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Contribution of the Blast Furnace Slag on the Behavior of HPC in a Hydrochloric Environment

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ABSTRACT

Most mechanical properties and durability of cementitious materials are related to the performance of the hydrated cement that coats the granular skeleton. However, different mineral additions are currently used in concrete. They are used as addition or substitution to cement. The use of these supplementary cementitious materials provides to concrete a denser matrix that will be more resistant to aggressive environments such as sulphates, chlorides and other aggressive agents. In mixtures containing finely ground of slag, 15% of cement by weight was replaced with finely ground of slag of El-Hadjar (Algeria). The main objective of this study is to investigate the effect of curing in the hydrochloric environment by subjugating its granular effect on the performance of concrete. Density, compressive strength, concrete surface, internal microstructure and ultrasonic pulse velocity were investigated in this research. The damage mechanisms of concrete have been related to the development of the microstructure of the material. The degradations were observed using a scanning electron microscope (SEM) and quantified by x-ray diffraction (XRD). The microstructural study concerns both the surface layer and the internal structure of the samples. The results have shown that slag of El-Hadjar present a pozzolanic activity and hence it affects favorably the microstructure of the paste which becomes denser and less permeable.

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1. Introduction

Sustainable development requires a balance between development of infrastructure and environmental protection. The challenge to the cement and concrete industry is to produce a durable concrete at a competitive cost having minimal environmental impact [1].

However, in a more general way, the improvement of the CO_2 emissions budget of the cement can be more easily achieved by the partial substitution of a part of the clinker by other constituents presenting hydraulic and/or pozzolanic properties [2,3].

Given its availability, it is likely that blast furnace slag contributes to reducing greenhouse gas emissions, limiting energy consumption and optimizing the use of non-renewable natural resources [4]. In addition, the replacement of a portion of the clinker with slag leads to improve the performance of the concrete by modifying their microstructure, as much by their mechanical properties as by their durability [5,6].

A high-performance concrete with a correct concrete dosage and good compactness, these two prescriptions could effectively guarantee a certain durability of the concrete material exposed to chemically aggressive environments [7]. It goes without saying that these considerations represent the first versions of a sustainable development policy in construction projects [8]. For a cementitious material, it is first of all about mastering its "genesis". This amounts to controlling the hydration processes and predicting the kinetics of their evolution with the consequences on the properties of the material, in this case the porosity [9].

However, the majority of recent studies concerning the influence of mineral additions on the properties of concrete consider the binding activity of additions resulting from their physicochemical and chemical effects without taking into account the action of the granular effect [10,11]. For this purpose, and to accentuate this activity, we milled the slag to a specific blown surface area of 8500 cm^2 / g with a grinding passing entirely through the 80 µm sieve.

This article reports on part of an ongoing research project on the reuse of mineral waste as an addition to cement for the development of sustainable concrete. We mainly examine the results of an experimental study on the effect of finely ground slag on the microstructure of hardened concrete in a hydrochloric salt environment. The evolution of the crystalline phases is analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM). The microstructural study concerns both the surface layer and the internal structure of the samples.

2. Used materials

2.1. Cement

The Portland cement used is a CEM I 52.5 from the Saint Pierre Lacour plant, whose chemical and mineralogical compositions are reported in Table 1.

Table 1
Chemical and mineralogical composition of CEM I 52.5 cement.

Elements	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	RI	PAF	CaO_l
%	64.50	21.01	4.90	2.80	0.90	3.00	0.90	0.20	0.20	1.10	0.45
Minerals	C_3S	C_2S	C_3A	C_4AF							
%	65.94	10.47	8.24	8.52							

2.2. Aggregates

The sand used is 0/3 alluvial sand having a fineness modulus of 2.47. Coarse aggregates are crushed gravel with fractions 3/8 and 8/15. However, obtaining the required characteristics for concrete is imperative through the development of its composition, which is to define the optimal mix of different aggregates.

2.3. Slag

Used slag is a by-product of the manufacture of cast iron. It comes from the factory of El-Hadjar (Annaba) Algeria; it is a sand of particle size 0/5 mm. Its chemical composition is shown in Table 2.

El-Hadjar slag (Algeria) has the advantage of being rather acidic, the CaO / SiO_2 ratio varies within the limits of 0.95 - 1.04; it is relatively stable.

Table 2
Chemical composition of the slag.

Elements	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	RI	PAF
%	39.77	41.69	7.05	1.41	5.49	0.15	0.44	0.10	0.12	0.11

However, the sudden quench cooling of the slag under a jet of water, allows obtaining a vitrified state (amorphous). This explains the absence (or very low intensity) of diffraction lines in the X-ray diffractogram (Figure 1) [12].

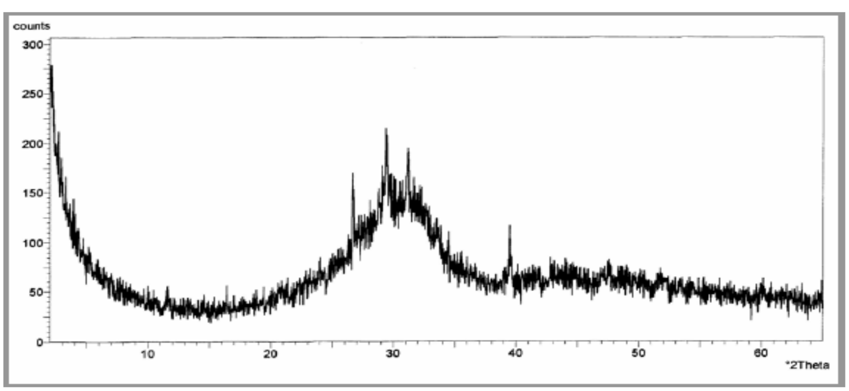

Fig. 1. Diffractogram of the slag.

The particle size analysis (Figure 2) carried out using a laser granulometer represents the partial and cumulative grain size curves of the slag.

A mean continuous particle size between 0.3 and 77 µm can be observed with the following granular classes:

- 90% of particles with a diameter of less than or equal to 77 µm.
- 50% of particles with a diameter of less than or equal to 22 µm.
- 10% of particles with a diameter of less than or equal to 2 µm.

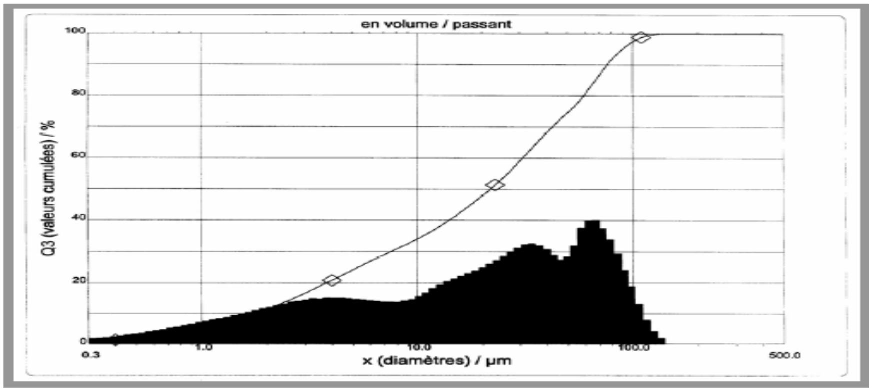

Fig. 2. Particle size distribution of the slag.

Besides its pozzolanic power characterized by the combined lime content, the slag having such a particle size ensures the densification of the matrix due to its fine particles which become embedded encrusted between the cement grains.

2.4. Superplasticizer

Superplasticizer is a water reducing plasticizer for high performance concrete according to NF EN 934-2 standard provided by the company SIKA. The SIKAMENT FF 86 allows the manufacture of concretes with very low E/C ratio and having very high mechanical strengths at all ages especially at young ages.

3. Experimental program

Two types of high-performance concrete were elaborated: control concrete BC without addition and one concrete BL using blast furnace slag. The compositions of the concretes with and without slag retained for experimental program after optimization are reported in Table 3.

Concrete specimens were kept in their mold in a humid room (20 ° C, 95% RH) for 24 hours. They were then demolded and immersed in the preservation medium at 3% sodium chloride (NaCl), at 20 ° C until fixed deadlines. This concentration corresponds to the average salinity of the oceans of 35g/l, including 27g/l of NaCl.

Compression tests were carried out at 28, 90 and 365 days, in order to study the strength evolution of the concretes in the aggressive medium. In parallel, hydration of the mixtures was followed by X-ray diffraction. The minerals are observed with SEM, micro analysis which is associated with it makes it possible to confirm their chemical composition.

Table 3
Composition of concretes with and without slag (kg/m^3).

Constituent	BC	BL
Cement	500	425
Sand	573	573
Gravel 3/8	130	130
Gravel 8/15	915	915
Water	150	150
Superplasticizer	8	8
Slag	-	75

4. Experimental results and discussion

In this work, the advocated approach in the context of sustainable development consists to enhance the blast furnace slag (industrial residue) used as a replacement for a part of cement in the concrete.

These concretes, designed, manufactured and used correctly, can offer higher performance to conventional concrete with Portland cement, both in mechanical properties and durability. Concretes manufactured with this addition can be used in a wide range of applications and in accordance with performance requirements.

4.1. Density

Addition of finely ground slag induced an increase of the concrete density (Figure 3). This is explained by the granular effect which is conditioned by the very high grinding fineness. Furthermore, produced Portlandite by the hydration of clinker grains reacts with Al^{3+} and Si^{4+} ions from the hydration of slag to form C-S-H and C_4AH_{13} increasing the density of the microstructure (pozzolanic effect). These products are major factors in the reduction of chloride ions permeability [13].

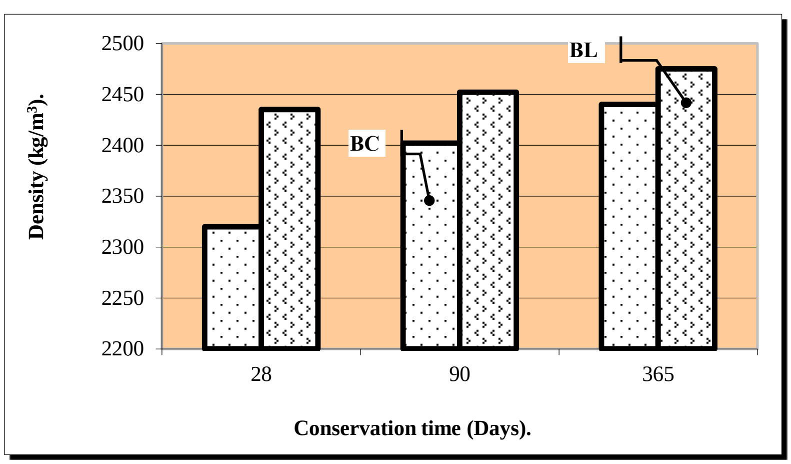

Fig. 3. Evolution of the concretes density as a function of curing time.

4.2. Mechanical strengths

The incorporation of slag in concrete generated the reduction of pore size of the hydrated cement paste and therefore, a decrease of permeability and infiltration rate of Cl^- ions. Concrete containing high volume of slag and correctly cured should, in general, have lower long-term permeability than the corresponding Portland cement concrete and thus provide better protection of the reinforcement against corrosion [14].

Figure 4 shows the increase of strength concrete specimens as a function as curing time in the hydrochloric acid medium. It can be seen that the compressive strengths of concrete with added slag are all higher than those of the reference concrete and exceed 75 MPa. These concretes are therefore considered as high-performance concretes. This quality is not affected by the aggressive environment. Thanks to the use of slag with high fineness in the cementitious matrix.

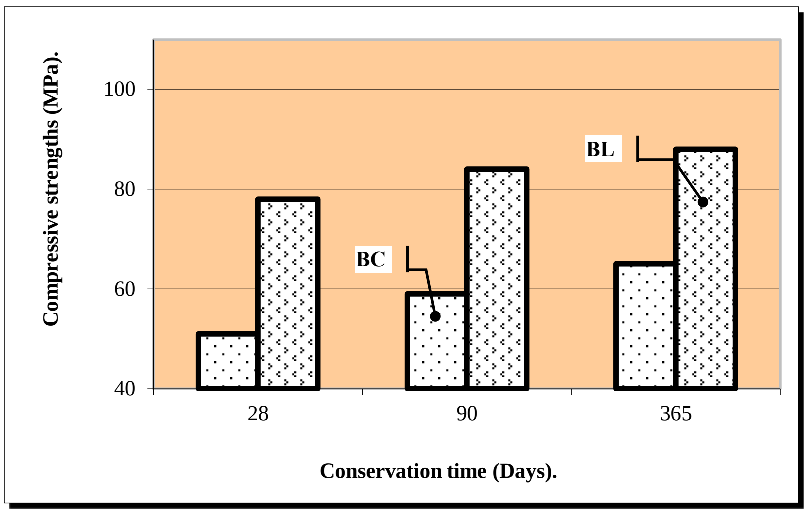

Fig. 4. Evolution of compressive strength as a function of curing time.

On the other hand, slag inclusion increase markedly compressive strength. Due to its high fineness, compressive strength value at 90 and 365 days are on average 50% higher than those of control concrete "which is degraded". This leads an improvement of strength, both from a mechanical point of view and in terms of physical and chemical aggression.

4.3. Concrete surface

The first part of this investigation will focus on an experimental study of the mechanical behavior of concrete surface exposed to hydrochloric acid medium. The surface of concrete is most sensitive because drying is faster there and it is more porous than the core of the concrete. Therefore accessible to Cl^- ions.

The Figure 5 showed that the surface degradation of concrete without slag is significantly increased compared to that of concrete with slag addition, revealing some of the CSH.

The mineralogy and texture of the surface solid for slag concrete are modified by calcium carbonate precipitation, the new surface compositions are characterized mainly by the formation of calcite, factor decreasing permeability of the concretes (Figure 6).

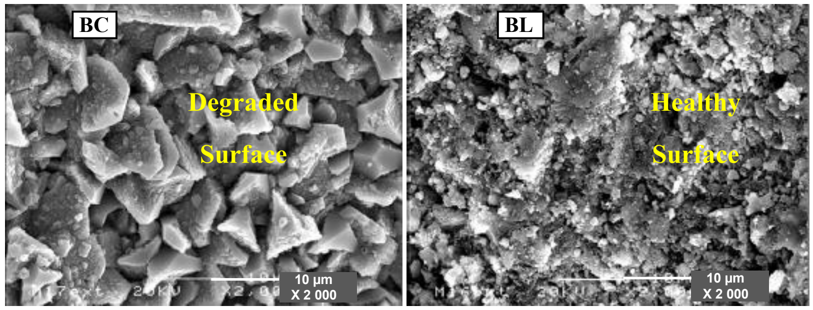

Fig. 5. SEM observation of the surface of concrete specimens after 365 days of curing.

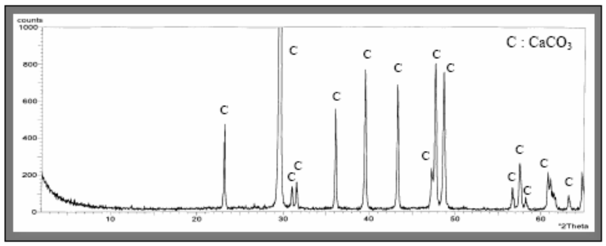

Fig. 6. Radiogram of the calcite observed on the surface of various concretes.

Measurements on ordinary concrete of structures regularly beaten by salty spray show that the concentration profile of chlorides generally shows a maximum at a depth of about 1 cm below the surface [15]. The maximum concentration is not measured at the surface because the chlorides are leached by precipitation.

4.4. Internal microstructure

The penetration of Cl^- ions into the concrete requires the presence of a liquid phase, it also depends on the characteristics of the material and humidification / drying cycles that it undergoes (duration, climatic conditions).

The chloride ions also interact with the cementitious matrix, they can be adsorbed by HSCs or chemically react with certain compounds to give new products (calcium chloroaluminates, in particular hydrated calcium monochloroaluminate, or Friedel salt, $C_3A.CaCl_2.10H_2O$) [16].

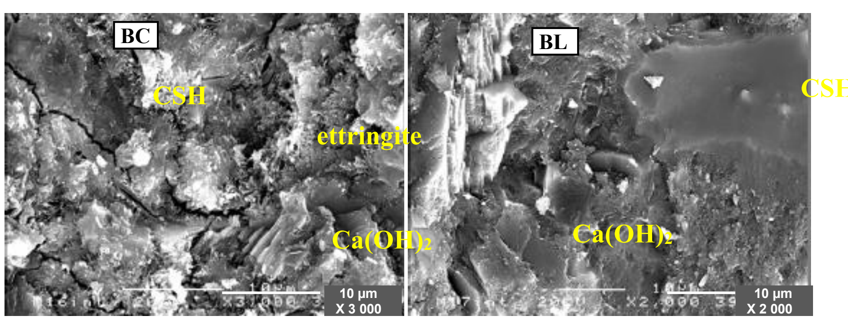

Fig. 7. SEM observation of the internal micro-structure of concrete specimens after 365 days of curing.

These chlorides are called "fixed chlorides" or "bound chlorides". Complex ions-matrix interactions are often described by a Freund lich-type non-linear interaction isotherm [17]. The fixing of Cl^- ions depends strongly on the nature of the cement used and mainly on its C_3A content but C_4AF calcium alumino-ferrite. Sulphates also play a significant role [18].

Figure 7 illustrates the shape of the different crystals observed at SEM, for slag concrete with a higher density (Figure 3). CSH are in vitreous form, with a less porous microstructure [19]. Unlike, concrete without slag, hydration products are formed of spiky heaps, with highly porous ettringite-rich zones containing portlandite preceding the healthy core.

The chemical reaction of slag with the Portlandite Ca $(OH)_2$ leads to production of additional CSH gel which was the main reason for the strength. X-ray diffraction analysis (Figure 8) illustrates the influence of the conservation medium on the different formations. The formed calcium hydrosilicates (CSH) are semi - crystalline or amorphous and difficult to identify by X - ray diffraction; only a few lines appear but they are superimposed on the lines of the other crystalline phases [20].

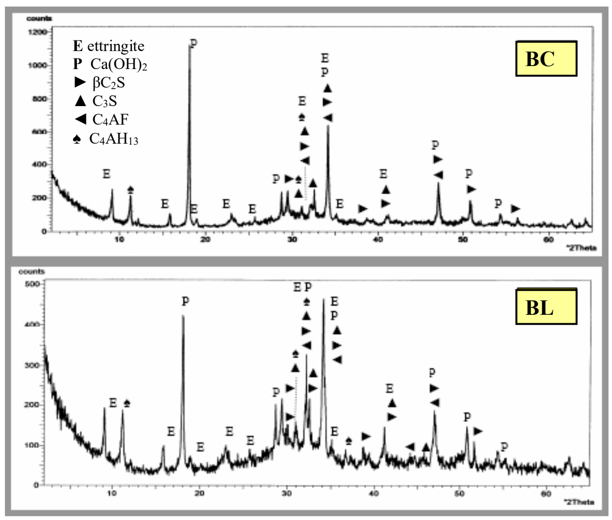

Fig. 8. Radiogram of concrete specimens after 365 days of curing.

By adding slag as a cementitious material in the concrete, an additional CSH gel is formed and lime is consumed, leading to a densification of the microstructure and a decrease in capillary porosity. In addition, the slag has Blaine fineness higher than that of cement, fills the tiny voids and accentuates the densification.

The crystalline phases (interior of the specimens) of the various concretes appear identical. However, as hydration develops and the size of the capillary pores decreases, the movements of water in the system become more and more difficult, so that the hydration of large cement particles becomes rather, by diffusion, and the hydration of the anhydrous compounds of the slag concrete is slowed, unlike that of the control concrete.

This is the consequence of the densification of the matrix by promoting the formation of a more compact skeleton and consequently much higher chemical strength (Figure 6). The absence of X-ray diffraction lines of the gypsum is noted; it is totally consumed during hydration and contributes to the formation of primary ettringite [21]. In this way, the results of X-ray diffraction analysis corroborate those of the SEM observations.

Ultrasonic propagation is directly related to the mechanical properties of the material; the phase velocity makes it possible to go back to the density and the compression and shear modules, while the attenuation is linked to its porosity, to its cracking micros and macros, or to the degree of heterogeneity of the material. All this makes it an excellent means of evaluating the properties of materials [22].

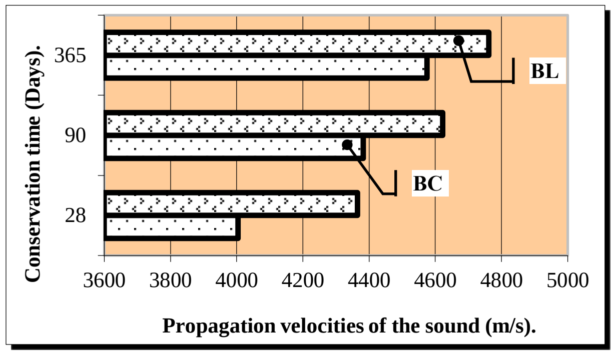

Fig. 9. Evolution of sound propagation velocities through concrete specimens as a function of curing time.

The compressive strength varies according to the binder class, the age of the concrete, the E/C ratio, the size of the aggregates and the compactness of the concrete. In Figure 9, there is a lower propagation speed for concrete without slag compared to concrete containing slag. This is the major consequence of the increase of the density of micro cracks or even porosities and which results in poorer mechanical characteristics.

If the pore volume and the micro cracks network strongly influence the mechanical resistance, they also condition the potential penetration of aggressive external substances with respect to the structure (water, chlorine, carbon, etc.). It should be noted that the first centimeters or millimeters of the material called "surface concrete" have a significant importance on the durability of the concrete, because they constitute a protective layer.

4.5. Transitional halo

The increase in the impermeability of concrete is also a reflection of the improvement of the transition halo. The hydration of the vitrified slag consumes some of the portlandite resulting from the hydration of the clinker to produce C-S-H. This homogenizes the microstructure of the transition halo (Figure 10), which decreases in thickness until it disappears and its density increases [23].

A global micro analysis is performed (x 1000) at the contact point matrix - granulate. The concrete incorporating slag addition has a higher Ca/Si ratio (3.9) compared to that of the concrete without slag (3.04), result of the new CSH formations.

For the control concrete, the porous space of the mortars is formed by the porosity (so-called capillary) of the cement paste, by air bubbles trapped during mixing and by the nanometric porosity of the hydrates. It also includes a particular porosity zone at the paste / granulate interface. Finally, there is the presence of microcracks.

On the other hand, the sulfur content in this zone is higher (0.90%) in the control concrete, which explains the strong presence of secondary ettringite in the transition halo observed at the SEM.

This weakens the matrix - gravel interaction and therefore limits the strength of the concrete and its durability to the hydrochloric medium.

It should be emphasized that the aggregate-matrix adhesion state and the state of health of these reinforcements are therefore important questions that builders and users of concrete structures face when carrying out sustainable constructions, especially in aggressive environments. It binds to the lime released during the hydration of the cement and thus contributes to the development of the strength [24].

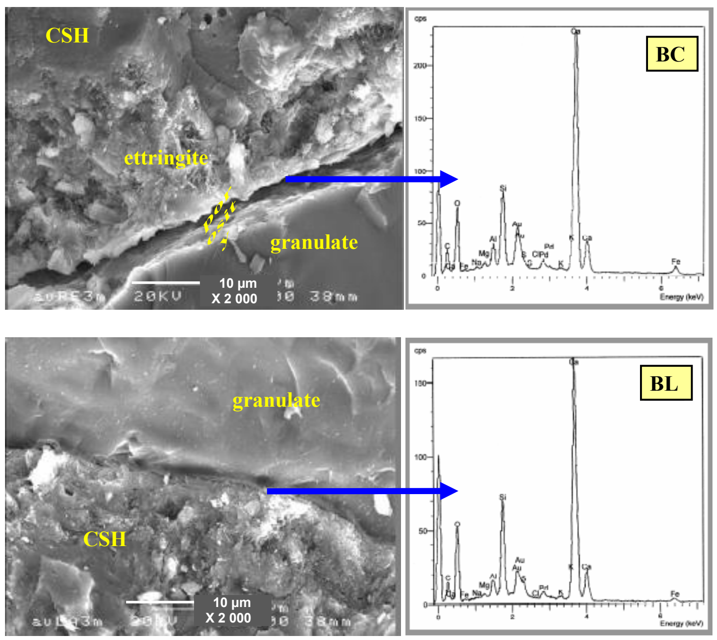

Fig. 10. SEM observation of transition halo of different concretes after 365 days of curing.

5. Conclusion

An experimental program has been undertaken to investigate the performance of concrete containing blast furnace slag as a partial replacement of cement.

The experimental results showed that the use of blast furnace slag in concrete is possible but it requires a high fineness to increase compactness.

The results have shown that:

The microstructure is the key to concrete performance. Its high density ensures a very low porosity as well as a high durability against external aggression.

Blast furnace slag has pozzolanic properties and its small size with large surface area, slag is more efficient. Its particle size varies between 0.3 and 77 µm.

In addition to compactness the hardened cement paste around the aggregates, these ultrafine particles also provide a generally more homogeneous filling of the granular skeleton in the thinnest zone. Compactness increases, improving durability.

The binding properties are highlighted when the slag is quenched and very finely ground, the temperature increases its kinetics. X-ray diffraction and SEM observations with micro analysis show that the products formed are semi-crystalline phases similar to those encountered with cement alone.

It should be specified that concrete with blast furnace slag leads to enhance durability against an externally chemically aggressive environment. This results from reducing porosity and consequently the increase of compactness which reduce permeability.

Blast furnace slag do not only contribute to forming a large volume of new hydrated products, capable of reducing the porosity of the concretes, which improves their mechanical strength, but they also help to restructure the bonds of the cement matrix.

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