Proceedings of the ASME 2010 3rd Joint US-European Fluids Engineering Summer Meeting and
8th International Conference on Nanochannels, Microchannels, and Minichannels
FEDSM-ICNMM2010
August 1-5, 2010, Montreal, Canada

FEDSM-ICNMM2010-31153

DIFFUSION ANALYSIS OF CHLORIDE IN CONCRETE FOLLOWING ELECTROKINETIC NANOPARTICLE TREATMENT

K. Kupwade-Patil
College of Engineering and Science
Ruston, LA, USA
kvk001@latech.edu

T.J. John
College of Engineering and Science
Ruston, LA, USA
tjj007@latech.edu

B. Mathew
College of Engineering and Science
Ruston, LA, USA
bma017@latech.edu

H. Cardenas
College of Engineering and Science
Ruston, LA, USA
cardenas@latech.edu

H. Hegab
College of Engineering and Science
Ruston, LA, USA
hhegab@latech.edu

ABSTRACT

Concrete is a highly porous material which is susceptible to the migration of highly deleterious species such as chlorides and sulfates. Various external sources including sea salt spray, direct sea water wetting, deicing salts and brine tanks harbor chlorides that can enter reinforced concrete. Chlorides diffuse into the capillary pores of concrete and come into contact with the rebar. When chloride concentration at the rebar exceeds a threshold level it breaks down the passive layer of oxide, leading to chloride induced corrosion. Application of electrokinetics using positively charged nanoparticles for corrosion protection in reinforced concrete structures is an emerging technology. This technique involves the principle of electrophoretic migration of nanoparticles to hinder chloride diffusion in the concrete. The re-entry of the chlorides is inhibited by the electrodeposited assembly of the nanoparticles at the rebar interface. In this work electrochemical impedance spectroscopy (EIS) combined with equivalent circuit analysis was used to predict chloride diffusion coefficients as influenced by nanoparticle treatments. Untreated controls exhibited a diffusion coefficient of $3.59 \times 10^{-12}\ \mathrm{m^2/s}$ which is slightly higher than the corrosion initiation benchmark value of $1.63 \times 10^{-12}\ \mathrm{m^2/s}$ that is noted in the literature for mature concrete with a 0.5 water/cement mass ratio. The electrokinetic nanoparticle (EN) treated specimens exhibited a diffusion coefficient of $1.41 \times 10^{-13}\ m^2/s$ which was 25 times lower than the untreated controls. Following an exposure period of three years the mature EN treated specimens exhibited lower chloride content by a factor of 27. These findings indicate that the EN treatment can significantly lower diffusion coefficients thereby delaying the initiation of corrosion.

NOMENCLATURE

A : area of the electrode surface
C_i : initial concentration
$C(x,t)$: Cl^-concentration at depth x and time t
$C(x,t_i)$: critical chloride threshold level
C_d : capacitance of electrode/electrolyte interface
C_s : Cl^- surface concentration
C_o : constant chloride content
$Erfc$: error function
D_a : achieved diffusion coefficient
d_o : constant diffusion coefficient
D_o : diffusion coefficient in oxidized state
D_R : diffusion coefficient in reduced state
F : Faraday's constant
k : constant
MC : mature concrete
MC^* : mature concrete through simulation
YC : young concrete
YC^* : young concrete through simulation
ω : angular frequency
R : gas constant
R_S : electrolyte resistance

R_S : electrolyte resistance
R_{ct} : resistance of charge transfer
t_i : time for initiation for corrosion
T : absolute temperature
Z' : real component of the impedance
Z'' : imaginary component of the impedance
Z_w : warburg impedance
Z_f : faradaic impedance
σ :coefficient of Warburg impedance

INTRODUCTION

Chloride laden environments can lead to chloride diffusion in concrete and cause a major durability issue [1-2]. A porous material like concrete can be highly susceptible to diffusion of deleterious species such as chlorides. The chlorides enter the capillary pores of the concrete and come into contact with the reinforcement as shown in Figure 1.

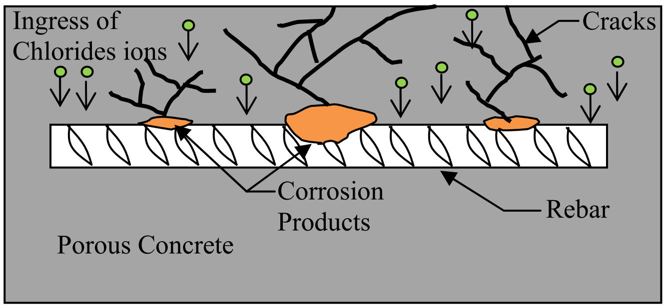


Fig 1. Concept of chloride induced corrosion

The chlorides react with the iron forming ferrous chloride [3]

$$\mathrm{Fe}^{2+} + 4\mathrm{Cl}^- \rightarrow (\mathrm{FeCl}_4)^{-2} + 2\mathrm{e}^- \qquad (1)$$

The ferric chloride reacts with the moisture to form ferrous oxide or rust $\mathrm{Fe(OH)}_2$

$$(\mathrm{FeCl}_4)^{-2} + 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Fe(OH)}_2 + 2\mathrm{H}^+ + 4\mathrm{Cl}^- \qquad (2)$$

The ferrous oxide builds up and develops tensile stress in the concrete. These stresses cause cracking in concrete and lead to the failure of the reinforced concrete structure.

The ingress of choride in concrete can be modeled using Ficks law of diffusion [4-6]. The chloride diffusion coefficient (D_a) at a specific distance from the rebar (x) is used to calculate the chloride content $\mathrm{C(x,t)}$

$$C(x,t) = (C_s - C_i)erfc\,\frac{x}{2\sqrt{D_a t}} + C_i \qquad (3)$$

Three common chloride diffusion models described in the literature are the Collepardi, LIGHTCON and HETEK models [4]. The Colleperadi model is preferred for relatively old reinforced concrete structures subjected to approximately 20 years of chloride exposure. The model assumes a constant chloride diffusion coefficient and chloride content. This model therefore uses a simple diffusion equation as shown below.

$$\frac{\partial C}{\partial t} = D_0 \cdot \frac{\partial^2 C}{\partial x^2} \qquad (4)$$

The LIGHTCON model uses a diffusion coefficient that is time dependent [4]. This diffusion coefficient is calculated using the power law.

$$D_a(t) = D_1 t^{-\alpha} \qquad (5)$$

Thus, the chloride contents were calculated using the modified diffusion equation,

$$C(x,t) = C_i + (C_o - C_i)erfc\left(\frac{0.5\,x}{\sqrt{D_a t}}\right) \qquad (6)$$

A drawback of the LIGHTCON model is that it cannot be used to predict the diffusion coefficient when exposed to a marine atmosphere. Constants need to be assumed for chloride contents when used for the marine splash zone and for concrete submerged in sea water. Piecewise linear diffusion coefficient functions are not used by the LIGHTCON model, but are important and present in the HETEK model.

The service life of a concrete structure can be organized into an initiation and a propagation period [7]. The time of exposure until chlorides have penetrated the concrete and the chloride content within the vicinity of the rebar is high enough to start corrosion is known as the initiation or diffusion period. The propagation period is the time from when the rebar starts to corrode until the end of the functional service life has been reached. Key parameters that govern the service life are the corrosion threshold limit, the chloride diffusion constant for initiation of corrosion, the transport properties of the concrete, and the distance of the reinforcement from the concrete [8]. The chloride deterioration process exhibits a diffusion period of 15 years for relatively low permeability concrete before the corrosion period starts as shown in Figure 2. In this case low permeability refers to concrete that is batched with a partial silica fume replacement of cement. The diffusion period is followed by a corrosion that averages 5 years leading to severe cracking and until the end of the functional service life [9].

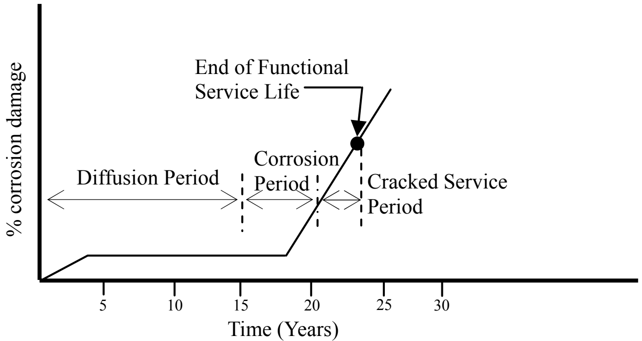


Fig 2. Chloride induced initiation process for reinforced concrete (Adapted from Weyers [8], pp.445-453 with permission).

The time in years to initiate corrosion (CI) is calculated using Equation No.7

$$CI\ (years) = \frac{Critical\ chloride\ threshold\ \left(\frac{kg}{m^3}\right)}{0.3\ \left(\frac{kg}{m^3}/year\right)} \qquad (7)$$

The chloride threshold contents are used to detect the corrosion initiation time in reinforced concrete based on estimated pH changes [9]. The critical chloride content can be predicted by,

$$C(x,t_i) = k\sqrt{t_i}\cdot\left\{exp^{\left(-\frac{x^2}{4Dt_i}\right)} - \left(\frac{x\sqrt{\pi}}{\sqrt{4D_a t_i}}\right)\cdot\left(1-\mathrm{erf}\left(\frac{x}{\sqrt{4D_a t_i}}\right)\right)\right\} \qquad (8)$$

ASTM C1556-04 was a traditional technique used to measure bulk diffusion coefficients of cementitious mixtures [10]. A new technique was used to evaluate the diffusion coefficients experimentally using the Nyquist plot (graph expressed in polar coordinates using gain and phase frequency response) which are obtained by electrochemical impedance spectroscopy (EIS) [11]. EIS is an experimental method for study of electrochemical systems using a range of frequencies. Equivalent circuits are used to represent the following equations as shown in Figure 3. The circuit is commonly referred to as the Randles equivalent circuit model.

$$Z' = R_s + R_{ct} + \sigma\omega^{-1/2} \qquad (9)$$

$$Z'' = \sigma\omega^{-1/2} + 2\sigma^2 C_d \qquad (10)$$

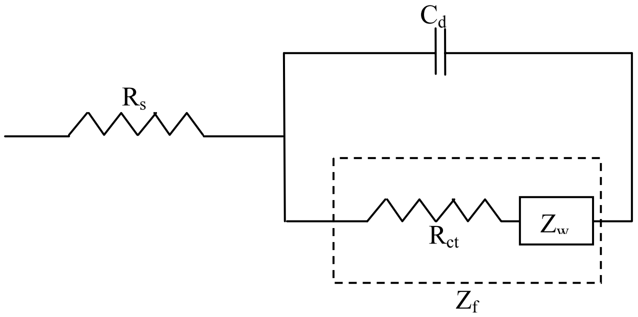


Fig 3. Randles circuit for measuring used for measuring diffusion coefficients

This equivalent circuit model consists of an active electrolyte resistance R_s in series with the parallel combination of double layer capacitance C_d and impedance, Z_f [12]. The equations 9 and 10 thus relate the coefficient of the Warburg impedance to the diffusion coefficient (σ).

Equations 9 and 10 can be solved for elimination of ω.

$$Z'' = Z' - R_s - R_{ct} + 2\sigma^2 C_d \qquad (11)$$

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}}\left(\frac{1}{D_0^{1/2}C_R} + \frac{1}{D_R^{1/2}C_R}\right) \qquad (12)$$

The Warburg impedance (Z_w) is also used to model the semi-infinite electrode resistance (R_s) of the Randles circuit and is obtained at a phase angle of 45 degrees in the low frequency region. Equation 12 can be used to determine the chloride coefficient (D_0 and D_R) which is one of the major factors used to predict the service life of the concrete.

Electrokinetic Nanoparticle (EN) treatment is a new repair strategy used to mitigate reinforcement corrosion in concrete [13-16]. This technique involves application of an electric field to inject the positively charged nanoparticles into the capillary pores of concrete (Refer to Figure 4). From a prior study, reinforcement removed from EN treated specimens are shown in Figure 5 and compared to untreated controls. The treated specimens showed less than 2 % corrosion product coverage of the surface area while the controls (untreated specimens) exhibited an average of 55% corrosion product coverage. The EN treated specimens formed a dense region near the vicinity of the reinforcement as compared to their untreated controls as shown in Figure 6. This dense region constituted a protective barrier surrounding the reinforcement, inhibiting the return of chlorides

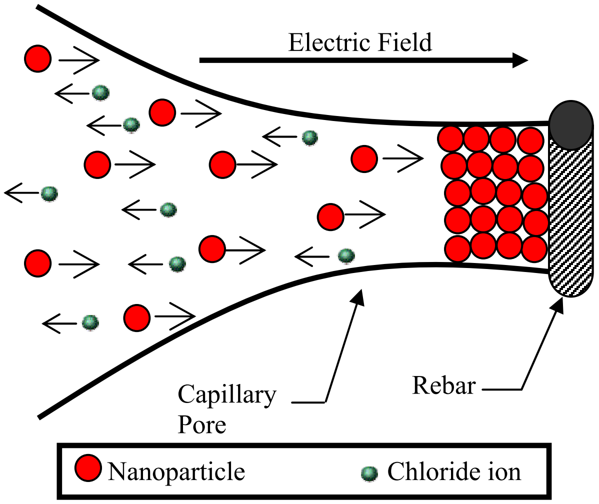


Fig 4. Electrokinetic transport of nanoparticles into the capillary pore.

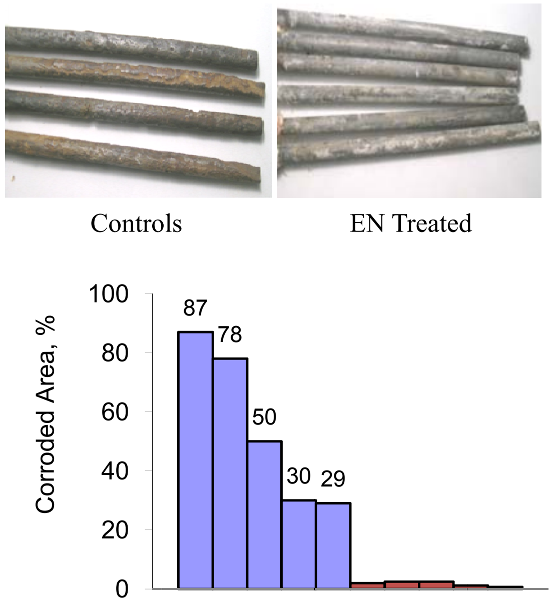


Fig 5. Electrokinetic nanoparticle treatment on controls and EN treated specimens [15].

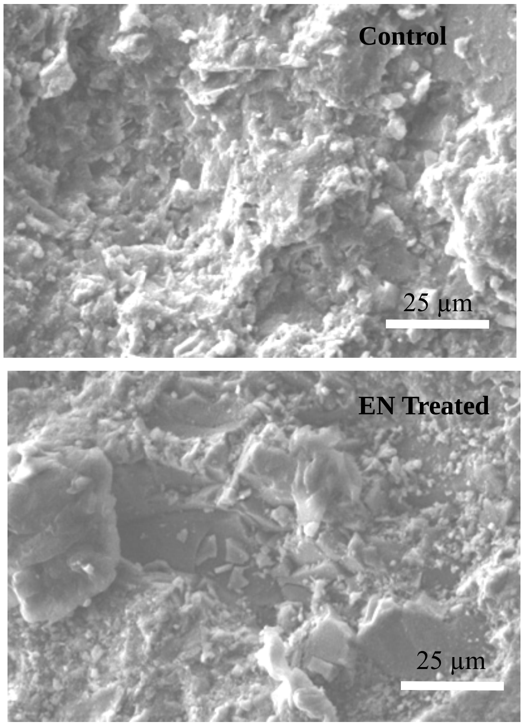


Fig 6. SEM microscopic analysis showing a relatively dense matrix due to EN treatment [15].

EXPERIMENTAL PROCEDURE

Cylindrical reinforced concrete specimens were batched using a 0.5 water to cement (w/c) ratio. The experimental flow chart of the EN treatment is shown in Figure 7. Mature cylindrical concrete was exposed to one year of initial saltwater of exposure. These specimens were subjected one week of ECE followed by a week of EN treatment and two years of post-treatment saltwater exposure. The alumina coated silica nanoparticles had a 20 nm silica core surrounded by a 2-nm layer of alumina particles. The young concrete was subjected to one week of EN treatment upon batching and then three years of post treatment saltwater exposure.

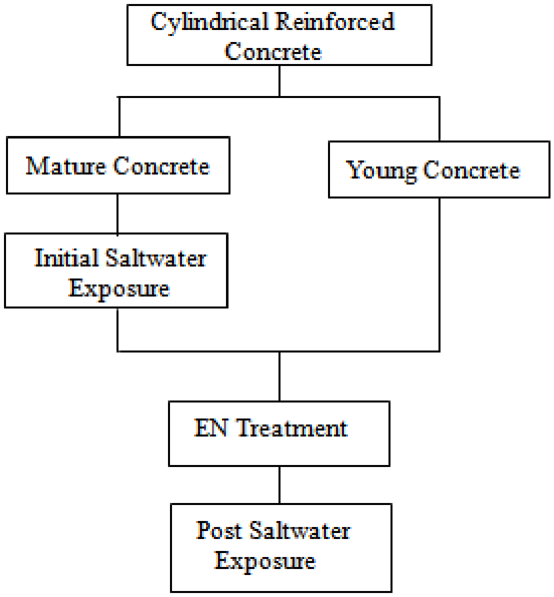


Figure 7. Experimental flow chart for control and EN treated specimens.

The circuit diagram used for EN treatment is shown in Figure 8. The positive pole of the power supply was connected to the titanium mesh (circumferential electrode) while the negative pole was connected to the working electrode. The nanoparticles were driven into the capillary pores using a current density of 1 A/m^2. During the course of the treatments diffusion coefficients were measured using EIS.

The Randles circuit model was used to determine the diffusion coefficients. Acid soluble chloride contents were measured in accordance with ASTM C 1152. Life 365 Version 2 simulation software (Silica Fume Association, Lovettsville, VA) was used to estimate the chloride distribution profiles and the chloride diffusion coefficients. Experimentally derived diffusion coefficients were obtained using EIS and compared with the simulation results. These diffusion coefficients were measured every thirty days during the course of the treatments. The measurements were taken using the sweep frequency mode using a Solartron SI 1260 impedance/ gain-phase analyzer, manufactured in Slough, Berkshire, UK. The potential was set to 0. The sweep was conducted from a frequency of 0.1 Hz (initial) to 10000 Hz (final) and amplitude of 10 mV. Equivalent circuit analysis using Z-view software (manufactured by Scribner Associates Inc of Southern Pines, NC) was used for estimating the diffusion coefficients.

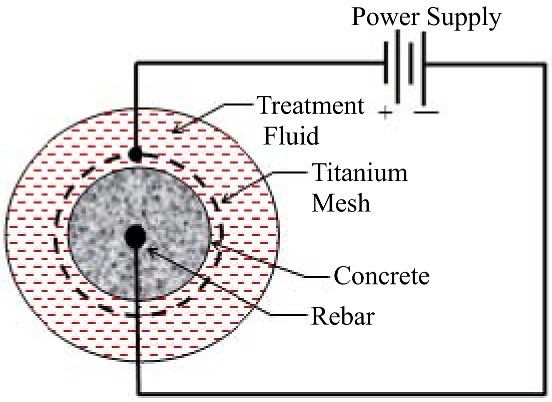


Fig 8. Electrokinetic Nanoparticle treatment setup.

RESULTS AND DISCUSSION

The EN and control specimens after post saltwater exposure are shown in Figure 9. The untreated mature controls exhibited severe cracking, while EN treated specimens demonstrated no signs of cracking. The diffusion coefficients of the specimens (young and mature concrete) were measured every 30 days for a period of 3 years as shown in Figure 10. The experimentally derived diffusion coefficients were compared to the coefficients obtained by "Life 365" simulation utilizing water to cement (w/c) ratio and specimen geometry.

Fig 9. Cracked control and EN treated specimens[14].

At the end of 30 days of initial saltwater exposure the mature and young controls exhibited diffusion coefficients of $9.34 \times 10^{-12} m^2/s$ and $6.60 \times 10^{-12} m^2/s$, while the EN treated specimens showed diffusion coefficients of $4.59 \times 10^{-12} m^2/s$ (Mature EN) and $1.74 \times 10^{-12} m^2/s$ (Young EN) specimens. After the first year of initial saltwater exposure the young EN treated specimens showed a diffusion coefficient of $4.45 \times 10^{-12} m^2/s$. This coefficient after EN treatment dropped to $1.01 \times 10^{-12} m^2/s$ (This was measured at the end of 60 days during the post treatment saltwater exposure.) The young EN treated specimens exhibited $1.41 \times 10^{-13} m^2/s$ after the post-treatment saltwater exposure period as compared to the untreated controls ($3.59 \times 10^{-12} m^2/s$). In the meantime, the mature EN treated specimens showed a value of $1.09 \times 10^{-13} m^2/s$ which was higher than the controls ($3.02 \times 10^{-12} m^2/s$).

The young and mature EN treated specimens showed lower diffusion coefficients which were under the threshold limit of $1.63 \times 10^{-12} m^2/s$ (Refer to Table 1). The untreated controls exhibited a higher value ($3.59 \times 10^{-12} m^2/s$) above the threshold limit indicating high susceptibility to chloride induced corrosion. During the post-treatment saltwater exposure period this value was below the threshold limit for EN treated specimens and did not appear to initiate corrosion. This diffusion coefficient value indicates that the EN treatment was effective in reducing the diffusion coefficient and acting as a protective barrier against chloride induced corrosion.

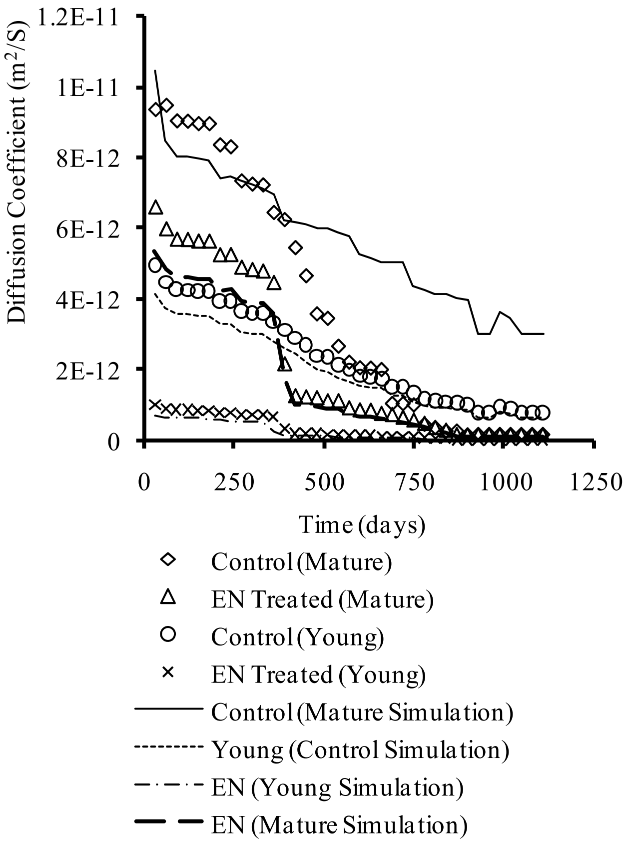


Fig 10. Diffusion coefficients obtained for EN treated (Young and Mature) and control specimens.

Table 1. Interpreting state of corrosion using diffusion coefficients

Diffusion coefficient (m^2/s)	State of Corrosion
$D_0 < 1.63 \times 10^{-12}$	implies “no corrosion”
$D_0 = 1.63 \times 10^{-12}$	implies “initiating corrosion”
$D_0 > 1.63 \times 10^{-12}$	Implies “ongoing corrosion”

The acid soluble chloride contents were measured as per ASTM C1152 and compared to the simulation results obtained by Life 365. The experimentally obtained chloride contents are shown in Figure 11. The chloride distribution profiles modeled using the Life 365 software is shown in Figure 12 and 13. The mature and young concrete controls were calculated to exhibit high chloride content in the range of 0.83-1.00 weight % of concrete. Chloride content in the range of 0.00-0.33 weight % of concrete was calculated for the young and mature EN treated specimens.

The distribution profile indicates that the chlorides were expected to diffuse through the capillary pores of the concrete and reach a concentration at the reinforcement that could initiate corrosion. The EN treated specimens exhibited values that were well below the chloride content corrosion limit (0.1 % wt of the cement) as compared to the controls (0.21 and 0.16 wt % of cement) as shown in Figure 11. The distribution indicates that the chlorides diffused through the capillary pores of the concrete and were available to break down the passive film on the reinforcement.

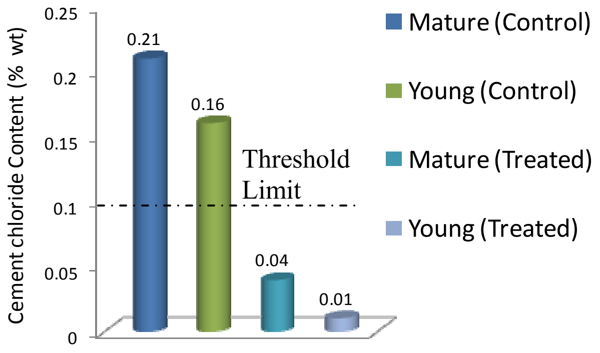
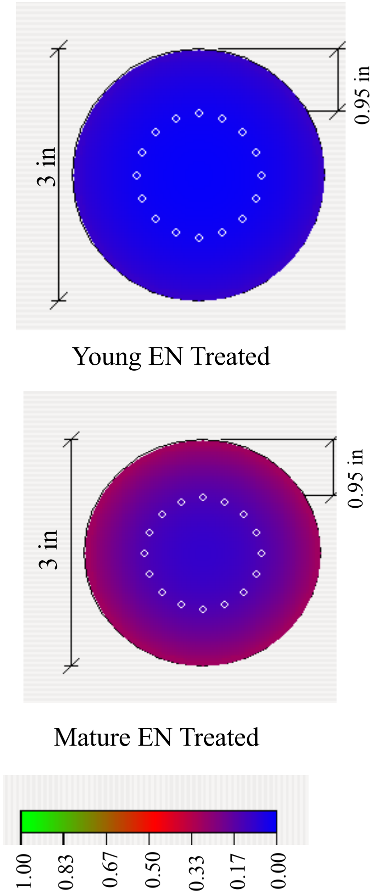


Fig 11. Cement chloride contents obtained experimentally through titration, after 3 years of saltwater exposure.



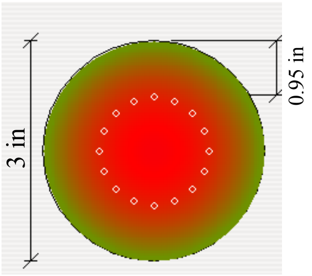
Young EN Treated

Mature EN Treated

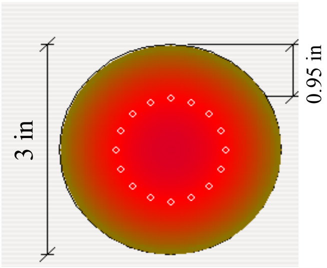
(Concentration with wt % of concrete)

Fig 12. Simulation results on mature EN Treated specimens showing the distribution of chloride contents ranging from 0.00 (Purple) to 1 wt % (Green).

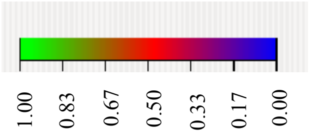
The results of the chloride contents versus time are shown in Figure 14. These values were calculated using equation no.8 from the diffusion coefficient data obtained from EIS. The young EN treated specimens showed chloride contents of 0.001kg/m^3 while 0.44 kg/m^3 was exhibited by the mature EN treated specimens at the end of the post-treatment saltwater exposure period. These values were below the corrosion threshold limit of 0.98 kg/m^3 for chloride content. The mature and young controls exhibited chloride contents of 9 kg/m^3 and 15 kg/m^3 respectively after the post-treatment saltwater exposure period.



Mature Control



Young Control



(concentration with wt% of concrete)

Fig 13. Simulation results on the control specimens of young and mature concrete.

A shift in chloride contents were observed after 660 days of saltwater exposure on the mature control and EN treated specimen as shown in Figure 14. This trend is associated with the change in the drying cycle of post-treatment saltwater exposure. The drying effect in concrete causes the pores to close and inhibits chloride ions. After 700 days the mature control experienced an increase in chloride content while the mature EN treated specimens showed a decrease in chloride contents. The mature controls were influenced by air induced carbonation in concrete which caused a drop in pH. Decrease in pH is attributed to the increase in corrosion in concrete.

These results indicate that the EN treatment had significant effect in reducing the chloride contents as compared to their untreated controls. The controls exhibited high chloride contents as compared to the EN treated specimens. This data indicates that the controls are in the high risk range of corrosion initiation at an early stage of chloride exposure and causing a decrease in the service life of the structure.

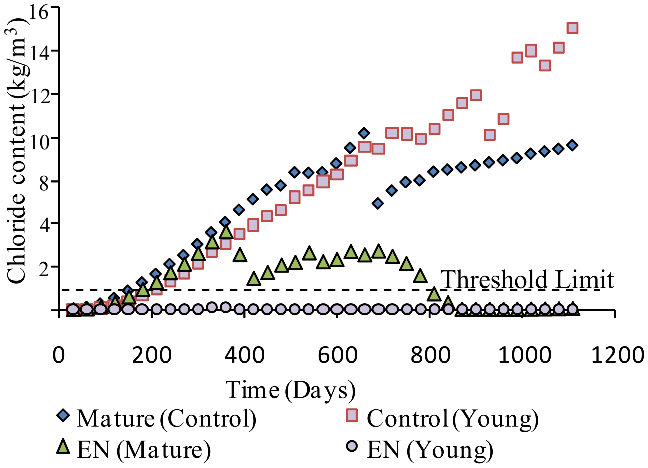


Fig 14. Chloride contents versus time for EN treated and untreated controls based on the diffusion coefficient data obtained by EIS.

CONCLUSION

The diffusion coefficients and chloride contents indicated that the EN treatment was effective in acting as a protective barrier against chloride induced corrosion in concrete.

REFERENCES

[1]. Bentur, A., Diamond, S., and Berke, N., 1998, Steel Corrosion in Concrete, Spon Publications, UK, pp.24-38.

[2]. Broomfield, J. P., 1997, Corrosion of Steel in Concrete: Understanding, Investigation and Repair, Taylor and Francis, London UK, pp.103-106.

[3] Ahmad, Z, 2006, Principles of Corrosion Engineering and Corrosion Control, *Elsevier Publications*, New York, pp.325-326.

[4]. Pooulsen E., and Mejlbro, L., 2006, Diffusion of chloride in concrete, Diffusion of chloride in concrete: theory and application, Taylor and Francis, London, UK, pp.241-330.

[5]. Tikalsky, P., and Marek,, P., 2005, Statistical variations in chloride diffusion in concrete bridges, *ACI Materials Journal*, **102** (S49), pp. 481- 486.

[6]. Goltermann, P., 2003, Chloride ingress in concrete structures: Extrapolation of Observations, *ACI Materials Journal*, **100** (M13), pp.114-119.

[7]. Maage M., Helland S., Poulsen E., Vennesland O., and Carlsen J. 1996, Service life prediction of existing concrete structures exposed to marine environment, *ACI Materials Journal*, **93** (M68), pp. 602-608.

[8]. Weyers, R., 1998, Service life model for chloride structures in chloride laden environments, *ACI Materials Journal*, **95** (M 42), pp. 445-453.

[9]. Trejo, D., and Pillai, R., Accelerated chloride threshold testing: Part I – ASTM A 615 and A 706 reinforcement, *ACI Materials Journal,* **100** (M60), pp. 519-527.

[10]. ASTM C1556-04, 2004, Standard test method for determining the apparent chloride diffusion coefficients of cementious mixtures by bulk diffusion, American Society of Testing and Materials, Philadelphia, **04** (02), pp. 7.

[11]. Shi, M., and Chen, Z., and Sun, J., 1999, Determination of chloride diffusivity in concrete by AC impedance spectroscopy, *Cement and Concrete Research,* **29**, pp.1111-1115.

[12]. Barsoukov, E., and Macdonald, J., 2005, Impedance spectroscopy theory, experiment, and applications, Wiley - Interscience, pp.343- 424.

[13]. Cardenas, H; and Kupwade-Patil, K., 2007, Corrosion remediation using chloride extraction concurrent with electrokinetic pozzolan deposition in concrete, New solutions for environmental pollution, 6th Symposium on Electrokinetic Remediation, pp.117.

[14]. Cardenas, H; Kupwade-Patil, K; and Eklund, S., 2010, Corrosion mitigation in mature reinforced using nanoscale pozzolan deposition, Second international conference on sustainable construction materials and technologies, Ancona, Italy.

[15]. Kupwade-Patil., 2007, A new corrosion mitigation strategy using nanoscale pozzolan deposition, Master of Science Thesis, Louisiana Tech University.

[16]. Kupwade Patil. K.; Gordon. K.; Xu. K.; Moral O.; Cardenas. H.; and Lee. L., 2008, Corrosion mitigation in concrete beams using electrokinetic nanoparticle treatment," Proceedings on Excellence in Concrete Construction through Innovation, September, London, UK, pp.365-371.

[17]. ASTM C1152, 2003, Standard Test Method for Acid-soluble Chloride in Mortar and Concrete, American Society of Testing and Materials, Philadelphia, **09** (69), pp. 4.

[18]. Bentz, E and Thomas, M, 2008, LIFE-365, V.2, Service life prediction model. User's Manual, Silica Fume Association, Lovettsville, VA.