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## Effect of mineral admixtures on resistance to sulfuric acid solution of mortars with quaternary binders

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### Abstract

This research consists to study the synergistic action of three mineral additions simultaneously added to the cement. This synergistic effect has a positive effect on the sustainability of limestone mortars. Tests were performed on mortars based on crushed limestone sand and manufactured by five quaternary binders (ordinary Portland cement and CPO mixed simultaneously with filler limestone, blast-furnace and natural pozzolan). The purpose of this research was to identify the resistance of five different mortars to the solution of sulfuric acid. Changes in weight loss and compressive strength measured at 30, 60, 90, 120 and 180 days for each acid solution were studied. We followed up on the change in pH of the sulfuric acid solution at the end of each month up to 180 days.

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### 1. Introduction

Concrete structures can be exposed to various acids because of to environmental pollution. Therefore, changes in physical and chemical properties as well as changes in weight, strength and microstructure of mortars and cements caused by interaction with various acids must be considered [1-3].

The reaction of sulfuric acid with calcium carbonate leads to the deposition of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). These gypsum coverings were studied in natural rocks such as limestone and marble [4,5]. The  $\text{H}^+$  ions of the sulfuric acid dissolve  $\text{CaCO}_3$  and  $\text{Ca}(\text{OH})_2$ , while the simultaneous reaction of  $\text{SO}_4^{2-}$  with  $\text{Ca}^{2+}$  causes deterioration due to the deposition of gypsum on the surface of cementitious material [6]. The capacity of the acid to separate the components of the cementitious material and the solubility of calcium salts also play an important role in the degradation of these materials.

It has been shown that the use of binary and ternary cements compound of 10% silica fume and 60% fly ash in concrete has better performance than other concrete incorporating mineral admixtures. The loss weight of concrete samples is 25% after 56 days of immersion in a solution of 1% sulfuric acid [7-9].

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Other research works [10-12] have shown a significant improvement in the resistance of fly ash concrete to the acid.

The greater resistance to a solution of 0.5% sulfuric acid was achieved by a binary binder mixture comprising over 60% of granulated blast furnace slag [13]. Conversely, Chang et al. [14] have recently reported that the binary binders of concrete prepared with 60% slag and the ternary binders with 56% slag and 7% of fumed silica had a lower yield compared to that of a mixture of 100% CPO when immersed in a solution of 1% sulfuric acid at pH 1.27.

In this research, crushed limestone sand was used with a quaternary binder to study the resistance of mortar to sulfuric acid attack.

## 2. Materials

The chemical and physical properties of the four components used in this research are presented in Table 1. Five mortars based on limestone aggregates were made. The compositions of different mortars are given in Table 2.

Clinker and mineral additions were ground separately in a laboratory ball mill to a fineness of Blaine  $3500 \pm 100 \text{ cm}^2/\text{g}$  for clinker and  $3800 \pm 100 \text{ cm}^2/\text{g}$  for mineral additions. The mortars were prepared from these binders according to European standard EN196-1. Crushed limestone sand which the diameter of the larger grain is 2.5 mm, the particle size thereof is continuous. The sand/cement ratio is equal to 3 and the water/cement ratio is 0.50. The specimens  $4 \times 4 \times 16 \text{ cm}^3$  were molded and maintained for 24 hours in the molds for 28 days after demolding, in lime-saturated water.

Tables 1. Chemical composition and mineralogy of the different compounds.

Composition	Binder			
	Clinker	Limestone	Slag	Pozzolana
SiO <sub>2</sub>	21,38	0,76	39,38	57,10
Al <sub>2</sub> O <sub>3</sub>	5,59	0,41	5,64	15,82
Fe <sub>2</sub> O <sub>3</sub>	3,21	0,23	2,3	6,16
CaO	65,26	54,9	40,3	5,95
MgO	1,72	0,61	4,50	2,09
K <sub>2</sub> O	0,47	0,24	0,46	2,0
Na <sub>2</sub> O	0,19	0,04	0,13	1,1
SO <sub>3</sub>	0,56	0,61	0,90	0,28
Cl <sup>-</sup>	0,02	0,005	-	1,40
PAF	0,58	36,3	0,8	1,2
Mineralogy of clinker (%)	C <sub>2</sub> S	C <sub>3</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
	15,64	60,97	9,39	9,76

Tables 2. Composition of cements

Composition (%)	0	1	2	3	4
Clinker	95	47,5	47,5	47,5	47,5
Gypsum	5	2,5	2,5	2,5	2,5
Limestone	0	30	10	10	16,67
Slag	0	10	30	10	16,67
Pozzolana	0	10	10	30	16,67

Table 3. Different compositions and environments of conservations

Preservation medium	Composition				
	0	1	2	3	4
A: Water + lime	A0	A1	A2	A3	A4
F: sulfuric acid solution	F0	F1	F2	F3	F4

An adjuvant modified polycarboxylates, unchlorinated water reducer and ready to use SIKA range VISCOCRETE 3045 was used. It complies with the EN 934-2, which will assess its influence on the performance of cementitious materials.

### 3. Experimental methods

Five mortars based on limestone aggregates were carried out (Table 3). The ratio sand/cement = 3 and W/C ratio is kept constant = 0.50. The dosage of superplasticizer added to the mixture is from 2 to 2.5% by weight of the binder so as to obtain handling plastic (normal consistency) mixtures Rates.

Mortar specimens prepared in the laboratory were kept at a temperature of  $23 \pm 1^\circ\text{C}$  for 24 hours. After demoulding, the specimens were immersed in saturated lime water for 28 days. After this period, a series of mortar specimens were preserved in a solution of 3%  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  for 180 days. Meanwhile, another series of similar compositions remains stored in lime-saturated water to make a comparative study.

The compressive strength testing was performed according to European standard EN196-1 on specimens  $40 \times 40 \times 160 \text{ mm}^3$ . Strength tests were performed at 28th day in lime-saturated water and 30, 60, 90, 120, and 180 days after 28 days of immersion in sulfuric acid solution.

## 4. Results and Discussion

### 4.1. Weight changes

As shown in Figure 1, there was a continuous increase in the weight of all mortars with age of exposure to different degrees during 90 days of exposure, except mortars F2 and F3 which showed a gain of weight at an early age, up to 120 days, then after this age there was a decrease in weight for all mortars.

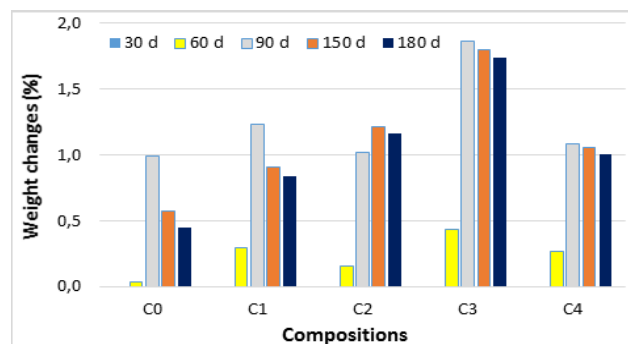


Fig. 1. Weight changes of mortar samples after immersion in the sulfuric acid solution

After 90 and 120 days of immersion, the replacement of a portion of Portland cement by mineral admixtures increased the capacity of mortars to resist to the acid attacks. However, the decrease in weight was lower than samples of mortars with quaternary binders. Samples F3, F2 and F4 showed a slight weight loss, While F0 and F1 samples show a greater loss, especially for the control mortar F0, because after 90 days of immersion, the weight reduction is well marked.

At 180 days of immersion, the weight increase was the highest recorded for mixtures containing more natural pozzolana F3 with 1.7% gain in weight. Samples F2 and F4 were 1.2% and 1.0% of weight gain respectively, whereas the sample F1 has 0.8% gain in weight. In contrast, the reference mortar F0 had the lowest weight gain of order of 0.4%.

It is interesting to note that gains weight relatively highest occurred with mortars F3 and F2, all of which had a high content of pozzolan and slag in cement. These results confirm the increased resistance to acid attack by other pozzolanic materials such as silica fume, metakaolin and fly ash as demonstrated by other researchers [11,13].

## 4.2. Compressive strength

### 4.2.1. Development of Compressive strength in lime water

The specimens were immersed in lime water, just after their demolding, up to 28 days. The strength values are summarized in Table 4.

Figure 2(a) shows the development of the compressive strength according to the immersion time of control mortar A0 and mortars with mineral additions immersed in water saturated with lime.

Table 4. Compressive Strength (MPa) at 28 days of mortars stored in water saturated with lime

Composition	Rc28j (MPa)
0	43,52
1	21,66
2	30,48
3	25,25
4	26,98

We note that the increase in compressive strength continues with time for different mortars. Since the hydration kinetics of binders does not occur in the same way, the development of the compressive strength of mortar will be different from one to another mortar. Mortar control A0 has a high compressive strength at all ages compared to mortars with quaternary binders. As for mortars with additions, the compressive strength of the mortar A2 is greatest followed by the mortars A3 and A4 and finally mortars A1. At 28 days of immersion in lime water, the compressive strength of mortar A2 is the best followed by that of mortars A4 and A3 and finally A1. At 180 days, the mortar A2 has the best compressive strength followed by A3 and A4 and finally A1.

### 4.2.2. Development of compressive strength in the sulfuric acid solution

Figure 2(b) illustrates the variation of the strength of mortars exposed to sulfuric acid solution. Mortars F2 and F3 show a continuous increase in compressive strength up to 120 days, from this age, the resistance of mortars began to fall, mortars F1 and F4 show a decrease in strength from 90 day except the control mortar F0 where we note a drop of compressive strength that to begins from the 30th day.

All mortar samples preserved in sulfuric acid solutions showed a compressive strength lower than that of the control mortar. Subsequently, the strength decreased at a later age (180 days).

The first increase in resistance can be attributed to two types of reactions, continuous hydration of the components of unhydrated cement to form more of the hydration products, in addition of the reaction of LHF or PN (in the case of quaternary binders ) with the lime released to form more C-S-H.

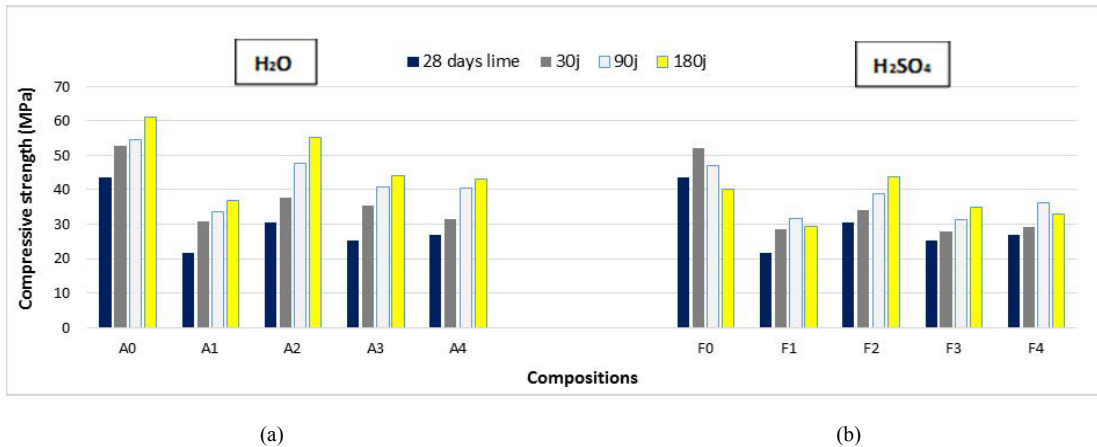


Fig. 2. Compressive strength of mortars according to the time of conservation (a) in lime water, (b) in sulfuric acid solution

In the solution of sulfuric acid as indicated in Figure 2(b), there is a reduction of the compressive strength of the control mortar F0, loss thereof is 5% at the age of 180 days of secondly, even if there is a decrease in compressive strength, it should be noted that the gain of the latter at the age of 180 days is 30, 27, and 22% for mortars F2, F3 and F4 successively, and 26% for the mortar F1. This means that the slag and pozzolana improve the resistance of mortar to the attack of sulfuric acid. Even if it is incorporated with the slag and pozzolana, the small effect of calcium on improving resistance to sulfuric acid is clear and therefore it must be both incorporated into the cement one or two additions mentioned above.

#### 4.2. Evolution of pH conservation solutions

The PH measurements were taken each end of month before to renew the consrvation solutions. In Table 5 are recorded the pH values of the solution of sulfuric acid taken every week until the 30th day after the immersion in lime water for 28 days.

Table 5. pH solutions of sulfuric acid after immersion of mortars for 30 days

	Time (days)			
	7	14	21	30
F0	1,96	4,03	7,22	9,92
F1	1,36	2,57	6,90	8,97
F2	1,44	3,48	5,91	8,35
F3	1,35	3,44	5,01	7,95
F4	1,38	3,97	6,34	8,46

The pH of the acid solution gradually increases with time until the 30<sup>th</sup> day of immersion. The pH of the solutions was changed to a pH of alkaline solutions. The highest value of pH was observed for the sample solutions F0, followed by those of samples F1, F2 and F4 show that pH values close to each other.

The pH measurements showed that solutions past from acidic solutions (pH = 1.30 to 1.96) to moderately alkaline solutions (pH = 7.95 to 9.92).

The sulfuric acid solutions were partially neutralized by alkali of cement and by reaction with the consumer from the clinker, mineral admixtures and aggregates. Therefore, after immersion of the samples in a solution of 3% sulfuric acid, the pH increases gradually with time.

For pH values of the solutions that have been taken up to 180 days each month. Figure 3(b) shows that after 30 days of immersion, the pH of acidic solutions begins to decrease slightly and gradually up to 180 days until the pH of the different solutions is between 2.6 and 4.8. Mortars F2 and F3 has a pH of about 2.6 and 3.0.

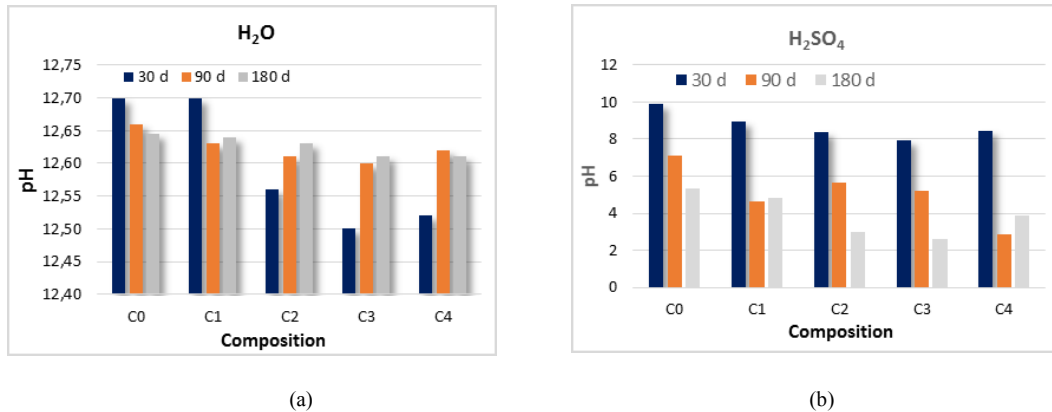


Fig. 3. Evolution of pH of solution during 180 days: (a): lime water, (b): sulfuric acid solution

On the one hand, the pH of the solutions of specimens F1 and F0 is the highest, it is of the order of 4.8 to 5.3, indicating that the solutions are always aggressive and secondly, mortars have been leached over time when exposed to the acidic environment. Unlike solutions of mortars with mineral admixtures, solutions of control mortars F0 show an increase in pH from 1.7 to 5.3 up to 180 days.

It is clear that the pH of conservation solutions of mortars with binders including that of solutions of the samples F2 and F3 decreased slightly with time, this may be due to leaching of cementitious materials where there is first a portlandite decalcification followed by the C-S-H. This decalcification results from the diffusion of Ca<sup>2+</sup> ions from the interior of the material to the external solution.

In the first step, the dissolution of Ca(OH)<sub>2</sub> and C-S-H leads to the formation of gypsum expansive. The gypsum is then reacted with C3A in an aqueous environment and form ettringite. In some cases, the presence of elemental sulfur, associated with gypsum and ettringite can be observed. In addition, the presence of acid can cause the reinforcement depassivation and corrosion. The sulfuric acid solutions were partially offset by alkali cement and reaction with the consumption of Ca<sup>2+</sup> ions derived aggregates.

The final product of degradation by a sulfuric acid can be a silica gel resulting from the total decalcification of C-S-H, which according Grube et al. may have a protective role of the surface of the concrete and retarder reactions. Transport conditions of the aggressive agent are more important than its concentration [12-15].

## 5. Conclusions

From the experimental results, it was shown that the simultaneous incorporation of limestone fillers, blast furnace slag and natural pozzolan play a complementary role in the development of resistance to sulfuric acid solution mortars containing limestone aggregates. The pozzolanic reaction of slag and

natural pozzolan is slow in the short term, it grows in the medium and long term, while the limestone is faster at a young age.

The compressive strength of mortar subjected to attack by sulfuric acid shows the positive effect of the simultaneous use of three mineral additives, in particular for mortar with 30% slag and 30% pozzolan, towards the attack of sulfuric acid. Slow hydration kinetic of these additions can be accelerated by the presence of limestone and prevents acquire high transfer properties.

The addition of a high rate of limestone in cement alone is detrimental to the durability of concrete. However, it has been shown that the simultaneous incorporation of limestone slag and natural pozzolan reduces the effect of undermining it, when added to the concrete at levels of about 30%.

## References

- [1] Bassuoni MT, Nehdi ML. Resistance of self-consolidating concrete to sulfuric acid attack with consecutive pH reduction. *Cement and Concrete Research* 2007;**37**:1070–1084.
- [2] Wang JG. Sulfate attack on hardened cement paste. *Cement and Concrete Research* 1994;**24** (4): 735-742.
- [3] Mostafa NY, Mohsen Q, El-Hemaly SAS, El-Korashy SA. P.W. Brown.High replacements of reactive pozzolan in blended cements: Microstructure and mechanical properties. *Cement and Concrete Composites* 2010;**32**:386–39.
- [4] Camuffo D. Physical weathering of stones. *Sci Total Environ* 1995;**167**:1-14.
- [5] Malaga-Starzec K, Panas I, Lindqvist JE, Lindqvist O. Efflorescence on thin sections of calcareous stones. *J Cult Herit* 2000; **34**:313–318.
- [6] Maravelaki-Kalaitzaki P. Hydraulic lime mortars with siloxane for waterproofing historic masonry. *Cement and Concrete Research* 2007; **37**:283-290.
- [7] Durning TA, Hicks MC, Using microsilica to increase concrete's resistance to aggressive chemicals. *Concrete International* 1991;**13**(3):42- 48.
- [8] Kazuyuk T, Mitsunor K. Effects of fly ash and silica fume on the resistance of mortar to sulphuric acid and sulphate attack. *Cement and Concrete Research* 1994;**24** (2): 361-370.
- [9] Tamimi AK. High performance concrete mix for an optimum protection in acidic conditions. *Materials and Structures*. 1997;**30**:188-191.
- [10] Makhloufi Z, Kadri EH, Bouhicha M, Benaïssa A, Bennacer R. The strength of the limestone mortars with quaternary binders: Leaching effect by demineralized water. *Construction and Building Materials* 2012; **36**:171-181.
- [11] Escadeillas G, Hornain H. The durability of concretes: The concrete durability vis-à-vis the chemically aggressive environments. In "Scientific basis for the formulation of concretes durable in their environment" edited by Jean-Pierre Ollivier and Angelique Vichot. Presses ENPC 2008. In French.
- [12] Caballero CE, Sanchez E, Cano U, Gonzalez JG, Castano V. On the effect of fly ash on the corrosion properties of reinforced mortars, *Corrosion Reviews* 2000;**18**(2-3):105-112.
- [13] Monteny J, De Belie N, Taerwe L. Resistance of different types of concrete mixtures to sulfuric acid, *Materials and Structures* 2003;**36** (258):242–249.
- [14] Chang Z, Song X, Munn R, Marosszeky M. Using limestone aggregates and different cements for enhancing resistance of concrete to sulphuric acid attack. *Cement and Concrete Research* 2005;**35**(8):1486–1494.
- [15] Pipilikaki P, Katsioti M. Study of the hydration process of quaternary blended cements and durability of the produced mortars and concretes. *Construction and Building Materials* 2009; **23**: 2246-2250.