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CHEMICAL ANALYSIS OF FINE AGGREGATE FROM RIO DOCE AND ITS INFLUENCE ON THE DURABILITY, STRENGTH AND CARBONATION OF CONCRETE

Claudinei Antonio Montebeller
http://lattes.cnpq.br/2547132665413519

Luan Rangel dos Santos
http://lattes.cnpq.br/6750980013574845

Lucas Soares Milanez
http://lattes.cnpq.br/7615578969927102

Adriana Zamprogno
http://lattes.cnpq.br/1071149366430504

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Abstract: This work aims to evaluate the influence of the fine aggregate extracted from the Rio Doce river in the possible appearance of pathologies of the concrete, since the river has a history of contamination by substances from mining waste. The probability of the emergence of pathologies in the concrete can be high depending on the physical and chemical characteristics of the fine aggregate used, such as the corrosion of the concrete and the reinforcement, putting its durability at risk. As the Rio Doce is the largest granulometric source of civil construction in the city of Colatina, a better analysis of the characteristics of the concrete used in local constructions is essential. For the analysis, three rivers were selected, in addition to Rio Doce, being them the Pancas , the Santa Maria and the Santa Joana rivers, in order to raise comparative and qualitative parameters between them. The concrete samples were submitted to axial compression strength tests, carbonation test and corrosion potential test through electrochemical method, being possible to evidence that, among the mentioned rivers, Rio Doce presented low values of carbonation velocity and results lower in the reinforcement corrosion potential test. The results obtained indicate that there is no influence of the contamination history of Rio Doce with the values presented in the tests.

Keywords: Concrete, carbonation, pathology, Rio Doce, fine aggregate.

INTRODUCTION

After the failure of the dams in the city of Mariana (MG), in 2015, a discussion was reignited regarding the environmental impacts that directly and indirectly affect the population dependent on natural resources from areas contaminated by industrial waste.

Rio Doce was the river most affected by the environmental disaster and, consequently, by the tailings from iron ore processing that were deposited on the banks and in its main channel, along almost its entire length. As the river is the main granulometric source of fine aggregate in the city of Colatina, this work intends to analyze the influence that the granulometric substances of Rio Doce exert on the concrete in terms of carbonation, corrosion and compressive strength, considering its history of contamination.

The low quality of the concrete can cause the appearance of pathologies, generated in the stage of conception, execution and use of the structure. One of the main causes of deterioration of concrete structures are those of natural origin, defined by chemical, physical and biological causes. The chemical combinations that occur in the pores of the material and the internal reactions to the concrete are one of the main reasons for the emergence of pathologies. Considering that the adhesion of concrete is obtained by the chemical reactions resulting from the mix of hydrated cement with the aggregates, it is extremely important to study how such reactions take place, as well as the factors that influence it (SOUZA and RIPPER, 1998).

The results allowed to raise comparative parameters of aggregates and comparative the corrosion potential of common and reinforced concrete made with fine aggregate from Rio Doce. Such conclusions will help in the research of the quality of the concrete produced with aggregates from rivers contaminated with the same substances and the survey of possible future pathological problems of concrete constructions in the city of Colatina (ES).

STRENGTH, CARBONATION AND CORROSION OF CONCRETE

Concrete is one of the most used materials in civil construction today and according to Gentil (2012), in the case of reinforced concrete, the reinforcement is susceptible to corrosion if there is contamination and/or deterioration of the concrete. The presence of impure substances can increase the chances of corrosion of the concrete and the steel inserted in it, through chemical reactions, and consequently cause its deterioration and compromise the durability of buildings. This corrosion is a pathological problem and can be defined, for the most part, as a spontaneous phenomenon of an electrochemical nature.

Considering such pathological problems, carbonation is one of the main and most common pathologies of concrete. It can be defined as a physical-chemical process from the reaction of acid gases, generally present in the environment, with alkaline concrete products, originated from the cement hydration reaction that form products with a precipitation pH lower than 9. The conditions under which the material is and the characteristics of the concrete are the factors that determine the speed of occurrence of the carbonation process (CADORE, 2008).

According to Kulakowski (2002), hydrogen sulphide (H2S), sulfur dioxide (SO2) and carbon dioxide (CO2) are the main acid gases that induce concrete to undergo carbonation. In this process, the alkaline compounds of the hydrated cement paste, such as potassium hydroxide (KOH) and calcium hydroxide (Ca(OH)2), are consumed in the reactions, and the ratio between carbon dioxide and calcium hydroxide is main carbonation reaction as shown below.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

In the process of making concrete, chemical reactions occur that generate excess calcium, which is released in the form of hydroxide (Ca(OH)2). After hardening, the material becomes alkaline inside the concrete, with a pH above 12.5. Carbon dioxide (CO2), from atmospheric air, can enter the concrete by diffusion and reach the moist pores that contain dissolved hydroxide, thus initiating a series of reactions that will transform the hydroxide into carbonate, decreasing the internal pH. If the pH reaches values below 9, the material is susceptible to dissolution of the iron oxide passivating film of the steel bars coating present inside the concrete, in the case of reinforced concrete (FUSCO, 2012). Thus, it leads to the anodyne reaction that leads to the solubilization of iron, represented below.

$$Fe \rightarrow Fe^{++} + 2e^-$$

To verify the carbonation, it is possible to detect the presence of free chlorides on the surface of the concrete or mortar through calorimetric tests. This qualitative method is carried out through the incidence of a solution containing chemical indicators, such as phenolphthalein and silver nitrate, applied on the surface of the cross-section area of the interior of the concrete. Such solutions, in the presence of free chlorides, change color through a photochemical reaction catalyzed by light (BOTELHO and SILVA, 2008).

According to Cadore (2008) the proportions used to prepare the phenolphthalein-based solution are: 30g of absolute ethyl alcohol; 70g of distilled water; 1 gram of phenolphthalein powder. When applied to the surface of the concrete, this substance remains colorless in acidic solutions, with a pH lower than 8.3, and becomes “magenta” when in contact with basic solutions, with a pH higher than 9.5, when the pH meets if between 8 and 9.5 the resulting color varies between pink and red. Thus, it is possible to measure the area with low pH, which indicates a probable carbonated region and more susceptible to chemical and electrochemical pathologies.

According to Vaghetti (2005), the depth of this corrosion may vary according to the concrete properties, such as porosity index, water/cement ratio used, characteristics of the curing environment, CO2 concentration, temperature, etc. The classical equation model for estimating the rate of carbonation comes from the integration of Fick's Law, resulting in the equation (1) (TASCA, 2012):

$$X_c = K_c \sqrt{}_t \qquad (1)$$

Which:
- Xc: depth of carbonation in mm;
- Kc: Kc: carbonation coefficient in mm /; √ year
- t: time of exposure to CO2 since molding, in years.

The value of Kc represents the speed at which the concrete, under specific conditions, undergoes carbonation from the environment in which it is inserted. Regarding the age at which the test was performed, according to Pauletti (2004), there are several studies, at the national level, that used natural and accelerated tests to verify carbonation, having the most varied types of curing and exposure of the test samples.

In relation to reinforced concrete, the corrosion process modifies the structure of metallic materials, altering the formation of electrically charged particles in the presence of a conductive electrolyte. In this way, an electrochemical corrosion cell can be formed, where there is the presence of an anode, a cathode, a difference in potential, a metallic bond between the anode and the cathode, and an external bond characterized by ionic conduction through the electrolyte. The anode is characterized by the passage of the material from the metallic state to the ionic state (oxidation) and the cathode by the consumption of electrons generated in the anodic region (reduction), being the anode with a more electronegative potential in the potential difference between both (GENTIL, 2012).

According to the American standard ASTM C876 (2009) it is possible to measure the electrical potential difference through the test method for corrosion potentials of uncoated reinforcing steel in concrete. The test consists of the use of a reference electrode, an electrical junction device, an electrical contact solution, a high impedance voltmeter and electrical wires. The standard indicates that the silver/silver chloride (Ag/AgCl) electrode can be used to perform the test and in this case the probability of corrosion is less than 10% when the measured value is greater than -119 (mV), uncertain when the value is between -119 (mV) and -269 (mV), and 90% probability when the measured value is greater than -269 (mV).

Nevertheless, in order to obtain more accurate results in a short period of time, it's necessary to accelerate the corrosion process, since this pathology occurs relatively slowly. The method consists of submitting the specimens to cycles of wetting in a solution with 3.5% NaCl and drying in a controlled laboratory environment, thus inducing the acceleration of corrosion by chloride ions, with the corrosion potential being measured after each half cycle. This is a procedure widely used in the academic environment when it is intended to obtain values of the corrosion potential in reinforced concrete (CABRAL, 2000; CASCUDO and HELENE, 2001; DOTTO, 2006; SILVA, 2010).

In addition to corrosion and carbonation tests, a method widely used for the quality control of concrete is the axial compression test, which consists of the use of standardized cylindrical specimens in laboratory tests. NBR 5738 (2016) and NBR 5739 (2007) establish all the necessary procedures for the preparation of concrete specimens and requirements necessary to perform the axial compression test. The presentation of the results must have information such as the identification and age of the specimen and the compressive strength expressed to the nearest 0.1 MPa.

MATERIALS AND METHODS

Five sediment samples were collected, two from Rio Doce, collected at different points, a sample from the Pancas River, one from Santa Maria and one from Santa Joana. The collection sites were chosen emphasizing points where there is legal extraction of fine aggregate for civil construction. Taking into account that three rivers (Pancas, Santa Maria and Santa Joana) chosen for the test are tributaries of Rio Doce, an extra sample of aggregate was collected from Rio Doce at a strategic point in the river bed that has no contact with the rivers. effluents from other rivers.

For the preparation of the specimens, complementary tests were carried out to characterize the aggregates to be used and for the preparation of the trace, according to the ABCP method. For standardization, high initial strength cement (ARI) CP-V was used, setting the slump at 80-100mm and the same type of coarse aggregate for all specimens, thus altering only the fine aggregate. All samples were cured for 28 days submerged in water in a curing tank. Table 1 specifies the number of specimens used for each test performed.

In making the specimens for the phenolphthalein carbonation test, wooden molds were used, fixed with threaded screws to assist in demolding. The test was performed 91 days after the preparation of the specimens, based on the methodology used by Cadore (2008), characterized by the application of a solution containing phenolphthalein on the perpendicular surface inside the ruptured test sample.

In the manufacture of the cylindrical specimens, for the axial compression test, steel forms were used, and the concrete was manually densified according to the procedures specified in NBR 5738 (2016). The concrete compression test was carried out in standard laboratory equipment, EMIC, 28 days after the preparation of the specimens, according to the specifications of NBR 5739 (2007).

For the preparation of the samples for the corrosion potential test by electrochemical technique, a wooden mold was used, fixed by means of threaded screws to facilitate the demolding and CA-50 bars obtained by hot rolling corrugated, with 10 mm in diameter. nominal and 100mm length. Four bars were placed in each specimen so that 20 mm of them were exposed. The bars were cleaned through an abrasion process using a sponge, steel brush and sandpaper in order to remove the iron oxide layer (rust) from the bars

Test type	Dimension	Test Sample Amount					Total
	Of test sample	Rio Doce A1	Rio Doce A2	Pancas	Santa Maria	Santa Joana	
corrosion potential	(15x15x15)	1	1	1	1	1	5
carbonation	(10x15x30)	1	1	1	1	1	5
compressive strength	(10x20)	2	2	2	2	2	10

Table 1 - Specification of the types of tests performed, dimensions and quantity of specimens made for each test.

Source: prepared by the author (2017).

(BOTELHO E SILVA, 2008).

The concrete covers of the steel bars in the samples followed the recommendations prescribed in table 7.2 of NBR 6118 (2014), where minimum covers are specified for various aggressive classes. Thus, 30mm of covering was used on the sides of the specimens and the lower covering of the specimen is 70mm thick, based on the methodology used by Silva (2010).

At the upper end of the bars, in the exposed part, flexible wires were connected to provide the electrical connection during the test. Insulating tape was used to protect the connection between the flexible wires and the bars, and epoxy resin was applied over the tape. The upper and lower faces of the specimens were also waterproofed with epoxy resin, preventing the entry of aggressive agents and inducing the corrosive process on the side of the specimen (DOTTO, 2006; SILVA, 2010). Stickers were placed on the bars of each specimen to facilitate the measurement, using the colors blue, yellow, green and red (Figure 1).

After curing, the cubic specimens were induced to corrosion through wetting cycles by partial immersion in a 3.5% NaCl solution for 2 days and drying cycles characterized by storage in an oven at 50ºC for 5 days, with the potentials measured after each half-cycle (SILVA, 2010; PEREIRA, 2012). Measurements were performed on all bars on only two sides of the specimen with the aid of distilled water, a sponge, a silver/silver chloride electrode and a multimeter. Soon after, the arithmetic mean of the potential values of each sample was obtained, in order to perform a global analysis by sample and not by bars. Due to a failure with the silver/silver chloride electrode, it was not possible to carry out the measurements in the first cycles, with the measurement started in the eighth cycle and ended 70 days after the beginning of the corrosion induction test.

Regarding the properties of the fine aggregate, there is a lack of materials and research in the academic environment on chemical analysis of sediments for making concrete, with only physical analysis being

Figure 1 – Waterproofing with epoxy resin in cubic specimens and measurement of corrosive potential test, respectively. Source: author’s collection (2017).

commonly adopted. In view of this, it was decided to carry out chemical analysis of the substances present in the sediments of the samples, in order to raise quantitative parameters for comparison between the samples of each river, in order to establish relationships of the influence of chemical elements in the pathological reactions that may happen on concrete.

RESULTS AND DISCUSSION

Figure 2 shows the images of the five specimens that were ruptured and submitted to the carbonation test, where five depth measurements were taken with a digital caliper on the surface of each specimen.

Through the carbonation depth data, it was possible to calculate the Kc coefficient, which represents the carbonation velocity of the studied concretes. The values of the carbonation depths, together with the respective Kc coefficients and the values of average concrete compressive strength, in MPa, are shown in Table 2.

The samples from the Rio Doce (A1) and Santa Maria show the highest average values of concrete compressive strength (MPa), while the samples from the Pancas and Santa Joana rivers show the lowest values. Samples from the Santa Joana and Pancas rivers showed higher values of carbonation depth, while Rio Doce (A2) and Santa Maria

Figure 2 - Photograph of the carbonation test of samples from Rio Doce (A1), Rio Doce (A2), Pancas, Santa Maria and Santa Joana, from left to right, respectively. Source: Author's collection (2017).

Sample	Axial Compression (Mpa)	Carbonation Test	
		Measured values (cm)	Kc coefficient
Rio Doce A1	42,55	0,486	0,973
Rio Doce A2	33,48	0,380	0,761
Pancas	31,24	0,554	1,110
Santa Maria	34,82	0,440	0,881
Santa Joana	32,62	0,760	1,522

Table 2 - Specification of the types of tests performed, dimensions and quantity of samples made for each test.

Source: prepared by the author (2017).

showed the lowest values.

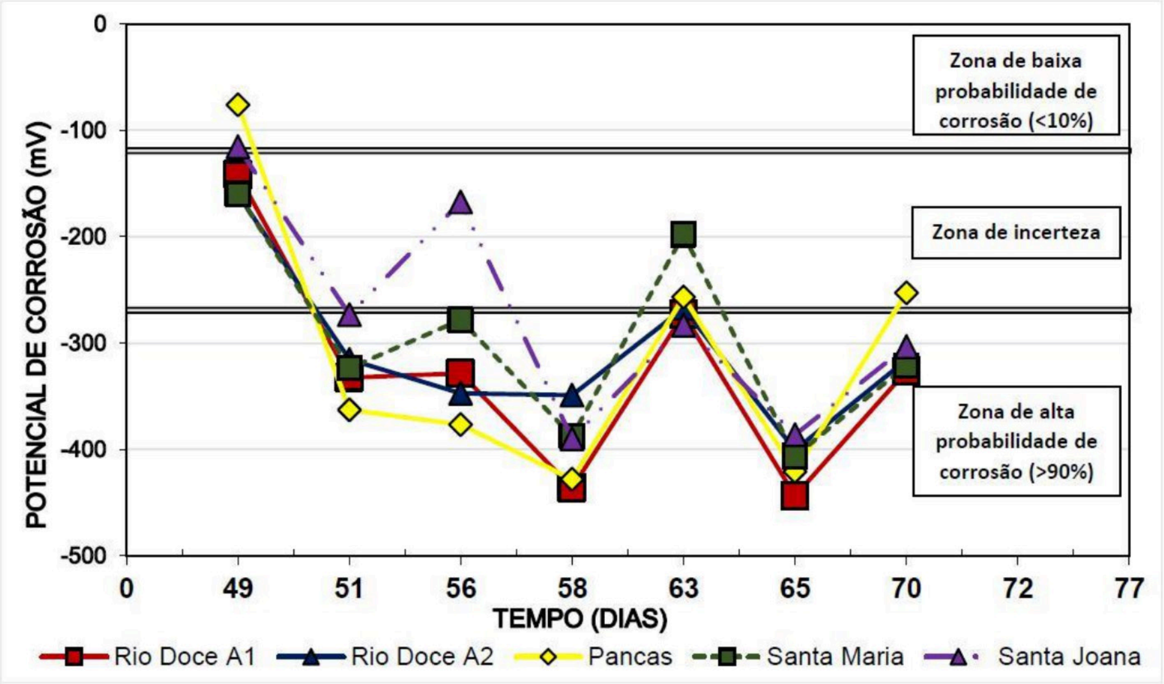
As for the corrosion potential test, it is noted that the Pancas and Rio Doce samples (A1) presented the most negative values located in the zone of high corrosion probability (>90%). The samples from the Santa Maria and Santa Joana rivers exhibited the most positive and most patterned values regarding the discontinuity caused by the wetting and drying cycles (Graph 1).

For the chemical analysis, priority was given to the general parameters of sediment analysis available on the market, in order to raise a quantitative form of comparison between the samples. The results of the analyzes are presented in Table 3.

The determining factors to start the process of carbonation of the concrete or corrosion of the reinforcement are related to the exposure conditions in which it is inserted and the characteristics of the material. As all specimens were subjected to the same environmental conditions for the same amount of time, it can be said that the measured values relate only to the characteristics of the material studied.

When analyzing Table 3, it is noted that the samples that presented the lowest average values of compressive strength (Pancas and Santa Joana) had the highest carbonation rates. However, only through statistical analysis will you, in fact, have the proof of these results. Thus, Pearson's correlation test was applied between the mean values of the tests performed, as shown in table 4.

When analyzing Table 4, it is noted that the test showed a moderate correlation between corrosion potential and compressive strength, with the value having a negative effect. Thus, the greater the compressive strength, the greater the corrosion potential of the material (more negative values), which



Graph 1 – Mean values of corrosion potentials according to the number of days after the beginning of the corrosion induction cycles of the different samples. Source: prepared by the author (2017).

PARAMETER	**UNITY**	**RIO DOCE A1**	**RIO DOCE A2**	**PANCAS**	**SANTA JOANA**	**SANTA MARIA**
TOTAL SULFATE	*L.Q.: 20,0 mg/Kg (SO4)*	93,0	35,0	66,0	55,0	72,0
PHOSPHORUS (P) - MEHLICH-1	*L.Q.: - mg/DM3*	6,0	6,0	10,0	5,0	4,0
SODIUM SATURATION (NA)	*L.Q.: - %*	1,0	1,6	0,6	1,3	1,0
BASE SATURATION	*L.Q.: - %*	58.5	39,6	21,1	40,4	45,7
SATURATION BY AL (M)	*L.Q.: - %*	0,0	0,0	48,0	0,0	0,0
CTC (EFFECTIVE)	L.Q.: - cmolc/dm3	1,3	0,7	1,3	0,5	0,8
SUM OF BASES	*L.Q.: - cmolc/dm3*	1,3	0,7	0,7	0,5	0,8
TOTAL ORGANIC MATTER	*L.Q.: - dag/dm3*	0,80	0,40	0,70	0,30	0,40
PH IN WATER	*L.Q.: -*	7,3	6,7	4,9	7,1	5,9
MANGANESE (MN) - MEHLICH-1	*L.Q.: - mg/dm3*	34,0	38,0	18,0	29,0	20,0
COPPER (CU) - MEHLICH-1	*L.Q.: - mg/dm3*	0,2	0,3	0,2	0,1	0,5
ZINC (ZN) - MEHLICH-1	*L.Q.: - mg/dm3*	2,2	1,4	2,5	0,6	0,9
H+AL	*L.Q.: - cmolc/dm3*	0,9	1,0	2,5	0,8	1,0
ALUMINUM (AL)	*L.Q.: - cmolc/dm3*	0,0	0,0	0,6	0,0	0,0
MAGNESIUM (MG)	*L.Q.: - cmolc/dm3*	0,1	0,1	0,1	0,1	0,2
CALCIUM (CA)	*L.Q.: - cmolc/dm3*	1,1	0,5	0,5	0,4	0,6
SODIUM (NA) - MEHLICH-1	*L.Q.: - mg/dm3*	5,0	6,0	5,0	4,0	4,0
IRON (FE) - MEHLICH-1	*L.Q.: - mg/dm3*	117,0	128,0	132,0	144,0	139,0
POTASSIUM (K) - MEHLICH-1	*L.Q.: - mg/dm3*	18,0	12,0	18,0	10,0	10,0
MAGNESIUM/POTASSIUM RATIO (MG/K)	*L.Q.: -*	2,2	3,3	2,2	3,9	7,8
CALCIUM/POTASSIUM RATIO (CA/K)	*L.Q.: -*	23,8	16,3	10,8	15,6	23,4
CALCIUM/MAGNESIUM RATIO (CA/MG)	*L.Q.: -*	11,0	5,0	5,0	4,0	3,0
BORON (B)	*L.Q.: - mg/dm3*	0,57	0,39	0,61	0,39	0,33
SULFUR (S)	*L.Q.: - mg/dm3*	19,0	18,0	16,0	16,0	19,0
CTC (PH7)	*L.Q.: - cmolc/dm3*	2,2	1,7	3,2	1,3	1,8
POTASSIUM SATURATION (K)	L.Q.: - %	2,2	1,9	1,5	1,9	1,4
MAGNESIUM SATURATION (MG)	*L.Q.: - %*	4,7	6,1	3,2	7,5	11,0
CALCIUM SATURATION (CA)	*L.Q.: - %*	51,3	30,7	15,9	30,2	32,9
TOTAL ACIDITY	*L.Q.: 25 mg/Kg*	<25	<25	97,50	<25	<25
CALCIUM CARBONATE CONTENT	*L.Q.: 6.000 mg/kg*	<6000	<6000	<6000	<6000	<6000

Table 3 – Analytical report of the chemical analysis performed on the sediments from each sample collected.

Source: prepared by the author (2017).

		Compressive Strength	Speed of Carbonation	Potential of Corrosion
Compressive Strength	**Pearson's Correlation**	1	-0,584	-0,603
	Sig. (2 extremidades)		0,301	0,282
	N	5	5	5
Speed of carbonation	**Pearson's Correlation**	-0,584	1	0,627
	Sig. (2 extremidades)	0,301		0,258
	N	5	5	5
Potential of Corrosion	**Pearson's Correlation**	-0,603	0,627	1
	Sig. (2 extremidades)	0,282	0,258	
	N	5	5	5

Table 4 - Results of Pearson's correlation test according to the tests performed.

Source: prepared by the author (2017).

goes against the literature because materials that tend to have better compressive strength have characteristics such as a good water/cement factor. and lower porosity indices, variables that influence concrete corrosion. Such characteristics are also opposed in the correlation between corrosion potential and carbonation velocity, that is, the lower the corrosion potential (more positive values), the greater the carbonation velocity.

However, when analyzing the p-values obtained through the Pearson's Correlation test, one cannot, statistically, say that this result applies in its entirety, that is, in a population. Thus, among the variables studied, the test showed that there is no correlation between them, which shows that the results presented in table 4 cannot be statistically generalized.

Considering the results of corrosion potential, graph 1, the analysis of variance (ANOVA) was performed to verify if there is a statistically significant difference between the samples in relation to the measured values of the corrosion potential. Thus, according to table 5, through analysis of variance per sample and considering that the data have a characteristic of normal distribution, it appears that at the 95% confidence level there is no statistically significant difference between the sediment samples against the measured values of corrosion potential of steel bars.

In addition to the analysis by specimen, there was an analysis of the correlation between the history of the rivers and the values of the tests carried out by the Pearson method. Considering that the samples Rio Doce (A1) and Rio Doce (A2) were collected in a river where it has a history of contamination by mining tailings and the samples Pancas, Santa Maria and Santa Joana do not show a history of contamination, it was verified the relationship between test results and river history, as shown in Table 6.

When analyzing the data presented in table 6, it appears that there is a moderate correlation between the history of river contamination and the values measured in the tests performed. However, the calculated p-values gave results lower than 5%, that is, it appears that the measure of the degree of association between the river contamination history with the measured results of compressive strength, carbonation velocity and corrosion potential inside the concrete are not generally applicable.

ANOVA VARIANCE ANALYSIS RESULTS							
Sample	*source of variation*	*SQ*	*gl*	*MQ*	*F*	*value-p*	*F critic*
Rio Doce (A1)	Between groups	5359,02	3	1786,34	0,139613	0,935301	3,008787
	Within the groups	307078,9	24	12794,96			
	Total	312438	27				
Rio Doce (A2)	Between groups	75840,54	3	25280,18	2,136965	0,12197	3,008787
	Within the groups	283918,6	24	11829,94			
	Total	359759,2	27				
Pancas	Between groups	9175,42	3	3058,47	0,182431	0,907281	3,008787
	Within the groups	402361,6	24	16765,07			
	Total	411537	27				
Santa Maria	Between groups	16657,51	3	5552,50	0,447866	0,721079	3,008787
	Within the groups	297544,6	24	12397,69			
	Between groups	314202,1	27				
Santa Joana	Between groups	21397,9	3	7132,63	0,558675	0,647415	3,008787
	Within the groups	306409,4	24	12767,06			
	Between groups	327807,3	27				

Table 5 - Analysis of variance data (ANOVA) according to the studied samples.

Source: prepared by the autho2017).

		Historic from The source	**Compressive Strenght**	**Speed of carbonatation**	**Potential of Corrosion**
Historic from the source	Pearson's Correlation	1	0,631	-0,653	-0,660
	Sig. (2 extremidades)		0,254	0,232	0,225
	N	5	5	5	5

Table 6 - Results of the Pearson's Correlation test according to the tests performed and the history of river contamination.

Source: prepared by the author (2017).

CONCLUSION

When considering all the tests carried out and the conditions used to verify the influence of the fine aggregate from Rio Doce in possible cases of concrete pathologies, it can be concluded that there is no statistically proven relationship between the carbonation speed of concrete, its resistance and the potential for corrosion of the bar inside it.

The history of the Rio Doce river, contaminated by mining tailings, is not associated with the speed of carbonation of the concrete, as well as the resistance to compression and the corrosion potential of the steel of the concrete, when they are used as a granulometric source of fine aggregate. In this way, the influence of the contamination of Rio Doce on the results of carbonation, corrosion of the bars and resistance of concrete to compression are negligible.

Regarding the chemical analysis of the sediments, it was possible to verify that the samples collected have similar values of the substances analyzed, showing that, chemically, there is not a relevant difference in the composition of the aggregates collected. And due to the scarcity of more comprehensive sediment chemical analyzes and academic references, it is not possible to make definitive conclusions about the influence of such substances on the appearance of concrete pathologies.

Based on the study carried out, it can be presented as a suggestion for future research, to carry out more detailed and comprehensive chemical analyzes of the fine aggregate from Rio Doce to verify punctually the substances

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