CONCRETE POROSITY REDUCTION BY COLLOIDAL SILICA NANO TECHNOLOGY, PART 2: ONE YEAR RESULTS FROM DJENO WHARF*

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ABSTRACT

The permeability of portland cement concrete has a direct impact on durability, especially in marine and corrosive environments. The petrochemical industry has specific challenges with concrete durability in marine structures and concrete exposed to sulfurous compounds. Marine facilities such as quays, jetties, wharfs, and water intake and outfalls have shown deterioration of reinforced concrete due to chloride or sulfate ingress leading to corrosion. Post-set applied colloidal nano-silica has demonstrated the ability to reduce permeability of concrete, and can subsequently be hypothesized to extend the life cycle of petrochemical and other concrete structures.

This paper presents scanning electron microscope image analysis of precast concrete from a marine petrochemical export facility at various depths from areas treated with a spray-applied colloidal nano-silica versus areas left untreated. Additionally, chloride content and permeability comparisons are made. The concrete structure was approximately one-year old when treated, with cores taken approximately one year after treatment. The concrete was treated with colloidal nano-silica as a mitigation measure due to non-compliance with contract documents.

Keywords: Colloidal Nano-Silica, Porosity, Permeability, Durability

*Part one of this paper (same authors) was presented at CONSEC 2016 in Lecco, Italy

INTRODUCTION

Colloidal Nano-Silica (CNS) is a stable dispersion of small particles of amorphous silicon dioxide, typically between 1 and 500 nm, but sufficiently small enough to remain suspended in water without settling[1]. Colloids consist of particles with a size sufficiently small (≤ 1 μm) not to be affected by gravitational forces but sufficiently large (≥ 1 nm) to show marked deviations from the properties of true solutions[2]. CNS has been in use since the 1970s, originally developed to reduce crude oil seepage from capped undersea wells. Recent academic research has shown the effectiveness of CNS in Portland cement concretes by reducing chloride diffusion rates, decreasing drying shrinkage, increasing surface resistivity, and increasing strength[3].

The principal constituents of hydrated portland cement pastes are Calcium Silicate Hydrate (C-S-H) gel and Portlandite (calcium hydroxide). C-S-H gel occupies about 50-60% of the hydrated paste by volume and is the major contributor to the behavior of the paste. Calcium hydroxide also makes up a significant amount of the hydrated cement paste[4]. CNS, along with other silica-bearing materials such as fly ash and silica fume are classified as pozzolanic materials. Pozzolanic additives contribute to strength enhancement by producing additional C-S-H from calcium hydroxide. The reactions involved are complex, and are related to a number of factors such as particle size and dispersion, chemical composition, minerology, and morphology among others[5].

CNS is an excellent generator of the pozzolanic reaction, with its very small particle size and surface chemistry making it among the most reactive pozzolan sources known. CNS reacts with calcium hydroxide in the pore space to form secondary C-S-H, reducing the size of capillary voids and pores, which leads to a denser and more homogeneous structure, greatly improving the mechanical properties of the concrete. CNS has much more surface area than silica fume, making it able to achieve a higher level of reactivity when concrete is treated with equal amounts of each[6]. Multiple studies have shown that even a small addition of colloidal silica can improve the mechanical properties of cementitious materials[7].

Of particular interest is the effect of utilizing CNS as a post-set applied spray treatment. As concrete durability is quickly becoming a design concern in the United States in consideration of recent assessments of critical infrastructure life expectancy, some attention has been focused on concrete structures that have been designed without proper consideration given to environmental-related durability[8]. Permeability of concrete is often greater than optimal, even in concrete structures where all other mechanical properties of the concrete are satisfactory. Permeability is widely recognized as an indicator of concrete durability, especially in reinforced concrete structures. If CNS can be shown to be a mitigative measure for existing concrete to improve durability and extend life cycle, it may be an important tool for infrastructure asset owners and stakeholders. While laboratory data has been conclusive from many research teams globally, field studies providing information on pre- and post-treatment permeability and other parameters promises to be useful to specifiers seeking to identify mitigative measures to improve the durability of compromised concrete structures.

DETAILS OF THE STUDY

A large petrochemical provider is evaluating the effectiveness of CNS to protect concrete infrastructure. The permeability of portland cement concrete has a direct impact on durability, especially in marine and corrosive environments. The petrochemical industry has specific challenges with concrete durability in marine structures and concrete exposed to sulfurous compounds. Marine facilities such as quays, jetties, wharfs, and water intake and outfalls have shown deterioration of reinforced concrete due to chloride or sulfate ingress leading to corrosion.

The petrochemical company discovered that there were non-compliance issues with precast concrete in salt water wharf in the Guinea Gulf (Djeno Wharf) in Africa as originally installed. With the idea of proving colloidal nano-silica technology as a potential mitigative measure, the petrochemical company and CNS provider partnered to treat a part of the concrete wharf with a spray-applied CNS approximately one year after its installation. The CNS chosen for use is a proprietary blend of nano-sized amorphous silicon dioxide particles and dispersing aids in a water carrier. Treatment involves spraying of the CNS to rejection, defined by the manufacturer as application of a flood coat sufficient to remain surface-saturated after fifteen (15) minutes of standing time. A total of approximately 1,000 m^2 was treated with a product usage of approximately 4.9 m^2/L.

Approximately one year after treatment, cores were extracted from the concrete and delivered to a laboratory in Arles, France for analysis. Both treated and untreated areas were studied, utilizing measurements of capillary absorption according to the AFREM procedure, resistance of water penetration (NF EN 12390-8), and examination of the penetration depth of CNS by Scanning Electron Microscope (SEM) and X-Ray Spectroscopy. The concrete studied is exposed to alternating wetting and drying cycles from seawater, and would commonly be characterized as being within the “splash zone”. A total of ten (10) cores were extracted, five (5) from treated areas, and five (5) from untreated areas.

Figure 1a and 1b: Underside (left) and Top (right) of Wharf

Capillarity

According to the AFREM procedure, samples were preconditioned by drying in a convection oven at 40° C until constant mass was achieved. The core specimens were then placed in sealed plastic bags and returned to the convection oven at 40° C for ten (10) days. At the end of the 10-day period, the cores were removed and stored at a temperature of 20° C, and the sides of the cores coated with resin to ensure moisture movement through the ends only. The surface of the core was then immersed in water with a maximum height above the sample of 3 mm inside a container covered with a lid. Mass measurements were then made at various times up to 24 hours. The capillarity water absorption coefficient, Ca, was then calculated:

$$C_a = \frac{M_x - M_0}{A} \quad \text{(Eq. 1)}$$

Where:

C_a: capillary water absorption coefficient (kg/m^2)

M_x: mass of the sample at a given time (kg)

M_0: initial mass of sample (kg)

A: cross-sectional area of sample (m^2)

Table 1: Results of Capillarity (Average)

Time (hours)	Untreated C_a (kg/m^2)	Treated C_a (kg/m2)	% Improvement (U-T/U)
1	0.48	0.16	66 %
4	0.67	0.29	57 %
8	0.84	0.42	50 %
24	1.12	0.64	42 %

Resistance of Water Penetration (EN 12390-8)

The resistance of water penetration test was performed by placing cores inside a machine that exposed the surface of the concrete to 5 bar hydrostatic pressure. The test was run for 72 hours then concrete was split open and the depth of water penetration is measured.

Table 2: Results of Water Penetration Testing

Average Untreated Depth of Penetration (mm)	Average Treated Depth of Penetration (mm)	% Improvement (U-T/U)
78	43	45 %

X-Ray Spectroscopy

The x-ray spectroscopy analysis of untreated versus treated concrete provides some interesting results. First, note the presence of a chloride (Cl) peaks in Figure 2a, below. When compared to the treated concrete (Figure 2b) the absence of a Cl peak is noteworthy. Additional information gained from the analysis includes the significant reductions of carbon (C), sodium (Na), sulfur (S), and the significant increase in silicon (Si) and aluminum (Al).

One explanation for both the disappearance of Cl and significant reduction of Na from the untreated to the treated x-ray spectroscopy results is that seawater containing salt (NaCl) has infiltrated the untreated concrete, while being either kept from entering or purged from the treated sample. There are peaks of Carbon (C) and Sulfur (S) in the untreated samples that are typically not seen in most concrete. When the use of the concrete wharf is examined, it can explain the potential explanation for the peaks. The concrete wharf is an active infrastructure asset in the petrochemical industry. Many petrochemical products contain high levels of sulfurous compounds. The untreated concrete may have allowed sulfur-bearing petrochemicals to enter, while the treated concrete may not have allowed as much to penetrate to the depth examined.

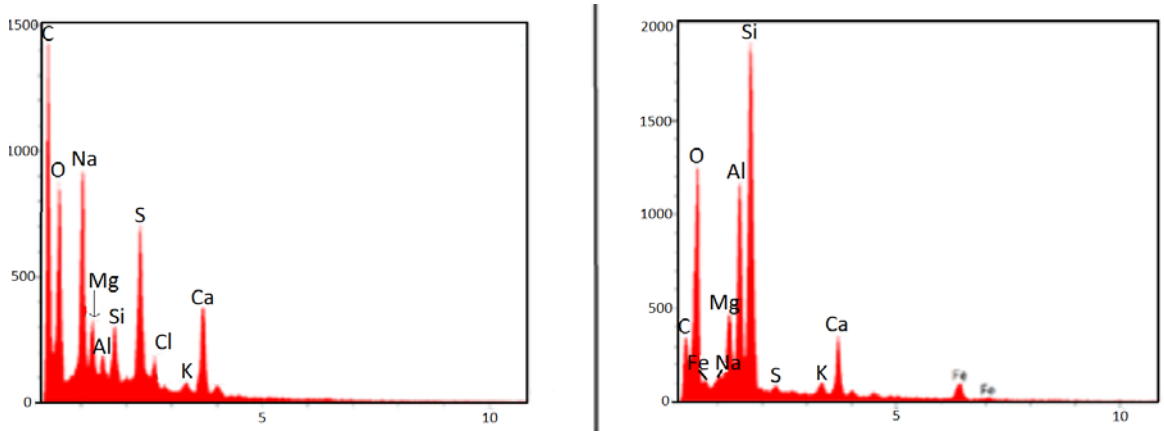

Figure 2a and 2b X-Ray Spectroscopy Results of Untreated (left) and CNS-Treated (right) Concrete

Also, exterior concrete can be susceptible to carbonation, and CNS treatment has demonstrated a slowing of carbonation effects in the laboratory. An explanation of the difference in the carbon (C) detected is that the untreated concrete has experienced a level of carbonation not present in the treated concrete. Additionally, the high silicon (Si) peak shown

in the treated concrete analysis can be explained by the addition of colloidal silica, and its reaction products, calcium silicate hydrate (C-S-H) and calcium aluminosilicate hydrate (C-A-S-H). The C-A-S-H reaction product is likely evidenced by the higher aluminum (Al) peak in the treated concrete.

Scanning Electron Microscopy

From the treated and untreated concrete, scanning electron microscope (SEM) digital images were obtained. The images were subjected to analysis utilizing ImageJ, a software product developed by the United States National Institute of Health. The procedure included sub-dividing each image into nine regions, analyzing each subdivision with the software, then combining results to obtain averages. A total of thirty-six (36) images were analyzed. Voids were identified visually, using a mapping tool included in the software package that allows outlining and filling of suspected voids. Images were identified by a numerical indicator only, with visual void identification run blind and only related to the area of extraction afterward. Results of number of voids and void area was supplied by exporting software data to a spreadsheet where calculations were performed.

Table 4: Image Analysis Results

	Average Number of Voids	Average Void Area μ^2	% Void Area
Untreated	95	0.53	5.2
Treated	77	0.25	3.3

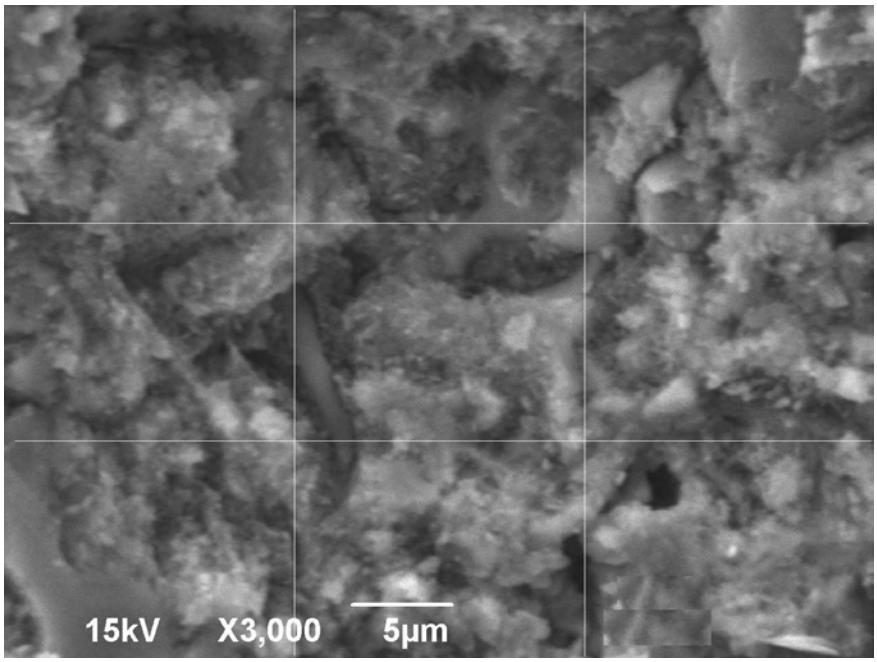

Figure 3: Untreated Concrete, 15mm depth

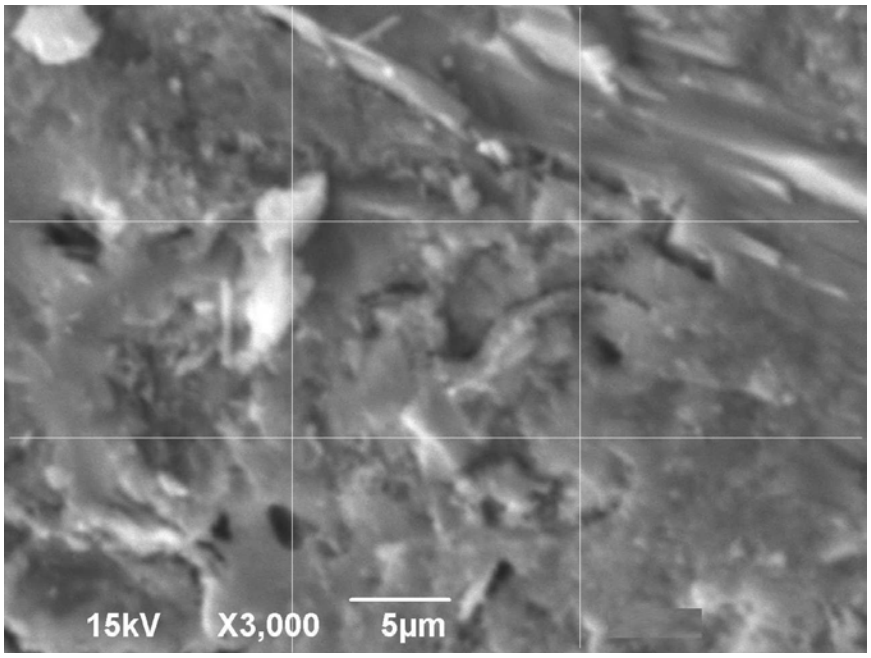

Figure 4: CNS-Treated Concrete, 15mm depth

Figures 3 and 4 above show the distinct difference between void space associated with untreated concrete (fig. 2) and treated concrete (fig. 3). The treated concrete exhibits a more uniform, solid appearance compared to the untreated concrete.

Life Cycle Corrosion Modeling Applied to Djeno Wharf

Life cycle prediction modeling was then performed using test results from untreated and treated concrete permeability to establish estimated chloride diffusion rates. Although chemical determination of chloride content was performed in the study, the depths examined were at too coarse a resolution to definitively determine diffusion, and sufficient time had not passed to establish a penetration gradient that would allow such calculations.

Life 365 was chosen as the software for lifecycle modeling. The service life (in years) produced by the Life 365 software assumes that the primary mode of degradation of concrete is by chloride ingress attacking the rebar. The calculations involved are based on 1st and 2nd order Fickian diffusion models. An initial period to rebar exposure to chlorides is predicted based on the diffusion coefficient and the depth of cover. The propagation time is then calculated to see how long the rebar will take to corrode enough to affect the structural properties of the concrete. Using a stochastic approach, Life 365 estimates the distribution of possible service life for a given concrete mix and corrosion protection strategy[9].

The first step was to establish a chloride diffusion rate for both untreated and treated concrete from available permeability data. Although theoretical, and significant debate exists about the effects of ions present in the chloride other than concrete, establishing a chloride

diffusion rate can be shown to be proportional within a given concrete for two separate samples given that the constituent materials are the same (i.e., the concrete is from the same load or production cycle). According to Lizarazo-Marriaga and Claisse, the relationship between chloride intrinsic diffusion ($D_{int\text{-}cl}$) and apparent diffusion coefficients ($D_{app\text{-}cl}$) is defined through the porosity of the material (ε) and the binding capacity factor (α)[10]. If the binding capacity factor (α) is assumed to be the same for the cores taken from the same concrete, the following equation from Lizarazo-Marriaga and Claisse can be applied to establish the proportionality of porosity to mean chloride diffusion rate (D).

$$\frac{\alpha}{\varepsilon} = \frac{D_{\text{int}-Cl}}{D_{app-Cl}} \qquad \text{(Eq. 2)}$$

Next, rebar cover was set to 50mm, with total thickness set to 350mm. Surface concentration was set at 1.0 % chlorides with an immediate (zero years) time to build-up which corresponds to the software's default values for seawater splash zones. The concrete design used was a 0.42 w/cm ratio 50% ground, granulated blast furnace slag mix. Weather conditions were set to reflect historical averages for the Congo near the Guinea Gulf. Corrosion propagation was left at the default six years from time of contact. Chloride diffusion rate (mean D) was allowed to be calculated for the untreated concrete for the mixture proportions. The mean D was then proportionally adjusted to reflect the EN-12390-8 results for hydrostatic pressure resistance for treated versus untreated concrete, a reduction in mean D of 45%. The software-calculated mean D value was 6.03 x 10^{-12}; the calculated mean D value for treated concrete was 3.32 x 10^{-12}.

Table 5: Life 365 Results

Condition	D (m^2/sec)	Init. (yrs.)	Prop. (yrs.)	Service Life (yrs.)
Untreated	6.03e-12	4.4	6.0	10.4
Treated	3.32e-12	14.1	6.0	20.1

Although unconventional, the above analysis corresponds well with chloride diffusion results obtained in previous laboratory chloride ponding experiments utilizing the same CNS product[11].

CONCLUSIONS

The analysis of concrete from a wharf structure treated after one year of age and examined after one year after treatment demonstrates the effectiveness of CNS in reducing capillarity and water penetration under hydrostatic pressure. The x-ray spectroscopy analysis is strong evidence of CNS's ability to deny access to contaminants like salt water and petrochemicals, and is also verification of the form taken by the CNS's reaction products. Finally, the SEM

image analysis shows a marked difference between the untreated and treated concrete void structures, establishing the CNS effectiveness at 15mm depth.

The capillarity results produced in this study indicate a possible trend of results merging over time, an effect not noted in previous studies. Further work should examine capillarity effects of CNS over longer periods.

Previous work has established improvements that can be made to the mechanical properties of concrete when CNS is applied at the time of concrete casting. Continued examination of CNS and its effects in the field are warranted to further explore this material's capabilities as a mitigative measure for existing structures, especially where a durability concern exists. By reducing permeability, CNS reduces chloride intrusion and thereby slows rebar corrosion rates. Other contaminants such as sulfates would likely be similarly be restricted in their transport. By taking away the pathways (capillarity) utilized for contaminant transport, CNS offers promise as a mitigative measure to extend the life of concrete infrastructure.

In general terms, the cost of application of CNS is reasonable compared to other corrosion mitigation strategies. Because CNS causes a change in the pore structure of the concrete through the pozzolanic reaction, a single application is typically all that is required. Other measures, especially coatings, often require multiple applications over the life of a structure. As field performance corroborates laboratory results, CNS is emerging as a technology that bears consideration for corrosion mitigation.

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