

# Use of nanomaterials for Concrete Pipe Protection

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## Abstract

This paper describes an innovative method for mitigating microbial induced corrosion (MIC) in concrete sewer pipes by driving nano-particles containing an antimicrobial agent into the wall of the steel-reinforced cementitious pipe using electrokinetics, an electrical deposition method. Electrokinetic coating involves the application of a weak electric field between the pipe reinforcement and a properly charged solution of nanoparticles. The electrical potential difference drives the nano-particles in the solution into the hardened concrete paste via its pore structure, simultaneously transporting the antimicrobial agent(s) into the pores. This new method of coating creates a mechanical anchorage between the coating liquid and the host matrix, which has inherent advantage over traditional brush or spray-on coating operations. The paper provides a brief overview of recent advances in spray-on coating and lining methods for protecting concrete pipe used in wastewater conveyance systems. Thereafter, a brief description of electrokinetics is provided. Preliminary results of an experimental testing program involving electro-kinetically coating of 35 mock concrete pipe specimens using cuprous oxide, a heavy metal oxide known to have a toxic effect on sulfate reducing bacteria (SRB), are presented. The preliminary testing program focused on examining the effectiveness of using electrokinetics for the treatment of new pipes, partially deteriorated pipes and pipes that exhibited moderate-to-severe deterioration due to sulfuric acid attack. The design of the experiment and the execution of the electrokinetic coating process are also described. The results suggest that the approach could potentially serve as an effective method for coating of new and partially deteriorated reinforced concrete pipes.

## Introduction

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Microbial induced corrosion (MIC) in concrete sewer conveyance systems is one of the most common types of deterioration encountered in such structures. This corrosion involves a chemical reaction between hydration products in the hardened concrete and biologically produced sulfuric acid, which alter the concrete chemical composition leading to early deterioration, loss of strength and, in extreme cases, pipe collapse due to inability to resist external earth and live loads.

MIC often involves two types of bacteria which are common to many sanitary sewer systems, namely sulfate reducing bacteria (SRB) *Desulfovibrio desulfuricans* and sulfide oxidizing bacteria *Thiobacillus thiooxidans* (also known as 'concretivorous', or 'concrete eater'). Sulfur present in sewage is transformed into hydrogen sulfide by sulfate reducing bacteria which tend to grow on the wet perimeter of the sewer pipe. In areas of turbulent flow, the hydrogen sulfide is released into pipe's head space. The *Thiobacillus* bacteria, which grow on the sewer crown region above the water line, convert the hydrogen sulfide to sulfuric acid in presence of oxygen (Pomeroy, 1946). The chemical reaction associated with production of sulfuric acid is (EPA, 1992):

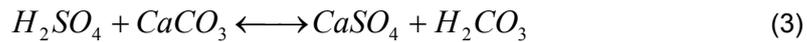
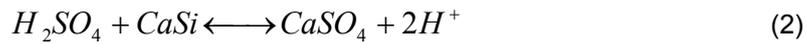


## The corrosion mechanism

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A freshly placed concrete has a pH of approximately 11 – 13, depending upon the mix design. This pH is due to the formation of a stable compound, calcium hydroxide  $Ca(OH)_2$ , a common by-product produced during the hydration of cement. This initial high pH on the surface of the concrete will not allow any bacterial growth; however, this high pH state lasts for only a short period of time and the pH level slowly declines over time, due to interaction with carbon dioxide ( $CO_2$ ) and hydrogen sulfide ( $H_2S$ ) gases. These gases form weak acidic solutions when dissolved in water (carbon dioxide forms carbonic acid and hydrogen sulfide forms thiosulfuric acid and polythionic acid), that lower the pH of the concrete surface to 9 or 9.5. *Thiobacillus* bacteria that have a unique ability to convert hydrogen

sulfide to sulfuric acid in the presence of oxygen start colonizing at a pH of about 9. The first colony of bacteria reduces the surface pH value from 9 to 6.5 by excreting sulfuric acid. These bacteria will not be able to survive at pH values lower than 6.5, and thus the colony dies and the residence is then taken over by another species that is capable of surviving below a pH of 6.5. This newly formed species of *Thiobacillus* further reduces the pH value from 6.5 to 4 before dying off. This process of colonizing and dying of bacteria continues, until the pH at the surface of the concrete can be brought to a value as low as 1 or 0.5 (Islander et al., 1991). The sulfuric acid produced by the bacteria interacts chemically with the hydration products in the hardened concrete paste. The chemical reactions involved in corrosion of concrete are:



The primary product produced during concrete decomposition by sulfuric acid is calcium sulfate ( $CaSO_4$ ), that when it hydrates becomes 'gypsum'. This material has low structural strength, especially when wet. It is usually present in corroded sewers as a pasty white mass at the crown region above the water line. Due to its lower shear strength and poor adhesion, the gypsum is washed off by the wastewater flow, exposing fresh concrete to further acid attack. An example of severe MIC in a 27 year-old concrete sewer pipe is shown in Figure 1.



Figure 1. Close-up of a 900 mm concrete sewer pipes that experienced severe MIC. The steel reinforcement ribs are either gone or in an advanced corrosion state. The white solids are MIC corrosion products (marked by red circles)

## Current approaches

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A large number of methods have been developed to mitigate MIC in wastewater collection systems. The following discussion will consider only approaches that involve applying a protective coat to the host pipe internal surface. Spray lining is the most widely used coating technique. However this method suffers from several disadvantages. It is often difficult to create proper adhesion between the coating material and the internal surface of the pipe. Also, the “rebound” effect from hurling the coating material at the pipe’s wall can result in uneven coating thickness. Combined with a non-uniform application, this uneven layer thickness tends to result in an uneven stress loading and subsequent premature failure. In summary, since the coating material does not penetrate the pipe surface, it tends to flake and fall down with time under loading from shrinkage, mechanical loading from the transported media and/or cracks induced by differential settlement of the pipe (Dietrich, 1989; James, 2003).

Another common method of protection is lining of the pipe internal surface with a chemically stable material. There are different methods of lining such as cured in place pipe (CIPP), fold and formed in place (FFP) and Deform-reform pipe (DRP), Rotaloc liner and Rib Loc Expanda liner. CIPP employs a chemically stable fabric with a thermosetting resin, where as FFP, DRP, Rotaloc liner and Rib loc expanda liner methods use PVC or HDPE pipe to internally line the deteriorated host pipe. Properly applied, these methods will serve their purpose for a long period of time. The short comings of lining methods include the relatively high costs associated with set up and installation and a close attention to quality control in the remote lining processes. In addition some methods require a by-pass.

## Literature review – Recent advances in surface treatment methods for concrete sewer pipes

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**Controlling Sewer Crown Corrosion Using the Crown Spray Process (James, 2003):** Originally proposed by Esfandi (1986) and later adopted and further developed by the sanitation group of Los Angeles County, California, the “crown spray” process involve a spray system mounted on a floating platform that sprays the crown region of the sewer pipe with magnesium hydroxide. The purpose of crown spray process is to neutralize the acid that has been generated by the Thiobacillus bacteria at the crown region of the pipe by spraying it with a high pH material (magnesium hydroxide), thus elevating the region’s alkalinity. The spray process needs to be repeated on the regular basis (time between applications approximately 6-9 months) due to depletion and washout of the magnesium hydroxide.

**Protection against MIC using 100% solid polyurethane (Shiwei, 2006):** A method of treating concrete pipes against MIC by employing 100% solid polyurethane instead of PVC and coal tar. The 100% solid polyurethane coating was developed at Madison Chemicals, and is claimed to be more economical than PVC and more reliable than coal tar. Test results are provided for pressure, performance and bond strength. The solid polyurethane coating was tested under laboratory and full-scale conditions for a 5-month period. During the tests, no defects such as blistering, cracking, spalling or sticking were noticed. The product was also reported to perform satisfactorily when tested for chemical resistance (vapor and liquid phase tests) and bond strength (ASTM D4541 and ASTM C321).

**Corrosion Control in Concrete Pipe and Manholes, (William, 1998):** Conshild is an antimicrobial chemical which is applied to the internal wall of the pipe to inhibit the growth of bacteria on the pipe surface. It is typically applied by mixing it with concrete and spraying it as shotcrete. Other application modes include mixing it with an epoxy, with the mixture applied to the concrete surface using spraying equipment.

**Effect of metal oxide coating on generation of sulfide in concrete sewer pipes (Hewayde et. al, 2005):**

Hewayde et al. studied coating a concrete pipe with copper oxide (CO) and silver oxide (SO) to provide bio-toxic surfaces. The experiment consisted of three concrete pipes, out of which two were internally coated with CO and SO, while the third served as a control. The heavy metal oxides were mixed with epoxy and sprayed on the internal surface of the pipe to a thickness of 350 microns. Specimens were then filled to a two third depth, with a nutrient solution that has a sulfate concentration of 350 mg/L and dissolved oxygen concentration of 0.5 gm/L. Next, six liters of bacterial solution that had *Desulfovibro Desulfuricans* bacteria were added to each of the tanks. The pipes were

then filled to the brim with a nutrient solution. The flow inside the pipe was maintained at 26 L/min, simulating a worse case condition in gravity sewer pipes. At the conclusion of the test period the bacterial growth in the coated pipes was found to be significantly lower (by up to 99%) than that of the control pipe. Also the formation of slime layer was almost absent in the coated pipes. This experiment proved that heavy metal oxides such as CO and SO at low concentrations have a considerable toxic effect on the bacteria species responsible for generation of the hydrogen sulfide and sulfuric acid. A potential problem identified during the study was the leaching of silver oxide into the nutrient solution due to poor bonding between silver oxide and epoxy, which led to SO flaking and mixing with the nutrient solution.

## **Electrokinetics – an overview**

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Electrokinetics is a technique that uses a low DC voltage across the electrodes to move particles or contaminants in a porous medium. Electrokinetics comprises three major processes – electrophoresis, electro-osmosis and electro-migration. Electrophoresis is the movement of colloids, or charged particles, under the influence of an electrical field; electro-osmosis is the movement of fluid, or, in this case, coating solution, through the capillaries and pores from the anode to the cathode. Electro-migration is the movement of ions or ionic complexes.

One of the earliest applications of electrokinetics took place during the 1960's, as part of an attempt to extract heavy metals and organic contaminants from soils and ground water (Acer 1993). Since then it has been used as basis for many other applications including:

1. Removal of heavy metals from mine tailings (Kim et al, 2002).
2. A permeation technique for injecting grouting material into silty soils to enhance their strength properties (Thevanayagam, 2003)
3. Chloride extrication and re-alkalization of reinforced concrete (Velivasakies et al., 1998).

## **Proposed work**

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This paper describes a innovative technique that can be used to coat a concrete pipe using electrokinetics. The process was developed to overcome problems such as poor adhesion, flaking and shrinkage of a coating material that were encountered in traditional spray-on coating processes. The benefits of coating a pipe with heavy metal oxides were demonstrated by Hewayde et al (2005). The present work aims to address the adhesion problem, and focuses on the development of a new coating process in which nano-scale particles of cuprous oxide are driven into the concrete under the influence of a weak electric field.

## **Experimental procedure**

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The experimental design involves a total of 35 mock concrete pipes. The results reported in this paper focus on the testing and results from a pilot study of three specimens, intended to provide an indication of the effectiveness of the proposed coating procedure for new concrete pipes, moderately deteriorated concrete pipes and severely deteriorated concrete pipes. Of the three specimens, one serves as a control (e.g., newly installed pipe), the second specimen was degraded to represent a partly corroded pipe (i.e., exposure of the coarse aggregates), while the third specimen was degraded to represent a moderate-to-severe corroded pipe (loss of coarse aggregates; random exposure of steel reinforcement). The degradation of the specimens was accomplished by filling a cavity in their center with sulfuric acid solution (pH = 0.7), which was refreshed regularly until the desired effect was reached. Following the surface preparation treatment, the three specimens were electrokinetically coated using a cuprous oxide solution. Following the coating process, a series of optical and chemical tests were undertaken to evaluate the effectiveness of this coating process in terms of the extent of penetration of the nanoparticles into the concrete and the concentration of the heavy metal as a function of depth.

Each of the mock concrete pipes was cylindrical in shape, 300 mm in height and 150 mm in diameter. A void was formed in the center of each cylindrical specimen. The void started at the top surface of the specimen, had a diameter of 37 mm and extended to a depth of 250 mm, allowing the specimen to serve as a liquid holding container. The concrete mix design for all specimens consists of Type II

Portland cement, water-cement ratio of 0.45, and 9.5 mm diameter coarse aggregates. A super plasticizer was added to the mix at a ratio of 240 cc per 45 kg to reduce the vibration force required for proper consolidation of the specimen. The total amount of concrete mixed to prepare 35 specimens was 420 Kg, which included 93 Kg of Portland cement, 42 Kg of water, 137 Kg of fine aggregate and 148 Kg of coarse aggregate. The ratio of fine to coarse aggregate was 1:1.08. (ACI 211.1-91)

Commercially available plastic cylindrical molds (300 x 150 mm) were used to prepare the specimens. The central void was formed by inserting a 37 mm diameter PVC pipe into the center of the mold. The lower end of the PVC pipe was blocked using expandable foam to prevent the fresh concrete from entering the cavity. The PVC insert was secured to the mold to prevent it from 'floating' during the casting of the concrete.

The steel reinforcement consists of fine gauge welded wire reinforcement fabric that served as both transverse and longitudinal reinforcement. The mesh was cut into rectangular shapes of dimensions 292 mm x 319 mm. The reinforcement fabric was then wrapped around four 6 mm diameter threaded rods to form a cylinder 100 mm in diameter. Steel ties were used to secure the reinforcement fabric and threaded rods. The threaded rods were 355 mm in length and served both as a longitudinal reinforcement as well as the terminals for the power supply. Figure 2 presents a schematic diagram of a mock pipe specimen.

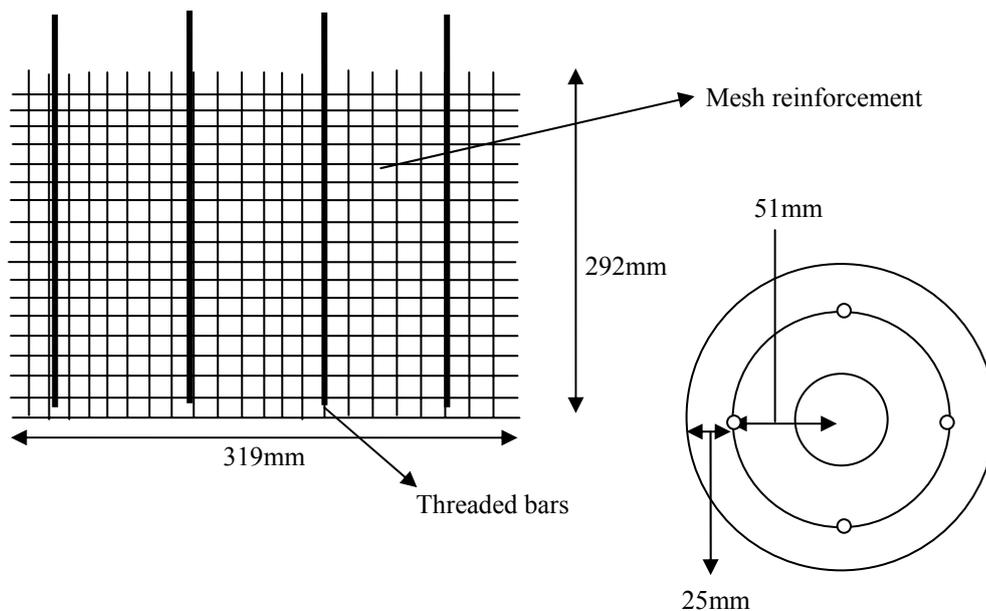


Figure 2. Schematic diagram of a mock pipe specimen

The reinforcement cage was placed inside the cylindrical mold and wet concrete was poured, while the PVC insert was maintained at the center of the mold. The PVC insert was removed three hours following placement of the concrete with care so as not to disturb the concrete specimen. The specimens were allowed to cure in a water holding tank for a period of 28 days (as per ASTM C 31). Following the curing period the specimens were removed from the tank and air dried. No breaking agents were applied to the PVC pipe inserts to avoid altering the surface characteristic of the specimens' inner wall. The 28 days compressive strength of the batch was obtained by conducting a standard compression test on 3 solid cylinder specimens, resulting in an average compressive strength of 37.6 MPa (5456 psi).

## Solution preparation

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The chemical solution used for cuprous oxide deposition was prepared based partially on work reported by Jongh et al (1999), which successfully electrodeposited  $\text{Cu}_2\text{O}$  (cuprous oxide) on a transparent conducting substrate using an alkaline Cu (II) lactate solution to keep the cuprous oxide in suspension. The pH of the solution was maintained between 8 and 9 to get a maximum amount of deposition. Forty five gm of  $\text{Cu}_2\text{SO}_4$  (copper sulfate) were dissolved in 75 mL of lactic acid to obtain the copper lactate solution. Next, 225 mL of 5 M NaOH (sodium hydroxide) was added in a titration-like fashion to maintain the pH of the solution. The final product was the dark blue colored solution shown in Figure 3.

The solution was stirred for 12 hrs prior to being poured into the void in the concrete specimens. A copper rod was placed in the solution to serve as the anode, while the steel reinforcement in the concrete served as the cathode. The electrokinetics process took place by applying 0.3 Amp of current continuously over a period of 5 hrs. The time of application of the electrical current was selected as the maximum beneficial period for such an electrokinetics process (i.e., optimal conditions). It is expected that in practical applications this time period will be greatly reduced while maintaining bulk of the benefits for the electrokinetics process.



Figure 3. cuprous oxide lactate solution poured into the a specimen (left); The electrokinetic coating process underway, note the copper electrode at the center of void (right)

## Preliminary results

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*Unaltered Specimen (control; fresh concrete pipe):* Following the electrokinetics coating process, the solution remaining in each of the specimen was removed and the inner wall of the “pipe” exposed by cutting ‘slices’ using a masonry diamond saw. The slices were inspected using a powerful optical microscope for evidence of copper particles deposited in the concrete matrix. The images from the optical microscopy examination revealed what appeared to be copper oxide particles deposition inside the concrete matrix. Figure 4 presents selected snap shots from the microscopy examination. Copper depositions can be identified as green color areas on the gray-white background of the hardened cement matrix. Images 4a and 4b display distinct green areas within the gray-white background typical for hardened Portland cement paste. These areas are suspected to be traces of copper oxide driven into the concrete matrix via the electrokinetics process. Images 4a and 4b were taken from the non-corroded and partially corroded specimens, respectively. In contrast, image 4c displays a uniform gray color, with no traces of green areas. This suggests that the copper-oxide did not penetrate into this specimen during the electrokinetics process. A possible explanation is that the weak electrical field is present between the anode and cathode only. Exposing the reinforcement resulted in a “short-

circuit” with the electrical current gradient flowing primarily to the partially exposed reinforcement rather than moving through the less conductive concrete material.

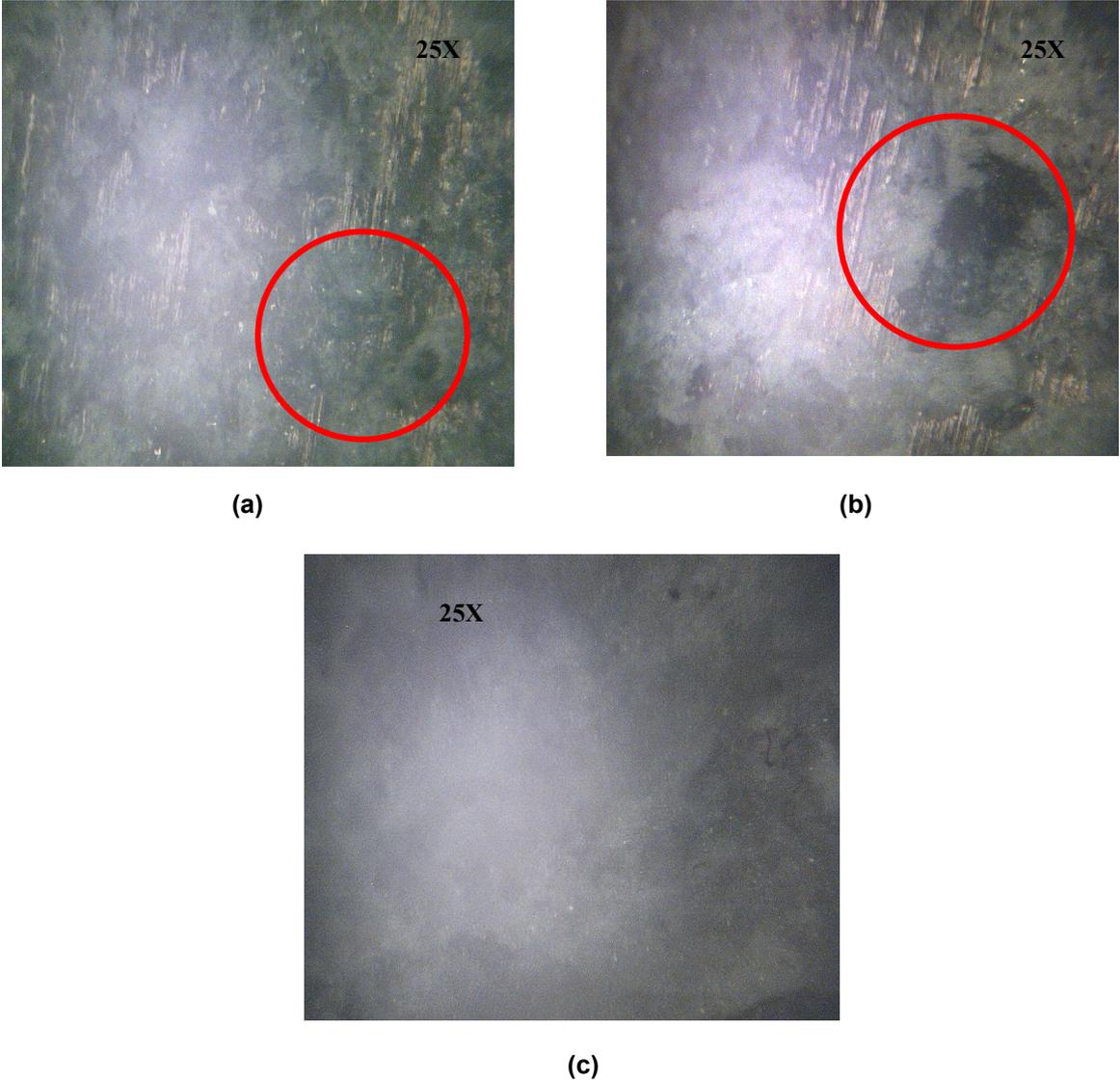


Figure 4. Images (a) and (b) showing copper-colored traces in the hardened concrete paste in the vicinity of the reinforcement in the new and partially corroded specimens, respectively; image (c) taken from the fully corroded specimen shows no traces of copper oxide. (All images taken using x25 optical microscope).

To confirm the hypothesis that copper oxide particles migrated into the concrete matrix, Atomic Absorption Spectroscopy analysis was performed on the three specimens, (i.e., non-corroded, partially corroded and fully corroded). The results of the AAS analysis are summarized in Table 1.

**Table 1. Results of Atomic Absorption Spectroscopy**

<b>SAMPLE (pre-treatment)</b>	<b>ABSORBANCE</b>	<b>PPM</b>	<b>% COPPER IN CONCRETE</b>
Non-corroded	0.012	1.231	0.022
Partially corroded	0.015	1.352	0.064
Fully corroded	0.003	0.312	0.009

## Discussion and conclusion

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The objective of this paper was to report on the study of a potential new coating process for pre-cast concrete pipes (dry-cast mix design; low w/c ratio; high compaction effort) using electrokinetics. The results demonstrated the feasibility of depositing copper oxide particles inside a dry-cast concrete matrix using a weak electric field. Optical microscopy images appeared to reveal the presence of copper oxide inside the concrete matrix in the case of new and partially deteriorated concrete pipe cylinders treated using the proposed coating process. No penetration of copper-oxide was detected in the fully deteriorated specimen, potentially due to the development of a "short-circuit" via the exposed reinforcement mesh that came into contact with the cuprous oxide lactate solution. Atomic absorption spectroscopy analysis proved that copper was deposited in the concrete matrix of all 3 specimens. However, in the case of the non-corroded and partially corroded specimens the percentage of copper was considerably higher than in the fully-corroded specimens. The treatment of the partially corroded concrete was shown to be the most successful than the non-corroded specimen that had added wall thickness and higher electrical resistance. Possible explanations are the larger surface area due to the corrosion process and the reduced wall thickness resulted in a higher concentration per unit volume between the pipe surface and the reinforcement. Further studies will include the durability of the coating under physical, thermal and chemical loadings, and a half-scale performance assessment where treated specimens will be exposed for simulated sewer and colonized with bacteria cultures. Research will also continue in terms of increasing the transport of copper into the concrete matrix and determining the level of copper in the matrix that will inhibit microbial induced corrosion.

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