In Situ Electrosynthesis of Polymethyl Methacrylate within Ceramic Launch Pad Materials

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ABSTRACT

Electrokinetic deposition of methylmethacrylate is used to mitigate corrosion in reinforced concrete. The methylmethacrylate (MMA) monomer deposits in the pores in the concrete where it is converted into its polymer, polymethylmethacrylate, thus creating a barrier that also enhances the mechanical properties of the concrete. Previous to the MMA treatment an Electrokinetic deposition is used to transport calcium, sodium and potassium hydroxide particles through the capillary pores of concrete directly to the concrete reinforcement. The intent is to use these compounds as a sacrificial electrode layer during the electrokinetic deposition of methylmethacrylate monomer. Cylindrical reinforced concrete specimens were subjected to electrokinetic treatment and the specimens were tested to characterize porosity reduction and tensile splitting strength showing an increase in the tensile strength. In addition, nine specimens treated electro-kinetically and in long-term atmospheric exposure testing at NASA's Kennedy Space Center, seaside atmospheric exposure test site were tested to determine their corrosion rate.

RELEVANCE TO NASA RESEARCH

Launch pad facilities are subjected to fallout containing hydrochloric acid expelled from the solid rocket boosters. This acidic environment, combined with salt spray from the Atlantic ocean, heat, ultraviolet radiation, and high humidity makes the launch pad highly susceptible to corrosion and is one of the most corrosive environments in the US. Maintenance associated with corrosion of the infrastructure used by NASA's Kennedy Space Center to launch rockets represents a large expenditure of manpower and money.

PURPOSE

The purpose of this research is to study a novel way of treating concrete in NASA facilities to prevent its corrosion. In addition the electrokinetic treatment improves the mechanical strength of the concrete as an added benefit.

RESEARCH METHODS

Twenty five specimens of concrete, reinforced with a steel rod (Figure 1) were treated by electrophoresis. A dc electrical power supply was connected to the specimens with the positive (cathode) connected to the steel reinforcement bar and the anode to a metal mesh strip placed around the specimens (Figure 2).

Fig. 1 Specimen

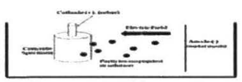

Fig. 2 Electroporesis

Fig.3 Experimental set up

The MMA electrodeposition process causes corrosion of the concrete reinforcement. To mitigate this corrosion, the reinforced concrete is treated electrophoretically with potassium hydroxide, sodium hydroxide and calcium hydroxide prior to the deposition of the methylmethacrylate.

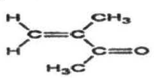

fig.4 Methylmethacrylate molecule

Methylmethacrylate is a monomer that is soluble in water and can be driven electroporetically inside the concrete. Specimens 1 to 20 were treated; specimens 21 to 25 were kept untreated as control.

Additionally nine specimens had been in long-term environmental exposure at the NASA's Kennedy Space Center seaside atmospheric exposure test site. Specimens 1 to 6 were submerged in seawater for 1100 days, specimens 7 to 9 were exposed to the atmosphere at the test site for 1492 days.

RESULTS

Table 1 Porosity and Tensile Strength of treated specimens

Type of Treatment	Average Porosity %	Standard Deviation for the Average Porosity %	Average Tensile Strength psi	Improvement in Tensile Strength Relative to Control
Specimens 1-5 NaOH 2.25 M, KOH 2.25 M, $Ca(OH)_2$ 1.125 M + MMA treatment	22.6	0.71	337	47%
Specimens 6-10 NaOH 1.5 M, KOH 1.5 M, $Ca(OH)_2$ 0.75 M + MMA treatment	21.0	0.37	366	60%
Specimens 11-15 NaOH 1 M, KOH 1 M, $Ca(OH)_2$ 0.5 M + MMA treatment	21.9	0.68	260	14%
MMA treatment (No hydroxides Treatment) specimens 16-20	23.4	0.26	213	-6%
Control specimens 21-25	23.5	0.17	229	

Table 2 Tensile Strength and corrosion rate of exposed specimens

Specimen	Tensile Splitting Test (psi)	Corrosion Rate (mils per year)
1	421	0.1177
2	381	0.0477
3	419	0.0237
4	394	0.3956
5	387	0.4450
6	290	0.3176
7	572	0.0473
8	732	2.0734
9	785	0.1709

DISCUSSION

The porosity of treated specimens did not vary much compared to the control specimens. This indicates that little methylmethacrylate (MMA) covered the concrete pores.

Even though little MMA entered the pores, it had a significant increase on the tensile strength of 60% and 47%.

CONCLUSION

The electrokinetic treatment has been shown as effective for strengthening the concrete even though the porosity has not changed much.

For the exposed specimens the steel reinforcement bars have visibly almost no signs of corrosion and the XPS results showed small peaks of iron, demonstrating the long term effectiveness of the corrosion prevention.

PROPOSED FUTURE WORK

It can be hypothesized that the hydroxides treatment had more to do with the strength increase than the MMA treatment. Further experimental work is needed to test this hypothesis. Also more work has to be done to achieve a better porosity reduction with MMA.

ACKNOWLEDGEMENT

I want to give thanks to Dr. Luz Marina Calle from the NASA Corrosion Technology Laboratory at Kennedy Space Center for her guidance and for letting me use her lab to perform the experiments. To Dr. Henry Cardenas from Louisiana Tech University for introducing me this very interesting topic of research and to Dr. Carlos Cabrera from the Center for Advanced Nanoscale Materials at the University of Puerto Rico, Rio Piedras for making this experience possible.

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Abstract

During the launch of rockets at NASA's Kennedy Space Center, the Launch Pad is exposed to enormous quantities of corrosion-causing chemicals expelled from the rocket engines. Electrokinetic treatments of methylmethacrylate is a method to mitigate corrosion in reinforced concrete. An electric field is used to transport calcium, sodium and potassium hydroxide particles through the capillary pores of concrete directly to the concrete reinforcement. The intent is to use these compounds as a sacrificial electrode layer during the electrokinetic deposition of methylmethacrylate monomer. The methylmethacrylate monomer deposits in the pores in the concrete where it is converted into its polymer, polymethylmethacrylate, thus creating a barrier that also enhances the mechanical properties of the concrete. Cylindrical reinforced concrete specimens were subjected to electrokinetic treatment and the specimens were tested to characterize porosity reduction and tensile splitting strength. In addition, nine specimens from long-term atmospheric exposure testing at NASA's Kennedy Space Center, seaside atmospheric exposure test site were tested to determine their corrosion rate.

INTRODUCTION

As a summer intern in the Corrosion Technology Laboratory of Dr. Luz Marina Calle at NASA's Kennedy Space Center, I performed experiments on the treatment of reinforced concrete with methyl methacrylate under the guidance of Dr. Henry Cardenas from Louisiana Tech University and Dr. Luz Marina Calle. This report concerns the experimental work performed during the summer intern experience.

Corrosion damages structures and, in some cases, can harm people. In the United States the annual direct cost of corrosion is $460 billion[1]. Maintenance of the infrastructure used by NASA's Kennedy Space Center to launch rockets represents a large expenditure of manpower and money. Launch pad facilities are subjected to fallout containing hydrochloric acid expelled from the solid rocket boosters. This acidic environment, combined with salt spray from the Atlantic Ocean, heat, ultraviolet radiation, and high humidity makes the launch pad highly susceptible to corrosion and one of the most corrosive environments in the US[2].

Launch pad facilities incorporate vast quantities of reinforced concrete. The porous nature of concrete allows corrosion causing species to pass through the bulk material and reach the steel reinforcement. Addition of polymethyl methacrylate to concrete creates a physical barrier inside the concrete by occupying part of the inherent porosity. An added benefit of dosing concrete with polymethyl methacrylate is an improvement in mechanical properties: the concrete acquires a higher compressive strength.

Dosing of existing reinforced concrete structures can be accomplished with electrophoresis. In electrophoresis, an applied electric field creates a potential difference that drives the particles from a solution into the concrete. This work involved a method of achieving the dosing of the methyl methacrylate to the concrete using electrophoresis.

EXPERIMENTAL PROCEDURE

Twenty five specimens of concrete, reinforced with a one quarter inch diameter steel rod, were prepared for this experiment (Figure 1).

Fig. 1 Reinforced concrete specimen

ELECTROPHORESIS TREATMENT

The specimens were treated by electrophoresis. Electrophoresis is the movement of charged particles in solution under the influence of an electrical field (Figure 2).

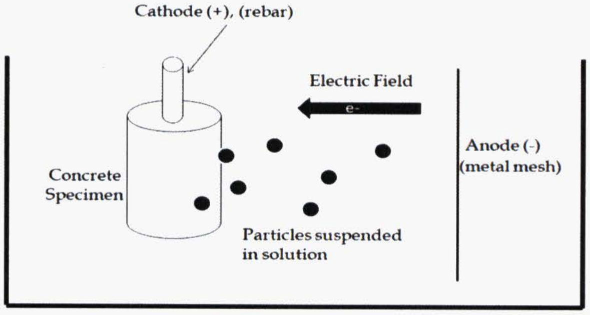

Fig.2 Graphical representation of electrophoresis

POTASSIUM HYDROXIDE, SODIUM HYDROXIDE AND CALCIUM HYDROXIDE TREATMENT

The polymethylmethacrylate electrodeposition process causes corrosion of the concrete reinforcement. To mitigate this corrosion, the reinforced concrete is treated electrophoretically with potassium hydroxide, sodium hydroxide and calcium hydroxide prior to the deposition of polymethylmethacrylate.

Specimens 1 to 5 were placed in a solution of 2.25 molar sodium hydroxide, 2.25 molar potassium hydroxide and 1.12 molar calcium hydroxide; specimens 6 to 10 were placed in a solution of 1.5 molar sodium hydroxide, 1.5 molar potassium hydroxide and 0.75 molar calcium hydroxide; specimens 11 to 15 were placed in a solution of 1 molar sodium hydroxide, 1 molar potassium hydroxide and 0.5 molar calcium hydroxide; specimens 16 to 20 did not receive hydroxides treatment and specimens 21 to 25 were kept as control. A dc electrical power supply was connected to the specimens with the positive (cathode) connected to the steel reinforcement bar. A flexible metal mesh strip was placed around the specimens and the negative (anode) was connected to this strip. The electrical circuit is completed through the solution (Figures 3 and 4). This treatment was performed for 9 days.

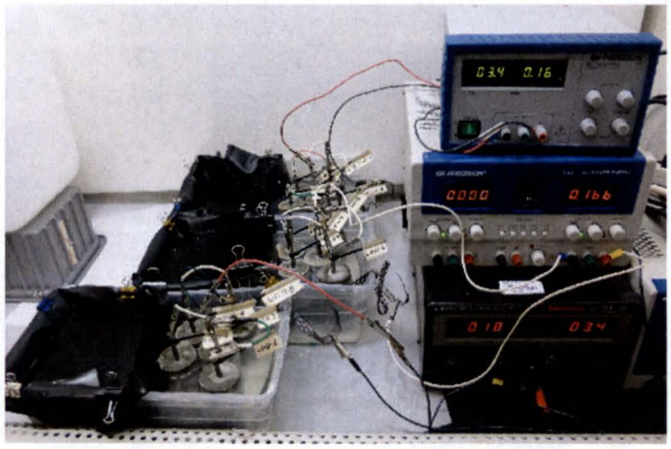

Fig.3 Specimens submerged in solution,
and exposed to an electrical current.

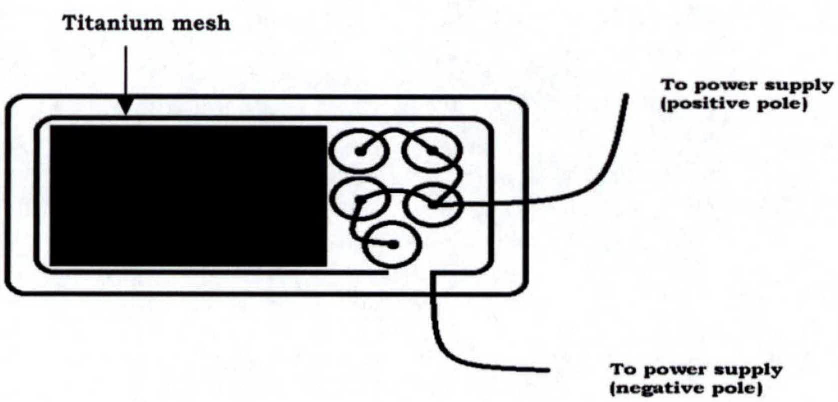

Fig.4 Top view of the experimental set up

METHYL METHACRYLATE TREATMENT

The hydroxides solution was removed and a solution of 1% by weight of methyl methacrylate (Figure 5) was introduced with a peristaltic pump to the tanks containing the specimens. Electrophoretic treatment was performed in three sessions of 8 hours of duration. Specimens 1 to 20 were treated; specimens 21 to 25 were kept untreated as control.

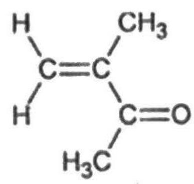

Fig.5 methylmethacrylate molecule

Methylmethacrylate is a monomer that is soluble in water and can be driven electroporetically.

SPLITTING TENSILE TESTING

The specimens were tested to determine the splitting tensile strength of the concrete. This is an indirect test since the specimen is subjected to a compression force on an Instron® universal testing machine. A constant rate force was applied to the specimens to determine peak load before breaking. This maximum load P is used to calculate the tensile strength (T)[3]:

$$T = \frac{2*P}{\pi*L*D}$$

Where L is the length of the specimen and D is the diameter of the specimen. This test was performed according to the test standard ASTM-C496 of the American Society for Testing and Materials.

X-RAY PHOTOELECTRON SPECTROSCOPY ANALYSIS

The specimens will be analyzed by X-ray Photoelectron Spectroscopy (XPS) to determine the atomic species present. At the time of this report the test has not been performed due to unavailability of the equipment.

ATMOSPHERIC EXPOSURE SPECIMENS

In addition to the twenty specimens treated, nine specimens that had been in long-term environmental exposure at the NASA's Kennedy Space Center seaside atmospheric exposure test site were analyzed. Specimens 1 to 6 were submerged in seawater for 1100 days, specimens 7 to 9 were exposed to the atmosphere at the test site for 1492 days. These specimens were tested using linear polarization to determine corrosion rate. They were also tested to determine splitting tensile strength and analyzed by X-Ray Photoelectron Spectroscopy (XPS) to determine the presence of iron and oxygen as evidence of corrosion.

RESULTS

POROSITY AND TENSILE STRENGTH

Table 1 Porosity and Tensile Strength of treated specimens

Type of Treatment	Average Porosity (%)	Average Tensile Strength (psi)	Improvement in Tensile Strength Relative to Control (%)
Specimens 1-5 NaOH 2.25 M, KOH 2.25 M, $Ca(OH)_2$ 1.123 M + MMA treatment	22.6±0.7	337	47
Specimens 6-10 NaOH 1.5M, KOH 1.5 M, $Ca(OH)_2$ 0.75M + MMA treatment	21.9±0.4	366	60
Specimens 11-15 NaOH 1 M, KOH 1 M, $Ca(OH)_2$ 0.5M + MMA treatment	21.9±0.7	260	14
MMA treatment (No hydroxides Treatment) specimens 16-20	23.1±0.3	213	-6
Control specimens 21-25	23.5±0.2	229	

LONG TERM EXPOSURE SPECIMENS

Table 2 Tensile Strength of long term exposure specimens

Specimen	Tensile Splitting Test (psi)
1	421
2	381
3	419
4	304
5	387
6	298
7	572
8	732
9	785

LINEAR POLARIZATION

Linear Polarization analysis was used to determine the corrosion rate of the steel reinforcement in mil per year. The specimens tested are from the Corrosion Technology Laboratory atmospheric exposure site. Specimens 1 to 6 were submerged in seawater for 1100 days, specimens 7 to 9 were exposed to the atmosphere at the test site for 1492 days.

Table 3 Corrosion Rate of long-term exposure specimens

	Corrosion Rate (mil per year)
1	0.1177
2	0.0477
3	0.0237
4	0.3956
5	0.4450
6	0.3176
7	0.0473
8	0.0734
9	0.1709

X RAY PHOTOELECTRON SPECTROSCOPY

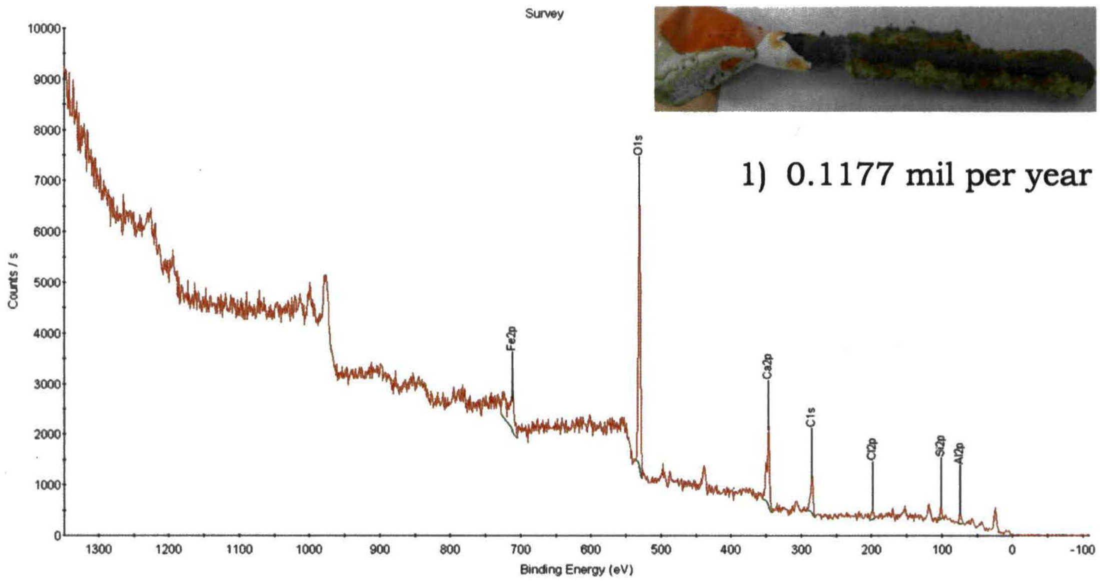

Fig.6 XPS of beach specimen 1 (immersed in seawater)

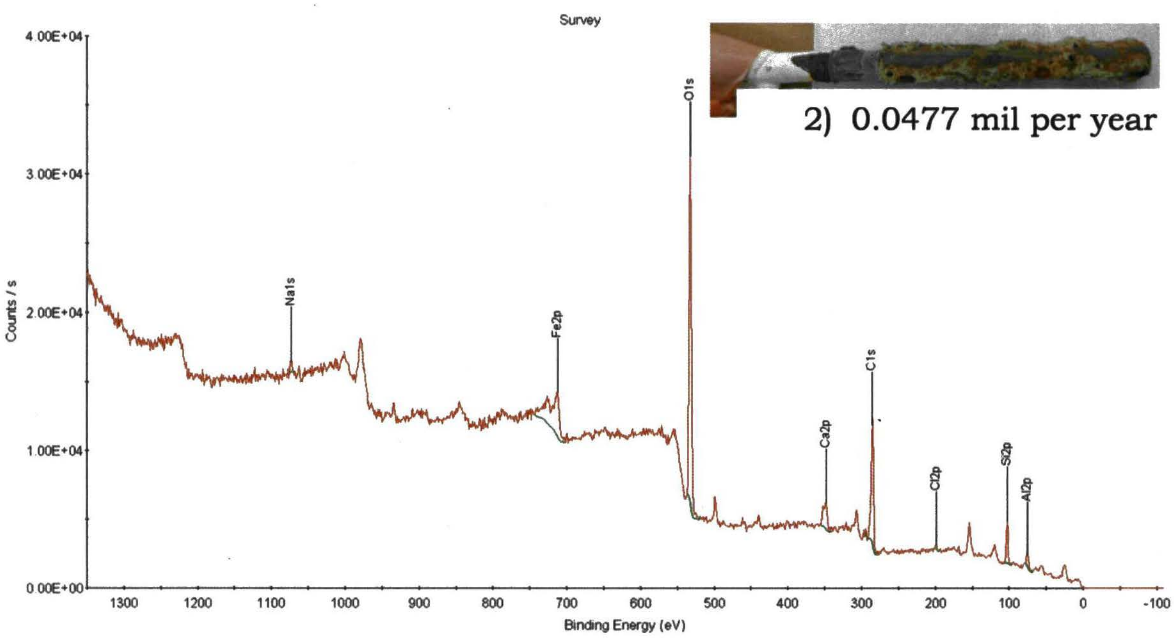

Fig.7 XPS of beach specimen 2 (immersed in seawater)

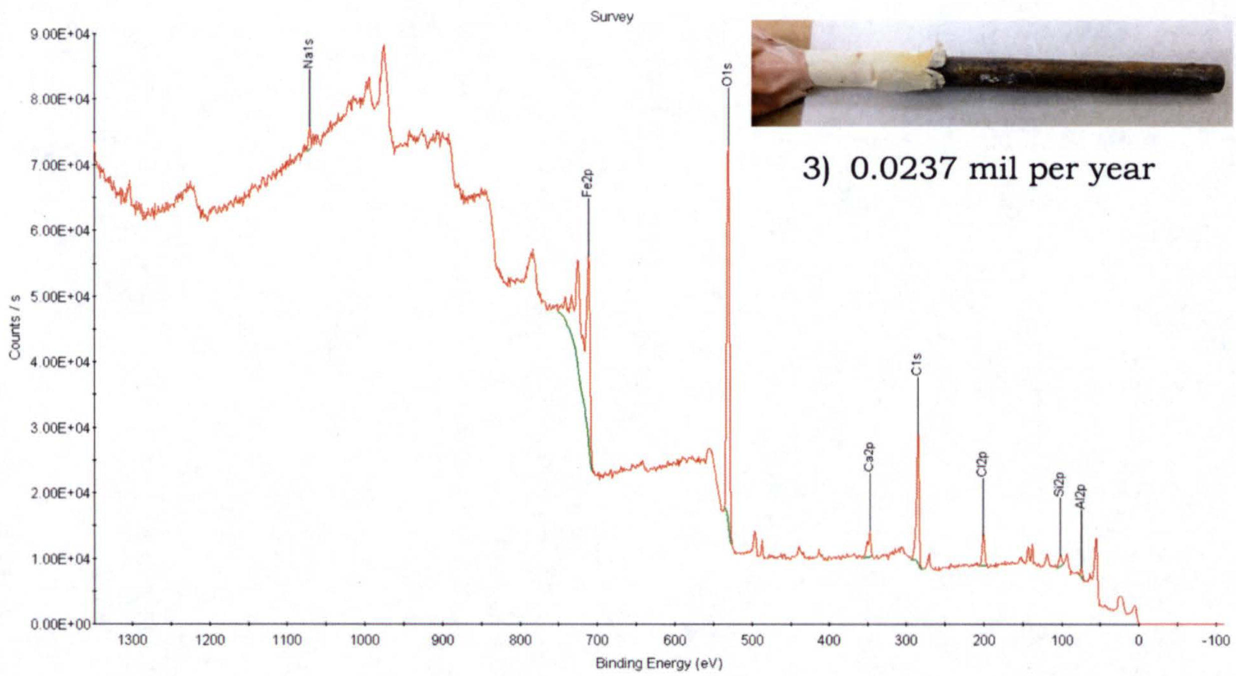

Fig.8 XPS of beach specimen 3 (immersed in seawater)

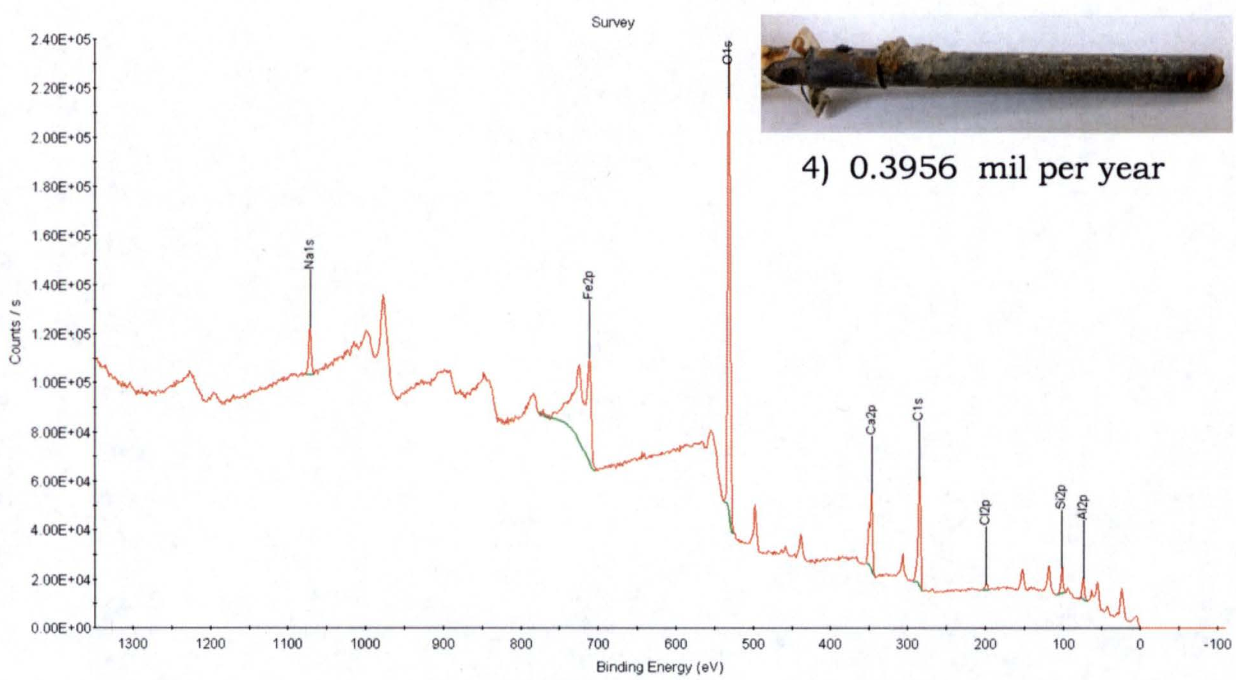

Fig.9 XPS of beach specimen 4 (atmospheric exposure)

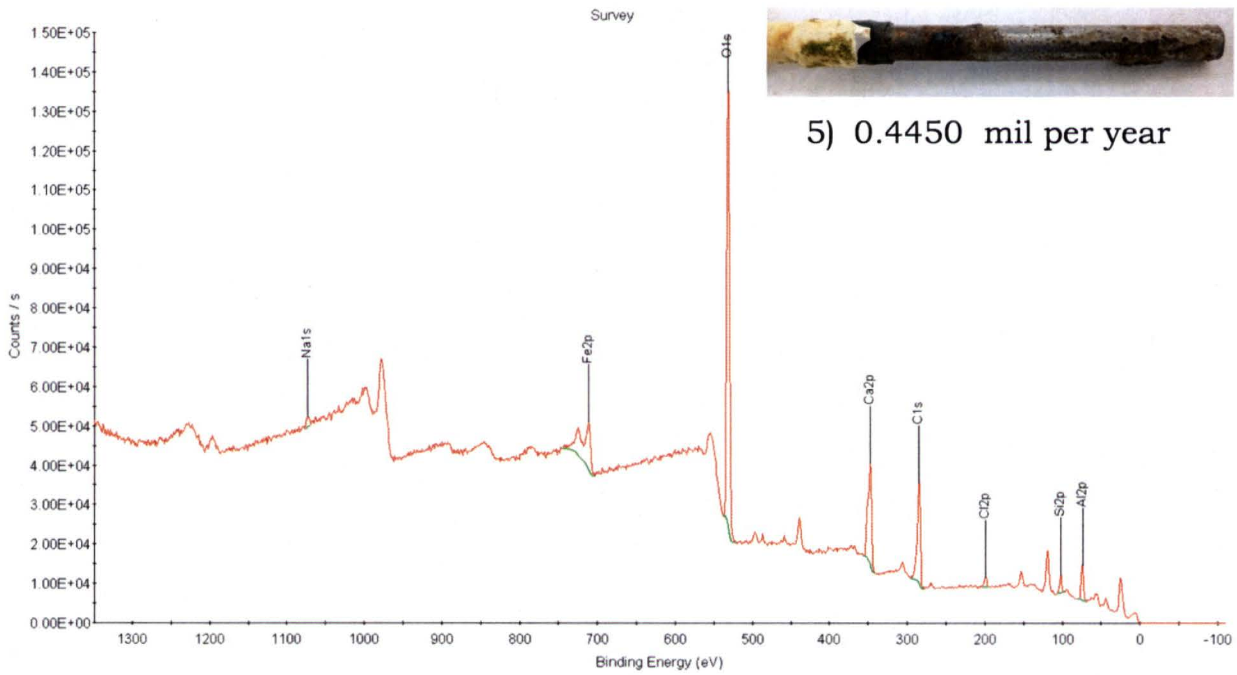

Fig.10 XPS of beach specimen 5 (atmospheric exposure)

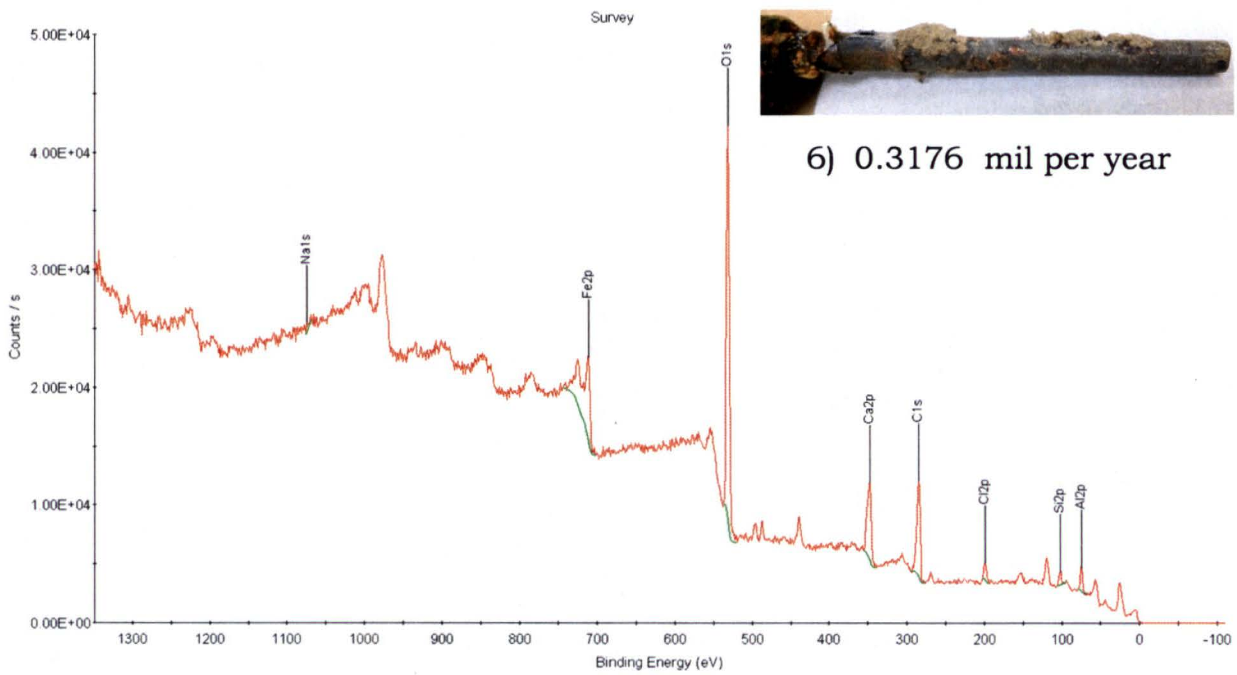

Fig.11 XPS of beach specimen 6 (atmospheric exposure)

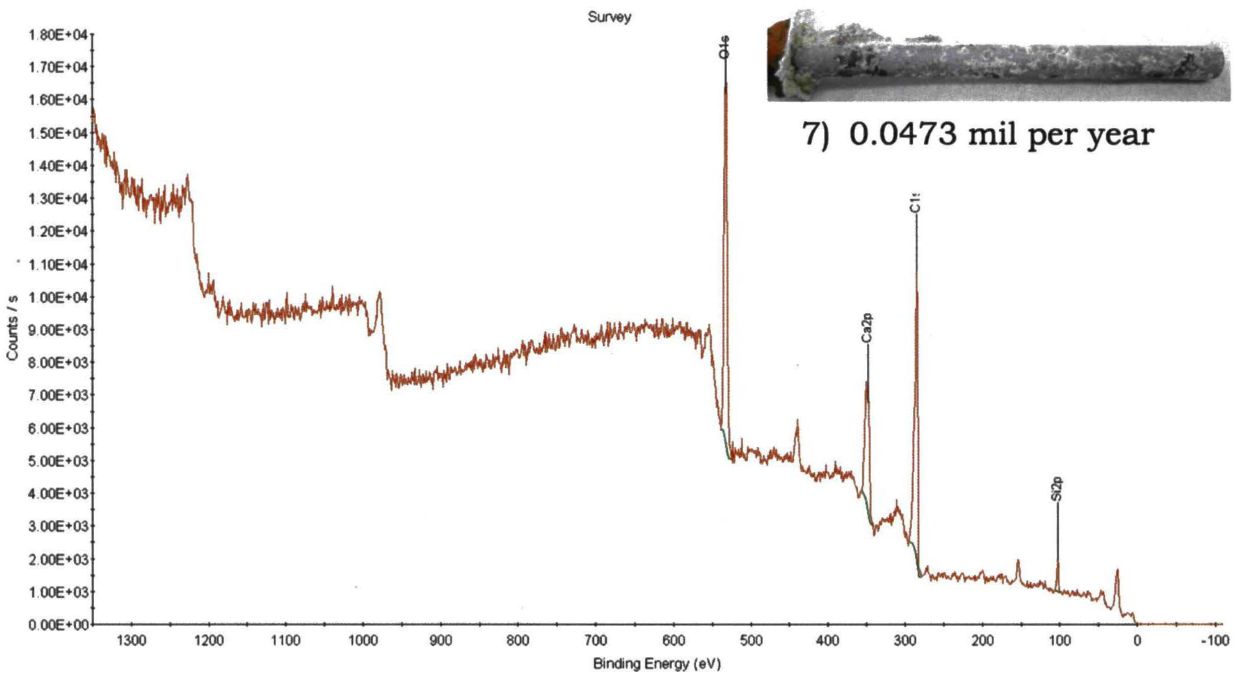

Fig.12 XPS of beach specimen 7

(atmospheric exposure)

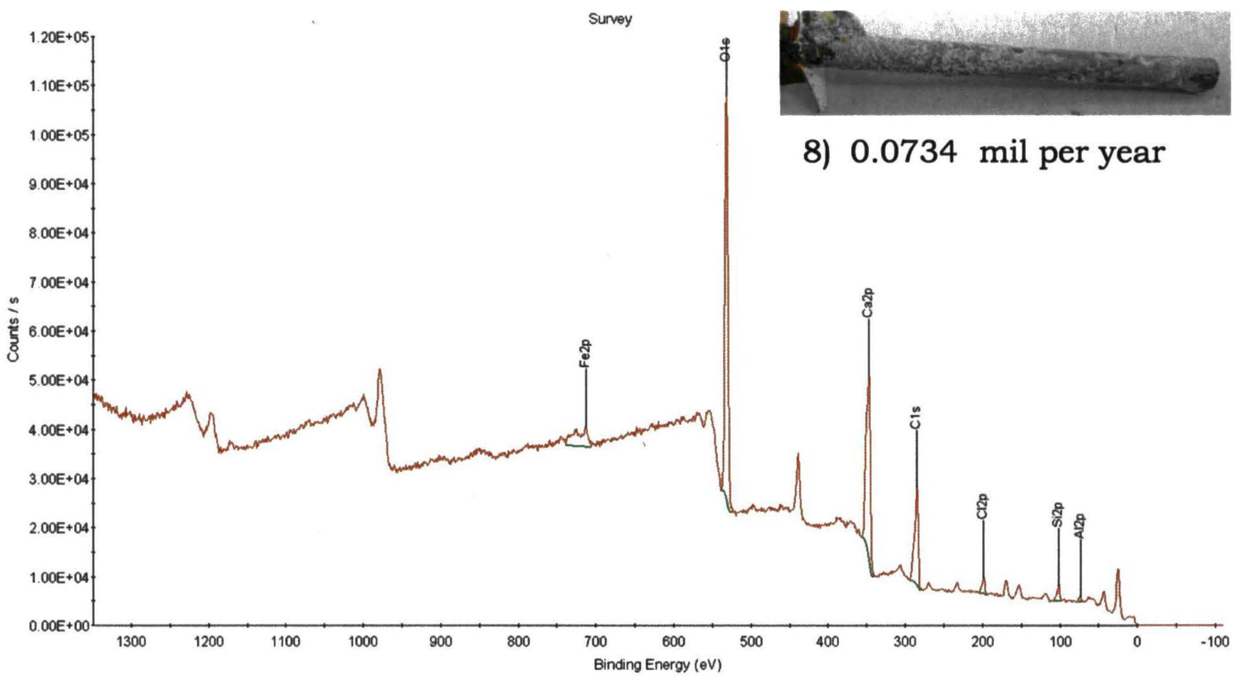

Fig.13 XPS of beach specimen 8 (atmospheric exposure)

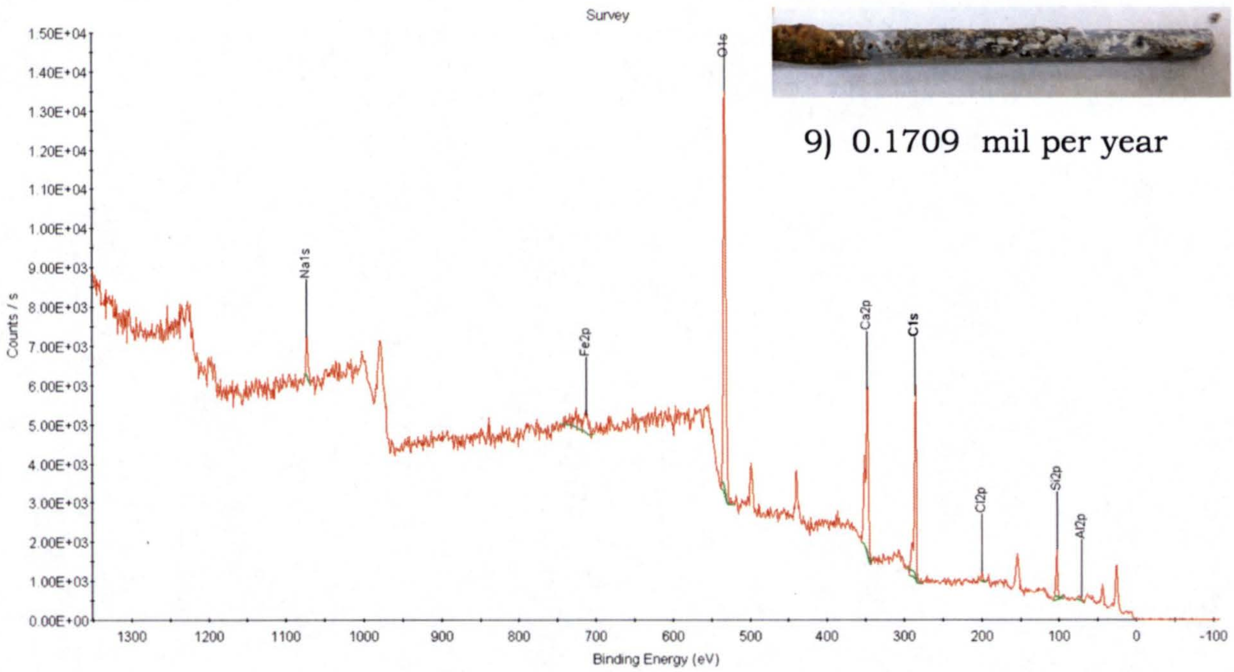

Fig.14 XPS of beach specimen 9 (atmospheric exposure)

CONCLUSION

The porosity of treated specimens did not vary much compared to the control specimens. This indicates that little methylmethacrylate (MMA) covered the concrete pores.

The specimens treated with hydroxides at a concentration of NaOH 1.5M, KOH 1.5 M, and $Ca(OH)_2$ 0.75M showed an increase of 60% in tensile strength. The specimens treated with concentrations of NaOH 2.25 M, KOH 2.25 M, and $Ca(OH)_2$ 1.123 M showed an increase of 47% in tensile strength. Even though little MMA entered the pores, it had a significant increase on the tensile strength. It can be hypothesized that the hydroxides treatment had more to do with the increase than the MMA treatment. Further experimental work is needed to test this hypothesis.

Specimens 1-3 that were exposed to the atmosphere (Table 2) had a higher tensile strength (average 409 psi) than the submerged ones (4-6) (average 330 psi), (7-10) (average 696 psi). The corrosion environment is more aggressive in the submerged specimens hence are weaker.

The corrosion rates in the specimens exposed to the atmosphere ranged from 0.0237 to 0.1709 mil per year. The highest corrosion was in the samples (4-6) (0.386 mil per year) that were submerged followed by (7-10) (0.0972 mil per year), again the corrosion being more aggressive in the submerged specimens. The steel reinforcement bars have visibly almost no signs of corrosion and the XPS results showed small peaks of iron, demonstrating the long term effectiveness of the corrosion prevention treatment in the beach specimens.

ACKNOWLEDGEMENTS

I want to give thanks to Dr. Luz Marina Calle from the NASA Corrosion Technology Laboratory at Kennedy Space Center for her guidance and for letting me use her lab to perform the experiments. To Dr. Henry Cardenas from Louisiana Tech University for introducing me this very interesting topic of research. Dr. Eliza Montgomery from NASA for her advice and facilitating my work by being always there to help me. Rick Johnston for his help and advice. Steve Trigwell for his help with the use of XPS. Dean Lewis and Jeff Sampson for their expertise in testing the strength of materials. To Rick Russell, Wendy Li, Mark Kolody, Jerry Curran and Jerry Buhrow, Paul Hintze and Pete Marciniak for being so kind and helpful. Also my thanks to Dr. Carlos Cabrera from the Center for Advanced Nanoscale Materials at the University of Puerto Rico, Rio Piedras for making this experience possible.

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