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Sulfuric acid's effects on the characteristics of regular Portland cement concrete under various environmental circumstances.

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ABSTRACT

An important component of environmental preservation and societal hygienic safety is the long-term resilience of sewage systems. As a result, engineers and authorities are highly concerned about the long-lasting performance of concrete sewer pipes. Acid resistance is a crucial factor in ensuring the sustainable quality of concrete used in sewage systems. In this paper, H_2SO_4 (a chemical) was utilized to investigate acid attack on concrete samples. The concrete samples were immersed in acid solution subjected to flowing and stagnant conditions having concentration of pH 1 and pH 2. Mass loss and strength loss studies were carried out. To demonstrate the survival of concrete in an aggressive environment (H_2SO_4) linear relation between acid concentration and degradation was established. It was found that the formation of gypsum has proven beneficial in reducing the degradation of concrete under acid attack.

***Keywords**:* Sulphuric acid, acid concentration, concrete.

Introduction

Acid resistance is an important durability property influencing concrete life cycle performance and maintenance in an aggressive acid environment. Aggressive environmental conditions with acid attacks occur in many industrial sectors like chemical industry, quarrying industry, mineral processing industry, cooling towers [1-3]), agricultural industry [4-7], and sewage systems. The variable nature of the hostile medium distinguishes acid attack in sewage systems made with concrete. The two primary zones of a sewer are (1). The sewer atmosphere (2). The sewage flow zone. There is a distinct type of acid corrosion in each of these zones. In the case of sewage flow zone, the most destructive media is wastewater which includes inorganic and inorganic acids, lime-dissolving carbonic acid, ammonium, magnesium salts, and fatty acids [8-9]. Strong acids, such as sulfuric acid can react with and dissolve many cement matrix components, resulting in calcium, aluminum, and iron salt precipitates, as well as silica gel. Weak acids such as carbonic and organic acids react with specific cement matrix components, such as calcium hydroxide and carbonate, to generate soluble hydrogen carbonates. The usual pH of municipal sewage lies between 7.0 and 8.0 [10], however, it may occasionally fall below this level due to industrial waste discharged into the sewage system [11].

Biogenic-produced sulfuric acid (BSA) attack, also known as microbially induced concrete corrosion (MICC), can cause disintegration of the hardened cement paste of concrete in sewers that are exposed to the atmosphere. In the direst scenario, this type of concrete degradation occurs on the order of several millimeters every year [12-17]. During the initial phase of MICC, hydrogen sulfide (H_2S) and carbon dioxide (CO_2) generated from wastewater adsorb on the surface of concrete sewer walls with a pH of around 12, causing acidification, carbonation, and a pH reduction to around 9. At this time, neutrophilic sulfur-oxidizing bacteria (NSOB) begin to colonize the concrete surface, producing a biofilm and converting reduced sulfur-containing molecules into sulfuric acid during respiration that is aerobic. The acid production causes the pH to fall even lower. When the pH drops to around 4, acidophilic sulfur-oxidizing bacteria (ASOB) begin to dominate the biofilm. This stage is regarded as the most active stage of concrete biodeterioration, characterized as the response of concrete to BSA [10, 18-20].

The mechanisms of acid attack are significant in determining concrete resistance because they are connected to the reaction of the aggressive medium with the components of the concrete matrix. The reactions follow a three-step sequence: (i) transporting the H_3O^+ ions to the reaction area (ii) chemically reacting the H_3O^+ions with concrete matrix and (iii) removing the reaction by-products from the area where the reaction occurs [21-22].

Ample research work is available on the acid attack on concrete but very less researchers known to author have worked simultaneously on stagnant and flowing conditions. The surrounding conditions of the aggressive medium considerably influence the corrosion process. With a continuous flow of wastewater through the sewer system, the dissolved concrete matrix, the attacking medium's reactivity, and the pace of dissolving are all influenced. Thus, this paper focuses on these parameters. To achieve this goal, concrete cubes were cast and subjected to acidic concentrations (pH 1) & (pH 2) in different surroundings (stagnant and flowing) and mass loss and loss of strength were measured.

Materials and methods

Raw materials

In this investigation, the concrete samples were prepared using Grade 43 (*Khyber*) Ordinary Portland Cement (OPC), which was accessible locally. The properties of the cement are outlined in table 1. The fine aggregate was made out of local river sand with a fineness modulus 2.47 and a density of 1789 kg/m^3[23]. The coarse aggregates with a maximum size of 20 mm were used having fineness modulus of 6.74, and a bulk dry density of 1945 kg/m^3 [23]. A polycarboxylic super-plasticizer (auramix 200) with a specific gravity of 1.04 was used to achieve the workability of fresh concrete.

Table 1. Chemical properties of cement

S.No.	Chemical Properties	Test Results
1	Ratio of percentage of lime to percentages of silica, alumina and iron oxide.	0.88
2	Ratio of percentage of alumina to that of iron oxide	1.20
3	Insoluble residue (% by mass)	2.80
4	Magnesia (% by mass)	1.40
5	Total sulphur content calculated as sulphuric anhydride (SO_3) (% by mass)	2.00
6	Loss on ignition (% by mass)	2.70
7	Chloride content (% by mass)	0.03
8	Tricalcium silicate (C_3S) (% by mass)	39.25
9	Tricalcium aluminate(C_3A) (% by mass)	9

Mix proportion and sample preparation

For preparing the concrete mix cement, sand and coarse aggregate were used along with water & superplastizer. The mixture was designed following the specifications outlined in [24]. Table 2 shows the proportions of the mix design. The coarse aggregate was used in the proportion of 60:40. 60% consists of an aggregate 10 mm and the remaining 40% consists of 20mm. Along with water super-plasticizer (auramix 200) with a weight percentage of 0.55% was added to the mixing water to improve cement's overall workability.

Table 2 Details of Mixture Proportions and Average Strength

W/C	Fine Aggregate (kg/m^3)	Coarse Aggregate (kg/m^3)	Superplasticizer (% weight of cement)	Average Compressive Strength 28 days N/mm^2
0.38	710	1120	0.55	44.12

The components were combined with an electrically driven mixer. The mixing operation's initial phase involved placing all the aggregates into the mixer. The components were then dry-mixed for 30 seconds to verify that the aggregates were distributed evenly. Fifty percent of the water (including superplastizer) was added first, followed by another minute of mixing. The mixer was then turned off for a bit to allow the aggregates to soak up the water. After adding the cement and running the mixer for 30 seconds, the remaining 50% of the water was added. 150 mm ×150 mm ×150 mm concrete cubes were made in well-greased cast-iron molds. Three layers of concrete were poured into the mold, and any trapped air was eliminated by vibrating the mold on an electrical counter for one minute. The casted samples remained undisturbed in the laboratory for 24 hours. Concrete specimens were hollowed out after 24 hours and stored in a curing tank with fresh water for 28 days. The tank's water was refilled every seven days.

After 28 days, these samples were removed and allowed to air dry for 12 hours. After drying the samples were kept at a 105 °C in an oven for approximately 24 hours to guarantee complete drying. After drying, the samples were allowed to cool in a laboratory under normal conditions for 6 hours before subjecting them to acid attack. After drying for 6 hours samples were placed in tanks with sulphuric acid solution (pH 1 & 2) under both flowing and stagnant circumstances for a predetermined time period. The samples were taken out of the tank and tested after a predetermined amount of time had passed.

Simulated method for sulphuric acid attack

A setup was devised to generate a flowing scenario similar to that of sewer pipes. Until present, no known author has used such an approach or setup in their work. Our arrangement consists of several steel tanks. These steel tanks were built by welding steel sheets together. In order to avoid any interaction between acid and steel tanks anti corrosive paint was used. Tanks intended for stagnant conditions contain just bib corks to replace the acidic water after a set period of time, whereas tanks intended for flowing conditions contain pipe and a motor system. The pipe diameter was one inch, and a 0.25 horsepower motor was employed. The line plan is presented in fig 1 and real images in fig 2.

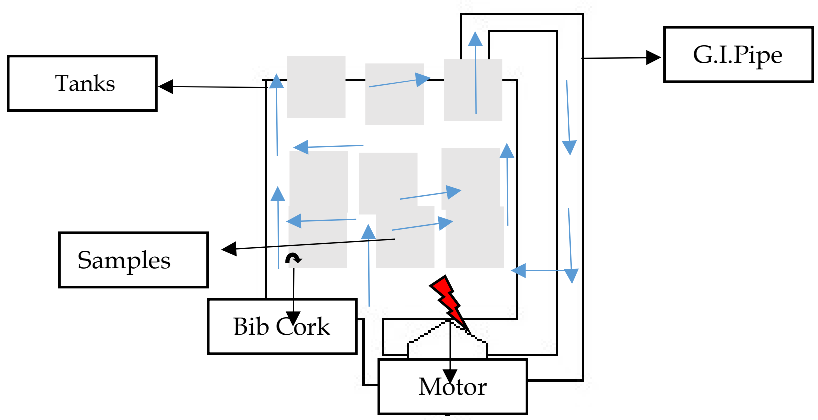


Fig. 1 Line plan of the setup

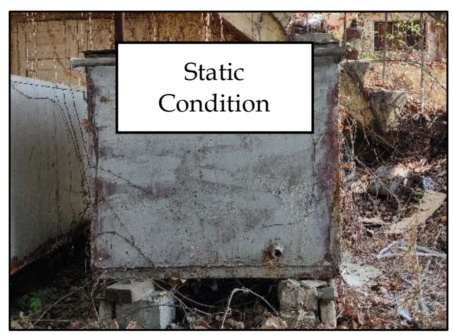


Fig. 2 Images of the setup

After the tanks were completely fabricated, a solution of sulphuric acid of desired concentration (pH 1 & 2) was prepared for both environments. This solution was created by combining the appropriate amount of acid with water to get the desired concentration. When the desired acid concentration was attained, concrete cubes were dipped in the tanks gently and steadily while wearing gloves. After soaking the cubes in acidic solution, the tanks were sealed with a lid to prevent any contact with the outside atmosphere. When the concrete cubes were immersed in the acid water the motor was connected to the electricity to maintain the flowing effect. Every day the motor used to run for 10 hours. As for stagnant condition the solution was not disturbed. After completing the desired period in acid, the concrete samples were taken out and evaluated for various durability parameters.

Exposure conditions

Four steel containers holding sulphuric acid solutions (pH 1 & 2) were prepared and concrete samples were engrossed in that solution. Figure 3 provides the details of the work procedure. The concrete samples were placed in the tanks for both surrounding conditions. For the tanks made for stagnant condition no disturbance was done to them while in case of flowing condition the concrete cubes experienced the shearing effect due to flowing of water. After finishing the required time period in the tanks, the samples were taken out and air-dried for a period of 6 hours before carrying out any testing on them.

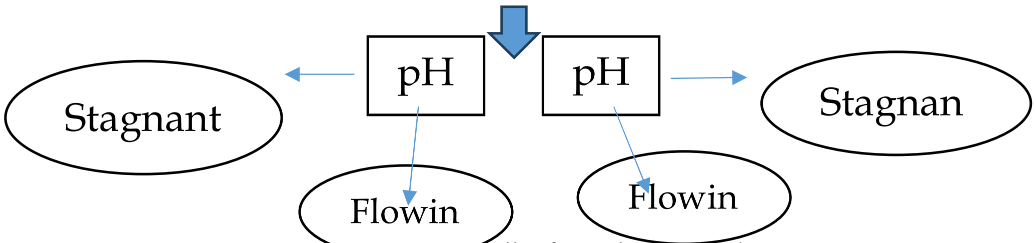


Fig 3 Details of experimental work

Testing &Test Results

1. **Mass loss:** The concrete samples were tested for degradation based on mass loss. After 1, 3, 5, 7, 9, and 12 months of immersion, samples were collected, part dried, and oven-dried for 24 hours at 105˚ C to achieve constant mass. Using a weighing scale with an accuracy of 0.01g, the dry mass (D_M) of the samples exposed to different sulphuric acid solution exposure circumstances was determined for all exposure ages.

$$\text{Mass Loss } \% = (D_M - D_T)/ D_M \times 100$$

D_M= Dry mass of sample before acid attack.

D_T= Dry mass of sample following acid attack at specific time interval.

2. Compressive Strength: All concrete samples were tested for compressive strength using an automatic compression test apparatus that complies with [25]. After the predetermined time for testing the samples were removed from the tank pat dried and kept in the lab for about 24 hrs before conducting a test. The load was gradually applied at the rate of 140kg/cm^2/min. For all ages, three replicate samples were analysed for each exposure scenario, with the average values reported as compressive strength. The compressive strength was calculated as:

$$\Theta = P/A$$

Θ= Compressive Strength (MPa)

P= Maximum Load in Newton

A=Area in mm^2

Discussions

a. Reaction of concrete with sulphuric acid solution.

When sulfuric acid attacks the concrete, it normally reacts with the alkaline components in the concrete via the following reaction [27].

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \quad (1)$$

$$CaSiO_2 \cdot 2H_2O + H_2SO_4 \rightarrow CaSO_4 + Si(OH)_4 + H_2O \quad (2)$$

$$3CaO \cdot Al_2O_3 \cdot 12H_2O + 3(CaSO_4 \cdot 2H_2O) + 14H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \quad (3)$$

It is evident from the preceding chemical equation that sulfuric acid dissolves concrete due to hydrogen ions as well as corrodes it with sulfate ions. The primary reaction result on the surface of concrete is in the form of gypsum, which has expanding properties. Gypsum further combines with calcium aluminate hydrate in the corrosion layer to create ettringite as the production of acid increases Ettringite crystals occur in high alkalinity pore fluids in deeper locations near the uncorded concrete [27]. The outcome is pitting and substantial volume expansion (i.e., 227%–700%), which is more detrimental than gypsum formation because it increases the surface area that is accessible to acid attack. [28-29] if the pH falls, ettringite loses its stability and eventually transforms into gypsum [30].

b. Effect of the flowing and stagnant condition on the properties of concrete.

The most significant factor influencing the degradation of any construction is its surroundings. In the case of the sewer system, the surroundings can be either stagnant or flowing. In the case of a stagnant condition, the gypsum formed as a result of a chemical reaction between acid and concrete gets accumulated all over the surface of the concrete specimen while as in the case of flowing condition the gypsum gets removed by the splash of water flowing through the pipeline. The amount of removal of the gypsum in case of flowing conditions mainly depends on the amount of velocity of the flowing fluid. In our experiment the removal of gypsum layer was not 100% but it was removed to great extent. Gypsum production after sulfuric chemical attack permits fewer sulfate ions to reach the inside of the concrete. When gypsum is removed during a chemical H_2SO_4 attack, new concrete surfaces are exposed to acid attack, causing progressive deterioration and increased corrosion rates. As pointed out by [31] the flow accelerated degradation by removing the protective layer of gypsum under high shear stresses. The same results are obtained in our experiment also. The samples submerged in stagnant conditions have undergone less degradation than the samples in flowing conditions. Many researchers have determined that the removal of gypsum deposits through wastewater flows can increase chemical corrosion [32].

c. Mass Loss

Because of its ease of testing and calculation, mass loss is one of the most commonly utilized indicators of the severity of concrete deterioration under sulfuric acid attack. Figure 4 depicts the results of the mass decrease of concrete specimen subjected to a sulfuric acid solution with a pH of 1and 2 over one year. Figure 4 shows that the proportion of mass loss in concrete during the initial stage of corrosion is slow, indicating the chemical reaction between sulphuric acid with the concrete is the time-dependent reaction. But as time passes the loss of mass also increases. The mass loss at the end of the year in case of the flowing condition was almost 6 % more than the stagnant condition for pH 1 and 4.53% for pH 2.

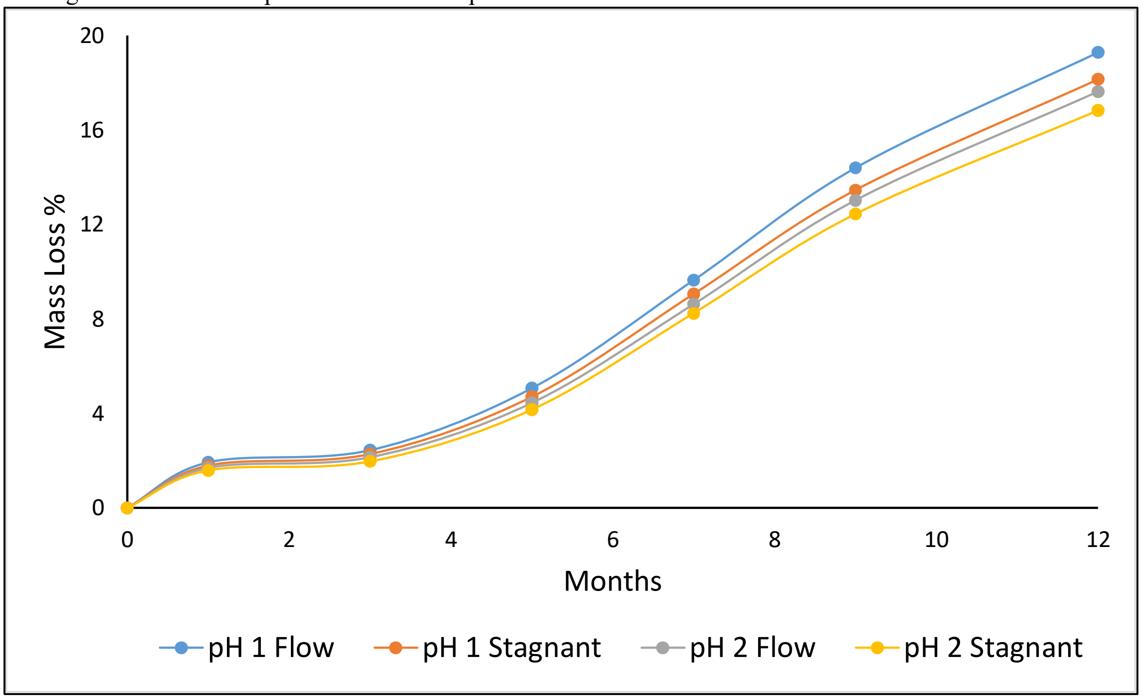


Fig. 4 Mass loss of concrete sample as a function of time under stagnant and flowing conditions for pH 1 and pH 2

Also from the graph, it is evident that the loss of mass in the case of pH 1 is more as compared to pH 2. This loss of mass is more because sulphuric acid at pH 1 level the concentration of hydrogen ions is more as compared to pH 2 which results in quick dissolution of calcium hydroxide and other components in the concrete matrix. Compared to pH 2, the mass loss was 8.65% more in pH 1 in the flowing condition and about 7.32 % in the stagnant condition respectively.

d. Compressive Strength

Fig.5 shows the influence of surrounding conditions on the strength loss of concrete in sulphuric acid. The compressive strength of the cubes decreases over time which is in line with the finding of [29]. Figure 5 also, shows that the percentage reduction in strength increases in both scenarios. As time in acid rises, cement hydration releases more C-S-H and CH, leading to severe degradation. This is consistent with [33,29] theory. Before exposure to an acidic environment, concrete specimens exhibited a uniaxial compressive strength of 44.12 MPa. After 365 days of exposure to underflow and stagnant conditions, the strength loss was 0.78% and 0.28% more in the case of flowing condition for pH 1 and pH 2 respectively.

Just like the mass loss the degradation of strength also was seen lower in case of pH 2 as compared to pH 1. The degradation was estimated as 0.90% and 0.40% more in pH 1 as compared to pH 2.

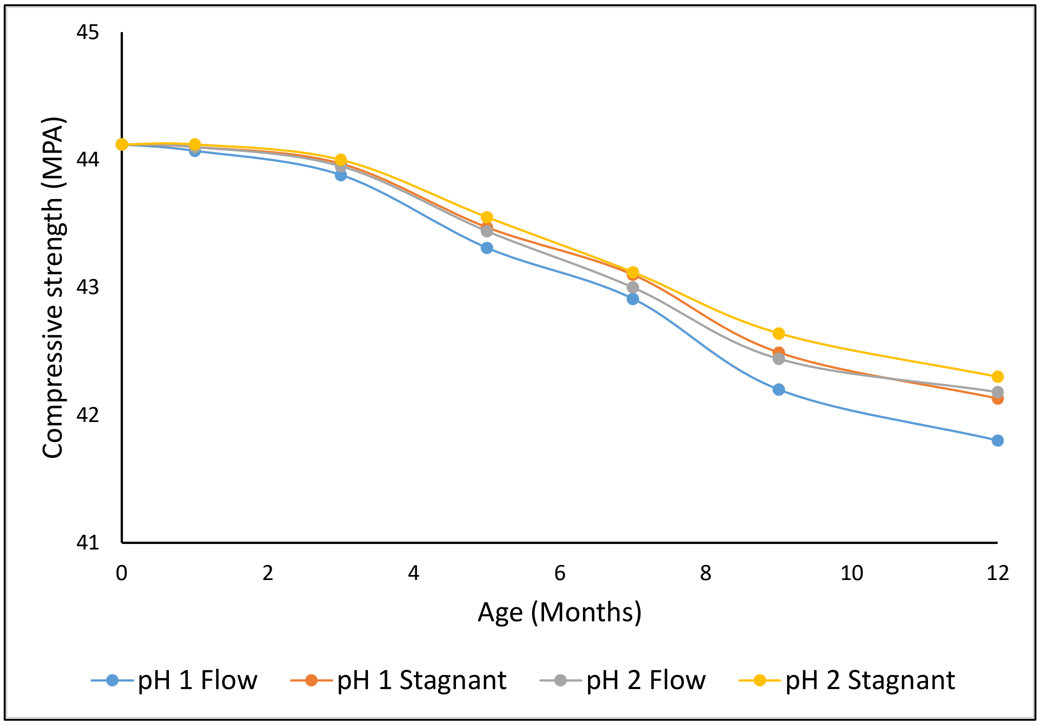
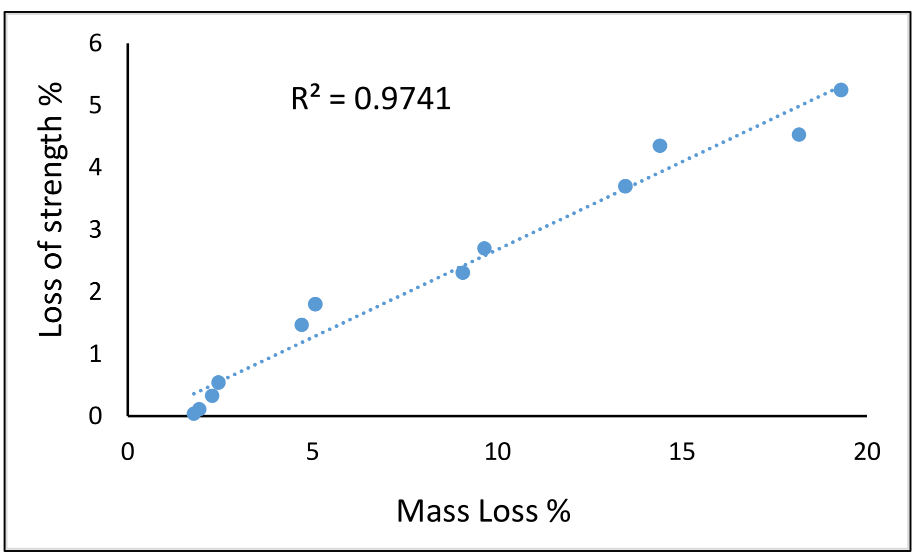


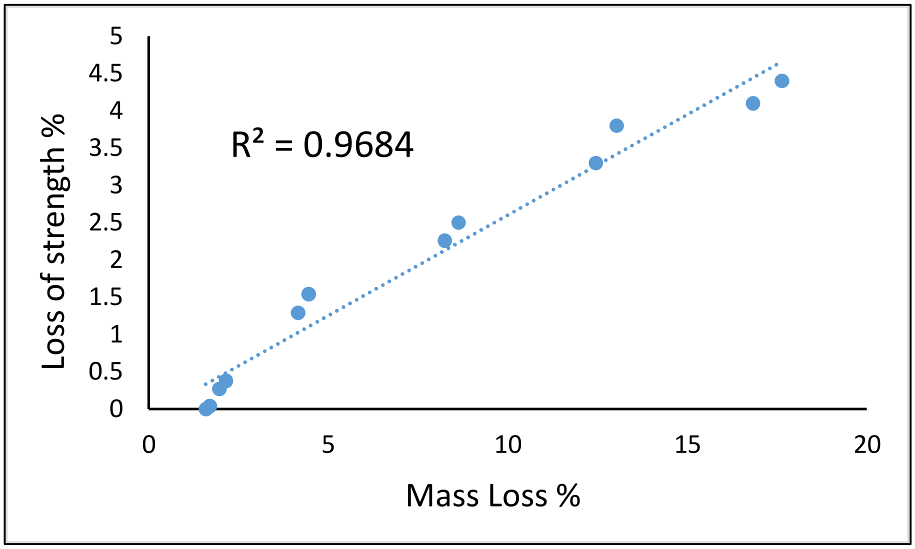
Fig. 5 Compressive strength loss of concrete sample as a function of time under stagnant and flowing surrounding conditions.

e. Relation between degradation and acid concentration

A linear relationship of time with degradation (mass loss %, loss of compressive strength % under different exposure situations was developed. Figure 6 (a & b) depicts the degradation over time at pH 1 and 2 for both surrounding conditions. The established equation for pH 1 yields a coefficient of determination (R^2) of 0.9741, indicating a nearly 3% significance level & co-efficient of determination (R^2) of 0.96884 indicating a nearly 4% significance level. From the value of R^2 it can be inferred that as the surrounding condition turns more acidic the losses are more.

(a)





(b)

Fig.6 Relation between acid and degradation in (a) pH 1 (b) pH 2.

Conclusion:

The primary goal of this study was to assess the durability of concrete in various environmental situations at different pH levels. The following observations were made:

1. The surrounding conditions in which the concrete has to be used play a significant role. For the same concrete mixture, the degradation losses were more for flowing surroundings as compared to stagnant ones thereby indicating the benefit of gypsum formation as a result of chemical reaction.
2. The acid concentration also affects the durability of concrete which is clear from the acid degradation relationship. The stronger the concentration the more degradation.
3. As the time of contact of the concrete increases the degradation also increases. This means time is also an important parameter when considering the durability of concrete in an acidic environment

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