THE NATURE OF CONCRETE AND ITS DURABILITY PERFORMANCE IN AN INLAND ENVIRONMENT – A LITERATURE REVIEW

Alhassan, Yunusa Aminu & Ibrahim A. Danjuma

Department of Civil Engineering Federal Polytechnic Idah, Nigeria **Email:** alhassanay@gmail.com **Corresponding author:** Alhassan, Yunusa Aminu

ABSTRACT

The process of reinforcement corrosion in concrete is partially controlled by the transport of ions through the concrete microstructure and its chemical composition. The rate of advance of aggressive agents in concrete depends on the permeability of the concrete and the quantity of the hydroxides, which are, in turn, controlled by the characteristics of the concrete making material and its processing, for example curing and compaction. This paper examines the nature of concrete and its influence on the durability performance and service life of reinforced concrete structures in an inland environment. Even though other types of degradation affect concrete as its affect it's physical and chemical properties and its consequences on the carbonation thus durability performance and service life of reinforced service and service life of reinforced concrete as its affect it's physical and chemical properties and its consequences on the carbonation thus durability performance and service life of reinforced concrete are also described. **Keywords:** Concrete; Carbonation; Durability performance; Service life; Degradation

INTRODUCTION

Durability performance and service life of reinforced concrete structures situated in the inland environment is often principally affected by the ingress of carbon dioxide (CO₁). When atmospheric air penetrates reinforced or unreinforced concrete, carbon dioxide in the air dissolves in the pore water of the concrete to form carbonic acid which then chemically reacts with alkalis (hydroxide) in the cement paste that are produced from the hydration reaction of cement to form carbonate with the release of water. This reaction is commonly referred to as "carbonation" and it moves as a "front" into the concrete (Ballim et al., 2009; Beckett, 1986;

Neville, 1981; Roberts, 1981). The rate of advance of the carbonation front in concrete depends on the permeability of the concrete and the quantity of the hydroxides, which are, in turn, controlled by the characteristics of the concrete making material and its processing, for example curing and compaction. In addition, carbonation rates also depend on the concrete condition environments exposure (Kobayashi & Uno, 1990; Neville, 1981; Roberts, 1981; Wierig, 1984). While the permeability of concrete depends on many factors among which the water/binder ratio are and processing of the concrete which influences its hydration, the amount of hydroxides (CH) available in the concrete depends on the type and content of the binder used. Some of the reasons for attention on concrete durability problems are the high cost of maintenance and repair of existing infrastructure; the need for current improvement in design specifications for concrete structures since design approaches of the past do account for the increasing not sophistication of modern materials; the increasing aggressiveness of the environment due to industrialization and; the need to prolong the service life of concrete structures. The paper discussed the nature of concrete with emphasis on the physical and chemical properties of its binder phase and its effect on concrete durability and service life.

LITERATURE REVIEW Concrete

Concrete is a composite material made of aggregate and the reaction products of the cement and mixing water (i.e. the porous cement paste). This makes concrete a multi-phase material comprising a binder, filler and transition interfacial zone as represented in Figure 1, taken from Mehta Monteiro and (1003).Discussion on the different phases in concrete is given below:

- A binder phase known as hardened cement paste (hcp) is made up of a solid phase (calcium silicate hydrates -CSH, calcium hydroxide - CH, calcium sulphoaluminate - CASHand unhydrated clinker grains); voids (interlayer space in C-S-H, capillary voids and air voids); and a water phase (capillary water, adsorbed water, interlayer water and chemically combined water);

- A filler phase, commonly consist of aggregates – coarse and fine, comprising mainly gravel and fine sand fractions of naturally weathered or crushed rock materials;

- The last phase in concrete is called the Interfacial Transition Zone (ITZ). The ITZ is the space between the bulk cement paste and aggregates (see Figure 1). The ITZ is composed of the same elements as the hcp but its microstructure and properties are different and it is weaker than the binder and filler phases. Hence the ITZ exercises a far greater influence on the mechanical and durability behaviour of concrete.



Figure 1: Representation of the transition zone and bulk cement paste in concrete (Mehta & Monteiro, 1993)

The deterioration of concrete and its long-term durability performance is dependent on the structure and composition of the hcp and ITZ. Similarly, the ability of concrete to embedded protect steel and withstands various types of degradation mechanisms depend also on the structures and compositions of the hcp and the *ITZ*. These phases in concrete also determine the concrete fluid transport and chemical properties (Mehta, 1988). Thus, the formation of *hcp* and ITZ in concrete, its structure and composition will be considered in more detail.

Physical and chemical nature of concrete

Concrete resists aggressive environments by its physical and chemical properties which are derived from its dense microstructure and complex pore system as well as from its chemical interaction. The structure of the *hcp* and ITZ determines concrete pore structure while their composition influences its chemistry. The durability performance of concrete therefore depends on the structure and composition of the hcp and ITZ. This is in turn influenced by the fluid transport properties of the hardened concrete and the chemical interaction between the constituents of the hcp and the aggressive agents. For instance, carbonation of reinforced concrete is responsible for the depassivation of reinforcing steel. The rate of advance of CO, into concrete is determined by both the ease of access for CO, (fluid transport properties) as well as the ability of the elements of the hcp (and ITZ) to bind CO_{i} (chemical interaction), thereby making the CO_{i} increasingly unavailable for depassivating the steel. The concrete chemical composition is influenced by the solid phase of the hcp and ITZ. While the structure of the hcp and ITZespecially its voids and water phases, dictates the pore structure hence the fluid transport properties of concrete. The aggregate phase in concrete acts as filler and is responsible for the unit elastic modulus weight, and dimensional stability of the concrete. This phase has no direct contribution to the chemical properties of concrete. The discussion below focuses on both these aspects (fluid transport properties and chemical interaction) in considering the influence of the structures and composition of the hcp and ITZ on the durability performance and service life of concrete.

The hydrated cement paste (hcp): Figure 2 as presented by Mehta and Monteiro (1993) shows a schematic outline of the micro structural development in port land cement paste. The end product of the developmental stage at 28 or 90 days is a reduced content of the unhydrated cement clinker and the water-filled capillary pores if properly cured. The largest volume of the hydration product in the hcp are C-S-H, CH and C-A-<u>S</u>-H which have the greater influence on the physical and chemical nature of concrete (Mehta & Monteiro, 1993). The larger part of this discussion is drawn from the work of Mehta and Monteiro (1993).

The C-S-H makes up 50-60% of the solid hep and has no defined stoichiometry but determines the phase property of the paste. While the CH phase of the solid constitutes 20-25% has a definite stoichiometry, and its strength contributing potential is limited. The CH crystals possess less adhesion capacity because of the lower surface area and correspondingly weak Vander Waal forces of attraction. The other solid product is the C-A-S-H which occupies 15-20% of the solid and plays minor role in the behaviour of concrete microstructure. The last phase is the inner cores of unhydrated clinker grains that exist in the microstructure of the hcp long after hydration. The percentage of unhydrated clinker depends on the cement particle size distribution and its degree of hydration. This phase of the hcp dictates on the chemical composition of the concrete and hence chemical interaction with its aggressive agents.



Figure 2: Schematic outline of Microstructural development in Portland cement paste

|C-A-S-Hare included as part of C-S-H for convenience, although they will crystallize as separate phases). The approximate times indicated are: (a) Initial mix; (b) 7 days; (c) 28 days; (d) 00 days (Mehta and Monteiro, 1993). Concrete with a well hydrated cement paste is composed of insoluble hydrates of calcium (C-S-H, CH and C-A-S-H that exist in a state of stable equilibrium with high-pH pore fluid. Depending on the concentration of $\mathcal{N}a^+$, K^+ and OH^- ions the pH value ranges from 12.5 to 13.5. The chemical composition of C-S-H is not well defined since the ratios between the oxides vary with the degree of hydration, w/c ratio and temperature (Mehta & Monteiro, 1993). However, C-S-H contributes to strength and it is volumetrically and chemically stable in non-aggressive environment. The hexagonal crystal of CH derived from

the hydration of calcium silicate is a constituent part of the hcp and has dimensions of the order of a few μ m. CH as well as NaOH and KOHthat are present in small amounts, are very important with regards to protecting the reinforcement because they cause an alkaline pH up to 13.5 in the pour liquid. In addition they also stabilize the C-S-H, the main binding agent of cement (Czernin, 1980; Moskvin, 1983). C-A-S-H presents a minor influence to the chemical properties of the concrete. The maintenance of the pH level in the pore fluid of concrete is important to the long-term durability of concrete. In blended concretes, the quantity of CHis low due to its consumption in the pozzolanic reaction and the dilution of clincker cement in the concrete. The chemical composition of concrete in terms of its CH content is important

to steel reinforcement embedded in concrete. Since the alkaline content in concrete protects the steel by passivation as well as buffering the ingress of CO_2 by going into reaction in the presence of water.

The *hcp* also consists of a void phase that represents the pore structure of the concrete. This phase plays major role in the physical properties of the *hcp* and hence the physical properties of the concrete in terms of its fluid transport. The different types of voids in the *hcp* are the interlayer pores in C-S-H (gel pores), capillary voids, entrained air voids and the entrapped air bubbles. Mehta and Monteiro (1993) prepared the schematic diagram shown in Figure 3, giving range of pore sizes for the different pore types.



Figure 3: Dimensional ranges of solids and pores in a hydrated cement paste (Mehta & Monteiro, 1993)

The interlayer pores in C-S-H have widths of approximately 18Å inbetween gel particles and account for about 28% of the porosity in the C-S-H phase as observed by Powers (Powers, 1958). Power's observation is however in contrast to Feldman and Sereda (1968) observation. Feldman and Sereda suggested that the pores in the interlayer of the C-S-H vary from 5Å - 25Å. Voids in the interlayer pores in C-S-H have no effect on the strength and permeation of the *hcp* but do contribute to the *hcp* drying shrinkage and creep. lons and gas molecules which are aggressive to

concrete are smaller than the size of typical gel pores. Thus, this void size range has no direct effect on the durability performance of the concrete, hence its service life. The capillary voids are the spaces not filled by the solid compound of the hardened paste, which is space not taken up by the cement or the hydration product. The capillary voids are irregular in shape and influences strength and permeability of the *hcp* when larger than 50 nm and are often referred to as macro pores (see Figure 4). The entrapped air voids and incomplete compaction voids have sizes greater than I mm and are created unintentionally. These voids are also irregular in shape and arise as a result of air trapped in the cement paste during concrete mixing. The entrapped air voids and compaction voids have substantial effects on concrete fluid transport property hence its degradation.



Figure 4: Schematic description of the structure of cement gel (Fernandez et al., 2004)

The third component of the *hcp* is water contained in the voids that exists capillary, adsorbed, as interlayer and chemically combined waters (see Figure 5 after Feldman and Sereda (1968)). The capillary water is present in voids that are larger than 50Å while the adsorbed water is water adsorbed onto the solid surface in the hcp by the influence of attractive forces. The removal or loss of the adsorbed water may cause shrinkage of the *hcp*. The interlayer water is the water that is associated with C-S-H

structure and is held by hydrogen bonding. This form of water can be lost only on strong drying and when this happens the C-S-H structure shrinks considerably. Chemically combined water is water that is an integral part of the microstructure of various cement hydration products. This water is not lost on normal drying, and is only released when the hydrates decompose on heating. This phase of the *hcp* also influence its permeation properties and hence that of the concrete.



Figure 5: Types of water associated with the calcium silicate hydrate (Feldman and Sereda, 1968)

The Interfacial Transition Zone (ITZ): The ITZ phase of the concrete represent a small region next to the particles of coarse aggregate and it is composed of the same elements as the hcp (see Figure 1). However, its microstructure and properties are different from those of the hcp. The ITZ, although similar to the hcp in terms of its components, is different in terms of morphology, composition and density (Mindess & Young, 1981). Thus, this phase present a zone of particularly high porosity (hence fluid transport) in concretes than does the hcp. This phase exist as a thin shell typically 10-15 μ m thick around large aggregate and is generally weaker than the aggregate and bulk hcp(Mehta & Monteiro, 1993). One of the reasons for the weaker microstructure of the ITZ is that, the water film that forms around large aggregate particles in the fresh concrete increases the ITZ w/c ratio and thus bleeding (Mindess & Young,

1981). Similarly, the dissolution of calcium sulphate and calcium aluminate compounds produced calcium, sulphate, hydroxyl and aluminate ions which combined to form C-A-S-H and CH. The higher w/c ratio in the vicinity of the coarse aggregate allows space for the crystalline products of C-A-S-H and CH to grow in the ITZ producing a relatively larger crystal. This forms a more porous framework in the ITZthan in the bulk *hcp*. The density and hence strength of the ITZ is however improved by the progress of hydration since the poorly crystalline C-S-H and a second generation of smaller crystals of C-A-S-H and CH start filling the empty space that exist between the framework created by the larger C-A-S-H and CH crystals (Mehta & Monteiro, 1993). During stress-induced cracking, the C-A-S-Hand CH crystals serve as preferred cleavage sites owing to their tendency to form an oriented structure. The

ITZ is therefore the main contributor to the fluid transport properties of concrete and hence the rate of concrete deterioration.

Nature of concrete on its fluid transport properties

The transport properties of concrete are important to predicting their deterioration thus durability, since deterioration mechanisms are all related to the ease with which a fluid or ion can move through the concrete microstructure (Mehta, 1988). The fluid transport property of concrete is predominantly influenced by the structure of the *hcp*, especially at the interface |ITZ| with aggregate particles. The passage of potentially aggressive species is primarily influenced by the penetrability of the concrete. Concrete penetrability is broadly defined as the extent to which the concrete permits gases, liquids or ionic species to move through its pore structure. It normally embraces the concepts of permeation, sorption, diffusion and migration and is quantified in terms of the transport parameters (Alexander & Mindess, 2005). The processes involved in fluid and ion movement include flow under pressure, distinct mechanisms of capillary action and flow under a concentration gradient. These mechanisms are characterised by the material properties of permeability, sorptivity, and diffusivity respectively (Richardson, 2002). There are a number of mechanism by which fluids move through the pore structure of concrete and the laws governing these movements are equally varied.

Nature of concrete on its chemical composition

The chemical composition of concrete depends on the mix constituents, especially the cement and/or binder content and its composition. In addition, the chemical composition of the binder also depends on the degree of hydration and degree of pozzolanic activity for blended cement. The hydroxide content in concrete also depends on the water/binder ratio and the degree of hydration; it increases with hydration as noted in Figure 1.3. However, the content of hydroxide in concrete depends more on the binder types used. While the hydroxide content increases with hydration in plain cement, it decreases in the case of blended cement. In either plain or blended cement concrete, hydration reduces the interconnectivity of the pore structure, with the rate of reduction being relatively slow for blended concrete. Generally, the amount of hydroxides and the concrete pore connectivity are functions of the cement hydration reaction which, in its turn, is time and curing dependent. Thus, the rate of carbonation in concrete may reduce as the water/binder ratio reduces and the degree of hydration increases. The chemical parameter limiting concrete carbonation is the amount of carbonatable material (hydroxides) that is available in the concrete matrix. Thus, the amount of hydroxide in the pore structure of the concrete has an influence on the rate of carbonation thus its durability performance in an inland environment.

Nature of concrete on its durability performance

One of the durability challenges faced by reinforced concrete structures situated in an inland environment is carbonation. Carbonation is the ingress of CO, into concrete pores and its reaction with hydroxide in the concrete pore water culminating into depassivation of reinforcing steel and corrosion. The hence rate of carbonation in concrete and thus its durability performance is controlled by the proportion of the binder phase (*hcp* and |TZ|, as well as its properties. The properties of the binder phase in concrete depend on its microstructure (i.e. the type, amount and distribution of solids and voids in the hcp and |TZ|. The size and continuity of the pores in the *hcp* and ITZ in concrete would determine its fluid transport properties and this is closely related to the capillary porosity and the solidspace ratio. The capillary pores and its degree of interconnectivity as well as the entrapped air influences the pore structure of the concrete. While the composition of the solid phase in the *hcp* and ITZ determine the concrete

chemical interaction. In determining the resistance to degradation of concrete, not only should the total porosity, capillary size and interconnectivity of the capillary pores he considered, but also the composition of the CSH and CH that exist in the *hcp* and *ITZ*.

The microstructure of concrete can be seen on three different scales. In increasing level of scale we have the microstructures of the *hcp*, mortar and then concrete. This scale is attributed to the decreasing *hcp* content and *ITZ* volume, increasing thereby making the fluid transport properties increasing with the scale. Most deterioration mechanisms involve the movement of gases or liquids into or out of the pore structure of concrete. Thus, the fluid transport properties of concrete are an important а determinant of its ability to resist deterioration (Mehta, 1993). The durability performance of a concrete exposed to a given aggressive environment is also influenced by the chemical interaction between the constituents of the hcp/ITZ and the The aggressive agent. chemical composition of concrete which is derived from the thermodynamic stability of its hydrates, determines the resistance to aggressive agents from the environment. Similarly, the nature of the interaction of the paste component of the concrete with the aggressive agents also contributes to

resistance of the concrete. Because of its strong alkaline character, hcp (and therefore, concrete) is easilv deteriorated in an acidic environment, or a pH- reducing environment which then de-stabilises the hydrates. In determining the resistance to degradation of concrete and its role in embedded the protecting steel reinforcement, the quantity of the hydrates is also very important. The composition of the *hcp* influences the concrete chemistry and is responsible for the chemical protection of the embedded steel reinforcement. It has been established that the perviousness of concrete as well as its chemical composition plays an important role in the control of concrete durability (Hilsdorf, 1989). Accordingly, testing of transport parameters for concrete, such as permeability, absorption or diffusivity behaviour in most cases has been done on the basis of durability consideration. Similarly, the control of concrete durability especially chloride diffusion and carbonation is also affected by binder chemistry of concrete (Dhir, et al., 1999; Parrott, 1994).

Mechanism of Carbonation in Concrete

Carbonation is a reaction between carbonic acid and hydroxides in cement paste that form carbonates. Carbonic acid can be introduced in the pore structure of *hcp* by dissolution of gaseous atmospheric CO_2 in pore

water or by direct penetration of rain water with dissolved CO_r Cementitious pastes are basic |pH| as high as 13.5) and the carbonation reaction reduces the pH of the paste to less than 8.5 when fully carbonated (Glass et al., 1991). Carbonates formed in the carbonation reaction are molecules larger and of lower solubility than the hydroxides, thereby increasing the density of the cement pastes of the concrete and locally, the strength (Neville, 1997). Reduction of the pH of the cement paste is a concern for reinforcing steel embedded in concrete because steel is more susceptible to corrosion at lower pHlevel. As a result, carbonation studies most often concern themselves with this potential corrosion and the rate at which carbonation progresses from the exposed concrete face towards the reinforcing steel. The chemical composition of the cover concrete depends on the mix constituents, especially the binder type and content, and the chemical composition of the binder. Additionally, the chemical composition of concrete also depends on the degree of hydration and degree of pozzolanic activity in the case of blended binders. Curing influences the degree of hydration and pozzolanic activity thus the chemical composition of the concrete. With the use of supplementary cementitious materials (SCM), hydroxide components in the cement paste are reduced due to its consumption. With this reduction,

carbonation rates would tend to increase, as there is less material to react with the CO_2 .

However, SCM have the effect of decreasing permeability of the cement paste which tends to decrease the diffusivity of the ingress of CO, If the reduction in permeability has a higher impact than the reduction in hydroxide components, then the overall carbonation is reduced. The chemical parameter of importance to is carbonation the amount of carbonatable material (hydroxides) that is available in the concrete matrix. It has been observed that, given a sufficiently high CO_{1} concentration, unhydrated products (C,S, C,S) as well as the CSH gel and other hydration products such as ettringite will carbonate. While at ambient CO, concentration, only the CH will mainly carbonate. Thus, the rate of carbonation is slow at low CO_{1} concentration. Considering the mentioned limitations in the derivation of the square-root of time law stated in section 2.4.2 for the progression of the carbonation front in concrete and the various factors that influences this progression as enumerated in section 2.4.3, numerous attempts to correlate the rate of carbonation with the concrete physical and/or chemical properties has been attempted in a bid to model the mechanism of carbonation in concrete (Ballim, 1994; Mackechnie, 1996; Parrott & Killoh, 1989; Bruno, 2010). In the following section, an attempt is made to review some existing empirical models on carbonation progression in concrete.

CONCLUSION

The structure and composition of the hcp and ITZ phases in concrete determines its pore structure and chemistry respectively. The durability performance of concrete depends on the structures and composition of the hcp and ITZ which are in turn influcend by the fluid transport properties and the chemical interaction between the hcp and ITZ and the aggressive agents. This paper has introduced some of the key aspects of the nature of concrete and their influence on the carbonation of thus concrete its durability performance and service life. The factors that influence the physical and chemical properties of concrete have been mentioned. How these factors affect concrete carbonation thus its durability performance and service life been extensively discussed. has Prevention or reduction of concrete deterioration depends on the undertstanding and quantification of the concrete physical and chemical properties.

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