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Environmental Performance of Zn-Contaminated Mortars Using Electrical Measurements –EIS.

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ABSTRACT

The utilization of industrial wastes in the construction materials have been studied and also the environmental evaluation of this incorporation. The costs of the new materials may be reduced with the wastes incorporation and the environmental impacts. However, the wastes contamination requires some precaution measures after incorporation, avoiding a new contamination. Through of the leaching tests, the leaching potential is evaluated, the final leaching concentration and the diffusivity of the contaminants. The electrochemical impedance spectroscopy evaluate the microstructure changes on the presence of heavy metals and can be explained the leaching process. This technique is sensible to microstructure changes of the cementitious materials. The results of the measures of electrical impedance are characteristics spectrums. Using these spectrums was possible to determinate the diffusivity of the zinc in the cement mortars. The mortars were produced with Portland cement (CPV- ARI), ratio w/c of 0.50 and the samples were contaminated with 50, 100 and 200 ppm of nitrate of zinc in relation to quantity of cement added in the cementitious matrices. The mortars were submitted to leaching tests (tank test) and during the renewal of the liquid, the electrical measures also was realized in the mortars. The spectrums of the contaminated mortars showed different crystalline phases and the diffusivities determined by electrical test were higher than the diffusivities of the leaching tests. The zinc showed a greater toxicity potential by electrical test.

INTRODUCTION

The electrical tests using Electrical Impedance Spectroscopy (EIS) are important in the evaluation of the microstructural changes in cementitious materials. The results of electrical tests, it is possible to analyze the resistive and capacitive parcels and their interpretation shows that the electrical measurements are sensible in relation to physical and chemical proprieties of the cementitious materials. Leaching tests are used as tools to estimate the potential release of constituents from waste materials with environmental perspective and for quality control purposes (KOSSON et al 2002). In present research an experimental approach is proposed for evaluation of waste leaching potential. For this purpose, mortars were contaminated with heavy metal zinc (0.50, 100 and 200 ppm) and EIS measurements were carried out on mortars during hydration and after leaching test. This contamination refers to mortars produced with wastes containing high concentration of the zinc.

The leaching test were realized with monolithic materials and has been used to evaluate the traces elements mobility from wastes materials, providing whether a heavy metal has been encapsulated in the cementitious materials. The diffusion is the main ionic transport that occurs during the leaching test. The concentration gradient between external environment and porous solution induce diffusion of main ionic species (alkalis, calcium, hydroxides) from the porous solution to the external environment (LARRARD et al., 2010).

In the cement paste, the diffusion occurs between these phases: porous, C-S-H and others solid phases (anhydrous cement grains). In the mortars, the solid phase consists of aggregates and interstitial zone aggregate-paste (KAMALI-BERNARD et al., 2009).

The determination of diffusion using the electrical impedance spectroscopy it is possible (SHI et al., 1999). The authors showed the correlation between the diffusion process and the electrical measurements through the Warburg coefficient (W). In the results spectrums of electrical measurements, the Warburg coefficient can be obtained from the intersection of the straight line on the real axis (figure 1).

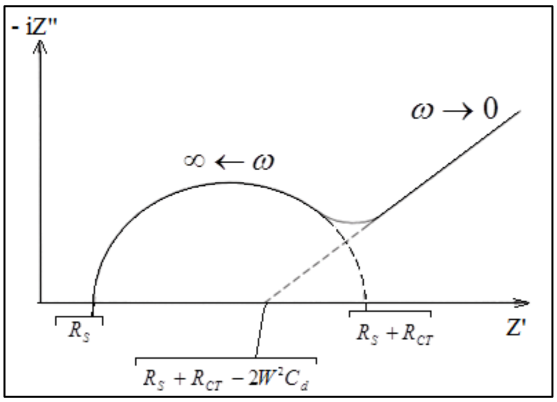

Figure 1. Warburg Coefficient (from: SHI et al., 1999).

The Warburg coefficient has been utilized in this research for the correlation between the leaching and electrical tests of the contaminated mortars.

EXPERIMENTAL INVESTIGATION

Materials. The cement mortars were prepared with a water/cement ratio of w/c= 0.50 and cement to sand ratio of 1:2 (by weight). The cement CPV is high strength cement and it was used to avoid a contamination from supplementary wastes materials. The heavy metals were added in the mortars through of nitrate (Zn $(NO_3)2.6H_2O$). The contamination concentrations were 50, 100 and 200 ppm of heavy metal by the weight of Portland cement.

Methods. The tank leaching test is usual static procedure used in the monolithic samples. According to standard NEN 7375, after of the first contact of the sample with the water, it were carried out eight extractions of the liquid and it your renewing at time periods established. For these investigations the test was adapted for 6h and 1, 4, 7, 16 and 28 days (six steps). The tests started at an age of 28 days, at temperature between 18-22°C and solid/liquid ratio of 10. At each step the pH, conductivity and concentration of leaching liquid (eluates) were immediately measured. The intervals of the time are increasing and the renewing of the liquid ensures a gradient of ionic concentration between the solid matrix and the leaching liquid, in order to be insured the diffusion of the ions. The eluates were filtered over a 0.45 µm filter before the chemical analysis and the concentrations of Calcium and Zn were determined by EDX- 900, using FP analysis.

The Electrical Impedance Spectroscopy (EIS) measures were carried out on mortars contaminated or not (reference sample, designate by REF). The electrical measurements were made during the six steps of renewing of the liquid, on leaching test. The electrical impedance is expressed in ohms [Ω] and represented by the symbol "Z". The electrical impedance indicates the total imposition that electrical circuit offers to flows of the AC in the time. Mathematically, the determination of the electrical impedance is presented in the Eq. 1.

$$Z = \frac{V}{I} \tag{1}$$

The resultant graphic of spectrum of electrical impedance are arcs, the Nyquist's diagram, resultant of the complex plain (real and imaginary). *Z'* is the real plain of impedance (electrical resistance, *R*), and *Z''* is the imaginary plain of impedance (electrical reactance, *X*) (Eq. 2 and Eq. 3).

$$R = |Z| \times \cos\theta \tag{2}$$

$$X = |Z| \times sen\theta \tag{3}$$

$$X = \frac{1}{2\pi f C} \tag{4}$$

The electrical capacitance (C, [F/m]) is determined by electrical reactance (Eq. 4) and the frequency band [Hz] of the electrical measurements. The frequency band utilized in this work was of 10 kHz to up to 40 MHz and the tension used was 10 V. The AC was generating in the tension generator and the sinusoidal signals of the electrical current and of the electrical tension were verified in the digital oscilloscope. All the instruments utilized are of model Tektronik®: TDS 3014C, AFG 3102 e P6022. With the time and the angle formed between the two sinusoidal, obtained through oscilloscope, it was possible calculate the resistive and capacitive portion of electrical impedance. When the electrical reactance is zero and the value of the electrical resistance is maximal, this electrical resistance is named "bulk resistance" that refers to total electrical resistance of the mortars.

RESULTS AND DISCUSSIONS

Leaching Test. In the figure 2 and figure 3 are showed the quantity leached of Zinc and Calcium, respectively, that were measured in the eluates of the leaching tests. In the figure 2 also is showed the total quantity of zinc leached in the end of leaching test. Figure 4 and 5 show the pH and conductivity that were measured at the same eluates, collected after each steps.

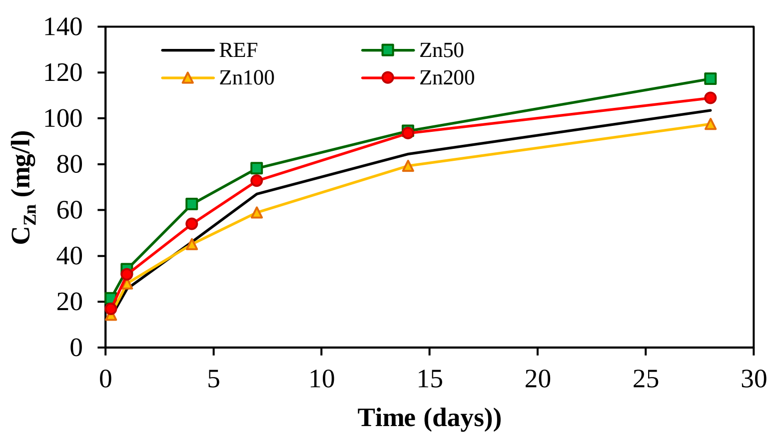

Figure 2. Zinc leached from mortars during the leaching test.

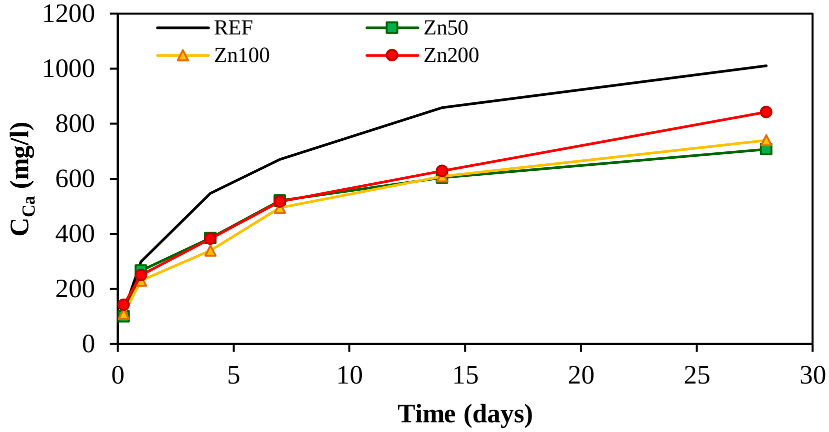

Figure 3. Calcium leached from mortars during the leaching test.

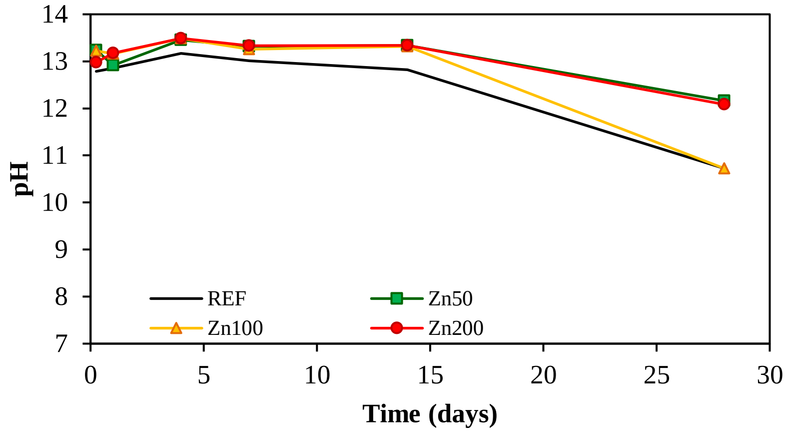

Figure 4. pH of the leached liquid during the six steps of renewing of the liquid of the tanks.

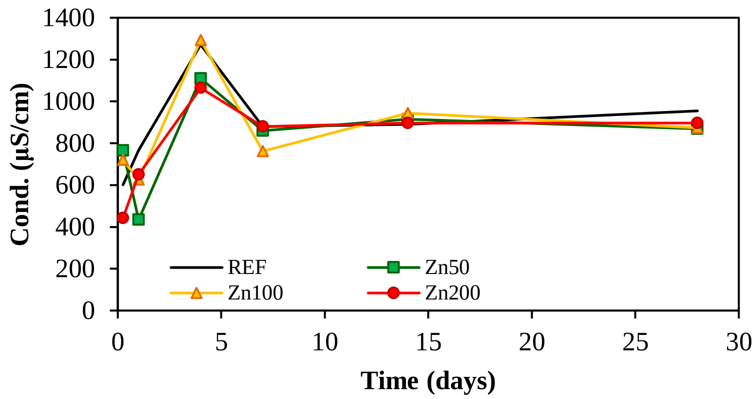

Figure 5. Conductivity of the leaching liquid on the six steps of renewing of the liquid of the tanks.

The presence of Zinc in REF is due a trace elements present in cement Portland. Mortar with 200 ppm of zinc contamination has not shown a higher leached zinc concentration. There is not a significate difference between the leached zinc concentration and the zinc contamination degree of the mortars. During leaching test the zinc leached from mortars are close to the reference mortar, even contamination with 200 ppm of zinc contamination. In this sense, occurred the stabilization of the heavy metals in the mortars.

During the leaching test it was observed that calcium liberation and its release decreased in the presence of the zinc. The zinc contamination reduced the calcium solubility. This fact can reflect to a possible chemical reaction of the zinc with the calcium. The release decreased of calcium in the mortar with more contamination of zinc resulted in the lower pH values in the end of leaching test (Zn 200, figure 4). The presence of the portlandite in the extraction solution results in high pH values.

The electrical conductivity showed a maximum value at the third extraction, when a highest liberation of the chemical elements was observed. After third extractions, the elements release decrease. Chemical elements releasing are responsible for the electrical conductivity of the solution. If the elements concentration in the solution decreases, the electrical conductivity also decreases.

Evaluation of diffusion process (leaching test x electrical impedance spectroscopy). The electrical behavior of the contaminated ortars, during the first and last extraction are showed in the figure 6 to figure 8.

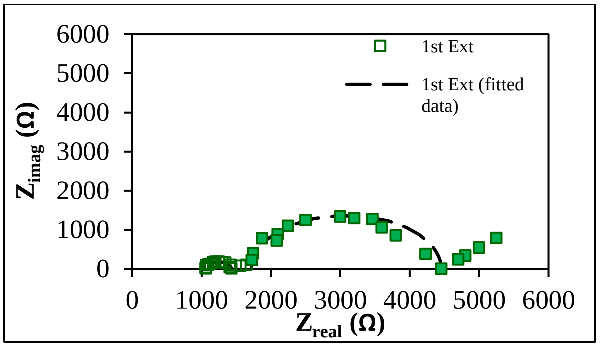

Figure 6. Spectrums of the mortars contaminated with 50 ppm of the zinc during the leaching test.

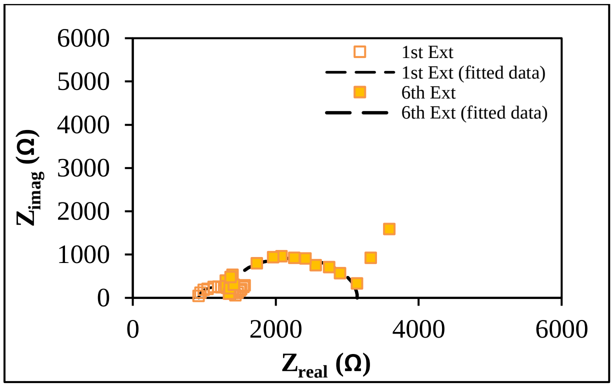

Figure 7. Spectrums of the mortars contaminated with 100 ppm of the zinc during the leaching test.

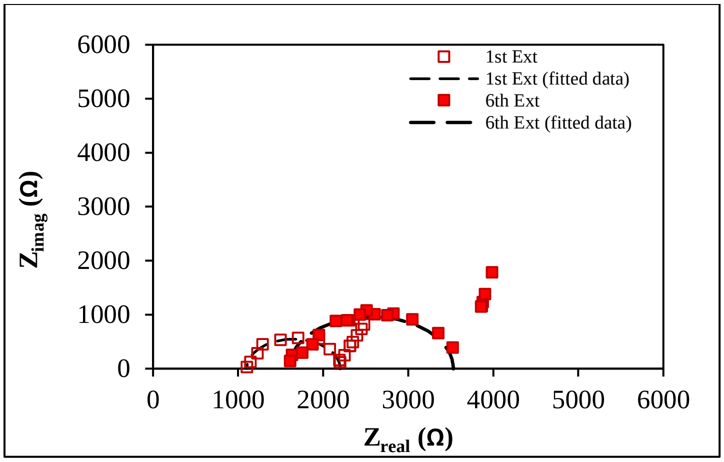

Figure 8. Spectrums of the mortars contaminated with 200 ppm of the zinc during the leaching test

The Warburg coefficient was determined by electrical impedance spectrums. The spectrums of the mortars contaminated with zinc showed the semi-circle and one line. The intersection of this straight line with the real axis determines the Warburg coefficient. In the figure 8, figure 9 and figure 10 are the Nyquist graphics of the mortars Zn 50, Zn 100 and Zn 200, respectively.

In the fitting data, the MatLab® was utilized. The equivalent circuit model of electrical impedance during the leaching test is presented in figure 11.

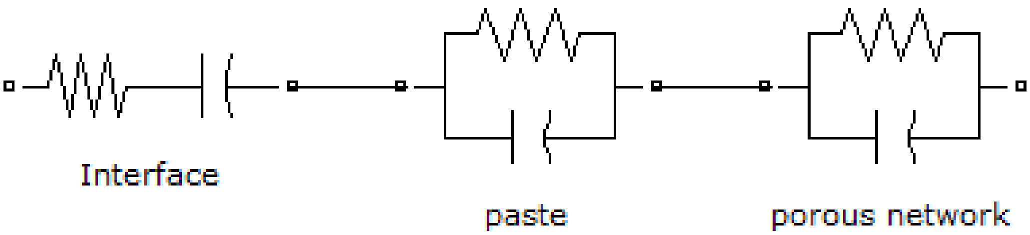

Figure 9. Equivalent circuit model of electrical impedance during the leaching test.

The interface show the parcels resistive and capacitive and these parcels affects the electrical results during the leaching test. The first circuit with electrical resistance and capacitance in parallel represents the evolution of cementitious matrices, for example the hidration degree. In the second circuit with electrical resistance and capacitance in parallel represents the porous network and interface zones. With the simulation by MatLab®, it is possible evaluate the parcels that affect mainly the electrical behaviour of the contaminated mortars. In the future, this fact can be more studied to identify the localization of the metalic ions in the cementitious matrices.

The figure 10 to figure 15, are showed the real and imaginary components of electrical impedance, of the contaminated mortars, during the leaching test, for the equivalent circuit model adopted.

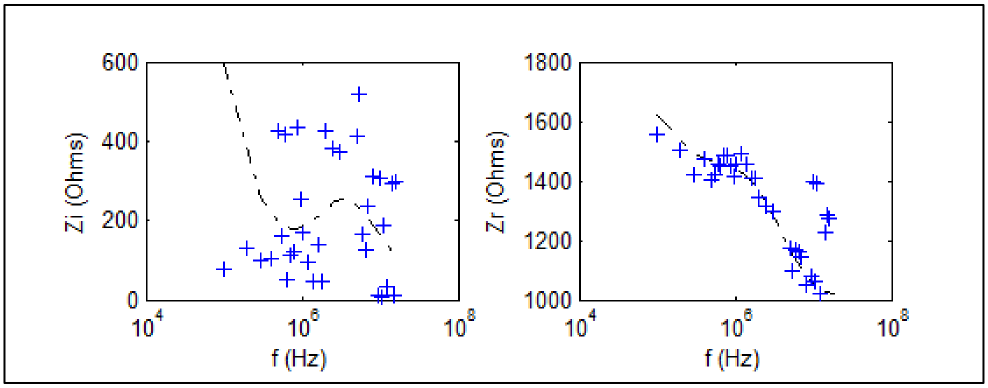

Figure 10. Electrical Impedance of the mortars contaminated with 50 ppm of the zinc during the 1st extraction of leaching test.

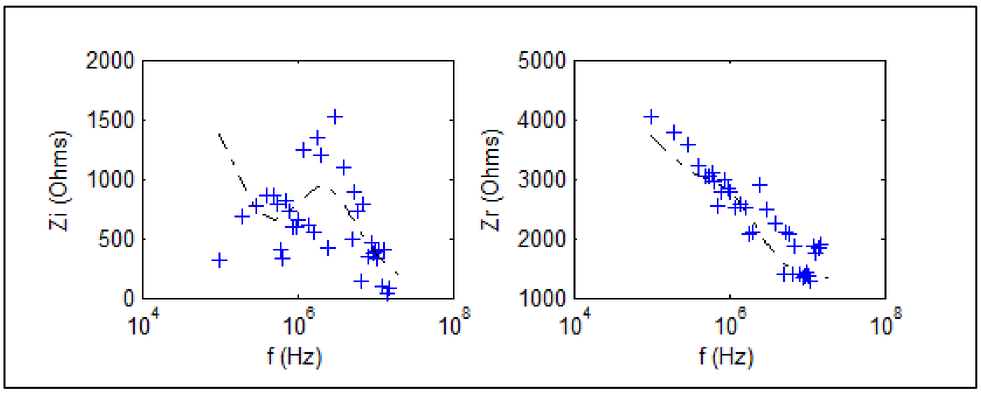

Figure 11. Electrical Impedance of the mortars contaminated with 50 ppm of the zinc during the last extraction of leaching test.

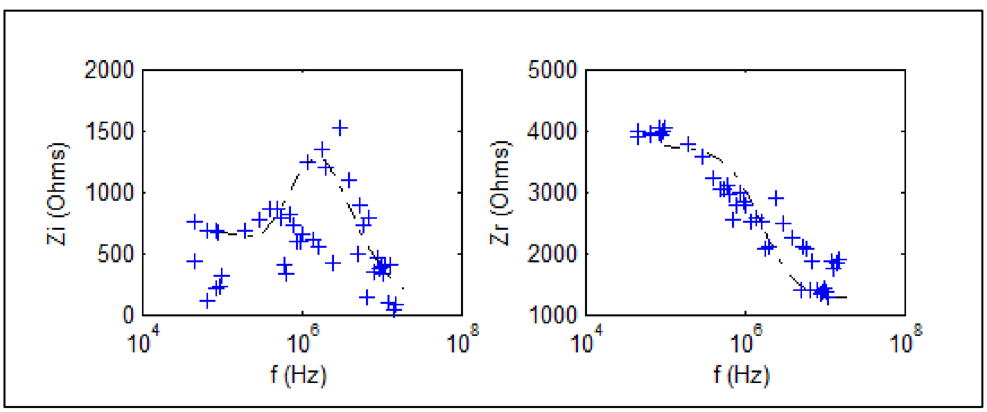

Figure 12. Electrical Impedance of the mortars contaminated with 100 ppm of the zinc during the 1st extraction of leaching test.

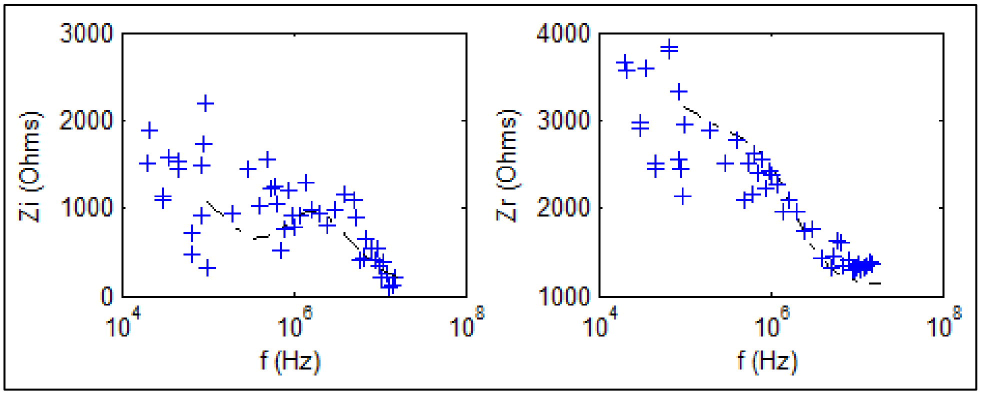

Figure 13. Electrical Impedance of the mortars contaminated with 100 ppm of the zinc during the last extraction of leaching test.

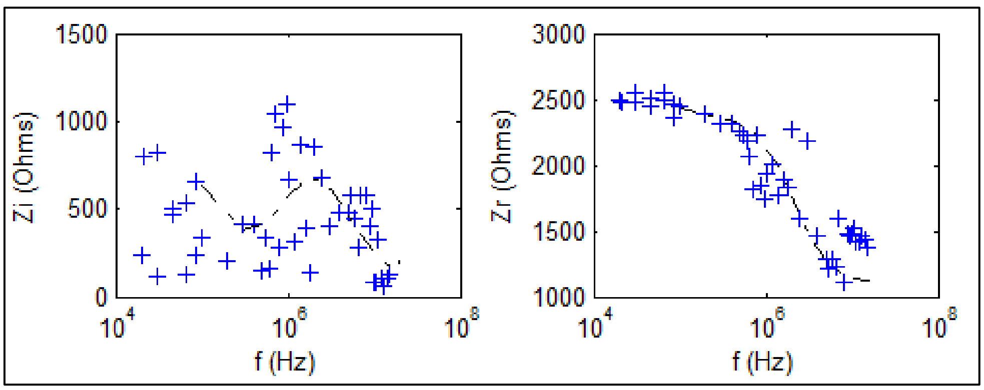

Figure 14. Electrical Impedance of the mortars contaminated with 100 ppm of the zinc during the 1st extraction of leaching test.

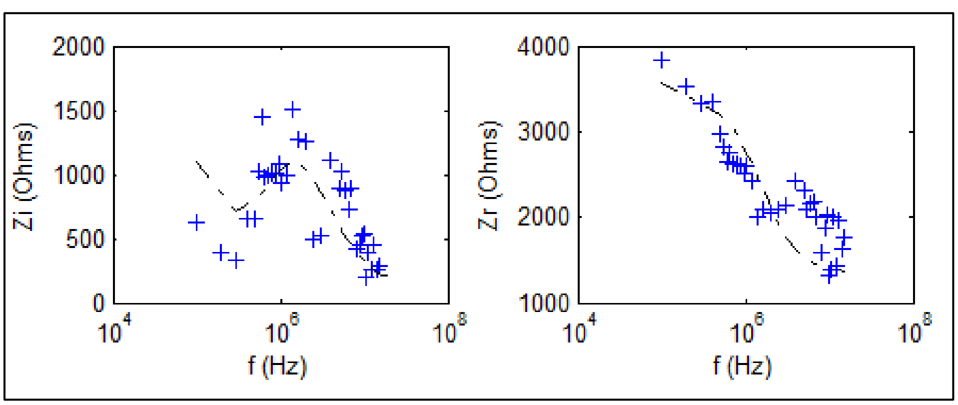

Figure 15. Electrical Impedance of the mortars contaminated with 100 ppm of the zinc during the 1st extraction of leaching test.

Figures 10 to 15, it can be observed that the equivalent circuit model adopted is valid and the main electrical proprieties as electrical resistance, capacitance and dielectric behavior needs to be better understood.

The spectrums of the mortars obtained in the course of the first and at the last extractions, showed higher impedance values at the end of leaching test. The electrical impedance represents the electrical reactance (capacitive proprieties of the cementitious matrices) and electrical resistance. The presence of ions into the mortars provides the current flow. When the transport of ions occurred (during leaching test), the electrical resistance increases. The parcel capacitive of the cementitious matrices is represented by gel-phases (Díaz *et al.*, 2013) and the presence of ions in this interface zones. Along zinc release during leaching test the capacitive parcel decreases and the electrical reactance increases.

During the leaching test, the coefficient of diffusivity was determined using the standard NEN 7375.

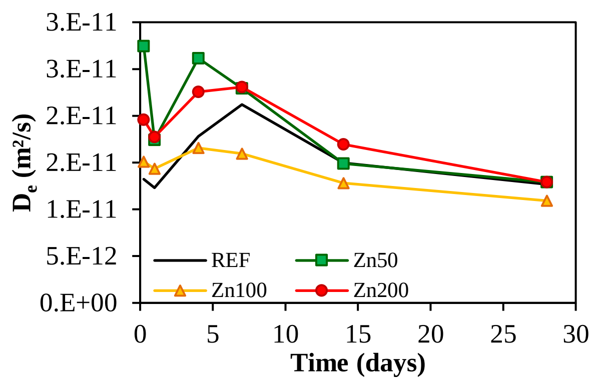

Figure 16. Diffusivity coefficient by leaching test.

The Warburg coefficient was determined through the electrical measurements and calculated according Shi et al. (1999).

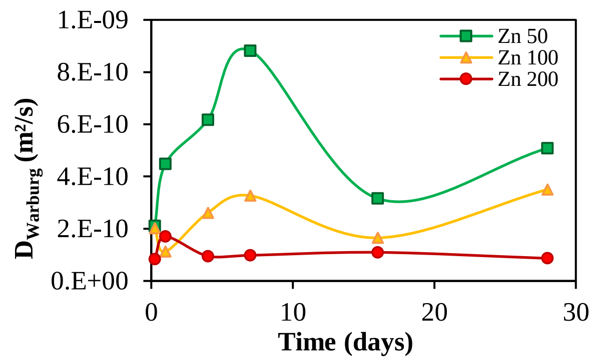

Figure 17. Warburg Coefficient by electrical impedance spectroscopy during the leaching test.

The diffusivity determined through Warburg coefficient (D_W) showed higher values at begin of the leaching test, similar to the diffusivity determined by leaching test (D_e). Higher values of diffusivity occurred until fourth extraction. This fact is due the higher concentration of zinc released at begin of leaching test. The mortar Zn 50 showed the higher values of D_W and D_e.

Negative logarithm (according to NEN 7375) of the D_W (ρD_W) and De (ρD_e) were determined Table 1. These values represent the potential of release and, in this case, zinc mobility.

Table 1. Leaching release by diffusivity coefficients.

Sample	ρDe (Tank Test)	Classification	ρD_W (Electrical Test)	Classification
Ref	10,90	High Mobility	-	-
Zn 50	10,89	High Mobility	9,29	High Mobility
Zn 100	10,96	High Mobility	9,45	High Mobility
Zn 200	10,89	High Mobility	10,06	High Mobility

According Vedalakshmi *et al.* (2009), the cementitious materials porous are filled with an ionic solution. The D_W will represent the ionic transport that occurs between the solid and gel phases of mortars, and, of none leached ions. It was observed that the increasing zinc concentration resulted in lowers values of leached zinc (close to the reference mortar), the stabilization of zinc and the presence of the ions in the cementitious matrices providing higher values of D_W. The D_e represents the heavy metal mobility of the ionic species that leached and the D_W represents the heavy metals remained stabilized and/or stabilization into the mortars.

CONCLUSION

- Lower concentration of the zinc and calcium were released from the contaminated mortars in comparison to reference mortar.
- Less calcium leached from the contaminated mortars reflects a possible chemical reaction between the zinc and the calcium.
- Warburg diffusion is more realistic than the diffusion coefficient determined during the leaching test.
- Electrical impedance spectroscopy can be used to analyse the ionic mobility and contaminants release.

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