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Durability of mortars containing blast furnace slags used as a partial substitute of Portland cement exposed to external sulfate attacks

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Abstract

This research study was conducted in order to evaluate the durability characteristics of mortars using ground granulated blast furnace slag (GGBFS) or crystallized slag with partial substitution of Portland cement in comparison with reference mortars prepared with Portland cement. All mixtures were exposed to the external sulfate attacks. The results obtained show that the physical and mechanical properties of the mortars vary according to the nature and the substitution rate of mineral admixtures. A drop in mechanical strength and a loss of mass of the mortars haves been noticed after a year of conservation in a high magnesium sulfate medium ($MgSO_4$). The mortars with GGBFS present the lowest drop in strength (≤10%), while the mortars with crystallized slag provide the major decreases with strength loss from 20% to 31%. At 28-day curing time in water before immersing the mortar in a sulfate solution allowed mitigating the damage. It was possible to characterize these mortars based on the macroscopic and microscopic analysis of the tested mortar samples. Two behaviors were observed: the first concerns the most resistant mortar and the second concerns the mortar which is most damaged by the external sulfate attack.

1. Introduction

To ensure the durability of cementitious materials, we need to focus not only on the formulation and manufacturing methods, but also on the environmental conditions. All external environments are considered aggressive to cement matrix.

External sulfate attacks covering all cementitious materials degradation phenomena in which aggressive agent is sulfate ion (SO_4^{2-}) coming from the surrounding medium such as: seawater, soil rich in gypsum, underground water... [1]. In Algeria, the gypsum soils occupy 12.2% of the total surface of the gypsum soils of the world, they are estimated at 7966.3 km^2 (representing 3.3% of the surface of the country) [2]. These attacks are associated with precipitation of secondary sulfate products, a significant expansion and physical chemical and mechanical deterioration (changes in transport properties of porosity, cracking, loss of strength and cohesion ...). [3,4].

The chemical attack of cementitious materials is mainly carried out on portlandite $Ca(OH)_2$ contained in the cement paste. The attack of silicates and hydrated lime aluminate C-S-H and CAH is not negligible where there is formation of gypsum and secondary ettringite as well as thaumasite from the surface exposed to sulfate. [5,6].

Several studies have been made to demonstrate the phenomenon of degradation of cementitious materials in sulfate-rich environments. For example: [7-10], have shown that there are many parameters which affect this degradation, namely the type and the concentration of the etching solution as well as temperature. They have demonstrated that the magnesium sulfate solution $MgSO_4$ is more aggressive than the sodium sulfate solution Na_2SO_4 and the increase in temperature accelerates the attack of these sulfates. Demene et al [11] have shown that the conservation process in the $MgSO_4$ solution significantly affects the durability of mortars and reduces mechanical behavior after two months of attack.

Other research [12-17] have shown that the type of cement and the mineral additions affect the degradation of the cementitious materials. The durability performance of mortars based on reactive mineral additions such as pozzolan and GGBFS exposed to a sulfate solution was better than that of mortars with cement without additions.

According to [18-20] the use of cement with slag or the addition of GGBFS as mineral admixtures improves the durability of materials. The granulated slag is a mineral addition which has several interesting qualities: chemical composition near to that of cement and a regularity of chemical composition. The GGBFS present a latent-reactive activated in the presence of Portland cement [21-23].

The use of compound cements or the addition of granulated slag is essential for improving the durability of concrete structures and it presents technical, economic and environmental advantages. [24-26]. The GGBS improves the resistance of concrete to sulfates by dilution of aluminates, by reducing the portlandite content and by increasing the compactness of hydrates in connection with the reduction of the pore volume [27,28]

This study aims at analyzing and evaluating the effect of the attack of magnesium sulfate ($MgSO_4$) on the physico-mechanical and microstructural degradation of mortars containing blast furnace slags and crystallized slag used as a partial substitute of Portland cement.

2. Materials and experimental procedure

2.1. *Materials*

2.1.1. ***Cement and mineral admixtures***: the cement used was a CEM I 42.5 /A the mineral admixtures used in this work are Ground Granulated Blast Furnace Slag (GGBFS) and crystallized slag. The main physical and chemical properties of cement and mineral admixtures are given in Table 1 and 2.

Table 1. Chemical composition of cement and mineral admixtures

Chemical composition (%)	Cement	GGBFS	crystallized slag
Fe_2O_3	3.52	1.49	0.60
CaO	63.81	40.82	41.71
SiO_2	21.23	40.34	41.00
MgO	0.96	5.53	4.80
Al_2O_3	5.04	7.70	8.16
MnO	-	1.58	1.93
K_2O)	0.58	-	-
Loss on ignition	0.47	-	-

Table 2. Physical properties of cement and mineral admixtures

Properties	Unit	Cement	GGBFS	crystallized slag
Apparent density	(kg/m^3)	1040	1030	950
Absolute density	(kg/m^3)	3000	2800	2390
Specific surface area	(cm^2/g)	3073	3650	3500

2.1.2. Sand: The sand used is a siliceous. Its chemical and physical characteristics are given in Table 3 and 4.

Table 3. Chemical composition of sand

	Fe	**CaO**	**SiO_2**	**MgO**	**Al_2O_3**	**MnO**	**PF**
siliceous Sand	1.69	4.95	84.08	/	3.31	0.11	4.30

Table 4. Physical properties of sand

	Fineness modulus	**Bulk density**	**Absolute density**	**Sand equivalent**
Unit	-	kg/m^3	kg/m^3	%
Sand	2 .25	1440	2590	92.26

2.1.3. Sulfates: the magnesium sulfate solution ($MgSO_4.7H_2O$), with concentration of 50 g/l according to the French Standard NF P18-837 [29], is used for external sulphatic attack.

2.2. Formulation of study mortars

The mortars of this study is composed by one part cement, three parts of sand and with a water/ Binder ratio = 0.5. The composition of the various types of mortars prepared with GGBFS or crystallized slag used in this study is given in table 5.

Table 5. Mix proportions of mortars

Name of mortars	**Binder/ Sand**	Water/ Equivalent Binder	**Constituent dosage in Kg/m^3**			
			Sand	Cement	**Mineral admixtures in**	
					GGFBS	**Crystallized slag**
MW	1/3	0.5	1888,02	629,34	0	0
MGGBS 30%	1/3	0.5	1888,02	440,54	176,19	0
MGGBS 40%	1/3	0.5	1888,02	377,61	234,95	0
MGGBS 50%	1/3	0.5	1888,02	314,67	293,69	0
MACS 10%	1/3	0.5	1888,02	440,54	117,47	50,17
MACS 20%	1/3	0.5	1888,02	377,61	117,47	100,27
MACS 30%	1/3	0.5	1888,02	314,67	117,47	150,41

2.3. Technical and experimental procedure

The experimental study was conducted on prismatic specimens of dimensions (4 ×4 ×16) cm^3 according to the European standard EN 12390-1 [30]. The approach of this comparative study is to quantify over time the resistance to external sulfate attack characterized by physico-mechanical and microstructural degradation of mortars with blast furnace slag (GGBFS) or crystallized slag as partial substitution of Portland cement, kept in water and in a magnesium sulfate solution-water ($MgSO_4.7H_2O$) according to the standard NF P18-837 [28] with replacement of solutions and PH control. The conservation mode is illustrated by the following chart:

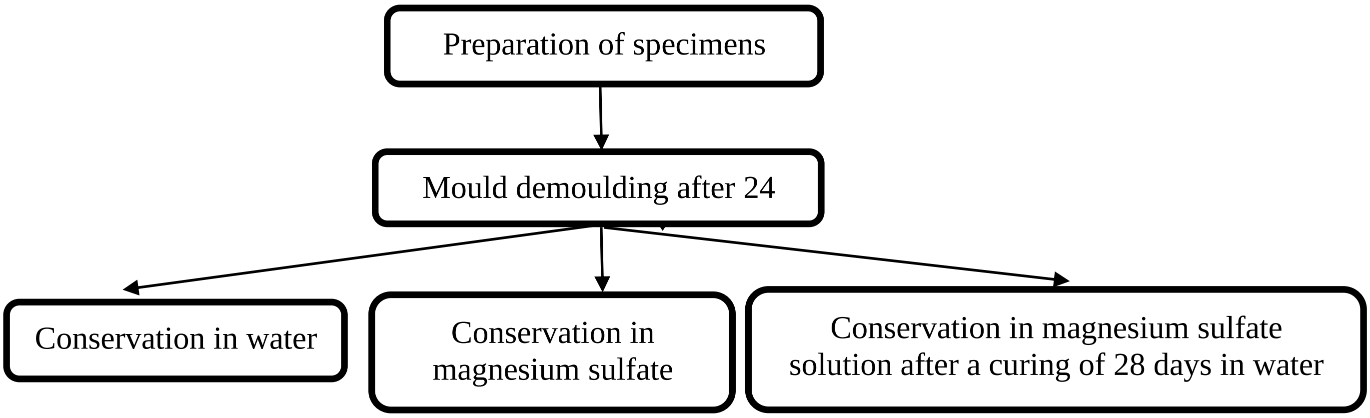


Figure 1. Diagram showing the method of conservation

The evolution of mechanical strength with time is obtained by exploiting the flexural strength and compression on specimens produced according to European standards NF EN 12390-5 [31] and EN 12390- 3 [32]. The mass variation of the samples according to the three conservation methods is carried out on prismatic specimens of dimension (4×4×16)cm. Weighing is carried out using an electronic scale.

3. Results and Discussion

Figures 2-13 show the effect of the nature and the rate of mineral admixtures (GGBFS and crystallized slag) as partial substitution to cement and the conservation mode in a medium rich in magnesium sulfate on the mechanical properties of mortar (compressive and flexural tensile strength).

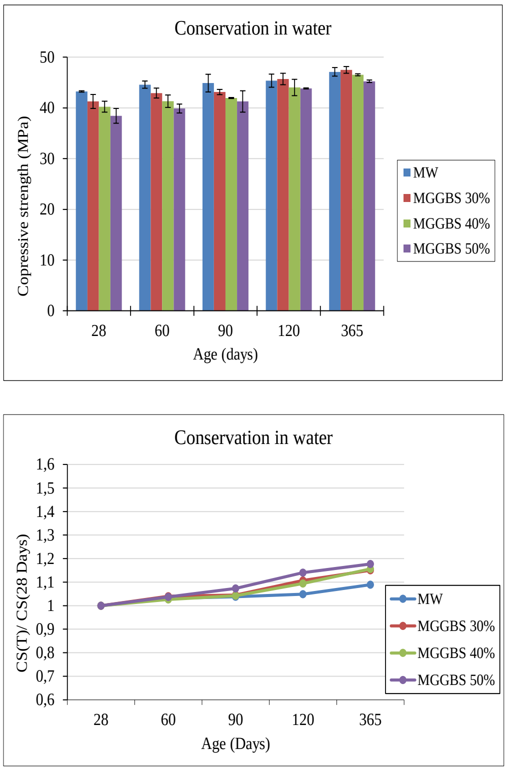


Figure 2. Compressive strength of mortars with GGBFS conserved in water

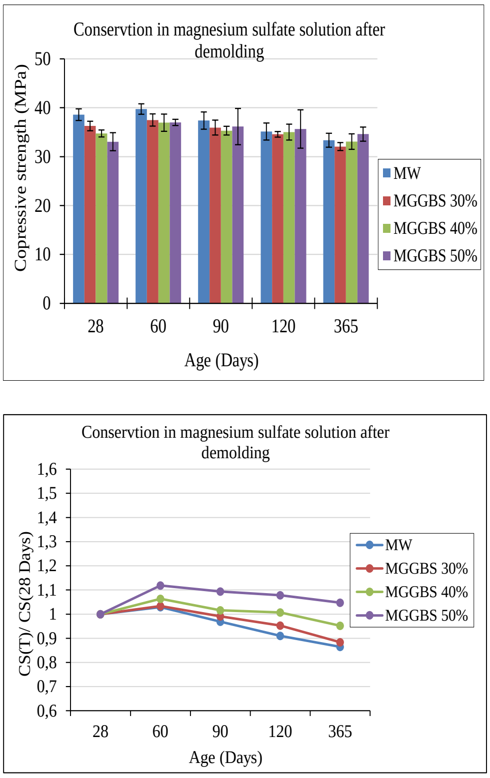


Figure 3. Compressive strength of mortars with GGBFS mortars conserved in magnesium sulfate solution after demolding

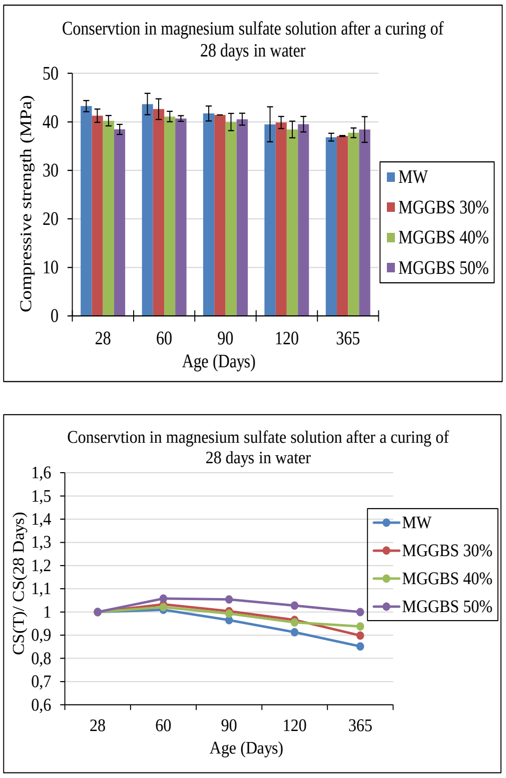
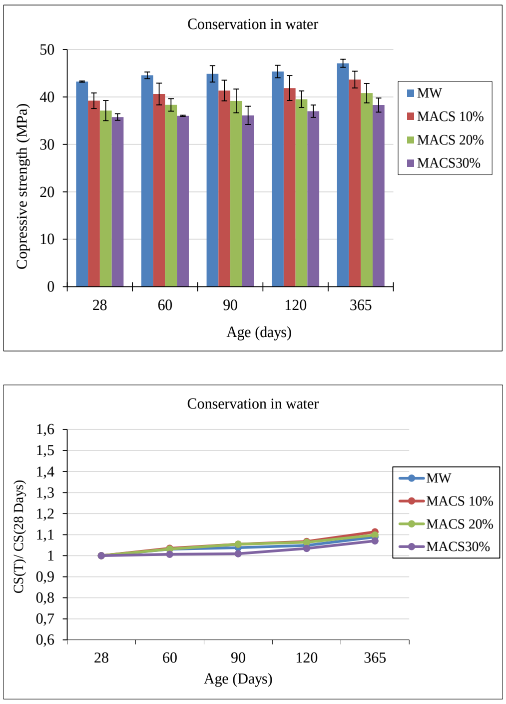
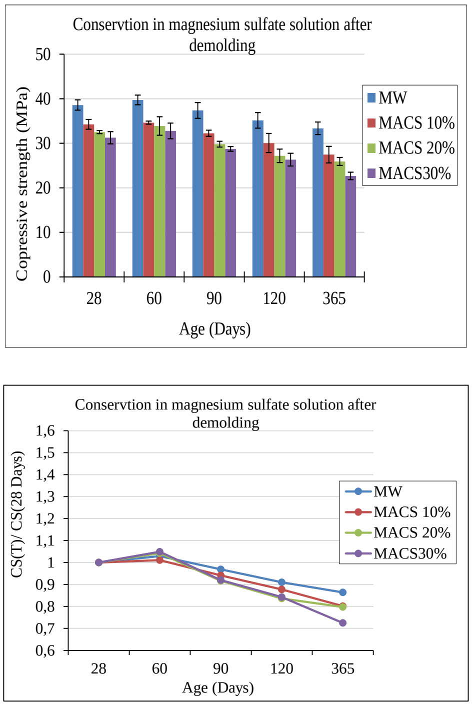


Figure 4. Compressive strength of mortars with GGBFS mortars conserved in magnesium sulfate solution after a curing of 28 days in water





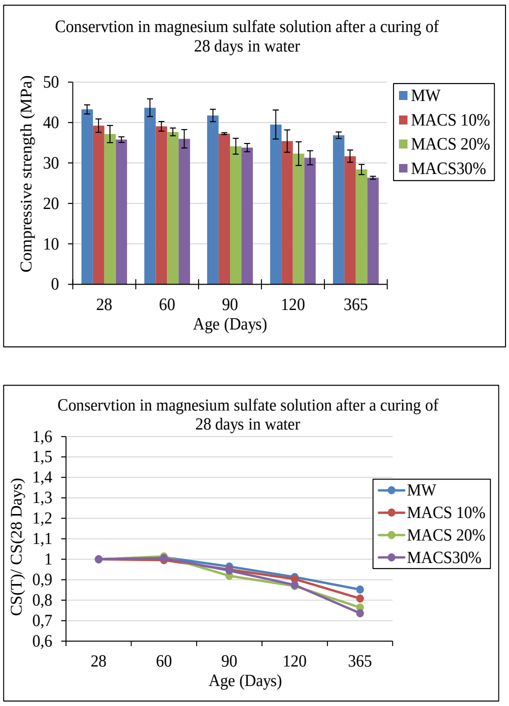
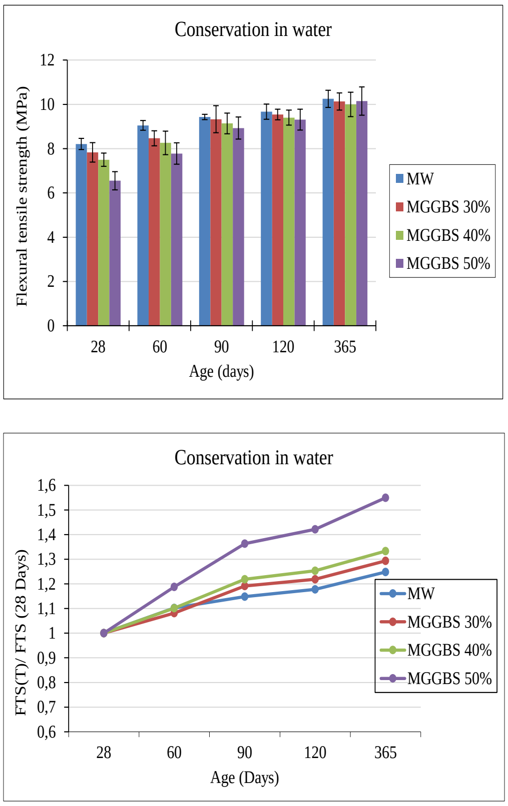
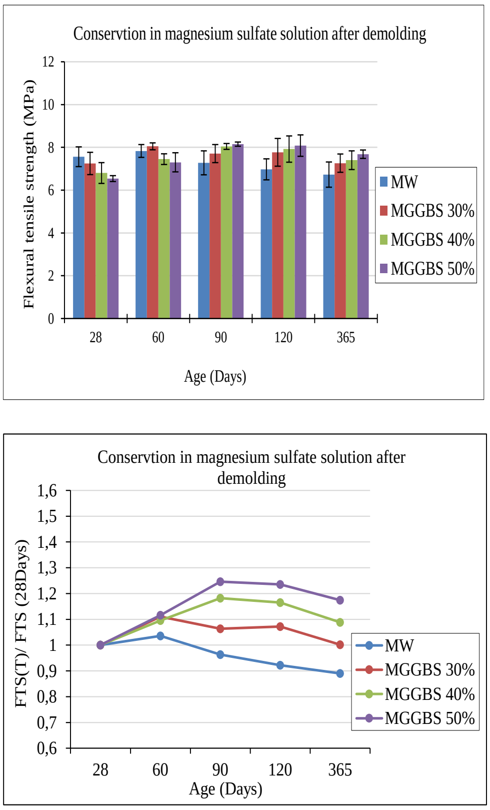


Figure 5. Compressive strength of mortars with crystallized slag conserved in water

Figure 6. Compressive strength of mortars with crystallized slag conserved in magnesium sulfate solution after demolding

Figure 7. Compressive strength of mortars with crystallized slag conserved in magnesium sulfate solution after a curing of 28 days in water





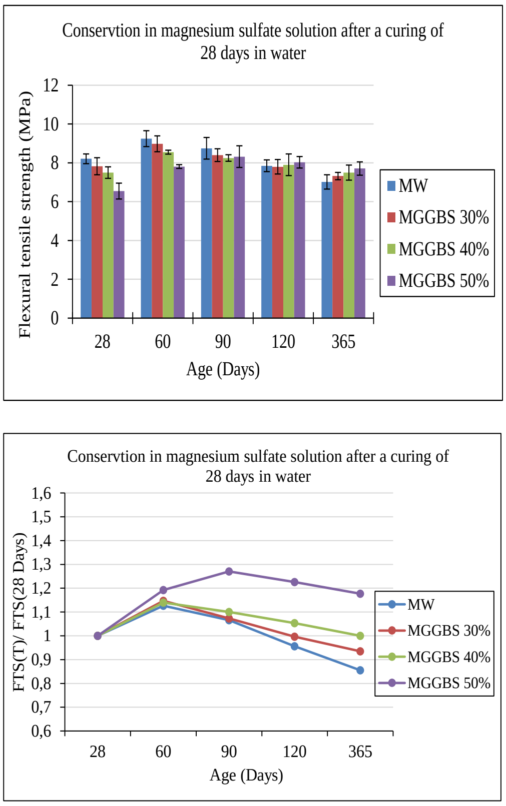


Figure 8. Flexural tensile strength of mortars with GGBFS conserved in water

igure 9. Flexural tensile strength of mortars vith GGBFS conserved in magnesium sulfate olution after demolding

Figure 10. Flexural tensile strength of mortars with GGBFS conserved in magnesium sulfate solution after a curing of 28 days in water

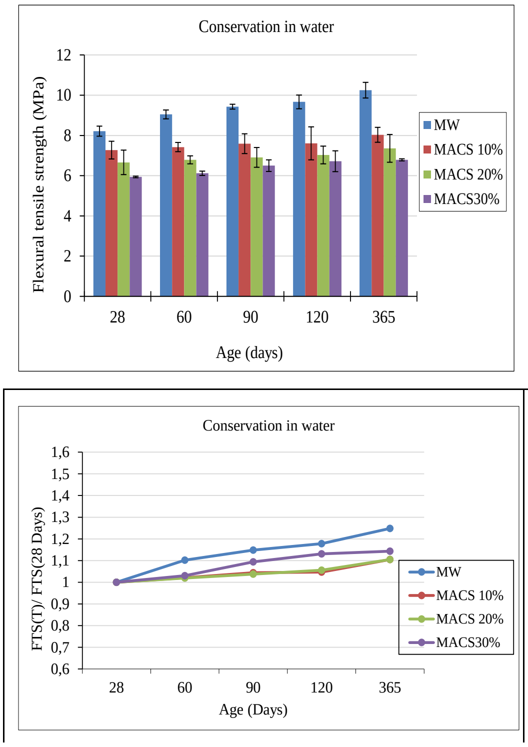


Figure 11. Flexural tensile strength of mortars with crystallized slag conserved in water

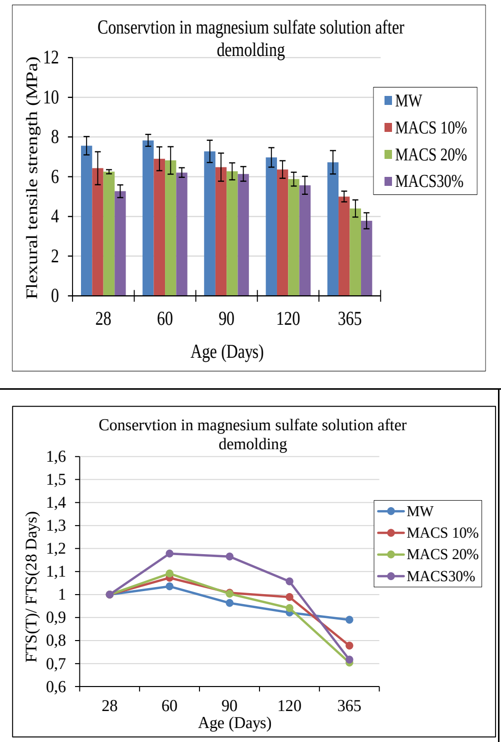


Figure 12. Flexural tensile strength of mortars with crystallized slag conserved in magnesium sulfate solution after demolding

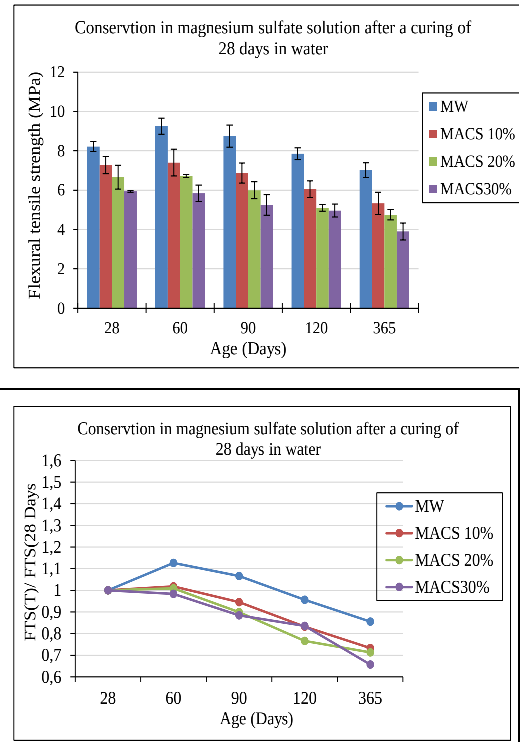


Figure 13. Flexural tensile strength of mortars with crystallized slag conserved in magnesium sulfate solution after a curing of 28 days in water

3.1.1. Case of conservation in water

Figures 2, 5, 8 and 11 show that the mechanical strength of mortars conserved within saturating humidity are highly influenced by the nature and the substitution rate of mineral admixtures.

In the case of mortars with GGBFS, the compressive and flexural tensile strength vary from 0 to 60 days is decreased by increasing the substitution rate of GGBFS. This is explained by the decrease in the amount of clinker or the clinker minerals (especially C_3S and C_2S) that strengthen the mortar, and very low hydraulic activity of GGBFS in the short term.

After 60 days, a progressive evolution of mechanical strengths with curing time takes place only on the mortars with GGBFS. On the other hand, the reference mortar presents a stationary or slow progression. The gains of compressive strength is in the order of 15%, 16% and 18% respectively with the rate of 30%, 40% and 50% of GGBFS compared to reference which is the order of 9%. This progress in the compressive strength of mortars with GGBFS can be explained by the finesse and latent hydraulic activity of GGBFS. These results are in good agreement with the literature [22] which demonstrated that the mortar with 30% of GGBFS can expect the compressive and flexural strengths compared with the reference mortar (without slag). These authors have also shown that the hydraulic activity and the specific surface area of GGBFS are the main factors responsible for the increase in the mechanical strength.

In the case of mortars with crystallized slag, the figures show a decrease in the mechanical strengths with increasing of the substitution rate of crystallized slag of up to 12%.This reduction can be explained by the slow hydration of cement with increasing ratio of crystallized slag. Consequently, the presence of crystallized slag disrupts the hydration process. This slag corresponds to a stable mineral form, it is chemically stable and hydraulic power, when it exists, can only be a modest one [33].

3.1.2. Case of conservation in magnesium sulfate solution after demoulding

The figures 3, 6, 9 and 12 show two phases:

1st phase ranging from 0 to 90 days

During this period, it can be noticed that a stabilization of the compressive strength and flexural strength for reference mortars and those with GGBFS (no significant drop was recorded) take place. However, a slight decrease in compressive strength for the mortars with crystallized slag after 60 days is observed. This can be explained by the formation of brucite, $Mg(OH)_2$ on an outer layer of the specimens exposed to the solution of sulfate, which can temporarily delay the penetration of sulfate ions. Brucite $Mg(OH)_2$ is the product of the reaction between the portlandite $Ca(OH)_2$ and magnesium sulfate according to the following reaction Eqn.1:

$$Ca(OH)_2 + MgSO_4 \longrightarrow CaSO_4 + Mg(OH)_2 \quad \text{Eqn.1}$$

The improvements in the mechanical behaviour in the mortars with GGBFS are mainly due to the hydraulic activity of GGBFS and the formation of secondary CSH, which consequently leads to the densification of the cement matrix.

2nd phase ranging from 90 to 365 days

During this period, a decrease in the mechanical strength for all mixtures is observed. However, this regression differs according to the nature and dosage of addition used. Mortars with GGBFS have the lowest decreases in strength (this decrease does not exceed 7%), for the mortar reference this drop of strength is about 18%.On the other hand, the mortars with crystallized slag give the largest declines with drop ranging from 20% to 29%.

The best mechanical behaviour of mortars with GGBFS to external sulphatic attacks is essentially due to the hydraulic activity of GGBFS, which will consume part of portlandite by pozzolanic reaction.

Several research papers have studied the reactivity of Algerian GGBFS, [34], [35]. The authors have shown that the Algerian blast furnace slag has a low hydraulic reactivity. To accelerate the speed of slag reaction, an external activation is required with a pH above 12.6 favouring the reactivity [36]. This justifies the high resistance of GGBFS in a sulfate environment.

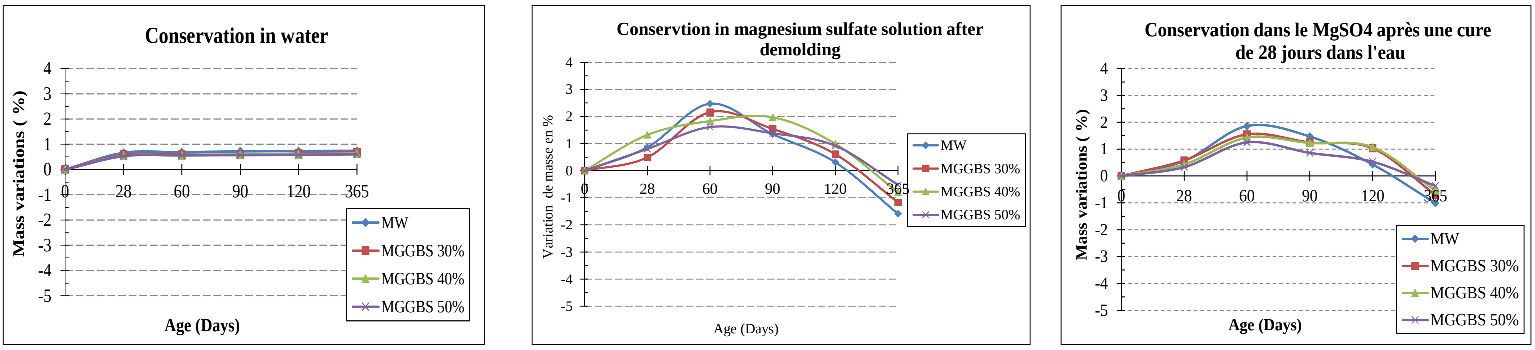
The GGBFS mixed with water does not hydrate, because of the formation of an acid layer around the grain of slag preventing the latter to hydrate. Portlandite ($Ca(OH)_2$) released during the hydration of Portland cement will dissolve the acid layer and reacts with the slag components, forming secondary hydrates and reduces the pH of the mixture and consequently improves the resistance in aggressive media. [1] [18]. On the other hand, the mortars with crystallized slag even with a percentage of 20% of GGBFS have a sharp reduction in the mechanical strength compared to the reference mortar or mortars with GGBFS. This drop can be explained by the decreasing cement hydration with increasing substitution rate of crystallized slag.

3.1.3. Case of conservation in magnesium sulfate solution after a course of 28 days in water

A curing time of 28 days in water before immersing the mortar specimens in a sulfate solution improves their mechanical behaviour. Figures 4, 7, 10 and 13 show that all mortars have higher compressive strength as well as flexural strength compared to that conserved directly in a sulfate solution. This can be accounted for by a correct hydration process and a maximum formation of hydrates that have a more stable crystalline structure and more resistant than that obtained directly after demolding.

3.2. Mass variation

Figures 14 and 15 give the results for the mass change of mortar with a substitution of GGBFS and crystallized slag according to the three conservation modes.

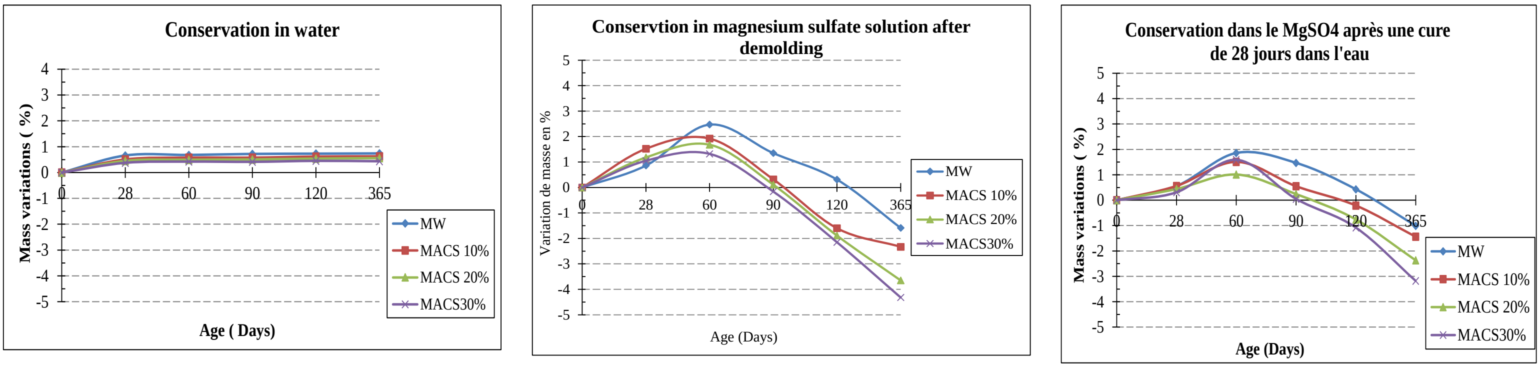


A/ Mortars conserved in water

B/ Mortars conserved in magnesium sulfate solution after demolding

C/ Mortars conserved in magnesium sulfate solution after a curing of 28 days in water

Figure14. Mass variation of mortars with GGBS



A/ Mortars conserved in water

B/ Mortars conserved in magnesium sulfate solution after demolding

C/ Mortars conserved in magnesium sulfate solution after a curing of 28 days in water

Figure15. Mass variation of mortars with crystallized slag

3.2.1. Case of conservation in the water

The results obtained show that in the short term (up to 28 days) there is a slight increase in weight with age for all mixtures. This may be due to the fixing of an amount of H_2O during the formation of hydrates over time. This fixed quantity of water is higher for the reference mortar than for the mortars with GGBFS. Beyond this period a stabilization of the mass up to 365 days is observed.

3.2.2. Case of conservation in magnesium sulfate solution

Figures 14 and 15 show the variation mass of mortars specimens conserved in magnesium sulfate solution after demolding and after a curing time of 28 days in water. Two phases are observed in the mass change:

1stphase ranging from 0 to 90 days:

A similar trend is observed for all the mortars, one notes also a significant increase in the mass of specimens. This increase is obtained following to the formation of ettringite and the secondary gypsum which results from the reaction between the portlandite $Ca(OH)_2$ and the solution of $MgSO_4$ in the presence of water. This reaction is accompanied by a swelling followed by damage to the mortar samples. Moreover, the formation of brucite $Mg(OH)_2$ can temporarily delay the penetration of sulphate and leads, consequently, to mass increase. This increase is less important for mortars incorporating more mineral admixtures and less cement.

2nd phase ranging from 90 to 365 days:

It is noticed that the mass begins to decrease gradually with the age of conservation. This decrease may be due to the leaching of portlandite $Ca(OH)_2$. The specimens are exposed to a low concentration of $MgSO_4$ solution compared to the specimens which are porous materials of basic character due to the nature of the hardened paste. During storage in the sulfate solution, this change in concentration causes the dissolution of the hydration products of the cement matrix mainly portlandite (strong base) which increases the porosity of the mortars over time. On the contrary, in this phase we can see that the mass begins to gradually decline with age of conservation, this mass loss may be due to the leaching of portlandite $Ca(OH)_2$. This phenomenon when the mortar specimens (porous cementitious materials) with basic character(pH between 12.5 and 13.5) are immersed in a sulfate solution $MgSO_4$ with low concentration and a pH of 5.73.This concentration change causes the dissolution of some hydration products and more particularly portlandite (strong base) which increases the porosity of the mortar over time.

3.3. Macrostructure and microstructure degradation

3.3.1. Macrostructure degradation (Visual observations)

Figure 16 show the photographs of mortar specimens exposed to the sulfate solution after 365 days of exposure. We can see that the degree of damage of this specimen differs depending on the composition of the mortars (the nature and rate of substitution of mineral addition). It is also observed the presence of the bruciteu layer of white colour at the surface of the specimens. This layer is formed following the reaction between portlandite CH and $MgSO_4$ (see Eqn. 1).

The least affected samples are those of mortars containing granulated slag, contrary the samples of mortar with crystallized slag are most damaged.

The damage observed (cracks and bursting) is attributed to the formation of expansive salts obtained following reactions between some components of the cement matrix (portlandite) and magnesium sulfates $MgSO_4$. The latter are particularly aggressive by a double action of cation Mg^{2+} with Ca^{2+}cations and SO_4^{2-}anions. These exchanges of Mg^{2+} with Ca^{2+} lead to the formation of brucite $Mg(OH)_2$ which can temporarily slow the penetration of sulphate's. They also cause the progressive transformation of CSH to magnesium silicate hydrate MSH without binding properties. Moreover, the crystallization of unstable ettringite in the presence of magnesium sulfate intensifies secondary gypsum formation reaction. This is in agreement with the results obtained by Santhanam [37].

Gollop and Taylor [38] have given a diagram (Figure 17) that represents the mechanism of expansion and degradation of the samples immersed in a sulfate solution. They have shown that the reaction of the components of the cement paste with the sulfate solution produce ettringite at the first place and subsequently gypsum. These two components are formed close to the external surface. This diagram explains the degradation of the mortars of this study especially those based on crystallized slag.

A/ witness Mortar B/ GGBS based Mortar C/Crystallized slag based Mortar

Figure 16. Visual observation of mortars exposed to magnesium sulfate solution

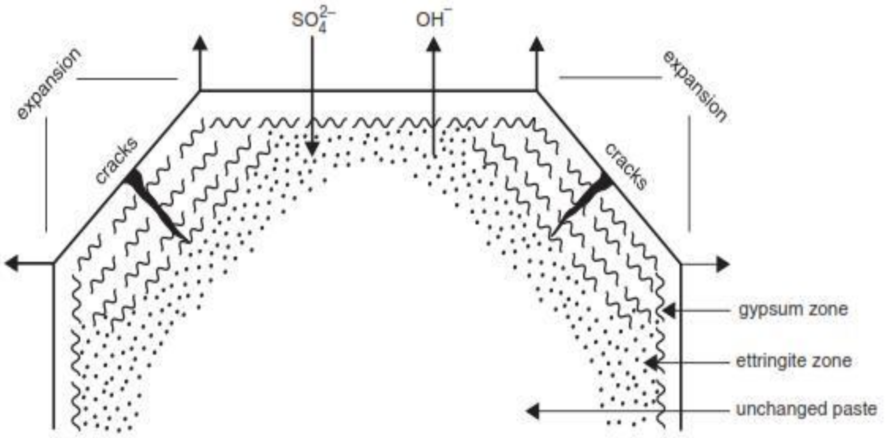
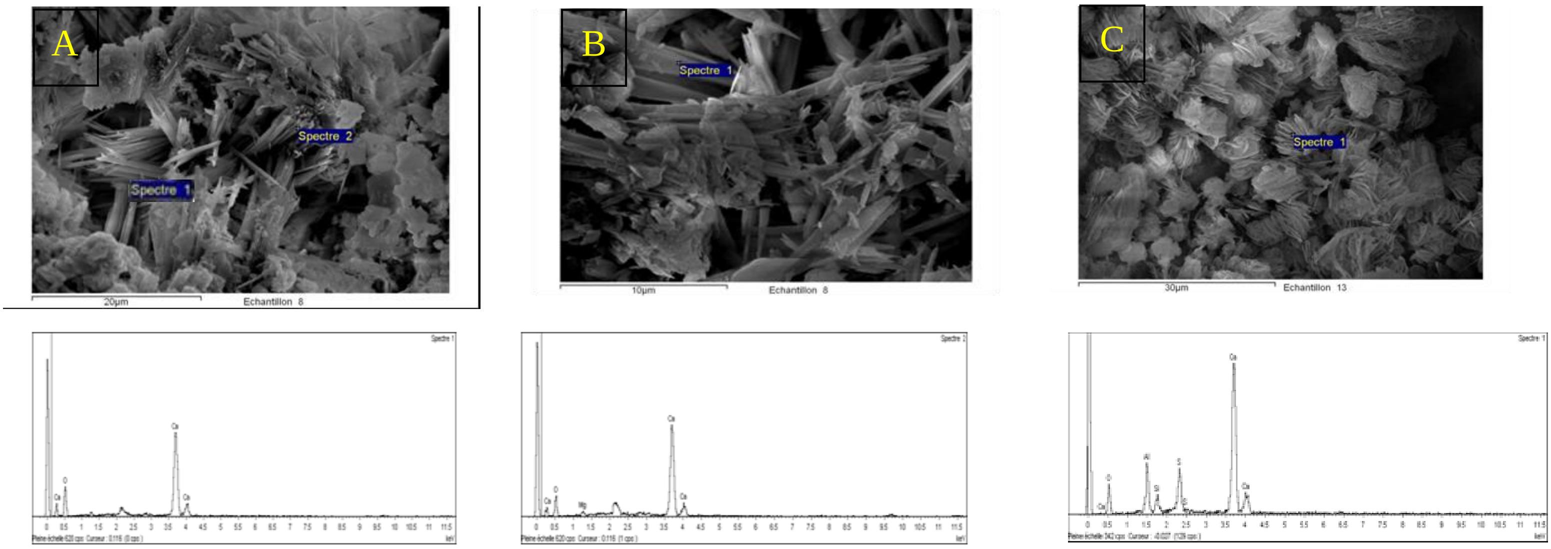


Fig.17. Schematic representation of the microstructure of a section of a specimen after immersion in a sulfate solution [38]

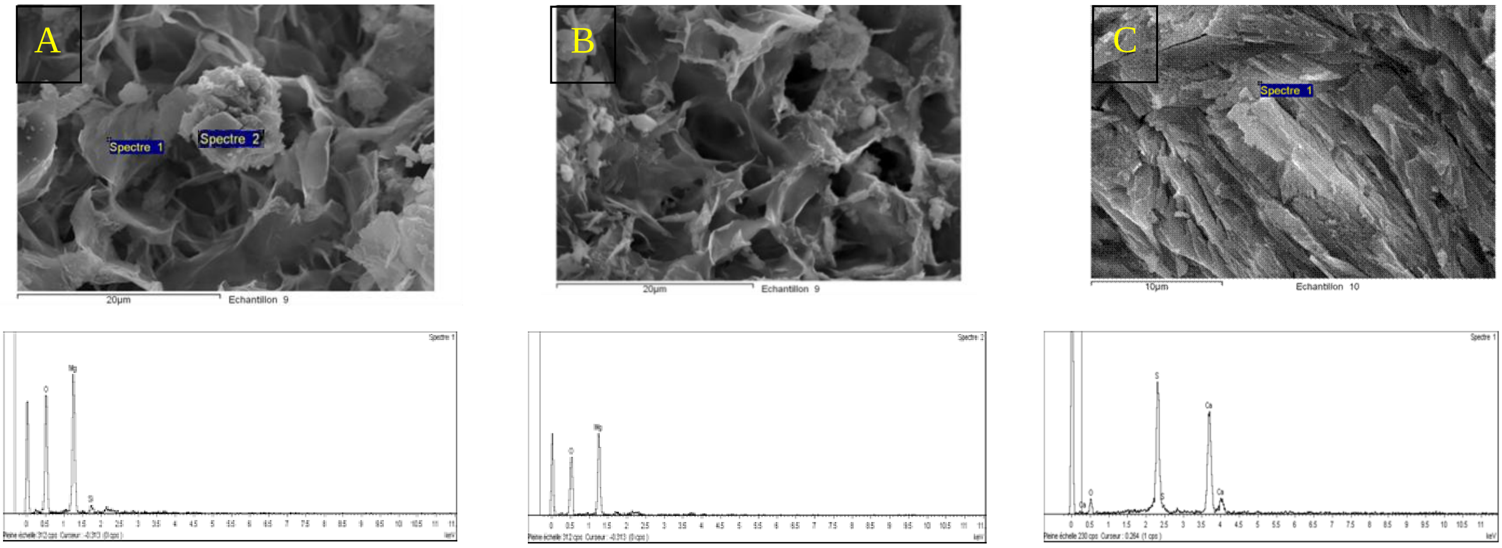
3.4. SEM observations

The microstructure analyses were performed on reference mortar samples, mortar with 50% GGBFS and with a mixture of 20% GGBFS and 30% crystallized slag in order to identify the sulfate attack deterioration products during a one year period. This analysis allowed us to identify new products of reactions between sulfate ions and cement hydration products. The Figures 18- 23 show the images of the SEM associated by EDX elemental analysis of the different samples analyzed. For the reference mortar (without mineral additions) conserved in the $MgSO_4$ solution after 28-day curing time in water, the microstructure is very affected by the sulfate attack. Figure 18/C, which characterizes the attack at the level of the outer layer, shows the formation of ettringite crystals in balls. Figure18/A and 18/B, which characterizes the attack at the heart of specimen, shows the abundant presence of portlandite with a very visible porosity. For the same type of mortar conserved in the sulfate solution $MgSO_4$ after demolding, it can be seen in figure19/A and 19/B the presence of brucite on the surface of the sample. The latter was formed following the reaction between Portlandite CH and $MgSO_4$ solution. This justifies the absence of portlandite at the sample surface. At the core of the sample, figure14/C shows the presence of the CSH gel. Concerning the mortar with GGBFS conserved in the $MgSO_4$ solution after a 28 day period in water, it can be noticed the presence of hydrous magnesium silicates MSH at the outer phase of the specimen (Figure20/A) following the transformation of CSH after leaching of portlandite. At the core of the specimen (Figure20/B and C), we can observe a very dense structure of the paste due to the formation of a large amount of CSH with the Presence of anhydrates slag grains. For the mortars with GGBFS conserved directly after demolding in the $MgSO_4$ solution presented in figure 21/A and 21/B, we can see the formation of ettringite crystals in the sample surface, and the CSH in the core, as shown in figure21/C. The high amount of CSH in the mortars with GGBFS may be due to granulated slag activity. This latter reacts with the released lime laying the hydration of the cement and forms the CSH. Figure 22 shows the presence of calcite on the outer surface of mortar with crystallized slag conserved in the $MgSO_4$ solution after 28 days in water and the CSH gel in the sample core.



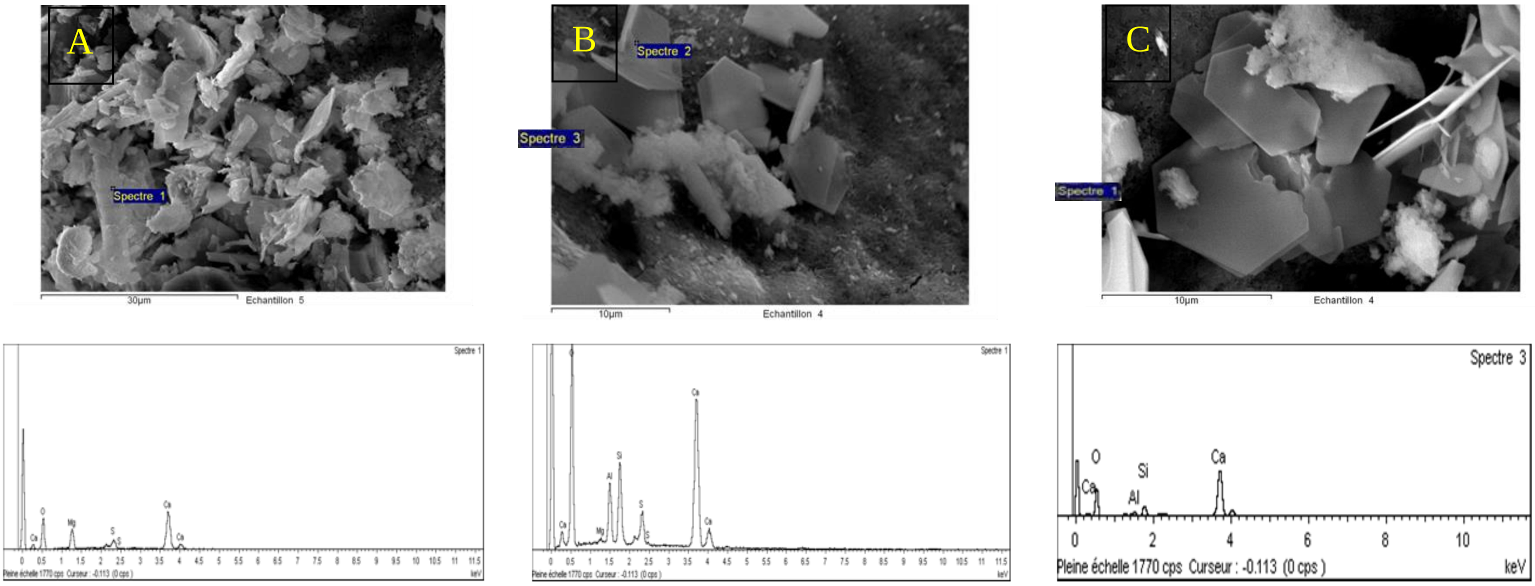
A-B/core of the test specimen C/ Outer layer

Figure18. SEM observation of witness mortar conserved in magnesium sulfate solution after curing time of 28 days in water



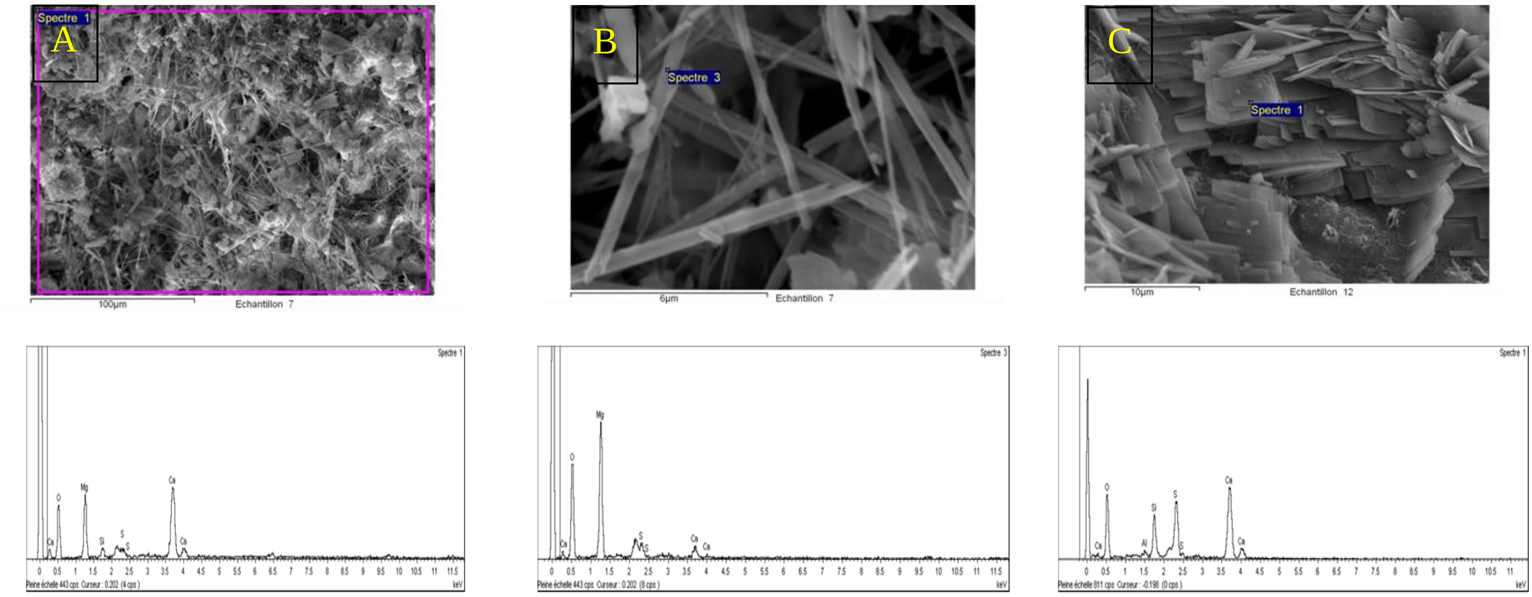
A-B/core of the test specimen C/ Outer layer

Figure19. SEM observation of witness mortar conserved in $MgSO_4$ solution after release



A/ Outer layer B-C/core of the test specimen

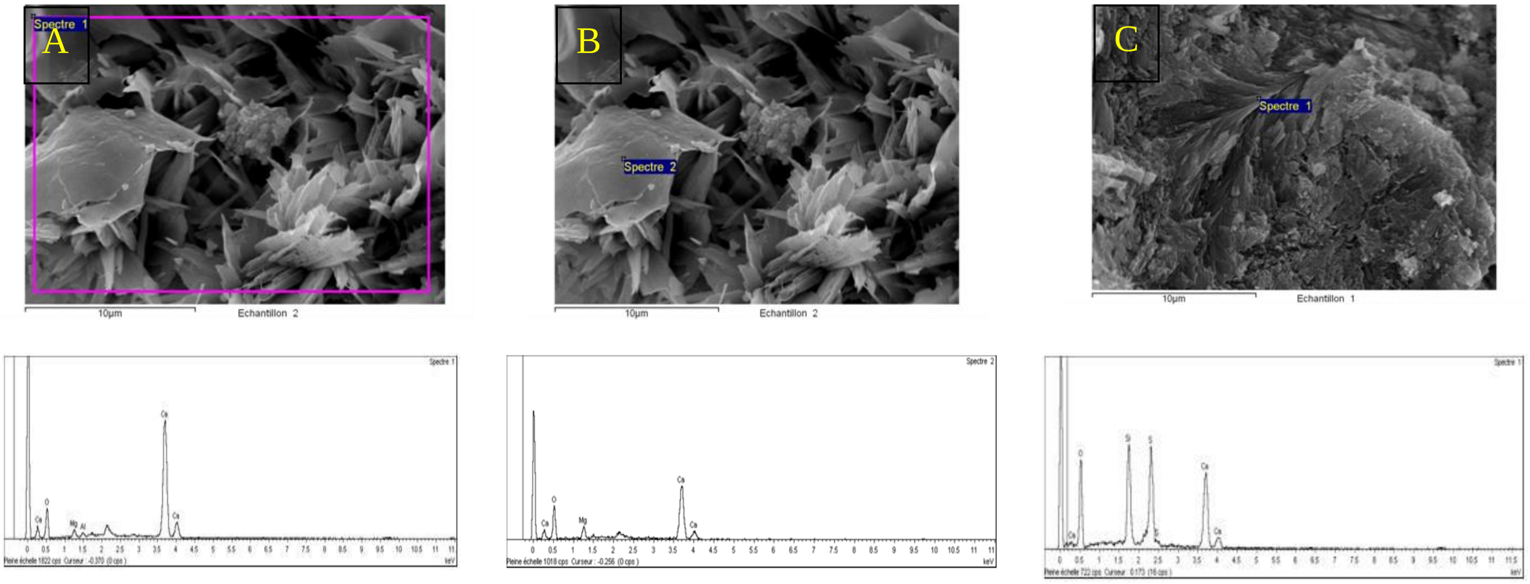
Figure 20. SEM observation of GGBS based mortar conserved in magnesium sulfate solution after curing time 28 days in water



A-B/ Outer layer C/core of the test specimen

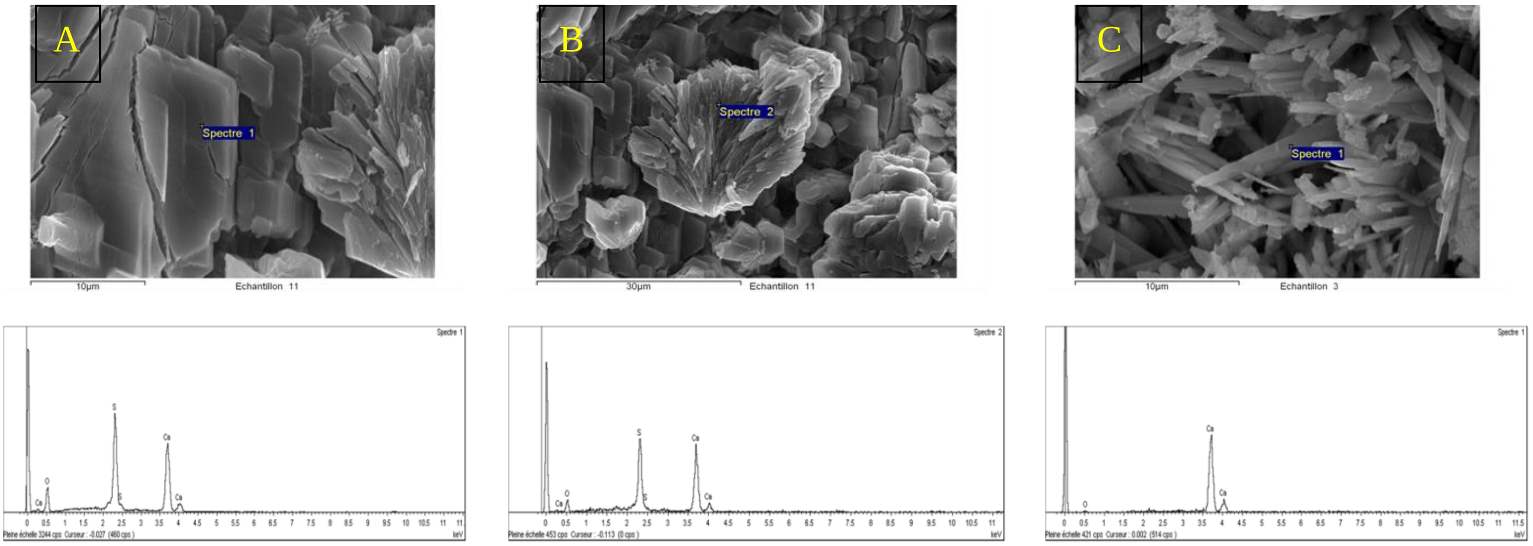
Figure 21. SEM observation of GGBS based mortar conserved in magnesium sulfate solution after demolding

Figure 23/A and B shows that the outer phase of mortar with the crystallized slag conserved in the $MgSO_4$ after demolding is marked by the presence of a large amount of gypsum formed. At the inner phase notice the existence of portlandite (Figure23/C). After one year of conservation of mortars in a sulfate medium, the specimens have been subjected to a superficial degradation following the formation of the expansive products, but the core remains more or less healthy.



A-B/ Outer layer C/core of the test specimen

Figure 22. SEM observation of crystallized slag based mortar conserved in magnesium sulfate solution after curing time 28 days in water



A-B/ Outer layer C/core of the test specimen

Figure 23. SEM observation of mortar with crystallized slag conserved in magnesium sulfate solution after demolding

Conclusion

This work highlights the resistance of mortars containing GGBFS or crystallized slag used as a partial substitute of Portland cement to the external sulfate attack. Based on analysis of the results obtained we can state:

The mechanical strengths of mortars conserved directly after demolding in $MgSO_4$ solution are very influenced by the nature and the rate of substitution with blast furnace slags (GGBFS or crystallized slag). For the period to 90 days, the mechanical strengths are slightly affected by external sulfate attack.

This is explained by the formation of a layer of brucite $Mg(OH)_2$ on the outer skin of the samples conserved in an $MgSO_4$ solution, which temporarily delays the effect of a sulfate ion and allows the continuity of the hydration kinetics.

Beyond 90 days, the degradation is clearly visible. Mechanical strength drop was recorded for all mortars studied. This drop is mainly due to the formation of gypsum and secondary ettringite which cause the expansion. This favors the onset and growth of the cracks followed by a drop of mechanical strength.

The effect of GGBFS substitution improves the mechanical strength of mortars to the sulfate attack. These mortars have the lowest mechanical strength decreases compared to those with crystallized slag. The mechanical strength of mortars with GGBFS to external sulfate attacks is essentially due to the hydraulic activity of GGBFS materialized by consumption of part of portlandite and formation of CSH's.

The SEM analysis of mortar samples allows us to identify new products of the reactions between the sulfate ions and cement hydration products to justify the results of physical and mechanical properties. After one year of conservation of mortars in a sulfate environment, the specimens were subjected to a surface degradation due to the formation of expansive products, but the core remains intact.

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