J. Mater. Environ. Sci. 6 (11) (2015) 3002-3014
ISSN : 2028-2508
CODEN: JMESCN

Resistance of two different types of concrete pipes used in sewer systems under sulfuric acid and sodium sulfate attacks

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Received 10 Jan 2015, Revised 12 Aug 2015, Accepted 13 Aug 2015
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Abstract

The behavior of two concrete used in sewer pipes was studied by immersion tests in acid and sulfate solutions at 25°C and 40°C, in order to study the influence of production method, cement and aggregate types used for each concrete. The gain of weight for concrete aged in Na_2SO_4 at 25°C which had been oven dried is explained by the absorption of solution into the empty pores of matrix. The delay in weight gain for concrete aged in Na_2SO_4 at 40°C is due to the fact that pores were initially filled with air, and the incoming solution had to compress/dissolve/diffuse air to allow the diffusion of solution into specimen. The mass loss for concrete aged in H_2SO_4 at 25°C and 40°C is due to acid reacting with alkaline substances. The weight gain for concrete aged in 50g/l Na_2SO_4 at 25°C result from water that fills the cracks and a mass of water used to precipitate a hydrated phase. These results allowed to obtain that: centrifugation method with a low w/c ratio, gave a dense and less porous concrete, characterized by a rapid diffusion of solution, that can be attributed to the disappearance of finer element's concrete during centrifugation (remove with water), which will facilitate the diffusion of solution into concrete. Portland cement with limestone and Portland cement with fly ash, limestone and dolomite aggregates, which were used, are sensitive to acid attack. These results prove that concretes' behavior mainly depends on the production method, cement and aggregate types and w/c ratio.

Keywords: Concrete, Sulfuric acid, Sodium sulfate, Visual observations, Gravimetric measurements, MEB.

1. Introduction

Biodeterioration of concrete sewer pipes is a major problem throughout the world [1–8]. The acidic environment in the inner walls of sewer pipes is the most destructive for concrete, which may damage the cementitious materials by mass loss and cracking, then reduce the materials service life which can cause the structural collapse and lead to structural failure [4,6,9,10]. According to the NM 10.1.008 standard [11] (EN standard 206), aggressive environments are divided into exposure classes and sewer pipes are categorized as exposure class XA3 [4,12]. The deterioration severely compromises the integrity of the infrastructure, which requires costly repairs and premature replacement of failed structures [5].

The processes leading to corrosion in concrete sewer pipes are highly complex [4]. As reported by several authors [4–9,13–19], the mechanism of the biogenic sulfuric acid corrosion (BSA) of concrete in sewer systems starts with the reduction of sulfate SO_4^{2-} to sulfide in domestic and some industrial waste waters by sulfate reducing bacteria (SRB). This biological reduction of sulfate to hydrogen sulfide occurs in the biofilm and the sediments under anaerobic conditions in the submerged part of the concrete pipe. Then, the hydrogen sulfide spreads to the atmosphere, condensates on the pipe wall above the waste water and is absorbed into the biofilm which covers the pipes surface, due basically to its low solubility and to the volatilization of the molecular form (H_2S_{aq}). Subsequently, the sulfur-oxidizing bacteria growing aerobically on this surface convert the hydrogen sulfide into sulfuric acid, which reacts with the concrete and causes the deterioration. In most cases, the pH on the surface of the pipe is very low, where the bacteria named *Thiobacillus thiooxidans* produces a vast amount of H_2SO_4 and reduces the surfaces' pH to 1 (as low as 0.5 in the worst case) [4,6,9,13].

Sulfuric acid has been identified as a corrosive agent in corroding sewer systems and it's responsible for the deterioration of sewer pipes [9,15,20].

An attack by sulfuric acid is a combined acid–sulfate reaction with the hydrogen ion causing a dissolution effect, coupled with a corrosive role played by the sulfate ion, which leads to the formation of two important corrosion products: gypsum and ettringite [10,15,16].

According to [4,8,15,20] the first step involves a reaction between the acid and the calcium hydroxide ($Ca(OH)_2$) and the C–S–H too, when portlandite is no longer available, forming calcium sulfate according to the following Eq. (1):

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

In the sequel of the attack, the gypsum reacts with the calcium aluminate hydrate (C_3A) to form ettringite, an expansive product (Eq. (2)) [8,15,20]:

$$3CaSO_4.2H_2O + 3CaO.Al_2O_3 + 26H_2O \rightarrow (CaO)_3.(Al_2O_3).(CaSO_4)_3.32H_2O \quad (2)$$

In contrast, calcium hydroxide reacts also with sodium sulfate or other sulfates, which are always present in wastewater, providing very high concentrations of SO_4^{2-} forming secondary gypsum, which can form secondary ettringite [17]. Sodium sulfate (Na_2SO_4) reacts with portlandite, monosulfate and unreacted C_3A to form gypsum and ettringite [20]. The formation of gypsum and ettringite can be expansive. The expansive products, that have filled the porosity of concrete, can cause expansion, cracking, deterioration, damage and finally a strength loss of the concrete [21,22].

Migration of sulfate ions into concrete has been reported to cause the following chemical reactions (Eq. (3) and (4)) [21]:

$$SO_4^{2-} + Ca^{2+} + 2H_2O \rightarrow CaSO_4.2H_2O \quad (3)$$

$$SO_4^{2-} + 2Ca^{2+} + Ca_4Al_2(OH)_{12}.SO_4.6H_2O \rightarrow Ca_6Al_2(OH)_{12}(SO_4)_3.26H_2O \quad (4)$$

According to Najimi et al. [23], the sulfate attack is one of several chemical mechanisms of concrete deterioration. The exposure of concrete structures in sulfate environments may lead to detrimental chemical, microstructural, and physical changes in the concrete matrix, resulting in serious deteriorations and a reduction of service life. As reported by Shanahan et al. [24], the resistance of concrete to sulfate attacks is determined by several factors, such as water/cement ratio, permeability and cement characteristics, which include the fineness and the composition of the cement.

According to [4,12,13] there are currently no methods available to evaluate the performance of hydraulic cements in acid- and sulfate-rich environments. In fact, the ASTM describes two test methods for assessing their performance in sulfate-rich environments (ASTM C452 and C1012). Girardi et al. [4,13] have criticized these test methods because they seem unable to predict the field performance adequately and they are performed on mortars, not concretes, taking into account only the expansion due to the formation of ettringite. Acid attack is generally ignored, though it causes mass loss and may accelerate the deterioration process induced by sulfate exposure.

This work presents the final phase of the biochemical attack of concrete and aims to study the behavior of two different types of concrete used in sewerage pipes in Morocco. To achieve this goal, an accelerated testing in the laboratory in sulfatic solutions (H_2SO_4, Na_2SO_4) was performed, to study the influence of the production method, the cement type, the aggregate type and w/c ratio on the corrosion of these two different types of concrete sewer pipes.

2. Materials and methods

2.1. Materials

The concrete pipes were especially prepared for this research with a composition that is frequently used by manufacturers of sewer pipes without reinforcement. Two pipes have been fabricated by using the method of centrifugation with a spin speed equal to 500 turns / min and the two others by using the vibration method. The centrifuged pipes were 100 cm in internal diameter and 300 cm long. Their thickness was 10 cm. The vibrated pipes were 80 cm in internal diameter and 250 cm long. Their thickness was 10 cm.

The manufacturing, removing from the mould and the storage of the pipes up to 30 days, were carried out in the factories, where these pipes are produced.

After 30 days, cylindrical specimens with a diameter of 95 mm and a height of 95 mm were cored directly from the pipes in transverse lines by the standard NF EN 12504-1 [25]. Figure 1 shows the coring phase of the test specimens using a core drill. To obtain linear surface, the thin layers not exceeding 5mm of the outer surfaces of specimens were eliminated, a small deviations localized were authorized. After rectification, the cored samples were stored in a keeping room with a temperature of 20±1°C and humidity ≥ 90 RH. Then, the samples were coded and weighed at the initial state. The mass absorption of three specimens added with a specimen for microscopic analysis for each test and for each material were monitored.

Figure 1: Coring of samples from: a) centrifuged pipes, b) vibrated pipes

Table 1 shows the characteristic parameters of the two different concrete specimens.

Table 1: Characteristic parameters of the two different concrete specimens

Code	Production method	Cement type (EN 197-1)	Cement (Kg/m^3)	Water (Kg/m^3)	w/c ratio	Aggregate type		Porosity (%) (NF P18-59)	Mass volume density (kg/dm^3)
						Gravel[1] 3/8 (mm) (Kg/m^3)	Gravel[1] 8/15 (mm) (Kg/m^3)		
VC	Vibration	CEMII/A-V 52.5N	300	150	0.5	350	750	12,5	2.352
CC	Centrifugation	CEM II/B-L 42.5N	400	170	0.425	Limestone (dolomite)[2]		7,76	2.503

[1] Gravel nature: limestone.
[2] More details were not given by the manufacturer.

2.2. Chemical test procedures

Three different types of accelerated tests were performed, to study the chemical resistance of concrete specimens:

a) Continuous immersion in 10 liters of sulfuric acid (H_2SO_4) solution 5g/l of SO_4^{2-}, with a pH=1 at 25°C. Continuous immersion in 10 liters of sodium sulfate (Na_2SO_4) solution 5g/l of SO_4^{2-} at 25°C. The specimens were kept in an oven at 105°C for 18 hours. Afterwards, the specimens were dried for a period of 3 hours to take the medium temperature. Then the specimens were placed in the test solutions. The solutions were renewed every month.
b) Continuous immersion in 10 liters of sulfuric acid (H_2SO_4) solution 5g/l of SO_4^{2-}, with a pH=1 at 40°C. Continuous immersion in 10 liters of sodium sulfate (Na_2SO_4) solution 5g/l of SO_4^{2-} at 40°C. The solutions were renewed every month.
c) Continuous immersion in 10 liters of 50 g/l sodium sulfate solution at 25°C, with a pH=7 (regulation was performed by addition of sulphuric acid). The solutions were renewed every month.

2.2.1. Gravimetric measurements

Every week, the weight of each sample was measured. After drying the samples with a cloth, their weight was recorded using a technical balance with a sensitivity of ±0.01 g.

The weight gain m(t) of each specimen was calculated by its initial weight M(0) and its weight after absorption M(t) as follows (Eq. (5)) :

$$m(t) = \frac{M(t) - M(0)}{M(0)} \times 100 \qquad (5)$$

M(t): Mass at time t (g)
M(0): Initial mass before exposure to sulfuric acid (g).

2.2.2. SEM-EDX

The microstructural analyses were performed using a SEM (FEI QUANTA 200) and a SEM (JEOL) which is equipped with devices for an energy-dispersive X-ray analysis (EDX).

3. Results and discussion

3.1. Visual observations

Figures 2 and 3 show the visual observations of the concrete specimens CC and VC respectively after nearly 300 days of aging in different test solutions carried out during this work.

On the other hand, the microscopic analyzes that follow later in this work were carried out on samples of concrete cut out from the most attacked areas of concrete specimens, in order to confirm the interpretation of visual observations.

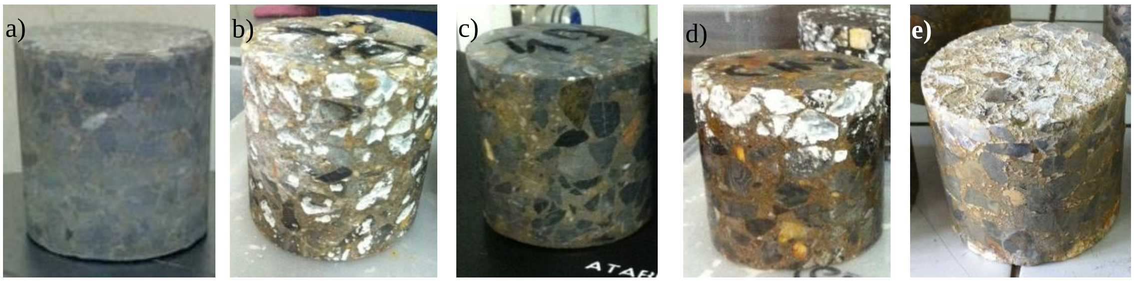

Figure 2: Visual observations of CC concrete specimens: a) initial state, b) aged in H_2SO_4 at 25°C, c) aged in Na_2SO_4 at 25°C, d) aged in H_2SO_4 at 40°C, e) aged in 50g/l de Na_2SO_4 at 25°C

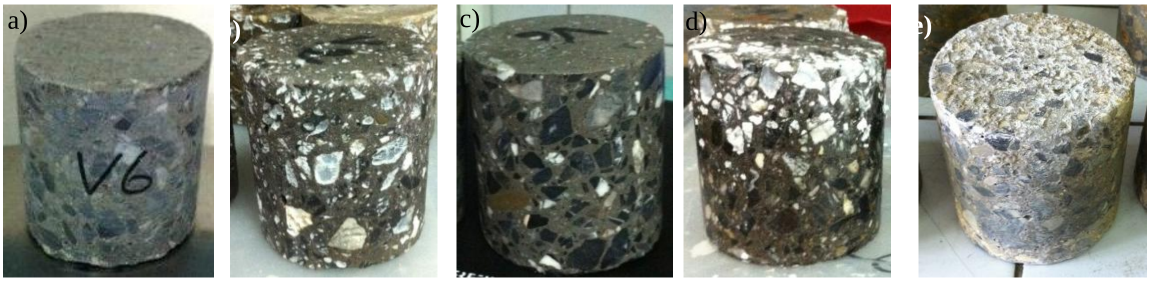

Figure 3: Visual observations of VC concrete specimens: a) initial state, b) aged in H_2SO_4 at 25°C, c) aged in Na_2SO_4 at 25°C, d) aged in H_2SO_4 at 40°C, e) aged in 50g/l de Na_2SO_4 at 25°C

According to figures 2 and 3, the same visual observations of the two types of concrete specimens in the various test solutions were found.

The deterioration of the concrete aged in H_2SO_4 (5g/l of SO_4^{2-}) solution at 25°C (figures 2.b and 3.b) was characterized after 55 days by a roughness of specimens' surface. The appearance of white deposits on the specimens and the leaching of the cement paste in the test solution proved that this degradation continued over the time. No cracking could be observed. For the concrete specimens CC and VC aged in Na_2SO_4 (5g/l SO_4^{2-}) solution at 25°C (figures 2.c and 3.c), a change in color of the specimens was observed due to the absorption of the solution, while the surfaces remained unchanged. For the concrete specimens CC and VC aged in H_2SO_4 (5g/l SO_4^{2-}) at 40°C (figures 2.d and 3.d), white deposits on the surfaces which were most exposed to the test solution and the leaching of the cement paste were observed. No cracking could be observed. For the concrete specimens CC and VC aged in 50 g/l of Na_2SO_4 solution at 25°C (figures 2.e and 3.e), a start of swelling and cracking of the surfaces which were most exposed to the test solution was found. For the concrete specimens CC and VC aged in Na_2SO_4 (5g/l SO_4^{2-}) solution at 40°C, a change in color of the specimens was observed while the surfaces remained unchanged.

According to O'Connell et al. [20] the acid deterioration of concrete cubes is characterized by the formation of a soft white substance (most likely gypsum) on the surface that is easy to remove. The regular examination of the concrete also revealed the complete loss of cohesion of the surface layer of the cement matrix after 12 weeks and there was no evidence of cracking at any point over the 6 months of the exposure period. Also, according to O'Connell et al. [20], white deposits began forming on the exterior of each prism as the attack progressed. These deposits were like a mushy substance, without any cohesive properties and have ''the consistency of cottage cheese", followed by a lack of cohesion and the spalling at the edges, possibly indicating the decalcification of the C–S–H phase. Irassar et al. [26] described the corrosion of the edges and corners and attributed this to the gypsum formation in the parallel veins to the sulfate attack front. According to O'Connell et al. [15], the experimental and in situ analysis of the concrete has confirmed that gypsum formation is one of the primary corrosion mechanisms involved in the deterioration of the cement matrix leading to a loss of cohesion in cementitious calcium compounds. Also [15] indicated that the build-up of gypsum can act as a barrier to further penetration, slowing an attack, however it has also been asserted that the rougher surface leads to a greater surface area to be attacked. According to Chang et al. [7], it could be observed by visual inspections that the specimens' surface of the concrete aged in 1% of H_2SO_4 becomes significantly rougher after only 21 days, which appeared to indicate that the surface layers of these portland cement concretes were more vulnerable to the acid attack. These visual observations show that both types of cements which were used are mainly vulnerable to acid attacks and the limestone aggregates which were used are reactive and they are degraded by the acid attack as indicated by [8, 18].

3.2. Mass variation

3.2.1. Immersion test in H_2SO_4 (5g/l SO_4^{2-}) and immersion test in Na_2SO_4 (5g/l SO_4^{2-}) at 25°C

Figures 4.a,b show the mass variation versus time of the concrete specimens CC and VC respectively exposed to sodium sulfate (5g/l SO_4^{2-}) and to sulfuric acid (5g/l SO_4^{2-}) solutions at 25°C. The evolution of the mass absorption of three specimens for each material was monitored.

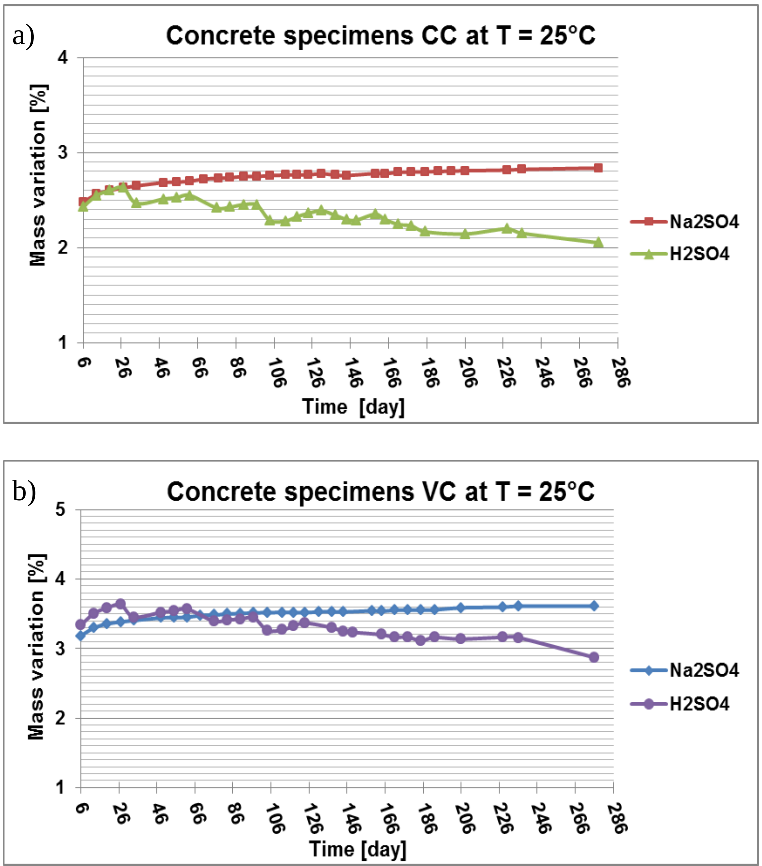

Figure 4: Absorption kinetics in H_2SO_4 (5g/l SO_4^{2-}) and in Na_2SO_4 (5g/l SO_4^{2-}) at 25°C of: a) CC specimens, b) VC specimens

For the concrete specimens CC and VC aged in Na_2SO_4 (5g/l SO_4^{2-}) at 25°C (figures 4.a and 4.b), a high absorption of the solution after 6 days of immersion was observed: About 2.48% for CC specimens and about 3.18% for VC specimens. During aging a slow and constant absorption of the solution was found. Thus, at the end of test an absorption of about 2.84% for CC specimens and an absorption of about 3.61% for VC specimens was noted.

The high absorption of the solution at the beginning of the test (specimens had been oven dried before being placed in the test solution) is explained by the filling of the empty pores of the matrix. Concrete specimens with a high porosity, have a high absorption after being oven dried. The delays in weight gains can be attributed to the bath solution seeping into the specimens. The process of the solution flowing into the specimens is slow due to the fact that the pores were initially filled with air, the air was trapped in the central part of the core and the incoming solution had to compress/dissolve/diffuse the air to allow the diffusion of more solution into the specimen.

On the other hand, for the concrete specimens CC and VC aged in H_2SO_4 (5g/l SO_4^{2-}) at 25°C (figures 4.a and 4.b), a same absorption of the solution after 6 days of immersion was observed: About 2.46% for CC specimens and about 3.34% for VC specimens. During aging, the weight gain for CC specimens (2.66% at 27 days) and VC (3.63% at 27 days) was still observed, until the first change of the solution after 4 weeks of immersion, when a decrease in mass of about 2.49% for CC specimens and of about 3.45% for the VC specimens was noted. Then, at the end of test, a decrease of about 0.40% for CC specimens and of about 0.47% for VC specimens was found.

The weight gain of the concrete specimens CC and VC (which had been oven dried before being placed in the solution bath), is explained as in the case of sulfate, by the filling of the empty pores in the matrix with the test solution. For the continuation of the gain in weight: That is just an intake of water by the specimens.

The mass loss is explained by the attack of sulfuric acid, which is an acid-sulfate reaction, namely, a hydrogen ion reaction causing an effect of dissolution and a corrosive reaction of the sulfate ions. When the acid reacts with the cement matrix [4,15], the first step involves a reaction between the acid, the calcium hydroxide ($Ca(OH)_2$) and the C-S-H too, when the portlandite is no longer available, forming calcium sulfate according to the following equation:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O \quad (6)$$

Subsequently, this quantity is hydrated to form gypsum ($CaSO_4.2H_2O$), whose appearance on the surface of the concrete pipe takes the form of a white pasty substance which has no cohesion properties. Thereafter, the gypsum reacts with calcium aluminate hydrate (C_3A) forming ettringite:

$$3CaCO_4.2H_2O + 3CaO.Al_2O_3 \rightarrow (CaO)_3.(Al_2O_3).(CaSO_4)_3.32H_2O \quad (7)$$

3.2.2. Immersion test in Na_2SO_4 (5g/l SO_4^{2-}) at 40°C

Figure 5 show the mass variation versus time of the concrete specimens CC and VC exposed to sodium sulfate (5g/l SO_4^{2-}) solution at 40°C. Three specimens for each concrete was followed.

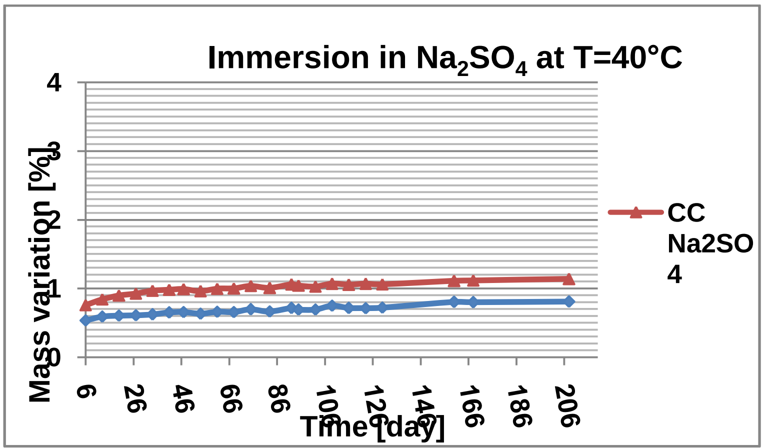

Figure 5: Absorption kinetics of CC and VC immersed in Na_2SO_4 (5g/l SO_4^{2-}) at 40°C

For the concrete specimens CC and VC aged in Na_2SO_4 (5g/l SO_4^{2-}) at 40°C (figure 5), an absorption of the solution after 6 days of immersion of about 0.76% for CC specimens and about 0.53% for VC specimens was observed. During aging, a slow absorption of the solution was found. At the end of test, an absorption of about 1.14% for CC specimens and an absorption of about 0.81% for VC specimens was noted.

Some authors have shown that the increase in mass in sodium sulfate [4] and in sulfuric acid solution [27] was due to the continuation of the cement hydration. These interpretations could not be used for our case, since the pipes were first cured for 30 days before the pipes were cored to obtain the specimens. Most of the hydration reaction would have been completed at that time. These interpretations were corroborated by the mass variation's results at 40°C (figure 5), because, if the weight gain was due to the continuation of the hydration reaction, the weight gains for the specimens at 40°C have to be higher (higher temperature means higher rate of reaction) when in fact the weight gains for specimens at 40°C were quite lower. Following these interpretations, different results and discussions of various authors, who can confirm our results, were summarized.

According to Girardi et al. [4], the specimens exposed to a sulfate solution showed a constant slow increase in mass, mainly due to the formation of calcium sulfate. As reported by Shanahan et al. [24], in the presence of sodium sulfate source, the main products are ettringite and/or gypsum. Depending on lime availability, calcium hydroxide interacts with sodium sulfate to form secondary gypsum. Consequently, the latter can also participate in secondary ettringite formation, which is responsible for the water adsorption and expansion. According to O'Connell et al. [15], in sodium sulfate solution calcium hydroxide primarily undergoes a decomposition to gypsum and subsequently to ettringite. Only when there is no sufficient source of calcium to continue the reaction the solution will start to attack the C–S–H phase. Finally, according to Brunetaud et al. [28], a sulfate attack may take a long time to damage concrete, especially in low w/c concretes.

3.2.3. Immersion test in H_2SO_4 (5g/l SO_4^{2-}) *at 40°C*

Figure 6 show the mass variation versus time of the concrete specimens CC and VC exposed to sulfuric acid (5g/l SO_4^{2-}) solution at 40°C. Three specimens for each material were monitored.

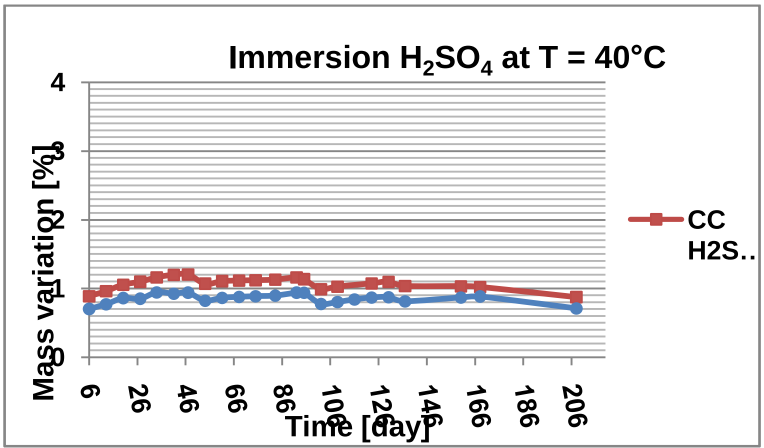

Figure 6: Absorption kinetics of CC and VC immersed in H_2SO_4 (5g/l SO_4^{2-}) at 40°C

As reported in figure 6, an absorption of the solution after 6 days of immersion for the both concrete specimens CC and VC aged in H_2SO_4 (5g/l SO_4^{2-}) at 40°C, was observed. The absorption was about 0.89% for CC specimens and about 0.70% for VC specimens. During aging, the weight gain due to the intake of water by the specimens was still observed, of about 1.20% for CC specimens and of about 0.94% for VC specimens followed by a decrease in mass. The decrease continued over time by the effect of sulfuric acid and temperature.

The mass loss was due to the sulfuric acid reacting with the alkaline substances in the concretes (cement paste and aggregate) [4]. As reported also by Girardi et al. [4] the portlandite reacts with sulfuric acid forming calcium sulfate more quickly than C–S–H. The aggregate also reacts with the acid, becoming coated with calcium sulfate. O'Connell et al. [15] indicated that the corrosive nature of a sulfuric acid attack has been well documented from both in situ observations and chemical testing on concrete. The dissolution effect of the hydrogen ion and the separate effect of the sulfate ion combine to create an aggressive set of chemical reactions, threatening the stability of a cement matrix. Munyck et al. [5] showed that the weight loss of the concrete is mainly attributable to the attack of the cement paste. Also, as reported by Fan et al. [29], the specimens submerged in water, pH 3.5 and pH 2.5 acid solutions show a slight mass gain at the initial immersion period, which is a result of the effect of cement hydrated heat. Then, the specimens show a steady rate of mass loss. The rate of mass loss goes up gradually with the increase of immersion time. Girardi et al. [13] found that the rate of mass loss is not constant and increases with time, due to the attack of C-S-H, which is the main binding component of the cement paste hardened, by the acid solution, when no more $Ca(OH)_2$ is available, mainly provoking its decalcification in the transition zone. According to Chang et al. [7], the increase in mass during the early period of immersion in 1% sulphuric acid solution, could be attributed to a number of factors, which include the continued hydration of cement, the formation of gypsum and the increase of absorbed water in the samples. Chang et al. [7] also showed, that the results of the mass change indicate that the dissolution caused by hydrogen ions lagged behind the action caused by the sulphate ions at the early days of immersion in acid. The first would mainly cause dissolution and mass loss, while the second could initially lead to mass gain and finally result in mass loss due to the excessive expansion and cracking. The combined actions of dissolution and expansion gradually caused the surface layer of cement mortar to fail, which brought about a significant mass reduction of the cylinders.

3.2.4. Immersion test in 50g/l de Na_2SO_4 at 25°C

Figure 7 shows the mass variation versus time of the concrete specimens CC and VC exposed to 50 g/l of sodium sulfate solution at 25°C with a pH regulating to 7 by addition of sulfuric acid. Three specimens were used for the monitoring of the mass absorption.

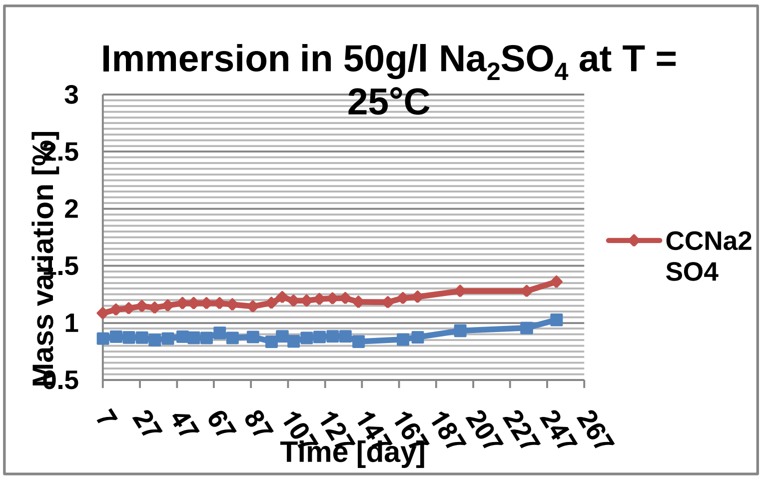

Figure 7: Absorption kinetics of CC end VC immersed in 50g/l Na_2SO_4 at 25°C

For the concrete specimens CC and VC aged in 50g/l of Na_2SO_4 at 25°C (figure 7), absorption of the solution after 7 days of immersion of about 1.08% for CC specimens and about 0.86% for VC specimens was observed. During aging, a slow absorption of the solution was found, which was explained by the fact that the pores have been initially filled with air. Until 177 days, when a dispersion in increasing of the mass for the two concrete specimens CC (1.36%) and VC (1.03%) was found. This dispersion was accompanied by a start of swelling on the most exposed parts of the samples.

This weight gain can be a result of the water that fills the cracks, but also a mass of water used to precipitate a hydrated phase as ettringite [30]. These accelerated results are also explained by the regulation at a pH below 12, which allows the destabilizing of the portlandite that is available to form gypsum and ettringite. The choice of pH 7 allows staying close to the pH encountered in natural sulfatic environments. It was shown that the attack was the more severe as the pH is low. If not controlled, the pH of the solution quickly joined a value of 12.5 due to the leaching of the portlandite [12].

3.2.5. Discussion of mass variation result's

In summary of the mass variation's results, the three parameters (production method, nature of the cement and the type of the aggregates) have an effect on the behavior of concrete.

Regarding the concrete specimens CC, the centrifuge process with the low w/c ratios gave a dense and less porous concrete, but it's characterized by a rapid diffusion of the solution (aging test in acid and sulfate solutions at 40°C and 50 g/l Na_2SO_4 at 25°C), which can be attributed to the centrifugation method, which causes the disappearance of the finer element's concrete and facilitate the diffusion of aggressive ions into the concrete. On the other hand, the filling of the pores with air of the cored specimens of these two types of pipes have delayed the diffusion of the solution into the materials, thereby slowing the degradation. Again, the portland cement with limestone filler and the portland cement with fly ash which were used are sensitive to acid attack **-** the limestone and dolomite aggregates are reactive aggregates in an acidic medium. As indicated by the study of Girardi et al. [4], it could be confirmed, that limestone filler and fly ash silica don't reduce the mass loss under acid attack. Several authors have found that the use of pozzolana or silica fume can reduce the percentage of the mass loss of concretes exposed to dilute acids, but not when concentrated acids are involved. According to the ACI Committee 201 [18], the deterioration of concrete by acids is primarily the result of a reaction between these chemicals and the calcium hydroxide of the hydrated portland cement, then the calcium sulfate formed will affect the concrete by the sulfate attack mechanism. Furthermore, where limestone and dolomitic aggregates are used, they are also subject to attack by acids. Moreover, as reported by the ACI Committee 201 [18], a dense concrete with a low w/c provides a degree of protection against mild acid attacks. Certain pozzolanic materials and silica fume in particular, increase the resistance of concrete to acids. Makhloufi et al. [31] showed that the simultaneous incorporation of slag and natural pozzolana with limestone filler reduces the compromising effect of this one, when it is added to concrete in high content in the order of 30%. Moreover, these three additions can decrease the total porosity of mortar and modifies the pore structure of the cement, mortar and significantly reduce the permeability which allows the transfer of harmful ions leading to the deterioration of the concrete matrix. As reported also by Makhloufi et al. [31], the simultaneous incorporation of the limestone filler, blast furnace slag and natural pozzolana in cement of limestone mortars has gained considerable importance because of the requirements of environmental safety and more durable construction in the future.

3.3. SEM-EDX

3.3.1. SEM-EDX for immersion test in Na_2SO_4 (5g/l SO_4^{2-}) *at 25°C*

Figures 8 and 9 show a SEM image accompanied by the EDX analysis respectively of CC concrete specimens aged in Na_2SO_4 (5g/l SO_4^{2-}) at 25°C after 192 days. Microscopic analyzes were performed on samples of concrete cut out from the most attacked areas of concrete specimens. The identification of the microstructure of the concrete was carried out from the polished surfaces with a carbon metallization.

3.3.1.a. SEM-EDX picture

According to figure 8, the product formed in abundance at the interface is rich in calcium, aluminum and sulfur, which allows concluding the formation of ettringite $(CaO)_3.AL_2O_3.3CaSO_4.32H_2O)$ in abundance, formed from aluminates.

These results are confirmed by the percentage of concrete elements found by SEM-EDX analysis. The initial state have a low percentages of the elements Al_2O_3 (6.23%) and SO_3 (1.52%) and after being aged in sodium sulfate at 25°C, a percentage of Al_2O_3 equal to 12.38 % and of SO_3 equal to 25.18% was found.

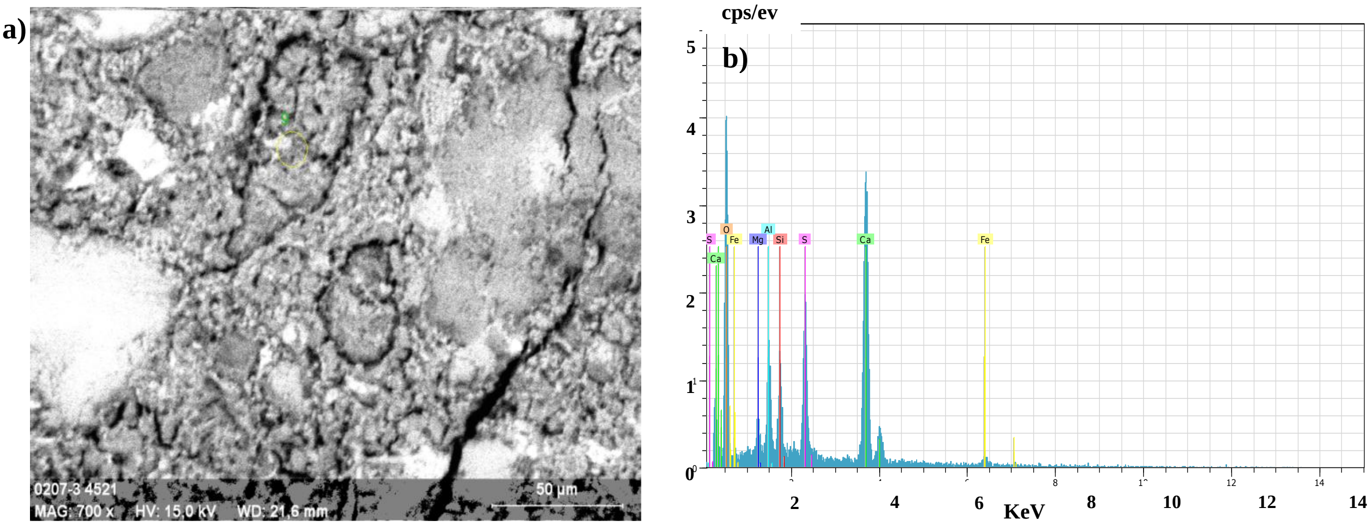

Figure 8: CC specimens aged in Na_2SO_4 (5g/l SO_4^{2-}) at 25°C: a) and b) SEM images, c) and d): EDX analysis

3.3.1.b. Cartography given by EDX

For figure 9, the cartography given by EDX analysis of the relative distribution of the concrete elements present different compositions of concrete named in figure 8 and identify the products formed during the sodium sulfate attack. The high concentrations of calcium are used to identify the cement paste. The product formed is rich in calcium, aluminum and sulfur (ettringite).

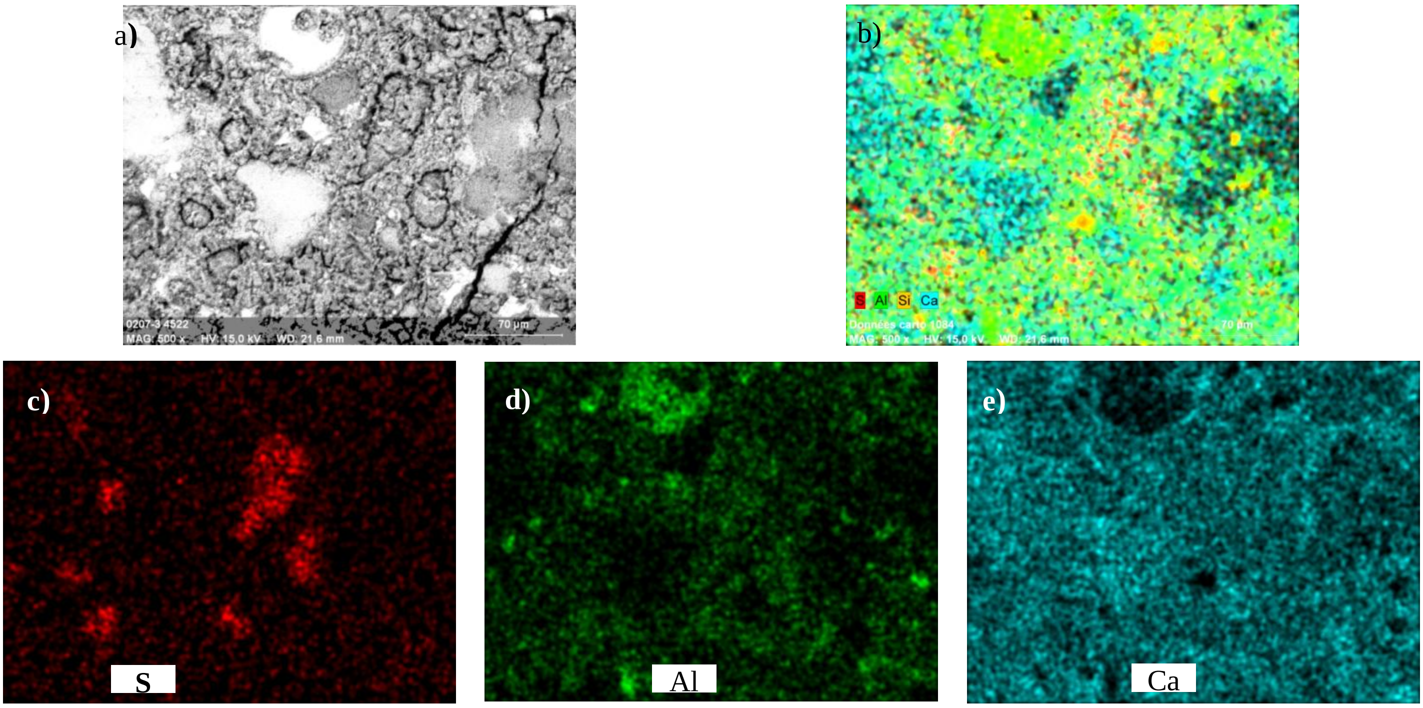

Figure 9: CC specimens aged in Na_2SO_4 (5g/l SO_4^{2-}) at 25°C: a) SEM picture, b) EDX cartography, c) sulfur, d) aluminum, e) calcium

3.3.2. SEM-EDX for immersion test in H_2SO_4 (5g/l SO_4^{2-}) *at 25°C*

Figure 10.a shows a SEM image accompanied by the EDX analysis (figures 10.b) of CC concrete specimens aged in H_2SO_4 (5g/l SO_4^{2-}) at 25°C after 192 days. The identification of the microstructure of the concrete was carried out from the polished surfaces with a carbon metallization.

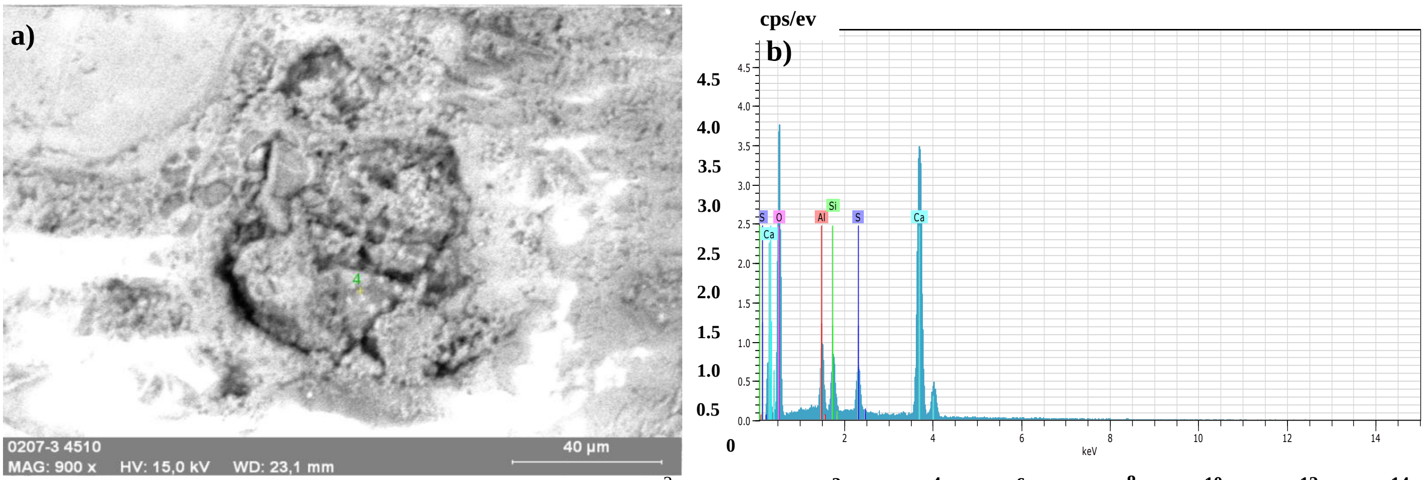

Figure 10: CC specimens aged in H_2SO_4 (5g/l SO_4^{2-}) à 25°C: a) SEM image, b) EDX analysis

In this analysis (figure 10), a small amount of ettringite (due to the amounts of oxygen (O), sulfur (S), calcium (Ca) and aluminum (Al) components) was found in a deeper section of the concrete. Furthermore, according to SEM-EDX analysis, a percentage of Al_2O_3 equal to 8.84% and of SO_3 equal to 11.45% was also found.

These observations are consistent with the work of O'Connell et al. [15] proving that in the sulfuric acid attack a limited quantity of ettringite is formed in the deeper sections of the concrete if the pH is high enough to maintain its stability. The gypsum, sufficiently formed in the initial stages of the attack, can move into the concrete. This evaluation is in accordance with other researchers reporting the inability of the ettringite to survive in an acidic environment [32] and even in an alkaline environment (pH as high as 10.6) [33].

3.3.3 SEM for immersion test in 50g/l of Na_2SO_4 at 25°C

On the other hand, a SEM analysis that was conducted on the fractures (metallized with carbon) of CC and VC concrete specimens after immersion for 302 days in 50 g/l Na_2SO_4 at 25°C with pH control (figures 11.a and 11.b), has shown the predominant formation of ettringite. These figures revealed the appearance of micro-cracks, which are due to the formation of secondary gypsum and the formation of ettringite in the concrete pores leads to a swelling and the expansion of the material.

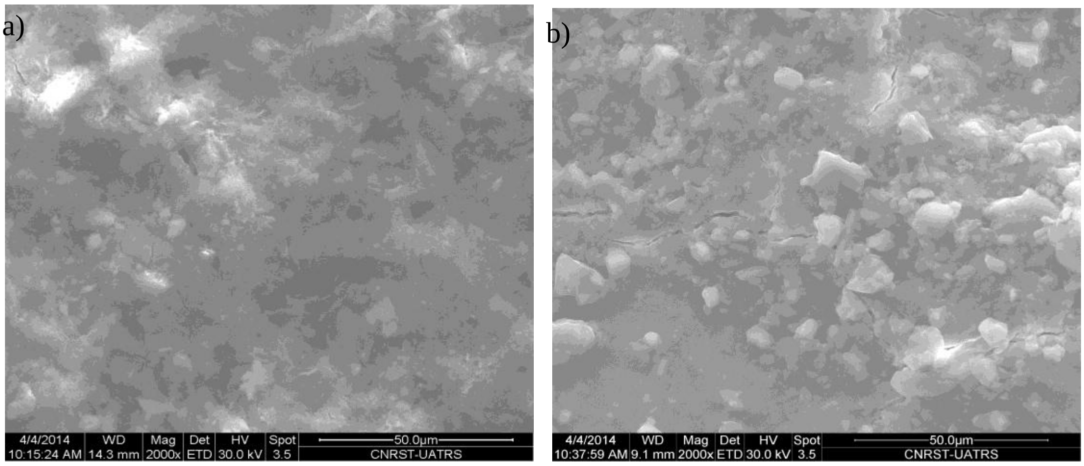

Figure 11: SEM Images: Micro-cracks after aging in 50 g/l Na_2SO_4 at 25°C: a) CC specimens b) VC specimens

For VC concrete specimens a magnification in areas with microcracks was performed which confirmed the presence of secondary ettringite needles (Figure 12).

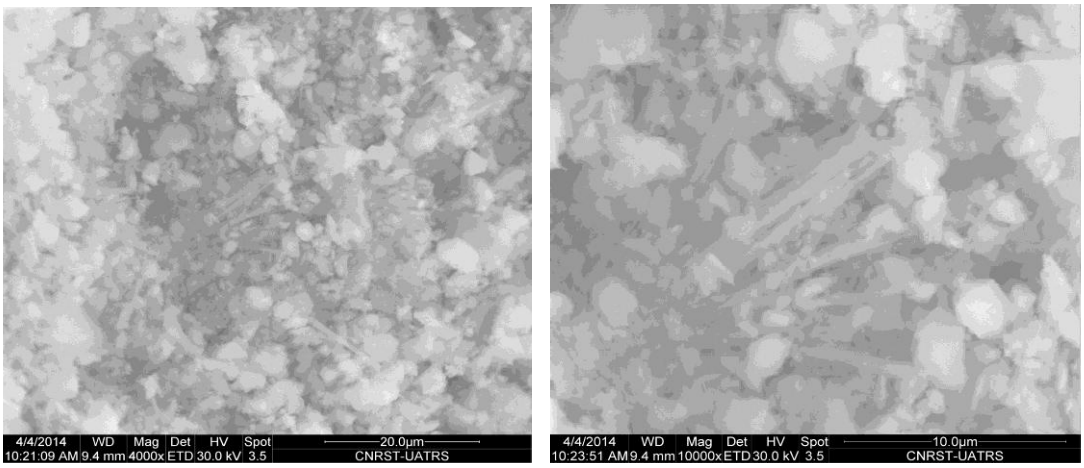

Figure 12: SEM Images of VC specimens after aging in 50 g/l Na_2SO_4 at 25°C: presence of the needles of ettringite

For CC specimens aged in Na_2SO_4 (5g/l SO_4^{2-}) at 25°C (figure 9) and for CC and VC specimens aged in 50 g/l of Na_2SO_4 at 25°C (figures 11 and 12), the existence of ettringite in abundance in both concentrations of sodium sulfate was found. The appearance of micro-cracks in the concrete surfaces in the case of 50 g/l of Na_2SO_4 at 25°C is due to the secondary gypsum and of ettringite formation in the pores of the material, resulting in the swelling and expansion of the material. However, the micro-cracks on the surface of the specimens aging in Na_2SO_4 (5g/l SO_4^{2-}) at 25°C were not seen. In this concentration, the degradation is very slow and the phenomenon of expansion of ettringite is lower. This allows concluding: The higher the concentration of sodium sulfate, the more important is the phenomenon of expansion. According to Girardi et al. [13] and Neville et al. [34], the diffusion of the sulfate ions into the concrete from sulfate-containing solutions causes the formation of gypsum, where calcium hydroxide is reduced. The ACI Committee 201 [18] showed that the two most recognized chemical consequences of the sulfate attack on concrete components are the formation of ettringite (calcium aluminate trisulfate 32-hydrate, $CaO.Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) and gypsum (calcium sulfate dihydrate, $CaSO_4{\cdot}2H_2O$). They indicated that the formation of ettringite can result in an increase of the solid volume, leading to an expansion and cracking, while the formation of gypsum can lead to a softening and the loss of concrete strength.

The microscopic observations have confirmed the macroscopic findings of mass variation and compressive strength obtained in this work.

Conclusion

The behavior of two different types of concrete used in sewer pipes was studied, by three different types of accelerated tests in acid and sulfate solutions, in order to study the effect of the production method, the nature of cement and type of aggregate used in each concrete. The most significant results of this work are cited below:

- The gravimetric measurements of CC and VC concrete specimens aged in Na_2SO_4 (5g/l SO_4^{2-}) at 25°C showed an increase of mass versus time. The gain of weight for this concrete specimens which had been oven dried is explained by the absorption of the bath solution into the empty pores of the matrix.
- The gravimetric measurements of CC and VC concrete specimens aged in Na_2SO_4 (5g/l SO_4^{2-}) at 40°C showed a slow increase of mass versus time. The delay in weight gain is due to the fact that the pores were initially filled with air, the air was trapped in the central part of the core and the incoming solution had to compress/dissolve/diffuse the air to allow the diffusion of more solution into the specimen.
- The gravimetric measurements of CC and VC concrete specimens aged in H_2SO_4 (5g/l SO_4^{2-}) at 25°C and at 40°C, showed an increase of mass in the first few months, followed by a mass loss versus time. The increase in mass in a sulfuric acid solution is due to a water intake. The mass loss is due to the sulfuric acid reacting with the alkaline substances in the concrete (cement paste and aggregate).
- The gravimetric measurements of CC and VC concrete specimens aged in 50g/l Na_2SO_4 at 25°C showed a dispersion in increasing of mass accompanied by a start of swelling on the most exposed parts of the samples. This weight gain can result from the water that fills the cracks, but also a mass of water used to precipitate a hydrated phase as ettringite.

The mass variation results showed that the three parameters (production method, nature of cement and aggregate types) of concrete have an effect on behavior of this material. The centrifuged concrete has a low w/c ratio and has a less porous concrete, but it's characterized by a rapid diffusion of the solution. This is can be explained by the fact that during centrifugation the finer elements of concrete depart with the water and facilitate the diffusion of solution into the concrete. On the other hand, the filling of the pores with air of the cored specimens from these two types of pipes have delayed the diffusion of solution into materials. Moreover, the Portland cement with limestone filler and the Portland cement with fly ash which were used are sensitive to acid attack and the limestone and dolomite aggregates are reactive aggregates in an acidic medium.

These results prove that the concretes' behavior mainly depends on the production method, the type of cement, the type of aggregate and w/c ratio.

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(2015) ; http://www.jmaterenvironsci.com