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The effect of SCMs and curing time on resistance of mortars subjected to organic acids

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ABSTRACT

Agricultural effluents such as liquid manure and ensilage effluents contain organic acids that constitute a severe chemical threat toward the concrete of agricultural structures. In contact with an acidic solution, the chemical equilibrium of the hydrates in cement paste is destabilized, causing negative effects on porosity, reinforcement corrosion, mechanical strength, and, in the long term, may result in the collapse of the structure. More durable concrete in this environment is needed. The purpose of this study is to examine the effect of the nature of the supplementary cementing materials (SCMs) as well as the curing time on the chemical and the physical modifications of cement pastes and on the compressive strength, mass loss, altered depth and microstructure of mortars immersed in acetic acid at a pH of 4.

This study concentrated on three types of hardened cement pastes or mortars made with ordinary Portland cement (OPC), slag and metakaolin cements, cured for period varying from 28 days to 1 year. The results show the beneficial effect of the curing time before the acid immersion, the better durability of metakaolin cement and the good chemical resistance of the slag cement against acid attack. The latter develops low compressive strength and is more sensitive to the curing time but the drop of its resistance due to the acid immersion is minimal due to its strong chemical resistance.

1. Introduction

Intensification of farming practice is at the origin of environmental problems directly linked to the excess of effluents such as liquid manure and ensilage effluent [1,2]. Although animal excrement recycling was recognized as a practice that maintains and improves the fertility of soils [2], current policies aim for storage in water-tight silos, often built in concrete.

The agricultural effluents are quickly transformed under the effect of bacteria into organic acids. Effluents such as liquid manure and ensilage effluents contain organic acids that constitute a severe chemical threat toward the concrete of agricultural structures. The pH of ensilage effluents is 4 and that of liquid manure is between 6 and 8 [3]. According to Zivica and Bajza [4] and Pavlik [5], the degree of aggressivity of an acid is dependent on the chemical character of anions present. The strength of the acid, its degree of dissociation in solution and, mainly, the solubility of the salts formed are dependent on the chemical character of the anion [6–8]. Organic acids react with hydrated and anhydrous compounds of the cement paste to give mainly calcium salts. Depending on their solubility, these salts may precipitate or may be dissolved in solution.

Acetic, and more so lactic acids, are known as very aggressive compounds [5,9]. Their reactivity was explained by the reaction with the free lime $Ca(OH)_2$ of the concrete producing very soluble calcium salts [9] which, because they are soluble, are leached away by the aggressive solution. This effect contributes to the progress of the acidic front. On the other hand, oxalic acid is very little or not at all aggressive to the matrix [10]. The action of the oxalic acid solution is beneficial because the formation of calcium oxalate salts is insoluble favoring a protective effect [10].

Bertron et al. [11] showed that the four acids of the liquid manure tested (acetic, propionic, butyric and iso-butyric acids) have an equivalent aggressiveness while lactic acid presents a greater aggressiveness according to its dissociation constant value (pKa). Moreover, it was demonstrated that an acetic acid solution of pH 4 mimics well the aggressiveness of organic acids found in animal manure [11].

The concrete is a strongly basic environment with a pH greater than 13. In contact with an acidic solution, the chemical equilibrium of the cement hydrates is destabilized. A variation of pH value means a change in the solubility of the various compounds, which can influence the stability of cement-based materials [12]. In contact with an acetic acidic solution (representing liquid manure composition), the concrete will undergo an acido-basic reaction leading to the formation of soluble to very soluble salts in water [4,6–8,13]. The stability of the different hydrates is variable. Portlandite is the most susceptible in an aggressive attack, with dissolution initiated at a pH below 12.5 [14]. Consequently, the porosity of the material and the corrosion of the rebar embedded in degraded concrete will increase, the mechanical strength will drop, and, in the long term, can result in the total collapse of the structure. Given that the concrete for agricultural constructions is

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subject to attack by organic acids, the selection of durable materials becomes essential.

Many factors affect the performance of concrete in an aggressive environment such as the type of cement, the amount, the fineness of any supplementary cementing material (SCM) used and especially the curing conditions [11,15]. According to Baron and Ollivier [12], the conditions and duration of curing are important for the quantity and stability of hydrates. The use of SCMs can considerably improve the performance of concrete in agricultural structures by improving properties such as workability, durability and permeability [12,16]. Pozzolanic and/or the filler effect can improve the chemical stability of the cement matrix in an acidic environment by the refinement of porosity and the reduced presence of calcium hydroxide, which is most vulnerable to acid attack [17,18]. Knowing that, the acidic alteration of the cement matrix is translated into a decalcification of the altered zone manifesting by the progressive dissolution of all phases portlandite, ettringite, C_4AH_x and C-S-H [19].

Today, the incorporation of SCMs has gained importance because it improves the durability of concrete [11,20,21] and leads to a significant reduction in CO_2 emissions [22]. The use of SCM can lead to densification of the mortar [23] and contribute not only to the decrease or disappearance of calcium hydroxide but can also modify the chemical composition of the cement matrix that should be beneficial against acid attack. Blended Portland cements containing pozzolans or slags are considered to be more resistant to the acidic attack than Portland cement [9].

During the first part of this research program on acid attack, we had the opportunity to study a large number of binders including a high-alumina cement, an ordinary Portland cement (OPC), alone or blended with silica fume, class F fly ash, blast furnace slag, and metakaolin as partial replacement [24]. Mixtures containing fly ash, silica fume and alumina cement were considerably more leached than the control OPC sample after acetic acid immersion [24,25]. Silica fume specimens were almost completely disintegrated which was surprising considering high pozzolanic activity and filler effect responsible for refined microstructure of silica fume blended cement. The best chemical performances determined from experiments on paste samples were obtained with blast furnace slag and metakaolin. For that reason, this study was only conducted on mixes that showed the best performances during the chemical resistance evaluation in acidic environment.

This study aims at identifying the chemical and the physical modifications of cement pastes submitted to organic acid attack and to evaluate the compressive strength, the mass loss, and the altered depth of corresponding mortars The effect of the nature of SCMs as well as the curing time is studied by comparing their effect on the chemical and mechanical resistance in order to develop mixture proportion rules for cement-based materials with SCMs subjected to acidic environments.

2. Experimental procedure

2.1. Materials

This study was conducted on cement pastes and mortars made with OPC, designated in American Standard as GU (General Use, containing a maximum of 5% limestone filler), blended with 80% of ground granulated blast furnace slag (GBFS) or 20% of metakaolin (MK) as partial cement replacement by mass. The control sample is made only of GU. The chemical composition of the binders is given in Table 1.

The immersion solution was composed of acetic acid (CH_3COOH), a weak organic acid, with a dissociation constant pKa of 4.76 at 25 °C. The concentration of the acetic acid was 0.5 M at a pH of 4. To bring the pH to 4, 5 g/l of solid NaOH was added to the solution.

Table 1
Chemical composition of binders.

Binder (%)	CaO	SiO_2	Fe_2O_3	Al_2O_3	MgO	K_2O	Na_2O	TiO_2
GU	62.5	19.6	2.27	4.9	2.61	0.9	0.24	0.25
MK	0.03	51.65	0.68	44.7	0.08	0.34	0.08	0.12
GBFS	37.31	36.77	0.85	7.77	13.91	0.43	0.31	0.36
MK-20	50.01	26.01	1.95	12.86	2.1	0.79	0.21	0.22
GBFS-80	42.35	33.34	1.13	7.2	11.65	0.52	0.30	0.34

The solution was renewed every week throughout the duration of the experiment in order to maintain the pH of the solution at a value of 4. Table 2 presents the solubility of salts susceptible to form during the acid attack.

2.2. Specimen making and treatment

Cement paste specimens were made at a water/cementitious material mass ratio (w/cm) of 0.27. Hardened paste specimens are cylindrical, 150 mm high and 100 mm in diameter.

Cubic mortars samples (50 × 50 × 50 mm) were made at a water/cementitious material mass ratio (w/cm) of 0.485 with 1375 kg/m^3 of uniformly graded Ottawa silica sand, Accusand C-109 from Unimin Corporation and 500 kg/m^3 of cementitious material. No superplasticizer was added. The procedure for making mortar was according to ASTM C192/C192M [26].

Paste and mortar specimens were demolded 24 h after pouring and stored in wet room at 23 °C and 100% RH for 27 days. At the end of each curing period of 28 days, 3 months, 6 months and 1 year, paste and mortar specimens were immersed for 3 and 2 months in the acetic acid solutions (0.5 M, pH 4) at solid–liquid volume ratio of 1/15 and 1/25, respectively. Control samples were kept in a wet room throughout the duration of immersion.

2.3. Test methods

The physical modifications of paste samples were analyzed by mercury intrusion porosimetry (Micrometritics AutoPore IV model) (MIP) with applying pressures up to 60000 psi. After 3 months of immersion in acetic acid, the samples were dried at 80 °C for 72 h priors to porosity measurement. The analysis was realized in the sound and altered zones of GBFS, MK and control cement pastes cured for 28 days, 3 and 6 months and immersed for 3 months in the acid solution.

The chemical modifications of the specimen were analyzed by a CAMECA SX 100 electron probe microanalyser (EPMA) at accelerating voltage of 15 kV, a current strength of 10 nA and a scanning volume of 5 × 5 × 5 μm^3. The measurements were done on polished sections, according to depth in the altered and sound zones. Particular care was given to the choice of the analyzed points to get only the hydrated paste and to avoid anhydrous grains. The following elements were analyzed: Ca, Si, Al, Fe, Mg, S, K, Na, Ti and O. The chemical data are expressed as percentages of oxide amounts in the volume sounded. Data in the altered zone were corrected according to the titanium content to represent the absolute variation of each element as suggested by Bertron et al. [27]. EPMA analyses were performed on three immersed specimens, for each type of paste, after 28 days and 3 months of curing and 3 months of acid immersion. Three control specimens for each type of paste were analyzed, at the rate of 100 points per specimen after 28 days and 3 months of curing.

Mineralogical phases were analyzed by a Siemens D5000 X-ray diffractometer using CuK$_\alpha$ radiation generated at 30 mA and 40 kV. Specimens were step-scanned as random powder mounts from 8 to 42° 2θ at 0.02° 2θ steps integrated at 1.2 s step^{-1}.

The altered depths and relative mass losses of mortar specimens were measured after the acid immersion. To quantify the altered

Table 2
Solubility of calcium, aluminum, magnesium and iron acetic acid salts (g/100 ml) [6,7,11].

	Ca salts $Ca(C_2H_3O_2)_2/Ca(C_2H_3O_2)_2 \cdot H_2O/Ca(C_2H_3O_2)_2 \cdot 2H_2O$	Al salts $Al(C_2H_3O_2)_3$	Mg salts $Mg(C_2H_3O_2)_2$ or $Mg(C_2H_3O_2)_2.4H_2O$	Fe salts $FeOH(C_2H_3O_2)_2$
Sol. cold water g/100 ml (T/°C)	37.4/43.6 (0 °C)/34.7 (20 °C)	Slightly soluble to soluble	Very soluble or 120 (15 °C)	Insoluble
Sol. hot water g/100 ml (T/°C)	29.7/34.3 (100 °C)33.5 (80 °C)	Decomposes	Very soluble or ∞	–

depth, three specimens were sawn perpendicularly to their axis and phenolphthalein was sprayed on the plane sections. The depth of the color change, considered to correspond to the altered depth, was measured with an optical videomicroscope on several points distributed around the perimeter of the cubes. The mass loss measurements were carried out on three immersed specimens that had first been dried.

Compressive strength measurements of mortar cubes were made according to ASTM C109M [28]. The tests were conducted on samples degraded for 2 months in acetic acid solution (pH 4, 0.5 M) and on control samples stored in wet room (23 °C, 100% RH) for the same period of time. After the conditioning time, samples were stored in a dry room (20 °C, 50% RH) for about 1 month until mass stabilization to <0.1% change. The compressive strengths were measured on three dry specimens per condition.

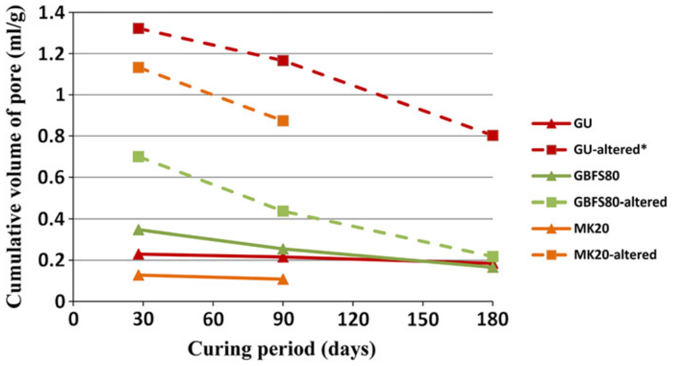
3. Results and discussion

3.1. Physical modifications of paste samples measured by MIP

Fig. 1 presents the MIP results measured on sound and altered zones of tested cement pastes. Data represent the cumulative volume of pores.

In a general way, the total porosity of cement pastes decreases for all samples with the extent of the curing time. This reduction is much more pronounced for GBFS samples with values decreasing by 52% with curing time from 28 days to 6 months due to the latent character of that binder. On the other hand, the total porosity reduction in the 28 day to 3 month curing period is weak with a decrease of only 15.6% for MK samples that react rapidly. The hydration degree is an important factor contributing to the improvement of the pore distribution. During the hydration period, the decrease of pore volume is relatively related to the increase in the volume of hydrates formed [29].

In sound zones of the specimen cured for 28 days, the GBFS samples show the highest total porosity without any improvement of the size of pores (40% of pores larger than 0.1 μm) contrary to MK samples which allow an important decrease of the total volume of pores as well as a large contribution to the refinement of pores (only 26.6% of pores larger than 0.1 μm). In altered zones, we note a net increase of the porosity for all specimens. The GU control sample presents the highest total porosity which should be more significant considering that the zone studied was an intermediate zone because the most degraded external zone was totally lost in solution. The altered zone of the MK samples was largely affected by the aggressive solution with total porosity values closed to that obtained with the intermediate zone of the GU control. Moreover, the proportion of the cumulative volume of pores larger than 0.1 μm increases to 41.4% in the altered zone of MK samples compared to 26.6% in the sound zone. The altered zone of the MK samples is by far more porous than the sound zone and the proportion of pore larger than 0.1 μm in the altered zone is also increased. The samples containing GBFS present the lowest total porosities of all the tested samples in the altered zone knowing that their contribution to the refinement of pores is low. MK cement pastes (MK-20) are more sensitive to the aggressiveness of the acetic acid than GBFS samples (GBFS-80) which may be due in part to its higher Ca content knowing that leaching of calcium, the most vulnerable element to an acidic attack, is responsible for loss of sample integrity [24].



* intermediate zone(external zone completely dissolved)

Fig. 1. MIP data measured on altered and sound zones of cement pastes cured for 28 days, 3 and 6 months prior to 3 months of immersion in acetic acid (pH 4).

After a curing period of 3 months, GBFS specimens always present the highest total volume of pore with an increase of 18% compared to GU sample. During the same period of time, a reduction of 50% was noted for MK specimen compared to GU control. A reduction of 28% of the total porosity was measured on GBFS samples in the 28 days to 3 months curing period. The porosity of the altered zone was largely decreased by the extent of the curing period to 3 months, although still important, with reduction of 23 and 37% for MK and GBFS samples compared to same samples cured for 28 days. Direct comparison is not possible for GU sample considering that the external zone of samples cured for 28 days was completely lost.

After 6 months of curing, total porosity of GBFS samples was comparable to that of GU with a weak refinement of the pore structure (54.1 vs 60.1% of pores smaller than 0.1 μm for GU and GBFS samples, respectively). Total porosity of altered zones continues to decrease with porosity reduction of 50 and 31% in the 3 to 6 months curing period for GBFS and GU samples, respectively. After 6 months of curing, the total porosity of the altered zone of GBFS sample is decreased by 72.9% compared to that of the GU sample. This emphasizes the importance of the chemical composition of the binder on the acid resistance with GU total porosity similar to that of GBFS sample in the sound zone but more than 3.7 times greater in the altered zone (0.80 ml/g for GU and 0.22 ml/g for GBFS). It is important to note that the MK sample goes from lowest to almost highest porosity in the unaltered and altered zones. This shows that a reduction of the porosity is important against chemical aggression but is not sufficient to assure the protection of the structure subjected to an acidic environment.

3.2. Chemical and mineralogical modifications of paste samples measured by EPMA and XRD

Figs. 2 to 4 present chemical composition profiles (as oxide equivalents) of cement pastes that were immersed in the aggressive solution with figures A and B corresponding to samples cured for 28 days while figures C and D are for specimen cured for 3 months prior to acid immersion. As notes previously, particular care was given to the choice of analyzed points to get only the hydrated paste. EPMA data are given as absolute percentages of oxide amount as a function of the distance from the surface of the specimen to their sound zone.

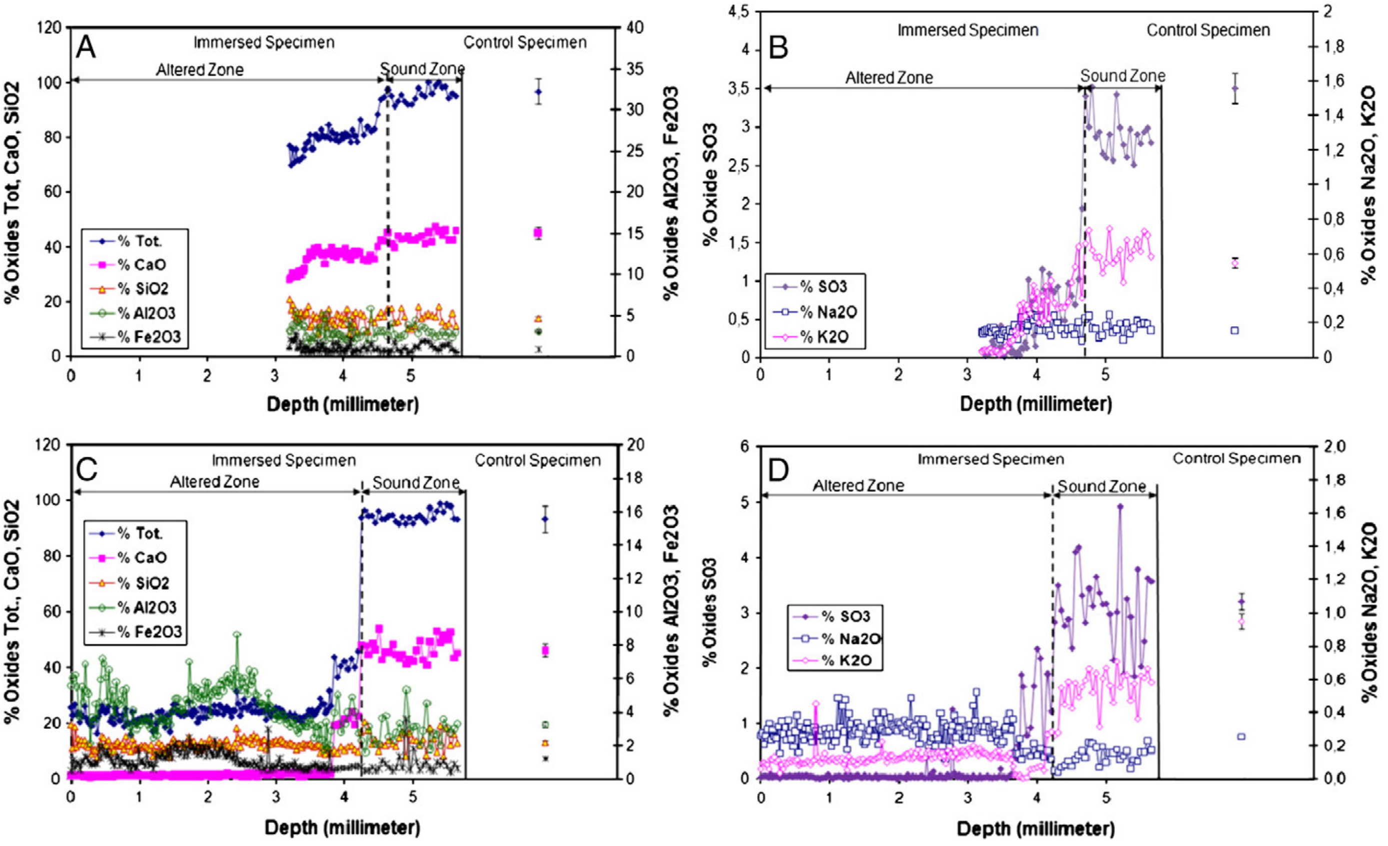


Fig. 2. Chemical composition profiles of GU paste samples immersed for 3 months in acetic acid solution according to the distance to the surface of the specimen – (A and B) GU pastes cured for 28 days – (C and D) GU pastes cured for 3 months.

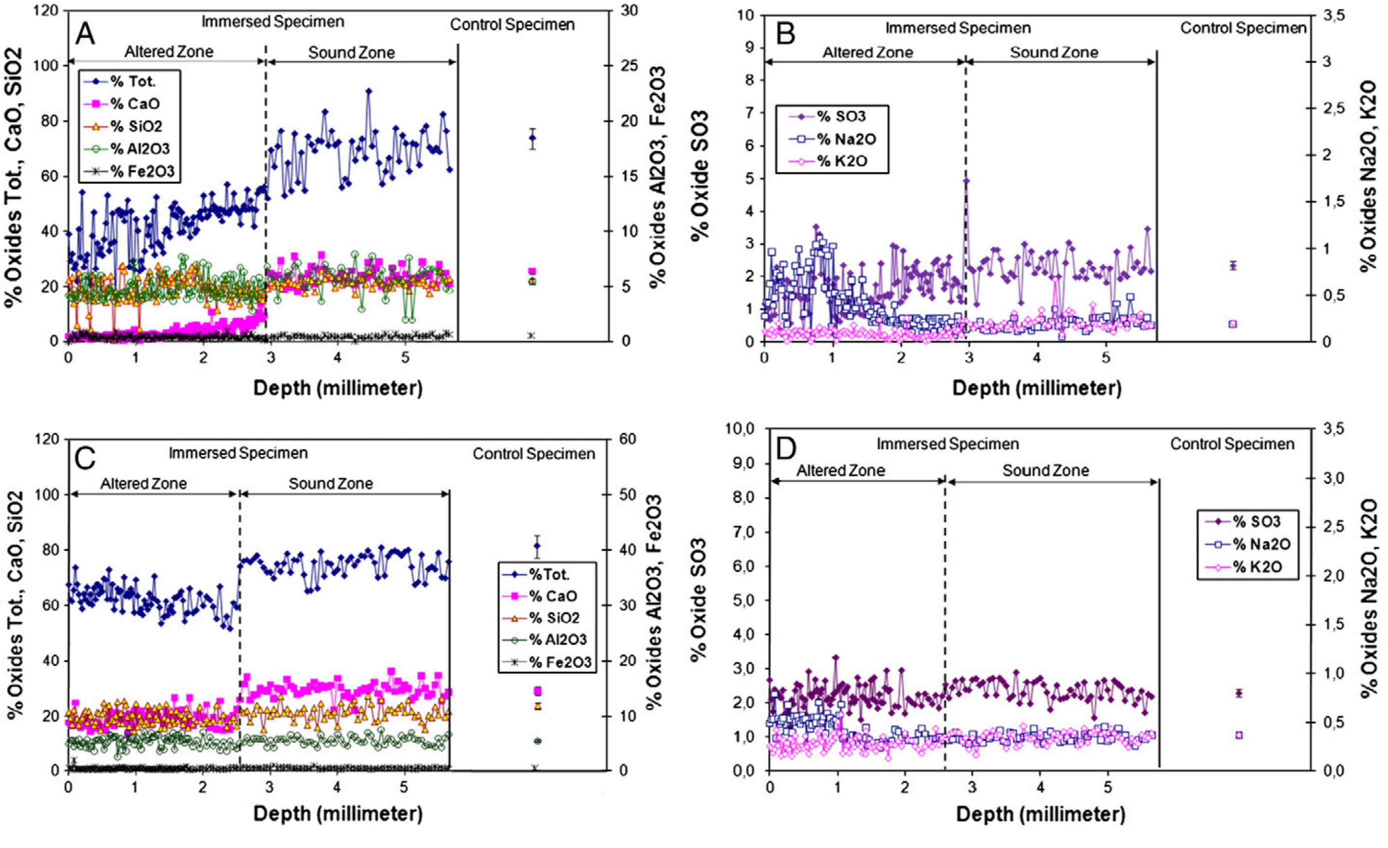


Fig. 3. Chemical composition profiles of GBFS-80 paste samples immersed for 3 months in acetic acid solution according to the distance to the surface of the specimen – (A and B) GBFS pastes cured for 28 days – (C and D) GBFS pastes cured for 3 months.

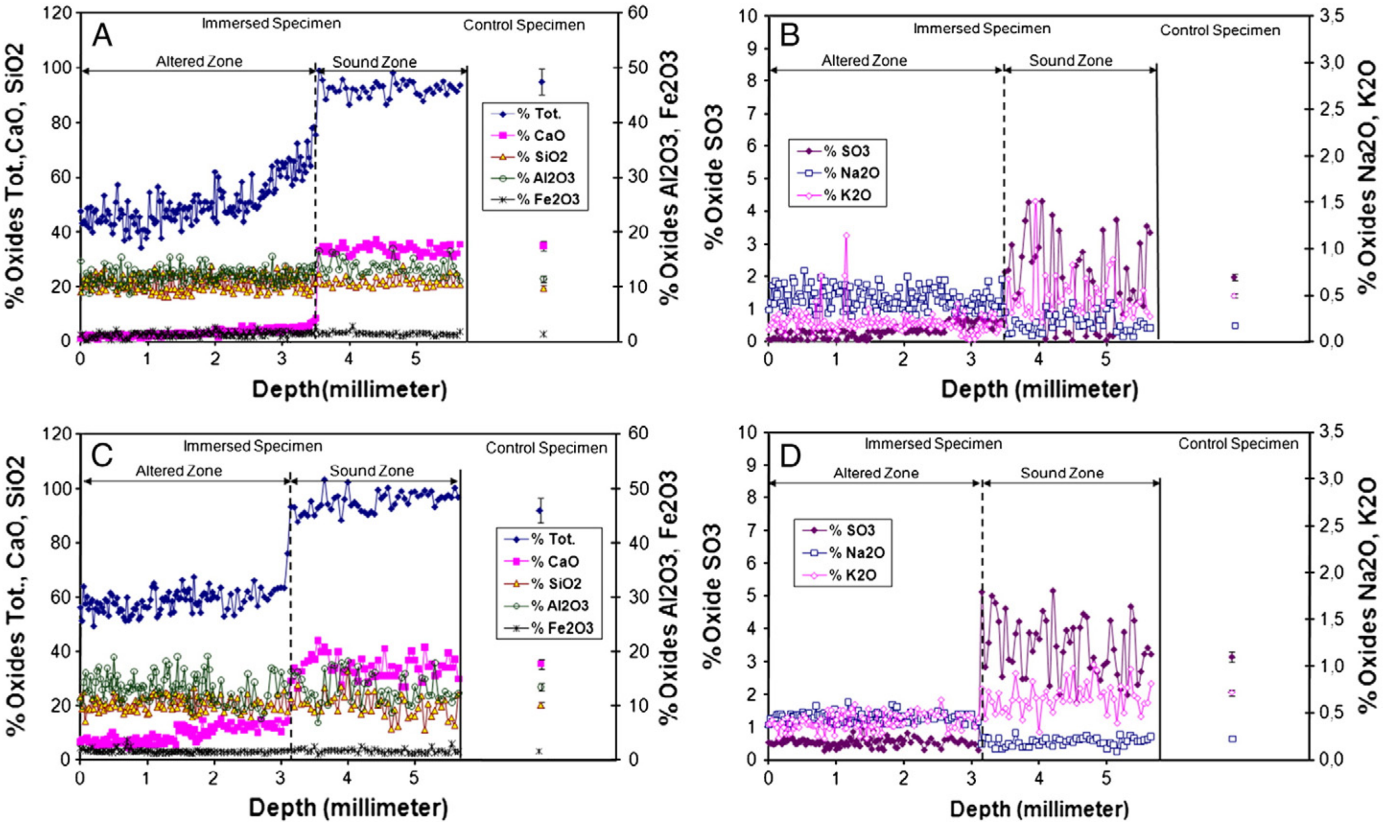


Fig. 4. Chemical composition profiles of MK-20 paste samples immersed for 3 months in acetic acid solution according to the distance to the surface of the specimen – (A and B) MK pastes cured for 28 days – (C and D) MK pastes cured for 3 months.

In general, EPMA data show that the sound zone has the same chemical composition as the control specimen that was kept in the wet room for the entire period of testing. The sum of all oxide amounts gives an indication of the compactness of the cement paste. The change in color of the phenolphthalein indicator marking the interface between the sound and the altered zones matched a brutal drop of the CaO amount and a large decrease of the total amount of oxides. Altered depth measurements done by observation of the indicator color change correspond exactly to the CaO and total amount of oxide drop measures by the electron microprobe.

For samples cured 28 days, the altered zone of each specimen is almost completely decalcified and the total amount of oxides drops reaching values of 30 and 40% for GBFS and MK samples, respectively. Lower value of the total amount of oxides is expected for the GU control sample as 25% was measured on paste samples cured for 3 months in a wet room prior to acid immersion (Fig. 1C). The drop in CaO content is directly linked to the dissolution of portlandite ($Ca(OH)_2$) and to the decalcification of the C-S-H phase, followed by the complete dissolution of C-S-H in the external parts of samples where CaO content becomes lower to near-zero percent. XRD data show that altered zones are completely amorphous (Figs. 5 to 7 are presented for samples cured for 3 months which are similar to those cured for 28 days (not shown)). These figures show that portlandite, ettringite, and cement anhydrous lines completely disappear while broad diffraction humps (in gray on Figs. 5 to 7) characteristic of amorphous phase can be observed at low-angle. EPMA data show that the amount of other oxides, SiO_2, Fe_2O_3, Al_2O_3 is unchanged while enrichments in Na_2O and depletion in SO_3 are observed next to the surface. Hong and Glasser [30] showed that alkali ion binding into C-S-H phase improves as its Ca/Si ratio decreases as it is the case here where Ca content decreases in the altered zone of MK and GBFS specimen. The enrichment in alkaline ions may also be linked with the sorption of alkaline ions on silica and/or alumina–silica gel [31] that covered the external part of degraded samples.

The increase of the curing period to 3 months improves the compactness of the specimen particularly in the altered zone where total amount of oxides is greater than it was for samples cured for 28 days. GU samples retain their integrity and it is now possible to analyze the composition of their altered zone. For all samples, the altered depth is reduced but it is still completely amorphous as seen on XRD traces (Figs. 5 to 7). MK and GBFS present significant CaO content in their altered zone, but this oxide was completely removed in samples cured for 28 days. The external zone of specimen is still enriched in Na_2O and depleted in SO_3.

Degradation occurs through the attack of phases. During the acid attack, the external part of samples cured for 28 days in direct contact with the acid solution is completely depleted in portlandite, ettringite, cement anhydrous phases and C-S-H as seen on the XRD traces and on microprobe data where CaO content is near 0%. The increased stability of MK and GBFS samples against acidic media seems related to their chemical composition rich in silicon, aluminum and iron favorable parameters for assessing the chemical resistance of binders and limited in calcium, the most vulnerable component with the highest dissolution rate of all the elements in an acidic solution.

3.3. Aspect, altered depths, mass losses and compressive strength of mortars

3.3.1. General aspect

Fig. 8 shows the aspect of mortar specimens after 2 months of immersion in the acetic acid solution. The mortar cubes containing GBFS or MK kept their integrity. However, the GU control samples show little dissolution but they were fairly cracked. The external zone of cubes in direct contact with the acid solution presents a yellowish

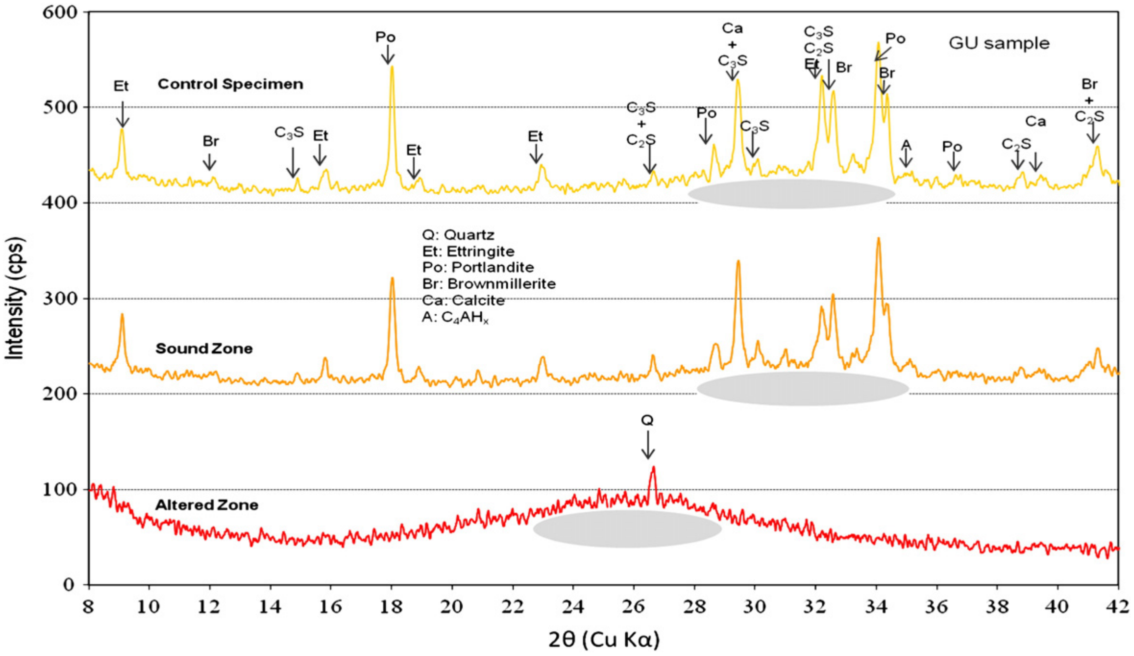


Fig. 5. XRD mineralogical profiles of GU paste samples cured for 3 months and immersed for 3 months in acetic acid solution.

coloration. This zone is susceptible to drying shrinkage, presents large open cracks and is easily removed from the cubes upon drying.

Fig. 9 shows the appearance of mortar samples cured for 3 months, 6 months and 1 year in a wet room (23 °C, 100% RH) prior to the 2 month acid immersion. After 3 months of curing, samples show a marked improvement of their durability against acid attack. However, opening cracks are still present in the GU control cubes. Samples cured for 6 months and 1 year have very little degradation; even the GU control samples do not show sign of cracking or degradation.

3.3.2. Altered depth

Fig. 10 presents the development of altered depths according to the curing time after 2 months of immersion of the different mortars tested. It is clear that the prolongation of the curing period is beneficial for the durability of mortars subjected to an acid solution. Moreover, the extension of the curing period is more favorable for some binders. For a curing period of 28 days, differences in the amount of alteration between the various mortars tested are significant with altered depth measurements on the GU control mortars which are approximately the double of that measured on the GBFS samples. The performance of MK samples is situated somewhere between the GBFS and GU samples. Both SCMs, GBFS and MK, significantly improve the acid durability in terms of altered depths.

Increasing the curing period to 3 months allows a clear improvement of the altered depths measured on all samples. The decrease in the dissolution front is more important for the GU mortars. However,

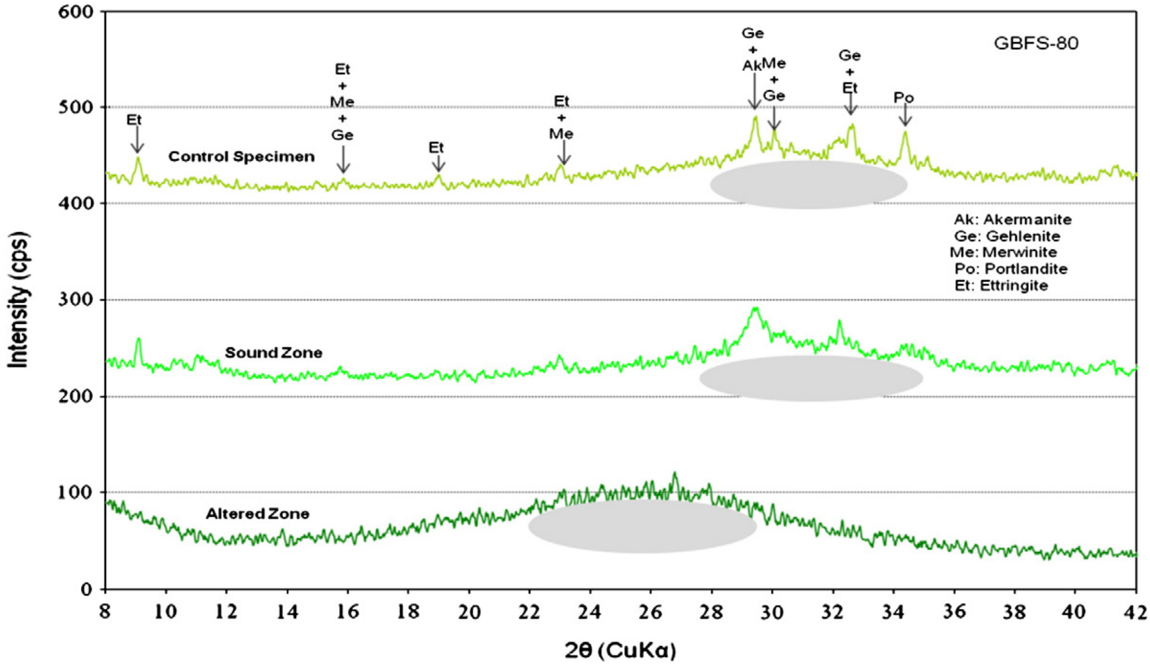


Fig. 6. XRD mineralogical profiles of GBFS-80 paste samples cured for 3 months and immersed for 3 months in acetic acid solution.

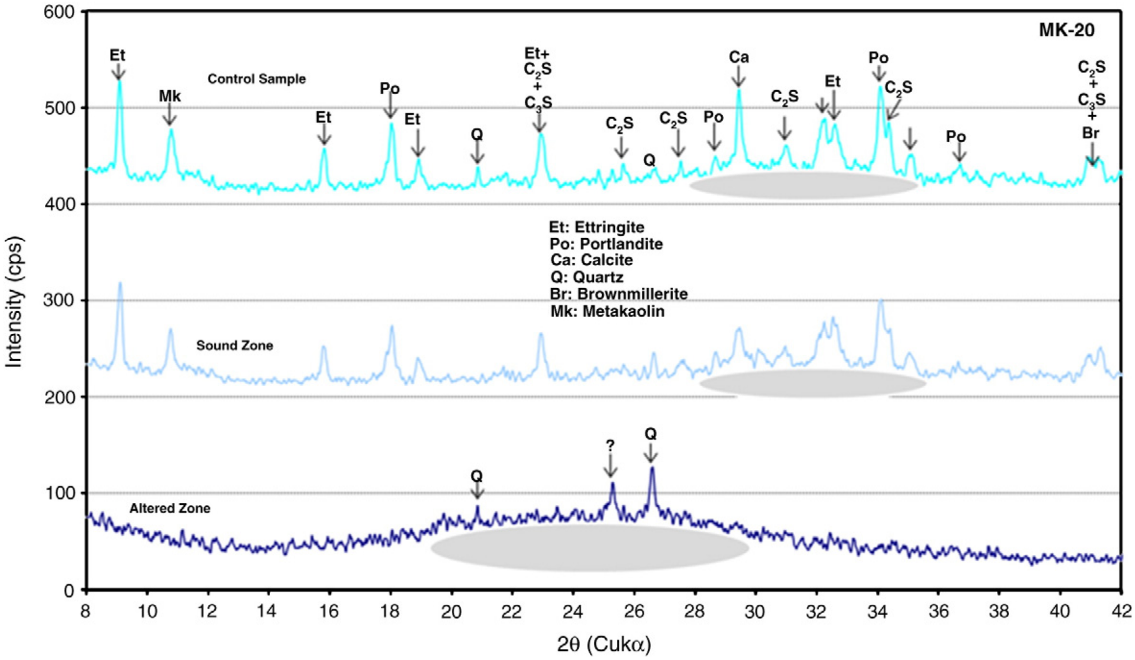


Fig. 7. XRD mineralogical profiles of MK-20 paste samples cured for 3 months and immersed for 3 months in acetic acid solution.

the improvement is less marked for the binder with MK. This is not surprising considering the high reactivity of MK which reacts quickly. The longer curing leads to reduce the altered depths. After 1 year of curing, the difference in altered depths measured between samples becomes minimal with values ranging from 2 to 3.7 mm. GBFS mortars have the lowest altered depths during the whole experience.

3.3.3. Mass variations

Fig. 11 presents the evolution of mass losses according to the curing time for different mortars tested. The mass losses of the GU mortars are by far the most important. Replacement of a part of the Portland cement by MK or GBFS reduced considerably the mass losses for samples stored in acidic solution.

As for the measurements of the altered depth, the prolongation of the curing time allows to decrease the mass losses of all the samples. The rate of reduction of the mass loss is more important between 28 and 180 days of curing but it is still significant between 6 and 12 months. Contrary to the data of altered depth, here the interval between samples is not reduced and it is the GBFS sample that benefits most of a prolonged curing period. Very low mass losses measured on GBFS specimens, particularly those cured for a long period of time, may be explained by the good chemical resistance of the material.

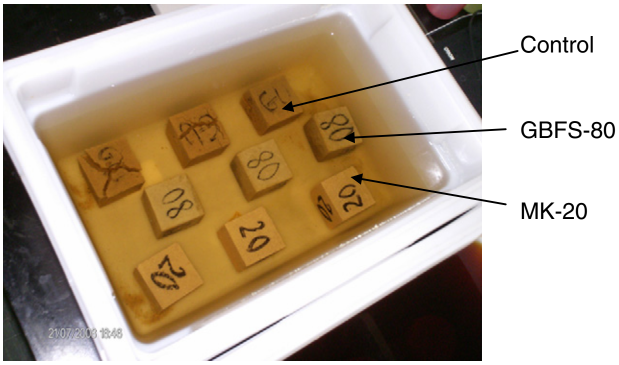


Fig. 8. Aspect of mortar specimens after 28 days of curing and 2 months of immersion in an acetic acid solution (0.5 M, pH 4). GU = general use Portland cement (control); GBFS-80 = GU blended with 80% of ground granulated blast furnace slag (GBFS); MK-20 = GU blended with 20% of metakaolin (MK).

3.3.4. Compressive strength

Fig. 12 shows the evolution of the compressive strength of samples stored in wet room for different curing time. The order of increasing compressive strength of various binders is always the same no matter of the curing time with GBFS mortars having a lower resistance than GU control mortars, than, MK mortars. For all samples tested, the compressive strength increases significantly with the increase of the curing period even for curing period as long as a year. After 28 days of curing, the compressive strength of the GU mortar reached 61% of its optimum resistance measured after 1 year of curing. This value is higher than that reached by MK or GBFS samples with 59 and 45%, respectively. The compressive strength values measured on GBFS mortars are about the half of that measured on GU mortars.

Fig. 13 presents the compressive strength of mortars immersed for 2 months in an acetic acid solution. As for results presented in Fig. 12, mortars were cured in a wet room for a different period time before the acid immersion. It is clear, from the comparison of these two figures, that the acid attack provokes a drop of the compressive strength of all samples. At a curing period of 28 days, the resistance drops by 69, 27, and 10% for GU, MK, and GBFS mortars, respectively. For all curing periods tested, mortars with MK present the far superior strengths. However, in the acetic acid solution, the compressive strength of GBFS mortars was less affected. For the different curing period, the resistance reductions between acid immersion and wet room samples were measured within a range of 12% for GBFS samples, 18% for MK samples and 60% for OPC samples. These results pointed out the beneficial effects of SCM addition and the prolongation of the curing time on compressive strength values of mortars subjected to acid attack.

The compressive strength of hardened concrete depends mainly on the porosity of the matrix [32]. According to the evolution of the compressive strength of mortar, the control GBFS mortars, stored in wet room, present very weak values of compressive strength due to the high porosity and the low rate of GBFS hydration. MK reacts very differently with a large increase in the compressive strength compared to GU or GBFS mortars. The high chemical reactivity

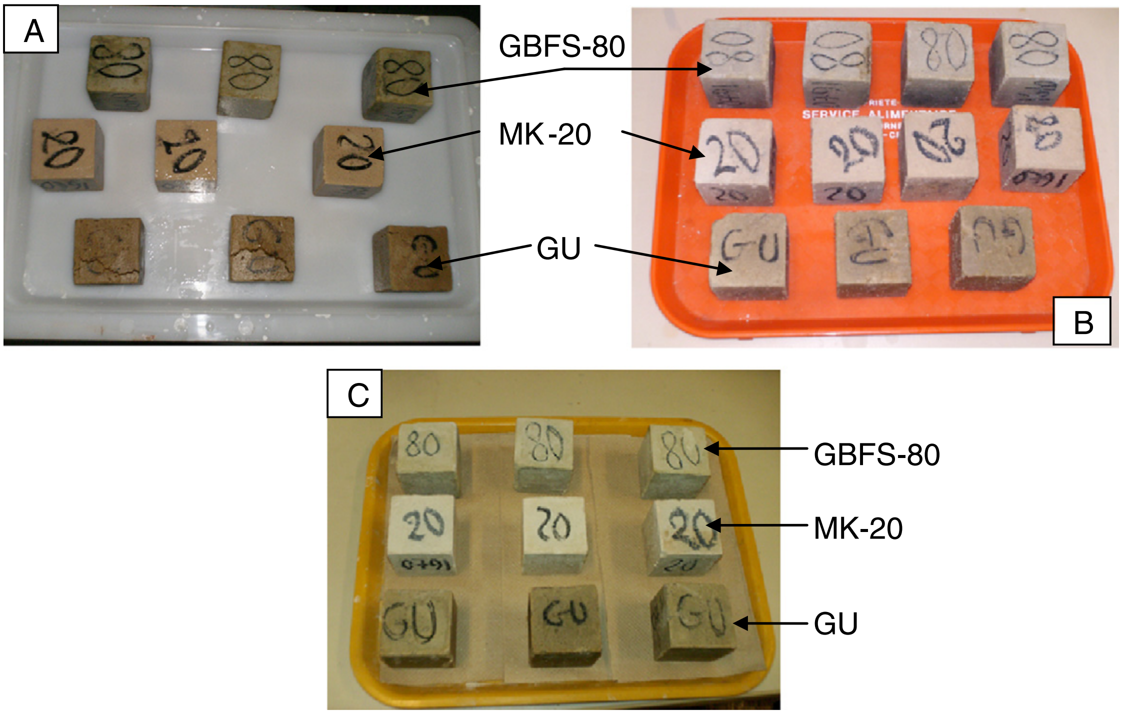


Fig. 9. Aspect of mortar samples after a) 3 months, b) 6 months and c) 1 year of curing in wet room and 2 months of immersion in an acetic acid solution of pH 4.

along with the high surface area of MK is responsible of the refinement of pores densifying the microstructure of the cement as demonstrated in Section 3.1 on MIP results.

In immersion in acetic acid, the compressive strength of all mortars dropped in a more or less important way according to the binder. The drop is really important for the GU samples caused by the heavy chemical damage due to the high calcium content of the binder. The drop of compressive strength of MK and GBFS samples is a lot lower than that of GU samples mainly due to their chemical resistance against acid attack and to the more compact microstructure of the MK mortars. Improving physical properties of cement paste by use of SCMs with large impact on the refinement of pores densifying is not enough to increase durability against acid attack. The chemical composition of the SCMs as well as that of the hydration products is of main importance as demonstrated by the low strength loss of GBFS samples during acid immersion in spite of their high porosity. Binders rich in Si, Al and Fe and poor in Ca and Mg resist better in acidic media where all Ca-bearing phases (portlandite, C-S-H, ettringite and cement anhydrous phases) are completely dissolved in direct contact with the acid solution.

Extending of curing time is beneficial for improving durability against acid attack. Methods for accelerating the curing process such as the use of physical processes (additional sources of heat/insulation) or use of chemical admixtures should be envisaged for agricultural infrastructures in contact with acidic environment.

4. Conclusions

In this study, the effects of the kind of SCMs and the curing time were investigated by comparing their effect on the porosity, chemical

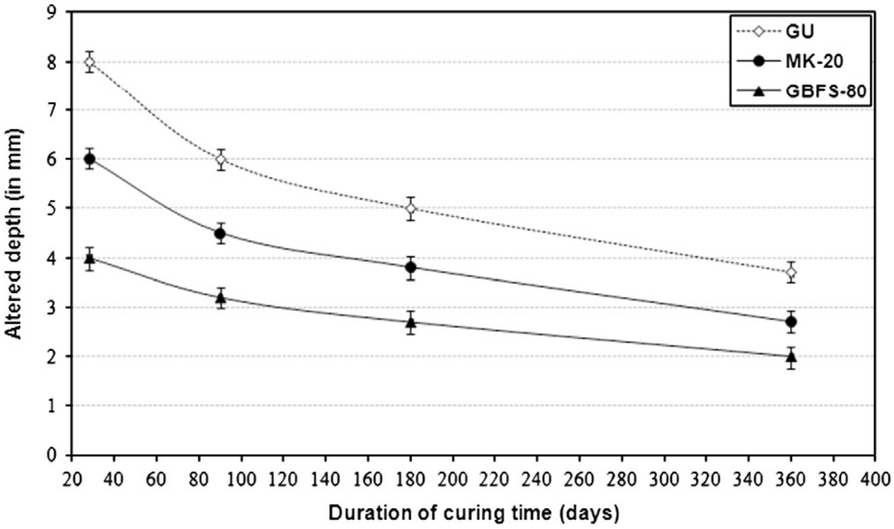


Fig. 10. Evolution of the altered depth measured on mortar cubes after 2 months of immersion in an acetic acid solution as a function of the curing time prior to acid immersion.

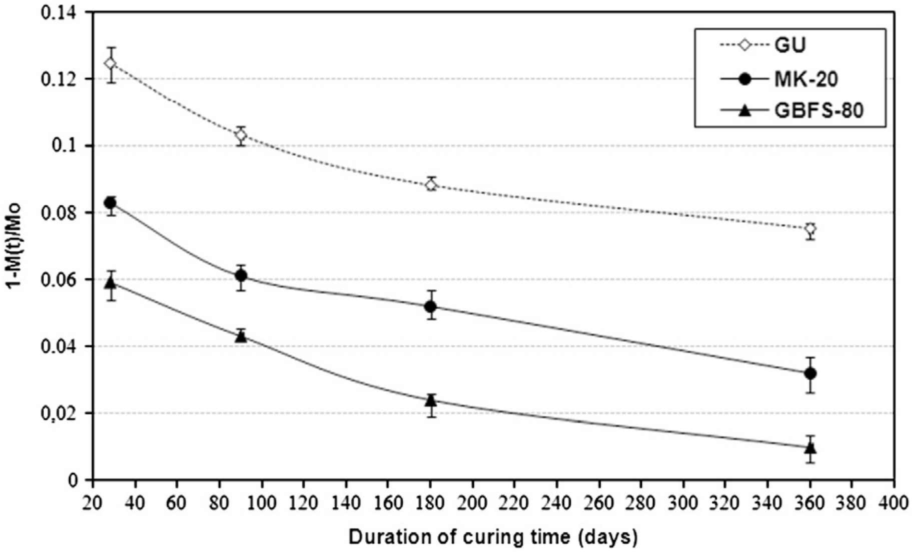


Fig. 11. Evolution of the mass loss measured on mortar cubes after 2 months of immersion in an acetic acid solution as a function of the curing time prior to acid immersion.

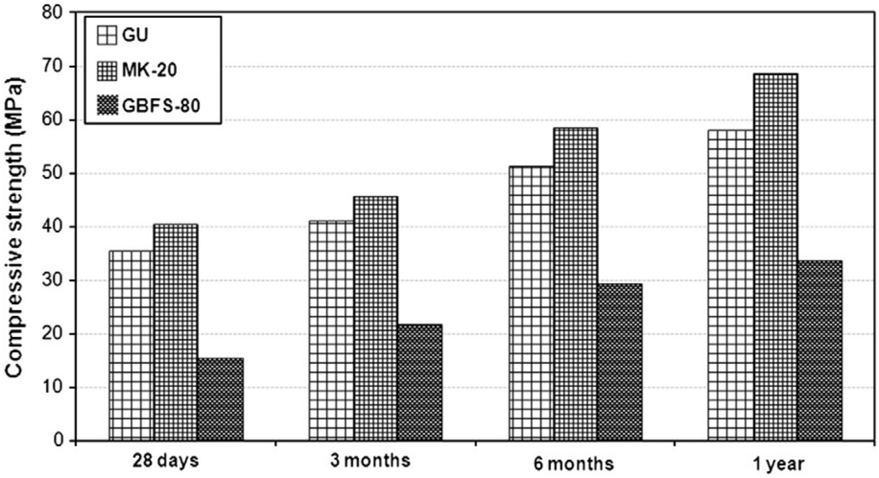


Fig. 12. Evolution of the compressive strength of mortar samples stored in a wet room (23 °C, 100% RH) as a function of the curing time.

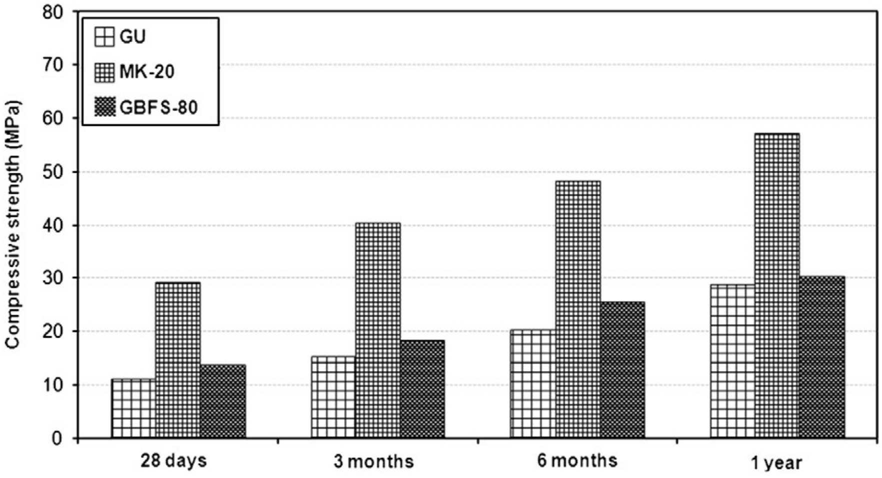


Fig. 13. Evolution of the compressive strength of mortar samples immersed for 2 months in acetic acid (0.5 M, pH 4) as a function of the curing time in a wet room prior to acid immersion.

and mineralogical composition of pastes and on the compressive strength, mass loss and altered depth of mortars immersed in acetic acid at a pH of 4.

The porosity of the binder is an important factor of the durability of concrete but the chemical resistance is also important. GBFS pastes present the most important total porosity but the best chemical stability. After 2 months of immersion, MK and GBFS mortars kept their integrity while GU mortars were fairly cracked. The prolongation of the curing period was beneficial for all samples decreasing significantly the porosity, mass losses and the altered depth while increasing the compressive strength. The slow hydration of GBFS is responsible of the high porosity of GBFS mortars which has a direct impact on the low compressive strength measured.

MK reacts very differently with a large increase in the compressive strength and a reduction of the total porosity for samples kept in moist conditions. However, after acid immersion, the MK sample goes from lowest to almost highest porosity in the unaltered and altered zones. In spite of an 18% drop of the compressive strength after acid immersion, MK samples present still by far the highest compressive strength.

In short, both GBFS and MK improve mortar resistance against organic acid attack. GBFS presents the lowest mass loss and altered depth while MK has the highest compressive strength after acid immersion.

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