Acid Attack on Concrete-A Review

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***Abstract* - Effect of acid on concrete is always studied as a part of research on concrete. This is because concrete is exposed to variety of environments from factories to sea structures. With Pollution in environment increasing every day, the rain has also become more acidic. Hence there is dire need to expose every kind of concrete we innovate to be tested in various percentages of acid solutions so that the durability and vulnerability aspects of the type of concrete invented is thoroughly studied. Acid is a substance which has sour taste and reacts with alkaline or bases to form salts which may be or may not be soluble in water. Acids are present in rain due to pollution of atmosphere. The acids predominant in the rain are carboxylic, sulphuric and nitric acids. These acids are deleterious to manmade concrete structures. This paper reviews various types of concretes tested with various types of acids.**

***Index Terms* - Acid, Concrete, Pollution, Durability.**

I.INTRODUCTION

Our Atmosphere is being polluted with industrial gases like never before. This results in water combining with gases such as sulphur dioxide (SO_2) and nitrogen oxides (NO_X) to form sulphuric and nitric acids respectively. Most of the SO2 and NO_X that cause acid rain is from the burning of fossil fuels. The major sources of SO_2 and NO_X in the atmosphere are:[1]

1. Burning of fossil fuels to generate electricity. Two thirds of SO_2 and one fourth of NO_X in the atmosphere come from electric power generators.
2. Vehicles and heavy equipment.
3. Manufacturing, oil refineries and other industries.

Winds carry SO2 and NO_X across borders making acid rain a problem for everyone.

Not all acidic deposition is *wet*. [1] Sometimes dust particles can become acidic as well, and this is called *dry deposition*. When acid rain and dry acidic particles fall to earth, the nitric and sulphuric acid that make the particles acidic can land on statues, buildings, and other manmade structures, and damage their surfaces and deterioration of internal structures of Reinforced cement concrete.

Concrete is basically an alkaline material. It undergoes degradation due to dissolution of calcium salts formed with related acids in acid rain.

The acids in acid rain causes Acid attack [2], which is the reaction of an acid and calcium hydroxide portion of the cement paste, producing a soluble calcium salt as shown below.

Acid X + CH   CX + H→

Acid + Calcium Hydroxide → Calcium Salt + Water

Acid attack [2] of concrete takes three forms.

a, In *acidolysis* hydration products react with the acid to form dissolved ions, leading to loss of solid material. Where acidolysis is the predominant mechanism, an acid solution penetrating the pores of concrete will start to cause some of the constituents to dissolve.

b, In *complexolysis,* insoluble salts form, some of which precipitate to cause expansion and cracking. Finally, some acids give complexes with calcium, aluminium, iron and silicate ions which produce much higher concentrations of these ions in solution than would otherwise be the case, again leading to dissolution. This can potentially occur at pH conditions under which cement would normally be relatively stable. Depending on the acid present, more than one of these deterioration mechanisms may be effective.

c, In *decalcification* Exposure to acidic solution also causes loss of calciumof C-S-H gel, leaving relatively weak silica gel behind.

Less aggressive acids such as phosphoric and humic acids (at foundation and basement part of structures) produce calcium salts with a low solubility. These low soluble salts can act as a partial inhibitor to the overall process by blocking tiny passage in the cement paste through which water flows. This reduces the amount of calcium salts that enter into solution and retard the overall process.

The calcium sulphate salt is produced by the reaction of the sulphuric acid and calcium hydroxide, which increases degradation of concrete due to sulphate attack. This reaction is shown below.

$H_2SO_4 + Ca(OH)_2 \rightarrow Ca(SO)_4 + 2H_2O$

Acid + Calcium Hydroxide → Calcium Sulphate+ Water (calcium sulphate product contributes to sulphate attack)

The dissolution of calcium hydroxide [2] caused by acid attack proceeds in two phases. The first phase being the acid reaction with calcium hydroxide in the cement paste. The second phase being the acid reaction with the calcium silicate hydrate. The second phase will not begin until all calcium hydroxide is consumed. The dissolution of the calcium silicate hydrate, in the most advanced cases of acid attack, can cause severe structural damage to concrete. Hence a detailed review of the various types of acids on concrete is need of the hour.

II. REVIEW

Michael John McCarthy, et al., [3] explain that reducing calcium content will potentially impart greater acid resistance to concrete. Pozzolanic materials are more effective in enhancing resistance to acid attack, since their combination with Portland cement will reduce free calcium hydroxide. Reduced rates of mass transport and enhanced strength achieved through the use of pozzolanic materials helps in improved acid resistance.

Hongguang et al., [4] modelled and tested concrete in sulphuric acid. Corrosion tests for concrete were carried out using uniform test design and nonparametric regression. Effects of water-cement ratio and pH value on the sulphuric acid corrosion mechanism for concrete were evaluated. Test results showed that when the pH value was 2.50, the sulphuric acid corrosion degree of concrete was the most serious. They found that, the whole process of sulphuric acid corrosion relies on the dissolution of $Ca(OH)_2$ out of concrete and consumption by H^+ in the soaking solution. Sulphuric acid reacts with $Ca(OH)_2$ in concrete, and the dissolution of generated soluble calcium salts causes the reaction process to continue and the alkalinity of concrete to decrease.

T.G. Nijland, et al, [5] explain that Acid attack is the dissolution and leaching of calcium hydroxide, from the cement paste of hardened concrete. This action results in an increase in capillary porosity, loss of cohesiveness and eventually loss of strength. In some situations, acid attack may be accompanied by crack formation and eventually disintegration, especially when the structure is subjected at one side to water pressure. Unlike sulphate attack the products formed from acid attack are not expansive, and leaching will only occur in structures that are relatively permeable. In high performance concrete systems containing cement pastes with a low content of calcium hydroxide, acid attack is relative slow and may involve only the finely divided calcium hydroxide crystals incorporated in the interstices of the calcium silicate hydrates, C-S-H.

Acid attack [6] on Portland cement concrete is not unexpected, since calcium hydroxide are readily dissolved by acids. Typically, acid attack leads to loss of binder and strength in concrete and eventually to loss of section. Unlike acid attack, sulphate attack commonly involves expansive reactions which fracture the concrete leading to ongoing degradation, loss of strength and function.

Jason Et al., [7] studied case of biological acid attack, anaerobic bacteria (found in the thin slime layer which develops on the sewer walls in direct contact with the effluent flow). Convert Sulphates in the sewage to sulphide. The sulphide is released in the form of dissolved hydrogen sulphide into the effluent stream. When the concentration is high enough, or due to turbulence, H_2S volatilises from the effluent and, carried by convection currents, it accumulates at the crown of the pipe, where it oxidises to elemental sulphur. A second set of aerobic bacteria (*Thiobacillus thiooxidans*) then uses the sulphur as food and excretes sulphuric acid as a waste product. This sulphuric acid goes on to attack the concrete.

Brian [8]suggests that the resistance to acid attack is related to the impenetrability of the concrete rather than the particular cement type used. Requirements for resistance to acid attack are thus often expressed simply in terms of limitations on concrete composition such as minimum cement content or maximum free water–cement ratio.

Resistance to other chemical attack is often only required in specialist applications such as chemical plants, or in contaminated land. The conditions may vary widely and most standards either do not address such issues or recommend the user to seek specialist advice.

Ravindra[9] explains that Portland cement-based concretes are vulnerable to acid attack and it is generally acknowledged that, for a given acid strength severity of attack, the acid attack resistance is not greatly influenced by the strength of the concrete. The depth of attack increases with Copper Slag content. The presence of Copper Slag increases the intensity of the acid attack. As the sulphuric acid leaching technique has been used in metal recovery from Copper Slag (Wang et al., 2013), this probably explains the low resistance of Copper Slag to H_2SO_4 acid attack.

Malkit Singh [10] concluded that, Sulphuric acid reacts with calcium hydroxide and produces calcium sulphate ($CaSO_4$). When sulphuric acid reacts with calcium silicate hydrate, silicate oxide in aqueous state is formed. Due to sulphuric acid attack, the concrete micro-structure becomes weak, cement paste is lost, and size of specimen reduces thereby resulting in reduction in compressive strength of concrete. He concluded that pozzolanic properties of both Coal bottom ash and Fly Ash causes reduction in permeability of concrete incorporating CBA which results in marginally lower percentage of loss weight compared to normal concrete.

Portland cement[11] concrete usually does not have good resistance to acids. Some weak acids, however, can be tolerated, particularly if the exposure is occasional. There are essentially three ways to improve concrete’s resistance to acids, (1) choosing the right concrete composition to make it as impermeable as possible, (2) isolating it from the environment by using a suitable coating or (3) modifying the environment to make it less aggressive to the concrete. Siliceous aggregates are resistant to most acids and other chemicals and are sometimes specified to improve the chemical resistance of concrete. Concrete deterioration increases as the pH of the acid decreases from 6.5. In fact, no hydraulic cement concrete, regardless of its composition, will hold up for long if exposed to a solution with a pH of 3 or lower. To protect concrete from such severely acidic environments, surface treatments are often used. German researchers tried to improve the resistance of concrete pipes exposed to long-term acid attacks in a pH range between 4.5 and 6.5. The fundamental solution of increasing chemical resistance by lowering concrete’s permeability was used to optimize concrete mix designs. The objective was to keep the erosion rate so low that a service life of about 100 years could be achieved It was found that a significant improvement in acid resistance can be achieved by carefully controlled use of fine supplementary cementitious materials. The main reason for the increased acid resistance of the concrete investigated was the formation of a very dense hardened cement paste and aggregate interface with very low porosities. The use of slag cement increased acid resistance as well as portland cements with silica fume (up to 8 percent by mass of cementitious material) or fly ash.

Carbonation by Contact with Water

Natural waters [11] usually have a pH of more than 7 and seldom less than 6. Even waters with a pH greater than 6.5 may be aggressive if they contain bicarbonates. Any water that contains bicarbonate ion also contains free carbon dioxide, which can dissolve calcium carbonate unless saturation already exists. Water with this aggressive carbon dioxide acts by acid reaction and can attack concrete and other portland cement products whether or not they are carbonated. A German specification, DIN 4030, includes both criteria and a test method for assessing the potential of damage from carbonic acid-bearing water.

Anthony Oswald, [12] states that, Every year, plants spend millions of dollars repairing or replacing failed concrete. The corrosive environment in many chemical plants subjects concrete to attack from a wide range of acids and alkalis. Because standard concrete is porous, non-corrosive chemicals pass through it easily contaminating the concrete itself and the ground below. A wide variety of coating and linings systems are available to protect concrete. The alternatives include thin-film coatings, filled and reinforced monolithic, membranes, acid brick, polymer concretes and sheet or moulded liners made of rubber or plastics. Generally, most of the coating and lining systems are epoxy, vinyl ester, polyester urethane, furan or silicate-based. The liners, for the most part, are natural or synthetic rubbers, polyvinylchloride, plastic or FRPs based on a variety of resins.

Singh, R., et al [13] performed durability tests in laboratory to evaluate the performance of pervious concrete made by blended cement containing limestone powder, silica fume, and metakaolin. Durability of pervious concrete exposed to sulphate and acid has been studied on specimen fully submerged in 5% sodium sulphate solution and 1% sulphuric acid solution respectively for 180 days. The study of partial replacement of cement by limestone blends shows that the ternary blends show good improvement against effect of sulphate and acid attack and presents good option of replacement as a substitution in pervious concrete. Due to densification of microstructure of cement paste in ternary blends, abrasion resistance is also improved.

Hewayde, E [14] studied five admixtures, which offer a range of potential improvement mechanisms, were used at various dosages to enhance the resistance of concrete made with Type 50E cement to chemical sulphuric acid attack. The resistance to sulphuric acid of concrete specimens incorporating these admixtures was measured and compared to that of control specimens. An attempt was made to determine whether there is a relationship between the effect of the various admixtures on mechanical strength and porosity and the resistance of concrete to H2SO4 attack. Results indicate that metakaolin reduced the mass loss of concrete specimens due to immersion for eight weeks in H2SO4 solutions having concentrations of 7% and 3% (by volume) by 38 and 25%, respectively, compared with that of the control specimens.

Ali Riza Erbektas et al., [15] compared biogenic and chemical acid attack for assessing the final stage of microbially induced corrosion of concrete (MICC). Paste specimens were exposed to either biogenic or sulphuric acid solutions. The solutions had an initial pH of 2. The biogenic acid attack caused higher changes in the chemical composition of the specimens. Flexural strength tests did not show a significant difference between the chemical and biogenic acid attack; however, this could be attributed to the short test duration.

S Xie, et al., [16] Deterioration of cement concrete specimens caused by simulated acid rain was investigatedby laboratory tests. Before and after cement concrete specimens were exposed to simulated acid rain, the neutralized depth, the compressive strength and the chemical compositions in the hardened cement paste were measured. The mineralogical composition of the concrete specimens was analyzed with XRD. The results lead to the following conclusions: the neutralized depth of the concrete specimens of all experiments can be described as a power function of exposure duration, CaO loss and the reduction rate of strength increased with H+ and decreased with SO_4^{2-} concentration in simulated acid rain. The original mineral compounds such as $[Na\ K]AlSi_3O_8$ and $[Ca\ Na][SiAl]_4O_8$ in the hardened cement paste are converted to $CaSO_4{\cdot}2H_2O$, $CaAl_2Si_2O_8$ and $Ca_3Al_6O_{12}{\cdot}CaSO_4$. And these are larger in volume so that the reaction with $SO_4^{2}-$ ions result in volume expansion and strength decrease.

Ravindrarajah, R,[17] propounded the results of a study on the corrosion of high strength concrete with silica fume subjected to 15% concentration of sulphuric acid, hydrochloric acid and lactic acid. Silica fume were used to replace 8% and 15% of the cement, by weight. The results showed that partial replacement of cement with silica fume had no effect on lactic acid resistance, improved the hydrochloric acid resistance and worsened the sulphuric acid attack. Sulphuric acid attack resulted in concrete disintegration at an almost constant rate, the hydrochloric attack rate was reduced with time, whereas the lactic acid attack resulted leaching of corrosion products, at a slower rate under stagnant condition.

Thomas Dyer [18] examined deterioration of buildings as a result of the deposition of bird excreta. Uric acid in bird excreta is broken down by fungi into urea and glyoxylic acid. This paper examines the effect of exposing stone and cement specimens to glyoxylic acid solutions. These materials were a limestone, a sandstone and two cement pastes – Portland and calcium sulfoaluminate cement. Specimens of these materials were submerged in acid solutions and deterioration characterised using mass loss measurements. The results indicate that the main processes involved in glyoxylic acid attack of the materials investigated are acidolysis and complex formation. No calcium glyoxylate salts were present in the degraded materials. Instead, a conversion of glyoxylate to oxalate occurred leading to precipitation of calcium oxalate compounds.

III. TEST PROCEDURES ADOPTED

1. Mortar specimens [19] in charters with dimensions of 12 × 6 × 6 cm moulded and kept in water for 5 days. Then in a lab environment with

a relative humidity of 55% and the temperature of 20°C they were cured. Tested samples were cut to expose the surface of aggregates. Comparison with conventional concrete has been done.15% solution of hydrochloric acid (HCI), 5% sulphuric acid (H2SO2) and 5% lactic acid (CH3CHOHCOOH) has been prepared and the samples were submerged in the solution. Weight changes of the samples have been investigated at specified intervals.. In all experiments, the concentration of acidic solution (pH) is kept constant by using red methyl as an identifier by titration against sodium hydroxide (Na OH).

2. 150 mm size cubes [20] were cast for all the mixes. Before immersion in the acidic medium, the specimens were subjected to a realistic curing practice, in which the specimens were cured in a water tank maintained at a temperature of 27 ±2°C for 7 days followed by continuous air curing in the lab environment at around 27 ±5°C and 50 ±10% RH until the age of 90 days. This curing regime was chosen so that the specimens would reach a consistent level of hydration before immersion in the aggressive solution. After subjecting the specimens to the above-mentioned curing regime for three months, the specimens were kept in the respective aggressive solutions for a period of up to one year. In order to evaluate the prepared specimens against resistance to acid attack, they were exposed to three environments, namely 1% sulfuric acid (H2SO4) solution, 1% hydrochloric acid (HCl) solution, and 1% nitric acid (HNO3) solution. Although many studies in the past have used pH value as an indicator of aggressiveness, recently it has been observed that the pH value being dependent on the degree of dissociation of radicals, it may not be a true indicator of the concentration of acid in the solution. Therefore, the concentration is used directly as an indicator of the aggressiveness of the exposure environment. The solution was renewed on a monthly basis in order to maintain uniform concentration and pH throughout the testing period. The specimens were stored in 200 litre capacity drums with up to 6 specimens immersed in about 120-100 litres of solution. The test program was concluded after 48 weeks. During this test period, measurements were done to study the effect of aggressive environments on the specimens. The tests were done in triplicate to confirm the reproducibility of the test results. Mass loss and compressive strength loss were evaluated.
3. During the chemical test [21] for each mixture three cylinders (Ø 270 mm, h = 70 mm) were subjected to a cyclic procedure of immersion in a 0.5% sulfuric acid solution and drying by air. The cylinders, fixed on horizontal axes, turned with a speed of 1 revolution per hour through separate recipients. Each point of the outer circumference was submersed during 1/3 of the rotation time. After each cycle, which lasted for 12 days, the cylinders were brushed with rotary brushes to remove weakly adhering concrete particles. The corrosion of the specimens was measured using laser sensors, connected with a computer. Out of those measurements the change of the radius of the different cylinders could be calculated. The measurements were performed before as well as after brushing the cylinders. In that way it was possible to determine the average change of the radius of the cylinders due to chemical reaction of the concrete with the sulphuric acid solution during the immersion as well as the change of the radius due to mechanical action of brushing the cylinders. The measurements with the laser sensors were also used to calculate the surface roughness of the concrete after brushing the cylinders. The surface roughness was expressed by means of the Ra-value.
4. The experimental program [22] for this research work is divided into two parts. In the first part, 60 number grade M20 concrete cubes of sizes 150mm x 150mm x 150mm, 18 number 150mm x 150 mm x 450mm concrete beams and 18 number 150mm x 300mm concrete cylinders for compressive, flexural and tensile strength tests respectively are casted using a water cement ratio of 0.69 and mix ratio of 1:3:4. The cubes, beams and cylinders were de-molded after 24 hours and cured for 7, 14, 28 and 60 days, the curing water having been mixed with 0, 5, 10, 15, and 20% of nitric acid by volume respectively. In the second part, for each percentage of acid, 12 cubes, 3 cylinders and 3 beams were cured in the water. And for each of the curing conditions above, 3 cubes each were tested for compressive strength after 7, 14, 28 and60 days and 3 beams

and 3 cylinders were tested for tensile and flexural strength respectively after 28 days of curing.

5. The relative acid resistance[23] was determined in accordance with ASTM C-267 (standard test method, for chemical resistance of mortars). Four types of acidic solutions were used: 5% sulfuric acid (H2SO4); 10% hydrochloric acid (HCl); 5% nitric acid (HNO3) and 10% acetic acid (CH3COOH), with the following pH values: 0.5, 0.25, 0.45 and 2.2, respectively. For each acidic environment and curing age, three concrete slices were subjected to each solution. The concrete slices were immersed in plexi-glass containers containing these acidic solutions for 90 days. These containers were kept covered throughout the testing period to minimize evaporation. After 2, 7, 14, 28, 56 and 90 days of immersion, each specimen was removed from the baths, brushed with a soft nylon brush, and rinsed in distilled water. This process removed loose surface material from the specimen. The specimen was then dried and weighed. The acid resistance was evaluated through measurement of the weight loss of the specimens.
6. A total of 162 cubes [24] were cast for this study. After about 24 hours, the steel moulds were removed and the cubes were cured by total immersion in water for the different curing ages of 3-day, 7-day and 28-day. Two different concentrations (75mg/l and 150mg/l) of hydrochloric acid (HCl) were prepared from 35% concentration of HCl and distilled water was used for the control solution. The choice of HCl for this study is based on the fact that it is staple acid on the shelf of many science laboratories and also it is one of the strong acids that can easily attack concrete. At 3-day, 7-day, and 28-day curing, the compressive strengths of the cubes were determined. Both crushed and uncrushed concrete cubes were soaked in the acid and water solutions for 48 hours after curing them in water. The dissolved solids concentrations were determined for both crushed and uncrushed concrete dissolved solids concentrations were determined by evaporating to dryness 25 ml of the thoroughly-mixed concrete solutions.
7. After 28 days of casting, [25]all the specimens were transferred to sulphuric acid environments in exposure solutions of very low pH (1.5), low pH (4.0) and neutral pH (7.0). The plain concrete tests were conducted with three replicates for each condition. For those, the level of deterioration of concrete was determined by the weight loss of material after drying and brushing the samples. Additionally, for tests on reinforced concrete samples, two replicates were used for each condition. In these cylindrical specimens, direct contact was not allowed between the acid and the reinforcement bars. In order to achieve this, the bottom and the top of the samples were covered with an acid resistant epoxy material, so, the acid would have to penetrate through the porous matrix in order to reach the concrete. The level of deterioration of the steel was determined by an indirect measure consisting on the corrosion electric potential. The specimens studied were immersed in tanks filled with their respective solutions of sulphuric acid and the pH was controlled at intervals of two days, time in which the pH increased about 15% through the release of alkalis and calcium from the concrete samples. Acid was added every two days while all the overall solutions were renewed every month.
8. The concrete cube specimens[26] of various concrete mixtures of size 150 mm were cast and after 28 days of water curing, the specimens were removed from the curing tank and allowed to dry for one day. The weights of concrete cube specimen were taken. The acid attack test on concrete cube was conducted by immersing the cubes in the acid water for 90 days after 28 days of curing. Hydrochloric acid (HCL) with pH of about 2 at 5% weight of water was added to water in which the concrete cubes were stored. The pH was maintained throughout the period of 90 days. After 90 days of immersion, the concrete cubes were taken out of acid water. Then, the specimens were tested for compressive strength. The resistance of concrete to acid attack was found by the % loss of weight of specimen and the % loss of compressive strength on immersing concrete cubes in acid water.
9. For acid attack, [27] for each percentage of glass fibre 6 concrete cubes of size 150x150x150 mm will be cast. Out of these, 3 cubes would be tested for 28 days compressive strength and remaining 3 concrete cubes were tested for residual

compressive strength after 10 days of acid immersion. The test program will consist of finding out residual compressive strength test due to immersion in 5 % concentration of acid. The moulds would be removed after 24 hours and the specimens will be kept in a clear water tank by immersing in a clear water. After curing the specimens in clear water tank for a period of 28 days, the specimens would be removed outside of the water tank and allowed to dry under shade. Also 9 cubes would be cast for each mix for durability studies. After water curing, the 3 cubes would keep in 5% concentration acid solution for 10 days acid curing.

10. Acid resistance [28] of concrete was determined in terms of weight loss and residual compressive strength. For this test, concrete cubes of size 150 mm x 150 mm x 150 mm were cast and stored in a place at a temperature of 27°C for 24 hrs and then the specimens were water cured for 28 days. After 28 days curing, the specimens were taken out and allowed to dry for one day. Initial weights of the cubes were taken. For acid attack test, 5% of dilute sulphuric acid (H2SO4) by volume of the water with pH value of about two was used (Fig. 2). After taking initial weights, the cubes were immersed in the above said acid water for a period of 28 days (Fig. 3). After immersion in the above said acid water, the weight loss and residual compressive strength of the cubes are determined.

IV. TEST PROCEDURES ADOPTED FOR ACID RAIN EFFECT

Various sulphurous pollutants[16] deposited over the samples can be oxidized and converted to sulfuric acid with higher acidity and SO_4^{2-}, concentration in some parts of sample’s surface. Such a fact is taken into consideration in cement concrete specimens exposed to simulated acid rain. Consequently, the effects of different H+ concentration as well as different SO_4^{2-} concentration at high acidity in simulated acid rain on deterioration of cement concrete are investigated in this study. All the cement concrete specimens used in the study were cast in cubes of 100 mm x100 mm x 100 mm using general Portland cement and slag cement as binders and crushed cobble stone with maximum diameter of 25 mm as coarse aggregate.

Periodic soaking experiment

The basis of the periodic soaking experiment [16] is that the erosion of concrete specimens can be accelerated by alternating between wetting and drying them. The concrete specimens subjected to a 6-day cycle; they are immersed in 20 L simulated acid rain solution for 5 days and then naturally dried them at room temperature for 1 day. The specimens were exposed to simulated acid rain solutions of pH 5.6 and 3.5 for 90 days and to solutions of pH 1.0 for 66 days. Experiments were carried out at room temperature C) and humidity (about 60%). It is very important to keep the pH value constant during the periodic immersion experiment process. The pH value of the immersion solution is hourly observed at the beginning of each experiment and adjusted to initial values with 6 mol l HNO3 every day by using a pHmeter. It is found from the observed results for 30 days that the pH changed greatly even after 1 day in the solutions of pH 5.6 and 3.5, while for the solution of Ph 1.0 the pH value hardly ever altered even after 5 days, so the experimental conditions are determined that the simulation acid rain solution is refreshed each day for pH 5.6 and 3.5 whilst for the pH 1.0 only after 5 days.

Spraying experiment

The spraying method [16] is based on several publications dealing with this methodology (Sersale et al., 1998; Johnson et al., 1996and Mart!ınez-Ram!ırez et al., 1998). The simulated acid rain solution is sprayed intermittently as small drops with diameter ranging from 0.2 to 0.5 mm by means of a proper ejector on specimen surface. The impact of the drops emulates the action of precipitation. As soon as the specimen is dry, the surface is sprayed again. The effects of acid rain are accelerated by means of these wetting and drying cycles. The concrete specimens were exposed to simulated acid rain solution at the flow rate of 60 ml h equivalent to the rainfall intensity of 7.7 mm day. In the same way as described for the soaking procedures, 6 day cycles are used consisting of 120 h (5day) spraying the acid solution and 24 h drying up at room temperature (about 1971 C) and humidity (about 60%). The exposure to the spraying drops is running continuously for 180 days. The total volume of sprayed solution is nearly equal to that of the annualrainfallin Guiyang, China (about 1198.9 mm)

V. REMEDIAL MEASURES ADOPTED

1. The intrusion[29] of a polyethylene or polyvinyl liner inside the existing pipe. This method is costly but much more economical, especially in large metropolitan areas, than pipe replacement.
2. The removal[29] of damaged concrete, the application of shotcrete and the roll on application of a protective plastic sheet.
3. Standard sealant[29] or epoxy coatings are a cost effective means to repair damaged concrete
4. Calcium silicates[30] can be used to fill the pores and decrease the permeability. This can be done by treating calcium hydroxide with diluted sodium silicate (also known as Water-Glass)
5. Pores [30]can also be filled by treating Calcium Hydroxide with Magnesium Fluosilicate followed by the formation of Colloidal Silicofluoric Gel to withstand acid attack
6. Allowing [30the concrete to dry before exposure causes the formation of a calcium carbonate film produced by the action of CO2 on lime. This film blocks the pores and reduces the permeability of the surface layer. Thus a precast concrete is appreciated.
7. The above method [30] is not a permanent solution. For more protection the concrete is subjected in vacuum to silicon tetra fluoride gas which reacts with the lime as follow.
   $2Ca(OH)_2 + SiF_4 \text{------>} 2CaF_2 + Si(OH)_4$
   This treatment can only be applied to precast concrete, which is then known as Ocrat-Concrete.
8. Surface treatments with Coal-Tar Pitch, Bituminous Paints and Epoxy Resins can be adopted
9. The w/c ratio [31] plays an important role in defining ac id resistance. For the majority of acids, a lower w/c ratio yields greater resistance to corrosion, principally as a result of a reduced rate of ingress through the corroded layer and a higher strength in this layer, resulting in reduced loss of mass as a result of mechanical wear.
10. The presence [31] of the polymer has the effect of enhancing a number of properties. however, in the context of acid attack, the main benefit to this approach is that the polymer components of the resulting cement matrix are largely unaffected by contact with acids, thus reducing the rate of deterioration. in addition, the polymer will usually fill the capillary porosity between cement grains to some extent, reducing porosity. range of polymeric materials can be used for polymer modification, including polymethyl methacrylate (pmma), polystyrene (ps), polyesters, styrene acrylic esters, styrene butadiene, polyvinyl acetate (pva), acryl ic polymers, polyacrylonitrile (pan) and epoxy resins
11. Resin injection[31] of cracked concrete is now an established repair technique, which is likely to provide renewed acid protection of concrete
12. Use surface hardeners [32] such as magnesium or zincfluosilicate or apply an oil-insoluble resin. Use high quality concrete; cement-rich mixes with entrained air generally perform better. Use carbonate aggregates Design system to prevent conversion of hydrogen sulfide to sulfuric acid. If industrial wastes are present, use cement with less than 8% tricalciumaluminate. Exclude moisture by providing roof shelter over sulphur bearing coal in cement based concrete storage bins. Cure concrete thoroughly. Then allow to dry at least 28 days in air. High alumina cement concrete has greater resistance, but may not provide a permanent remedy.
13. Unlike[33] limestone and dolomitic aggregates, siliceous aggregates are acid-resistant and are sometimes specified to improve the chemical resistance of concrete, especially with the use of chemical-resistant cement. Properly cured concrete with reduced permeability experience a slightly lower rate of attack from acids.
14. Anwar Khitab [34] mentions Silica concrete, Air entraining concrete , Blast Furnace concrete, High performance concrete for acid resistance.
15. New cement composites [34]have been developed during the recent years by combining it with nano-Titania (TiO2), Carbon nanotubes, nano-silica (SiO2), nano clay and nano-alumina (Al2O3), which have significantly improved the performance of these materials [6,13]. Besides nano composite cementitious materials, efforts are also going on to introduce nano-cement at commercial scale. The present commercial cement particle has its size in micrometers. It is a well-established fact that finer particles (nano) having more specific surface area can fill more effectively the pores in cement matrix, densify its structure, and might lead to superior strength due

to faster chemical reactions with water (hydration reactions). Or in other words nano materials might enhance the chemical resistance of concrete against acid attack.

VI. CONCLUSION

This paper has elaborately covered the various research works carried out. This has also covered the various basic test procedures adopted and also acid rain effect process. Remedial measures adopted to prevent acid attack on concrete is enumerated.

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