

STARCH MODIFIED CONCRETES EXPOSED TO AGGRESSIVE ACIDIC ENVIRONMENT

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Abstract

The deterioration processes are linked with transport mechanism of various fluids: gas, ionic diffusion, water absorption and permeation. Dense and durable concretes are required for concrete structures to be able to adequately resist aggressive sulphate environment. The effects of starch extracted from cassava and maize on concretes with starch introduced as admixtures in various concentrations (0%, 0.5%, 1%, 1.5% by weight of cement) were produced. The concrete samples were subjected to an aggressive environment by placing them in 10% sulphuric acid solution for accelerated assessment of the suitability or otherwise of this organic admixture in such an environment. Compressive strength tests were carried out on the cubes at 7, 28, 56, and 90 days, respectively. In order to assess the depth of penetration of the sulphuric acid solution into the concrete cubes, a set of concrete cubes was cast and cured for 7, 28, 56, and 90 days, respectively, in the same acidic (10% sulphuric (H_2SO_4)) solution. Another set of concrete cubes was cast and cured for the same number of days for a wet and dry curing regime in the same solution. The outcome showed that maize starch (MS) concrete of 1% and cassava starch (CA) concrete of 1% gave greater compressive strength, and the 1% maize starch concretes provide better resistance to sulphate attack. For the concretes cured by wet and dry method, CA 1% concretes gave the optimum result both in increased compressive strength and enhanced durability.

Keywords: concrete, starch, compressive strength, durability test, sulphate concentration.

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1. Introduction

Marine environments, sulphate contaminated ground water or sulphate effluents from fertilizer or mining industries are known to cause deterioration of concrete structures. Therefore, durability of concrete requires extra attention in such an environment. Susilorini et al. [12] pointed out that concrete deterioration due to sulphate attack may cause concrete to expand and result in mass loss. Chen and Liew [2] noted that sulphate attack on concrete structure may be physical in the form of crystallization of salt. It may also be due to chemical reactions of sulphate ions as a result of late decomposition of gypsum in the cementitious system or due to reaction of sulphate ions from external sources. External attack will depend on the resistance of the concrete to migration of sulphate ions from the surrounding aggressive environment and their concentration around the concrete. Clifton et al. [3] reported that the conditions under which the concrete is exposed such as permanent immersion or wet and dry cycles will determine the extent of manifestation of degradation of the concrete. Sulphate attack on concrete cause loss of strength of the concrete, which is associated with the decalcification of hydration products. According to Tixier and Mobasher [15] because substantial portion of calcium silicate hydrates has been destroyed the hardened concrete is changed into a crumbly mass.

One of the ways to take care of sulphate attack in concrete is through the use of sulphate resisting cement or the use of blended cements. Pozzolanic materials such as fly ash, metakaolin, and condensed silica fume added at certain percentages into the concrete mix have proved to offer good resistance to sulphate attack (Owens [7]). Kerkhoff [6] pointed out that surfaces of the concrete can also be protected from sulphate with coatings, while other chemical admixtures have also been suggested. The effect of organic admixtures such as polysaccharide and starch ether in concrete have been examined by Peschard et al. [8]. Starch consists of a large number of glucose units joined together by glycosidic bonds. By dissolving starch in warm water, starch paste is formed, which can be used as a thickening, stiffening or gluing agent (Teixeira et al. [14]). This

renewable material has various industrial applications, in the construction industry. Rols et al. [9] found starch to be a very good and cheap alternative to welan gum as a viscosity modifying and water retention agent in self-levelling concrete. Simonides and Terpstra [11] noted that starch as a viscosity modifying agent gives cohesion against deformation, segregation, and bleeding in concrete. Izaguirre et al. [4] noted that starch based concrete finds useful applications in grouting, rendering, and shotcreting because of its thickening or plasticizing ability which depends on application. Akindahunsi et al. [1] also reported on the use of starch modified concrete for repair works in that it improves durability properties of the concrete. Hence, this paper examines the effect of starch extracted from cassava and maize as an admixture in concrete in an aggressive environment of acidic solution.

2. Experimental Procedure

2.1. Materials

Ordinary Portland cement (OPC), CEM I 52.5N used as the binder for this study was supplied by the Pretoria Portland Cement Company PTY (PPC) in Johannesburg, South Africa. Crushed granite was used as the coarse and fine aggregates. The aggregates were obtained from AfriSam aggregates Johannesburg were in compliance with South African National Standards SANS 1083 [10]. The maximum coarse aggregate size used is 22mm (compacted bulk density of 1750kg/m^3 and specific gravity of 2.67). Potable water was used for the mixing of the materials. The starches (cassava and maize) used are from Nigeria. In this investigation, a 10% sulphuric acid (H_2SO_4) solution was prepared and used as the curing solution to mimican extreme aggressive environment. Epoxy coating made of two components, namely, a base and an activator (StonhardStonkote 681) was used to coat the concrete cubes used for durability tests cured in acidic solution and the other set of concrete cubes cured by a wet and dry method in the same solution. The cassava and maize starch powders are shown in Figures 1 and 2, respectively.



Figure 1. Cassava starch powder.



Figure 2. Maize starch powder.

2.2. Methods

2.2.1. Starch activation

The maize starch powder is factory pre-treated and the starch properties are activated in water at ambient room temperature, the required dosage was added directly to the mix. Cassava starch however, has to be activated with hot water of temperature between 70 to 90°C. Therefore, the required dosage was specially prepared separately and allowed to cool down in order not to contribute to temperature rise in the mix in which it was used. The quantity of water used in the cassava starch activation was deducted from that required for the concrete mix. Particle sizes of the CA and MS starch were determined by using Malvern mastersizer 2000 particle size analyser.

2.2.2. Concrete mixes

The mix proportion used for the concrete mixes for compressive strength and durability tests is presented in Table 1. A total of 96 concrete cubes (100mm × 100mm × 100mm) containing 0%, 0.5%, 1%, and 1.5% MS and CA starch by weight of cement were cast and compacted by using a vibrating table and demoulded after 24 hours. The concretes cubes were cured in a 10% concentration of H₂SO₄ solution. This was done in order to accelerate the effect of H₂SO₄ on the concrete cubes within the time frame of the test (i.e., 7, 28, 56, and 90 days). Another set of concrete cubes of the same number were cast for wet and dry curing in the same acidic solution. For example, for a 7 day curing, concrete cubes were cured for the first 4 days in the acidic solution and then taken out and kept in ambient environment for 3 days. Same process was carried out for all the cubes used in the wet and dry curing. Two sets of 56 no concrete cubes (0%, 0.5%, 1%, and 1.5% of MS and CA) were cast for durability tests. The concrete cubes for the durability tests were coated on 5 sides with epoxy paint, the epoxy was mixed as 4 parts of base to one part activator. One side left uncoated was to ensure that

penetration of H_2SO_4 solution into the concrete was from that particular side of the concrete, the coated concrete cubes were left to dry for a day. A set of the concrete cubes was cured (by permanent immersion) in the acidic solution and tested at the earlier stated ages. The other set was cured in the same solution but by a wet and dry curing regime as also explained previously. Water-cement ratio of 0.54 was used because addition of starch into the concrete modifies the viscosity of the concrete to give more cohesiveness and stability.

Table 1. Mix proportion

Water/cement ratio	Water (kg/m ³)	Cement (kg/m ³) CEM I 52.5N	Fine aggregates (kg/m ³)	Coarse aggregates (kg/m ³)
0.54	205	379	764	1024

2.2.3. Compressive strength tests

At the end of each curing age, the concrete cubes were taken out of the curing bath, wiped and weighed and for compressive strength tests using a 2000kN hydraulic Amsler machine. The concrete cube to be tested was placed centrally on the base loading plate. The loading plate was kept in even contact with the specimen and the load was applied without shock. The load was increased continuously at a constant rate of about 5kN/s until the concrete cube failed and the load at failure was documented to the nearest of 0.1kN. The same process was repeated for all concrete cubes.

2.2.4. Durability test

In order to investigate how much of the H_2SO_4 solution had penetrated into the concrete cubes cured in the solution, tests were conducted to determine the concentrations of sulphate (SO_4^{2-}) that has been absorbed by the concrete cubes. The concrete cubes (0%, 0.5%, 1%, and 1.5% of MS and CA) were split approximately into two equal parts by

using the 2000kN hydraulic Amsler machine. Mortar samples were taken from the centre of the concrete cubes. The mortar samples for each concrete cube was finely ground, placed and labelled in each beaker. A condition reagent was prepared: 25ml of glycerol was measured, mixed with 15ml of concentrated hydrochloric acid in the same beaker. To the same beaker, 50ml of 95% isopropyl alcohol was added and properly mixed. 37.5g of sodium chloride was weighed and then dissolved in the distilled water. The contents were all mixed together and filled to the final volume of 100ml with distilled water. A standard sulphate solution containing 1.479g of anhydrous sodium sulphate was measured and dissolved in distilled water to a 1000ml mark of the standard flask. 50ml of distilled water was added to the finely ground samples in the labelled beakers, properly mixed, 5ml of the conditioning reagent was added to each beaker. Prior to testing the samples in an UV spectrometer shown in Figure 3, a spatula amount of barium chloride was added to the mix in the beakers, distilled water was filled to the 100ml mark of the beakers. The UV spectrometer is standardized with the standard sulphate solution prepared, the output from the spectrometer gives the absorbance value for the sample that was tested.



Figure 3. UV absorption spectrometer.

Each beaker containing the samples was properly mixed and poured into sample tubes, placed in the UV spectrometer one after the other for the test. From the absorbance value, the concentration of sulphuric acid in each sample was calculated by using Equation (1)

$$A = \varepsilon l c, \quad (1)$$

where

A = absorbance;

ε = molar absorption coefficient at 405nm;

l = cell width (mm);

c = concentration (mg/L).

3. Results and Discussion

3.1. Particle sizes test

The result of the particle size of the CA and MS starch measured are presented in Figures 4 and 5. From Figure 4, the average particle size for cassava starch indicated as D50 is 14.294 μm . The D10 and D90 give the lower and upper boundaries of the particle size available in the starch, which is 5.282 μm and 21.876 μm , respectively. The specific surface area of the cassava starch is 0.444 m^2/g . Figure 5 shows the average particle size of maize starch (D50) to be 25.051 μm , while the lower and upper boundaries of the particle size are 13.967 μm and 41.752 μm , respectively. The specific surface area of the maize starch is 0.266 m^2/g . The obtained results showed that cassava starch has smaller particle sizes and greater specific surface area than maize starch.

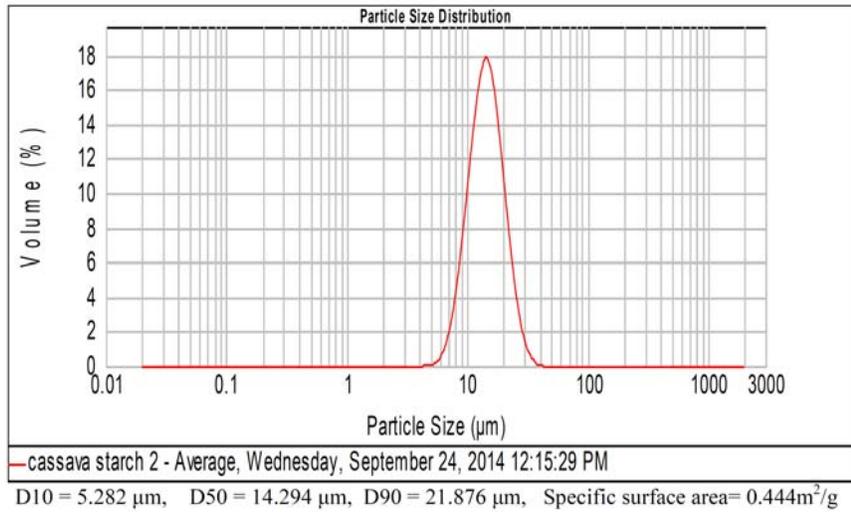


Figure 4. Particle size of the cassava starch granules.

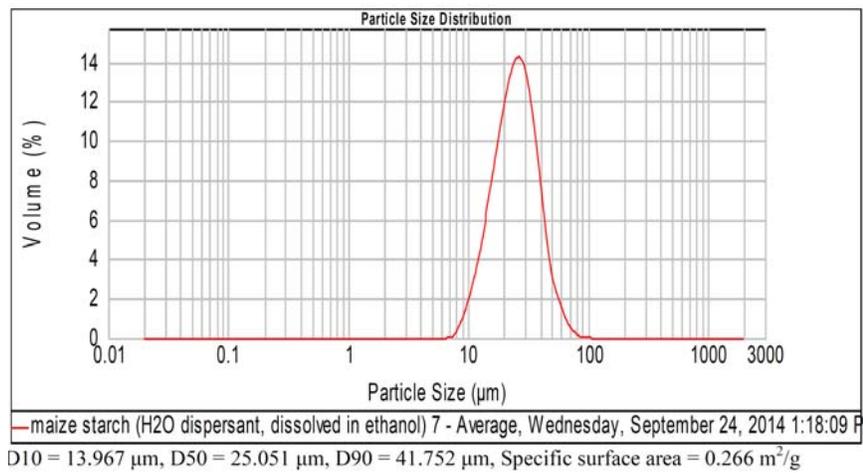


Figure 5. Particle size of the maize starch granules.

3.2. Effect of slump measurement

Figure 6 presents the measured slump for all the concretes. It can be seen generally that there is progressive decrease in slump measurement as the starch concentration increases. This shows starch gives cohesion

and stability against segregation and bleeding of concrete and this view is supported by several authors, such as Khayat [5] and Rols et al. [9] among others. Swinkels [13] reported that starch provides thickening and gluing effect in materials. Cassava starch has greater specific surface area than maize starch (Figures 4 and 5), this makes more of the cassava starch to be absorbed onto the surfaces of the cementitious system. As a result of which at the same concentration, CA concretes has lower slump measurements when compared to MS concretes. It was however, noted that MS 1.5 and CA 1.5 concretes especially require longer compaction time in order to make well compacted concretes.

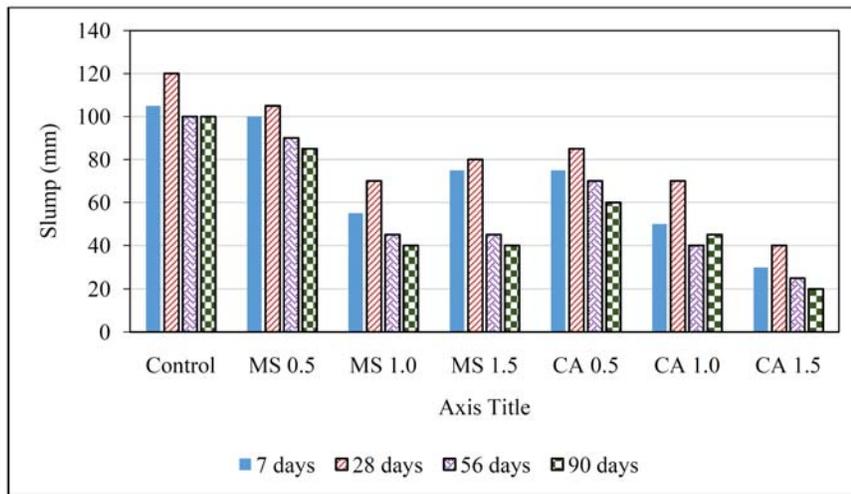


Figure 6. Slump measurements for the concretes.

3.3. Effect of H_2SO_4 solution on compressive strength

The typical effects of sulphate attack on the tested concretes is depicted in Figure 7, the degree of degradation of concretes in H_2SO_4 solution with time is very glaring. Progressive mass loss of concretes can be observed especially from 28-90 days cured concretes cubes, this confirms the findings of Tixier and Mobasher [15] that sulphate attack in concrete destroys calcium silicate hydrates in the hardened concrete

transforming it into a breakable mass. The sludge formed as a result of deterioration of the concretes caused by the disintegration of hydration products of the hardened concretes is shown in Figure 8. The enormous volume of sludge seen in Figure 8 shows the effect of high concentration of the acidic environment on the concretes. It also shows that the hydration products are very susceptible to sulphate attack especially when the concentration is high.

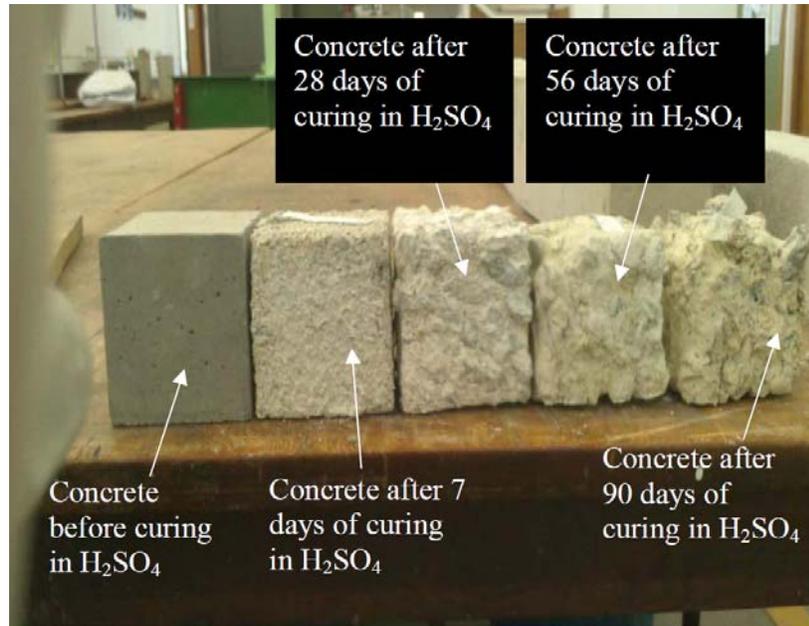


Figure 7. Typical change in shape and mass of concrete cubes exposed to H_2SO_4 solution after 7, 28, 56, and 90 days of curing, respectively.



Figure 8. Sludge formed by concrete cubes in H_2SO_4 solution.

The compressive strength tests results for the concretes cured continuously in H_2SO_4 solution and those cure by wet and dry method in the same solution are as presented in Figures 9 and 10, respectively. General observation from Figure 9 shows progressive decrease in compressive strengths of all the concretes as curing age progresses. This is to be expected because degradation of the concretes will continue as long as they are under this aggressive sulphate environment. It is also noticed that there is a sharp decline in strengths of the concretes of 7 days curing to that of 28 days curing. This may be due to the high concentration of sulphate in the solution and because the solution has penetrated into the concretes to cause substantial damage. Observations from Figure 8 show that MS 1.0, CA 0.5, and CA 1.0 concretes have greater compressive strengths when compared to the control concrete of the same age. This shows that starch offers additional benefit to the concretes subjected to sulphate attack. This may be due to the additional thickening and gluing properties of the starch, which are provided to the concretes. This is also supported by Rols et al. [9] that starch is a good

and cheap viscosity modifying agent that can be used in concrete. This is because starch gives cohesiveness to concrete in that it prevents bleeding and segregation.

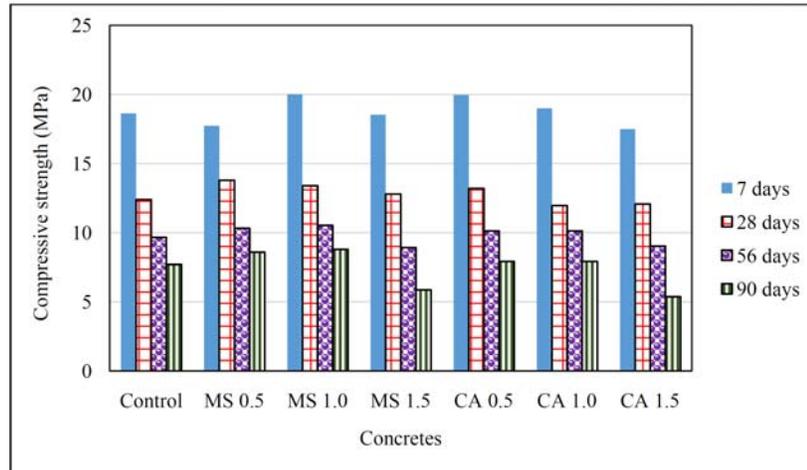


Figure 9. Compressive strengths of concretes in H_2SO_4 solution.

The results of the compressive strengths of concretes cured under the wet and dry cycle in the acidic solution is as shown in Figure 10. It can be seen that while high compressive strengths were recorded for all the concretes at 7 days of curing, there was a general substantial reduction in the strength at 28 days curing onwards, which is similar to the observation of the concretes in Figure 9. Another generally observed trend was that the compressive strengths from 28 days curing for concretes in Figure 10 were mostly lower than that of the corresponding periods in Figure 9 for the same set of concretes. This is due to the effect of wet and drying on the concretes as shown by some of the typical concretes cured under the wet and dry cycle in the acidic solution in Figure 11. The deterioration due to cracks on the concretes and the mass loss will significantly affect the strength of the concretes. It is seen from this investigation that concretes exposed to wet and dry cycles in sulphate environment suffer more degradation than the concretes

continuously exposed to the same environment. This also agrees with some of the findings of Clifton et al. [3] that wet and dry cycles in sulphate attack has more detrimental effect in concretes. Observations from the results showed that starch modified concretes especially MS 1.0, CA 0.5, and CA 1.0 concretes all had greater compressive strengths at corresponding days than the control concretes. However, the compressive strengths of MS 1.5 and CA 1.5 concretes decreased by 13% and 5% in comparison to the control at the end of 90 days, respectively. This may be due to difficulty in compaction since the mix becomes stiffer as shown by the slump measurement in Figure 6.

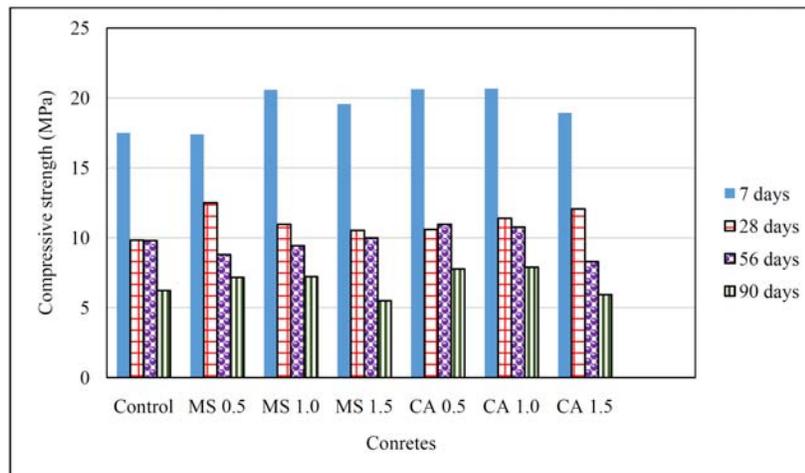


Figure 10. Compressive strengths of concretes in wet and dry cycle in H_2SO_4 solution.



Figure 11. Sludge formation when concrete is immersed in 10% H_2SO_4 solution, and cracking of the concrete cubes were exposed to the ambient air.

3.4. Effect of H_2SO_4 solution on durability of concretes

One of the effects of H_2SO_4 solution on the durability of concretes is shown in Figure 11. It weakens the concretes due to loss of hydration products and leads to mass loss and cracks. It should be noted that all the concretes tested to assess the quantity of sulphate absorbed into the concretes had earlier been coated with epoxy as stated in Subsection 2.1 of this paper. A common observation on all the concretes when the concretes were taken out to be tested at 28, 56, and 90 days was that the coatings on the concretes had peeled off. This shows coating applied to these concretes cannot prevent the effect of sulphate attack on concrete. It may also be due to the effect of high concentration of H_2SO_4 in the solution to accelerate the attack. However, this finding is in contrast to the observation of Kerkhoff [6] that coatings can protect concrete surfaces from sulphate attack. Observations from Figure 12 shows there is an increase in concentration of sulphates in all the concretes with curing time across board. However, MS 1.0, CA 0.5, and CA 1.0 had the lower concentrations of sulphate in comparison to the others this may be because these concretes are less permeable. Figure 13 presents the sulphate concentrations in the wet and dry cycle of cured concretes in the

acidic solution. It can be seen that starch concretes especially MS 1.0, CA 0.5, and CA 1.0 absorbed lower concentrations of sulphate when compared to the control concrete. This shows that starch thickening and gelling properties offer more cohesion and stability to the concretes a view also noted by Peschard et al. [8] and Akindahunsi et al. [1].

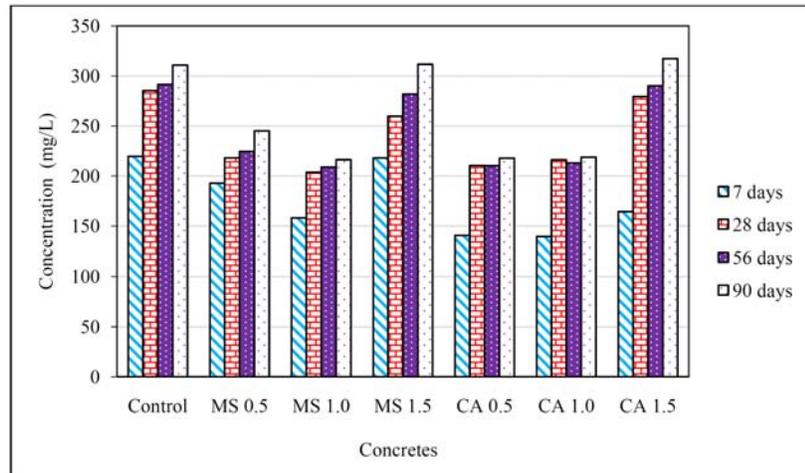


Figure 12. Concentration of concretes in 10% H₂SO₄ solution.

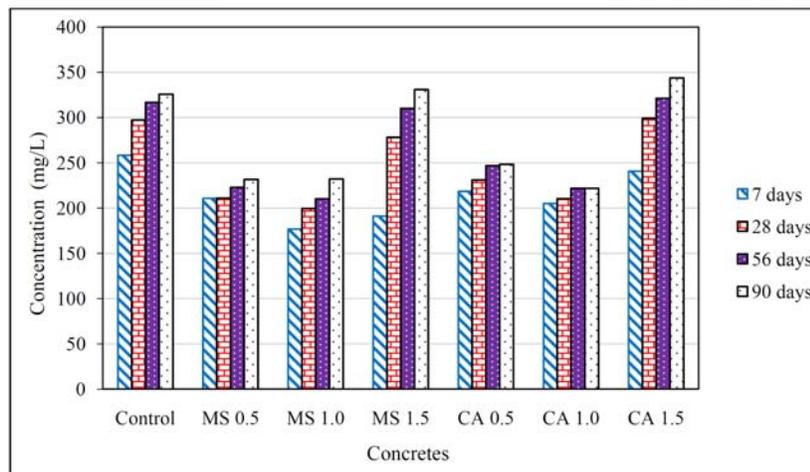


Figure 13. Concentration of concretes in 10% H₂SO₄ solution in wet and dry cycle.

4. Conclusion

The effects of concentrated sulphate solution on starch modified concretes have been examined in this paper and the following conclusions can be drawn:

(i) Sulphate attack generally affects all the concretes, however, starch concretes offer improved resistance to the attack.

(ii) MS 1.0 and CA 1.0 gave greater compressive strengths, 7.23MPa and 7.9MPa, respectively, after 90 days of curing when compared to the control of 6.23MPa in wet and dry curing regime.

(iii) Epoxy coatings applied on the concretes used for durability tests did not seem to provide any resistance to deterioration of the concretes.

(iv) Starch concretes gave better resistance against the ingress sulphate ions as shown by the lower concentrations of sulphate obtained in the concretes.

(v) Concretes exposed to wet and dry curing method had the lowest set of compressive strength results. The concretes also had the highest absorbed sulphate concentration when compared to the concretes cured in continuous sulphate environment.

(vi) In comparing the relative performance of the MS and CA concretes, MS 1% and CA 1% concretes showed better resistance to sulphate attack.

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