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A review of the impact of carbonation, chlorine, and sulfur attacks on reinforced concrete

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ABSTRACT

Concrete is the material that has the greatest versatility and widespread use in construction worldwide. The durability of concrete structures has become a major concern in recent years . Particularly in environments with high levels of aggression. Traditionally, a large number of natural and Chemical admixtures are used to enhance concrete's properties.

In the majority of concrete failures are caused by mistakes in material design and installation . workmanship, environmental impact, usage, and poor maintenance strategy are all factors to consider. The durability of concrete can be influenced by a range of physical and chemical factors. Relevant choice of Concrete's strength and durability can be improved by adding admixture .

The purpose of this paper is to review the literature of several published studies on the impact of chemicals aggression to reinforced concrete structures.

1. Introduction

Reinforced concrete structures are typically designed with a specific expected lifespan when operating under normal conditions. However, exposure to harsh environments can unexpectedly shorten this lifespan due to durability issues, with the most prominent being the corrosion of steel reinforcement. Corrosion of steel reinforcing bars leads to concrete cracking and spalling, resulting in significant performance degradation and a substantial increase in rehabilitation costs.

Traditionally, steel within reinforced concrete (RC) has been assumed to remain passive and protected from corrosion. This is attributed to the formation of an extremely thin (approximately 10 nm) self-renewable film at the interface between the steel and concrete, which has a protective electrochemical nature. The alkalinity of concrete (pH 13-14) and the appropriate electrochemical potential further guarantee the effectiveness of this passivating layer.

The durability of concrete structures can be compromised by chlorides, which initiate corrosion of the steel reinforcement, and sulfates, which deteriorate the concrete itself. Sulfate attack occurs as a result of the interaction between sulfate ions and the hydrated cement components. The extent and manifestation of sulfate attack in concrete can vary, depending on the chemical composition of the sulfate and the atmospheric conditions to which the concrete is exposed.

Carbonation occurs when carbon dioxide from the environment infiltrates the concrete and reacts with calcium hydroxide to form calcium carbonate. The infiltration of chloride ions poses a significant risk to reinforced concrete, particularly in structures located in marine environments or those prone to elevated salt concentrations. Carbonation and chloride exposure are the primary factors that initiate the corrosion of steel reinforcement.

2. Review previous studies

2.1 Carbonation

Carbonation is the result of the interaction of carbon dioxide gas in the atmosphere with the alkaline hydroxides in the concrete. Like many other gases carbon dioxide dissolves in water to form an acid. Unlike most other acids the carbonic acid does not attack the cement paste, but just neutralizes the alkalies in the pore water, mainly forming calcium carbonate that lines the pores:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$$

2.2 Chloride ion

Chloride ion (Cl^-) is formed when the element chlorine gains an electron or when a compound such as hydrogen chloride is dissolved in water. Concrete with high concentrations of chloride ions can be very problematic. The passive layer of reinforcing steel is broken down by chloride ions due to their electro-chemical nature, without the need to lower pH levels. The formation of hydrochloric acid through a chemical process occurs as a result of chloride ions interacting with the steel and the surrounding passive material, which leads to corrosion. The hydrochloric acid eats away at the steel reinforcement and thus leads to concrete cracking, spalling, and eventually failure **(SHI, X., XIE, N., FORTUNE, K and GONG, J. (2011)**) **.**

The concrete mix components and the surrounding environment are both major sources of chloride ions. Unwashed aggregates and sand, admixtures, and even using seawater in concrete processing could be the primary causes. The second comes mainly from being exposed to marine environment such as sea salt spray, direct seawater wetting, when concrete is in contact with soils rich with chlorides deposits, or it can come from deicing salts and use of chemicals. It is by the process of diffusion that chloride penetrates the concrete.

2.3 Sulphate attack

It has been demonstrated that sulphate attack on concrete results from a chemical reaction between the sulphate ion and hydrated calcium aluminate and/or the calcium hydroxide components of hardened cement paste in the presence of water. The results of these reactions are calcium sulphoaluminate hydrate, which is commonly referred to as ettringite, and calcium sulphate hydrate, which is better known by the name gypsum. These solids have a very much higher volume than the solid reactants and, as a consequence, stresses are produced that may result in breakdown of the paste and ultimately in breakdown of the concrete.

According to **(Goudie, A., and Viles, H. (1997))**, there are multiple sources of salt weathering or sulphate attack on concrete structures. Sulphates from natural sources that are either present in soil or dissolved in ground water are included in this group. Chemically aggressive sulphates are derived from agricultural wastewater (such as ammonium sulphates that enter the groundwater after being utilized as fertilizer). Sulphates are also found in the coal and metallurgical industries. The presence of atmospheric pollution could lead to an increase in sulphate concentrations in the soil and groundwater .

The rate and degree of sulphate attack depend on the concentration of sulphate present, the type and availability of the sulphate ion, the accessibility of water, and the type of cement and quality of concrete. To protect against sulfates, it is common to adopt preventative measures such as using sulphate-resistant cement, having a low water-cement ratio, having a minimum cement content, entrainment of air, and paying attention to reinforcing cover.

2.4 Effect of carbonation, chloride and sulphate attacks on hydration products of concrete

The combination of chlorides and carbonation action in the cementitious material is a complex chemical and physical phenomenon. On the one hand, the transformation of $Ca(OH)_2$ and others hydrates into carbonates, decreases the porosity of concrete **[C. Ngala, V. & Page,1997]** and, consequently, contributes to reduce the amount of penetrated chlorides. On the other hand, the pH decrease caused by carbonation **[B. Johannesson, P. Utgenannt,2001]** can contribute towards releasing chemically fixed chlorides and increasing free chlorides content, which may actively ingress into concrete. When these aggressive agents act at the same time, or in short intervals one after the other.

In a study conducted by the two researchers **(E.M. Mbadikea, A.U. Elinwa, 2011)**, about the effect of saltwater in the production of concrete was investigated. A total of ninety (90) concrete cubes were cast for compression strength test i.e. forty five cubes were cast using fresh water and the other forty five cubes were also cast using salt water. Similarly, a total of ninety (90) concrete beams were cast for flexural strength test i.e. forty-five beams were cast using fresh water and the other forty-five beams were also cast using salt water. The concrete cubes and the beams were cured at 7,21,28,60 and 90 days respectively. The result of the average compressive strength of concrete obtained using fresh water of mix ratio (1 : 1.51 : 4.01), water-cement ratio (0.47) ranges from 27.35-42.34 N/mm^2 while that of salt water ranges from 25.24-38.81 N/mm^2 for the hydration period of 7, 21, 28, 60 and 90 days. The flexural strength of concrete obtained using fresh water of the same mix ratio and water cement ratio ranges from 6.60 - 11.20 N/mm^2 for 7, 21, 28, 60 and 90 days hydration period while that of salt water ranges from 5.98-11.04 N/mm2 for the same hydration period. For the mix ratio (1 : 1.61 : 4.03) and water-cement ratio (0.55), the average compressive strength of concrete obtained using fresh and salt water ranges from 27.26 - 40.80 N/mm^2 and 24.68 - 39.13 N/mm^2 respectively while the flexural strength ranges from 6.55 - 11.13 N/mm^2 and 6.26 - 10.76 N/mm^2 for fresh and salt water respectively. The initial and final setting time of cement using fresh water is 50 mins and 587 mins while that of salt water is 55mins and 605 mins respectively.

The conclusion of the study can be summarized as follows: The strength development in the concrete produced increases with the increase in the hydration period, The higher the setting time, the lower the strength of concrete produced, The use of salt water in concrete production will reduce the strength of concrete produced to approximately 8%, Curing is very necessary in concrete in order to ensure the complete hydration of cement, The strength development in concrete depends on the percentage chemical composition of cement, The presence of chlorides and sulphates.

(Liu et al,2017) studied the combined effects of chlorides and carbonation on normal Portland cement concrete with different w/b (0.38, 0.47, 0.53). They found that the samples with higher w/b have higher chloride binding capacity before carbonation. The chloride binding capacity of all samples with different w/b decreased with the influence of carbonation. Comparatively speaking, the degree of decrease of chloride binding capacity was greater in lower w/b (0.38).

Previous studies have suggested that concrete with low w/c ratio is more vulnerable to damage by physical sulphate attack since lowering the w/c ratio reduces the pore size diameter, which can behave similar to rocks with fine pores **(Hime, 2003).** However ,a laboratory investigation by **Folliard and Sandberg (1994)** showed that concrete made with w/c = 0.30 had better performance than concrete made with w/c = 0.50 under an environment prone to physical sulphate attack. Yet, a study by **Nehdi and Hayek (2005)** showed that concrete mortars with an intermediate w/c = 0.45 had an extensive efflorescence formation compared with w/c = 0.30 and w/c = 0.60 as shown in Figure 1. Therefore, more research is needed to investigate the main role of the w/c in concrete exposed to physical sulphate attack.

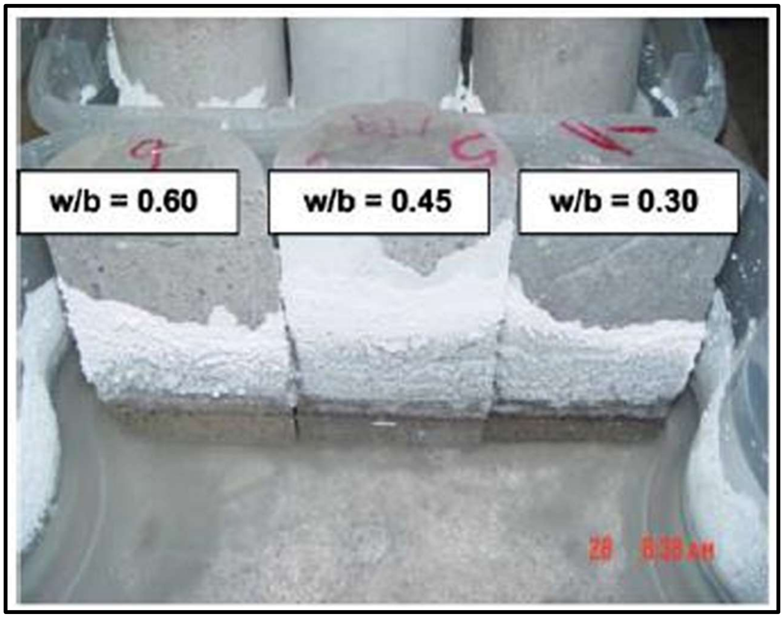


Figure 1: Salt efflorescence of concrete cylinders partially immersed in a sodium sulphate solution **(Nehdi and Hayek, 2005).**

A study by QCL Group of Companies in 1999 delved into the role of sulphate attack and the penetration of chloride ions in concrete durability. The research introduced performance tests aimed at facilitating the assessment of concrete's resistance to these chemical actions, considering various cementitious binder options now available for inclusion in concrete. Data from a CSIRO research project suggests that when specifying concrete to withstand sulphate attack or resist chloride ion penetration, an effective approach might involve achieving a compressive strength (f'c) of 40 MPa to limit the water/cement ratio to a maximum of 0.45, thereby reducing permeability. Additionally, incorporating at least 20% fly ash or 60% slag is recommended, as either of these additives can also help mitigate the potential for alkali-silica reaction.

(Khalid Hawi 2014), This research is deliberate the effect external sulfate attack on Compressive strength concrete with 1 : 1.5 :3 mix ratio and cement content 380 kg /m^3 with curing age 28 days in ordinary water then complete immersed in three different sulfate solutions of magnesium, sodium and calcium at four Solution concentration (0%, 2%, 4% and 6%) each for three exposure periods of (60, 90 and 120) days. Results tests of Compressive strength for all specimens immersed in different sulfate solutions show that Magnesium sulfate had the most deleterious effect on the concrete compressive strength especially when exposed in 6% for 120 days which record 24.44 MPa compare with referential 30.87 MPa with strength loss 20.82 % . Calcium sulfate had the least effect with strength reduction most 9.43 % for specimens which immersed in it , and 16.74 % strength loss with in sodium sulfate in 6% for 90 days for each of them compare with referential .

Compressive strength(MPa) of samples after immersion in solution			**Solution concentration %**	**Sample name**	**Type of salts**
120 days	90 days	60 days			
30.87	30.82	30.75	%0	R	Without the use of sulfates
27.04	27.68	30.17	%2	M_2	$MgSO_4$
25.74	26.83	29.95	%4	M_4	
24.44	25.81	29.59	%6	M_6	
27.95	27.75	30.36	%2	N_2	Na_2SO_4
27.80	26.88	30.18	%4	N_4	
27.22	25.66	29.60	%6	N_6	
28.73	28.29	31.15	%2	C_2	$CaSO_4$
29.50	27.98	30.97	%4	C_4	
28.97	27.91	30.96	%6	C_6	

Table 1: The table shows the results of the compression test for concrete exposed to sulfate solutions at different concentrations and ages

2.5 Effect of carbonation, chloride and sulphate attacks on steel reinforced concrete

The impact of carbonation, chloride, and sulphate attacks on steel-reinforced concrete is undeniably a prominent challenge in the field of structural engineering. This challenge has significant repercussions on the safety and reliability of structures under normal operational conditions, as well as in the face of both human-induced and natural hazards. Particularly, the corrosion of reinforcement steel within concrete structures presents a multifaceted problem. This damage initiates internally within the structure, often escaping visual inspection, and for a considerable period, the corrosion of reinforcement steel was not considered a major concern. This was due to the belief that the steel was shielded by the concrete cover. However, the presence of chlorides originating from marine environments or de-icing salts, the use of contaminated sand, aggregates, or mixing water in concrete formulations, historical utilization of chlorides as accelerators in concrete binding, or even the natural carbonation process of concrete all contribute to the deterioration of the protective alkaline environment within the concrete.

In a study conducted by **Verma et al. in 2013,** the effect of chloride attack and the concrete cover on the probability of corrosion was evaluated. The authors highlighted the penetration of chloride ions in concrete structures as a significant threat to their durability. Corrosion in reinforced concrete structures occurs when the passive protective layer is compromised by the ingress of chloride. Most researchers employ Fick's laws of diffusion to model chloride ingress, which is primarily dependent on the diffusion coefficient. Based on numerous studies and field survey results related to chlorination, enhancing the chloride resistance of concrete structures is advised through measures such as increasing the depth of the concrete cover, incorporating supplementary materials, and using pozzolanic substances.

In another study, it was found that there is a lot of calcium hydroxide in concrete pores that can dissolve in the pore water. This helps maintain the pH at its usual level of 12-13 while the carbonation reaction occurs. However, when carbon dioxide reacts with calcium hydroxides (and others) in solution, all of the calcium hydroxide eventually reacts, precipitating calcium carbonate and allowing the pH to fall to a level where the steel corrodes. This is illustrated in Figures 2 (a) and (b) which show the decrease in steel corrosion rate with increasing pH and the change in pH across the carburizing front.

Carbonation damage occurs most rapidly when there is little concrete cover of the reinforcing steel. It can also occur when the cover is high but the pore structure is open, pores are well connected together and allow rapid CO_2 ingress and when alkaline reserves in the pores are low. This occurs when there is a low cement content, high water cement ratio and poor curing of the concrete. **(Shalon and Raphael J ACI, 1959).**

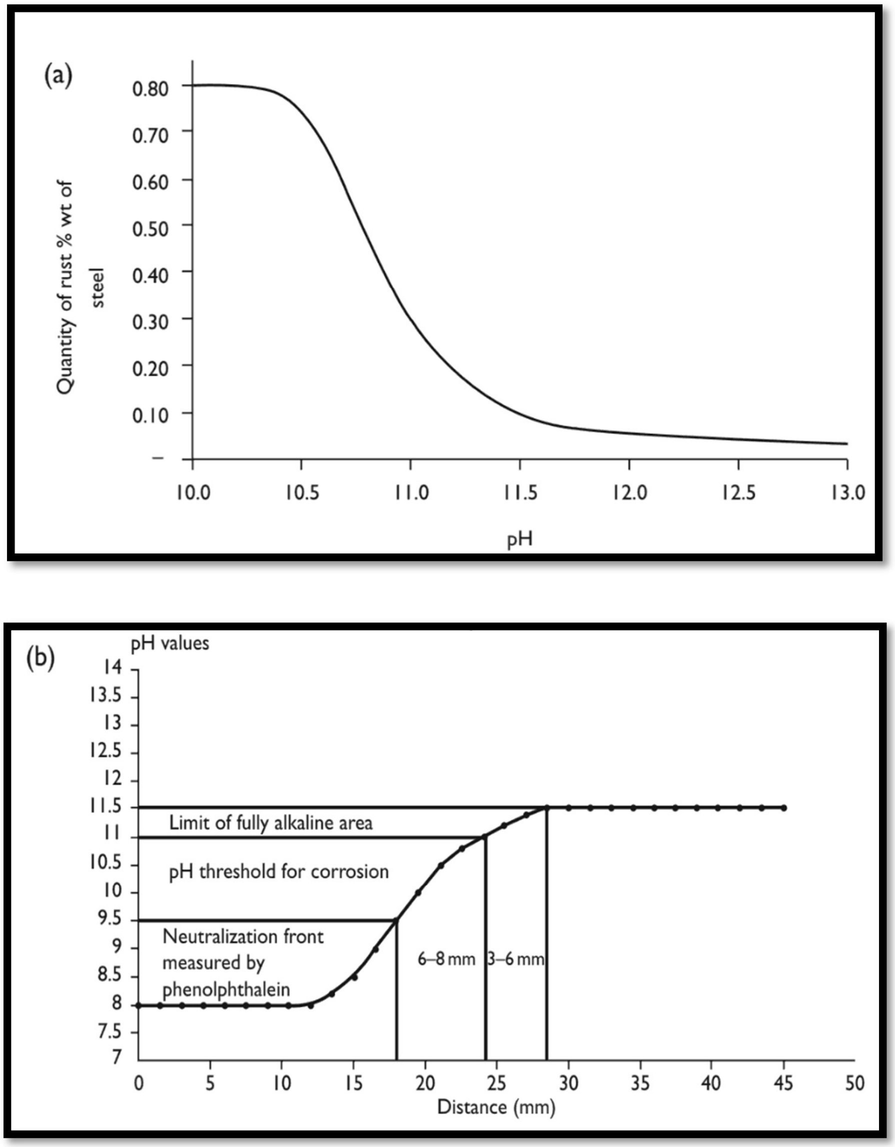
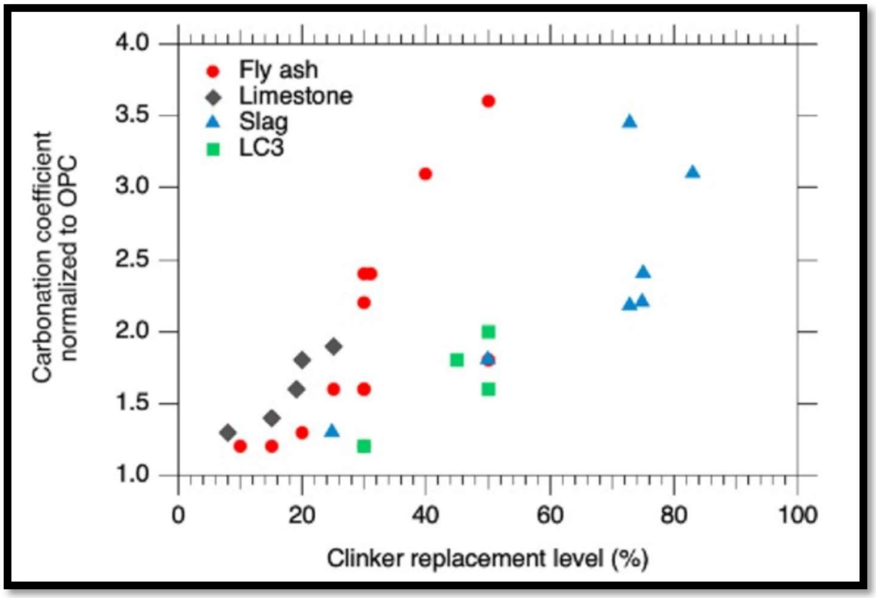


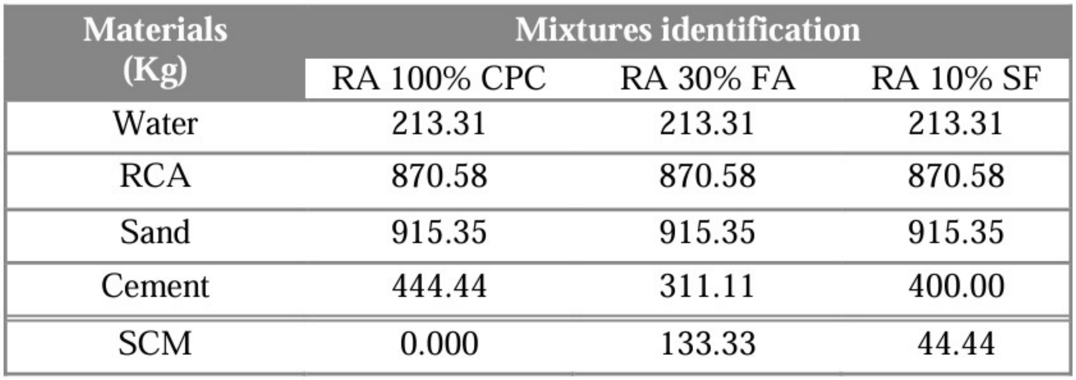
Figure. 2: (a) Corrosion of steel in aqueous solutions as a function of pH, showing the effect of the passive layer above pH 12.5. (b) The pH levels for carbonation, corrosion and phenolphthalein indicator.

In a recent study **[Z. Zhang, P. Trtik, F. Ren,2022],** the ingress of capillary water into a carbonated mortar sample was monitored using neutron radiography, while the corrosion state of an embedded steel electrode was simultaneously observed through electrochemical techniques. The results confirmed a remarkable increase in the instantaneous corrosion rate of the (depassivated) steel, rising from a negligible 0.16 µm/year in the initially dry state to over 30 µm/year precisely when the water reached the steel. In summary, the current state-of-the-art knowledge supports the idea that carbonation alone does not induce corrosion; rather, a certain moisture content must be attained for corrosion to occur. This understanding, exemplified by documented cases in practice **[U. Angst, F. Moro, M. Geiker, S. Kessler,2020],** provides an opportunity to address the "carbonation dilemma." The author envisions establishing a new engineering approach that allows for reduced alkalinity (thus enabling increased levels of clinker substitution (Figuer 3)) while simultaneously controlling corrosion.



Figuer.3: Effect of clinker replacement on the resistance against carbonation.

In a study by **Corral-Higuera,2011**, three sets of samples were produced with a water cement ratio of 0.48: one series.Made from 100% Recycled Rough Concrete Aggregate (RCA) and 100% Portland Cement Composite (CPC), a series made of 100% RCA and 30% FA as a partial replacement for CPC, and finally, Series made of 100% RCA and 10% SF as a partial replacement for CPC. These were samples Cured for 28 days in a room temperature of 23±2°C and 98±1% relative humidity. Characteristics and The proportions of the mixtures are given in Table 2.



Materials (Kg)	Mixtures identification		
	RA 100% CPC	RA 30% FA	RA 10% SF
Water	213.31	213.31	213.31
RCA	870.58	870.58	870.58
Sand	915.35	915.35	915.35
Cement	444.44	311.11	400.00
SCM	0.000	133.33	44.44

Table 2: Characteristics and proportion of the test mixtures (by 1m^3 of concrete).

Concrete cylinders with a diameter of 15 cm and a height of 30 cm were used, with two embedded in the middle. Reinforcing bars were used to study the effect of sulfur environment on concrete weight loss and corrosion of steel reinforcement. Test samples were exposed to 3.5% $Na2SO_4$ Aqueous solution and reducing/increasing the weight of reinforced concrete samples was they are evaluated periodically, with samples retrieved and air-dried for one day in the laboratory environment (21±2 °C) and weighing. According to the results obtained in concrete test samples made from 100% recycled rough materials. Overall, it can be concluded that: Fly ash and silica fumes contribute to the increase in resistance of recycled aggregate concrete to sulphate attack. The addition of 10% of SF as a partial replacement of cement, reduces around 20 times the weight loss, whereas the addition of 30% of FA as a partial replacement of cement, reduces around 8 times the weight loss by sulfate attack, with respect to the concrete without supplementary cementing materials.

Silica fume contribute significantly in increase the steel corrosion resistance, due to cementing matrix densification and pore refinement. Therefore ,the durability of the reinforced recycled aggregate concrete structures exposed to underground water or filtrations with high sulfate content can increase significantly using supplementary cementing materials, as a partial replacement of cement, contributing to the concrete industry sustainability.

Conclusions

Grounded on reviewed studies related to deterioration of corroborated concrete due to chemical aggression, there's a major change in strength properties and thus the continuity of exposed concrete structures. The deterioration medium depends on material ingredients and exposure conditions. In utmost concrete structures, chemical attacks are initiated by different causes similar as unsuitable choice of cement type for the conditions of exposure, high concrete porosity and permeability, cement content, type and quality of constituent materials.

The results from epitomized studies show that increase in compressive strength and objectification of supplementary cementitious materials can enhance the resistance of concrete to aggressive chemical conduct.

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