

DEVELOPMENT OF AN ACID RESISTANT CONCRETE: A REVIEW

Anwar Khitab*, Muhammad Tausif Arshad, Faisal Mushtaq Awan, Imran Khan

Department of Civil Engineering, Mirpur University of Science & Technology, Mirpur, Azad Kashmir, Pakistan

*Corresponding E-mail: anwarkhitab@yahoo.com

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Abstract

This review paper addresses the measures taken to prevent or minimize the deterioration of concrete, which confronts an acidic environment. Primarily, the mechanism of reaction between alkaline concrete and acid is clearly demonstrated. The mechanism of reaction clearly sets guidelines as to how the chances of this disastrous reaction should be minimized or eliminated at all. The suggested preventive measures are two-fold i.e. the improvement of the basic microstructure of concrete and the provision of barriers against acids. Concrete can be made acid resistant using classical as well as novel techniques like nanotechnology. There exists an immense need that these measures are recognized and implemented by the construction industry to put a stop to huge money losses.

Keywords: *Concrete, Acid attack, mechanism of reaction, preventive measures, nanotechnology*

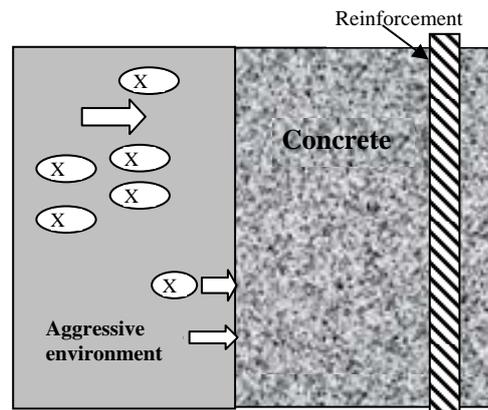
1.0 Introduction

Concrete is defined as a mixture of cement, sand, gravels, water and sometimes admixtures and additives. Concrete has long been used in civil engineering industry for construction of foundations, footings, retaining walls, slabs, pavements, tunnels, bridges, basins, canals, dams, drains, sewerage lines and many other structures and structural members. Concrete is the backbone of any country's infrastructure. Concrete hardens and gains strength within days. Its relative low cost, ease of application and relative long term service life compared to other materials is the main cause of its popularity. The disadvantage of using concrete is that the micro structure of concrete allows the penetration of water and other destructive species that will cause premature failing of the concrete surface. A permeable concrete will allow infiltration of aggressive agents (chlorides, carbon dioxide and acids) to the steel reinforcement bars causing complete failure of the structure [20].

In general, concrete has a low resistance to chemical attack. The common forms of chemical attack on concrete and the embedded reinforcement in reinforced concrete are chloride attack, sulphate attack, Carbonation due to Carbon dioxide, Alkali-aggregate reactions and acid attack [9, 22].

Chlorides in de-icing salts or in soils, sea water and ground water can enter concrete and destroy the passive oxide film, which normally protects the steel against corrosion. Chloride can enter either through its ingredients (like chloride containing aggregates, and water) or through the environment (such as de-icing salts or seawater). As a result, rust layers build up on steel, whose volume is enough to exert disruptive tensile stresses on surrounding concrete causing it to crack or even spall [8, 23].

Sulphates present in soils, groundwater and seawater react with Tricalcium Aluminate (C_3A) of cement to form expansive compounds. The reaction leads to an increased volume of the products resulting in disintegration of the concrete. Sulphate resisting cement, which has a lower content of C_3A (ASTM Type V cement) is best suited in conditions where an extensive exposure to sulphates is expected [1, 21].



Note: X is an aggressive species

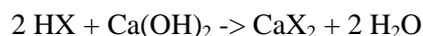
Figure 1: Reinforced concrete exposed to an aggressive environment

The pore solution of concrete is alkaline in nature due to the presence of portlandite or Calcium hydroxide ($\text{Ca}(\text{OH})_2$). This alkaline solution protects steel from corrosion. The presence of CO_2 may lead to the destruction of this alkalinity. This process of loss of alkalinity due to the reaction between $\text{Ca}(\text{OH})_2$ in concrete and CO_2 from air is known as carbonation [24]. Carbonation leads to the formation of Calcium Carbonate and water, as a result the alkalinity of concrete is lost. The steel thus becomes vulnerable to rusting in the presence of oxygen and moisture.

The reaction between the silica of aggregates (in siliceous aggregates) and the alkali content in cement is called alkali-aggregate reaction. The product of the reaction expands by absorbing water and increases in volume leading to cracking of concrete [1].

2.0 Mechanism of acid attack

As mentioned earlier concrete is alkaline in nature due to the presence of Calcium Hydroxide ($\text{Ca}(\text{OH})_2$). If attacked by an acid HX (where X is the negative ion of the acid), the components of the cement matrix break down in accordance with the following famous acid-base reaction [25]:



The decomposition of the concrete depends on the porosity of the cement paste, on the concentration of the acid, the solubility of the acid calcium salts (CaX_2) and on the fluid transport through the concrete [2]. Insoluble calcium salts may precipitate in the voids and can slow down the attack. Acids such as nitric acid, hydrochloric acid and acetic acid are very aggressive as their calcium salts are readily soluble and removed from the attack front. Other acids such as phosphoric acid and humic acid are less harmful as their calcium salt, due to their low solubility, inhibits the attack by blocking the pathways within the concrete such as interconnected cracks, voids and porosity. Sulphuric acid is very damaging to concrete as it combines an acid attack and a sulphate attack [26].

3.0 Special concretes for acid attack prevention

The risk of acid attack on concrete can be minimized by providing due consideration to concrete porosity. Lesser the porosity, lesser will be the chances of acid attack on concrete. In general it is said that all high performance concrete mixtures show a better resistance against acid

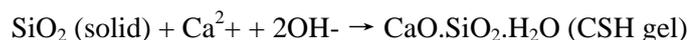
attack than the reference ordinary type concrete [9]. By High performance concrete is meant a concrete with superior qualities including low permeability and low diffusion [2]. In another way, the concrete resistance to acids can also be provided by giving its surface an acid resistant coating. In Fig. 2, two ordinary concrete cylinders having the same mix design are shown. The cylinder on left was immersed in 5% sulphuric acid for 28 days having a 6% loss of mass at the end of the immersion period.



Figure 1: Concrete cylinder immersed in 5% H₂SO₄ for 28 days (Left)

3.1 Silica concrete

Silica fume (SF) is an industrial byproduct obtained from an electric arc furnace process. During this process, high purity quartz are reduced to silicon at high temperatures producing silica vapors. These vapors oxidize and condense in the low temperature zone to tiny particles known as silica fumes [27]. Fly ash are fine solid particles of ash carried into the air during the combustion of pulverized fuel in power stations. Silica fume and fly ash have proved to be very useful additives for concrete. Using fly ash in combination with micro silica fume, results in an improved resistance against acid attack [14, 15]. Fly ash produces a densely packed mixture of cement paste and aggregates, while silica fume reacts pozzolanically and transforms the calcium hydroxide into Calcium-Silicate-Hydrate (CSH) gel in accordance with the following equation [31]:



The CSH gel is the source of strength in concrete. On one hand it increases the bond between the cement paste and aggregates and on the other hand, it increases the compressive strength and chemical resistance of the concrete. The additional CSH produced by silica fume is more resistant to attack from aggressive chemicals than the weaker CH. Therefore, the combination of silica fume and fly ash results in a denser concrete having lesser quantity of calcium hydroxide, which considerably increases the acid resistance. Silica fume without fly ash produces micro cracks in concrete, which increase the path of acid attack.

3.2 Air entraining concrete

Air entrainment is the process of incorporating minute air bubbles into concrete. Although, air entrainment is mainly practiced to increase freeze-thaw resistance of the concrete, it can also be used as a means of acid resistance. The air entrainment increases the acid resistance because the air voids block micro capillaries and prevent the acid from invading the concrete through these canals. Air-entraining agents are available as additives as well as admixtures. As additives, the agents are interground with cement in fixed proportions, as in cements Type IA, IIA and IIIA [32]. Requirements and specifications of air-entraining agents to be used in concrete are covered in

ASTM C 260 [17]. As admixtures, Vinol resin and fatty acid salts were used as air-entraining agents, which have now been largely replaced by synthetic admixtures: Alkyl sulphates, olefin sulphonates, Diethanolamines etc. [16].

3.3 Blast Furnace concrete

Blast Furnace Slag is formed when iron pellets, coke and limestone/dolomite flux are melted together in a blast furnace. During this process, the lime chemically combines with the aluminates and silicates of the ore and coke ash to form blast furnace slag [18]. Blast furnace slag significantly increases the durability of the concrete. It has been found to be very effective against chloride and sulphate attack; however it does not provide any considerable improvement in acid resistance [19]. The reason for this is probably that the slag does not change the amount of calcium hydroxide in the concrete. In addition to the use of slag as admixture, it is also used as additive by intergrading with the Portland cement clinker. The combined cement is known as slag cement [32].

3.4 High performance concrete

High performance concrete (HPC) is defined as a concrete having properties much superior than an ordinary concrete [28]. Along with other properties like strength and durability, it is supposed to have higher resistance against chemical attack. High-performance concretes are made with carefully selected high-quality ingredients and optimized mix design. The concrete is batched, mixed, placed, compacted and cured to the highest standards. Typically, such concretes will have a low water-cement ratio of 0.25 to 0.4 [1]. Various admixtures are usually used to make these concretes fluid and workable [29]. Owing to lesser porosity, HPCs also offer significant acid resistance. The low porosity is achieved by cement contents in excess of 500 kg/m³ of concrete, low water to cement ratio, adequate compaction and curing and the incorporation of a super plasticizing admixture [32]. With this combination, the strength as high as 10000 psi or above can be achieved.

4.0 Use of nanotechnology for acid attack prevention

Nanotechnology is a new branch of material sciences that promotes the use of nano particles in different domains. As obvious from its name, nano particles have their sizes in nano meters. A nano particle is defined as the one, which has at least one of its dimensions in nanometers or 10⁻⁹ m [11]. Materials at nano scale display properties somewhat different from those at micro or macro scale. For example, inert titania is used for pigmentary purposes while a nano titania is a photo-catalyst. Similarly, opaque copper becomes transparent when ground to nano size [12]. Knowing that, attempts were made to apply nanotechnology in different fields including construction engineering. Apart from other beneficial effects, nanotechnology has also found its importance in increasing the acid resistance of concrete as given below.

4.1 Significance against acid attack

In construction materials, the materials density and strengths are the most important properties in which the experts are interested. As mentioned under heading 3.4, the High performance concrete is quite effective against acid attack. However, it is a common observation that materials having high strengths are also associated with higher densities and thus the dead weight of the structure considerably increases. On the other hand, nanotechnology offers quite interestingly certain materials with higher strength while possessing low to medium densities. The examples are carbon nanotubes (CNTs) and carbon nanofibers (CNFs) [7]. As an example, it is

believed that the design life of a concrete bridge can be increased from 30 to 45-50 years, using nanotechnology [30].

4.2 Nano cementitious materials

Cementitious materials in civil engineering include concrete, mortar and cement paste. These materials were developed due to strong bonding characteristics and very rapid hardening and setting of cement. Several new cement composites have been developed during the recent years by combining it with nano-Titania (TiO_2), Carbon nanotubes, nano-silica (SiO_2), nano clay and nano-alumina (Al_2O_3), which have significantly improved the performance of these materials [6,13]. Besides nano composite cementitious materials, efforts are also going on to introduce nano-cement at commercial scale. The present commercial cement particle has its size in micrometers [1]. It is a well-established fact that finer particles (nano) having more specific surface area can fill more effectively the pores in cement matrix, densify its structure, and might lead to superior strength due to faster chemical reactions with water (hydration reactions) [33]. Or in other words nano materials might enhance the chemical resistance of concrete against acid attack.

4.3 Nano coating materials

With the help of nanotechnology, coatings with a molecular structure which simply rejects adhesion by foreign bodies have been created. Many nano-coatings are in the market, which effectively provide effective resistance against acid attack. [34]. Appropriate nanotechnology can be used to create eco-friendly sealers and coatings that deliver pure Performance on concrete. These coatings can be applied by spraying, rolling or brushing [4, 5].

4.4 Nano food additives

New concretes with nano food additives are being developed at National Institute of Standards and Technology (NIST) USA [3]. The technique is named as VERDiCT (Viscosity Enhancers Reducing Diffusion in Concrete Technology). With nano additives in concrete pores, the viscosity of the concrete pore solution can be increased, which will slow down the ingress of external species (including acids).

5.0 Conclusions

This review paper has attempted to collect the state of knowledge and information in the field of concrete, confronting an acidic environment. Emphasis was given to understand the problem and to identify a compatible solution. The solutions include the improvement of internal structure of the concrete or the provision of an external acid resistant membrane. Additionally, the paper also describes the novel nanotechnologies that can be used to achieve acid resistance goals for concrete.

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