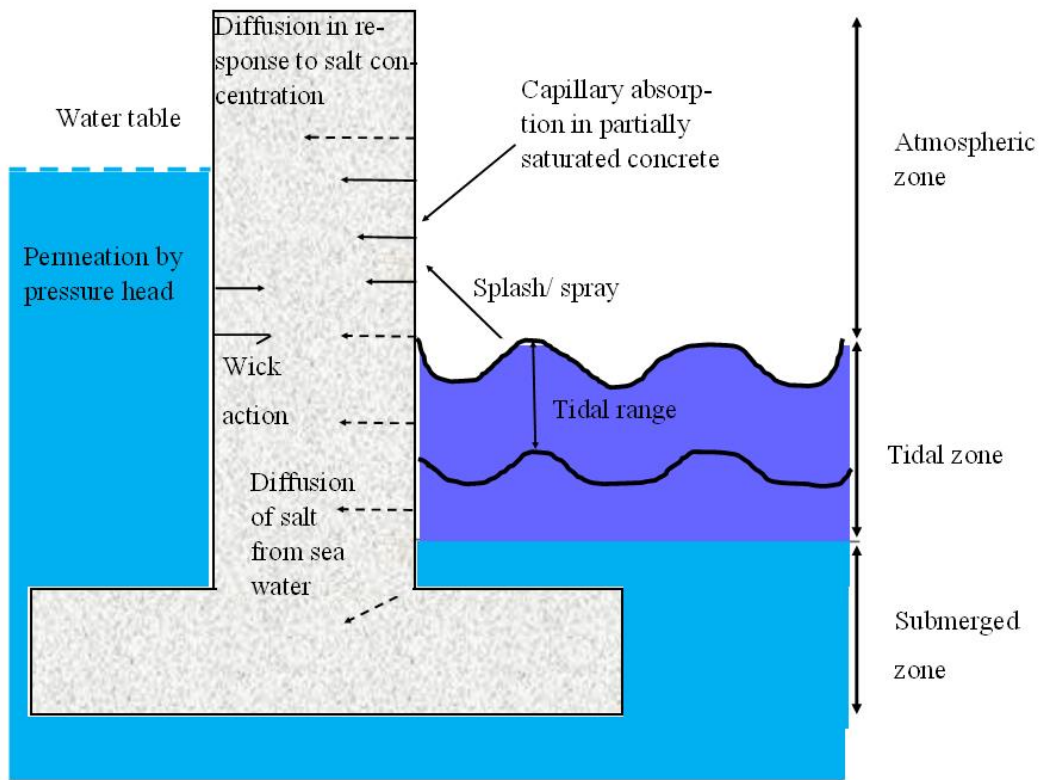
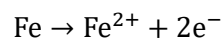


Fig.4: Different exposure conditions that occur in a marine environment (20)

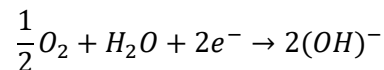
When the threshold quantity of chloride ions reaches the surface of the reinforcing bars then it leads to localized breakdown of the passive layer resulting in the initiation of the corrosion process. There are two states of chlorides present in the concrete: free chlorides, and bound chlorides. Free chlorides get dissolved in the pore solution and are only responsible for the initiation of corrosion. Bound chlorides on the other hand are chemically and physically bound to the cement hydrates and their surfaces (21).

As the cathode region is larger than the anode region, that results in severe corrosion of the anode region. The metal ions will be in excess in anode region and chloride ions also migrate to that area. When hydrolysis of metal ions takes place that will lead to the formation of the acid solutions and will enhance the conductivity in that region. These factors are responsible for promoting corrosion (22).

The reaction that occurs at the anode is:



The reaction that occurs at the cathode is:



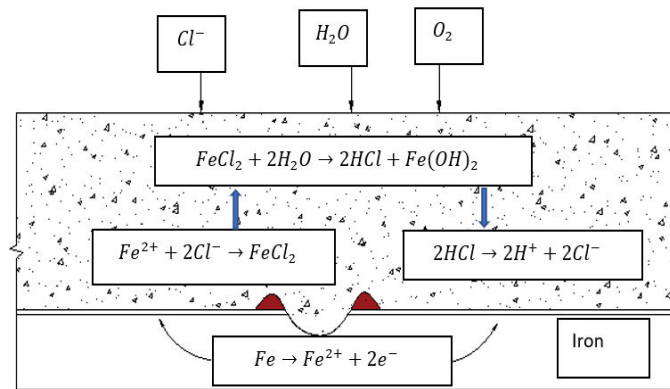


Fig.5: Mechanism of Chloride-Ion Induced Corrosion

The process shown in the Fig.5 is regenerating and instead of spreading along the reinforcement, corrosion continues at local anodes and deep pits are formed.

Once corrosion is initiated by depassivation of reinforcement, propagation phase begins. Factors affecting propagation phase are:

- pH of concrete
- presence of moisture
- presence of oxygen
- chloride content

3.2 Effect of supplementary cementitious materials on Chloride Ion Penetration

Li and Roy (23) have conducted an experiment in which Type I Portland cement (PC) and low-calcium fly ash (FA) were combined in the following weight ratios: 100:00, 80:20, 70:30, and 60:40, with respective w/s ratios of 0.3, 0.5, and 0.6. With a w/s ratio of 0.5, cement and silica fume are mixed 90:10. The best ratio of cement to fly ash discovered in this study is 60:40 percent (by weight), which has a great potential for minimizing chloride ion transport. This is caused by the influence of multivalent cations on chloride ion transport in the pore solution, and the clogging of pores by gel created by the pozzolanic reaction.

Byfors (24) Conducted an experimental tests using Ordinary Portland Cement (OPC), OPC/10%CSE, OPC/20%CSE, OPC/15%PFA1, and OPC/40%PFA2 with various water to binder (w/b) ratios. The outcomes of the tests show that as compared to pure Portland cement paste, the rate of chloride diffusion is decreased when silica fume (SF) or FA are added while maintaining the w/b ratio. When the w/b ratio is lowered, the rate of diffusion likewise falls off dramatically. For samples with 40% FA and a w/b of 0.40, the lowest diffusion rate was discovered. A little amount has no noticeable impact, but additions of silica in amounts more than 20% may cause the pH to drop to a point where steel is no longer passive.

Thomas and Bamforth (25) carried out research using samples that were submerged in sea water and in a lab. The time of exposure significantly increases the differences in chloride penetration rates between plain PC concrete and concrete incorporating either FA or slag. During a 100-year service life, the diffusion coefficients for FA or slag concretes are likely to drop to one or two orders of magnitude less than those for similar grade PC concrete.

Leng et al. (26) conducted experiments using three different cement mixtures: only PC, PC and FA, and PC and GGBS. FA and GGBS concretes have chloride ion diffusion coefficients significantly lower than PC concrete alone. The increased ion concentration, which as a result restricts chloride ion movement, the pore size effect, the formation of more Calcium Silicate Hydrate(C-S-H) gel, and the fact that FA and GGBS has more C_3A content, which absorbs more chloride ion and produces Friedel's salt, are all factors that contribute to the decrease in chloride ion diffusion coefficient.

Nath and Sarker (27) carried out experiment using two separate series of mixes: mix A had a different w/b ratio and a different amount of binder, while mix B had the same w/b ratio and the same amount of binder. At 28 and 180 days, the FA concretes produced better results in terms of resistance to chloride ion penetration. As a result, high strength concrete with reduced permeability can be designed by adding up to 40% Class F FA to the total binder.

Zhou et al. (28) performed experiment by replacing cementitious materials with FA by 0%, 15%, and 30%. When the compressive stress ratio was less than 0.6, the chloride diffusion coefficient decreased with an increase in FA replacement level. However, at a stress ratio of 0.8, concrete specimens with a 30% FA replacement had a higher chloride ion diffusion coefficient than those with a 15% FA content under the same loading conditions. At the elastic stage, an approximately linear connection between the chloride diffusivity and FA content was visible.

Otieno et al. (29) conducted experimental works with the replacement of cementitious materials by 20%, 35%, and 50% GGBS. At a given w/b ratio, chloride conductivity and porosity reduced with rising GGBS replacement levels (from 20% to 35% to 50%), improving resistance to chloride penetration.

4. Exposure of RC structures to urban environment

RC structures exposed to urban environment are susceptible to carbonation induced corrosion of the reinforcement.

4.1 Carbonation induced corrosion:

Carbon dioxide present in the atmosphere diffuses into the concrete through pores of cover concrete. The calcium hydroxide that is formed during hydration of cement keeps the pH of concrete between 12.5 and 13.5 which is sufficient to make the passive protective layer around the reinforcement bar. When CO_2 enters into the concrete it reacts with calcium hydroxide and converts it to calcium carbonate which will reduce the pH of concrete below 8.3 and at with this low level of pH the passive layer will be destroyed, and the initiation of corrosion takes place in the reinforcement as illustrated in Fig.6.

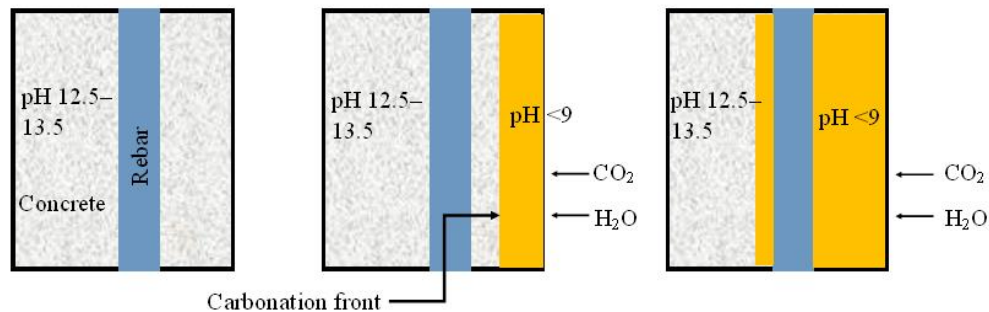
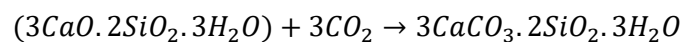
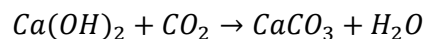


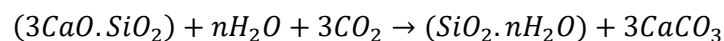
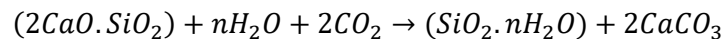
Fig.6: Mechanism of Carbonation

Chemical reaction for carbonation is:

For hydration products,



For residual unhydrated compounds present in concrete



Ingress of carbon dioxide in the concrete is the function of Relative Humidity (RH). The most suitable range of relative humidity for carbonation is the RH between 50% and 70%. Below RH 40% the CO_2 cannot be dissolved and at above RH 90% diffusion of CO_2 will be blocked by the pore water and hence prevents the entry of CO_2 . Other factors that affect the carbonation in concrete are binder types, degree of hydration, and water to cement ratio (w/c) (30).

The depth of carbonation can be determined using phenolphthalein solution, which when spread on the freshly broken surface if the color turned to pink then it indicates no carbonation if it turned to colorless then it is fully carbonated.

4.2 Effect of supplementary cementitious materials on carbonation

Khunthongkeaw et al. (31) conclude with their experiment that concrete's carbonation coefficient rises as FA content, w/b, and atmospheric CO_2 concentrations rise. However, when a little quantity of FA (10%) is included, the carbonation coefficient remains similar when compared to the cement-only concrete.

Reis et al. (32) conducted experimental studies with PC type I and two different types of FA mainly with different CaO content. The depth of carbonation was higher in mixtures containing mineral additions, especially FA. The incorporation of hydrated lime has potential to develop strength to carbonation of concrete with high volume of fly ash (HVFA) and therefore assure the production of eco efficient and durable concrete.

Khan and Siddique (33) conclude during their laboratory investigation revealed that SF concrete had higher carbonation rates than concrete without SF for a given compressive strength.

Khalil and Anwar (34) conclude on their experimental studies conclude that the carbonation process increased as the FA content increased. Additionally, compared to both mixes of OPC only and OPC with FA, the carbonation process is higher when SF is added to the only and OPC with FA. Comparing unicast and ternary systems, ternary systems exhibit higher carbonations.

Lye et al. (35) concluded on their review paper that in comparison to concrete that just contains PC, the depth of carbonation increases as FA portion increased. While the degree of carbonation varies with exposure conditions, field observations on the carbonation of 2.5 to 30-years old in-service concrete structures produced with PC and FA in the UK and Australia suggest that FA concrete tends to carbonate rapidly than PC concrete. This is due to the consumption of Calcium hydroxide ($Ca(OH)_2$) created during the hydration of Portland cement (PC) by both the pozzolanic reaction and the carbonation process, and this can cause corrosion by depassivating the steel reinforcement.

Singh and Singh (36) concluded that due to pozzolanic reaction of SF occurring simultaneously with cement hydration, it produces significant pore refinement, or the transformation of larger pores into smaller ones, upon addition. Alkali silica expansion and long-term corrosion resistance are both enhanced by SF, while carbonation depth is also increased. As FA replacement increased, the depth of carbonation also increased.

Zhao et al. (37) conducted experiment with the replacement of cementitious materials by 0%, 30%, 50%, and 70% GGBS with the specimen size $100 \times 100 \times 100$ mm. Carbonation depth was measured in every 3, 7, 28, and 56 days. Under the same experimental settings, replacing OPC with GGBS causes an increase in the carbonation depth of concrete.

5. Service Life of RC structures.

The initiation period and propagation period as shown in Fig.7 are the two main periods that are typically estimated when calculating service life models. The initiation period is the amount of time needed for the chlorides to penetrate the concrete cover and build up at the surface of the rebar in a sufficient quantity (threshold amount) or carbonation depth that is equal to the concrete cover, capable of breaking down the passive protective layer and starting corrosion. Among these, the penetration of chloride ion is the most serious and harmful related to corrosion of reinforcement. The beginning of the corrosion of reinforcement

by either reaching of carbonation front or the threshold amount of chloride at the surface of the reinforcement is the main stage for the prediction of the service life of the reinforced concrete structure. When there is a large concentration of chlorides close to the reinforcing bar or when the carbonation depth is equal to the concrete cover, the propagation phase begins (38). At this point, corrosion starts and quickly increases over time. Corrosion phase starts with initiation of corrosion followed by cracking, spalling and collapse of the RC structure (39). The factors that affect the initiation phase are:

- a) Environmental exposure condition
- b) Concrete cover
- c) Quality of cover concrete, permeability, alkalinity, and diffusion characteristics
- d) Steel types and threshold chloride content
- e) Existing cracks in the structure.

Typically, concrete structures can prevent deterioration for long periods of time. However, premature corrosion and the resulting deterioration in the strength and serviceability performance of concrete structures can occur due to the use of poor-quality materials and poor construction practices (40).

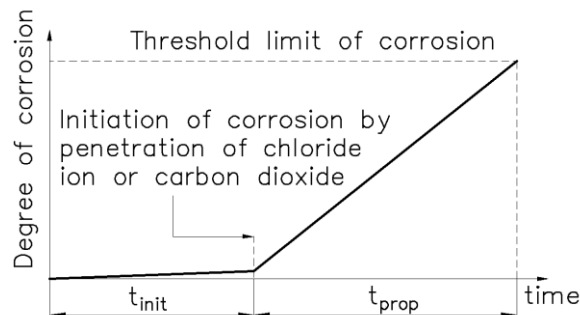


Fig.7 service life model by Tutti (1982) (41)

Prediction of remaining service life

By deducting the age of the concrete from the anticipated service life obtained from the service life prediction models, one can determine the remaining service life of the reinforced concrete structures. While predicting the service life of the RC structures initiation phase is more important as propagation phase is short.

6. SUMMARY AND CONCLUSIONS

This paper included the protection provided by the concrete to the reinforcement by introducing thin passive protection layer due to its high alkalinity, mechanism of chloride induced corrosion or reinforcement (pitting corrosion), mechanism of carbonation induced corrosion (uniform corrosion), corrosion products, and effects of SCMs on chloride ion penetration and carbonation in the RC structures.

Some conclusions obtained from the above comprehensive reviews are:

The service life design of RC structure needs the movement from prescriptive approach to performance-based approach.

The paramount concern among the various environmental deterioration mechanisms for RC structures is chloride ion penetration, leading to rapid reinforcement corrosion, followed by carbonation as the subsequent threat in terms of corrosion.

Use of SCMs such as FA, SF, and GGBS reduces the potential of chloride ion penetration by obstructing the diffusion of chloride ion due to their pore filling effect and production of secondary CSH gel.

Use of SCMs such as FA, SF, and GGBS increases the potential for carbonation attack by consuming calcium hydroxide during its pozzolanic reaction and reducing pH of concrete.

By deducting the age of the concrete from the anticipated service life obtained from the service life prediction models, one can determine the remaining service life of the reinforced concrete structures.

7. ACKNOWLEDGEMENTS

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