Influence of Concrete Mixture Composition on Acid Resistance of Concrete: A Review

Chinnu Mariam Ninan[1*], K P Ramaswamy[2], R Sajeeb[3]

[1] Doctoral Scholar, Department of Civil Engineering, TKM College of Engineering, Kollam, Kerala, India
[2] Assistant Professor, Department of Civil Engineering, TKM College of Engineering, Kollam, Kerala, India
[3] Professor, Department of Civil Engineering, TKM College of Engineering, Kollam, Kerala, India

*Corresponding author: chinnuninan@gmail.com

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ABSTRACT

Cementitious materials are highly susceptible to rapid and severe degradation by a wide range of acids that are found immensely in ground water, sewage systems, industrial effluents, acid rain etc. which may cause microstructure deterioration. The factors influencing acid attack is generally categorised as material related factors and test related factors. Material related factors can be either related to acid solution or concrete mixture composition. Composition of concrete mixture greatly impacts the acid resistance of concrete. Factors related to composition of concrete mixture are type of cement, type and proportion of binders, water binder ratio, aggregate binder ratio and mineralogical nature of the aggregates. Even though the type of cement influences acid attack, the magnitude of variation is negligible. Consumption of calcium hydroxide and refinement of pore structure makes the use of supplementary cementitious materials favourable for acid resistance. Decrease in water binder ratio and increase in aggregate binder ratio reduces the porosity of concrete and thereby improves the acid resistance of concrete. Calcareous aggregates are preferred for concretes exposed to acids having less soluble salts and not preferred for acids forming soluble salts. This paper highlights the influence of composition of concrete mixture on acid resistance of concrete. A proper formulation of concrete is expected to enhance its acid resistance.

Keywords: degradation, deterioration, acid attack, leaching, decalcification

1 INTRODUCTION

Acid attack is one of the major causes of deterioration of concrete. Acid attack is the process of dissolution and leaching of acid-susceptible hydrated products in cement matrix of the concrete (Nijland and Larbi, 2010). Concrete is an alkaline material whose pH is above 12.5 and is highly vulnerable to aggressive acidic environment. When the concrete is exposed to an acid, the acid upsets the chemical equilibrium of the cement matrix causing dissolution of the hydrated products, particularly complete disintegration of calcium hydroxide and partial dissociation of calcium silicate hydrate, followed by calcium aluminate and alumino-ferrite hydrates (Ramaswamy and Santhanam, 2018). This results in the decalcification of hydrated products, leading to a loss of mechanical properties and increased concrete porosity (Duchesne and Bertron, 2013). Increased porosity causes increase in permeability which results in microstructural deterioration and affects the strength, durability and structural integrity of concrete.

The major sources of acids that may come in contact with concrete are industries, ground water, sewer systems, acid rain etc. Acids are generally categorised as organic and inorganic acids. Organic acids, which are considered to be weak acids such as citric acid, acetic acid etc. are commonly found in agricultural and agro-food industries. Inorganic acids such as sulphuric acid, hydrochloric acid, nitric acid etc. are strong in nature and mostly found

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in manufacturing industries. But, the damaging effects due to organic acids like acetic acid are higher compared to inorganic acids such as sulphuric or hydrochloric acid because of the acid buffer action and the high solubility of the reaction products (Koenig and Dehn, 2016). The solubility of major calcium salts that may be formed during acid attack and the associated phenomena for the reactions of various acids are provided in Table 1.

Table 1. The solubility of major calcium salts of various acids and the associated phenomena (Bertron et al. 2009; Menendez et al. 2013; Bertron and Duchesne, 2013; Dyer, 2016; Ramaswamy et al. 2017)

Acid	Acid dissociation constant (25^{o}C)	Aggressiveness	Major calcium salts	Solubility of products	Associated phenomena
Sulphuric	-	Very high	Calcium sulphate (Gypsum)	Soluble	Expansion, Ettringite formation
Acetic	4.76	Moderate	Calcium acetate monohydrate	Highly soluble	Leaching
Citric	3.14/4.77/ 6.39	Very high	Calcium citrate tetrahydrate	Slightly soluble	High molar volume, Fragmentation
Succinic	4.16/5.61	High	Calcium succinate trihydrate	Slightly soluble	Transition zone with SO_3
Lactic	3.86	Moderate	Calcium lactate pentahydrate	Soluble	Well defined zones of degradation
Tartaric	3.04/4.37	Moderately low	Calcium tartarate tetrahydrate	Insoluble	2 phase degradation
Oxalic	1.23/4.19	Very Low	Calcium oxalate monohydrate	Insoluble	Low molar volume, Protective coating

Table 1 exhibits the changes in concrete on exposure to various acids and the solubility of reaction products formed. It signifies the importance of understanding the degradation mechanism. It also helps to identify suitable materials that perform well in aggressive acidic environments. In order to recognise the performance of these materials on acid exposure, a precise knowledge on the factors influencing acid attack is essential.

2 FACTORS INFLUENCING ACID RESISTANCE

Factors influencing acid resistance of concrete can be categorised as material related factors and test related factors (Ramaswamy et al. 2017). Material related factors deals with the materials used for the study and test related factors deals with the testing environment and methods adopted for the same. Factors such as replenishment of acid, temperature, effects of abrasion, type and nature of specimen, shape and size of specimen, volume of acid solution to the specimen, interchangeability of acids and acid exposure period are some of the test related factors. Test related factors can be categorised as test condition related factors, specimen related factors and acid related factors.

Material related factors can be either related to acid solution or concrete mixture composition. Acid related factors are associated with the material properties of acid such as aggressiveness of acid, type of acid, its acid dissociation properties, poly-acidity etc. Factors related to concrete mixture composition include both binder related factors and aggregate related factors. This can be illustrated as shown in Figure 1.

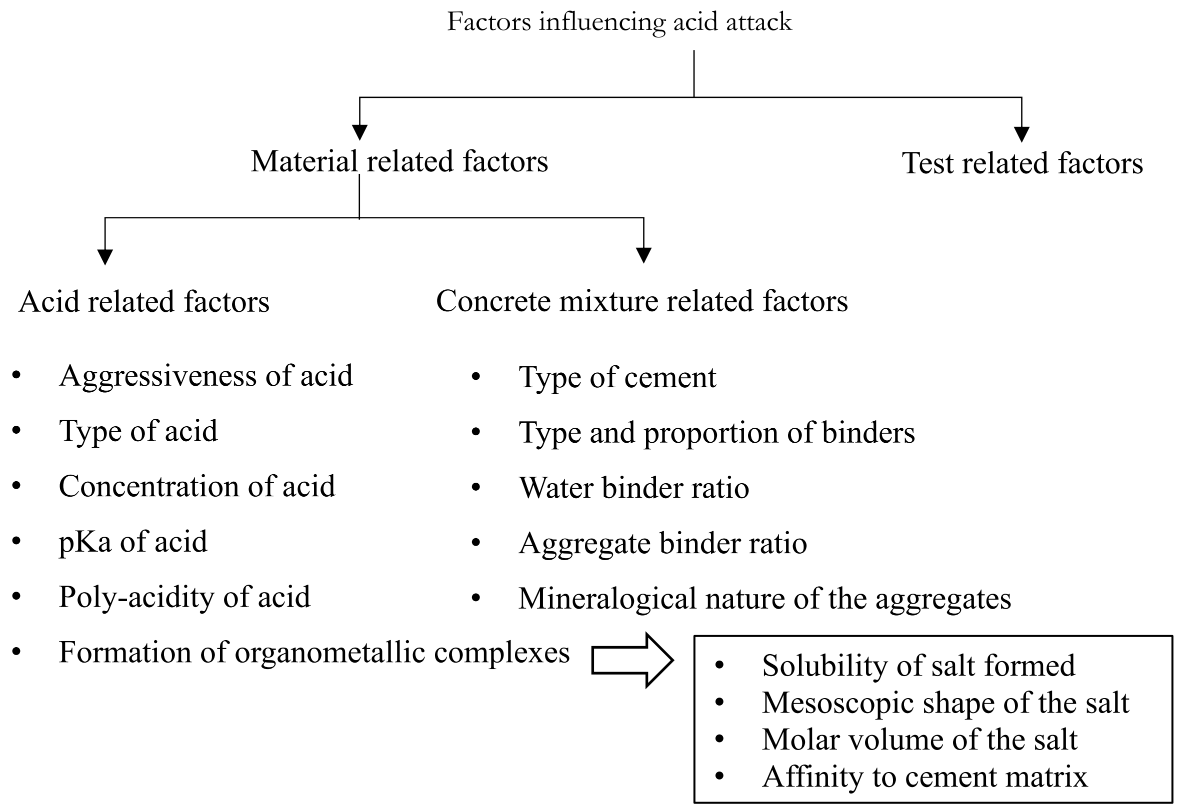

Figure 1. Factors influencing acid attack in concrete (Larreur-Cayol et al. 2011; Bertron and Duchesne 2013; Ramaswamy et al. 2017)

The quality of cement matrix influences acid resistance of concrete to a great extent. Good quality cement paste lowers the fluid (acid) ingress into the concrete, thereby improving the acid resistance of concrete. So, the chemical and mineralogical nature of the cement matrix is the major factor to be considered in respect of materials selected, which depends on the type of cement, type of binders and its proportion (Ramaswamy et al. 2017). Well-cured and compacted concrete with low to moderate water to cement ratio have a good quality cement matrix which is relatively dense with low permeability, thereby limiting the rate of acid penetration and the degree of acid attack on the concrete (Bensted et al. 2007). The effect of specific concrete mixture related factors are discussed below.

2.1 Type of cement

Acid attack can occur in Portland cement concrete mainly because the cement matrix is alkaline in nature and most of the hydrated products are dissolved by acids either partially or completely. The presence of acid, attacks the concrete by reacting with and dissolving the basic constituents like calcium hydroxide, calcium silicate hydrates, calcium aluminate hydrates, monosulfate and ettringite (Bensted et al. 2007). Calcium hydroxide is the most reactive of all products and completely dissociates in acids leading to increased porosity of concrete.

According to cement chemistry, C_3S hydration produces about three times calcium hydroxide than C_2S hydration. Thus, acid attack can be higher in magnitude for concrete prepared with high C_3S cement such as Ordinary Portland cement (OPC). Calcium silicate hydrates (CSH) also undergoes acid attack and decalcification occurs resulting in an amorphous silica gel, causing severe structural damage to concrete (Ravindrarajah, 2012). Special cements like high alumina cement (HAC) and calcium sulphoaluminate cement (CSA) provides better acid resistance when compared to Ordinary Portland cement. This is mainly because of the absence of calcium hydroxide in the hydration products (Mehta and Monteiro, 2006). Also the presence of high Al content in these special cements improves acid resistance. The acid resistance of HAC is also associated with the intrinsic physicochemical properties like reactivity, porosity etc. of the phases initially present or precipitated during the deterioration process (Buvignier, 2019). Dyer (2017) studied the acid resistance of three cement pastes namely, OPC paste, OPC blended with fly ash paste and CSA paste on exposure to acetic and butyric acids. The results of the study indicate that CSA cement shows superior performance to acid resistance as it has greater cross sectional area of the inner core. CSA cement showed better performance on exposure to different concentrations of both acids (Dyer, 2017). A micro-computed tomography (CT) slice image of the cement pastes exposed to butyric acid is shown in Figure 2.

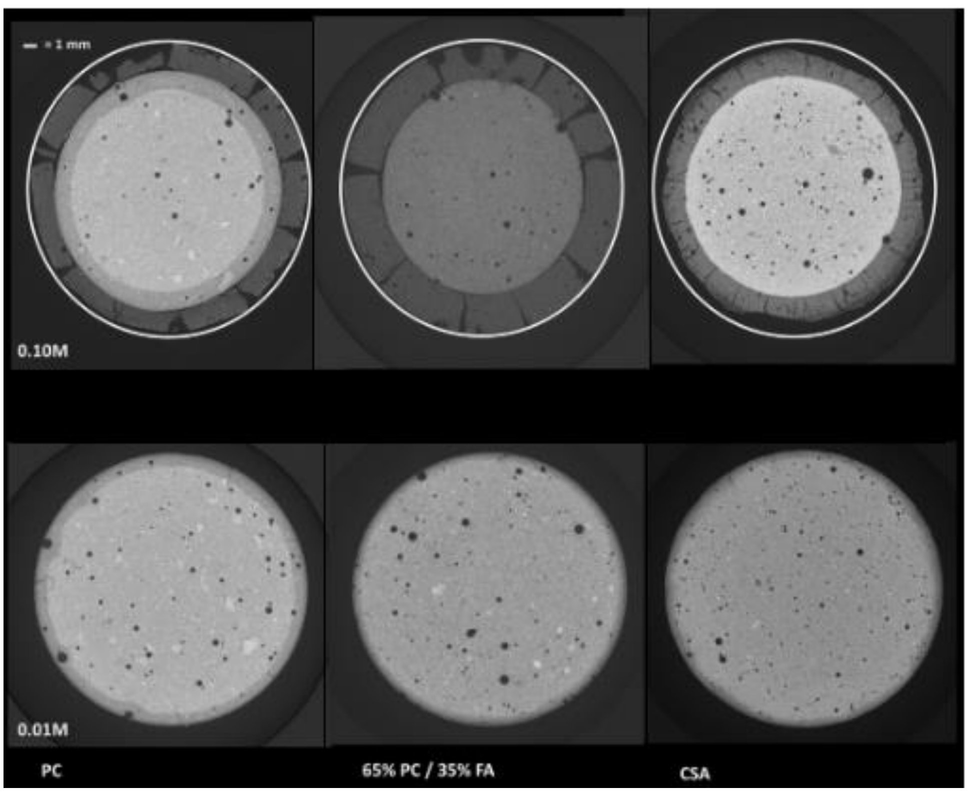

Figure 2. Micro-CT scan showing superior performance of CSA cement (Dyer, 2017)

According to Dyer (2016), different cements have different levels of acid resistance and, in most cases, the extent of this variation is negligible. Therefore, the design of concrete mixes to withstand acid attack requires approaches that extend beyond cement type selection, the most evident being the selection of the water/cement ratio.

2.2 Water to binder ratio

Concrete permeability is the most important aspect to be considered to achieve better acid resistance. Permeability of concrete depends on its water to binder ratio. Lower the ratio, lower is the interconnected porosity and thereby lesser will be the permeability. A reduction in permeability results in a decrease in the penetration of acid into the concrete, thus reducing the extent of damage of acid attack in concrete. So, for improving acid resistance, water to binder ratio should be lowered.

But there should be enough water to ensure proper hydration of concrete. Slightly high amount of water causes bleeding in concrete resulting in microscopic pores and shrinkage cracks, which affects the material properties of concrete whereas lower water content restricts the process of hydration. So the water to binder ratio needs to be suitably designed to achieve the target strength and the desired material properties (Sahoo, 2020). Study conducted by Sahoo (2020) presented the optimized w/b ratio was found as 0.36 for minimum percentage strength loss in acidic environment.

2.3 Type and proportion of binders

Supplementary cementitious materials (SCM) like slag, fly ash, silica fume etc. are used to reduce cement content in concrete and also to refine the pore structure of concrete thereby improving the resistance to penetration and hence acid resistance of concrete. Also, these pozzolanic materials consume calcium hydroxide in presence of moisture resulting in an increase in strength and durability aspects of concrete. In order to improve acid resistance, SCM with the proper fineness and prolonged curing can be used (Ramaswamy et al. 2017).

Inclusion of ground granulated blast furnace slag (GGBFS) and metakaolin enhance the resistance to acid attack (Oueslati, 2012). Oueslati (2012) found that slag presents the lowest mass loss and altered depth on acid exposure while MK has the highest compressive strength after acid immersion. Also, enhanced resistance to acids (lactic and acetic) in silage effluent has also been reported for the addition of metakaolin to Portland cement concrete (De Belie et al. 2000).The increased stability of MK and GGBFS samples against acidic media appears to be due to their silicon, aluminium and iron rich chemical composition and limited calcium content which is the most vulnerable component of concrete.

Ravindrarajah (2012) studied the acid attack in silica fume admixed concrete and found that silica fume do not improve the behaviour of cement paste to acid attack particularly in case of lactic acid attack and only negligible improvement is observed in case of hydrochloric acid attack. Figure 3 illustrates the variation of silica fume concrete exposed to lactic and hydrochloric acids.

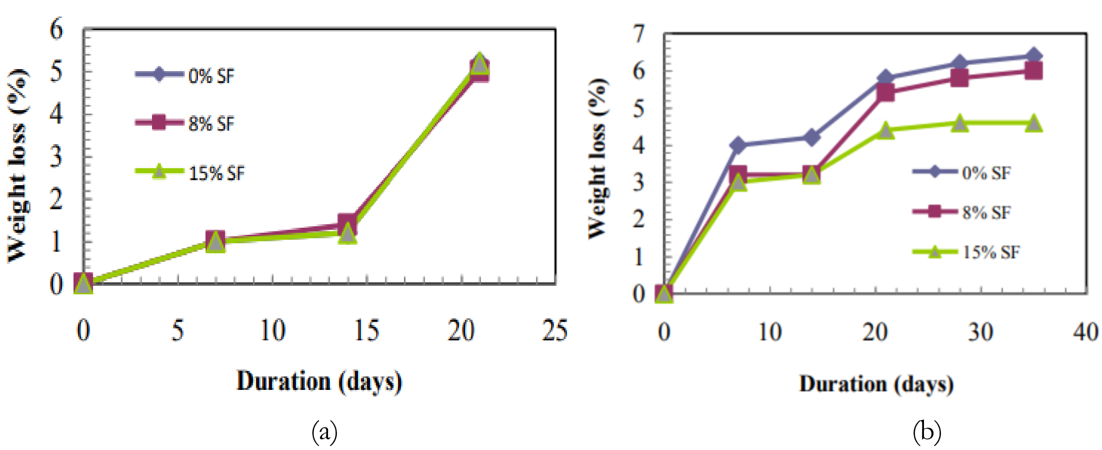

Figure 3. Silica fume concrete exposed to (a) lactic acid and (b) hydrochloric acid (Ravindrarajah, 2012)

Use of fly ash in concrete improves the sulphuric acid resistance of concrete (Murthy, 2007). Sahoo also studied acid resistance for fly ash replaced concrete and obtained the optimum combination of concrete as 40% fly ash replacement for a water to binder ratio of 0.35 (Sahoo, 2020). The results relating to the efficacy of SCMs are not yet fully convincing and further study needs to be carried out (Ramaswamy et al. 2017).

2.4 Properties of aggregates

Aggregates used for the concrete can influence the acid resistance of concrete. For example, limestone aggregates are easily attacked by aggressive acids than siliceous aggregates. In certain cases, aggregates being attacked by acids are advantageous mainly because the carbonates present in aggregates prolong and enhance the acid neutralisation capacity of concrete (Bensted et al. 2007). This helps to extend the service-life of concrete. Also, in conditions like pipelines subjected to acid attack, if both cement and aggregates degrade evenly, a smooth and hydraulically efficient surface can be maintained (Bensted et al. 2007). Uniform rates of dissolution of both binder and aggregates are preferred to eliminate aggregate bulging out of concrete (Alexander and Fourie, 2011). The main factors related to aggregates that influence the acid resistance of concrete are mineralogical nature of the aggregates and aggregate binder ratio (Ramaswamy et al. 2017), and these are discussed below.

2.4.1 Mineralogical nature of aggregates

Aggregates normally used for concreting are either calcareous (limestone) or siliceous in nature and they behave differently when exposed to aggressive acidic environments. The use of calcareous aggregates such as limestone exhibits sacrificial protection as the attack on cement hydrates are shared by the calcium bearing aggregates also (Ramaswamy and Santhanam, 2018). Siliceous aggregates are considered to be inert to acidic environments, mainly because of the very low amount of calcium in siliceous aggregates. During acid attack, the paste will dissociate leaving behind the siliceous aggregates which protrude out of the surface of concrete. Study by Ramaswamy and Santhanam (2018) shows that on exposure to sulphuric acid, mortar with limestone displays a lower depth of degradation than the mortar with siliceous river sand. Also, mortar with limestone exhibits higher mass loss than that with siliceous aggregates when exposed to acetic acid. During acetic acid attack, limestone aggregates creates a buffering environment thus making a sacrificial protective effect and limits the acid dissociation in the cement paste (Ramaswamy and Santhanam, 2018). Hence limestone aggregates are preferred for concretes exposed to acids having less soluble salts and not preferred for acids forming soluble salts.

2.4.2 Aggregate binder ratio

Quality of surface concrete has a great role in resisting penetration of aggressive acids into the concrete. Study conducted by Kreijger (1984) on surface properties shows that as the depth of concrete from surface increases, aggregate to cement ratio also increases. This contributes to the surface aggregate binder ratio being significantly lower than interior and a large volume of paste at the surface. Since, the cement paste is typically more porous than the aggregate, higher surface porosity is observed (Dyer, 2014). Increased porosity of the skin of concrete (surface) provides greater erosion and wear while aggressive solutions can penetrate faster into the concrete and increase chemical reactions in the skin (Kreijger, 1984). The variation of porosity and aggregate/cement ratio with depth is shown in Figure 4.

As the aggregate binder ratio increases, a limited reduction in porosity is observed. Hence, the acid resistance of concrete can be improved by reducing the surface porosity, which can be achieved by increasing the volume of aggregates at surface, or by providing surface pore filling or protective coatings at the surface of concrete.

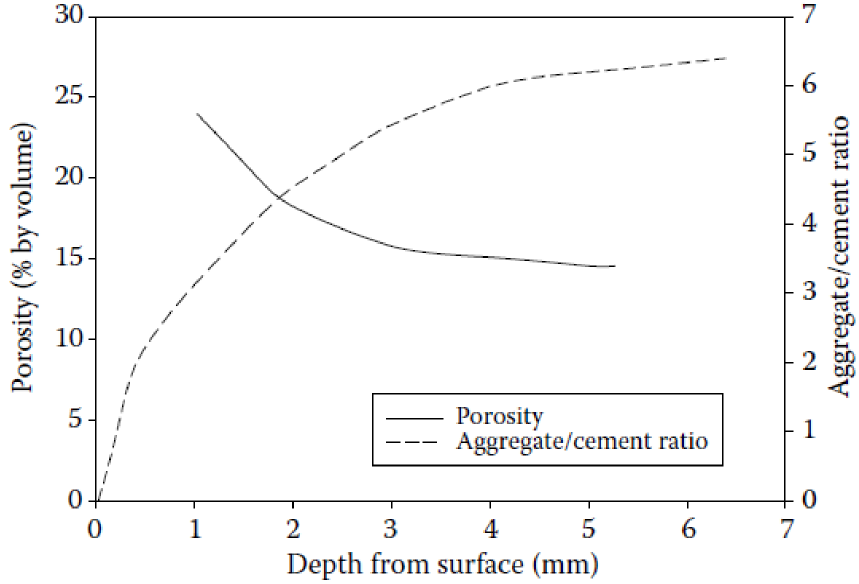

Figure 4. Changes in the porosity and aggregate/cement ratio with the depth (Dyer, 2014)

3 CONCLUSIONS

Acid attack is a severe cause of deterioration of concrete. This causes dissolution and decalcification of hydrated products resulting in loss of mechanical properties, durability and structural integrity of concrete. This eventually results in destruction of the concrete structures. This exhibits the need to study degradation kinetics and mechanism of acid attack and to develop suitable materials that are resistant to aggressive acidic exposure conditions. The factors influencing acid attack are to be identified at first. Factors influencing acid attack can be categorised as material related factors and test related factors. Material related factors deals with the materials used for the study and test related factors deals with the testing environment adopted for the same. Material related factors can be either related to acid solution or concrete mixture composition.

Use of supplementary cementitious materials is preferred to improve acid resistance mainly due to the consumption of calcium hydroxide and refinement of pore structure of concrete. A reduction in water binder ratio decreases the porosity of concrete which improves the permeability and hence improves the acid resistance of concrete. An increase in aggregate binder ratio reduces the porosity of concrete and thereby improves the acid resistance of concrete. Calcareous aggregates are preferred for concretes exposed to acids having less soluble salts and not preferred for acids forming soluble salts. The significance of each factor with respect to acid resistance will vary. Therefore, further research is required to establish a link between these variables in the study of the characteristics of concrete degradation. Understanding the effect of each factor on concrete degradation and identifying methods to solve the detrimental effects will impact tremendously on acid resistance of concrete.

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