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FEW ASPECTS OF STRUCTURAL CONCRETE IN ACIDIC ENVIRONMENTS

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Abstract- *Structural concrete exposed to aggressive environment including acidic environment is often reported to be deteriorated in practice and repair/rehabilitation of them is very costly and sometimes may be impossible. Proper case must be taken during design and construction of such structures so as to ensure its durability. The paper discusses and reviews the acidic attack on structural concrete mentioning the mechanism, factor influencing the attack, causes and effects, few remedial measures in the light of past study/existing literature. It is revealed that among all the acids' coming in contact with concrete, sulfuric acid is considered more aggressive for its critical reaction on hardened concrete. The action of acids with hardened cement paste leads to the formation of some expansive and leachable compounds responsible to the degradation of concrete. The use of supplementary cementitious materials including fly ash, slag etc are reported to increase the durability of structural concrete in such location.*

Keywords: Strength, Durability, Structural Concrete, Permeability, Acidic Environment

1. INTRODUCTION

Concrete is a manmade building material that looks like stone. It is a composite material composed of coarse granular material (the aggregate or filler) embedded in a hard matrix of material (the cement or binder) that fills the space among the aggregate particles and glues them together. The strength, durability and other characteristics of concrete depend upon the properties of its ingredients, on the proportions of mix, the method of compaction and other controls during placing, compaction and curing. The structural concretes are often subjected to different aggressive environments such as acidic environments, marine environments etc. Concrete structures, specially situated in coastal areas, are exposed to marine environments worldwide. Although it is not just over the sea but it could be deemed to be extended over the area where concrete becomes wet with sea water and wherever the wind will carry salt water spray which may be as far as some kilometers inland. But most of the concrete structures for practical application particularly in industrial region are more or less affected by acid attack. In addition, the structures those are not directly exposed to acidic environments are also affected by different acids coming from acid rain. Due to climate change, acid rains are frequent phenomena now a days.

Concrete is generally well resistant to chemical attack, provided an appropriate mix is used and the concrete is properly compacted. There are however, some exceptions. Concrete containing Portland cement, being highly alkaline, is not resistant to attack by strong acids or compounds which may convert to acids. Consequently, unless protected, concrete, should not be used when this form of attack may occur.

Concrete is also attacked by water containing free CO_2 such as moorland water or mineral waters, which may also contain hydrogen sulfide. Not all CO_2 is aggressive because some of it is required to form calcium bicarbonate in the solution. Flowing pure water, formed by melting ice or by condensation and containing little CO_2 also dissolves $Ca(OH)_2$, thus causing surface erosion. Peaty water with CO_2 particularly aggressive, it can have pH value as low as 4.4. This type of attack may be of importance in conduits in mountain regions, not only from the standpoint of durability but also because the leaching out of hydrated cement leaves behind protruding and increase the roughness of the pipe. To avoid this, the use of calcareous, rather than siliceous, aggregate is advantageous because both the aggregate and the cement paste are eroded.

Concrete is generally resistant to microbiological attack because its high pH does not encourage such action; nevertheless, under certain, fortunately rare, tropical conditions, some algae, fungi and bacteria can use atmospheric nitrogen to form nitric acid which attacks concrete. Lubricating oils and hydraulic fluid, sometimes split on concrete aprons at airports, break down when heated by exhaust gases and react with $Ca(OH)_2$, thus causing leaching.

Various physical and chemical tests on the resistance of concrete to acids have been developed, but there are no standard procedures. It is essential that tests are performed under realistic conditions because, when a concentrated acid is used, all cements dissolve and no assessment of their relative quality is possible. For this reason, care is required in interpreting the results of accelerated tests.

Use of blended cements which include ground granulated blast furnace slag, pozzolanas and especially silica fume, is beneficial in reducing the ingress of aggressive substances. Pozzolanic action also fixes $Ca(OH)_2$, which is usually the most vulnerable product of hydration of cement in so far as acid attack is concerned. However, the performance of concrete depends more on its quality than of the type of cement used. The resistance of concrete to chemical attack is increased by allowing it to dry out before exposure, but following proper curing. A thin layer of calcium carbonate (produced by the action of CO_2 on lime) then forms, blocking the pores and reducing the permeability of the surface zone. It follows that pre-cast concrete is generally less vulnerable to attack than concrete cast in situ. Good protection of concrete from acid attack is obtained by subjecting pre-cast concrete in a vacuum to the action of silicon tetra fluoride gas. This gas reacts with lime.

$2Ca(OH)_2 + SiF \rightarrow 2CaF_2 + Si(OH)_2$

$Ca(OH)_2$ can also be fixed by treatment of with diluted water-glass (sodium silicate). Calcium silicates are then formed, filling the pores. Treatment with magnesium fluorosilicate is also possible. The pores become filled and the resistance of the concrete to acid is also slightly increased, probably due to the formation of colloidal silicofluoric gel.

2. ACID ATTACK ON STRUCTURAL CONCRETE

Chemical attack of concrete occurs by way of decomposition of the products of hydration and formation of new compounds which, if soluble, may leach out and, if not soluble, may be disruptive in situ. The most vulnerable hydrate is $Ca(OH)_2$, although C-S-H can also be attacked. Concrete can be attacked by liquids with a pH value below 6.5 but the attack is sever only at a pH below 5.5; below 4.5, the attack is very severe [1]. Concrete is also attacked by water containing free CO_2, such as moorland water or mineral waters, which contain hydrogen sulfide.

Acid rain, which consists mainly of sulfuric acid and nitric acid and has a pH value between 4.0 and 4.5, may cause surface weathering of exposed concrete [2]. Although domestic sewage by itself is alkaline and does not attack concrete, severe damage of sewers has been observed in many cases, especially at fairly high temperatures when sulfur compounds become reduced by anaerobic bacteria to H_2S [3]. This is not a destructive agent in itself, but when dissolved in moisture films on the exposed surface of the concrete and undergoes oxidation by aerobic bacteria, finally producing sulfuric acid. The attack occurs, therefore, above the level of flow of the sewage. The harden cement paste is gradually dissolved, and progressive deterioration of concrete takes place [4]. A somewhat similar form of attack can occur in offshore oil storage tanks [5].

Sulfuric acid is particularly aggressive because, in addition to the sulfate attack of the aluminate phase, acid attack on $Ca(OH)_2$ and C-S-H takes place. Reduction in the cement content of the concrete is therefore beneficial, provided, of course, that the density of the concrete is unimpaired [6].

3. MECHANISM OF ACID ATTACK

Concrete being very alkaline in nature, is extremely susceptible to acid attack. The mechanism for this process is very simple. The products of cement hydration are shown below.

$$\mathbf{CS + H \Rightarrow C\text{-}S\text{-}H + CH}$$

Calcium Silicate + Water → Calcium Silicate Hydrate + Calcium Hydroxide

Acid attack is caused by the reaction of an acid and the calcium hydroxide portion of the cement paste which produces a highly soluble calcium salt by product. These soluble calcium salts are easily leached out from the cement paste thus weakening the paste’s structure as a whole. This basic reaction is shown below.

$$\mathbf{Acid\ X + CH \Rightarrow CX + H}$$

Acid + Calcium Hydroxide→ Calcium Salt + Water

A more aggressive and destructive case of acid attack occurs when concrete is exposed to sulfuric acid. The calcium salt produced by the reaction of the sulfuric acid and calcium hydroxide is calcium sulfate which in turn causes an increased degradation due to sulfate attack. This process is illustrated below.

$$\mathbf{H_2SO_4 + Ca(OH)_2 \Rightarrow Ca(SO)_4 + 2H_2O}$$

Acid + Calcium Hydroxide→ Calcium Sulfate+ Water

Calcium sulfate product contributes to sulfate attack.The dissolution of calcium hydroxide causes by acid attack proceeds in two phases. The first phase is being the acid reaction with calcium hydroxide in the cement paste. The second phase is being the acid reaction with the calcium silicate hydrate. As one would expect the second phase will not begin until all calcium hydroxide is consumed. The dissolution of the calcium silicate hydrate, in the most advanced cases of acid attack, can cause severe structural damage to concrete.

Corrosion of rebar is an electrochemical reaction that occurs at anodic spot due to the development of anodic and cathodic regions on its surface as shown in Fig.1. The transformation of metallic iron to rust is accompanied by an increase in volume as large as 600% of the original metal consumed that result in cracking, spalling and ultimately structural failure. But concrete normally provides a high degree of protection to rebar against corrosion due to highly alkaline environment (pH ≈ 13). The passivity of steel is maintained as long as definite amount of aggressive ions do not reach the steel surface. In acidic environment, the rebar corrosion may be mainly initiated by the carbonation and chloride penetration process. In carbonation process the high pH value of concrete around rebar may be reduced by the ingress of acid (CO_2 in air) from the surrounding environment as per following reaction

$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$

As a result, pH changes from (12-13) to neutrality and the passivity of steel is lost. The penetration depth i.e. carbonation depth when exceeds the cover depth, aggressive ions including chloride find a suitable environment leading to greater corrosion. In chloride penetration process, chloride ions from acidic environment (HCl solution) gradually diffuse into concrete with time leading to a condition when the concrete no longer able to protect rebar from corrosion. Various researchers proposed different values of threshold chloride concentration that varies from 75-3640 ppm [7].

However, establishing a universally applicable threshold concentration of chloride is very difficult as it depends on several factors including pH of concrete, water content and properties of water soluble chlorides. Combined with carbonates even small chloride concentration may depassivate the steel and accelerate the corrosion process.

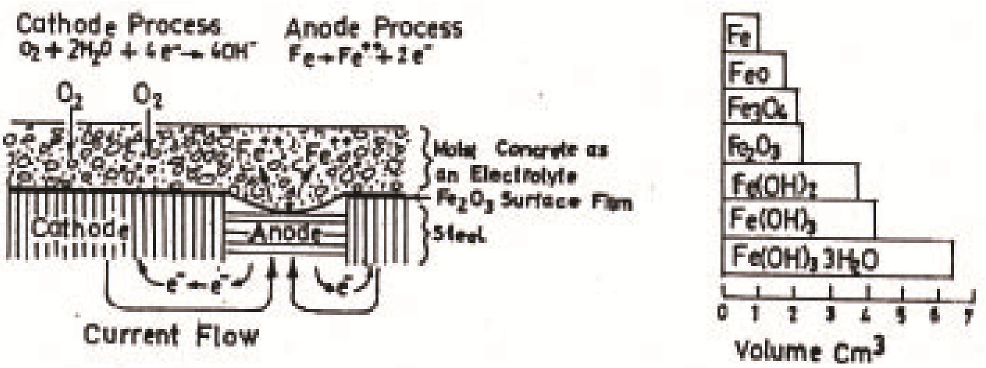

Figure 1: Expansion and Cracking of concrete due to corrosion of the embedded steel [7]

4. FACTORS CONTROLLING ACID ATTACK

The rate of acid attack and hence corrosion of concrete or cement paste depends on many factors such as the aggressivity of medium, the resistance of cement based materials, the choice of protective measurement, solubility of the calcium salts formed by the hydration of cement based materials etc. [8]. The aggressivity of medium is influenced by the dissociation characteristics of acid and thereby value of pH, quantity of acid. But the concentrations of aggressive species are more sensible to acid attack than pH value of the acidic solution [9]. A very porous layer of corrosive products remains on the surface and contribute to further development of the deterioration process. In the case of the formation of insoluble calcium salts such as calcium oxalate and fluoride, the effect of the acidic solution is entirely different. A dense insoluble layer is formed enhancing the development of the acidic attack showing a protective effect.

Other important factors for acid attack are quantity and action mode of acting solution. More the quantity of solution gives greater possibility of contact of aggressive species with surface of concrete which contributes to greater attack. In principle, two action modes are possible: (1) static conditions indicating no practical movement of the acting solution; (2) dynamic conditions means the change of the level or flow of the acting solution. The flow rate may have a greater influence than the concentration of the solution [10]. The water running with high velocity disrupts the corroded layer and contributes to the development of the attack on the uncorroded concrete. Dynamic conditions contribute to the transport of the aggressive species into the pore system of concrete and to the drainage out of the decomposition products [10, 6]. The drying of concrete leads to the crystallization of products formed by the acid attack. The corroded products may be expanded due to crystallization resulting tension cracks in the concrete. This crack helps the aggressive species to ingress in the unaffected concrete which again attacks the unaffected concrete. Alternate wetting and drying caused by repeated changes of the level in the acting solution may contribute to the severity of the processes [9]. Ambient temperature and relative humidity may influence the acidic attack, especially in the presence of the changes of the level of the acting solution [11]. The level of the ambient relative humidity is of special significance in an attack by air pollutants like CO_2, SO_2 and NO_x because the quantity of pore liquid in the attacked material is dependent on the ambient relative humidity[11]. The presence of humidity as a solution medium is a fundamental condition of the development of the process of the attack by gaseous species [12, 13].

The type of cement has no significant effect on acid resistance. All types of cement behave more or less similar way i.e. bad [14, 12]. But blended Portland cement containing pozzolana and or slag shows better performance against acid attack although the efficiency of performance is characterized by some other factors such as type and quantity of cement, amount, type and properties of admixture and curing conditions [8]. Curing conditions including time and temperature influence the porosity thereby permeability of the concrete which are directly related to the engineering properties of concrete. If the ambient temperature is high or if there is insufficient time for curing, the surface of the concrete will be dried resulting pore development and surface cracking which accelerate the acid attack [8]. The permeability of concrete depends on the properties of pore structures which include the pore size and its distribution affecting the engineering properties of concrete [15]. The transport phenomenon of concrete is directly related to its pore structure which permits easy access of aggressive species in the concrete resulting acid attack [8].

5. EFFECT OF ACID ATTACK ON STRUCTURAL CONCRETE

Acids affect the structural concretes by two ways. One way, the acid produces calcium salts such as gypsum by the reaction with Portlandite [$Ca(OH)_2$] which in turns produces ettringite (C3A·3CaSO4·31H2O) by reacting gypsum with C_3A, hydrated aluminates, or monosulfate (C3A·CaSO4·12H2O). The volume of this ettringite is higher than the reactants they replace. Due to this volume expansion cracks may be developed in the structural concrete leading more acid attack by more ingress of acid in the concrete. As a result, the concrete losses compressive load bearing capacity due to its weak structural condition. In the second way, the salts developed by the reaction of acids with hydrated cement product produce thaumasite (CaSiO 3·CaCO3·CaSO4·15H2O) by reaction of the calcium-silicate hydrates (C-S-H) with this calcium salts such as calcium sulfate in the presence of carbonate ions. Therefore, the amount of C-S-H is reduced. But the strength of concrete depends mainly on C-S-H. So the formation of thaumasite ultimately reduces the load bearing capacity of concrete. Besides these, sometimes some acids including H_2SO_4 produce gypsum by reacting with C-S-H leading to the formation of more ettringite and hence less C-S-H result in degradation of concrete.

More aggressive acids such as hydrochloric, acetic, nitric, and sulfuric acids produce calcium salts that are very soluble. This solubility leads to leaching out of the salts from the concrete and hence contributes to the greater porosity and thereby permeability of concrete. Less aggressive acids such as phosphoric and humic acids produce calcium salts with a lower solubility. These low soluble salts can act as a partial inhibitor to the overall process by blocking tiny passage in the cement paste through which water flows. This reduces the amount of calcium salts that enter into solution and retard the overall process. Some examples of concrete deterioration/degradation by acid attack as reported by several researchers are shown in the following figures.

Figure 2: Deterioration of concretes in sewage treatment plant [16]

(a) Deterioration in Sulfuric Acid (b) Deterioration in Hydrochloric acid

Figure 3: Deterioration of different concretes in acidic environments [17]

6. REMEDIAL MEASURES FOR ACID ATTACK ON STRUCTURAL CONCRETE

Several methods are reported to be applied to protect the concrete against acid attack or to retard the acid attack of structural concrete. Some of the methods are briefly explained below.

(a) Addition of Mineral Admixture to concrete: From the above discussion it is clear that the severity of acid attack mainly depends on the amount of lime present in cement. So to reduce the acid attack quantity of cement may be reduced by the partial replacement of cement with supplementary cementitious materials which imparts strength to concrete. Mineral admixture such as slag, fly ash, silica fume, metakaoline etc can be used as the supplementary materials of cement. Because all of these admixtures have plenty of silica in lieu of lime which form C-S-H gel directly by the pozzolanic action according the following equation.

Portlandite + Silica + Water → Calcium silicate hydrate (C-S-H)

(b) Providing protective coating: As penetration of aggressive spices is regarded as an important cause of concrete deterioration, to prevent the ingress of acid into the concrete, a layer with sufficient thickness of coating may be provided. Antibacterial additives can be incorporated in the coating mix to reduce the formation of acids in some structures like sewers lines [18, 19]. Adequate concrete cover must be provided in case of reinforced concrete structures to achieve greater level of corrosion protection.

(c) Mix proportions: Low water-cement ratio should be selected during mix design of the concrete to reduce the porosity/permeability and increase the density of concrete thereby increasing the acid resistance of concrete [16].

(d) Improving the properties of mix ingredients of concrete: The aggregate to be used in the mix design should be well graded, chemical ion free and having low alkalinity as acid attack is accelerated by the alkalinity of concrete. The mixing water must be free from objectionable salt ions.

(e) Proper quality control: Although durability of concrete depends on several factors including aggregate type, cement type, water-binder ration, air entrainment, period of procuring, quality of mixing water, proper quality control at every stages of concrete making is mandatory in order to get densed, less permeable, good quality concrete for the use as structural concrete in the acidic environment.

7. SUMMARY AND CONCLUSION

Structural concrete when exposed to acidic environment are reported to undergo degradation/destruction process unless it is protected with appropriate measure. A lot of studies have been conducted on the ill effects of acidic environment on structural concrete used for various applications. Existing literatures also covers the effectiveness of supplementary cementitious materials as partial replacement of cement to produce durable concrete as remedial measures. However on the basis of the previous research/existing literature discussed, the following findings/recommendations can be noted.

(a) Concrete being very alkaline in nature (pH:12-13) is extremely susceptible to acid attack.

(b) A more aggressive and destructive case of acid attack occurs when structural concrete is exposed to sulfuric acid. HCl leads to rebar corrosion and is initiated by carbonation and chloride penetration from acidic environment

(c) The rate of acid attack and hence corrosion of concrete depends on several factors including the aggressivity of the of the medium, the resistance of the cement based materials, solubility of calcium salts formed during hydration, dissociation characteristics of acid i.e. value of pH, quantity of acid etc.

(d) Alternate wetting and drying caused by repeated changes of the level in the acting solution of the environment may contribute to severity of the corrosion/deterioration process.

(e) The type of cement has no significant effect on acid resistance. But blended Portland cement containing pozzolana including fly ash, slag shows better performance against acid attack.

(f) Acid reacts with hardened cement matrix and form complex products including Friedel's salts, ettringite etc which are being leachable/expansive in nature causes degradation of structural concrete.

(g) Addition of mineral admixture (fly ash, slat etc) with cement, proper protective coating, adequate cover to rebar, good quality concrete having low permeability, use of chemical free ingredient materials for concrete, proper quality control etc. are the suggested remedial measures for making structural concrete in acidic environment.

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