Durability of high-performance concrete to an attack by a mixture of sulfuric acid and acetic acid

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Érkezett: 2022. 03. 24. ▪ Received: 24. 03. 2022. ▪ https://doi.org/10.14382/epitoanyag-jsbcm.2023.01

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Abstract

Agrifood and industrial effluents, such as acetic acid (CH_3COOH) and sulfuric acid (H_2SO_4), are very aggressive media for concrete structures. The mixture of sulfuric and acetic acids (strong acid and weak acid) can be encountered in the environment due to industrial and agrifood effluents; the behavior of cementitious materials in particular high performance concrete under the combined effect of sulfuric (H_2SO_4) and acetic (CH_3COOH) acid is not studied until now. In this regard, the present study was devoted to investigating (i) the durability of two high performance concrete (HPC) based on maximum compactness granular mix with and without silica fume to the unique effects of two types of acid, sulfuric acid (H_2SO_4) and acetic acid (CH_3COOH) and (ii) the durability of HPC with and without silica fume to the effects of a mixture of 5% H_2SO_4 and 5% CH_3COOH at an ambient temperature of 20±2 °C. The chemical resistance to acids was determined by monitoring the relative mass loss, compressive strength loss, and macroscopic changes (altered depth and porosity). A microscopy study including x-ray diffraction and scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDS) analysis was also performed. The experimental results showed very good compressive strength of HPC to the acid attack by CH_3COOH. The physico-mechanical properties were slightly influenced by the acetic acid attack. In contrast, the durability of HPC to attacks by H_2SO_4 and the mixture of the two acids (CH_3COOH) and (H_2SO_4) showed a remarkable modification in the initial properties of the HPC. The deterioration of HPC by the acid mixture was the most serious, with the maximum value of the mass loss reaching 6 times the mass loss due to acetic acid and almost twice the mass loss resulting from the sulfuric acid attack. X-ray diffraction analysis (XRD) showed the presence of calcium sulfate $CaSO_4{\cdot}2H_2O$ (gypsum) in the samples after the attack by sulfuric acid and after the attack by a mixture of the sulfuric acid and acetic acid.

Keywords: high performance concrete (HPC), durability, strong acid, weakacid, mixture of acids
Kulcsszavak: nagy teljesítményű beton (HPC), tartósság, erős sav, gyenge sav, savak keverék

1. Introduction

An increase in damage to concrete structures by acids has been observed around the world, as a consequence of the increase in sources of acidic environments due to the evolution of urban and industrial activities. Acidic media can come, for example, from agriculture. Since cementitious materials are very sensitive when in contact with acidic environments, acid attacks on concrete is a very important subject to study [1], [2]. Many authors have been interested in the durability of cement materials to different types of acids with a solution pH of less than, equal to, or greater than 4 [3], [4]. Some authors have studied the effect of attacks by strong acids, such as sulfuric (H_2SO_4), hydrochloric acid (HCl), carbonic acid (H_2CO_3), and phosphoric acid (H_3PO_4) [8], on various cement materials, mortar, and concrete with no mineral additions[12], [13].

Other researchers have studied the harmful effects of organic acids. Those studies investigated the effect of a single acid or a mixture of two or more types of organic acids [3], [16].

The compound formed is calcium acetate salt, which is very soluble in water *Eq. (1)*; therefore, the porosity increases with an alteration of the concrete. The corrosion of concrete due to acetic acid can generally be characterized by the following reactions [5]:

$$2CH_3COOH+Ca(OH)_2 = Ca(CH_3COO)_2+2H_2O \tag{1}$$

Monteny et al [6] characterized the attack with sulfuric acid (H_2SO_4) by the following chemical reactions:

$$CaCO_3+H_2SO_4+2H_2O = CaSO_4{\cdot}2H_2O+H_2O+CO_2 \tag{2}$$

$$Ca(OH)_2+ H_2SO_4 = CaSO_4{\cdot}2H_2O \tag{3}$$

$$3CaO{\cdot}Al_2O_3{\cdot}12H_2O + 3(CaSO_4{\cdot}2H_2O) + 14H_2O = 3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O \tag{4}$$

$$3CaO{\cdot}SiO_2{\cdot}3H_2O+H_2SO_4 = CaSO_4{\cdot}2H_2O+Si(OH)_4 \tag{5}$$

The primary reaction product manifested on the concrete surface is gypsum, which is associated with volume expansion *Eq. (3)* and can induce tensile stresses in concrete, resulting in cracking and spalling. Further reaction of gypsum with calcium aluminate phases in the cementitious matrix can form ettringite *Eq. (4)*, which has a larger volume increase than that of gypsum, thus leading to more micro- and macro- cracking. In addition, sulfuric acid decomposes the cementitious matrix by decalcifying calcium silicate hydrate (C–S–H) *Eq. (5)*, thus contributing to strength loss [6].

Previous research

Achoura.D et al [8] found a reduction in the mechanical resistance of mortars based on blast furnace slag under the effect of attacks by different types of acids. The maximum decrease was observed in the samples immersed in the H_2SO_4 solution followed by hydrochloric acid (HCl), phosphoric acid (H_3PO_4), and finally byacetic acid CH_3COOH. The attack by H_2SO_4 leads to the formation of gypsum and ettringite, the attack by hydrochloric acid HCl leads to the formation of calcium chloride and iron hydroxide, the attack by acetic acid CH_3COOH leads to the formation of calcium acetate, and the attack by phosphoric acid H_3PO_4 leads to the formation of calcium phosphate.

Ammonium nitrate (NH_4NO_3) is an aggressive agent for cement paste, of which an acceleration of Ca leaching was observed during attack. In addition, the degraded depth and the leached Ca linearly increased as a function of the square root of the immersion time of the samples in the Ammonium nitrate (NH_4NO_3) solution. An increase in water permeability and sample porosity after attack by Ammonium nitrate (NH_4NO_3) was noted for all samples [7].

Zivica.V [9] compared the aggressiveness of organic acids to that of inorganic acids. He demonstrated the aggressive power of acetic acid solution, which he compared to that of lactic acid.

We found in a previous study that the relative loss of mass of HPC under attack by a 4% sulfuric acid H_2SO_4 solution did not exceed 4%. Crystallization of calcium sulfate (gypsum) and thaumasite were detected by X-ray diffraction (XRD) at the end of the test [10].

Acid attack on high strength concrete with and without silica fume is mainly influenced by the type of acid even though they may have the same high concentration of 15%. Partial replacement of cement with silica fume up to 15% by weight caused no effect of the lactic acid ($C_3H_6O_3$) attack, reduced the HCl attack, and worsened the H_2SO_4 attack [11].

Kazuyuk et al [12] showed that using silica fume as a replacement cementitious material can increase sulfuric acid resistance. Zivica. V [13] reported that the use of chemically modified silica fume reduced the intensity of the hydrochloric acid attack. E. Hewayde et al [14] showed that the presence of silica fume in the concrete mixture had a minor effect on the resistance to the 7% H_2SO_4 solution. L. Mlinárik et al [32] studied the influence of combined of metakaolin and silica fume on the durability of mortars. The mortar specimens were exposed to two different types of acidic solutions, sulfuric acid and to acetic acid up to 390 days. The sulfuric acid caused increase in mass, the best results were provided by the metakaolin mixture. In acetic acid attack, the combined use of metakaolin and silica fume did not result better resistance, than for the other mixtures. On the other hand after almost one year of exposure, the differences are not significant.

Yasser Sharifi et al [15] studied the durability of mortars containing ceramic waste powder (CWP), like other cementitious materials, to attacks by sulfuric acid with a pH = 1.5. The cement was replaced with CWP powder in amounts of 0, 5, 10, 15, 20, and 25% (by weight of cement). This study presented the mechanical resistance tests, loss of mass of cement mortars, and a microstructure analysis (SEM and XRD). The results showed that mortar samples containing 5% CWP exhibited the lowest mass loss at all ages (0 days to 56 days). Crystallization of gypsum was observed by XRD in samples at the end of testing.

The addition of fly ash to mortars and concretes increased their chemical resistance to attacks by a mixture of organic acids (acetic acid CH_3COOH and lactic acid $C_3H_6O_3$), reducing the degradation of concrete and mortar samples compared to compositions without fly ash [16].

Sara Irico et al [17], studied the durability of two self-compacting concrete (SCC) by severe sulfuric acid attack at pH 2. The (SCC) types that are based on ordinary Portland cement (OPC) and granulometrically optimized blast-furnace slag cement was evaluated by three complementary tests that were performed in different research institutes. The use of granulometrically optimized slag cement provided a moderate increase of the concrete resistance against acid attack.

Compressive strength loss did not have a direct relation with mass loss of Self-consolidating concrete (SCC) specimens under sulfuric acid attack [18].

William G.Valencia-Saavedra et al [19], studied the acidic attack behaviour of alkali-activated concretes, based on a low-quality fly ash (FA), using as sources of calcium granulated blast furnace slag (GBFS) and Portland cement (OPC), which were incorporated in a 20% by weight proportion. A mixture of sodium silicate and sodium hydroxide was used as the activating solution. The specimens were exposed to solutions of sulfuric acid H_2SO_4 and acetic acid CH_3-COOH at concentration 1 M for 360 d. The results indicate that alkali-activated concretes show better performance compared with that of OPC. M. Nasir et al [28][29] combined blast furnace slag with silico-manganese fume to produce alkali-activated mortars. Slag free specimens were also studied. After exposure to H_2SO_4 (5%), they found that the slag free specimens exhibited high resistance attributed to the lack of Ca in silico-manganese fume. The blended specimens were reported to have underwent deal-umination along with gypsum formation which resulted in severe spalling.

L.Wu et al [29][30] found that adding up to 10% calcium aluminate cement had a positive impact on the H_2SO_4 (pH =2.0) resistance of alkali-activated metakaolin. This was attributed to the reduced volume of permeable voids and the enhanced neutralisation capacity. Khan et al [31] investigated the replacement of fly ash with waste glass (GP up to 40%) in alkali-activated fly ash/slag. They exposed mortars to H_2SO_4 (3%) and HCl (3%) for one year and found that waste glass improved the acid resistance in terms of the mass and strength losses observed. The inclusion of 10%–20% GP as a replacement of fly ash (FA) substantially reduced the physical, mechanical and microstructural damages of the specimens due to acid attack.

The effect of acid rain simulated by a mixture of sulfuric acid H_2SO_4 and nitric acid (HNO_3) was applied to concrete samples with a pH equal to 1. A slight increase in tensile strength was observed for immersion up to 10 days. Beyond 10 days, a decrease in tensile strength with increasing immersion time in the solutionwas observed [20].

The development of industrial, agricultural, food-processing activities, urban evacuations producing large quantities of effluents, these effluents are loaded mainly with organic acids and sulfuric acid used for the manufacture of fertilizers, also used in the petroleum industry…, thus the evacuation of waste water loaded with acetic acid used in cleaning products, certain medicines, food additives and preservatives, acid rain loaded with sulfuric acid, consequently, waste of great quantities loaded with acetic and sulfuric acid are stored before treatment in reinforced concrete structures, or evacuated into nature, and infiltrated under the foundations of the structures. Concrete structures exposed to these acid laden effluents are generally degraded very quickly. Acetic and sulfuric acids are aggressive environments for the cementitious matrix and the limestone aggregates, the salts resulting from the chemical reactions are soluble and insoluble salts (calcium acetate and calcium sulphate). The combined effect of attack by two sulfuric and acetic acids on a cementitious material little encountered in the environment, thus, it is not yet studied. In this respect, the study of the durability of cementitious materials, in particular HPC, under the combined effect of sulfuric and acetic acids is very important.

The originality of this research consists of studying the durability of HPC with and without silica fume to attacks by acid mixtures composed of acetic acid and sulfuric acid at a temperature of 20±2 °C in presence of low-pH solutions <4.

2. Materials and methods

2.1 Materials

2.1.1 Aggregates

The aggregates used to manufacture the different concrete compositions are of limestone origin of classes 0/4, 4/8, 8/16 and 16/20 with the addition of naturals and from rivers 0/4 in order to increase the compactness of the aggregates mixture and improve workability.

2.1.2 Cement and silica fume

The chemical analysis of cement and silica fume are summarized in *Table 1*.

	CEM II/A 52,5	Silica Fume
SiO_2	19.58%	85%
Al_2O_3	4.52%	-
Fe_2O_3	2.76%	-
CaO	61.63%	-
K_2O	0.61%	-
Na_2O	0.09%	-
Na_2O-equ	0.50%	-
Loss on ignition	3.34%	-
MgO	1.75%	-
SO_3	2.59%	<2.5%
Cl^-	0.019%	<0.2%

Table 1 Chemical compositions of CEM II/A 52.5 cement and silica fume
1. táblázat A CEM II/A 52.5 cement és szilikapor kémiai összetétele

2.2 Formulation of high-performance concrete (HPC)

The HPC formulation method used was inspired by the HPC formulation method developed at the university of Sherbrooke [21] follows the same approach as the American standard ACI 211[22]. Overall, the formulation of HPC was based on a combination of empirical results and calculations based on the method of absolute volumes. Determination of the optimal dosage of the different granular classes used was based on the maximum compactness of the mixtures in the dry state. Combinations of aggregate mixtures were prepared; we started with binary mixtures, then ternary, quaternary, and ended with pentagonal mixtures. The maximum compactness in the dry state was observed for a pentagonal mixture. The determination of the dosage of superplasticizer MEDAFLOW 30 was conducted according to the grout method [21]. The main objective of the grout method is to experimentally determine the optimal dosage of superplasticizer (saturation dose) [21]. The compositions of the various concretes formulated, and which will be the subject of a characterization study both in the fresh and hardened state, are presented in *Table 2.*

Mix HPC	HPC	HPC FS
Crushed aggregat 16/20, kg/m³	432.05	426.21
Crushed aggregat 8/16, kg/m³	259.23	255.72
Crushed aggregat 4/8, kg/m³	388.84	383.59
Crushed limestone sand C0/4, kg/m³	344.22	339.59
Sand naturel R0/4, kg/m³	344.22	339.59
Cement, kg/m³	470	423
Silica fume, kg/m³	0	47
Water, l/m³	164.5	164.5
SP, kg/m³	5.64	8.46
e/c	0.35	0.38
e/l	0.35	0.35
Slump, mm	300	300

HPC: high performance concrete without silica fume
HPC FS: high performance concrete with silica fume

Table 2 Mix proportions and slump for high performance concrete (HPC)
2. táblázat Keverési arányok és süllyedés nagy teljesítményű betonhoz (HPC)

2.3 Test method

The test was devoted to investigating the durability of two high HPC with and without silica fume to the unique effects of two types of acid, sulfuric acid and acetic acid and the of mixture of 5% sulfuric acid and 5% acetic acid at an ambient temperature of 20±2°C. The test of chemical resistance to acid attack was carried out on two types of prismatic samples of dimensions 7x7x28 cm and cubic dimensions 10x10x10 cm. The shape, dimensions of the test pieces and the molds comply with European standard NF EN 12390-1 [23]. The acid concentration of the solutions was 5%; the test samples aged 56 days conserved in water were immersed in the solution in closed plastic tubs for 120 days. The solution was renewed every 15 days for the attack by sulfuric acid and the acid mixture, and renewed after 1 week for the attack by acetic acid. The samples were placed in a climatic chamber where the temperature was set at 20±2°C.

3. Results and discussion

3.1 Mechanical resistance of HPC before durability testing

The compression test was carried out on cubic specimens of dimensions 10x10x10 cm^3 cured for 1 week in water for 28 days and 56 days after demoulding. The three-point bending test was carried out on prismatic specimens 7x7x28 cm^3 aged 28 and 56 days. The compression and bending tests were carried out in accordance with the standards [24][25]. The results of the tests are the average values obtained on three test specimens. *Table 3* shows the evolution of the mechanical compressive strength and flexural strength, respectively.

Mix HPC	Compressive strength MPa		Flexural strength MPa	
Age	28 days	56 days	28 days	56 days
HPC	68.90	74.48	4.66	4.95
HPCFS	68.87	81.33	4.85	4.99

Table 3 Mechanical strength
3. táblázat Mechanikai szilárdság

3.2 PH evolution

Fig. 1 shows the change of pH of the acid solutions after immersion of the samples with and without HPC silica fume. According to the results, there is a rapid increase in pH for the acetic acid based solution because it reaches the value of 4 after 24 h of immersion of the samples. While, the pH values remained stable up to 10 days of immersion of the samples in solutions based on sulfuric acid and mixture of acids, the pH reached the value of 4 after 15 days. This can be explained by the phenomenon of the dissociation of strong and weak acids.

3.3 Exterior and interior appearance of the sample after the tests

Fig. 2 shows the appearance outside and inside the sample at the end of the trials.

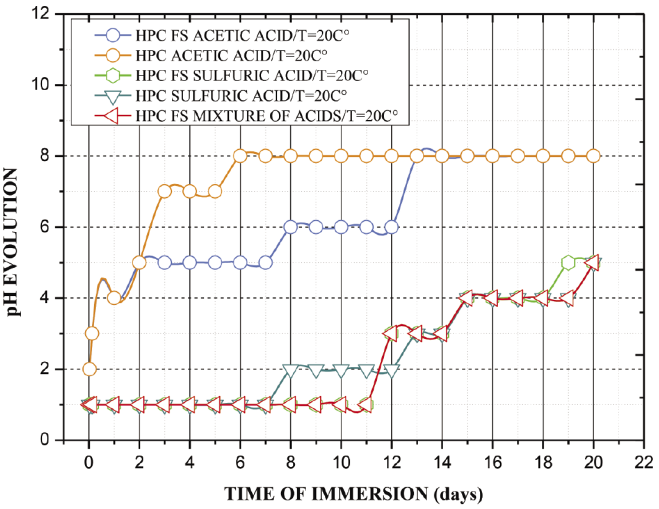


Fig. 1 pH evolution of acid solutions after sample immersion
1. ábra Savas oldatok pH-változása mintabemerítés után

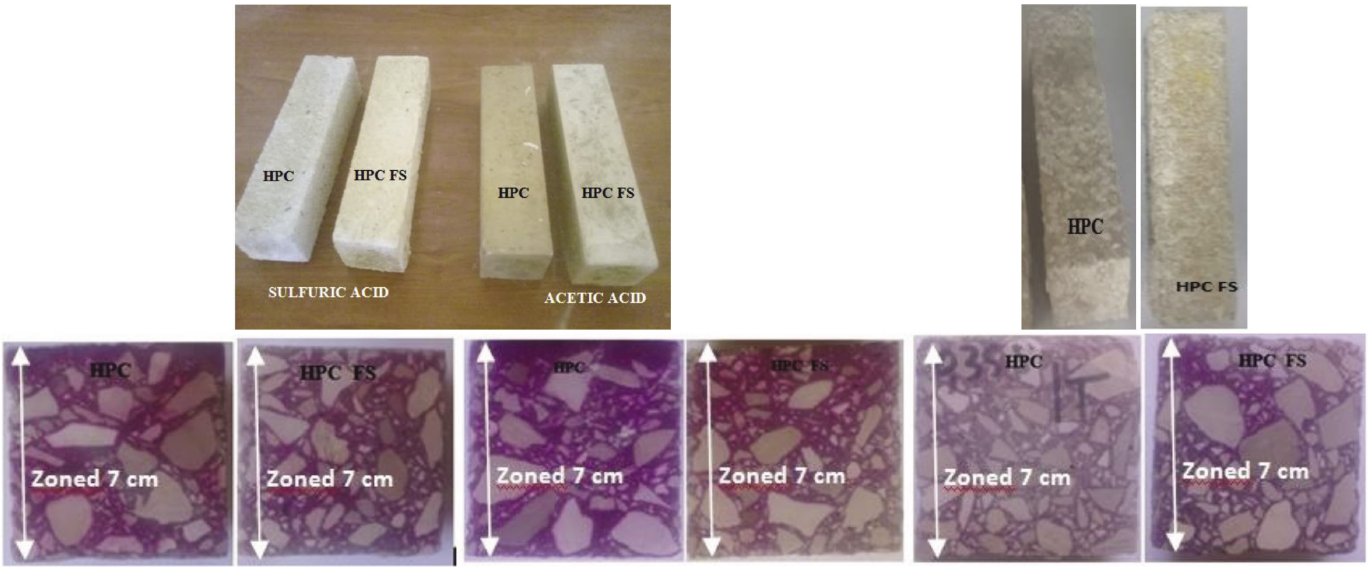
Acetic acid

The test samples preserved in the acetic acid based solution were characterized by a smooth, clear, brown surface without cracks. After cutting the samples, no change was observed inside the HPC samples. The color change appears only on the surface (see *Fig. 2*).

Sulfuric acid and acid mixture: The test samples were characterized by a whitish appearance and a rough surface. Inside the samples, no degradation was observed (i.e., degradation appears only on the surface, see *Fig. 2*).

3.4 Altered depth

At the end of the test, the samples were sawn perpendicularly and sprayed with a solution dosed at 1% of phenolphthalein in order to check the healthy and degraded areas of the test pieces. The phenolphthalein test applied to the sections of the



Acetic acid Sulfuric acid Mixture acids

Fig. 2 Exterior and interior appearance after cleaning the samples sprayed the cut surface with phenolphtalein solution
2. ábra A minták külső és belső megjelenése tisztítás után, a vágási felületet fenolftalein oldattal permetezték be

samples at the end of the attack test by acetic and sulfuric acid showed the coloring of the entire sawn section (see *Fig. 2*). This was explained by the dissolution of the entire degraded surface of the samples. The histogram in *Fig. 3* shows the change in the altered depth. According to the results, the altered depth for the attack by acetic acid does not exceed a few micrometers for the two compositions of HPC, while the alteration of concrete by sulfuric acid reached 1.2 mm after 120 days of immersion of the samples in the aggressive solution. The curve in *Fig. 3* illustrates the longitudinal evolution of the altered depth of the different compositions of the HPC tested in the acid mixture; the range of its variation was between 1.5–2 mm.The layer of corrosion products on the surface of HPC increased faster in the solution of sulfuric and mixture acids than in the solution of acetic acid. this is explained by the formation of gypsum $CaSO_4{\cdot}2H_2O$ on the surface of the sample, which results from the reaction of sulfuric acid, calcite $CaCO_3$ and portlandite $Ca(OH)_2$.

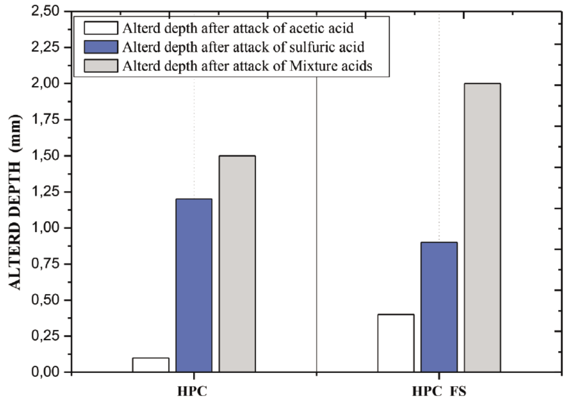


Fig. 3 *Altered depth*
3. ábra *Változott mélység*

3.5 Mass loss

The cumulative mass loss at each month (^{TM}Mt) was calculated by:

$$\delta M_t = \left(\frac{M_t - M_i}{M_i}\right) \times 100 \qquad (6)$$

M_t: Mass at time t (kg).
M_i: Initial mass before exposure to acid (kg).

Fig. 4 shows the evolution of the variation rates of the masses of the different compositions of HPC tested in an aggressive solution of acids: acetic acid, sulfuric acid, and acid mixture.

- **Acetic acid:** In the first month, the mass losses are almost identical for the two compositions with and without silica fume. From the second month of the acid attack, it is observed that the mass loss is slightly lower by the incorporation of silica fume in the composition of HPC. The mass losses do not exceed 1.5% after 120 days of immersion in the acid solution. The loss of mass in the specimens is mainly due to dissolution of the calcium upon exposure to acetic acid.
- **Sulfuric acid:** The maximum mass losses were observed in the compositions with silica fume; its maximum value reached 5% after 120 days of immersion of the samples in the acid solution, the differences are not significant. These mass losses were noted to be significant compared to samples attacked by acetic acid.
- **Acid mixture:** The results show an increase in the mass loss of the samples as a function of the duration of the immersion of the samples in the acid mixture solution. The maximum mass loss is 10.26% after 120 days of immersion of the samples with silica fume in the acid mixture solution. This marked increase in mass loss is mainly due to with the reduction of the pH, results from the addition of sulfuric acid.

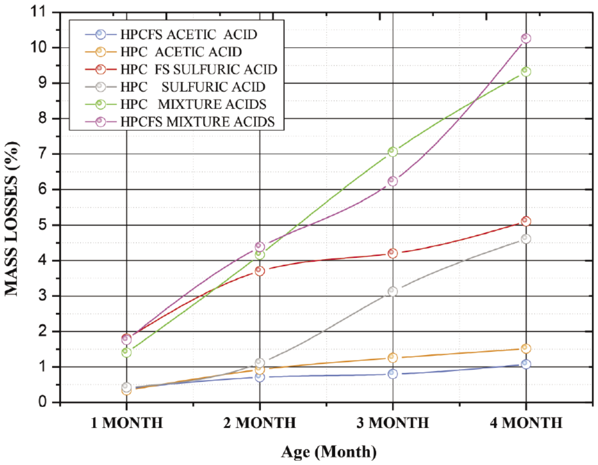


Fig. 4 *Relative mass losses*
4. ábra *Relatív tömegveszteségek*

The attack of HPC with sulfuric acid causes mass loss of the order of 5%, i.e., 3.4 times the mass loss resulting from the attack of acetic acid after 120 days in the solution. While the deterioration of HPC by the acid mixture was noticed, the maximum value of the mass loss reached 9.39%, which is 6 times the mass loss by the aggression of acetic acid and almost twice the mass loss resulting from the aggression of sulfuric acid (see *Fig. 5*). The increase in mass loss recorded to attack by the mixture of acids can be explained by the decrease in pH during the fifteen days, and therefore the increase in the speed of deterioration of the samples.

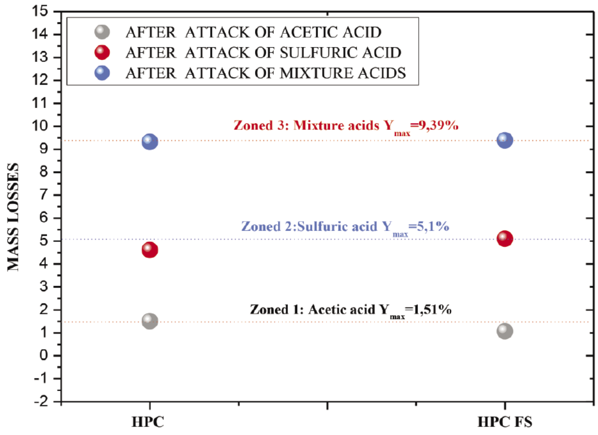


Fig. 5 *Relative mass loss*
5. ábra *Relatív tömegveszteség*

3.6 Porosity accessible to water

The histogram of *Fig. 6* shows a slight increase of the porosity accessible to water samples before and after the attack by acetic acid, sulfuric acid, and the acid mixture. A slight increase in the porosity of the HPC was observed after attack by the acids. According to the results illustrated in *Fig. 7*, the maximum increase in porosity of HPC without silica fume does not exceed 0.56% compared to the value of the initial porosity before immersion of the samples in the acid solution. This value is 0.65% for HPC with silica fume. The measurements of porosity have shown that HPC formulated has good resistance to attack by acids, and this thanks to its dense structure.

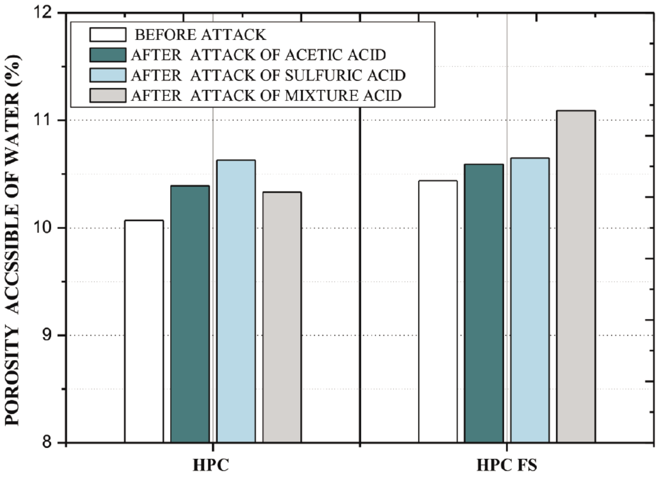
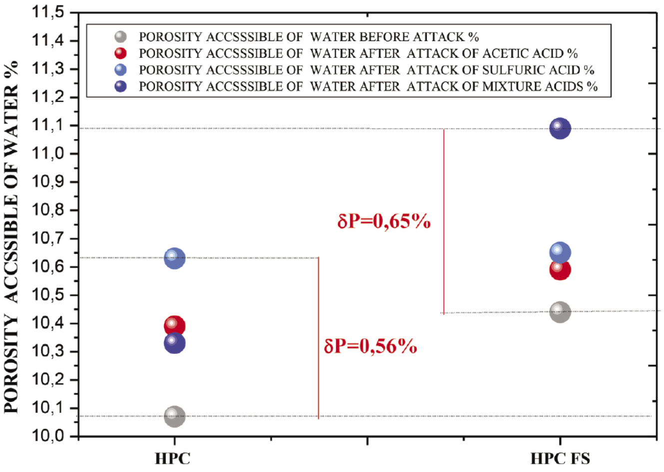


Fig. 6 *Porosity accessible to water of the specimens before and after the attack*
6. ábra *A próbatestek víz számára hozzáférhető porozitása a savazás előtt és után*



Fig, 7 *Variation of Porosity accessible to water*
7. ábra *A víz számára elérhető porozitás változása*

3.7 Compressive strength

The histogram in *Fig. 8* shows the variation in the compressive strength of HPC compositions tested before and after attack by both acetic and sulfuric acid and also for the acid mixture over 120 days. It can be seen that the compressive strength of the HPC samples under the attack of acetic acid is slightly changed; the maximum reduction rate is δσ = 3.73% (see *Fig. 9*). A remarkable drop in compressive strength was recorded for the HPC immersed in a solution of sulfuric acid and the acid mixture. The decrease of the compressive strength reached δσ = 46% after the attack by sulfuric acid and δσ = 54.35% after the attack by the acid mixture despite the sample cores remaining healthy and degradation appearing only on the surface. This result can be explained by the importance of surface degradation, which decreases the toughness of the material and, consequently, the ease of the propagation of cracks at the moment of crushing of the test pieces, which accelerate the rupture of the material.

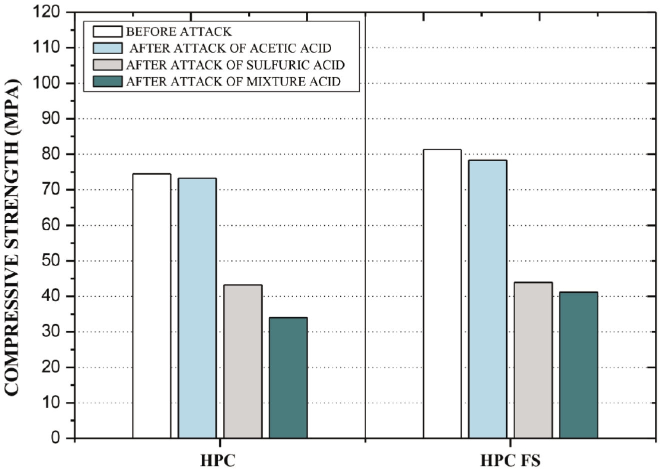


Fig. 8 *Mechanical compressive strength*
8. ábra *Mechanikai nyomószilárdság*

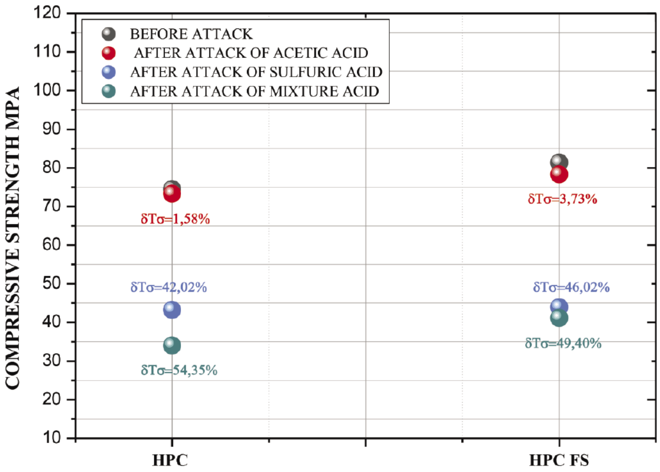


Fig. 9 *Variation of compressive strength*
9. ábra *A nyomószilárdság változása*

The formulated HPC compositions exhibit very good resistance to attack by sulfuric acid despite the fact that the aggregates used are reactive. The relative mass loss does not exceed 5% after 4 months of immersion in the dosed solution of 5% sulfuric acid. A comparison of the results obtained by some authors, in the framework of studying the durability of HPC to attacks by sulfuric acid, are summarized in the following: Shweta Goyal [26] studied the durability of HPC to attacks by sulfuric acid with a solution concentration of 1%. These HPC were formulated with and without 5% silica fume substitution, with granite-type crushed aggregates and natural river sand. According to the results obtained by Shweta Goyal [26], the relative mass losses reached 7% after 4 months of immersion in the dosed solution of 1% sulfuric acid for composition M2-II (composition with 5% silica fume, w/c= 0.35, compressive strength R_{c28} = 83.5 MPa, slump = 20.4 cm). E. Hewayde [14] showed that the relative mass loss for a HPC reached 19% after 61 days of immersion of the samples in a solution of 3% sulfuric acid and 30% after 61 days of immersion of the samples in a 7% sulfuric acid solution, although this HPC was made of siliceous aggregates (composition with and without silica fume 15%, w/c = 0.35, R_{c28} = 57.6 MPa and 68 MPa, slump = 5 ± 1 cm). R. Sri Ravindrarajah [11] performed research on the durability of high performance concrete based on silica fume to attack by sulfuric acid. The concentration of the acid solutions was maintained at 15%. The results showed that the incorporation of silica fume had a negative effect for the attack of HPC by sulfuric acid; the maximum mass loss for the HPC reached 20% after 30 days of immersion in the aggressive solution.

The good resistance to attacks of sulfuric acid observed for our HPC, results from the use of granular mixture with maximum compactness, the latter minimizes the speed of deterioration of material and consequently its lifespan.

	Mass loss (5% Acid) sulfuric Research		Mass loss (1% Acid sulfuric) Shweta Goyal [26]		Mass loss (3% acid sulfuric) E. Hewayde [14]		Mass loss (15% acid sulfuric) E. Hewayde [14]	
	HPC	**HPC FS**	**HPC**	**HPC FS**	**HPC**	**HPC FS**	**HPC**	**HPC FS**
After 30 days	0.42%	1.8%	-2%	-2%	10%	10%	20%	14%
After 60 days	1.11%	3.7%	5%	3.5%	18%	19%	-	-
After 90 days	3.12%	4.2%	7%	6%	-	-	-	-
After 120 days	4.61%	5.1%	11%	7%	-	-	-	-

Table 4 Comparison of the results
4. táblázat Az eredmények összehasonlítása

4. Microstructure analysis by SEM/EDS and XRD after attack by acids

Microstructure analysis by SEM/EDS and by XRD were carried out at the end of the acid attack tests in order to verify all types of modification within the material at the microscopic scale. We chose the composition HPC FS for our microscopic study, from the cut of the sample sawn perpendicularly. The results obtained are as follows:

4.1 Acetic acid

The SEM image in *Fig. 10a* shows that the HPC FS sample always remained healthy with very little appearance of micro-cracks and small pores characterized by lengths of a few micrometers. According to the EDS atomic spectrum, HPCFS contains peaks of Ca, O, and C, which are the main elements in the composition of hydrates and calcium acetate resulting from the reaction of portlandite and calcite with acetic acid. Another smaller scale SEM image was taken on the same sample. *Fig. 10b* shows crystallization of a dense regular texture in sheets with very little crystallization from a gel. Since the EDS analysis shows the richness of the sample by calcium and a low percentage of silicon SiO_2, we believe this is the crystallization of portlandite with very little of the calcium acetate crystallizing in the pores. An X-ray diffraction analysis was performed on a ground sample (in average sample) in order to further validate the results obtained by EDS. *Fig. 11* shows the spectrum of HPCFS obtained by XRD. According to the results, the components detected by XRD are calcite $CaCO_3$, silicon SiO_2, and calcium silicate $CaSiO_3$. Calcium acetate is not detected in this analysis; this can be explained by its solubility in water.

4.2 Sulfuric acid

The presence of a few long micro-cracks in the paste and in the limestone aggregates was observed in the HPC FS sample. These micro-cracks were characterized by lengths of the order of 600 µm (see *Fig. 12a*). EDS analysis shows that the HPC FS sample contains peaks of Ca, O, Si, Al, and C, which are the main components in the composition of hydration products. The absence of sulfur (S) was noted in the EDS analysis. Sulfur is a major component in the composition of ettringite and gypsum. In contrast, the second full-scale SEM image shown in *Fig. 12b* shows the crystallization of hydrates and gel. For this purpose, XRD analysis was performed to confirm the results; actually, according to the spectrum in *Fig. 13*, the XRD analysis detects the crystallization of calcium sulphate $CaSO_4 \cdot 2H_2O$ (gypsum) and calcium-aluminum-silicate-hydrate $CaAl_2Si_2O_8 \cdot 4\ H_2O$ (gismondine [27]) within the material.

4.3 Acid mixture

After observing the SEM image presented in *Fig. 14a*, we noticed the appearance of a large field of micro-cracks at the level of the paste, at the level of the calcareous aggregates, and at the interface of the paste aggregates siliceous. The lengths of the micro-cracks exceeded 600 µm. The EDS spectrum of HPCFS contains peaks of Ca, O, Si, Al, and C, which are the main building blocks of hydration products and calcium acetate. As in the single attack by sulfuric acid, there is no sulfur in the EDS analysis. The large scale SEM image shown in *Fig. 14b* also shows gel crystallization within the sample, which we believe to be hydrates and $CaSO_4 \cdot 2H_2O$ (gypsum). However, the XRD analysis in *Fig. 15* detects the crystallization of calcium sulfate $CaSO_4 \cdot 2H_2O$ (gypsum) and calcium-aluminum-silicate-hydrate $CaAl_2Si_2O_8 \cdot 4\ H_2O$ (gismondine [27]) within the ground concrete sample.

The salts, which were detected only by X-ray diffraction analysis on the ground sample, can be explained by the crystallization of salts on the surface of the sample.

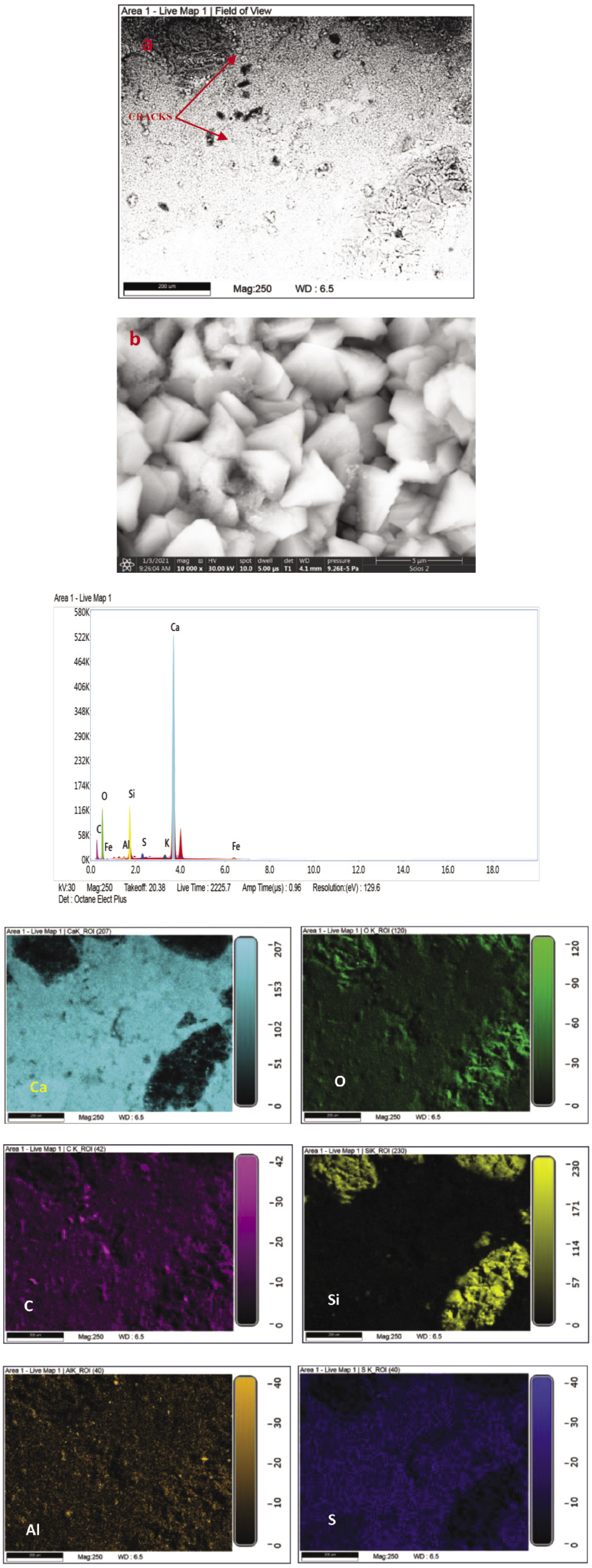


Fig. 10 *SEM observation accompanied by EDS analysis for the HPC FS sample after 4 months of immersion in a solution of 5% acetic acid*

10. ábra *SEM megfigyelés kíséretében EDS analízis a HPC FS mintánál 4 hónapig 5%-os ecetsav oldatba való merítés után*

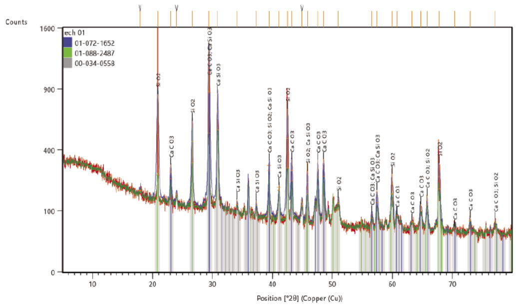


Fig. 11 *XRD observation for the HPC FS sample after 4 months of immersion in a solution of 5% acetic acid*

11. ábra *XRD megfigyelés a HPC FS mintánál 4 hónapig 5%-os ecetsav oldatba való merítés után*

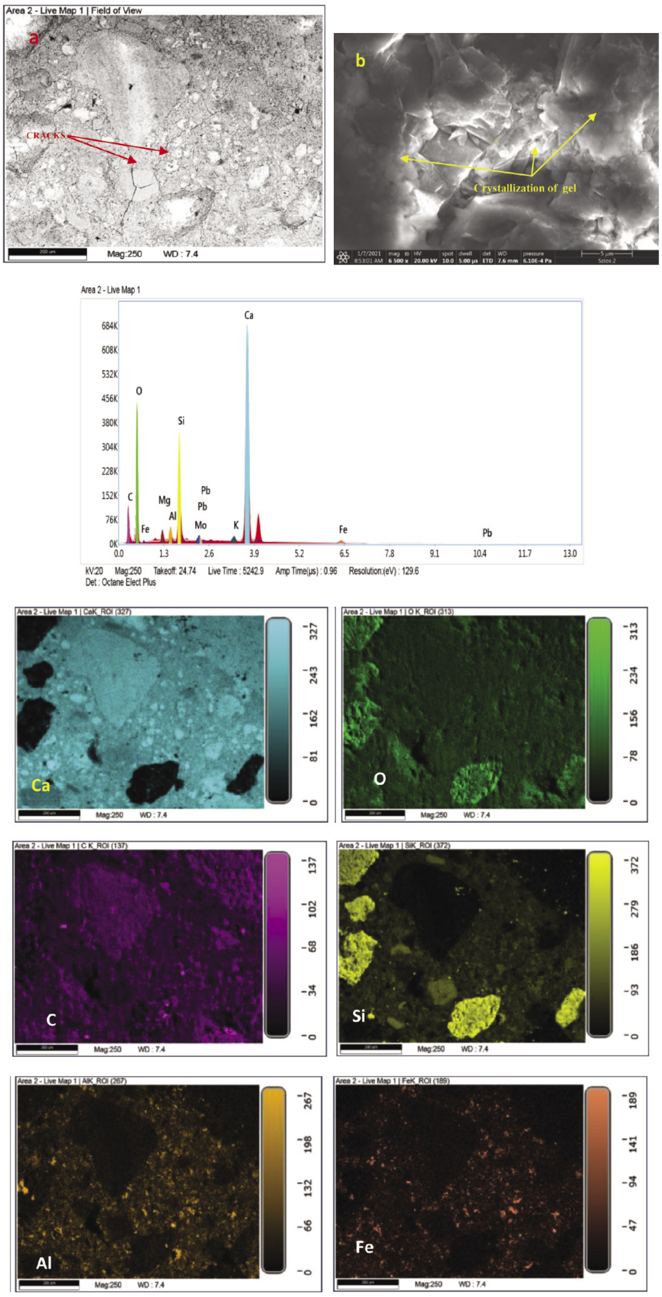


Fig. 12 *SEM observation accompanied by EDS analysis for the HPC FS sample after 4 months of immersion in a 5% sulfuric acid solution*

12. ábra *SEM megfigyelés kíséretében EDS analízis a HPC FS mintánál 4 hónapig 5%-os kénsavoldatba való merítés után*

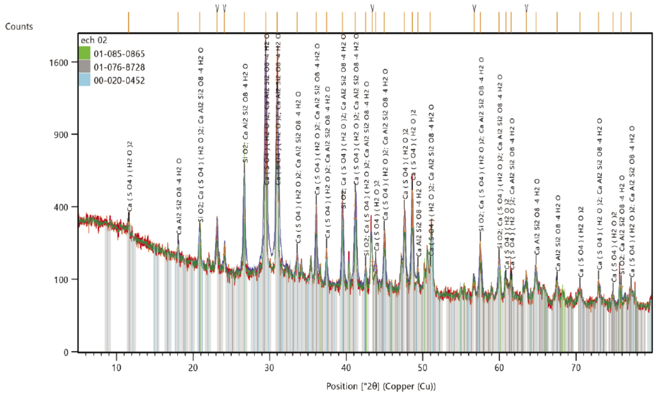
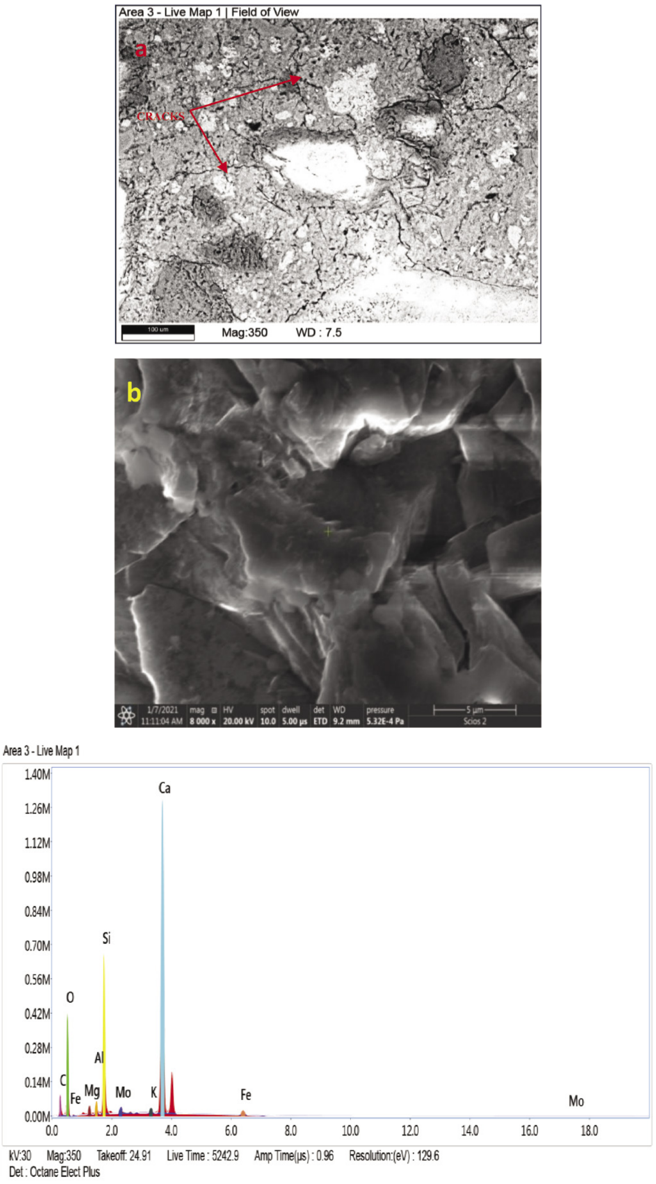


Fig. 13 *XRD analysis on the HPC FS sample after 4 months of immersion in a 5% sulfuric acid solution*

13. ábra *XRD analízis a HPC FS mintán 4 hónapig 5%-os kénsavoldatba való merítés után*



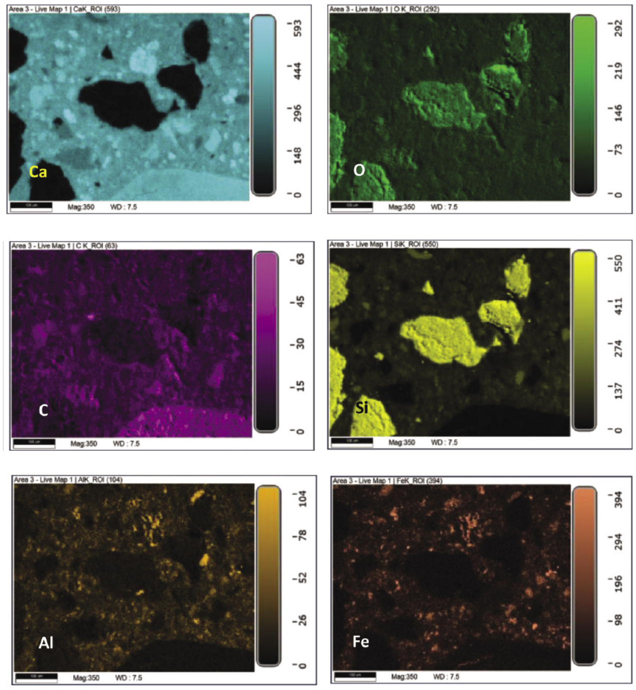


Fig. 14 *SEM observation accompanied by EDS analysis for the HPC FS sample after 4 months of immersion in a solution based on 5% acetic acid and 5% sulfuric acid*

14. ábra *SEM megfigyelés kíséretében EDS analízis a HPC FS mintánál 4 hónapig 5% ecetsav és 5% kénsav alapú oldatba való merítés után*

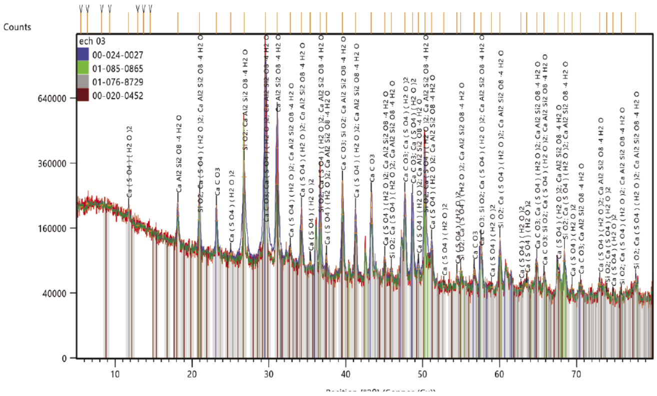


Fig. 15 *XRD analysis on the HPC FS sample after 4 months of immersion in a solution based on 5% acetic acid and 5% sulfuric acid*

15. ábra *XRD analízis a HPC FS mintán 4 hónapig 5 % ecetsav és 5% kénsav alapú oldatba való merítés után*

5. Conclusions

This work was focused on evaluation of durability of HPC under the single and combined effect of two types of acetic and sulfuric acids which are encountered in the environment. A comparative study was presented after the presentation of the results. From the obtained results following conclusions can be drawn:

- The study of the durability of different compositions of HPC formulated to the unique attacks of acetic and sulfuric acids showed us that the chemical and mechanical resistance of HPC was slightly affected by the attack of in the solution of acetic acid dosed 5%; while a remarkable drop in the physico-mechanical characteristics were observed for the attack of sulfuric acid. The rate of reduction of the compressive strength reached 46% and the relative loss of mass reached 5%. HPC made in the context of this study show very good resistance to attack by sulfuric acid, although the aggregates used responsive, and that compared to other results obtained by the researchers.

- The durability tests of HPC to attacks by a mixture of acids (acetic and sulfuric) at an ambient temperature of 20±2 °C showed an increase in the weathering rates or the rates of mass change at the end of the test to be almost double that compared to attacks by sulfuric acid and six times higher compared to attacks by acetic acid. A considerable drop in compressive strength was observed in all HPC compositions tested.
- The use of silica fume in HPC somewhat reduces the intensity of the acetic acid attack. The relative losses of the masses were observed to be minimal compared to the samples formulated without silica fume, the differences are not significant.
- In contrast, the addition of silica fume in HPC decreases the chemical resistance to the attack by sulfuric acid and the acid mixture. The maximum values of the relative mass losses were obtained for the samples attacked by a mixture of sulfuric and acetic acid.
- The microstructure analysis performed on the HPC FS sample after the attack with acetic acid, sulfuric acid, and the mixture of the two acids showed the following:
- The HPC FS sample after the acetic acid attack was characterized by a dense microstructure with the appearance of very few micro-cracks. No salt was detected by XRD, this can be explained by the solubility of calcium acetate in water.
- The presence of long micro-cracks and the crystallization of calcium sulfate ($CaSO_4 \cdot 2H_2O$) (gypsum) and gismondine ($CaAl_2Si_2O_8 \cdot 4\ H_2O$) within the HPC FS sample were detected by XRD at the end of the sulfuric acid attack. The modifications in the microstructure of HPC FS are the causes of the modification of the physico-mechanical characteristics of the sample (increase in porosity accessible to water and decrease in compressive strength).
- A significant development of micro-cracks within HPC FS after the attack by a mixture of acetic acid and sulfuric acid was observed compared to the appearance of the samples after the single attack of the two acids. As in the case of the sulfuric acid attack, crystallization of calcium sulfate ($CaSO_4 \cdot 2H_2O$) (gypsum) and gismondine ($CaAl_2Si_2O_8 \cdot 4\ H_2O$) was observed in the HPC FS sample by XRD. The remarkable changes in the microstructure justify the drop in strength resulting from the combined effect of the acetic acid and sulfuric acid.

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Ref.:
Djerfaf, Nadjat – **Nafa**, Zahreddine – **Belaidi**, Akram Salah Eddine: *Durability of high-performance concrete to an attack by a mixture of sulfuric acid and acetic acid*
Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 75, No. 1 (2023), 6–16. p.
https://doi.org/10.14382/epitoanyag-jsbcm.2023.01

Welcome notes to XVIII ECERS

The XVIIIth Conference of the European Ceramic Society will take place in Lyon, on 2-6 July 2023.

Lyon, where the Rhőne and the Saőne rivers meet, has always been a city of exchanges and industrial development, with major historic landmarks. 'Lugdunum' was founded in 43BC by the Romans and served as the capital of Gaul. It was also famous, as the world capital of silk, during the French Renaissance. Lyon's cuisine is famous all over the world, the cinema was invented by the Lumiére brothers in this City of Lights, surrounded by prestigious wine areas where you can taste Beaujolais, Burgundy and Cőtes-du-Rhőne, not far from the Alps and of course Mont Blanc. Lyon is also the city of cutting edge industry and engineering, especially in the fields of chemistry and materials, bio-technology and medicine, mobility systems, with numerous schools and faculties created to answer technological and societal needs.

Thus, it is a great pleasure to welcome ceramists in the City of Lights, to share the latest discoveries in ceramic science and technology, reconnect with colleagues from around the world, in a convivial conference atmosphere. The conference, hosting ceramic experts from industry and academia, offering a unique opportunity to participate in an international event covering the development and applications of ceramic-based systems.

In addition to the now traditional symposia dealing with innovative processing, thermo-mechanical properties, modelling and ceramics for different high-tech applications, emphasis will also be given to advanced characterization techniques, silicate-based ceramics and materials for building applications, as well as the place of ceramics in necessary sustainable development. Lyon has been growing and evolving for 2,000 years: it is today a leading sustainable destination. Therefore, intent on reducing our environmental impact, we will make this XVIIIth ECerS conference a truly "think green" event.

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