Athens Institute for Education and Research
ATINER

ATINER's Conference Paper Series
ENG2016-2095

The Use of 1% Nano-Fe_3O_4 and 1% Nano-TiO_2 as Partial Replacement of Cement to Enhance the Chemical Performance of Reinforced Concrete Structures

Mariana d'Orey Gaivao Portella Braganca
Researcher
Institutos Lactec
Brazil

Kleber Franke Portella
Researcher
Institutos Lactec
Brazil

Camila Marcal Gobi
Researcher
Institutos Lactec
Brazil

Evandro de Mesquita Silva
Technician
Institutos Lactec
Brazil

Emerson Alberti
Researcher
Centrais Elétricas do Rio Jordão
Brazil

An Introduction to ATINER's Conference Paper Series

ATINER started to publish this conference papers series in 2012. It includes only the papers submitted for publication after they were presented at one of the conferences organized by our Institute every year. This paper has been peer reviewed by at least two academic members of ATINER.

Dr. Gregory T. Papanikos
President
Athens Institute for Education and Research

This paper should be cited as follows:

d'Orey Gaivao Portella Braganca, M., Portella, K. F., Marcal Gobi, C., de Mesquita Silva, E. and Alberti, E. (2016). **"The Use of 1% Nano-Fe_3O_4 and 1% Nano-TiO_2 as Partial Replacement of Cement to Enhance the Chemical Performance of Reinforced Concrete Structures",** Athens: ATINER'S Conference Paper Series, No: **ENG2016-2095.**

Athens Institute for Education and Research
8 Valaoritou Street, Kolonaki, 10671 Athens, Greece
Tel: + 30 210 3634210 Fax: + 30 210 3634209 Email: info@atiner.gr URL: www.atiner.gr
URL Conference Papers Series: www.atiner.gr/papers.htm
Printed in Athens, Greece by the Athens Institute for Education and Research.
ISSN: 2241-2891
11/1/2017

The Use of 1% Nano-Fe_3O_4 and 1% Nano-TiO_2 as Partial Replacement of Cement to Enhance the Chemical Performance of Reinforced Concrete Structures

Mariana d'Orey Gaivao Portella Braganca
Kleber Franke Portella
Camila Marcal Gobi
Evandro de Mesquita Silva
Emerson Alberti

Abstract

The buildings can be exposed to ionic agents present in the environment (soil, water and air), such as chloride and sulfate, or even to the intern ones, added in the dosage process due the usage of some contaminated materials, such as alkalis and sulphur minerals presented in some aggregates. The contaminants tend to react with the cement hydrates and could modify the concrete or mortar properties, dropping the materials' lifetime. Especially in reinforced structures, these agents influence the double layer (concrete/bar) quality, promoting the bar corrosion due the ionic interaction or the modification of the environment alkalinity. Because of this, there is a necessity of stopping or avoiding these chemical reactions between the products of cement hydration and the aggressive agents. Currently, the most promising techniques involve the enhancement of concrete quality, especially from the permeability. Although, there are some advances in the nanoscale compound studies, which have raised the development of more chemically resistant concretes and also special treatments for the material presented on structures in early stages of degradation. The present article aimed for the development of a cause and effect study of distress mechanisms in concrete, with and without additions of nano-Fe_3O_4 and nano-TiO_2 in 1% partial cement replacement, used to enhance the material's durability. For that, the nanoscale ceramic oxides were characterized and added in concrete dosages, as a partial replacement of cement. The obtained material was analyzed for physical and chemical measurements, to evaluate the structural performance and the durability characteristics under laboratory aggressive exposition. The obtained results showed there developed a new kind of concrete, with more homogeneous microstructure produced even in the early ages, by the reaction between the cement hydrates and the nano-materials. It improved the concretes mechanical and physicochemical properties, enabling the dosage of more durable materials.

Keywords: Chemical resistance, Nano-Fe_3O_4, Nano-TiO_2, Reinforced concrete.

Acknowledgments: The authors would like to thank PIPE-UFPR (Programa Interdisciplinar de Pós-Graduação em Engenharia e Ciência dos Materiais of Universidade Federal do Paraná), the Lactec Institutes (Institutos Lactec), ANEEL (Agência Nacional de Energia Elétrica), ELEJOR (Centrais Elétricas do Rio Jordão; PD 2945-0004/2013) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, law 8010/90) for financial support and infrastructure. We also acknowledge financial assistance from the CNPq productivity fellowship grants that were awarded to Kleber F. Portella (grant number 305718/2011-8).

Introduction

Durability is the life time expectation of a specific material, exposed to environmental conditions. Specifically to Portland cement concrete, according to the American Concrete Institute (ACI), this property represents the capacity to resist weathering action, chemical reaction, abrasion or any other condition of service, without losing the functionality and the original format (ACI Committee 201, 2008).

Because of the microstructural properties, the conventional concrete (CCV) is, usually, a low permeability material (the permeability coefficient is around 10^{-8} cm.s^{-1}). Although, it allows the entry of water through their pores, which can affects the durability (Carvalho, 2008). In spite of, many studies indicates that even in aggressive conditions, this composite life cycle is between 50 and 100 years, without major structural maintenance actions (Monteiro and Kurtis, 2002).

Among the many factors that can reduce the CCV life cycle, there are: i) the occurrence of distress because of the chemical reactions between the aggressive agents of the environment and the concrete components, such as the cement alkalis (Mehta and Monteiro, 2008); ii) the cement paste leaching process, that occurs due to the direct contact of the concrete with running water, resulting in hydrolysis and mass loss of the paste components, such as calcium hydroxide and hydrated silicate (Yang et al., 2011); and iii) the carbon dioxide concentration and of other pollutants, into the environment, which tend to penetrate through the concrete pores, reducing the pH to values below 9, due to the salinization of the portlandite $Ca(OH)_2$ and of other hydroxides components (Monteiro et al., 2012).

Specifically in coastal regions, problems of degradation and corrosion are usually related to the diffusion of chloride ions (Cl^-) through the surface of the buildings. With the natural wetting and drying cycles, promoted to the exposure to rainwater, dew and solar radiation, these anions can penetrate through the pores of the material by capillarity and can accumulate in pores and voids; or even diffuse through the preferential path, until reaching the reinforcement (Meira et al., 2010).

Another important reaction that can affect the concrete durability is the one that occurs between the cement hydrates (such as alumina and calcium hydroxide) with sulfate ions (SO_4^{2-}), that can be present, as a contaminant, in industrial effluents (water and air); in the soil, due the decomposition of organic matter; or even in some materials used to prepare the concrete, such as many types of minerals used as aggregates. Similar to chloride, these ions tend to penetrate through the concrete pores, across its surface, generating new products and, in many cases, localized tensile forces, that can generate expansion and the appearance of fissures (Monteiro and Kurtis, 2002; Ahmad, 2003).

The great challenge to the conventional concrete durability is related to the interruption or the prevention of the occurrence of these chemical reactions between the cement hydrates and the aggressive agents. Techniques that involve the increase of the concrete quality, specific related to permeability coefficient (adequate thickness, high consumption of cement, low water/ ement ratio, good densification and cure process) are also rated as the most promising forms of enhancement of the material life cycle (Aitcin, 2003). In this context, the progress that have been made in the study of nano compounds, such as silicon dioxide, have enabled the development of, not only higher chemically resistant concretes, but also enabling the treatment of structures subjected to early stages of degradation (Sanchez and Sobolev, 2010).

Melo and Triches (2012), studied nanometric titanium dioxide (TiO_2), added to cement materials for surface modification, to develop structures that can photo-catalyze the NO_x gases from the atmosphere. The use of this addition to increase the mechanical properties was proposed by Li and collaborators, which developed concretes with 1, 3 and 5% of nano-TiO_2 and enhanced the abrasion resistance, the axial compressive and the flexural fatigue strength of the material.

The nano-Fe_3O_4 preliminary studies were on cement pastes, to investigate the hydration characteristics, the axial compressive strength and the tensile strength by diametral compression and the penetration of chloride ions, which were improved for additions of 1.5% (Amin et al., 2013; Shekari and Razzaghi, 2011; Rashad, 2013). Braganca et al. (2016) studied the electrochemical stability of Portland cement concretes with 1% nano-Fe_3O_4 addition under chloride and sulfate environments trough impedance spectroscopy and cyclic voltammetry. It was verified enhanced properties, resultant from a more homogeneous microstructure, produced by the byproducts of the reaction between the cement hydrates and the nano-material.

Then, the present article aimed for the development of a cause and effect study of distress mechanisms in concrete with and without additions of nano-Fe_3O_4 and nano-TiO_2 in 1% partial cement replacement that was used to enhance the material's durability. For that, the nanoscale ceramic oxides were characterized and added in concrete dosages, as partial replacements of cement. The obtained material was analyzed for physical and chemical measurements, to evaluate the structural performance and the durability characteristics under laboratory aggressive exposition.

Experimental Methodology

The effect of using nano-Fe_3O_4 and nano-TiO_2 as cement partial replacement (1%) to improve the physicochemical properties of reinforced concretes was evaluated, starting with the characterization of the precursor materials, followed by the dosages and by the development of aging studies.

Materials Properties

The oxides used in this research, as partial replacement of cement, were the commercial Fe_3O_4 and TiO_2, nanoscale, provided by Sigma-Aldrich. The both material has a particle size between 25 and 100 nm and an average surface area of 55 $m^2.g^{-1}$. The specific gravity of them, respectively, were 4,800 $g.cm^{-3}$ and 3,900 $g.cm^{-3}$.

The applied binder was a commercial pozzolanic Portland cement (CP IV 32), and, as aggregates, it was used basaltic rocks, crushed into fine (ABF) and coarse (ABG) phases. These materials, cement and aggregates, were fully characterized, in accordance with Brazilian standards (NBR 6118, 2014).

Concrete Dosage

The reference concrete (RC) was prepared with the characterized materials and the used proportions were 1 part of cement to 5 parts of aggregates, by mass (1.46 ABF and 3, 55 ABG), similar to the methodology used by Li et al. (2014). The concretes with the addition of nanoscale oxides were prepared in a similar manner of RC. The additions were made in partial replacement of cement in the proportion of 1%, by mass, for both nanosized oxides studied (nano-Fe_3O_4 and nano-TiO_2), also similar to the methodology adopted by Li et al. (2014). The nanoscale materials were manually mixed with cement, to improve the dispersion of the particles. In Table 1 is presented the data for the materials consumption and for the fresh concrete properties.

Table 1. *Materials Consumption and Fresh Concrete Properties*

Materials Consumption	Water (l)	Cement (kg.m^{-3})	ABF (kg.m^{-3})	ABG (kg.m^{-3})	w/c	Addition (kg.m^{-3})
RC	218	383	560	1360	0.57	0
1% nano-oxides	217	381	563	1367	0.57	4

Fresh Concrete Properties	Mixing temperature (°C)	Specific gravity (kg.m^{-3})	Slump test (mm)
RC	22.3	2818	50 ± 10
1% nano-TiO_2 (TC)	21.5	2765	40
1% nano-Fe_3O_4 (FC)	21.6	2792	30

The prepared concretes were molded in cylindrical forms (100 x 200) mm and (150 x 300) mm for the characterization tests of mechanical and physical properties; and prismatic molds (50 x 90 x 100) mm, containing carbon steel (CA 50) and graphite electrodes for the study of electrochemical properties. After, the concrete was cured in air for 24 h, and then, molded. The healing was performed in a humid chamber until it aged for 28 days (or until the corresponding age to the specific performed test).

Concrete Characterization

The mechanical properties of prepared concretes, after molding and healing, were evaluated through the following tests: (i) compressive strength, after 1, 7, 28 and 91 days of healing; (ii) tensile strength by diametrical compression, after 28 days of healing; and (iii) static modulus elasticity, after 28 and 91 days of wet cure. The mechanical tests were performed on equipment EMIC PC 200. The physical properties of the concretes were evaluated after 28 days of healing for determining the water absorption, the void index and the water permeability.

Exposure Studies and Characterization

The reinforced concretes were divided into groups and subjected to different processes of healing and accelerated aging processes:

- Desiccator: some samples of each material was kept as a reference standard, in a desiccator, after 28 days of moist curing;
- SO_2 chamber: in cycles of wetting (8 h at 40° C in a saturated moist atmosphere, with a concentration of 2% SO_2) and drying (16 h, at ambient conditions) in adapted Kesternich procedure;
- Salt-spray chamber - under daily cycles of wetting (8 h at 40° C in a saturated moist atmosphere, with a concentration of 5% NaCl) and drying (16 h at 25° C).

Then, the relative durability of the concretes was studied, aiming the comprehension of the established deterioration mechanisms and to study the electrochemical stability. For that, the materials were characterized for corrosion potential and the test was developed in procedure adapted from ASTM C876 (2009). The test was performed in an electrochemical system Ecochemie AUTOLAB, model - PGSTAT-100, interfaced with a computer for the acquisition and recording of data. The measurements were performed with wet samples, relative to a saturated calomel reference electrode.

Results and Discussion

Materials Characterization

The cement and the aggregates used in this study presented properties in accordance with the Brazilian standard recommendations. The results of XRF chemical characterization of these materials are shown in Table 2.

Table 2. *Cement and Aggregates Chemical Characterization, by XRF*

Materials (%)	**CaO**	**SiO_2**	**Na_2O**	**Al_2O_3**	**MgO**
Cement	45.2	28.4	1.31	10.3	3.2
Aggregate	9.1	47.1	2.5	13	2.8
(%)	**Fe_2O_3**	**SO_3**	**TiO_2**	**Others**	**Lose in Ignition**
Cement	3.7	2.4	--	2.2	3.2
Aggregate	18.3	0.3	3.2	3.7	0.8

Concrete Characterization

The results for the compressive strength, modulus of elasticity, tensile strength by diametrical compression, water absorption, void ratio, and water permeability of concrete reference (RC) and nanometric additions are shown in Figures 1 and 2 and in Table 3.

Figure 1. *Compressive Strength Results for Concretes. Performed after Healing for Ages of 1 (RC only), 7, 28 and 91 days. Error Bars Inserted for Each Point, relative to the Standard Deviation of the Results Obtained for Different CPs Analyzed (3 CP's age)*

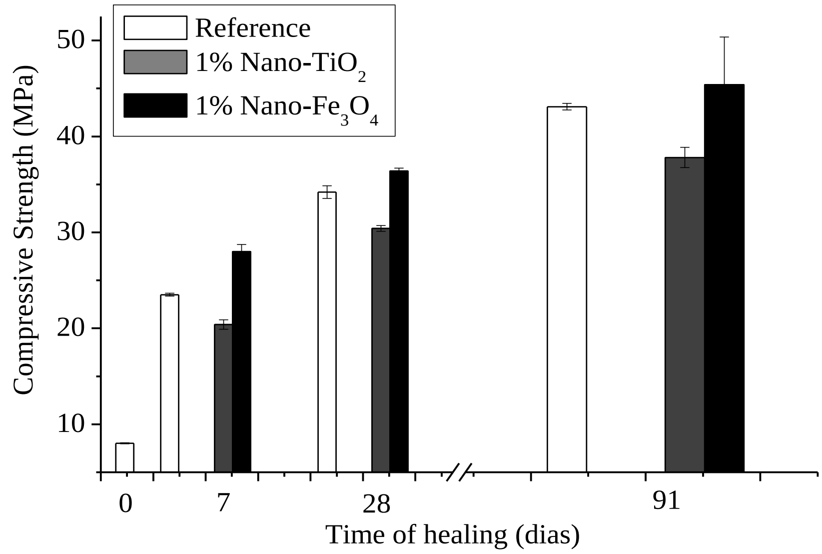


Figure 2. *Modulus of Elasticity Results for Concretes. Tests Performed after Healing for Ages of 7 (RC Only), 28 and 91 days. Error Bars Inserted for Each Point, relative to the Standard Deviation of the Results Obtained for Different CPs Analyzed (3 CP's Age)*

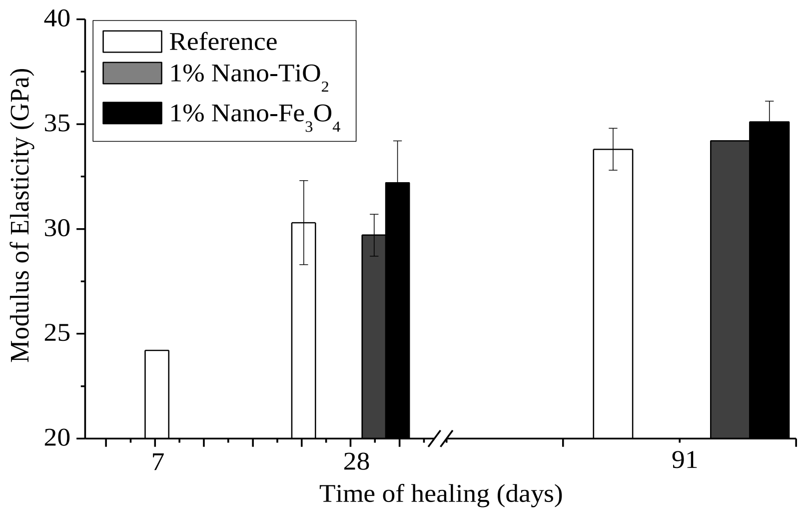


Table 3. *Tensile Strength by Diametrical Compression, Water Absorption, Void Ratio, and Water Permeability Results for Concretes. Tests Performed after 28 Days of Healing. Error Bars Inserted for Each Point, relative to the Standard Deviation of the Results Obtained for Different CPs Analyzed (3 CP's Age)*

Property	Reference	Nano-TiO_2	Nano-Fe_3O_4
Tensile strength (MPa)	3.28 ± 0.11	3.36 ± 0.06	3.18 ± 0.14
Water absortion (%)	6.39 ± 0.38	4.86 ± 0.08	5.04 ± 0.19
Void ratio (%)	15.06 ± 0.95	11.85 ± 0.19	12.34 ± 0.43
Water permeability ($cm.s^{-1}$)	$3.25x10^{-11}$	$3.55x10^{-11}$	$1.93x10^{-11}$

The results for the compressive strength, modulus of elasticity, tensile strength by diametrical compression, water absorption, void ratio, and water permeability, presented in the Figures 1 and 2 and in the Table 3, showed that the properties of all of the concretes that were consistent with the technical norms (NBR 6118). According to NBR 6118 (ABNT, 2014), developed materials can be classified as "conventional concrete of normal strength", which allows general use.

Specifically, for compressive strength (Figure 1), observed a tendency to increase the property value to concrete with additions of nano-TiO_2 (4.18%) and nano-Fe_3O_4 (12.30%) was observed, in relation to the reference material. For these two, the same behavior was observed to the modulus of elasticity (Figure 2), especially at 28 days, with an increase of 5.90% nano-TiO_2 and 2.26% for nano-Fe_3O_4.

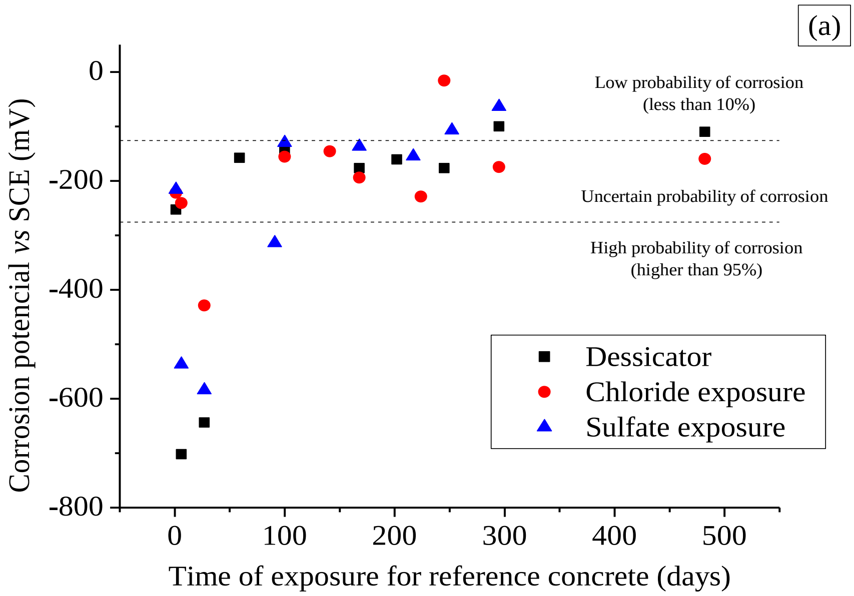
For the physical properties, the decrease in water absorption was observed in 21.1% (nano-Fe_3O_4) and 23.9% (nano-TiO_2); and the reduction of voids in 18.1% (nano-Fe_3O_4) and 21.3% (nano-TiO_2). These water absorption properties and voids ratio can be related to the decrease in the amount of pores in the cement paste, because of the addition and homogeneous dispersion of the nanomaterial particles in concrete, to which, according with the work of Li et al. (2004; 2006) tend to favor the growth control calcium silicate hydrates (C-S-H) crystals, increasing the density of interface transition zone (ITZ) and effect as filler in concrete. These features allow obtaining a cement paste with a homogeneous microstructure, which may have better physicochemical and mechanical performance (Li et al., 2004; 2006).

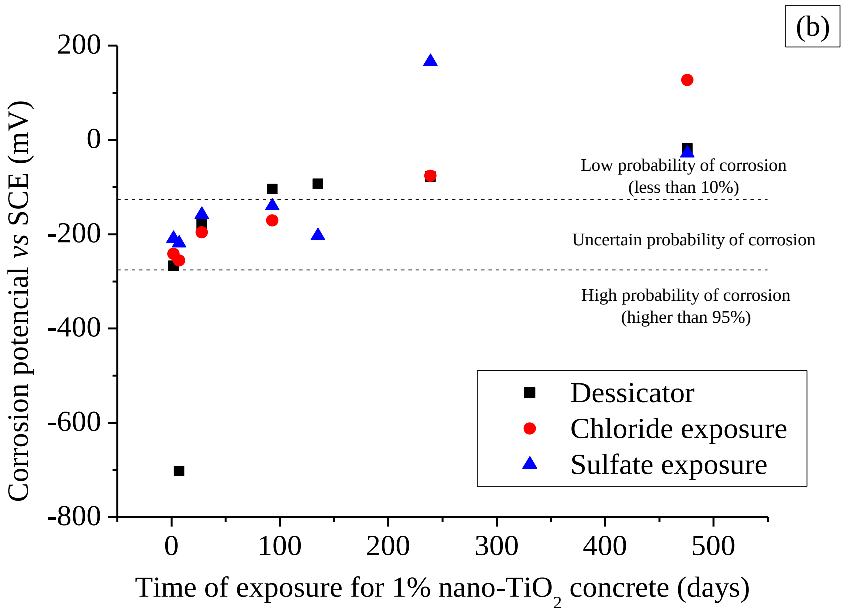
The results of tensile strength by diametrical compression and water permeability (in terms of order of magnitude), the concrete properties with additions were kept in similar values to reference material and according to the data presented by Aslani and Nejadi (2012), characteristic of conventional concrete.

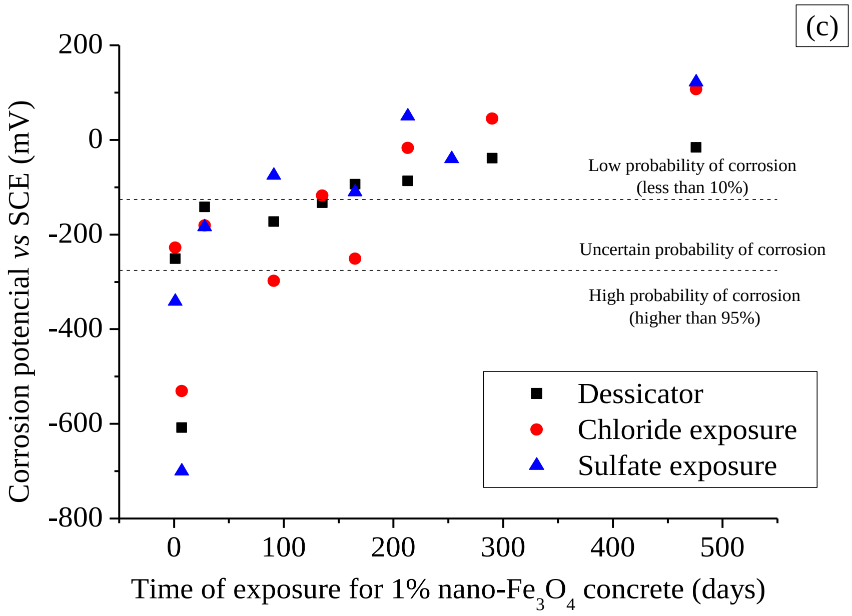
Exposure Studies and Characterization

The relative durability of the exposed to aggressive environments containing chloride and sulfate ions was characterized by corrosion potential, in relation to the saturated calomel electrode, as presented in Figure 3.

Figure 3. *Corrosion Potential Results for Concretes, in relation to the Saturated Calomel Electrode, (a) the Reference One, (b) the Nano-TiO_2 and (c) the Nano-Fe_3O_4. Tests Performed during the Exposition Studies to Aggressive Environments Containing Chloride and Sulfate Ions, for 500 Days of Exposure*







Conclusions

The preparation of concretes with additions of 1% nano-Fe_3O_4 and nano-TiO_2 by partial replacement of cement was possible and it obtained a similar material to the mechanical properties of the reference concrete after healing.

The concretes with nanomaterials presented a lower water absorption and void ratio (around 20%), and superior electrochemical stability, even with the exposure to environments containing chloride and sulfate ions, for 500 days. It could be concluded that the nano-Fe_3O_4 and nano-TiO_2 enhanced the microstructure of the cement pastes, increasing the corrosion resistance and, consequently, the durability of the materials, relatively to the reference one, when exposed to industrial and marine environments.

References

ABNT. (2014). NBR 6118. Projeto de estruturas de concreto - Procedimento [Design of concrete structures - Procedure]. Brazil.

ACI Committee 201. (2008). 201-2R-08. Guide to Durable Concrete. Farmington Hills, Michigan, Estados Unidos: American Concrete Institute.

Ahmad, S. (2003). Reinforcement corrosion in concrete structures, its monitoring and service life prediction - a review. Cement and Concrete Composites, pp. 459-471.

Aitcin, P. C. (2003). The durability characteristics of high performance concrete: a review. Cement & Concrete Composites, pp. 409-420.

Amin, M. S., El-Gamal, S. M. A., Hashem, F. S. Effect of addition of nano-magnetite on the hydration characteristics of hardened Portland cement and high slag cement pastes. J Therm Anal Calorim 2013; 112: 1253-59.

Aslani, F., Nejadi, S. (2012). Mechanical properties of conventional and self-compacting concrete: An analytical study. Construction and Building Materials, pp. 330-347.

ASTM. (2009). ASTM C 876-09. Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete. United States: Standard Worlwide.

Braganca, M. O. G. P., Portella, K. F., Bontato, M. M., Alberti, E., Marino, C. E. B. (2016). Performance of Portland cement concretes with 1% nano-Fe_3O_4 addition: electrochemical stability under chloride and sulfate environments. Construction and Building Materials, v. 117, 152-162.

Carvalho, J. D. (2008). Sobre as Origens e Desenvolvimento do Concreto [About the Origins and Development of Concrete]. Revista Tecnológica, 19-28.

Li, H., Xiao, H., Guan, X., Wang, Z., Yu, L. (2014). Chloride diffusion in concrete containing nano-TiO_2 under coupled effect of scouring. Composites: Part B, 56, pp. 698-704.

Li, H., Xiao, H., Ou, J. (2004). A study on mechanical and pressure-sensitive properties of cement mortar with nanophase materials. Cement and Concrete Research, 34, pp. 435-438.

Li, H., Zhang, M., Ou, J. (2006). Abrasion resistance of concrete containing nano-particles for pavement. Wear, 260, pp. 1262-1266.

Mehta, P. K., & Monteiro, P. J. (2008). Concreto - Microestrutura, Propriedades e Materiais [Concrete - Microstructure, Properties and Materials]. São Paulo: IBRACON.

Meira, G., Andrade, C., Alonso, C., Borba JR., J. Padilha JR., M. (2010). Durability of concrete structures in marine atmosphere zones: The use of chloride deposition rate on the wet candle as an environmental indicator. Cement & Concrete Composites, pp. 427-435.

Melo J., Triches G. (2012). Evaluation of the influence of environmental conditions on the efficiency of photocatalytic coatings in the degradation of nitrogen oxides (NOx). Build Environ; 49: 127-33.

Monteiro, I., Branco, F., Brito, J., Neves, D. (2012). Statistical analysis of the carbonatation coefficient in open air concrete structures. Construction and Building Materials, 29, pp. 263-269.

Monteiro, P., Kurtis, K. (2002). Time to failure for concrete exposed to severe sulfate attack. Cement and Concrete Research, pp. 987-993.

Rashad A. (2013). Review: A synopsis about the effect of nano-Al_2O_3, nano-Fe_2O_3, nano-Fe_3O_4 e nano-clay on some properties of cementitious materials – A short guide for Civil Engineer. Mater Design; 52: 143-57.

Sanchez, F., Sobolev, K. (2010). Nanotechnology in concrete - a review. Construction and Building Materials, pp. 2060-2071.

Shekari A. H, Razzaghi M. S. (2011). Influence of nano particles on durability and mechanical properties of high performance concrete. Pro Eng, 14: 3036-41.

Yang, H., Jiang, L., Zhang, Y., Pu, Q., & Xu, Y. (2011). Predicting the calcium leaching behavior of cement pastes in aggressive environments. Construction and Building Materials, pp. 88-96.