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A critical review on the effect of organic acids on cement-based materials

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Abstract. Ingression of acids into concrete structure arrests its long-term durability by the progressive degradation of the highly alkaline cementitious materials. Acid attack results in the decalcification of hydration products leading to higher inherent porosity and both micro-macro cracks, providing a path for the passage of aggressive ions into the interior of concrete. Amplification of agriculture and food industries such as the breeding, dairy or sugar industries produce large quantities of effluents that are the major sources of organic acids. These effluents have complex acidic compositions leading to serious degradation of structures made for their production, collection, storage and treatment. New binder systems that are capable of proposing extensive long term durability in aggressive acidic environment and also being a sustainable option need to be evolved. From earlier studies, application of various binder systems containing materials such as fly ash, ground granulated blast furnace slag, silica fume, bagasse ash etc. has an influence on the hydration products, micro-structural and macro-structural changes in cement-based materials when subjected to aggressive acidic media, thus enhancing the performance and durability of concrete structures. This paper outlines the basic mechanism of organic acid attack and highlights the influence of various binder systems on the alteration of degradation kinetics when exposed to various organic acids.

1. Introduction

Acid attack on concrete structures is a global concerned research area due to the prominent degradation of concrete structures caused by the aggressive species over time. The growth of enormous industries has led to higher production of effluents and when untreated becomes the major sources of pollution as well as primary cause of deterioration of concrete. Concrete is found to be in disequilibrium with its environment due to its alkaline nature. For the hydrated compounds to be stable, there should be proper defined ranges of concentration for Ca^{2+} and OH^- ions. As the pH of the solution decreases, the hydrated compounds undergo hydrolytic decomposition causing distortion of the cement matrix equilibrium and thus leading to degradation of concrete. The aggressiveness of the



acids in the cementitious matrix depends on their solubility in water, their acid dissociation constant, mono/poly acidity of acids and the physical properties of salts they form. Formation of salts will have an influence on alteration kinetics and these salts may either precipitate or leach out depending on its solubility in the acid solution. Weak acids such as organic acids dissociate only partially as compared to strong acids. Even though organic acids are destructively inferior to inorganic acids, they promote corrosion of the embedded reinforcements and disrupt production facilities. The effluents from agricultural and agro food industries are the usual source of organic acids. India has about 620 sugar mills and about 400 molasses based distilleries with an installed capacity of 400 billion litres of alcohol and a potential to generate, on an average, 40 billion litres of spent wash annually [1]. Generally spent wash is disposed untreated on land and is exposed as a toxic effluent that is hazardous to vegetation and ground water quality due to dissolved leachates and colour. Waste waters such as whey and white and green waters generated by the dairy industries, or molasses and vinasses from distilleries and the sugar industry, liquid manure and silage juice produced by stock-rearing activities, contain a broad range of organic acids, that are responsible for acid attacks on concrete. Table 1 gives the list of various sources of organic acids that can attack the concrete.

Table 1. Predominant acids in agro-food industries. [2]

Industry	Waste waters	Acids	Concentration (mmol/L)	pH	
Wine industry	Vinasses	Tartaric	3.2–8.73	4-6	
		Acetic	3.1–5.0		
		Lactic	2.2–5.6		
		Succinic	0.3–6.8		
		Malic	0.5–0.8		
		Total (max.)	26.9		
Sugar industries	Sugar cane vinasses	Lactic	18–80.4	4-7	
		Glycolic	12–25		
		Citric	1.7–10.4		
		Trans-Aconitic	0.2–4.8		
		Cis-Aconitic	0.1–2.8		
		Oxalic	0.08–0.8		
		Fumaric	0.1–0.4		
Total (max.)	124.2				
Dairy industries	Whey	Acetic	14.0	4–6	
		Citric	9.2–9.6		
		Lactic	3.4–5.7		
		Propionic	1.0		
		Butyric	0.6		
		Total (max.)	30.9		
Animal rearing	Silage juice	Lactic	55.3–63.7	4–5	
		Acetic	25.3–28.3		
		Butyric	43.4		
		Propionic	3.1		
	Total (max.)	99.1			
	Liquid manure	Liquid manure	Acetic,	31.7–213	5-8
			Butyric	1.1–28.8	
Propionic			5.4–37.8		
Total (max.)	279.6				

Liquid manure and silage effluents contain acetic acid, lactic acid and butyric acid. The distillery and fermentation industry produces winery wastewaters whose pH is around 4.5 and contains acetic, lactic, citric and tartaric acids [3]. Silage acids cause most of the deterioration problems in conventional cast-in-place and precast concrete silos. Larger silos are more prone to acid deterioration

than smaller silos due to the increased horizontal pressure [4]. When moist plant material is placed in a silo, it goes through the ensiling process which produces silage acids, namely lactic and acetic acids. Conditions such as temperature, aeration and time of storage in the silo influences the pH of the silage acids released. These acids, on contact with concrete silo walls, react with the cement matrix, causing a decrease in strength with increase in time. Liquid manure is also a predominant source of organic acids, mainly acetic acid. These waste waters include mixture of acids and the resulting attack need not be defined as the summation of alteration caused by each acids individually. To adequately ascertain the complex mechanisms involved, each acid needs to be examined discretely before exploring acid mixtures.

Although organic acids are considered to be weak acids, they are often detrimental to the cement matrix. The attack by weak organic acids such as acetic acid is comparable to that of strong acids such as hydrochloric and nitric acids [1]. So accordingly the degradation kinetics should be explored to ascertain the degradation mechanisms for developing new materials to resist organic acid attack. Mass loss and altered depths are considered to be the main parameters to study the degradation kinetics. Koenig et al. defines depth of degradation (DD) as the summation of the depth of erosion (DE) and depth of reaction (DR) and arises with increase in exposure time [5]. From the literature review, it is observed that very less number of studies is done to investigate the effect of organic acids on cement-based materials.

2. Mechanism of organic acid attack

Concrete, particularly the cement matrix is highly vulnerable under acid attack. The basic mechanism of deterioration due to acid attack is acidolysis, where the hydration products in the matrix reacts with the incoming organic acid resulting in the release of ions onto the solution, thereby losing the solid mass of the matrix. Two other mechanisms are also found to be effective in organic acid attack. First of which is complexolysis, where the acid ions forms complexes with the metal ions which are extracted during the acidolysis phase, allowing more of the solid phase to dissolve in the solution.

The second mechanism is the precipitation of expansive reaction products, which is specifically significant when the salt formed has a higher molar volume than the hydration products it replaces, leading to expansion and cracking [6]. Organic acids have the potential to include all these mechanisms simultaneously, which enhances the curiosity towards its study. Table 2 gives the solubility data of salts that may be formed as a result of the reaction of hardened cement paste with an organic acid. The attack by each acid is specific and their mechanisms are briefed below.

Table 2. Solubility of calcium and aluminium salts of various organic acids.[1], [6], [7]

Acid	Acid dissociation constant (25°C)	Aggressiveness	Major calcium salts	Solubility (g/L)
Acetic	4.76	Moderate	Calcium acetate monohydrate {Ca(CH ₃ COO) ₂ ·H ₂ O}	436 (0°C)/ Highly soluble
Citric	3.14/4.77/6.39	Very high	Calcium citrate tetrahydrate {Ca ₃ (C ₆ H ₅ O ₇) ₂ ·4H ₂ O}	0.095 (25°C) / Slightly soluble
Lactic	3.86	Moderate	Calcium lactate pentahydrate	0.97 (25°C) / Soluble
Tartaric	3.04/4.37	Moderately low	Calcium tartarate tetrahydrate {CaC ₄ H ₄ O ₆ ·4H ₂ O}	Insoluble
Succinic	4.16/5.61	High	Calcium succinate trihydrate	0.193 (0°C) / Slightly soluble
Oxalic	1.23/4.19	Very Low	Calcium oxalate monohydrate {CaC ₂ O ₄ /CaC ₂ O·H ₂ O}	Insoluble
Butyric	4.82	Moderate	Calcium butyrate monohydrate {Ca(CH ₃ CH ₂ CH ₂ CO ₂) ₂ ·H ₂ O}	0.04 (25°C) / Slightly soluble

2.1 Acetic acid

Acetic acid, which is a monocarboxylic acid, cause dissolution of the calcium hydroxide present in concrete that are leached away exposing fresh concrete surface to acid attack [7]. Acetic acid also reacts with the other hydrates present in the cement paste such as C-S-H gel and hydrated aluminates to form water soluble calcium and aluminium salts, leading to increase in porosity and reduction in mechanical strength. This is a quick degradation process and no protective layer is formed on the external surface of specimens in this process.

2.2 Citric acid

It exhibits high degradation kinetics and causes very severe alteration of the cementitious paste leading to rapid deterioration. Citric acid forms strong complexes with calcium (Ca), aluminium (Al) and iron (Fe) ions. A large amount of salt precipitation occurs at the surface, which gets detached from the specimen in substantial quantities without any trace of salt inside or at the surface of the altered specimen. Hence, it does not seem to have any protective effect on the matrix [2]. The high molar volume of the salt formed, leads to the breaking of outer parts of the matrix, leading to fragmentation. As a result, the deterioration of cement exposed to citric acid is mainly because of fragmentation due to precipitation of this salt [6].

2.3 Tartaric acid

Tartaric acid is a chiral compound having dextro- (D-), levo- (L-) and meso- forms. The levo-tartaric acid is naturally occurring whereas the dextro-tartaric acid and meso-tartaric acid forms are artificially synthesized. Two phase deterioration is observed in case of tartaric acid. The first phase exhibits no signs of visible deterioration whereas the second phase actively participates in deterioration process. Of the salts formed, calcium tartarate tetrahydrate is more significant, since it yields a protective layer at the surface of the concrete. But it is found to be less protective to the matrix than the layer formed by calcium oxalate [6].

2.4 Succinic acid

While discussing the degradation characteristics of succinic acid, the area between the inner core and the degraded zone, represented as the transition zone, shows slight enrichment in SO_3 , leading to ettringite formation and elimination of calcium hydroxide from that zone. Further, the degraded zone is divided into an inner and outer degraded zone. The inner degraded zone precipitates the salt and the outer degraded zone is found to be amorphous and made of an aluminium and iron bearing silica gel skeleton with an orange colour, without any traces of calcium compounds [7]. Moreover, this acid is less investigated by the researchers.

2.5 Oxalic acid

The calcium oxalate monohydrate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), which is formed during the degradation process, forms a protective coating around the concrete. The calcium oxalate is formed by the reaction between calcium hydroxide or CSH gel and oxalic acid, but it does not leach out of concrete, instead acts as the protective layer. This leads to the elimination of calcium hydroxide and/or decalcification of CSH gel in the degraded zone [7]. Also, the calcium oxalate salts formed have very low molar volume exerting only less pressure on to the matrix. Hence, the total deterioration occurring in concrete is the least when it is exposed to oxalic acid [2].

3. Effects on various binders

The resistance of concrete to an organic acid also depends on the binder composition. In order to explore the resistance of various binder systems, they are categorized into four, namely, Ordinary Portland Cement (OPC) system, blended cement systems, special cement systems and alkali activated systems. The responses of these binders on exposure to various organic acids are explained in the sub sections.

3.1 Ordinary Portland cement system

Dyer conducted a study comparing the degradation kinetics and mechanism of various binder systems on exposure to acetic and butyric acid [8]. The results of the study projects that, Ordinary Portland cement (OPC) shows large amount of mass loss for organic acids, even at low and high acid concentrations when compared to other binding systems. Larreur-Cayol et al. analyzed the degradation mechanism of cementitious materials exposed to four organic acids: citric, acetic, oxalic and tartaric acids [2]. Figure 1 depicts the visual aspects of the OPC samples in various solutions (0.28 M) after one month of immersion.

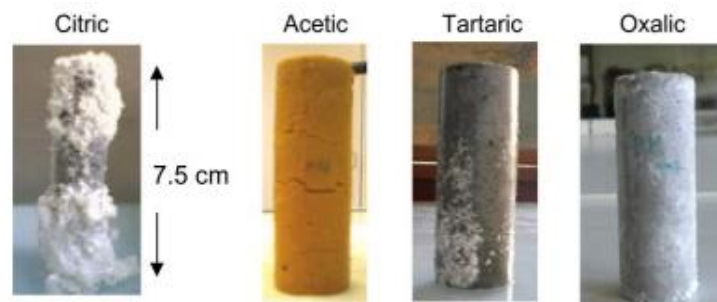


Figure 1. Aspects of the specimens immersed for 1 month in various acids.[2]

From the visual observations, oxalic acid was found to be least aggressive to the matrix due to the formation of thin layer of calcium oxalate salt that act as a cover, sealing the capillary porosity. Larreur-Cayol et al. and Bertron et al. performed immersion tests on cement paste specimens in six different organic acids: citric acid, malic acid, acetic acid, oxalic acid, tartaric acid, succinic acid, to identify the relative aggressiveness of the acids, degradation depths and mass losses of the specimens were monitored over time (Figure 2) [2], [9].

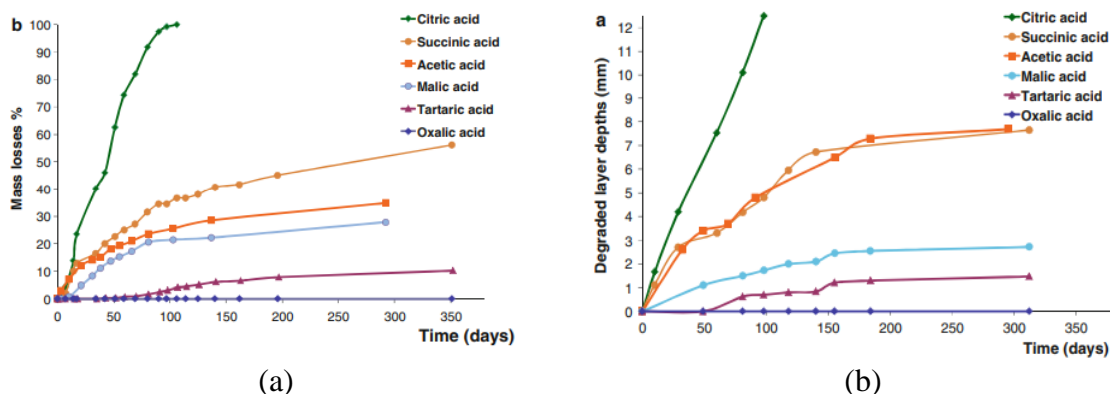


Figure 2. Alteration kinetics of OPC paste specimens immersed in organic acids – (a) relative mass losses and (b) degraded layer depths.[9]

The increasing order of aggressiveness of the six acids on the cement matrix was as follows: oxalic acid < tartaric acid < malic acid < acetic acid < succinic acid < citric acid. However, from Figure 2, it can be noted that the degraded depth for acetic is higher than that of succinic but the mass loss of OPC on exposure to acetic is found to be lower than succinic acid. Therefore, the relevance of parameters i.e. mass loss and altered depth in investigating the degradation kinetics need to be further ascertained in the future researches.

While reviewing the degradation mechanism of OPC system exposed to various acids, a clear distinction is observed between the inner core zone and outer degraded zone. The inner core zone has

least cross sectional area for OPC systems which shows its inferior performance comparing to other systems. A progressive reduction in calcium content from the inner core till the outer surface is observed in the case of OPC system. The outer surface is a wholly decalcified silica gel layer. The whole degraded zone is mainly amorphous in nature, which retains a higher amount of iron and aluminium [8].

3.2 Blended cement system

According to Dyer, a binary system containing OPC and fly ash (FA) showed better performance than the OPC system on exposure to acetic and butyric acid [8]. Even though it showed considerable mass loss at low concentration, it exhibits superior performance at high concentrations comparing all other systems. Ramaswamy and Santhanam examined the influence of role of binders on alteration kinetics on exposure to citric acid. Binders such as Class F fly ash (30% replacement, FA30), densified silica fume (10% replacement, SF10), ground granulated blast furnace slag (50% replacement, BFS50) were considered as mass replacements to cement in addition to the control mix containing OPC [10]. Cement paste specimens containing 10% silica fume on exposure to citric acid showed enhanced resistance as compared to cement paste specimens containing other binders. This may be due to high concentration/low pH of the acid solution and the absence of interfacial transition zone (ITZ) in the paste of other binders. For the tests with and without brushing, the thickness loss was found to be lesser in case of the SF10 mix.

Bertron et al. evaluated the alteration mechanisms of ordinary cement (CEM I), blended cement paste specimens containing 68% slag (CEM III/B) and 10% silica fume (CEM I + 10 % SF), for 18 weeks in an aggressive solution of Synthetic Liquid Manure (SLM-pH 4) composed of acetic, butyric, propionic, isobutyric and valeric acids [11]. Figure 3 represents the variation in mass loss and altered depth of different systems exposed to SLM.

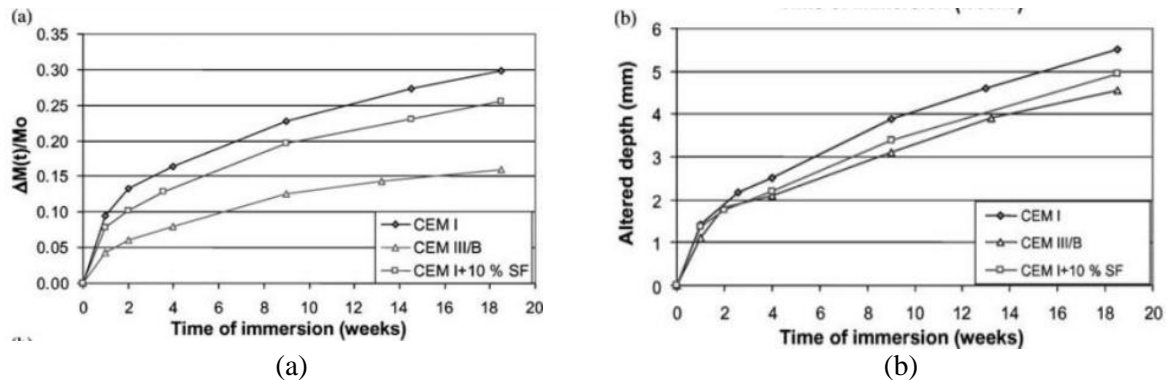


Figure 3. Evolution of durability criteria: a) mass losses and b) altered depth, according to the immersion time.[11]

Results show that, the mass losses of CEM I specimens were twice higher than CEM III/B and 1.15 times higher than CEM I + 10 % SF. On the other hand, altered depths of CEM I pastes were 1.14 and 1.26 times higher than CEM I + 10 % SF and CEM III/B respectively. Although the mass loss variation for CEM I seemed higher than other systems, altered depth variation was found to have lesser variations. Therefore, the acceptance of mass loss and altered depth parameters for measuring kinetic degradation of various systems on exposure to acids needs to be ascertained.

3.3 Special cement system

High alumina cements (HACs) such as calcium aluminate cements (CACs)/ calcium sulphoaluminate cement (CSA) are called the refractory cements that are most suitable for high temperature applications. In these systems, various crystalline and amorphous hydrates are formed in the process of hydration, which depends on the water to cement ratio, curing time and temperature [12].

Dyer examined the performance of three types of cement paste namely, Ordinary Portland Cement, combination of Portland cement with fly ash and Calcium sulphoaluminate cement (PC, PC/FA and CSA) using laboratory experiments when exposed to acetic and butyric acids [8]. CSA cement exhibited least mass loss at lower acid concentrations and high mass loss at higher concentrations as depicted in figure 4.

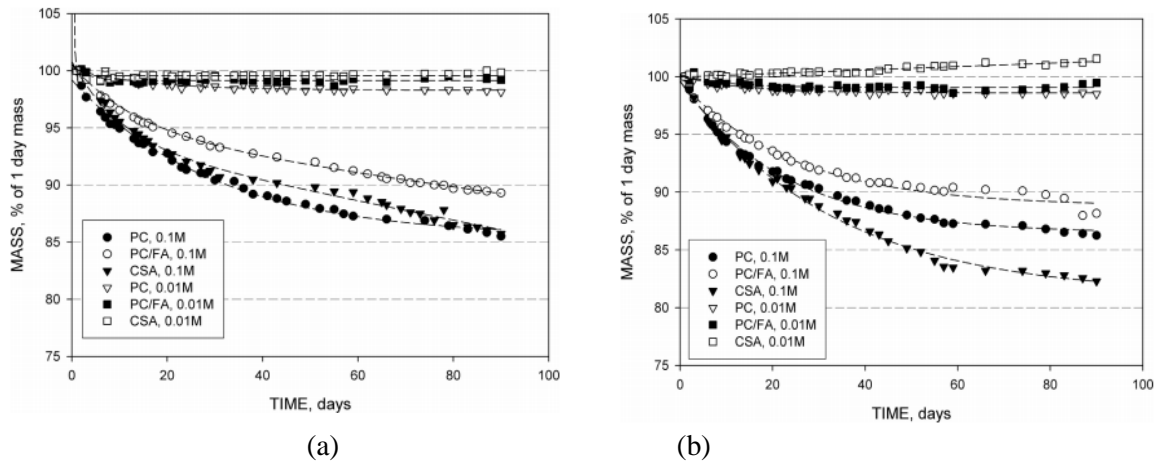


Figure 4. Mass loss from paste specimens exposed to (a) butyric acid (b) acetic acid.[8]

The high mass loss is not due to increased rate of degradation, but due to complete dissolution of silica gel from the degraded surface to a certain depth into the specimen. Abrupt erosion of degraded layers and significant cracking due to drying shrinkage has been observed. So, the depth of the degraded layer attached to the specimen will be comparatively lower. Hence, not only calcium compounds, but silica and other materials also leach out of the system, leading to a heavy mass loss. Also, CSA exhibits larger cross sectional area of inner core indicating superior performance of special cement systems at lower concentrations of acids [8].

3.4 Alkali activated system

Recently, alkali-activated binders became a promising alternative for highly durable concretes due to their high resistance within aggressive environments. Alkali activation is the generic term which is applied to the reaction of a solid aluminosilicate (termed the ‘precursor’) under alkaline conditions (induced by the ‘alkali activator’), to produce a hardened binder [13]. Geopolymers are considered to be a subset of alkali activated binder system. Sodium aluminosilicate hydrate (N-A-S-H) gel is the main reaction product of the alkali-activated aluminosilicates.

Koenig et al. examined the resistance of alkali-activated binders under organic acid attack (acetic, propionic, lactic acid with pH 3) [5]. Despite having the lowest strength class and highest porosity, Alkali activated fly ash (AAFA) exhibited lowest mass loss and degradation depth. They also displayed a steady increase in strength over time. The results ascertain that the acid resistance increases with decrease in CaO content i.e., calcium silicate hydrate (C-S-H) < calcium aluminosilicate hydrate (C-A-S-H) < sodium alumina silicate hydrate (N-A-S-H) and there is a continuous decrease in strength over time for all specimens immersed in acid solution, except for AAFA.

According to Reju, fly ash based geopolymer (FGP) specimens exhibited superior performance in acid resistance with respect to mass loss in mortar specimens (only 0.8%) exposed to 0.5 M acetic acid [14]. Mass loss for slag based geopolymer (SGP) specimen was found to be higher when immersed in acetic acid solution. These findings are in alignment with the findings depicted in Koenig et al. [5]. The durability performance of FGP specimens was found to be better against acetic acid attack. The altered depth variation in the specimens was experimented by spraying phenolphthalein to the freshly fractured surfaces. Figure 5 depicts the altered depth variation of mortar specimens before and after acid attack exposed to acetic and citric acids.

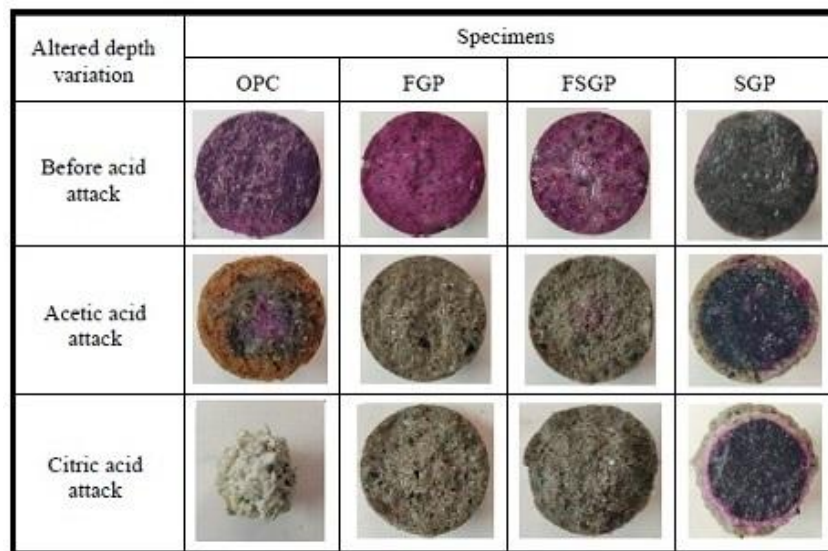


Figure 5. Altered depth variation of mortar specimens before and after acid attack.[14]

Based on altered depth, as a pink colour is found towards the core (pink colour indicates that the core is not attacked) it is inferred that SGP specimens have lower rate of degradation on exposure to both acetic and citric acid. However, results from the microstructural analysis showed that, FGP specimens has a better performance in resisting citric acid as no expansive products were formed unlike OPC and SGP.

4. Conclusion

Acid attack results in rapid deterioration of concrete structures. OPC is hardly resistant to acids and hence, more studies are to be conducted on the effect of other binder systems on exposure to various organic acids. Also, the parameters to express the degradation kinetics are to be explored further. The rate of degradation is dependent on the type of acid, concentration, chemical composition of binders and solubility of the salts formed. Also the degradation kinetics caused by acids depends on the type of binders used and their properties. Based on the aggressiveness of acids, citric acid is found to be the extremely aggressive from most studies due to the high molar volume of expansive calcium citrate tetrahydrate salts. Acetic acid was also found to be aggressive as the attack leads to considerable mass loss and increase in porosity.

In general, blended cementitious systems with OPC partially replaced with supplementary cementing materials (SCM) perform better on exposure to lower concentrations of organic acids. The performance of SF (10%) was superior than other binders on exposure to 0.5M citric acid. Fly ash based alkali activated system showed highly improved performance against acetic and citric acid attack. The acid resistance of the strength-forming phases was linked to the binder composition. Thus, acid resistance increased with decrease in CaO content i.e. C-S-H < C-A-S-H < N-A-S-H. Alkali activated systems and CSA are found to be more durable in contrast with OPC and blended systems.

However, there is no actual comparison between the performance of alkali activated systems and CAC or CSA. The ranking of acid resistance could vary based on the parameters chosen. Therefore, further researches are required to ascertain the correlation between mass loss and altered depth parameters in studying the kinetics of degradation.

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