Tratamiento superficial con nanopartículas base silicio inducido durante el curado: Efecto en la durabilidad de materiales base cemento portland

D. Cruz-Moreno¹, G. Fajardo¹*, I. Flores-Vivián¹, A. Cruz-López¹, P. Valdez¹

*Autor de Contacto: gerardo.fajardosn@uanl.edu.mx
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RESUMEN
El efecto de la introducción de nanopartículas base silicio (NBS) preparadas por sol-gel en la permeabilidad de materiales base cemento portland fue estudiado. La introducción de NBS en morteros fabricados con una relación a/c de 0.65 fue inducida durante el curado por 72h, utilizando suspensión de [NBS]=0.1% vs. el volumen del agua. Posteriormente, las muestras siguieron un periodo de inmersión en agua potable con el fin de promover la reacción de la NBS con la matriz cementante y la resistividad fue medida frecuentemente. Después, fueron expuestos en ambientes con Cl⁻ o CO₂. Los resultados indicaron una disminución en la penetración de estos agresivos y un incremento de la resistividad en los especímenes tratados; por ende un incremento de la vida útil.

Palabras clave: Durabilidad; tratamiento superficial; nanopartículas; curado; permeabilidad.


¹Universidad Autónoma de Nuevo León, Facultad de Ingeniería Civil, México.
Surface treatment with silicon-based nanoparticles induced during curing: Effect on durability of portland cement based materials.

ABSTRACT

The effect of the introduction of silicon-based nanoparticles (NBS) prepared by the sol-gel method was studied. The introduction of NBS was induced for 72 hours during curing by using mortar specimens with a w/c ratio of 0.65 and a suspension prepared at [NBS] = 0.1% with respect to the volume of the curing water. Subsequently, the samples followed a period of immersion in potable water to promote the reaction of NBS inside mortar. Frequent measurements of electrical resistivity were made. Subsequently, a series of specimens were exposed in environments rich in Cl⁻ or CO₂. The results indicated a decrease in the penetration of aggressive agents into the mortar specimens. This coincides with increasing resistivity specimens treated with respect to the reference

Keywords: Durability; surface treatment; nanoparticles; curing; permeability.

Tratamiento superficial com nanopartículas à base de silício induzidas durante a cura: efeito sobre a durabilidade dos materiais de base cimento Portland

RESUMO

O efeito da introdução de nanopartículas à base de silício (NBS) preparado por sol-gel sobre a permeabilidade dos materiais de base de cimento Portland foi estudado. A introdução de NBS em argamassas feitas com uma relação a / c de 0,65 foi induzida durante a cura por 72 h, usando [NBS] = 0,1% vs. o volume de água. Posteriormente, as amostras seguiram um período de imersão na água potável para promover a reação do NBS com a matriz de cimento e a resistividade foi medida com frequência. Posteriormente, foram expostos em ambientes com Cl ou CO2. Os resultados indicaram uma diminuição na penetração destes agressivos e um aumento da resistividade nos espécimes tratados; aumentando assim a vida útil.

Palavras-chave: durabilidade; tratamento de superfície; nanopartículas; curado; permeabilidade.

1. INTRODUCTION

Problems of durability in reinforced concrete structures (RCS) begin with the interaction of the medium with the surface of the portland cement base materials (Cai et al., 2016; Hou et al., 2015; Hou et al., 2016). In the short to medium term, this interaction causes the deterioration of the RCS, generating further annual expenses between 18 to 21 billion USD in renovations or repairs due to the corrosion of reinforcing steel (Barnat-Hunek et al., 2016; Khaloo et al., 2016). More than 50% of these RCS present deterioration problems because of the high permeability or low quality concrete (Fajardo, et al., 2015; Rtimi et al., 2016), which favors the transport mechanism of aggressive agents as to the carbon dioxide (CO₂), chloride ion (Cl⁻) and sulphate (SO₄²⁻), these being, the main cause of deterioration in the RCS (Achal et to the., 2015; Trapote-Barreira et al., 2014). However, we must remember that the important properties, such as strength, permeability and durability, are linked directly with the concrete porosity (Fajardo et al., 2015; Rtimi et al., 2016). However, the porosity is determined by the type and the amount of cement used, the level of compaction, transportation, time and type of curing, with the latter being one of the main stages of the construction system of the RCS, since it is of great help and contributes to the achievement of many of their properties, (Fajardo et al., 2015; Zahedi et al., 2015). Curing is the mechanism used to promote hydration of cement; taking
control of the temperature and the movement of moisture from the surface to the inside of the concrete. Curing occurs in a period where the RCS usually lost moisture by evaporation, bleeding or hydration. During this period, there is a demand for water to continue with hydration. The gradient of moisture generated promotes the movement of water into the interior, coupled with the absorption originating the porosity of the matrix of concrete. This technique is not new, but allows the hydration, in a way that maximizes the potential properties that can be developed on a cement portland based matrix (Kong et al., 2016; Kupwade-Patil et al., 2016; Wyrzykowski et al., 2016). However, an improper curing process (or absence) of concrete can result in a high porosity, especially on the outer surface of the concrete. Today there are a wide variety of products that claim to offer a series of benefits to the surface of the concrete; from increase in the mechanical properties to permeability reduction. However, these products added during or after the curing process, are not achieving the benefits offered and the needs of the construction industry. Indeed, problems were found associated with improper application, degradation caused by constant exposure to UV rays, chemical incompatibility and therefore loss of adhesion between it and the substrate (Lakshmi et al., 2012; Zhu et al., 2016; Zhu et al., 2013). So, a wide variety of research has been generated over the last decades, mainly due to the economic impact caused by the problem of durability, where a variety of ways to improve the RCS were proposed and that they are more long-lasting. However, the most common strategy adopted, is to slow down the process of degradation of concrete reinforced by the decrease of porosity by reducing the water/cement ratio or the addition of nanoparticles (Efome et al., 2015; Franzoni et al., 2014; Jia et al., 2016; Pacheco-Torgal et al., 2009; Pigino et al., 2012; Pour-Ali et al., 2015). Nanoparticles through migration in hardened mortars have been entered in previous studies and found to be blocking the pores, causing a decrease in permeability (Fajardo et al., 2015; Sanchez et al., 2014). Other methods have been developed since the introduction of nanoparticles into the interior of cement base materials applied at early ages (Hou et al. 2015; Jalal et to the. 2012). These techniques have demonstrated the beneficial effects of the interaction of nanoparticles with certain phases of the matrix of the cementitious materials. However, present difficulties associated mainly to the complexity of the application in situ or real elements. Therefore, this paper explores the influence of the movement of moisture from the curing with water in cement portland base materials making it an enabling way for the induction of nanoparticles with the aim of improving the properties that increase durability.

2. EXPERIMENTAL PROCEDURE

2.1 Materials
Ordinary portland cement (CPO 40), with a chemical composition similar to a type I cement was used for this study and comply with ASTM C150 and NMX-C-414-ONNCCE respectively. It is used as aggregate, standard sand (silica's Ottawa) that conforms to ASTM C 778. In the case of the mixed water, deionized water for the preparation of mortar specimens was used, complies with the norm NMX-C-122-ONNCCE and as well to prevent the intrusion of ions Cl to the mix.

2.2 Manufacture of specimens
Designed cylindrical specimens of mortar with a diameter of 50 mm and 150 mm in length. Specimens were manufactured with a 0.65 water/cement ratio (w/c) as shown in table 1, this in order to maintain a characteristic of a conventional concrete porosity. Mixing of mortars was carried out following the procedure described in ASTM C 305 and ASTM C 109 standard. After being cast, specimens were kept at 20 ° C for 24 h as set out in the standard ASTM C171.

Table 1. Proportions of the mixture for a relationship w/c = 0.65 (PCA method).
2.3 Producción de nanopartículas base silicio (NBS)

Para obtener amorfos NBS y tamaños que varían entre 8 y 50 nm, se utilizó el gel en un proceso descrito en un trabajo previo (Fajardo et al., 2015).

2.4 Preparación del especímen y aplicación de curado.

Los especímenes fueron demoldados una vez cumplidas 24 horas desde su fabricación. Posteriormente, se realizaron cortes en las extremidades (a 25 mm) en cada especímen, esto para evitar los efectos de la bordadura producidos durante la preparación y la moldura. Luego, se realizaron los cortes para obtener especímenes de 50 mm de largo, como se muestra en la Figura 1.

![Figura 1. Obtaining of the cross sections from the specimen of mortar for the implementation of treatment with NBS.](image)

La aplicación de la solución con NBS se realizó durante el proceso de curado. Se preparó una solución utilizando 0.1% de NBS del volumen de agua utilizado en el curado. La aplicación de la solución se realizó sobre la superficie formando un film de agua de 20 mm de altura (véase Figura 2), que se mantuvo durante 3 días. Se utilizaron especímenes de referencia (CNT) donde se empleó agua potable para curado.

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2.5 Caracterización de CNT y NBS tratados especímenes

Después de realizar el tratamiento con NBS, los especímenes fueron cortados para determinar la resistividad eléctrica en 3 zonas de 16 mm cada una (véase la Figura 3). Zona 1 (Z1), siendo la más cercana a la área donde se realizó el curado con NBS, zona 2 (Z2) tratamiento intermedio, mientras que zona 3 (Z3), es la más lejana a la superficie tratada. Las secciones obtenidas fueron colocadas en inmersión en agua para saturar los especímenes. Posteriormente, los especímenes fueron monitoreados constantemente durante 112 días para determinar el efecto generado por el NBS.

Figure 3. Secciones de los especímenes de yeso para la evaluación de resistividad.

Physisorpción de N$_2$ y pruebas de resistividad eléctrica fueron realizadas en los especímenes de CNT y NBS tratados como se describió en el estudio previo (Fajardo et al., 2015).

2.6 Exposición a medios agresivos

Una vez que las mediciones de resistividad eléctrica mostraron un cambio en la microestructura de los especímenes de yeso (un aumento en la resistividad eléctrica), estos fueron expuestos a un ambiente rico en CO$_2$ o Cl$^-$ para determinar el efecto del NBS en dos medios agresivos diferentes.

En el caso de tratamiento con CO$_2$, se tomaron 3 especímenes para los morteros de CNT y NBS, que fueron cubiertos en el perímetro con pintura epoxi (Epoxacryl E-6000) y sellador con Alkafín (sellador acrílico, Comex®) para promover un cruzamiento de carbonatación. Subsecuentemente, las muestras fueron colocadas en un ambiente a 30°C con una humedad relativa de 60 ± 5% y una concentración de CO$_2$ del 10%. Al final, la profundidad de la carbonatación fue determinada.
using the procedure described in a previous work using phenolphthalein as indicator (Fajardo et al., 2015).

Figure 4. a) Specimen exposed in aggressive environments and b) sections obtained to determine chlorides content after exposure.

Another series of specimens were placed in water for a period of 56 days in a 165 ± 1 g/l NaCl solution as indicated in the standard ASTM C 1556. In order to determine the concentration of chlorides, 10 g of powder from each zone of the manufacture tablets were obtained. Then, the content of chlorides (total vs % by weight of cement) was obtained in a X-ray fluorescence - Epsilon 3 X. It is noteworthy that for this test 50 mm sections were divided into 3 zones called Z1, Z2 and Z3 approximately 16 mm thickness (see Figure 4b).

3. RESULTS AND DISCUSSION

Figure 5 presents the results obtained from the electrical resistivity in mortar specimens corresponding to different areas of the CNT and NBS specimens. The 10 kOhm.cm electrical resistivity threshold (URE) was set as a dotted horizontal line in the figure. This value is commonly used as an effective parameter to evaluate the risk of corrosion of steel embedded in concrete, particularly when corrosion was induced by aggressive agents (Polder, 2001; Koleva et al., 2008). A concrete matrix that will exceed this threshold goes from a high to low/moderate corrosion risk of reinforcing steel. The time expressed in the figure, represents the immersion time from 1 to 112 days after having been subjected to curing with NBS for 72 hours. In general, there is an ascending behavior during the first 56 days, achieving an increase in resistivity ranging from 34-36 kΩ.cm in the NBS treated specimens, while CNT specimens remained around 5.0 kΩ.cm. It can be observed that after 28 days the NBS treated specimen resistivity increased up to 7 times above the CNT specimens for the case of zones 1 and 2. This increase was superior to that obtained in a previous work where up to 3.5 times was achieved using a more complex system of introduction (Fajardo et al., 2015).
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Figure 5. Evolución de la resistividad eléctrica de los especímenes CNT y NBS durante el tiempo de inmersión.

Similarmente, un incremento en la resistividad eléctrica en los especímenes NBS tratados desde el día 3 por colocarlos por encima de la URE, siendo más notable para Z1 y Z2, con una resistividad que oscila entre 12-15 kΩ.cm, lo que indica un incremento en la durabilidad a partir de la reducción de la permeabilidad. Es importante mencionar que durante esta fase, el cementante aún presenta reacciones de hidratación, por lo que se puede inferir que la inducción de NBS durante el curado podría ser más efectiva que otras técnicas relativamente más complejas basadas en aplicaciones de campos eléctricos o sistemas de huecos en concreto endurecido (Fajardo et al., 2015; Kawashima et al., 2013; Kupwade-Patil et al., 2016; Sanchez et al., 2014; Zhu et al., 2016).

Aunque los mecanismos no son totalmente definidos, algunos autores inferen mecanismos generados por la rápida interacción del NBS con la matriz cementante generando precipitación y reacciones secundarias de floculación del NBS con la solución de poros. Así, el NBS impide y bloquea un gran número de pequeños poros capilares, exponiendo la porosidad > 90 Å (9 nm). Cerrando el acceso principal a los poros interconectados y los poros de la gel. Esto, debido a la interacción del NBS durante las reacciones de hidratación reduciendo 90% de la adsorción de N₂ en los especímenes tratados con NBS respecto a los especímenes CNT (Cai et al. 2016; Zhang et al., 2011).

Figura 6 presenta los resultados del diámetro y área de poros obtenidos mediante la técnica de Physisorption de N₂ en zona 1 de los especímenes CNT y NBS tras 14 días de inmersión. La porosidad en el rango de 25 - 450 Å (2.5 a 45 nm), se observa con un comportamiento bimodal, destacando la área de poros mesoporósos (< 10 nm). Los especímenes tratados con NBS disminuyen la permeabilidad, al bloquear un gran número de poros capilares pequeños, exponiendo la porosidad > 90 Å (9 nm). Cerrando el acceso principalmente a los poros interconectados y poros de la gel. Esto, debido a la interacción del NBS durante las reacciones de hidratación reduciendo 90% de la adsorción de N₂ en los especímenes tratados con NBS respecto a los especímenes CNT (Cai et al 2016; Zhang et al., 2011).
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Figure 6. The pore size distribution for CNT and NBS specimens obtained after 14-day of immersion.

Figure 7 shows the isotherms of adsorption of nitrogen in CNT and NBS treated specimens, showing the presence of isotherms of type IV (according to IUPAC) concerning the characteristics of mesoporous and macroporous materials of bottle or irregular neck type.

In general, there is a reduction in the volume of adsorption nitrogen around 90% in samples treated with NBS during the first 14 days of immersion with respect to sample CNT, indicating a reduction in pore diameters and therefore reduction permeability. Therefore, it is confirmed that, under the experimental conditions, using NBS in aqueous solution during curing promotes the entry of NBS reduce small capillary pores in accordance with the results obtained by Hou, these being responsible of the permeability in portland cement base materials (Cai et al 2016; Hou et al., 2013, Hou et al., 2015).
In Figure 8 are shown the results of mortar specimens that were exposed in an environment rich in CO$_2$ with the objective of evaluating their effect.

![Figure 8. Carbonation depth in the CNT and NBS specimens.](image)

There is a clear decrease in the depth of carbonation on mortar specimens treated with NBS regarding the CNT sample. It is therefore possible to conclude that the effect generated in the mortars by the NBS treatment is due to a decrease in permeability due to obstruction of bottleneck pore type. The obstruction causes a decrease of the interconduictivity and therefore an increase in the electrical resistivity of the cementing matrix.

Table 2 shown the results of mortar specimens exposed in an environment rich in Cl$^-$.  

<table>
<thead>
<tr>
<th>Zones</th>
<th>Total Cl$^-$ (% by weight of cement)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CNT</td>
</tr>
<tr>
<td>1</td>
<td>17.23</td>
</tr>
<tr>
<td>2</td>
<td>12.85</td>
</tr>
<tr>
<td>3</td>
<td>10.72</td>
</tr>
</tbody>
</table>

The results confirm a decrease in the concentration of chlorides, which represent a decrease in the diffusion of Cl$^-$ ions through the binder matrix in the specimens treated with NBS and consequent decrease of transport of aggressive agents through the mortar. Therefore, the decrease in the concentration of chlorides evidence a decrease in permeability, which is consistent with the results presented above.

The increase of the service life of newly placed RCS could be obtained when applying a treatment as described here. The curing process using NBS could be considered a new option to increase the durability during the construction process, which is the main problems of the loss of durability.

4. CONCLUSIONS

The NBS application induced during outer curing through a solution, according to the experimental conditions used here, leads to the conclusion that:

- The transport of moisture during the curing process favors the entry of the NBS towards the interior of the matrix binder.
- The resistivity of mortar treated with NBS increased up to 7 times above the CNT specimens from their first 21 days of immersion in water.
- The decrease in the adsorption of N$_2$ was attributed to the reduction of interconnection of
the porosity and therefore reducing the permeability, thus avoiding the introduction of ions Cl\(^-\) & CO\(_2\).

The NBS application during the curing process, may be promising in the increase of the durability in the RCS.

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6. REFERENCES


