Effect of temperature and acidity of sulphuric acid on concrete properties

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ABSTRACT

Concrete corrosion caused by sulphuric acid attack is a known phenomenon in sewer systems, resulting in significant economic losses and environmental problems. However, there is a scarcity of reported laboratory simulations and experimental work investigating the contributing factors controlling the corrosion. In this EPSRC (Engineering and Physical Sciences Research Council, UK) funded investigation the effect of temperature and the acidity of sulphuric acid solution on concrete specimens extracted from brand new concrete sewers has been investigated. In this investigation the concrete samples are submerged in three sulphuric acid solutions (pH = 0.5, 1 and 2) for 91 days under different temperatures (10ºC, 20ºC and 30ºC). Mass loss and compressive strength of the concrete specimens were tested and recorded at 7, 14, 28, 42, 56 and 91 days providing interesting data for visualising the changes taking place in the concrete samples (change in properties) during the time of immersion. The results revealed that samples overall mass increased at the early stages of the corrosion process. It also was observed that the overall mass of the samples decreased significantly at the later stages of the testing process with respect to the acidity of the solutions used.

Although the change in temperature did not have a significant effect on the compressive strength of the tested samples , rise in temperature however, had considerable effect on the mass loss of the concrete samples which were immersed in the most aggressive solution (i.e., pH=0.5 and temperature = 30ºC) at 91 days. This research clearly demonstrated a high correlation between the acidity of the solution and the rate of corrosion with respect to time.

KEYWORDS

Concrete corrosion, sulphuric acid attack, corrosion rate, mass loss, compressive strength

1. **Introduction**

The degradation of concrete sewer pipes by sulphuric acid attack is a substantial challenge globally, resulting in environmental impacts and economical losses of billions of dollars annually. Replacement and rehabilitation requirements related to the corrosion of concrete sewer pipes result in annual costs of $130 million in the UK (Water UK, 2013a, 2013b) and $120 million in Germany (Kaempfer and Berndt, 2013), which is a constantly growing threat for aging pipe sewer networks.

Concrete sewer pipe structural vulnerability is predominantly caused by sulphide corrosion which is dictated by the presence and high activity of sulphuric acid on the pipe wall and crown surfaces.

Generally the corrosion process goes through a three step chemical process: the sulphate contained in the wastewater transforms into sulphide (Figure 1), before the sulphide is released into the air in gas form, where the hydrogen sulphide is oxidised on moist surfaces into sulphuric acid (Parker, 1945a, 1945b; Vollertsen and Nielsen, 2008). The surface pH of new concrete pipe is generally between 11 and 13. Cement contains calcium hydroxide, which neutralises the acid. In active corrosion areas, the surface pH can drop to 1 or even lower and can cause a very strong acid attack. The corrosion rate of the sewer pipe wall is determined by the rate of sulphuric acid generation and the properties of the cementitious materials. As sulphides are formed and sulphuric acid is produced, hydration products in the hardened concrete paste (calcium silicate, calcium carbonate and calcium hydroxide) are converted to calcium sulphate, more commonly known by its mineral name, gypsum [ASCE 1989]. Gypsum provides little structural support, especially when wet. It is usually present as a pasty white mass on concrete surfaces above the water line. As the gypsum material is eroded, the concrete loses its binder and begins to spall, exposing new surfaces. This process will continue until the pipeline fails or corrective actions are taken.

To understand the process of concrete corrosion and its rate, accelerated experiments with the use of sulphuric acid have been undertaken. Jahani et al (2001a&b) exposed concrete samples to a sulphuric acid solution of 2-3 pH over 72 days, where a corrosion rate of 0.82mm/year was observed. In a research by De Belie et al (2004) subsequent steps of immersion and drying, combined with mechanical abrasion, were applied to simulate events occurring in sewer systems. To simulate sulphuric acid attack, three cylinders of each concrete type were subjected to 10 attack cycles consisting of an alternated immersion in a 0.5% sulphuric acid solution (initial pH 0.9–1.0), drying by air and brushing. They also assessed the effect of W/C ratio and the cement type on the corrosion rate. Gutierrez-Padilla et al (2009) estimated corrosion rates of 2.19, 0.76 and 0.18mm/year for concrete samples exposed for 64 days in 0.5%, 0.2% and 0.05% sulphuric acid solution. Most research on the resistance of concrete to sulphuric acid attack has considered the effectiveness of the change in concrete mix design on concrete resistivity (Bassuoni and Nehdi, 2007; Hewayde et al, 2007; Nnadi and Lizarazo-Marriaga, 2013). However, more rarely investigated is the effect of the main practical environmental factor (i.e., temperature) on chemical corrosion.

The current study is a part of an extensive project supported by the Engineering and Physical Sciences Research Council (EPSRC) on the assessment of the remaining life of the cementitious sewer pipes in the UK. The research involves both lab and field experiments and investigates the parameters affecting sulphide corrosion of concrete sewers and consequently the structural reliability of the sewers. In this paper the results of the lab experiments are presented. The aim is to assess the establishment of the corrosion process on concrete samples exposed to sulphuric acid solution with different temperature regimes and different levels of acidity, which has not been investigated in depth previously.

The deterioration of concrete could be evaluated by percentage of mass loss with respect to time (time of exposure to acid solution) under laboratory conditions. This also could be extended to the variations in the compressive strength of the samples tested within the context of the mechanical property of the concrete.

The output of this study can be helpful for research in the area of modelling the deterioration of concrete sewers as well as service life prediction and reliability analysis of these types of corrosion affected pipelines (Mahmoodian and Alani, 2013; Yuan et al, 2013; Alani et al, 2014; Mahmoodian and Alani, 2014).

2. Experimental work

To consider the effect of temperature and level of acidity on concrete properties, a test plan is proposed in this study based on the immersion of concrete samples into sulphuric acid and measurement of the mass and strength loss of the specimens. The concrete samples are submerged in three sulphuric acid solutions (pH = 0.5, 1 and 2) for 91 days under 10ºC, 20ºC and 30ºC temperature regimes. Therefore, a total of nine series of test specimens will be investigated (three temperature levels and three pH levels). Mass loss and compressive strength of the concrete specimens are measured after 7, 14, 28, 42, 56 and 91 days of immersion.

2.1. Sample preparation

Manufacturing process of concrete pipes has a significant effect on durability related properties of concrete pipes such as permeability, porosity and water absorption (Binici et al 2012). While in the most of the laboratory based experimental investigations the concrete specimens are fabricated in-situ (in the laboratory) (Jahani et al 2001a&b, Hewayde et al, 2007 and Nnadi and Lizarazo-Marriaga, 2013), in order to simulate the real field condition, in this research however, concrete cubes were cut from a brand new sewer pipe. This approach ascertains the high quality as well as the uniformity (in size) and homogeneity (consistency of the mix) of the samples used in this research.

A brand new non-reinforced concrete pipe produced by a concrete pipe manufacturer in the UK was selected for sample preparation. The diameter and the length of the pipe were 0.7m and 2.5m respectively and the manufacturer did not declare the concrete mix design due to commercial sensitivity of the design mix. It is important to point out that the aim of this investigation was not to investigate concrete design mixes and/or finding the optimum concrete design mix resistant against acid attack. The main aim of this research was to investigate the effect of environmental conditions (temperature and acidity) on the mechanical properties of concrete sewer pipes, therefore as long as the samples used were of similar dimensions and ingredients, the concrete mix design should not impose or be considered as a technical challenge or shortfall. Nevertheless, the samples used for this research were all in compliance with the sewer pipe design standard and code of practice in the UK.

Considering three samples for testing at six different immersion times for nine series of solution conditions, a total number of 162 cubic specimens were cut from the brand new circular concrete sewer pipe to be used in the experiments. In order to ascertain the compressive strength of the concrete before immersion, six extra samples were also prepared. Each cube had approximate dimensions of $100 \times 100 \times 100$mm and was cut with a diamond-blade rotating saw. However, as the process of cutting a circular pipe is very challenging and labour consuming, a tolerance of 10% for each side measurement of the cube was allowed (Figure 2).

2.2. Sulphuric acid baths

Nine containers made of acid resistant PVC with dimensions of 700x700x400mm and a volume of 196 L were filled to two-thirds of their height with sulphuric acid solutions (Figure 3). All sulphuric acid solutions were prepared by mixing de-ionized water with predetermined amounts of condensed sulphuric acid to gain the desired pH level. The temperature and pH levels of the sulphuric acid solutions were monitored daily using a digital thermometer with accuracy of ±0.1 and a digital pH meter with ±0.05 accuracy. Figures 4 and 5 show examples of pH and temperature monitoring records for sulphuric acid baths with pH=0.5 and temperature=10, 20 and 30^oC, respectively. Concentrated sulphuric acid was added periodically to the solutions to maintain the pH level within an acceptable range of the designated concentration.

2.3. Test procedure

As previously mentioned, 18 concrete specimens were immersed in each of the nine sulphuric acid tanks containing 130L of solution. Therefore, a total of 162 test specimens were oven dried at 105^0C until they reached constant mass, weighed using a digital scale (accuracy of ±0.01 g) and then immersed into the sulphuric acid tanks with pH = 0.5, 1 and 2 and three different temperature levels (i.e., 10^0C, 20^0C and 30^0C).

Measurements were performed at 7, 14, 28, 42, 56 and 91 days of sulphuric acid immersion; at each date three specimens were removed from each tank, rinsed and carefully brushed and oven dried at 105^0C until constant mass was achieved. The specimens were subsequently cooled at room temperature, weighed and prepared for compressive strength testing.

The percentage of mass loss at each date was calculated according to the following equation:

$$Mass\ Loss\ (\%) = \frac{M_1 - M_2}{M_1} \times 100 \tag{1}$$

where M_1 is the mass of the specimen before immersion and M_2 is the mass of the specimen after immersion. Mass loss is commonly used to evaluate the deterioration of concrete under acid attack (Ehrich et al, 1999; Hewayde et al, 2007; Nnadi and Lizarazo-Marriaga, 2013).

Compressive strength tests were also performed at 7, 14, 28, 42, 56 and 91 days using a hydraulic machine with a loading rate of 14.4 MPa/min as per ASTM C39 guidelines. Three identical specimens from each series were tested at each date and the average value is reported. The reduction in compressive strength of the corroded specimens was calculated as follows (ASTM C267):

$$\text{Reduction in compressive strength (strength loss)} = \frac{\acute{f}_o - \acute{f}_t}{\acute{f}_o} \tag{2}$$

where $\acute{f}_o$ is compressive strength of control samples (before immersion) and $\acute{f}_t$ is compressive strength after t days of immersion in sulphuric acid.

3. Results and discussion

3.1. Effect on mass loss

Figure 6 shows the evolution of the mass loss of the specimens for each temperature level. In the early stages, mass gain occurred for all the specimens. This mass increase had been found in other research undertaken by Nnadi and Lizarazo-Marriaga (2013). They describe this reaction as producing a decrease in density and an increase in volume. If the increase in volume is greater than the loss of density, mass increase could occur. However, the authors of the current research believe that the mass gain during the early ages can be explained by the ability of concrete to absorb the acid via micro-pores and the formation of gypsum that occurs under the concrete surface. The corrosion products under the surface layer of each specimen are not loose enough to be easily washed away, resulting in mass gain. As acid reaction continues, corrosion products at the surface become greater than what has been formed in the micro pores; they are loose enough to be washed away and so subsequent mass loss occurs. In Figure 7, degradation of the concrete samples with time is visually investigated. The production of a white coloured material on the concrete surface at the early ages of immersion is evidence of the creation of gypsum, but this corrosion product is not large enough or loose enough to be washed away from the surface of the specimen. At later stages, for example after 91 days (Figure 7g), the progress of corrosion has resulted in relatively substantial gypsum production; as this is washed away significant mass loss occurs.

It can also be observed that, within the first 56 days, the rate of mass change is not affected by temperature. However for 91 day specimens in pH=0.5, much greater mass loss is observed at higher temperature levels. This result, together with a visual inspection of the samples, reveals that, during the acid degradation process, the temperature of the sulphuric acid solution accelerates the mass loss by loosening the bonds between aggregates and cement paste. The main focus of large proportion of the available literature within the field has been on the effect of temperature on the bacterial degradation of concrete (Alexander et al 2013, Alani et al 2014 and House and Weiss 2014) and to the best of the authors' knowledge there are rather limited investigation results available on temperature effect on chemical acid attack progression in concrete specimens (Okochi et al. 2000 and Zhang et al. 2012). However, in practice concrete can potentially degrade differently in various climate and temperature conditions regardless of presence of bacteria. It also should be appreciated that the investigation of bacterial degradation of concrete, and in particular in cementitious sewer pipe scenarios, is a major research and development field which requires specialist and dedicated infrastructure and equipment as well as expertise.

The results of mass loss measurements presented in Figure 6 also clearly show that the trend of mass loss for the most acidic solutions (i.e., pH=0.5) is considerably higher than for the other two pH levels.

3.2. Effect on compressive strength

Figure 8 shows the change in compressive strength of concrete samples in each condition within time of immersion. The results confirm that the effect of temperature change on corrosion progress is negligible. However, the trend in the graphs demonstrates that the more acidic the solution, the greater the reduction in compressive strength. This is similar to the mass loss and can be also illustrated in the form of Figure 9. In this figure the mass loss and compressive strength after 91 days immersion in the three temperature conditions are illustrated. Both bar charts show the maximum effect caused by the most acidic solution (i.e., pH=0.5) on the concrete properties.

3.3. Relationship between mass loss and compressive strength degradation

The relationship between the mass loss experienced by all concrete specimens subjected to sulphuric acid and the reduction in their compressive strength is shown in Figure 10. It is observed that compressive strength declined as mass loss increased. This directly proportional relationship can be attributed to the fact that immersing concrete specimens in sulphuric acid results in loss of cement paste and structural integrity, weakening of the concrete matrix and a reduction in the specimen's diameter.

The graph in the figure is divided into four quadrants, with their point of intersection represented by the average compressive strength and mass loss of all the samples. It is clear from the figure that all the points for solutions with pH=0.5 are located in the upper right quadrant, which have above average values for both mass loss and loss in compressive strength. The mass loss and loss in compressive strength at the other two pH levels (i.e., pH=1 and pH=2) are considerably lower. This confirms the fact that the effect of acidity level on concrete resistance does not follow a linear correlation and, as the pH of the acid reduces, the chemical reaction occurs progressively.

4. Conclusion

This study investigated the effect of temperature and acidity level on the resistance of concrete to chemical sulphuric acid attack. Mass loss and loss in compressive strength of concrete samples extracted from a brand new concrete pipe were checked after immersion in solutions of three pH levels (pH=0.5, 1 and 2) and kept at three temperature levels ($T=10^{o}C$, $20^{o}C$ and $30^{o}C$) for 91 days.

It was noted that, at the very early stage of the corrosion process, concrete mass increased for all conditions. For the higher temperature acid solutions, greater mass loss was observed in the long term.

Overall, in the acid degradation process, the temperature of the sulphuric acid solution accelerates the mass loss by loosening the bonds between aggregates and cement paste. This results in aggregate loss and eventually higher depth of corrosion. This finding confirms the mechanical effect of temperature on the degradation process in concrete sewers.

It was also found in this study that the level of acidity of acid solutions progressively affects the concrete properties (i.e., mass loss and compressive strength).

It needs to be noted that mass loss and compressive strength were used in this research as major and common indicators for change in durability and mechanical properties of concrete subject to acid attack. However, other measures such as water absorptivity and permeability as well as chemical and/or microstructural analysis also can be used in future studies to further investigate concrete behaviour in an acidic environment.

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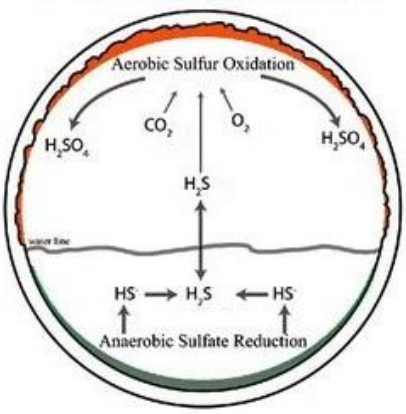


Figure 1. corrosion process in concrete sewers, [Water Stinks, Understanding sewer condition, http://waterstink.com/tag/concrete-sewers/]

Figure 2. cube specimens extracted from a brand new concrete pipe

Figure 3. Sulphuric acid bath with controlled pH value and temperature

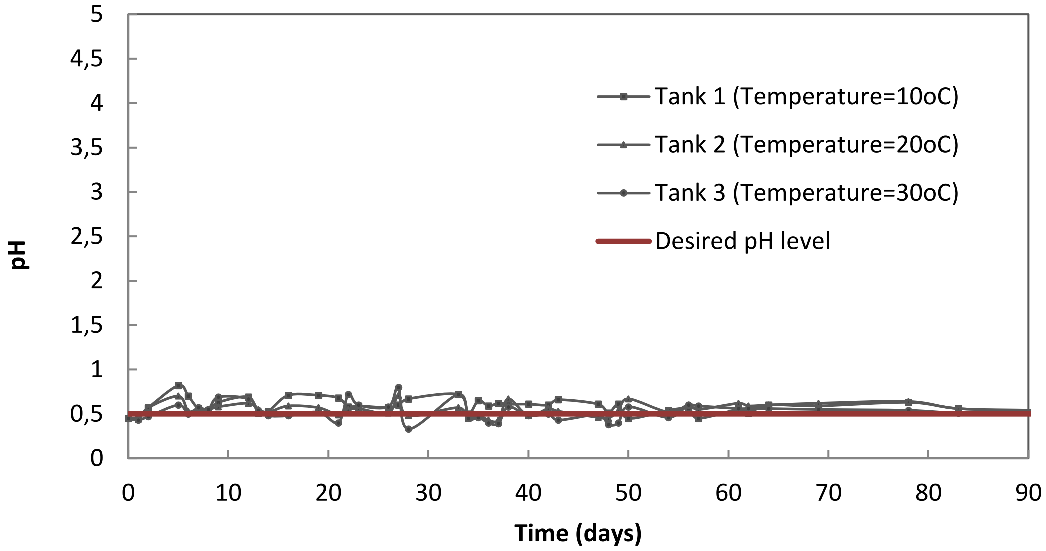


Figure 4.pH monitoring records for the three temperature regimes during period of immersion

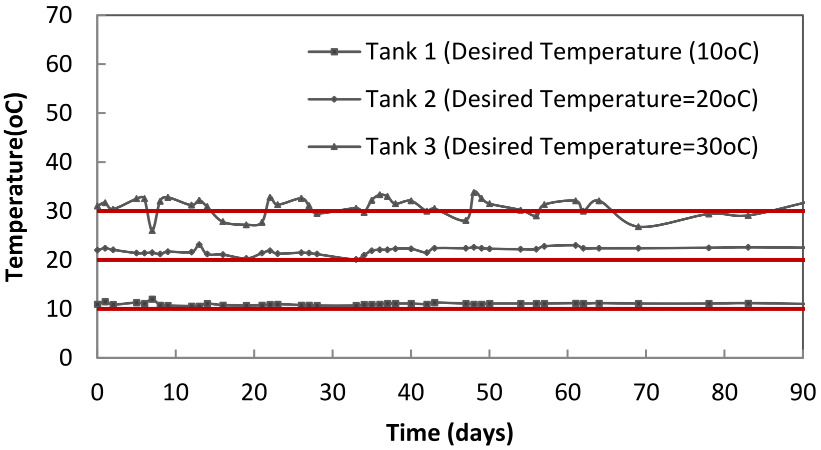


Figure 5.Temperature monitoring records for sulphuric acid solutions with pH=0.5 during period of immersion in the three temperature regimes

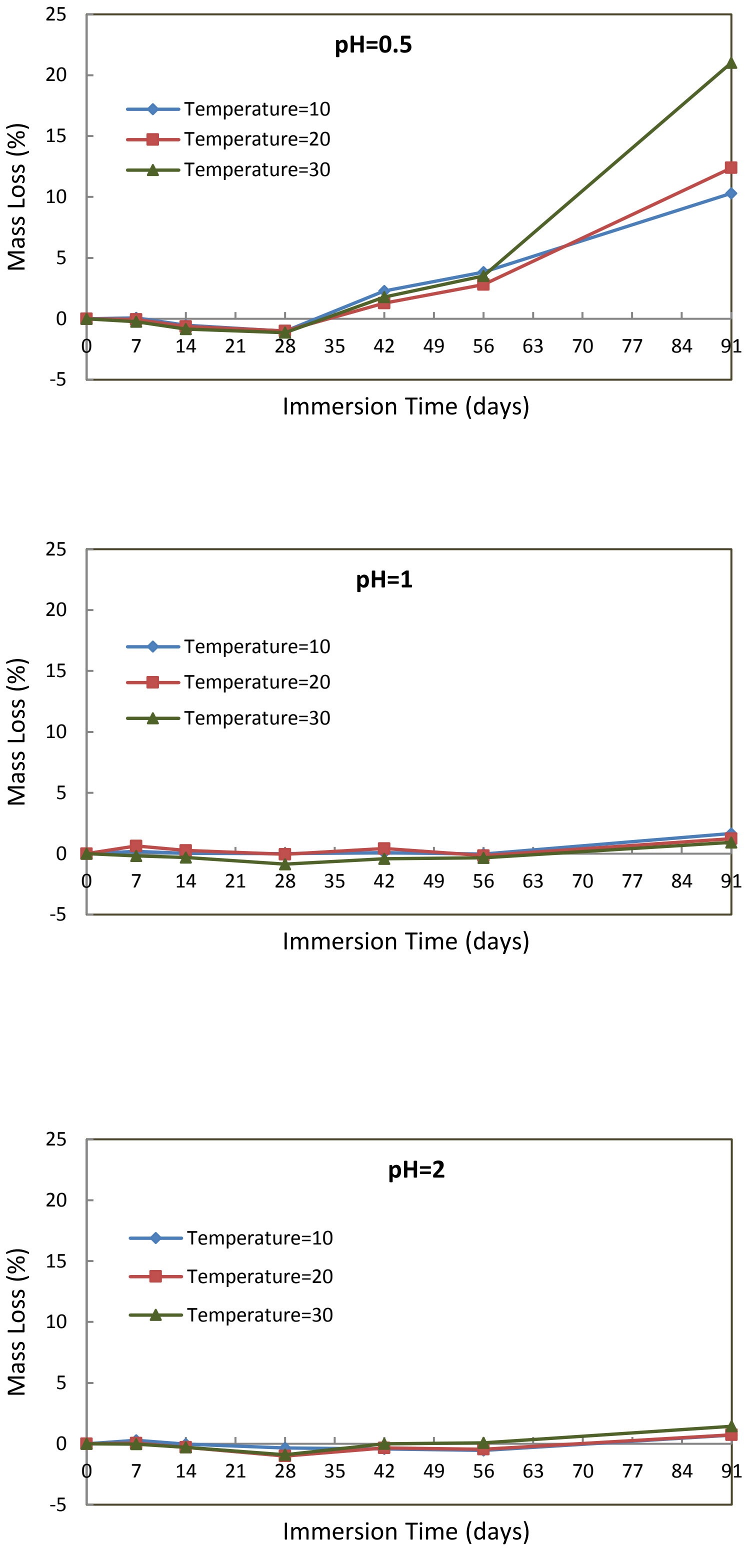
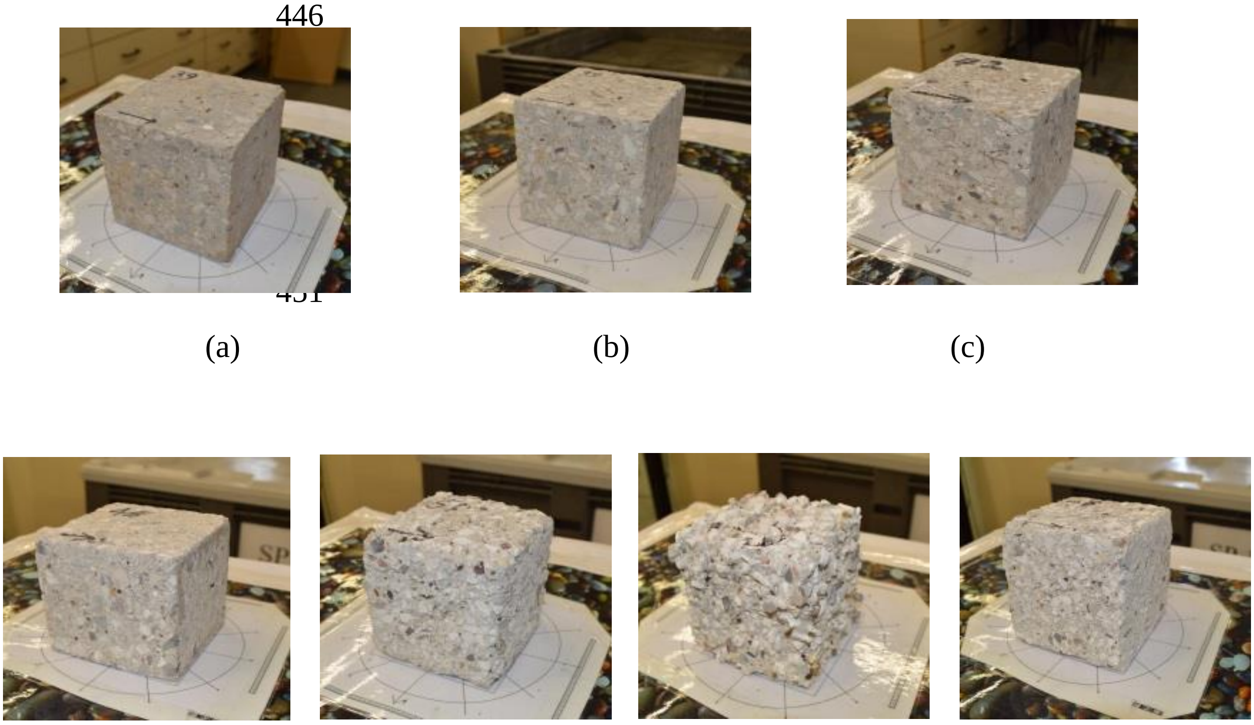


Figure 6. Mass loss of the specimens in three different sulphuric acid solutions and three temperature regimes


(a) (b) (c)

(d) (e) (f) (g)

Figure 7: (a) control specimen before immersion, (b) to (g) specimens after 7, 14, 28, 42, 56 and 91 days immersion in sulphuric acid, respectively.

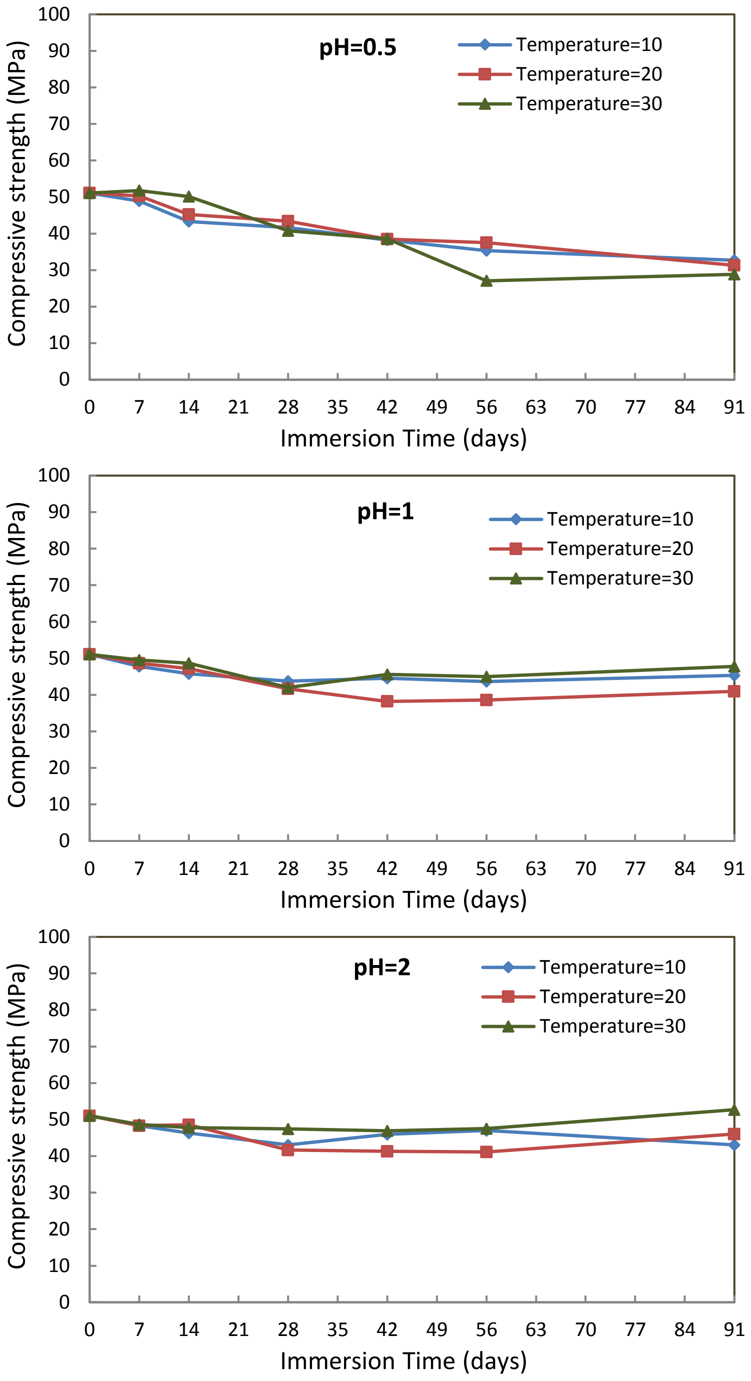


Figure 8. Compressive strength of the specimens in three different sulphuric acid solutions and three temperature regimes.

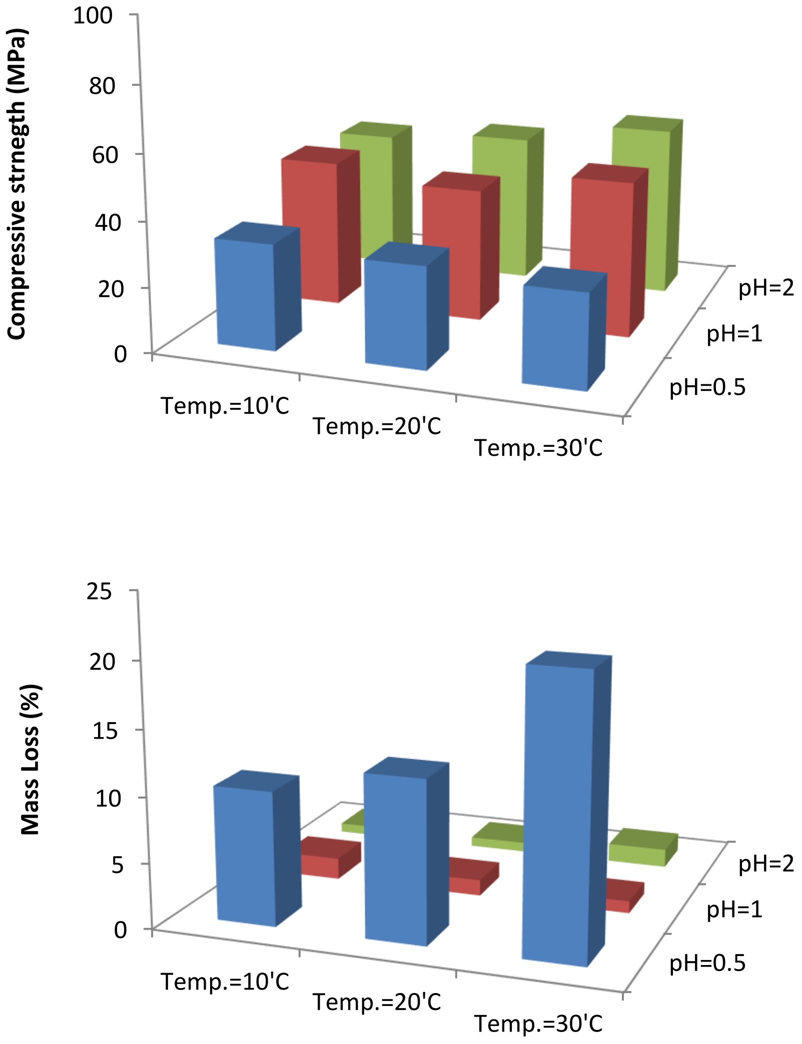


Figure 9. Variation in compressive strength and mass loss after 91 days immersion

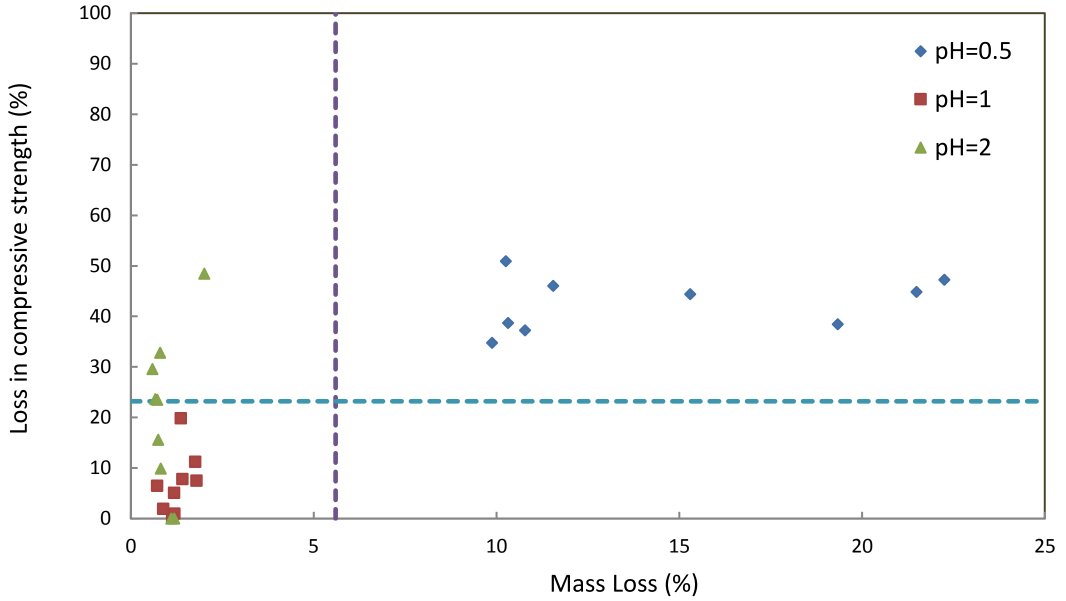


Figure 10. Relationship between mass loss of concrete specimens and loss in their compressive strength due to 91 days of immersion in sulphuric acid solutions