Methodology for simulating the process of microbiologically induced degradation of concrete by chemical exposure of specimens under controlled laboratory conditions

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Abstract. Research studies on the kinetics of the corrosion process that attacks concrete coincide in the amount of variables that interfere with the process, such as the impact of the pH levels of the corrosive environment and the surface of the concrete and the concentrations of biogenic sulfuric acid at the site. For this reason, it is vitally important to know the resistance of concrete to this attack in controlled laboratory conditions, defining a methodology that contributes to the development of new research related, for example, to the degradation of concrete in component elements of a sewer system.

1. Introduction

Considering the diverse environmental conditions to which concrete structures in sewerage systems are exposed, it is important to know the causes, consequences and solutions that can apply to corrosion caused by the action of biogenic sulfuric acid (BSA); for this it is necessary to note that the first evidence or record of corrosion in sewage systems was documented by Olmstead and Hamlin in 1900 [1]. This phenomenon is intense and has a great economic impact, in countries such as Germany 40% of 100 billion dollars are spent in repairing damages caused by BSA; in Flanders, Belgium, the biogenic corrosion represents a cost of 10% of the total cost of wastewater treatment. In Los Angeles, USA, about €400 million is spent on the restoration of pipelines affected by BSA [2].

Concrete is a construction material that looks like rock; it is a material composed of a coarse granular material, embedded in a cement paste, which serves as glue for the materials [3], and, in turn, is one of the most used materials in sewerage systems because of its high strength, low cost, great durability compared to other materials, and at the same time holds greater volumes of water compared with polyvinyl chloride (PVC) and metal tubes. Evidence has shown that corrosion is present in many concrete structures related used with water and in wastewater treatment. The alarming fact is that some of these facilities are significantly deteriorating after less than a decade of use [4].

The corrosion process that occurs in concrete structures by the action of sulfuric acid (SA), H₂SO₄, mainly in the pipes of sewerage systems, water treatment plants and inspection chambers, is known by different names such as: biogenic sulfuric acid corrosion, hydrogen sulfide corrosion and microbial induced/influenced corrosion [5].

This research seeks to establish the resistance of concrete mixtures, used in Colombia for the manufacture of sewer pipes, with reinforcements and the addition of antimicrobial compounds such as zeolites, to attack under controlled laboratory conditions and on-site exposure. Reviewing the behavior
of the types of reinforcement that will be implemented, in addition, evaluating the characteristics of the mixtures with zeolites to determine their efficiency without increasing production costs.

2. Methodology

This research work has an effect not only on the technological development of new concrete mixtures aimed at increasing the durability of concrete pipes exposed to biogenic sulfuric acid, but also on the sustainable and resilient development of sewage systems. Likewise, it allowed us to find a way to improve the physical simulation for the exposure to a corrosive medium of concrete specimens through chemical tests, as well as, the optimization and choice of the type of zeolite that would be incorporated into the mixture with which Concrete pipes are normally manufactured for wastewater drainage systems in Colombia, improving their durability conditions.

This research project is based on a quantitative methodology, since it responds to hypothetical deductive parameters, and seeks to analyze by experimental means, under controlled conditions, the phenomenon of corrosion that occurs in sewage systems. To conduct the research, the theoretical and practical procedures are established to determine results.

According to the above, the proposed experiments indicate that the concrete specimens are immersed in three sulfuric acid solutions with different concentrations; the weight of each concrete specimen is taken before immersion on an electronic balance accurate to ±10 Kg, as well as the moisture levels and compressive strength of the three specimens. The solutions are prepared with distilled water in three cylindrical tanks $\Phi = 1.03$ m, $h = 0.73$ m. with a capacity of 500 L, the concentrations of SA at 98% are 1%, 5% and 10%. 309 L of solution is prepared in each tank as shown in Table 1, as well as the amounts of solute and solvent, with the greatest amount of $\text{H}_2\text{SO}_4$ being used in the 10% solution with a total of 30.9 L of this chemical component as shown in Table 1.

| Solution concentration | Tank 1 | Tank 2 | Tank 3 |
|------------------------|--------|--------|--------|
| Volume of solvent in L  | 305.9  | 293.5  | 278.1  |
| Volume of solute ($\text{H}_2\text{SO}_4$ at 98%) in L | 3.1    | 15.5   | 30.9   |
| Solution in L           | 309    | 309    | 309    |

The pH and temperature of the solution are recorded before immersing the concrete specimens. The duration of the test period is two months; during this period the pH and temperature values of the solution with the specimens are measured, three times a day, to establish the changes that occur. The data collection is performed with a pH meter (brand HANNA, instruments reference HI 8013); a piece of equipment that measures temperature, conductivity and pH of solutions with a reliability level of 95%.

In each tank, the concrete specimens are placed, on a plastic base, in a grid pattern. The base is placed in order to prevent accumulation of particles, which are produced by the acid attack on the concrete surface, around the bottom of the cylinders. Subsequently, the proposed exposure time is waited before performing the tests and evaluating the corrosion of concrete cause by this phenomenon.

3. Experimental design

The SA is an aggressive chemical agent that has the ability to change the properties of strength and durability of concrete structures in sewerage systems. In order to propose the series of experiments the number of experiments, it is necessary, as a first step, to make a list of variables as can be seen in Table 2. In this way, it is easier to determine which variables can be controlled by the people conducting the tests.

Chemical corrosion tests on concrete specimens have a reliability rate of 95%, in which the techniques and events will be applied several times expecting the same result in all the phases; likewise, to ensure a high level of reliability in the data it will be necessary to have homogeneous conditions when applying the tests or measurements, in other words, at the same time, in the same place, with the same
analysts and with the same equipment. Regarding the validity of the data, the criteria used is the predictive model because the obtained data will have to be correlated with each other, and also the calculated variance should not mark a high value and should not generate a significant error in the respective analysis.

Table 2. Variables defined for the chemical tests.

| Variable/Environment generation chemical tests | Variable Independent |
|-----------------------------------------------|----------------------|
| pH solution                                   | X                    |
| Temperature                                   | X                    |
| Sulfuric acid concentration                   | X                    |

| Environment generation chemical tests         | X                    |
|-----------------------------------------------|----------------------|
| Physical characteristics of the specimens    |                      |
| Exposure time                                 | X                    |
| Dimensions of the cylinder                    | X                    |
| Resistance of the cylinders                   | X                    |
| pH of the concrete surface                    | X                    |
| Mix type (standard mixture for pipes and mix for marine environments) | X |
| Cylinder weight                               | X                    |
| Type of reinforcement (steel or metallic fiber) | X           |

For this reason, a certain number of specimens are used to be exposed to the environment, where the two variables (exposure time and concentration) are the most important factors for calculating a representative sample used for the tests.

The concrete cylinders shall be exposed to the following types of tests:

- Compressive strength.
- Mass loss.
- Permeability.
- Electrochemical tests (corrosion in the metal reinforcements).
- Detection of corrosion in the concrete.

The concrete specimens are 66 per tank, because two types of mixtures (33 cylinders of a standard mixture for pipes and 33 cylinders of a mixture resistant to sulfates for marine environments) will be used. For each of the two compositions, 5 samples will be used for the compression test, as a representative sample is needed that is reliable for a subsequent calculation of averages, to obtain a low random error, so for three exposure times 15 cylinders are needed for this test. To calculate the permeability after exposure to the environment, 3 cylinders supported in NTC Standard 4483 [6], are needed, and as 3 times are specified 9 cylinders are necessary to have reliable data in this test; and therefore 198 concrete cylinders are needed for exposure with the 3 concentrations per mixture, and this is the experimental arrangement of the two levels with mixtures without reinforcement.

Initial analysis of the specimens will be performed with eight cylinders, 5 of which will be for the compression test, which also serve to measure the initial mass of the specimens; and 3 for the permeability test, with the results being used to compare the impact of chemical sulfuric acid at 98% in concrete specimens according to the type of mixture. The amount of concrete cylinders to be used during the chemical tests are 144 of $\phi = 10$ cm and $h = 20$ cm, and 54 of $\phi = 7.5$ cm and $h = 15$ cm which must be handled appropriately to avoid affecting the reliability of the data can be seen in Figure 1.

Solutions of 1%, 5% and 10% will be implemented in short tanks of 500 L. To calculate the amount of solute and solvent it is necessary to predict the volume displaced by the cylinders upon being introduced into the tanks volume. According to this, solution volume per tank is 309 L and the volume of the solute varies in each of the tanks.
The factorial arrangement in this experiment phase consists of all the possible combinations of the levels and the treatment factors, in the tests of mass loss and strength it is a $3 \times 3 \times 2 \times 8$ arrangement; and in the permeability test the arrangement is $3 \times 3 \times 2 \times 3$. These combinations are useful to generate the number of specimens that should be used for a specific phase of experiments.

**Figure 1.** Exposure of concrete specimens.

### 4. Materials, safety equipment, and test methods

#### 4.1. Materials

**4.1.1. Concrete test specimens.** In the tests, cylindrical concrete specimens are used, which are used to assess the corrosion in the concrete mixtures. All the concrete specimens are prepared under the NTC 550 [7], standard and will be supplied by the cement manufacturing company TITAN S.A., with the specifications of the mixture used for making concrete pipe and a mixture for marine environments that is resistant to sulfate attack; these mixtures are dry with a low water cement ratio, to obtain a concrete with high density, low absorption, low permeability and long durability, produced under NTC Standard 1022 [8]. The cylinders used have a drying period of 28 days and a resistance of 350 Kg/cm$^2$. A total of 198 cylinders are exposed to chemical attack.

**4.1.2. Sulfuric acid.** For this research is necessary to use 49.5 L of sulfuric acid, with a purity of 98%, this chemical component has a brownish color, is a highly corrosive mineral acid and is an oily liquid. It is available in aqueous solutions of between 33% and 98%, its properties can be seen in Table 3; the acquisition of this chemical in Colombia involves various permits and certificates required by the State in order to handle this substance. All this is carried out through the Ministry of Justice, as it is the body in charge of and responsible for ensuring that this tool is used for a proper purpose.

**Table 3. Physical properties of sulfuric acid at 98%.**

| Property                          | Value  |
|----------------------------------|--------|
| Molecular weight in g/mol        | 98.08  |
| Physical state                   | Liquid |
| Boiling point (°C, 760 mmHg)     | 310-335|
| Melting point in °C              | 3      |
| Specific density at 15.60 °C     | 1.84   |

There are two methods of industrial manufacture or production of sulfuric acid; the lead chamber process and the contact process. This acid is used as a catalyst in the manufacture of fertilizers, herbicides, glue, oil purification, in the leather industry and as an agent in the production of explosives.

**4.1.3. Water.** The water that is used to prepare the solutions is distilled, because a high level of purity so that the acid does not react with other minerals contained in drinking water from the aqueduct of the
municipality of Tunja. The distillation process guarantees the removal of minerals, and if done correctly, the water should contain only oxygen and hydrogen molecules, and have a pH level of 7.

4.2. Safety equipment
The handling of sulfuric acid is a process that requires individuals to protect themselves from this chemical, which is why safety equipment is a mandatory requirement so that no part of the body is affected by this substance, and is necessary in order to conduct this research. The minimum protective equipment necessary can be seen in Figure 2 and it includes:

4.2.1. Plastic masks. Plastic masks which function to protect the face, which is the body part most susceptible to damage during the handling of SA.

4.2.2. Rubber clothing. A complete set of rubber clothing (trousers and jacket) is responsible for safeguarding the skin; rubber gloves are also used for the hands for a better handling of this substance.

4.2.3. Rubber boots. Resistant to chemicals, which are certified against any risk and also include a steel toecap to protect the toes from blows.

4.2.4. Storage and final disposal. The storage of sulfuric acid is carried out in a suitable cabinet for this purpose, with the key only being accessible to people who will conduct the project and who have the proper knowledge of the dangers of this product. Signs are placed all around the laboratory, but in places near to the sulfuric acid it is increased indicating the substance and the risk that a person faces if they are not sufficiently cautious. Notices are placed on the access door leading to the tanks, where the tests are carried out in the mentioned project, and the information placed there is preventive and informative.

As a precautionary measure, a fire extinguisher should be placed at the exit to the room where the experiments are carried out, and should have an adequate distribution in order to minimize risks. The labelling of the substance includes information about the associated risks and actions to be taken in an emergency; according to current international legislation for the handling of chemicals, a notice is placed at the entrance to the testing room with all these specifications of the international chemical safety cards (ICSC) reference: 0362 of the international programme on chemical safety (IPCS).

4.3. Test to be performed

4.3.1. Compressive Strength Test. The compression test of the concrete cylinders is conducted under NTC Standard 673 [9]. Prior to testing, the cylinders are subjected to a process of cleaning, brushing and drying. The capping that is used is neoprene in accordance with NTC Standard 504 [10]. The equipment used for the test is a digital hydraulic press with a reliability level of 95.45% [11,12].

4.3.2. Mass loss. A positive value in the average change in radius (either decrease or increase of the radius with regard to the initial radius) of the different cylindrical specimens versus the number of measurements means that the concrete swelled and a negative value indicates a loss of material of the concrete [13].
4.3.3. **Permeability test.** The method for the permeability test is specified in NTC Standard 4483 [6]; this test aims to determine the permeability coefficient $K$, by applying a pressure to one face of the specimen equivalent to 0.5 MPa, for 4 days. Once the specimen is saturated, and the flow has been adjusted to the opposite side, successive measurements of the volume flow are made to verify that the flow has been constant. Once the flow is established to be constant, the volume of water passing through the specimen in a given time period is determined.

4.3.4. **Test to determine the pH of a concrete surface.** NTC Standard 3696 [14], describes the method for determining the pH of a concrete surface attacked by an acid. The process described by the Standard is performed with litmus paper. However, there are other methods to record the pH variations in materials; one of those is the phenolphthalein test.

Phenolphthalein is a colorimetric pH indicator. It is an organic molecule which has two different structures depending on the pH, one of which is stable at an alkaline pH above 9, and the other at an alkaline pH less than 9. The test uses a 1% phenolphthalein solution in alcohol and is applied by spray or drops on the concrete surface; if the surface becomes pink, the pH is less than 9.

5. **Data collection and analysis**

The indicated time for the collection of data depends on when the specimens are introduced into the tanks, given that one hour too long or one hour too little in the exposure of the cylinders can affect the reliability of the data.

All data will be organized in Excel due to its wide applications in areas such as data analysis, probability and statistics, and an analysis of variance (ANOVA) will also be performed to determine the variance of the data and its reliability level. The ANOVA is a very flexible method that allows statistical models to be created for the analysis of experimental data whose values have been observed in various circumstances.

Essentially, it is a method for dividing the variance of the dependent variable in two or more components, each of which can be attributed to an identifiable source (variable or factor); in turn, the well-known analysis of variance is the most accurate method for calculating the variability of a measurement system, because it has the advantage of quantifying the variation due to the interaction between the operators and the parts.

For every cycle, the cylinders are measure twice: once before and once after brushing. The alternating increase and decrease of the radius correspond to alternating expansion and material loss of the concrete. The expansion of the cylinders occurs during the immersion in the sulfuric acid due to the production of expansive reaction products, such as gypsum. The decrease of the radius is mainly due to brushing of the cylinders but also is occur partially during immersion (see Figure 3). Once the expansion of the concrete is too large, loss of adhesion of the expanded part occurred.

![Figure 3. Variance analysis end error bars.](image)
6. Conclusion
The corrosion of concrete structures is very common in the world; it is a silent phenomenon that must be fought because of the large amount of money that is lost by performing ongoing maintenance works. The experimental design in a research project based on laboratory tests is essential because it identifies the number of treatments that are done during the practice phase.

The test specimens are submerged in a sulfuric acid solution are replenished at regular times, often one every week, or the pH of the solution is kept at a certain level by titration. The deterioration of specimens is followed up mainly by investigating the mass loss and change in compressive strength of the specimens a key for has good results is the methodology of develop of process in the lab between the different test procedures.

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