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Doping Technique in the Interfacial Transition Zone Between Paste and Lateritic Aggregate for the Production of Structural Concretes

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This paper discusses the use of doping technique in the interfacial transition zone (ITZ) between Portland cement paste and lateritic aggregates with the objective of promoting the implementation of structural concrete. Doping technique consists of establishing the initial impregnation of the aggregate with a high performance paste in order to improve its binding to the matrix. A Scanning Electron Microscope (SEM) equipped with an energy dispersive X-ray (EDX) analysis system is used to observe the results of the technique in the ITZ. The results are observed through an analysis of the cement hydration products formed in the ITZ. An ITZ with high concentration of large crystals of calcium hydroxide (CH) is observed in plain concrete, whereas in concrete prepared with doping technique the ITZ is rich in calcium silicate hydrate (CSH). This result confirms the possibility of using this material, which has no commercial value nowadays, as an alternative aggregate for elaborating structural concrete.

Keywords: *laterite, concrete, interfacial transition zone, doping technique, SEM*

1. Introduction

Surveys conducted since 2002 at the Laboratory for Cement-Based Advanced Materials of São Carlos Engineering School (São Paulo University) indicate that there is great potential in the application of materials doping technique to increase the performance of concrete properties[1-6].

Lateritic concretions are materials found in abundance on the surface of earth, but they have not been used in the production of structural concrete due to deficiencies of the material compared to aggregates currently utilized in the practice of construction. However, the use of crushed materials or those which require long distance transport is increasingly expensive.

Laterites, as presented in Figure 1, occur in the region of the tropics. However, it is clearly observed that they have always existed in regions marked by the motion of tectonic plates[7,8]. Water action on the banks of flooded regions shows soil separation and a good degree of material for immediate use - if granulometrically characterized, as indicated in Figure 2. Nevertheless, this material presents various defects if seen at higher magnification, as shown in Figure 3.

The mixture of this aggregate with conventional mortars results in poor ITZ, marked by voids and large formations of CH. Doping with high performance paste corrects the defective region, enhancing it with the formation of a large amount of additional CSH and building resilience[5,6].

To verify doping technique performance on concrete, an analysis of its effect on the ITZ structure between the aggregate and the cement matrix is presented.

According to Monteiro and Metha[15], prior to conducting any systematic work on the understanding of the cement matrix microstructure in order to increase concrete properties, one should prioritize studies which address the improvement of ITZ between the aggregate and the cement matrix. Such studies are pertinent because various important properties of concrete are significantly influenced by the characteristics of ITZ.

Several studies point to a strong relation between the cement hydration products and the quality of the ITZ. The studies also present some properties of concrete, such as compressive strength, elastic modulus, crack propagation mechanisms and permeability to aggressive agents. These properties justify the importance of the study of aggregate-matrix ITZ[10,11].

Some research results have demonstrated that mineral additions may produce significant changes in ITZ, such as restricting the size of CH crystals, reducing the concentration of the product and increasing the production of the CSH compound. Thinning and densification of ITZ are consequences of mineral additions, contributing to the improvement of properties related to mechanical strength and concrete durability[10-13].

Silica fume is considered an effective mineral addition, reducing aggregate-matrix ITZ thickness and altering hydration products of this region. The results obtained by Monteiro and Mehta[14,15] present ITZ thinning. Its thickness was reduced from 50 µm - in concrete without mineral addition - to values below 10 µm in concrete with silica fume. Furthermore, Larbi and Bijen[16] demonstrated that the CH crystal orientation index decreased, which implies in paste densification in the aggregate-matrix ITZ and CH consumption.

Through scanning electron microscopy, Bentur and Cohen[17] demonstrated changes and improvement in the ITZ

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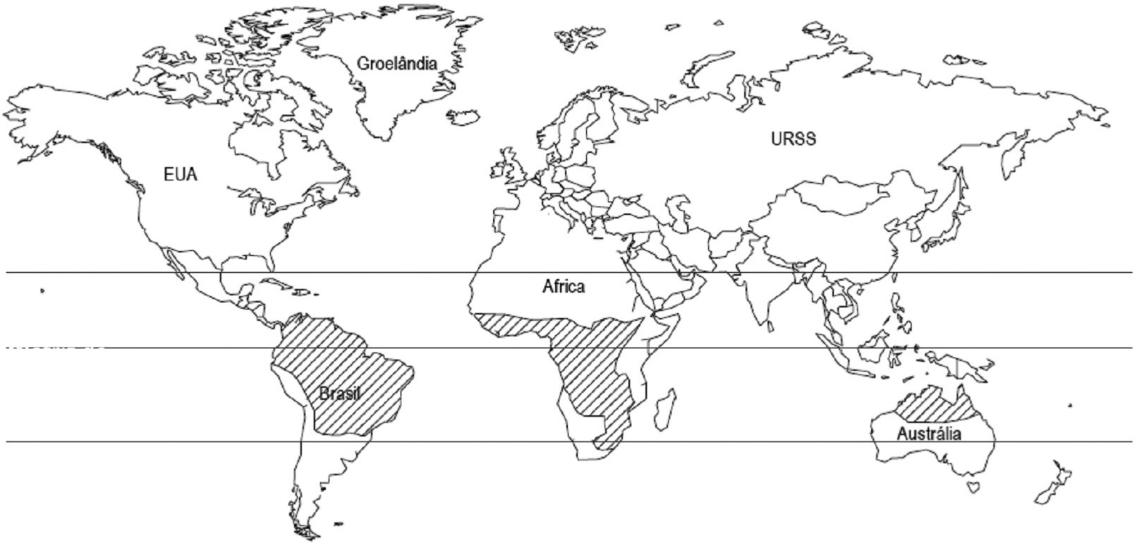

Figure 1. World map of the occurrence regions of lateritic soils[7,8].

Figure 2. Lateritic concretions distribution.

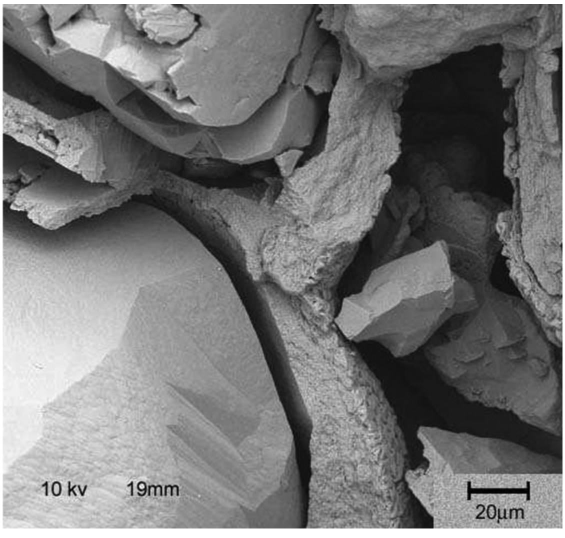

Figure 3. Porous characteristic of laterite seen with SEM[9].

with the use of silica fume between fine aggregate (sand) and paste, as shown in Figure 4.

Chemical additives such as water-reducing superplasticizers can also contribute to the aggregate-matrix ITZ region. By acting directly on the cement particles, additives enable the reduction of the amount of water in the system, maintaining the consistency index and contributing to the decrease of voids[18-20].

The simple treatment of the coarse aggregate used in concrete enables alterations in the aggregate-matrix ITZ. That is because the treatment (doping technique) allows the creation of a high performance layer with mineral addition and low water/binder ratio[7,8].

Although material doping technique is considered simple, it is innovative in the area in which this work is inserted. This technique is of great importance since studies which address doping low quality aggregates in order to improve their performance in structural concrete have not been found[1,2]. Scientifically treated, the technique is emerging and should solve various myths related to the use of other types of aggregates, not listed as suitable for structural concrete[4-6].

It is possible to observe an improvement of the aggregate-matrix ITZ characteristics in concrete treated with doping technique. Such improved characteristics may be described as reduction of both porosity and the amount of CH; and effects attributed mainly to the presence of silica fume in the doping layer. The ITZ between the aggregate and the cement matrix presents large amounts of silica fume as a result of applying the doping technique to the aggregate, which is already available at the start of hydration reactions. Therefore, the reduction of CH may be observed due to the reactions of silica fume to the Ca^{2+} ions released during the process of cement hydration, reducing the amount of Ca^{2+} available for the formation of CH and promoting densification of the region with additional CSH[7,8].

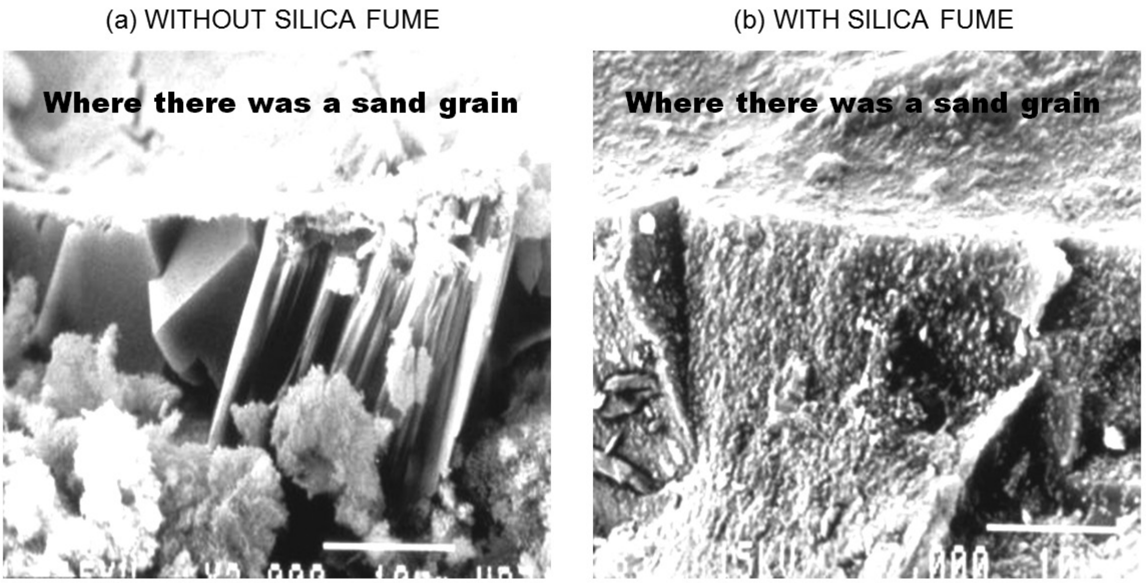

Figure 4. Transition zone micrographs of concrete with and without silica fume[17].

Thus, this paper presents the application of doping technique in the ITZ between the lateritic aggregate and the cement matrix. A quantitative analysis was performed through EDX associated to SEM to analyze the aggregate-matrix ITZ. The study was conducted in the Laboratory for Cement-Based Advanced Materials (LMABC - Advanced Materials Laboratory-Based Cement) based in São Carlos, Brazil.

2. Materials and Experimental Program

In this experiment, a sulphate resistant Portland cement was used for the manufacturing of concrete. Its density and Blaine cement fineness were 2960 kg/m^3 and 4371 cm^2/g, respectively. To prepare the high performance paste used in doping the coarse aggregates, a high resistance Portland cement was used. Its density and Blaine cement fineness were 3120 kg/m^3 and 4743 cm^2/g, respectively. The density, Blaine fineness and SiO_2 ratio of the silica fume used were 2180 kg/m^3, 180000 cm^2/g and 94.3%, respectively. Quartz sand (d_{max} = 2.4 mm) and lateritic concretion (d_{max} = 19.0 mm) were the aggregates used. The density and total solids of the polycarboxylic superplasticizer (SP) were 1.08 g/cm^3 and 31.0%, respectively.

The lateritic aggregates were immersed in paste prepared with 0.35 water/binder ratio (W/AGL), silica fume at a dosage of 10% in volumetric replacement to the cement mass and superplasticizer additive at a dosage of 0.8% of the binder mass.

Four mixtures with 1:5.5 ratio of cement to aggregate were prepared (Table 1). The aggregate fraction for concrete consisted of 42% sand, 58% lateritic aggregate, in weight. The dosage of silica fume was 10% (SA/C) in volumetric replacing to the cement mass. A superplasticizer at a dosage of 2.0% (SP/AGL) of the binder mass was added to the concrete with silica fume.

Table 1. Dosage of concretes.

Type	Doping Technique	W/B	SF/C (%) (per weight)	SP/B (%) (per mass)
1	without	0.57	-	-
2	with	0.57	-	-
3	without	0.40	10	2.0
4	with	0.40	10	2.0

The microstructure of the ITZ was examined with a Scanning Electron Microscope LEO-440 connected to an analysis system with Energy Dispersive X-ray (EDX). Fractured and polished samples were tested. The tested samples of 20 × 20 × 5 mm were cut from 30 × 30 × 100 mm prisms, which were taken from 100 (diameter) × 200 mm cylinders tested with tensile strength by diametral compression. The fractured samples were obtained from the manual fracture of the 30 × 30 × 100 mm prisms. Tests were conducted on samples prepared 28 days before testing. Hydration was interrupted with alcohol. The specimens were carefully vacuum impregnated with a low viscosity epoxy resin and polished with diamond paste.

Backscattered and secondary electron images were obtained from polished and fractured sections, respectively. Quantitative analyses of X-rays were performed at points located in the ITZ. At each point, quantitative analyzes of Na, Mg, Al, Fe, S, Ca, Si, Mn and K (oxygen was stoichiometrically calculated) were made. Three polished and three fractured samples were used for each type of concrete, and the points of the ITZ region of the samples were arbitrarily chosen.

Analyzes of the compositions of the main cement hydration products (CSH, CH, AFm and AFt) were used to compare the characteristics of the ITZ of the concretes. Based on studies of Kjellsen et al.[21], Taylor and Newbury[22] and Wasserman and Bentur[23] the following compositions were assigned to the main hydrated phases:

C-S-H:	$0.8 \leq Ca/Si \leq 2.5$	$(Al + Fe)/Ca \leq 0.2$	
CH:	$Ca/Si \geq 10$	$(Al + Fe)/Ca \leq 0.04$	$S/Ca \leq 0.04$
Afm:	$Ca/Si \geq 4.0$	$(Al + Fe)/Ca > 0.04$	$S/Ca > 0.15$

3. Results and Discussions

Figures 5 to 8 show micrographs of the polished samples for the four types of concrete, obtained with SEM from backscattered electrons. The result of semi-quantitative analyzes through EDS/SEM performed at certain points of the ITZ of the studied concrete are in Table 2.

The values obtained for the ratios (Al + Fe)/Ca and S/Ca indicate that none of the studied concrete presented significant amounts of AFm or Aft due to the fact that elements Al, Fe and S are present in the cement matrix predominantly in phases AFt and AFM. Furthermore, there was no preferential region for forming AFt or Afm as, for example, in the aggregate-matrix ITZ. Thus, the hydration products formed were identified through the behavior analysis of the Ca/Si relation, which presented significant variation, especially in the case of compound CSH.

The variations in the Ca/Si relation are due to the presence of mineral and chemical additions, particularly referring to C-S-H, which is the product this study focuses on. As an example, the C-S-H produced in cement hydration in the presence of blast furnace slag is distinguished by the Ca/Si relation, according to the origin, reducing its relation in the order of Portland cement to the slag for the pozzolan[24].

In concrete treated with aggregate doping - Figures 2 and 4 - it was found that the relation between the elements Ca and Si decreased in regions near the aggregate-matrix ITZ. This fact is attributed primarily to the presence of silica fume in the doping layer. This decrease is consistent with the literature[25-28].

The results indicate that doping technique causes a significant reduction in the porosity of aggregate-matrix ITZ. Furthermore, it decreases the proportion of CH in the region, compared to the corresponding concrete without doping. This can be verified in the reduction of the Ca/Si ratio values in ITZ (Table 2).

Figures 9 to 12 show micrographs of the fractured samples for the four types of concrete obtained with SEM

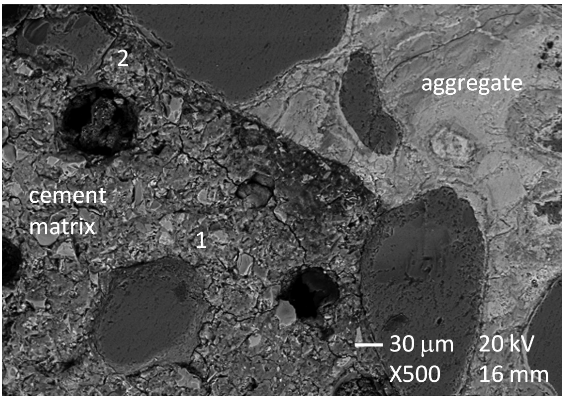

Figure 5. SEM-BSE analyses of concrete 1 (without doping).

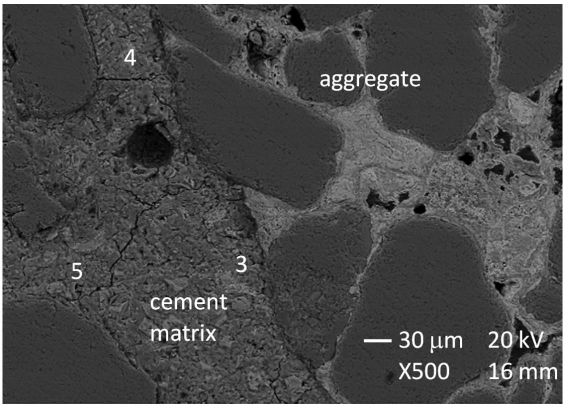

Figure 6. SEM-BSE analyses of concrete 2 (with doping).

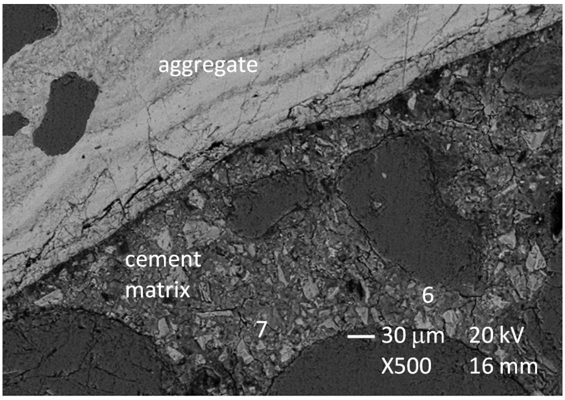

Figure 7. SEM-BSE analyses of concrete 3 (without doping, S/C = 10% and SP/B = 2%).

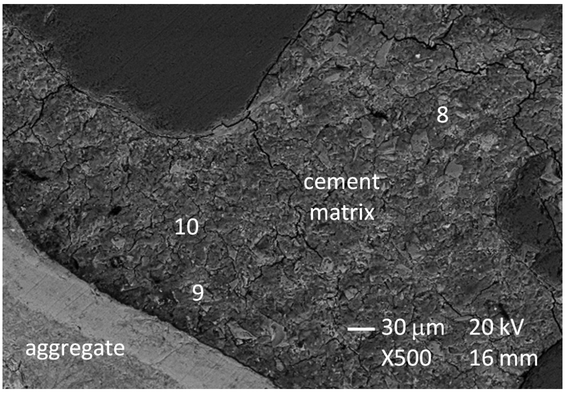

Figure 8. SEM-BSE analyses of concrete 4 (with doping, S/C = 10% and SP/B = 2%).

from secondary electrons, and confirm the results presented earlier.

Concrete 1 (Figure 9) is not doped. Therefore, it presents a large amount of CH which is characterized in geometrically defined piles of plates. The fracture of the sample indicates the weak link, which coincides with the CH plates. However, in doped concrete (Figures 10 and 12) both the quantity and the size of the CH crystals decreased. This factor favors the absence of ITZ and contributes to a stronger aggregate-matrix bond.

The morphology of the C-S-H in doped concrete is different from the morphology in concrete without doping, in the form of short acicular crystals (Figures 10 and 12) and compact fibrous bundles or almost not crystalline fibers (Figures 9 and 11), respectively. The results are attributed to the presence of silica fume in the doping layer.

The alteration in cement hydration products in the ITZ with 10% of silica fume in the doping layer can be explained by the following: i) low permeability of fresh concrete, thus causing less water accumulation on the surface of the aggregate, ii) the presence of multiple nuclei of crystallization, contributing to the formation of smaller CH crystals with lesser tendency in preferential orientations iii) gradual densification in the hydration products through pozzolanic reactions between CH and silica fume.

In Figure 13 the alteration in cement hydration products in the ITZ with 10% of silica fume in the doping layer can be observed through strength tests on specimens subjected to compression strength which has achieved $f_{c,91} = 59$ MPa. This result confirms the possibility of using defective aggregates - which have no commercial value - to produce durable high-strength concrete through doping and the improvement of high performance mortar.

Thus, the treatment of ITZ enables the possibility of using lateritic aggregates in structural concrete. It results in the refinement of porosity in the ITZ cement matrix and modification of cement hydration products, represented by the reduction of both quantity and size of CH plates and the increase of more compact and strong C-S-H. Doped concrete,

Table 2. SEM-BSE analyses of ITZ points.

Concrete	Point	Phase	Ca/Si	(Al+Fe)/Ca	S/Ca
Type 1	1	CH	35.08	-	0.03
	2	C-S-H	1.78	0.15	-
Type 2	3	C-S-H	1.35	0.20	-
	4	CH	13.10	-	0.08
	5	C-S-H	1.80	0.08	-
Type 3	6	CH	25.30	-	0.04
	7	C-S-H	1.53	0.07	-
Type 4	8	C-S-H	2.48	0.04	-
	9	CH	15.84	0.01	0.09
	10	C-S-H	1.63	0.08	-

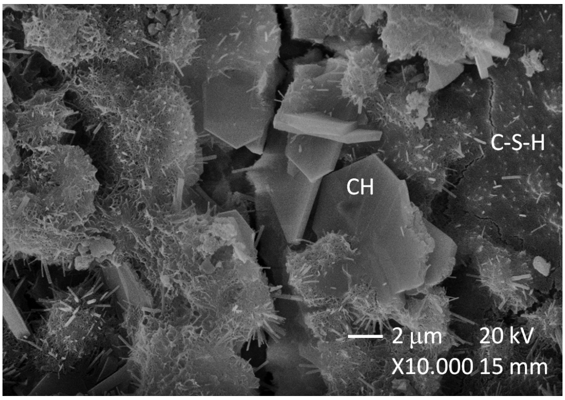

Figure 9. SEM-SE analyses of concrete 1 IZT (without doping).

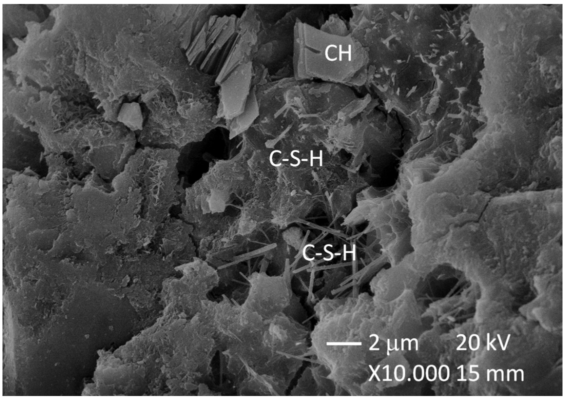

Figure 10. SEM-SE analyses of concrete 2 IZT (with doping).

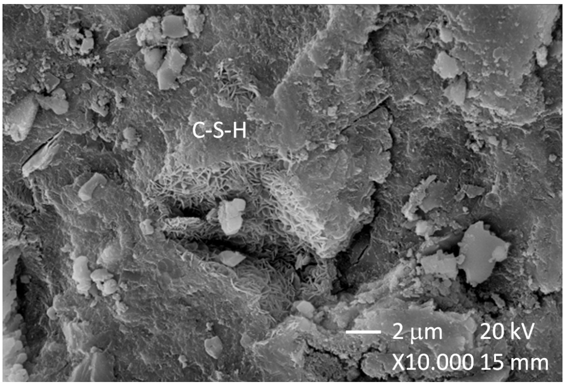

Figure 11. SEM-SE analyses of concrete 3 IZT (without doping, S/C = 10% and SP/B = 2%).

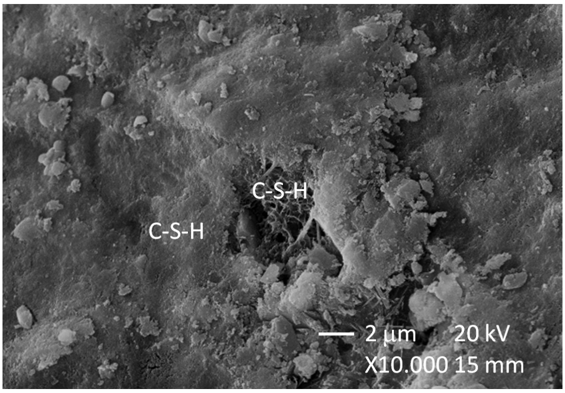

Figure 12. SEM-SE analyses of concrete 4 IZT (with doping, S/C = 10% and SP/B = 2%).

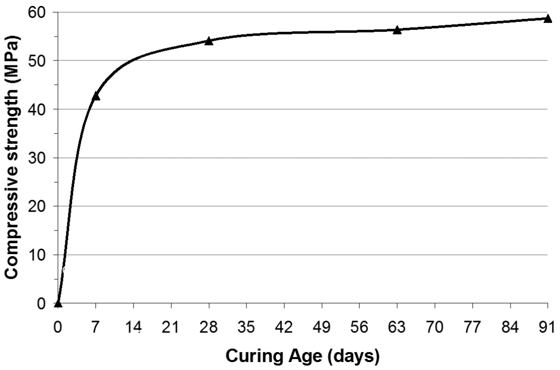

Figure 13. Compressive strength of concrete 4 versus curing age.

at the age of 28 days, exceeded 30 MPa – considered the strength limit for class III aggressiveness according to ABNT NBR 6118:2007. Therefore, most of the current construction works with lateritic concrete, treated as herein, may be perfectly utilized.

The success of this technique leads the way for treating other materials, whether they are construction waste, ceramic plates bonding, or improved pre-molded bonding.

4. Conclusions

In the results obtained from the microstructural analyzes of concrete it was observed that using doping technique for coarse aggregate, through the application of high performance layer containing 10% of silica fume, caused a reduction in the porosity of aggregate-matrix ITZ region, compared to concrete which received no treatment.

In addition to porosity reduction, it was observed that doping technique modified the hydration products in the aggregate-matrix ITZ. The modification is most evident in current concrete, that is, concrete with poorer cement matrix, such as type 1. The modification is simpler in concrete with richer cement matrix, that is, concrete elaborated with silica fume and superplasticizer additive, such as type 3. The matrix of such concrete is already a high performance matrix.

Concrete elaborated with doping technique presents ITZ richer in C-S-H compared to concrete which was not doped. The low water/binder ratio in doping layer and the pozzolanic reaction that occurs between CH and silica fume were the main responsible for the formation of a dense transition zone with small, not targeted crystals of CH.

Acknowledgments

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