Resistance of limestone mortars with quaternary binders to sulfuric acid solution

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ABSTRACT

The synergistic action of three mineral admixtures simultaneously incorporated in cement has a positive effect concerning the durability of limestone mortars. Tests were carried out on limestone mortars made from five quaternary binders (ordinary Portland cement and OPC blended simultaneously with limestone filler, blast furnaces slag and natural pozzolana). The purpose of this investigation was to identify the resistance of five different mortar mixtures to sulfuric acid solutions. The changes in weight loss and compressive strength values measured at 30, 60, 90, 120 and 180 days for each acid solution were studied. The pH variation of the sulfuric acid solution has been monitored during the tests and several phases are determined by XRD.

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1. Introduction

It is now well established that the evaluation of the concrete performance is not limited to the determination of its mechanical properties since it is of primordial importance to characterize the material in term of durability. The service life of a reinforced concrete structure and its performance over the time are closely connected with the properties that define durability (permeability to various agents), reaction to sulfates, acids and others [1]. Concrete structures can be exposed to various acids because of the environmental pollution. Therefore changes in physical and chemical properties and also variations in weight, strength and microstructure of the mortars and cements caused by interaction with various acids should be examined [2,3].

It is well known that there are acid attacks in mortars, concrete and many building materials that form part of the urban landscape and Cultural Heritage [4,5]. The reaction of sulfuric acid with calcium carbonate leads to the gypsum deposit. Such gypsum coatings have been studied in natural stones, such as calcareous stones and marbles [6–8]. The ability of the acid to disassociate and the solubility of calcium salts play also an important role in degradation.

Limestone filler and pozzolana also show different durability properties with the content and type of active silica present in their composition. In relation to the effect of pozzolana on concrete strength, it should be stated that the type, amount and fineness of pozzolana, and also the type of cement are factors that affect the strength of concrete [9]. The use of mineral admixtures such as silica fume and fly ash in concretes has been shown to improve the resistance of concrete to sulfuric acid attack in terms of the reduced presence of calcium hydroxide, which is over time vulnerable to acid attack [10].

It was recognized that the use of binary and ternary cement consisting of silica fume and fly ash had a better performance than concretes with other mineral admixtures, toward weight loss of the concrete samples up to 25% after 56 days immersion in 1% sulfuric acid solution [11–14].

The highest resistance to a 0.5% sulfuric acid solution was achieved by a binary binder mixture comprising more than 60% ground granulated blast furnace slag [15]. Conversely, Chang et al. [16] recently reported that binary binder concrete mixtures prepared with 60% slag and ternary binder mixtures with 56% slag and 7% silica fume had inferior performance compared to that of a 100% OPC mixture when immersed in a 1% sulfuric acid solution with a pH of 1.27.

The reaction between the amorphous glassy silica in slag and pozzolana and CH, which is the result of the hydration of cement, produced the CSH. This product is also effective on the durability of concrete [17,18].

Data on the resistance of quaternary binder concrete mixtures to sulfuric acid solutions are extremely limited. In this experimental study, crushed limestone sand was used with a quaternary binder
to investigate the resistance of mortars to acid attack. Five mortars were measured during the testing period of 180 days. All mortars were immersed in 3% sulfuric acid solution over 180 days and the samples were regularly investigated by mass change, compressive strength, pH and XRD.

2. Experimental investigation

2.1. Materials

Portland cement, limestone filler, blast furnace slag and natural pozzolana, crushed limestone sand, water, and superplasticizer were used in the production of mortar. The cement used in this investigation is the ordinary Portland cement (OPC) prepared from clinker and 5% of gypsum. Clinker with gypsum and all mineral mixtures were ground in a laboratory mill to a specific surface area of 350 m²/kg and 380 m²/kg respectively. The chemical analysis of the cement and mineral admixtures are presented in Table 1.

The specific gravities of cement, limestone filler, slag and natural pozzolana are approximately 3, 2.7, 2.6 and 2.8 respectively. The sand used in mortar mixtures was a crushed limestone sand of 2.5 mm maximum size aggregate. SIKA Viscocrete 3045 which is a water reducing plasticizer based on modified polycarboxylates and tap water were employed for the mixing. Sulfuric acid solution (3%), (pH = 1.30) was chosen for formal testing and prepared in order to test the resistance of mortars to the chemicals attack.

2.2. Preparation of specimens and test procedure

All substitutions were made by mass. The water/binder (w/b) ratio was kept constant at 0.5. The binder/sand (b/s) ratio was 1:3 for all specimens. Plasticizer was added to the mixture in order to obtain a comparable workability. The plasticizer content ranged between 2% and 2.5% of the binder weight. Mortars were mixed according to the EN 196-1 standard and 40 × 40 × 160 mm prisms were produced. After casting, the mortar samples were cured 24 h in laboratory at 20 ± 2 °C and relative humidity about 50%. After demolding, the specimens were cured in lime-saturated water during 28 days.

Five specimens of mortars for each blended cement were prepared. The mix design of mortars is given in Table 2. After 28 days of curing in lime water, both series of specimens were immersed in lime water and sulfuric acid solutions during 180 days in order to effectuate a comparative study. Samples of each composition were immersed separately in solution tank. Before carrying out the weighings and the mechanical tests, the specimens were washed with water then dried during 3 h in the laboratory.

Changes in weight of mortar specimens and pH of solutions were measured during the testing period of 180 days. All specimens at 28 days of their hardening in lime water, then after 28 days where they have been subjected to different solutions, we determined their compressive strength at 30, 60, 90, 120 and 180 days.

3. Results and discussion

3.1. Weight changes

Most investigations have considered weight loss as an acceptable indicator for evaluating the resistance of concrete to sulfuric acid attack [17]. Weight change was determined for all mortars stored in 3% sulfuric acid solutions. The results of weight changes of mortars specimens according to exposure time are presented in Fig. 1. As shown in this figure, there was a continuous weight increase for all mortars with exposure age with different extents until 90 days except mortars C2 and C3 showed a weight gain at earlier ages, up to 120 days, then at later age there was a decrease in weight for all mortars.

After 90 and 120 days of immersion, the replacement of part of Portland cement by the mineral admixtures increased the mortar’s ability to resist to acid attack. However, the decrease in weight was less with blended cement specimens. The mortar specimens C3, C2 and C4 show a slight weight loss whereas mortars C0 and C1 show an important mass loss especially for the mortar specimen C0 where after 90 days of immersion, the decrease in weight is well marked.

At 180 days immersion, the highest weight increase was found in mixtures containing natural pozzolana C3, with 1.7% weight gain. The specimens of mortars C2 and C4 had 1.2% and 1.0% weight gain respectively, while the mortar C1 has 0.8% weight gain. In contrast, the reference mortar C0 had the smallest weight gain of 0.4%.

It was interesting to note that the relatively higher weight gains occurred with the mortar C3 then C2, all of which had a high proportion of slag and pozzolana in the cement. These results confirm the increasing resistance to acid attack by other pozzolanic materials such as silica fume, metakaolin and fly ash obtained by other

### Table 1

Chemical compositions of cement and mineral additions.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Binder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clinker</td>
</tr>
<tr>
<td>SiO₂</td>
<td>21.38</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.59</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.21</td>
</tr>
<tr>
<td>CaO</td>
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<tr>
<td>MgO</td>
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</tr>
<tr>
<td>K₂O</td>
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</tr>
<tr>
<td>Na₂O</td>
<td>0.19</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.56</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.02</td>
</tr>
<tr>
<td>PAF</td>
<td>0.58</td>
</tr>
</tbody>
</table>

### Table 2

Composition of different binders.

<table>
<thead>
<tr>
<th>Composition</th>
<th>C₀</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clinker</td>
<td>95</td>
<td>47.5</td>
<td>47.5</td>
<td>47.5</td>
<td>47.5</td>
</tr>
<tr>
<td>Gypsum</td>
<td>5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Limestone</td>
<td>0</td>
<td>30</td>
<td>10</td>
<td>10</td>
<td>16.67</td>
</tr>
<tr>
<td>Slag</td>
<td>0</td>
<td>10</td>
<td>30</td>
<td>10</td>
<td>16.67</td>
</tr>
<tr>
<td>Pozzolana</td>
<td>0</td>
<td>10</td>
<td>30</td>
<td>30</td>
<td>16.67</td>
</tr>
</tbody>
</table>

Fig. 1. Weight changes of mortar samples after immersion in sulfuric acid solution.
The high content of SiO₂ of pozzolana and slag in the mortars binder C2 and C3 makes that the pozzolanic reaction will be more important than that of the mortars binders C0 and C1. This pozzolanic reaction will generate a high rate of CSH in the mortar binders C2 and C3 than that of mortars binders C0 and C1. CSH is the most abundant product in blended cement pastes. Its C/S ratio is generally lower than that in the Portland cement paste. However, the C/S ratio in CSH is still higher than the C/S ratio in the pure slag, indicating additional calcium demand by the slag hydration. This calcium demand is supplied either by the CH formed by the Portland cement hydration, or by the lower C/S ratio in the CSH [20]. The effect of the pozzolanic reaction produces more cement gel (C-S-H and C-A-H) reducing the pore size, blocks the capillary and produces denser concrete, responsible for the development of strength, thus making it stronger and more durable [21]. It is known that the CSH are less soluble than CH in aggressive solutions. On the other hand the pozzolana and the slag contain high percentages of alumina, thus the content of anhydrous and hydrated aluminate (C₃A and C₆AHF) in the mortars binders C2 and C3 will be higher. The rate of ettringite produced from these aluminates will be more important. The ettringite is formed in situ in contact with the calcium aluminates [22]. The high CaO amount of clinker makes that the amount of Ca₃(AlOH)₆ will be higher in mortars C0 than other mortars.

The differed ettringite can be formed by the transformation of the monosulfoaluminate or the hydration of the residual C₃A following the contribution of sulfate ions coming from the external environment. The precipitation of ettringite in a hardened and confined media can generate constraints then an expansion within cementitious material. SEM observations highlight a massive form of ettringite completely filling the pores, then initiating cracks which develop over time [23].

The weight gain during 90–120 days in sulfuric acid solution could be attributed to a number of factors, which include continued hydration of cement, action caused by the sulfate ions leading to the formation of gypsum and ettringite and to the increase in absorbed water in samples. The weight loss after 90–120 days may be due to the dissolution caused by the hydrogen ions which comes later than the action caused by the ions sulfates. The effect of sulfuric acid on concrete is more detrimental than that of sulfate attack; in addition to attack by sulfate ions, there is a dissolution effect caused by hydrogen ions [24]. H⁺ ions from sulfuric acid dissolves CaCO₃ and Ca(OH)₂ in the mortar, while the simultaneous reaction of SO₄²⁻ with Ca²⁺ provokes deterioration due to gypsum deposits on the mortar surface [9].

The mass change results of concretes, included a Portland cement, binary and ternary cements containing GBFS, silica fume and fly ash and silica fume exposed to the sulfuric acid solution, indicate that the dissolution caused by hydrogen ions lagged behind the action caused by sulfate ions at the early days of immersion in sulfuric acid. The former action would mainly cause dissolution and mass loss, however, the latter could initially lead to mass gain and finally result in mass loss due to excessive expansion and cracking [16], however the formation of gypsum and ettringite could initially lead to a weight gain and finally to involve the mass loss which is due to the excessive expansion cracking.

3.2. Compressive strength

3.2.1. Development of compressive strength in lime water

Fig. 2 shows the compressive strength development in relation to the time of immersion of control mortar C0 to Portland cement and blended cement mortars with mineral admixtures, immersed in lime water (LW). We note that the compressive strength increases continuously versus time for various mortars. Considering that the hydration kinetics of binders does not occur in the same way, Control mortar C0 has a high compressive strength at any age in comparison with that of blended cement mortars. Concerning the latter, the compressive strength of mortars C2 is the most increased followed by those of C3 and C4 and lastly the mortars C1.

The compressive strength development of mortar cement paste is strongly affected by the volume of CSH formed during cement hydration. The long-term compressive strengths were measured for the mortars made from blended cement/limestone filler (LF), ground blast furnace slag (GBFS) and natural pozzolana (NP). In general, for the same surface area of the mineral admixtures, the compressive strength decreased from GBS to NP to LF. Pozzolanicity of the mineral admixture influences the hydration rate [25]. The lower long-term strength for LF may be attributed mainly to its low reactivity.

The addition of LF as partial substitution of cement exhibits higher early strength. The opposite effect is caused by the addition of pozzolana. In the long term, cements with pozzolanic materials exhibit significantly higher compressive strength than the Portland cement and the Portland-limestone cement [26,27]. Concerning the reactivity of LF, there is a partial substitution of the sulfate ion by the carbonate ion during the formation of ettringite [28,29]. Calcium carbonate accelerates the hydration of tricalcic silicate and modifies the Ca/Si ratio of lime silicates hydrated (CSH) [30,31]. The precipitation of carbonate during the hydration highlighted by many authors [32,33] and the partial substitution of sulfate ions by the carbonate ions during the formation of ettringite. A new hydrate can be formed and the reactional sequences of the hydration are not modified [28,34,35].

The addition of CaCO₃ at C₃S accelerates the hydration of cement and modifies the Ca/Si ratio of hydrated lime silicates. The fine fillers such as limestone accelerate the initial reactions of hydration. These last studies confirm the significant effect of the limestone fillers on cement hydration at early age [30,36,37].

Replacements of mineral admixtures such as BFS and NP with cement are generally favorable to the resistance of concrete to the aggressive solutions. The lime consumption resulting from the hydration of clinker, which leads to a reduction in portlandite content, composed vulnerable with respect to the aggressive solutions and produce a greater quantity of CSH with lower CaO/SiO₂ ratio [38,39]. This results in a change of the binder paste microstructure by reducing the average size of pores and thus to increase the compactness of the hydrates whose densification will be very important over time reducing greatly the permeability and diffusivity and consequently the transfer capacity of aggressive ions in the mortar and concrete [40,41].

Simultaneous addition of LF and NP or LF and BFS in Portland cement has certain shortfalls. LF causes an increase of hydration at early ages improving the earlier strength, but it can reduce the later strength due to the dilution effect. On the other hand, NP
and BFS contribute to the hydration after 28 days inducing the strength at medium and later ages \[16,42,43\]. The combination of LF and GBFS or of LF and NP or LF and FA is complementary: the LF improves the early strength of cement while the BFS, the NP or the FA improves the later strength by the cementing reaction that refines the pore systems. It is proved that the ternary cemen-
titious blend of LF offers advantage over the binary blended ce-
ments and plain Portland cements \[44,45\].

The synergic interaction between LF and FA and its persistence over time was confirmed. LF interacts with the AFm and Aft hydra-
tion phases, leads to the formation of mono or hemicarboalumi-
nate hydrates instead of AFm hydrate and stabilizes thereby the ettringite. This leads to an increase in the volume of hydrates
and a subsequent decrease in porosity and an increase in strength. Fly ash, on the other hand, can provide additional aluminates which will lower the sulfate/aluminate ratio and thereby amplify the impact of the limestone. The XRD patterns show a larger amount of AFm and Aft phases when FA is present. However, alu-
minates liberated by fly ash do not go only into AFm and Aft phases as part of it is also incorporated in the C-S-H gel as observed by the increase of the Al/Si ratio of the C-S-H \[46,47\].

3.2.2. Development of compressive strength in sulfu-
ric acid solution

Fig. 3 illustrates strength variation of mortars exposed to sul-
phuric acid solution. The mortars C2 and C3 showed a continuous in-
crease in compressive strength up to 120 days, from this age the
resistance of mortars start to decrease slightly, the mortars C1 and
C4 showed a decrease in strength from the 90th day, excepted the
control mortar C0, where the downfall of compressive strength starts from the 60th day. All mortar samples stored in the sulfuric acid solutions showed a lower compressive strength than those of the control mortar. Thereafter, the strength decreased at the later age (180 days).

The first increase in strength may be attributed to two types of
reactions, the continuous hydration of unhydrated cement compo-
nents to form more hydration products in addition to the reaction
of BFS or NP (in case of blended cements) with the released lime to
form more CSH.

The hydration of C3S saturates the interstitial solution with cal-
cium hydroxide what confers the high pH of the cement paste. In
the case of blended cements, these conditions are favorable to the
solubility of NP and BFS. These additions then constitute a new source of silica to precipitate CSH and alumina, and to form
ettringite and/or AFm which will contribute to the increase of the
compressive strength \[40\].

3.3. Relationship between weight change and compressive strength
change

After 12 weeks of exposure to sulfuric acid solutions, the results revealed that it has a significant correlation between weight loss and compressive strength loss \[48\]. On the contrary, discrepancy between weight loss and strength loss after exposure to acidic media was also reported in other studies \[16,49\].

The relationship between weight loss and compressive strength
loss is shown in Fig. 4. It may be noted that there is a correlation between weight loss and strength loss for mortars C2 and C3 and an absence thereof for other mortars containing a high proportion of calcium carbonate. The correlation coefficients which have been determined are 0.96 and 0.94 for mortars C2 and C3 respectively and 0.72 and 0.42 for mortars C4, C1 and 0.86 for mortars C0 during 180 days of attacks.

Weight loss reflected the successive decomposition of mortars
specimens starting from the exposed surface and moving inwards. The fundamental factors controlling weight loss from the exposed
surface were the calcium hydroxide content and the existence of a
deteriorated or protective zone. Latters had a significant role in
slowing down the kinetics of the acidic reaction by reducing the
acid diffusion into the sound mortar matrix.

In the first slices, we note the increase in the strength loss, this
can be due to dissolution of Ca(OH)\textsubscript{2} and in the second part the reduction of strength loss can be due to the formation of new CSH, which will contribute to the rise of the compressive strength since compressive strength development of cement is strongly af-
fected by the volume of CSH formed during cement hydration. The addition of mineral admixtures GBFS or (GBFS + FA) in cement re-
sulted in the formation of decreased amount of CH in the hydration
product. This is attributed to the dilution effect and to the con-
sumption of CH by pozzolanic reaction. At 3 days, both C-S-H and
CH of all OPC specimens substituted by mineral additives were
lower than control concrete without any mineral admixture (CTR) indicating no pozzolanic reaction has taken place at this stage. While at age of 91 days, C-S-H of all OPC specimens containing
mineral admixtures was higher than CTR and their CH was comparatively lower than that at 3 days, denoting increase in C-
S-H at the cost of CH due to the pozzolanic reactivity \[50,51\].

The formation of a protective zone on the sample surface by
reducing the diffusion of acid inside the mortars can cause this de-
crease in strength loss. Any relationship between weight loss and compressive strength loss should be taken cautiously since the two manifestations are governed by different factors and are not directly related \[16,49\].

3.4. Evolution of conservation solutions pH

The influence of immersion time on pH change was also studied
to evaluate the rate of degradation. It is recognized that the hydra-
position products of Portland cement concrete are alkaline and the hydration reaction takes place in a basic medium with a pH ranging between 12 and 13, so that any other environment the pH of which is lower can be regarded as aggressive because of the solubility of some hydrates increase strongly in the acid environment, such as the portlandite [40]. Nevertheless, the rapid change in pH reflects the effect of the portlandite dissolution and by this fact decreases quickly the chemical aggressiveness of the conservation media. To bring back this aggressiveness to its initial state i.e. to maintain the pH constant, we followed the pH evolution and renewed periodically the solution baths.

The pH measurements were taken each end of the month before renewing lime water and acid solutions. The pH variation of lime water up to 180 days is shown in Fig. 5. Initially, as envisaged, the pH values are included between 12.5 and 12.7. At the 180th day the pH of all solutions are included between 12.60 and 12.65.

Table 3 gives the pH of the sulfuric acid solutions measured every week until 30 days after immersion in lime water during 28 days. After immersing mortar samples in sulfuric acid solutions, the pH values gradually increased with time. Until the 30th day of immersion and as it was expected the pH of acidic solutions has changed to the pH of alkaline solutions. The greatest pH value was observed for samples C0, follow-ups by samples C1, C2 and C4 that show pH values close to each other; in the end the samples C3 have the lowest pH. The pH measurements have shown that solutions have passed from acid solutions, (pH = 1.30–1.96) to moderately alkaline solutions (pH = 7.95–9.92). It is known that when the pH > 9, the degradation kinetics will be slow. The indications given in the bibliography show that it is not a very aggressive pH for cementitious materials, that's why we carried out the renewal of the baths of cure each 30 day.

The sulfuric acid solutions were partially neutralized by the alkalis of the cement and by reaction with consumption which come from the clinker, mineral admixtures and aggregates. Therefore, after immersing the samples in the 3% sulfuric acid solutions, the pH values gradually increased with time, as it was expected.

Other measurements of pH were taken each month in order to follow the pH evolution of the conservation solutions up to 180 days. Fig. 6 shows that after 30 days of immersion, the pH of acidic solutions begins to decrease gradually and slightly, up to 180 days where the pH of different solutions will be between 2.6 and 4.8. Mortars C2 and C3 have a pH of about 2.6 and 3.0. The specimens C1 and C0 have a higher pH about 4.8 to 5.3, showing that the solutions are still aggressive on the one hand and on the other, mortars that have been leached with time during exposure to the acid environment. Unlike solutions of mortars with mineral admixtures, solutions of control mortars C0 show an increase in pH from 1.7 to 5.3 up to 180 days.

It is clear that the pH of solutions conserving blended cement mortars including those of samples C2 and C3 decreased slightly with time, this can be due to the leaching of cementitious materials where there is, at first time, a decalcification of portlandite followed by that of the CSH.

### 3.5. XRD analysis

The analysis by X-ray diffraction (Fig. 7) of a milled powder from the surface samples of up to 1 mm thick, shows the influence of environment conservation on the different formations in the superficial part of various mortars after 180 days of immersion in sulfuric acid solution. It should be noted that at several times that spectral lines are superimposed on lines of other crystalline phases.

The diffractograms show the existence of large peaks of calcium carbonate (calcite) for all samples of mortars, which is quite obvious, since mortars are all made from limestone sand and limestone filler. The highest peak of intensities of calcite concerns mainly mortars C0, while mortars C2, C3 and C4 are close to each other. While those of C1 mortars are less important, this can be explained by the fact that part of CaCO$_3$ was used for forming carboaluminates.

Several peaks of carboaluminates C$_2$A·CaCO$_3$·11H$_2$O type were detected for mortars C1; this implies the presence of this mineral in mortars C1. We note the disappearance of some peaks and decreasing the intensity of these peaks in mortars C0 and the other mortars with mineral admixtures, including mortars C3.

Peaks of quartz are present in the diffractograms which means that the mineral exists in the superficial part of the material, because the clinker, slag and pozzolan contain a significant proportion of silica, the latter is found mostly in CSH which we'll talk about later.

The portlandite is found in small amounts in the superficial part of the mortars C0 and lesser amounts in samples C1 and C4. In mortars C2, the amount of portlandite is less than that of mortars C1, while it has few parallels in the mortars C3. The presence of lime in the mortar leads to the formation of carboaluminates, as
observed by XRD. This reaction may cause the decrease of portlandite as reported by previous studies [52–54].

The ettringite was found in trace, and at 180 days of immersion in sulfuric acid solution begins to be dissolved. We note the existence of some minor peaks. These are mainly secondary ettringite. The mechanism involved, is the formation of secondary ettringite. The precipitation of this salt under specific conditions can lead to swelling and cracking more or less important of the concrete. The water-cement ratio and the concentration of sulfate play an important role in the formation of secondary ettringite and gypsum [55].

The CSH peaks are present in all the mortars, but their intensities are greater in mortars with mineral admixtures than in controls mortar (C0). In mortars C3 quantities of CSH are higher than those of mortars C2, and they are more important than in mortars C1 and C4. This is probably due to the presence of SiO₂ in amounts higher or lower in the binders of samples C3, C4 and C2 in comparison with other samples.

The passage in solution of portlandite, the progressive decalcification of CSH, accompanied by the dissolution of the sulfoaluminate phases especially AFt, lead to the formation on material surface of a layer of gypsum (CaSO₄·2H₂O) more or less abundant depending on the type of mortar is detected by XRD and often manifests visually by the formation of concretions of whitish color. The CaSO₄·2H₂O peaks superpose with those of CaCO₃ peaks. The highest intensity of CaSO₄·2H₂O peaks concerns mainly mortars C0 followed by mortars C2 and C3, and then finally C4 C1. The lowest amount of gypsum concerns therefore limestone mortars C1, this can be explained by the transformation of a certain amount of tricalcium aluminate, CaCO₃ with ions of SO₄ to carboaluminates type C₃A·CaCO₃·CaSO₄·H₂O and type C₃A·Ca(OH)₂·CaSO₄·H₂O since peaks of these carboaluminates were detected by XRD.

3.6. Mechanism of sulfuric acid attack of blended mortars

The sulfuric acid very aggressive with respect to the concrete depending on a dual mechanism of acid attack and sulfate attack. Corrosion of concrete can generally be characterized by the following reactions:
\[
\text{Ca(OH)}_2 + H_2SO_4 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}
\] 

(1)

and

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{CaSO}_4 + 3\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}
\]

(2)

The evaluation of deleterious reactions can be divided into two parts (Eqs. (1), (2)). At the first stage, lime dissolution of \(\text{Ca(OH)}_2\) and CSH resulted with expansive gypsum formation. Moreover \(\text{CaCO}_3\) may react with \(\text{H}_2\text{SO}_4\) to generate gypsum and carbonic acid, \(\text{CaCO}_3 + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O} + \text{H}_2\text{CO}_3\). The gypsum then reacts with \(\text{CaA}\) in aqueous environment and forms a more expansive product called ‘ettringite’. In some cases, the presence of elementary sulfur, associated with gypsum and ettringite, can be observed. In addition, the presence of acid may cause the depassivation of steel reinforcement and their corrosion [40].

The immersion of the specimens in the sulfuric acid solutions led to the ion species of the sulfuric acid (\(\text{SO}_4^{2-}\) and \(\text{H}^+\)) being consumed. Although reduction in \(\text{SO}_4^{2-}\) may be compensated by Ca²⁺ extraction from calcite or portlandite, the \(\text{H}^+\) ions from sulfuric acid react with carbonates to form neutral species, such as \(\text{CO}_3^{2-}\) and \(\text{H}_2\text{O}\), which provokes a large drop in \(\text{H}^+\) concentration. The sulfuric acid solutions were partially neutralized by the alkalinity from the cement and by reaction with consumption which come from the aggregates.

The use of supplementary cementitious materials (SCM) such as LF, BFS and NP in limestone mortars has improved the resistance of mortar to sulfuric acid attack because of the reduced presence of calcium hydroxide, which is most vulnerable to acid attack.

As reported in the literature, the Portland limestone cements show competitive concrete properties and improve the durability of the concrete [26,27]. The concrete made with limestone aggregates and the ternary cement containing silica fume and fly ash have an excellent acid resistance in 1% sulfuric acid solution and the best of the concretes made with silicate aggregates [16]. Blended Portland cements with pozzolana and slag are considered to be more resistant to the acidic attack than Portland cements. It should also be considered that, the efficiency of blending for acid resistance may be affected by other factors, e.g. the type of cement used for blending, the amount and fineness of pozzolana used and especially the curing conditions [56].

Regarding the LF, of which calcium carbonate is the main component, which reacts very little with cement hydrates, their effect may be essentially a "filler effect", that is to say an increase in compactness [40]. Some results are contradictory and the effect seems to depend on other parameters, the cation nature and the cement type, for example. Moreover, additions of carbonate or calcium sulfate, in low substitution rate, are able to maintain the strength figure of cement paste [40].

The compressive strength of quaternary binder mortars shows that the simultaneous use of three mineral additives, especially mortars C2 and C3 showed a positive effect of these two additions with respect to the sulfuric acid attack. The slow hydration kinetics of these additions can be accelerated by the presence of limestone filler and does not acquire high performance in terms of transfer properties.

The addition of a high rate of limestone filler alone in cement is prejudicial to the durability of concrete. However, it was shown 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 concretes matrix.

Finally, 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.

### References


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