Galvanic Liquid Applied Coating Development for Protection of Steel in Concrete

Joseph John Curran and Jerry Curran
ASRC Aerospace
Chemical Instrumentation and Processing Lab, M/S ASRC-15
Kennedy Space Center, FL 32899

Louis MacDowell
National Aeronautics and Space Administration, M/S YA-C2-T
Kennedy Space Center, FL 32899

ABSTRACT

Corrosion of reinforcing steel in concrete is a major problem affecting NASA facilities at Kennedy Space Center (KSC), other government agencies, and the general public. Problems include damage to KSC launch support structures, transportation and marine infrastructures, as well as building structures. A galvanic liquid applied coating was developed at KSC in order to address this problem. The coating is a non-epoxy metal rich ethyl silicate liquid coating. The coating is applied as a liquid from initial stage to final stage. Preliminary data shows that this coating system exceeds the NACE 100 millivolt shift criterion. The remainder of the paper details the development of the coating system through the following phases:

- Phase I: Development of multiple formulations of the coating to achieve easy application characteristics, predictable galvanic activity, long-term protection, and minimum environmental impact.
- Phase II: Improvement of the formulations tested in Phase I including optimization of metallic loading as well as incorporation of humectants for continuous activation.
- Phase III: Application and testing of improved formulations on the test blocks.
- Phase IV: Incorporation of the final formulation upgrades onto large instrumented structures (slabs).

Key Words: cathodic protection, coating, galvanic, inorganic zinc, sacrificial anode, corrosion, corrosion protection.

INTRODUCTION

Corrosion of reinforcing steel in concrete is an insidious problem facing Kennedy Space Center (KSC), other government agencies, and the general public. These problems include KSC launch support structures, highway bridge infrastructure, and building structures such as condominium balconies. Due to these problems, the development of a Galvanic Liquid Applied Coating System (GLACS) would be a breakthrough technology having great commercial value for the following industries: Transportation, Infrastructure, Marine Infrastructure, Civil Engineering, and the Construction Industry.

This sacrificial coating system consists of a paint matrix that may include metallic components, conducting agents, and moisture attractors. Similar systems have been used in the past with varying degrees of success. These systems have no proven history of effectiveness over the long term. In addition, these types of systems have had limited success overcoming the initial resistance between the concrete/coating interface. The coating developed at KSC incorporates methods to overcome the barriers of previous systems.

The experimental effort was directed at solving reinforcing steel corrosion in concrete for structures at KSC. The experimental design incorporated methods typically used to protect steel structures and reinforcing steel by the use of inorganic zinc coatings and sacrificial anodes. The reinforced concrete test samples included modified ASTM G109 blocks and larger concrete slabs to simulate condominium balconies as shown in Figures 1 and 2 respectively. This new coating has metal particles suspended in the paint matrix. The main metallic constituents are zinc, magnesium, and indium in a specified ratio.

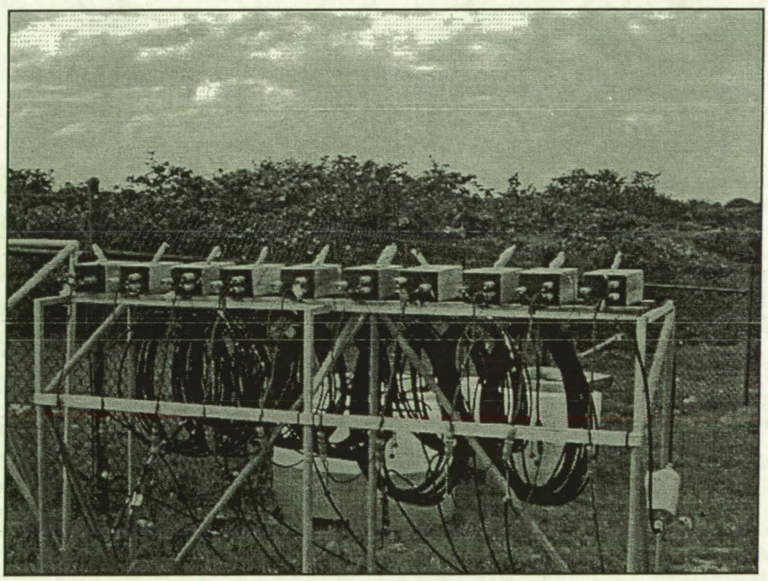


Figure 1. Test Blocks

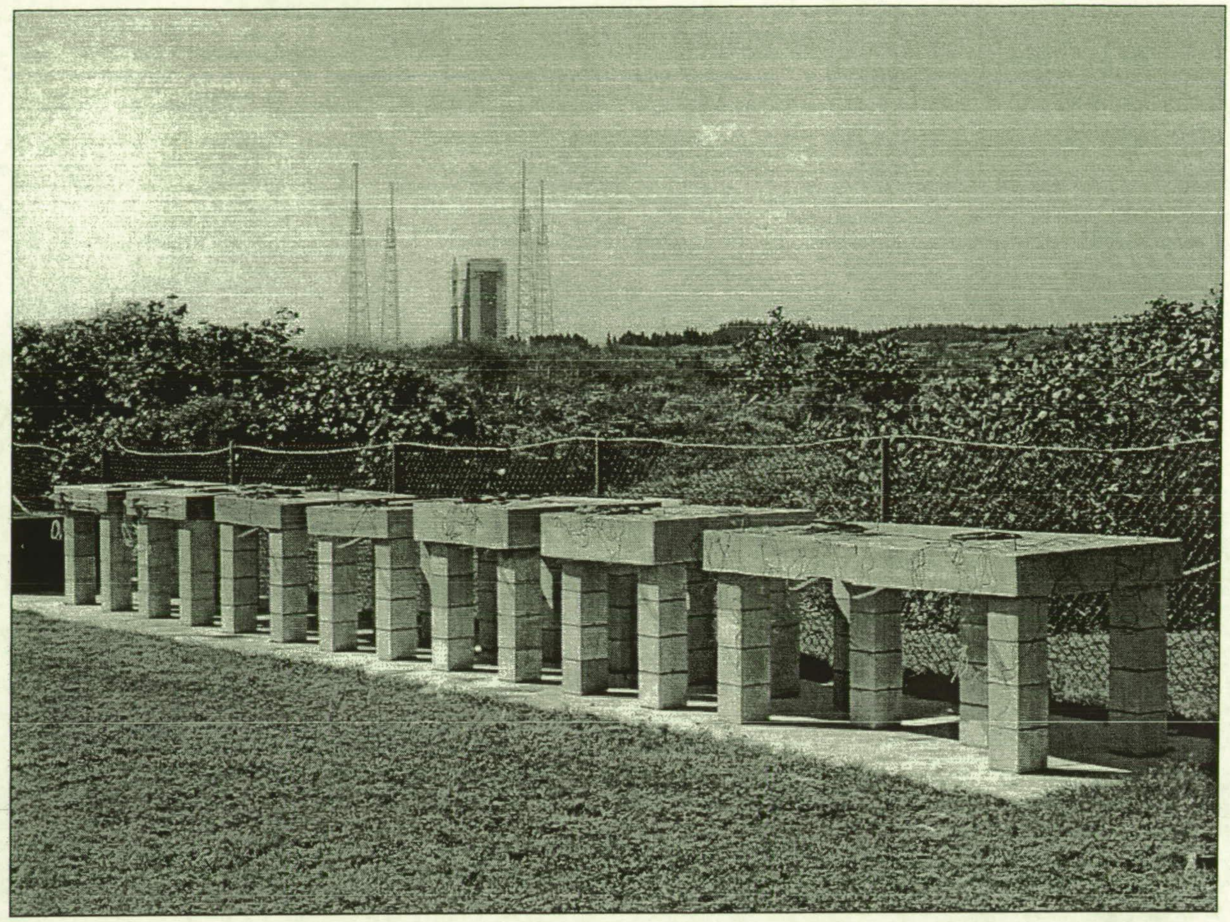


Figure 2. Simulated Reinforced Concrete Structures

EXPERIMENTAL PROCEDURE

The present effort is directed at several phases:

- Phase I concentrated on formulation of coatings with easy application characteristics, predictable galvanic activity, long-term protection, and minimum environmental impact. These new coating traits, along with the electrical connection system successfully protected the embedded reinforcing steel through the sacrificial cathodic protection action of the coating for the test blocks.
- Phase II focused on improving on the coating formulations and included optimizing metallic loading as well as incorporating a moisture attractor (humectant) into the coating for continuous activation.
- Phase III incorporated improvements from the previous two phases to the test blocks.
- Phase IV incorporated the final upgrades onto large reinforced concrete structures that were heavily instrumented. The Phase IV goal was to move the testing from small blocks (11"x 6" x 4.5") to seven larger slabs, six- 4'x 4' x 7" and one- 4'x8'x7". The new concrete design mix included chlorides, at 15-lbs/yd^3, to simulate contaminated reinforced concrete structures. Monitoring the effectiveness of the coating on the blocks and slabs was included in Phase IV.

Phase I

Task A. Formulate Coating With Different Ratios Of Magnesium And Zinc That Have Easy Application Characteristics, Predictable Galvanic Activity, Long-Term Protection, And Minimum Environmental Impact. The test results of Phase I are shown in Table 1. These potential and current measurements were performed Jan. 10-16, 2000, at the KSC Beach Corrosion Test Site. The blocks were exposed to the outdoor environment for approximately six days, during which there were two rain events, one minor and one major. The data for the major event is shown in Table 1, both before and after the rain. When the current and potential data are graphed and correlated with weather data, it can be seen that coatings with magnesium included have a longer protection period. This protection period starts sooner and ends later than the coatings without magnesium added. This phenomenon indicates two things: The weather does influence corrosion of materials and the addition of magnesium gives a longer reaction time than the zinc, effectively providing corrosion protection for a longer period of time. This effect starts earlier and continues longer than zinc alone.

Table 1.
Results Summary of Phase I Measured in Concrete Test Blocks

TEST PARAMETERS Phase I Designations				BEFORE RAIN		AFTER RAIN		CHANGES [1]		PROTECTION SUMMARY[2]	
Block #	Mg %	Zn %	Active[3]	I (uA)	V (mV)[4] $Ag/AgCl^-$	I (uA)	V (mV)[4] $Ag/AgCl^-$	uA	mV	Corrosion	Protection
1	25	75	No	0	-30	270	-260	270[5]	-230[5]	?	Good
3	0	100	Yes	na	-300	na	-330	na	-30[5]	Yes	na
4	0	100	Yes	400	-300	700	-350	300	-50[5]	?	Good
5	100	0	Yes	[6]	[6]	[6]	[6]	[6]	[6]	[6]	[6]
6	100	0	No	0	-30	5	-40	5	-10	No	Fair
7	0	100	No	0	-50	5	-130	5	-80[5]	?	Fair
8	50	50	No	5	-60	20	-100	15	-40[5]	No	Fair
9	50	50	Yes	0	-170	350	-350	350[5]	-180[5]	No	Good
10	25	75	Yes	[6]	[6]	[6]	[6]	[6]	[6]	[6]	[6]

[1] Change in current and voltage occurs from time rain starts to about 0.7 days later.
[2] *Protection* denotes a subjective evaluation of the current and voltage at the rebar, whether there is sufficient negative voltage and sufficient current to prevent rebar corrosion. The NACE standard, RP0169-96, was used as a guideline for determining protection (with a sacrificial coating in place) potential of the rebar.
[3] *Active* denotes salt-ponded to induce corrosion.
[4] Referenced to an $Ag/AgCl^-$ half cell (manufactured by Broadley James) at 199 mV vs. standard hydrogen electrode (SHE).
[5] Sharp peak occurred after each rain.
[6] Bad electrical connections caused invalid data.

Task B. Determine Which Formulation Will Give The Best Corrosion Protection. The final selection of 25 % Mg and 75 % Zn was made on the basis of the depolarization method (instant-off). The results of these measurements, made in the field on Jan. 21, 2000, are shown in Table 2. A graph of the depolarization test is shown in Figure 3. The best performer was considered to be the largest positive change in the rebar potential after disconnection from the anode, i.e., instant-off measurement.

Table 2.
Results Summary of Phase One Depolarization Test Conducted at the KSC Beach Corrosion Test Site (Procedure reference: NACE RP0290-90)

Mg/Zn	Active	Block #	Depolarization, mV[1]
25/75	NO	1	156
0/100	YES	4	78
100/0	YES	5	Bad Connection
100/0	NO	6	35
0/100	NO	7	47
50/50	YES	9	28
25/75	YES	10	145
50/50	NO	8	Not measured

[1] Referenced to an $Ag/AgCl^-$ half cell at 199 mV vs. standard hydrogen (SHE) (manufactured by Broadley James).

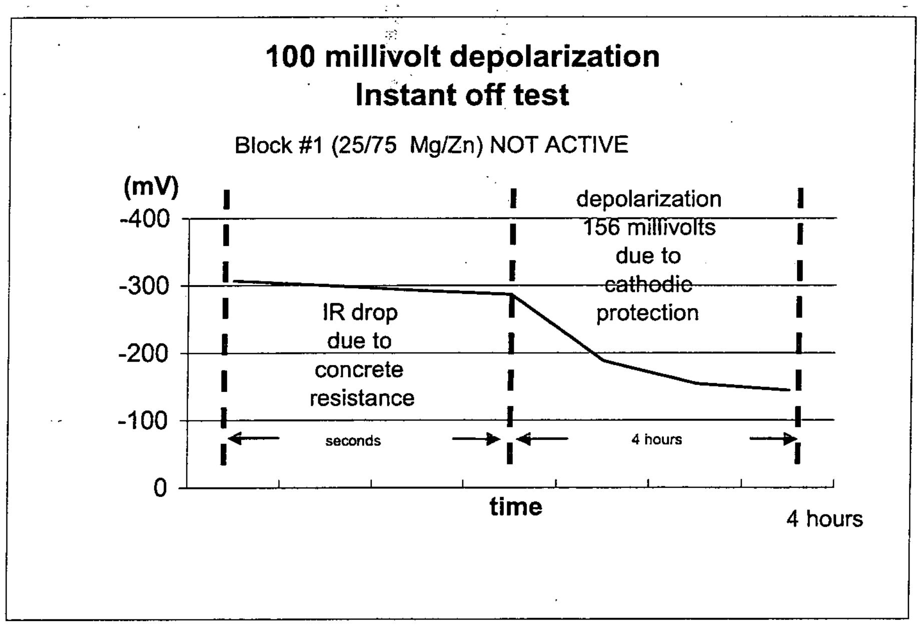


Figure 3. Results of Phase One Depolarization Test

Phase II

Task C. Identify Moisture-Attracting Agents For Incorporation Into The Liquid Applied Coating Formulation. Table 3 shows the seven humectants selected for incorporation in the coating.

Table 3.
Humectants chosen for Phase Two evaluation

Our Abbreviation	Name	Humectant Type
CaS	Calcium sulfate	Inorganic salt, hygroscopic
LiN	Lithium nitrate	Inorganic salt, strongly hygroscopic
CuSPH	Copper sulfate pentahydrate	Inorganic salt, already fully hydrated
SG	Silica gel, grade 62, 60-200 mesh, 150 Angstroms	Silica alumina solid powder, inorganic drying agent
PSS	Polystyrene sulfonic acid	Polystyrene sulfonic acid-co-maleic acid) sodium salt, 1 to 1 styrene/ MAH mole (Aldrich), polymer drying agent
TEG	Tri-ethylene glycol	Organic liquid, hygroscopic
CuS	Copper sulfate	Inorganic salt, unhydrated
NoPB	No paint, blank	Control 1
NoHC	Coated, no humectant	Control 2

Lithium nitrate was one of the humectants in the published study (B. S. Covino, et al., *Materials Performance*, Dec., pp 28-32, 1999). Upon mixing the lithium nitrate in the coating containing zinc and magnesium, the mixture got warm and appeared grainy. Thus, the mixture with lithium nitrate was brushed on the test block instead of sprayed. We also tried lithium bromide, but it reacted with and solidified the mixture, becoming hot and eventually flaming slightly after a few hours in the mixing beaker. PSS and TEG were listed as desiccants in 1997 ASHRAE Fundamentals Handbook, section 21.3.

Task D. Redesign Coating Formulation. The same basic formula for coating ingredients in Phase I was re-used in Phase 2, but the humectant was added to the coating matrix. The chosen metal combination was "75 % zinc and 25 % magnesium" (see Table 4). The volume of metal was the criterion to hold roughly constant in the coating formula; the base volume was 151 mL of Zn (441 g of Zn powder), enough to ensure that the coating will be electrically conductive. The original table of metal ingredients is shown below in Table 5. These amounts were put into 150 grams of coating vehicle.

Table 4.
Phase I metal designations and actual weights used in coating formulations with 150 grams of commercial coating vehicle.

PHASE ONE DESIGNATION, % volume of total metal volume	MAGNESIUM, g	mL	ZINC, g	mL	THINNER, mL
Mg100 %	102	210	0	0	15
Mg75 % Zn25%	76	156	110	38	12
Mg50 % Zn50 %	50	103	220	75	10
Mg25 % Zn75 %	25	51	331	113	7
Zn100 %	0	0	441	151	5

Table 5.
Phase Two coating matrix ingredients.

PHASE TWO INGREDIENT	WEIGHT, g	VOLUME, ML
Commercial Coating Vehicle	100	112
Mg	17	35
Zn	167	57
Thinner	18 **	18
Humectant	45	55
TOTAL	347	190

**Approximate amount; added to enhance flow

<u>Task E. Coat Test Blocks With New Formulation</u>. Table 6 shows the concrete block test matrix with humectants and the polarization values. Block ID numbers 19 and 2 were controls, number 19 with no coating or humectant, and number 2 with coating but no humectant. Characterization of open circuit potential (OCP) is done by placing the given block in a 3-liter pool of 3.5 % sodium chloride in DI water.

Table 6.
Circuit Potentials: ref. Calomel Electrode (mV)

ID #	Anode Dis-connected	Anode Connected	Delta	DATE 1st OCP	CHEMICAL	STATUS 09/06/2000
14	-528	-716	-188	07/14/2000	CaS	Coated
15	-385	-496	-181	07/14/2000	LiN	Coated
16	-516	-568	-52	07/14/2000	CuSPH	Coated
17	-539	-649	-110	07/14/2000	SG	Coated
18	-308	-493	-185	07/14/2000	PSS	Coated
24	-509	-661	-152	07/31/2000	TEG	Coated
20	-383	-510	-127	07/14/2000	CuS	Coated
19	-392	-436	-44	07/14/2000	NoPB	Uncoated
2	-355	-817	-462	08/02/2000	NoHC	Coated/No Hume.

Task F. Monitor New Coating Formulation For Effectiveness. The blocks were connected to the remote data acquisition system (DAS) at the Beach Lab, and were exposed to the outdoor environment for a few weeks until a lightning strike. The blocks were re-characterized in the NASA MSL Lab, re-placed on the racks at the BCTS, and connected to the remote DAS in the Beach Site Lab. Potential, current, and weather data generated is being recorded and accessed remotely. The results continue to be positive, showing the Liquid Galvanic Coating System to be functioning properly.

Task G. Design Test Slabs To Evaluate New Coating Formulation. Test slabs simulating balconies have been designed and are presently being monitored. Each slab contains two #5 mats of reinforcing steel, two to four embedded reference half-cell electrodes and a current density probe. Five slabs were designed with 2" cover and the remaining two with 3" cover.

Task H. Fabricate Test Slabs. A contractor was selected to construct the slabs off site. The test slabs were fabricated according to specifications, delivered, and installed at the NASA Beach Corrosion Test Site (BCTS) in December 2000. Two additional slabs were ordered and were built onsite in March, 2001. The blocks are numbered one thru five and the additional slabs lettered "A" and "B" (see Figure 4). They were protected from the weather using tarps and remained covered until the application of the Liquid Galvanic Coating System.

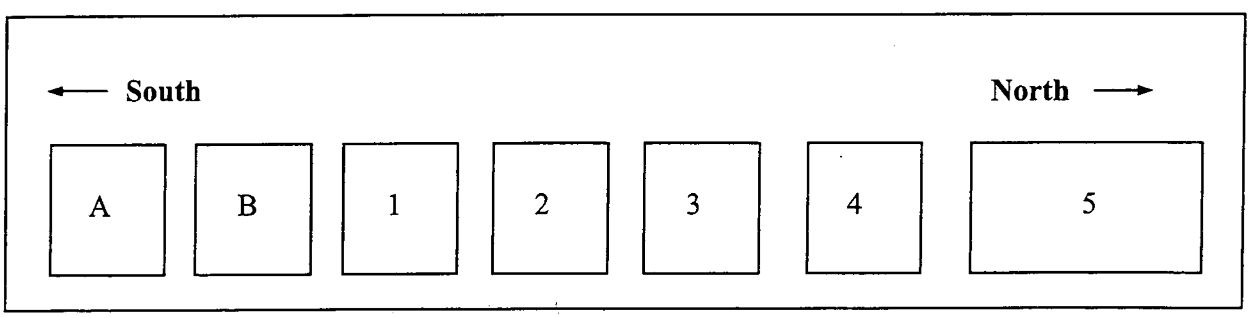


Figure 4. Simulated Reinforced Concrete Structure Layout.

Phase III

Task I. Monitor Phase II Test Blocks For Effectiveness. The LAC test blocks were brought in to the laboratory from the beach exposure racks on January 10, 2002 for performance testing. All blocks were allowed to depolarize over a 48-hour period. Each block was then soaked in a tub with four liters of DM water for 24 hours. The coating potential and embedded reference electrodes were checked using an $Ag/AgCl^-$ reference electrode. All embedded $Ag/AgCl^-$ reference electrodes were determined to be malfunctioning except for one in block 24. Open circuit potentials of the internal reinforcing steel were measured using an external $Ag/AgCl^-$ reference electrode on the surface. The blocks were polarized for approximately 45 minutes or until the potentials stabilized (+/- 5mV) then allowed to depolarize over a four-hour period. Current and potential measurements were taken at specific time intervals for analysis (see Table 7). Data collection on test blocks that did not meet NACE RP290 criteria for a 100mV potential shift were stopped and considered for refurbishment of the coating.

Table 7.
LAC Test Blocks w/ 75% Zn, 25% Mg Coatings (Jan. 2002)

Loc.	Block ID#	Humectant	Potential, mV vs. Ag/AgCl-					IR drop	pol/depol delta (minus ir drop)
			Coating	OCP	Polarized	ocp/pol delta	Depol.(4hr.)		
1	2	None	-725	-193	-610	-417	-202	78 mV	330 mV
2	10	None	-675	-345	-358	-13	stopped		
3	14	CaS	-395	-383	-383	0	stopped		
4	15	LiN	-263	-390	-348	42	stopped		
5	16	CuSPH	-420	-274	-283	-9	stopped		
6	17	SG	-480	-324	-330	-6	stopped		
7	18	PSS	-340	-200	-266	-66	stopped		
8	19	No Coating	n/a	-245	-255	-10	stopped		
9	20	CuS	-385	-212	-322	-110	-157	22 mV	143 mV
10	24	TEG	-375	-309	-311	-2	stopped		

Task J. Refurbish Test Blocks (if needed). Blocks 2, 19, and 20 had new C-Probe $Ag/AgCl^-$ reference cells embedded, were placed back on the exposure racks at the beach site, and were re-connected to the data acquisition system (DAS) computer on March 4, 2002. The remaining blocks were completely stripped and re-coated on March 7, 2002 with either a Zn/Mg or Zn/Mg/In coating. New C-Probe $Ag/AgCl^-$ reference cells were embedded into the remaining blocks and potential measurements were recorded before placing on the racks at the beach (see Table 8). The blocks were reconnected to the DAS computer on March 11, 2002. All blocks except #20 have no humectants. Block #20 has CuS as a humectant in the coating.

Table 8.
Refurbished Block Status (March, 2002)

Location	Block #	Coating % Zn/Mg/In	Coating Dry Thickness	OCP- Rebar ($Ag/AgCl^-$)	Coating Potential ($Ag/AgCl^-$)	Rebar Polarized Potential ($Ag/AgCl^-$)
1	2	75/25/0	old	-193 mv	-.725 v	-610 mv
2	10	75/25/0	38 mil	-213 mv	-1.25 v	-642 mv
3	14	75/25/0	38 mil	-267 mv	-1.23 v	-590 mv
4	15*	75/25/0.2	39.5 mil	-254 mv	-1.28 v	-870 mv
5	16	75/25/0	35 mil	-150 mv	-1.23 v	-615 mv
6	17	75/25/0	38 mil	-282 mv	-1.25 v	-587 mv
7	18*	75/25/0.2	37 mil	-299 mv	-1.29 v	-900 mv
8	19	Uncoated	0	-245 mv	n/a	-255 mv
9	20	75/25/CuS	old	-212 mv	-.385 v	-320 mv
10	24*	75/25/0.2	34.5 mil	-343 mv	-1.27 v	-740 mv

*Indium Added

Task K. Compare And Analyze Initial And Current Data. Potentials of the LAC test blocks, Phase II, from July, 2000 were compared with potential measurements of the same blocks, Phase III, in January, 2002 and in June, 2003, to evaluate the amount of protection (see Table 9). The potential measurements show a positive shift in resting potential of the reinforcing steel. This indicates that the immediate environment surrounding the reinforcing steel has changed to a protective nature due to the success of the anode protecting the reinforcing steel.

Table 9.
Potential Comparisons Phase II.

Block #	Potential, mv vs. $Ag/AgCl^-$ OCP 7/2000	OCP 1/2002	OCP 6/2003	Protection*
2	-315	-193	-345	
10	n/a	-345	-375	n/a
14	-490	-383	-322	Fair
15	-345	-390	-390	Corroding
16	-480	-274	-245	Good
17	-500	-324	-375	
18	-270	-200	-82	Great
19	-350	-245	-380	
20	-343	-212	-182	Good
24	-470	-309	-272	Fair

* Effects of phase II and phase III

Phase IV

Task M. Prepare Test Slabs For LGCS. The bottoms of the slabs were cleaned by water jet blasting using a gas powered pressure washer with a head pressure of 2250 psi.

Task N. Design And Install Optimum Electrical Connection For The LGCS And Rebar. A pair of titanium mesh strips (2" x 45") were installed to the underside of the slabs. These strips will be used to serve as an electrical contact between the GLCS and the rebar. The titanium strips were chosen because of its superior corrosion resistance and electrical properties.

Task O. Identify And Label Wires For Installation To Computer For Data Collection. The wires for the rebar connections and electrochemical devices have been identified and labeled.

Task P. Perform Initial Tests On Slabs And Collect Data To Use For Reference. Resting potentials have been measured using ASTM C-876 procedures and show evidence of corrosion of embedded rebar (see Table 10). Chloride profiles and pH analysis has been performed in at depths of 0.5", 1.0", 1.5", and 2.0", from the top surface, at various locations (see Table 11). Further testing using electrochemical techniques was performed and used as baseline data.

Table 10.
Rebar Potentials (OCP) referenced to an Ag/AgCl half cell electrode at 199mV vs. standard Hydrogen

Rebar Potentials Ag/AgCl (mV)	Test Slabs						
	A	B	1	2	3	4	5
Top Mat	-381	-350	-150	45	-375	182	-175
Bottom Mat	-345	-350	-220	135	-320	110	-220

Task Q. Apply LGCS To Test Slabs, Expose To Environment, And Activate System. The slabs were coated in the 4th quarter 2002.

Task R. Monitor LGCS For Effectiveness. Slab and block current and potential measurement data are being monitored at this time. Initial measurements showed that the coating was not effective in supplying protective current to the reinforcing steel. Dr. Alberto Sagues from USF was contacted and arrangements were made for his assistance here at KSC. It was speculated that the high resistance measurements may be do to carbonization of the concrete. We tested the slabs and found that they were indeed carbonated. The slabs were re-alkalized by the ponding of NaOH solution directly to the top of the slabs. Then the coating was applied to the top surface of two slabs on August 7, 2003. Again this did not improve the supply of protective current to the reinforcing steel.

Table 11.
Simulated Reinforced Concrete Structure Chloride Content and pH Data (October, 2001)

Slab A 2" Cover

Depth:	Cl^- (ppm)	PH
0.5"	5632	11.2
1.0"	2492	11.4
1.5"	2492	11.6
2.0"	3480	11.5

Slab 3 3" cover

Depth:	Cl^- (ppm)	pH
0.5"	2208	11.4
1.0"	3856	11.5
1.5"	3128	11.6
2.0"	2800	11.7

Slab B 2" Cover

Depth:	Cl^- (ppm)	PH
0.5"	3480	11.6
1.0"	3128	11.6
1.5"	2800	11.6
2.0"	2208	11.6

Slab 4 3" cover

Depth:	Cl^- (ppm)	pH
0.5"	188	11.4
1.0"	360	11.6
1.5"	360	11.7
2.0"	360	11.8

Slab 1 2" Cover

Depth:	Cl^- (ppm)	PH
0.5"	1464	11.6
1.0"	3480	11.6
1.5"	2800	11.7
2.0"	1944	11.6

Slab 5 South 2" Cover

Depth:	Cl^- (ppm)	pH
0.5"	1696	11.4
1.0"	3128	11.6
1.5"	2208	11.6
2.0"	2800	11.6

Slab 2 2" Cover

Depth:	Cl^- (ppm)	PH
0.5"	360	11.4
1.0"	360	11.7
1.5"	360	11.8
2.0"	360	11.9

Slab 5 North 2" Cover

Depth:	Cl^- (ppm)	pH
0.5"	320	11.4
1.0"	360	11.4
1.5"	360	11.6
2.0"	360	11.6

RESULTS

Coating Adhesion

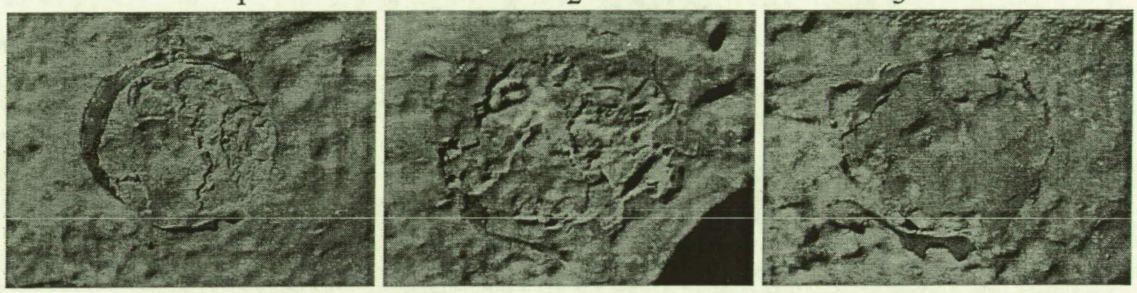
Coating adhesion test were performed, using ASTM D4541-02, on blocks 16, 20, and 24. The adhesion tests showed the coating having a good bond with the substrate. The pull-off strength of the GLAC blocks was performed on three test blocks at the KSC Beach Corrosion Test Site on November 22, 2002. The ASTM D4541-02 Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers was used as a guideline. The coating surfaces were prepared by lightly sanding the test area with 400-grit sandpaper and then wiped clean with an alcohol damped tech wipe. The JB weld adhesive was mixed according to manufacturers recommendations, applied on the loading fixtures (dollies), and secured to the coating surface. Three dollies were installed on each test block. The adhesive was allowed to cure for 24 hours. The pull-off tester, Elcometer adhesion tester (0-500 psi range), was placed over the dollies one at a time and set in motion by turning the hand wheel clockwise in a smooth and constant motion until the system failed. The data was recorded and photographs of each area and dolly were taken (see Figure 5). The possible failures are listed below.

Possible Failures:

- Substrate– Coating Layer One
- Coating Layer One– Coating Layer Two
- Coating Layer Two– Dolly Adhesive
- Adhesive

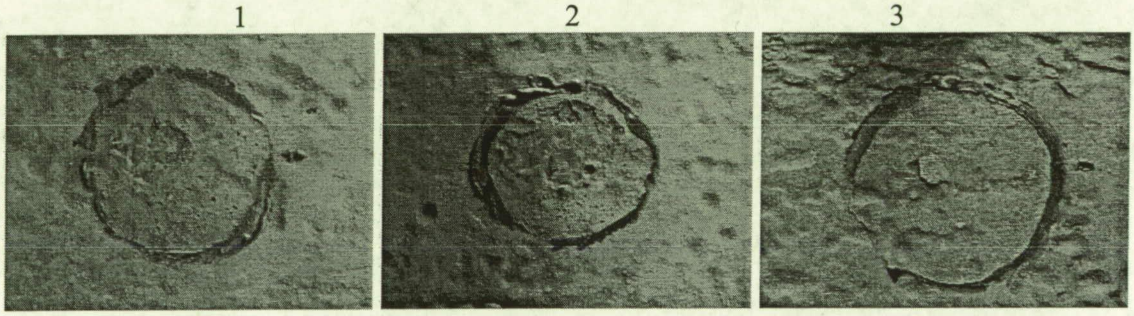
Location 5/ Block 16
Dolly/ Coating Interface

1 2 3



Location 10/ Block 24
Dolly/ Coating Interface

1 2 3



Location 9/ Block 20
Dolly/ Coating Interface

1 2 3

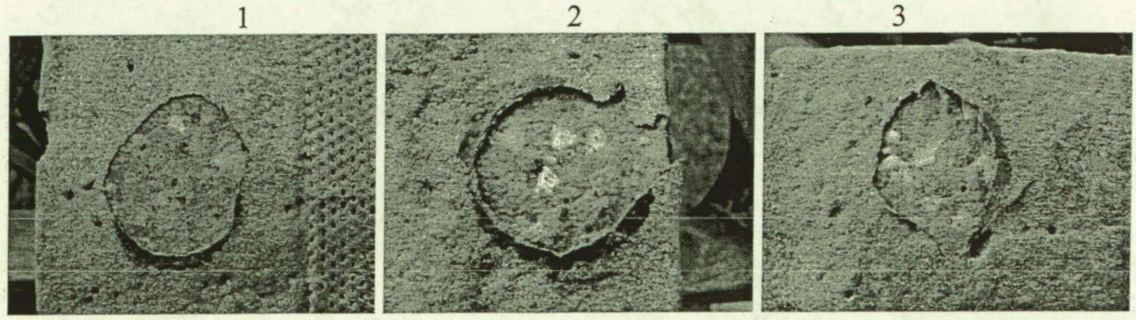


Figure 5. Dolly/Coating Interface

The test blocks have a substrate of concrete and are typically covered with two coats. Table 12 gives the dry film thickness of the respective test blocks. Table 13 gives the failure modes of each test.

Table 12.
LAC Blocks Tested

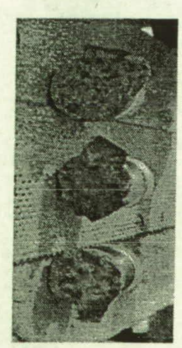
Location #	Block #	Coating	Layer 1 (dft)	Layer 2 (dft)
5	16	Zn/Mg	10 mils	9 mils
9	20	Arc Sprayed Zn	na	na
10	24	Zn/Mg/In	10 mils	7 mils

Table 13.
Failure Modes

Loc 5/ Blk 16		Failure Mode:	
Dolly 1	275 psi	40% cohesive between layers 1 & 2 60% adhesive bonding to topcoat	1
Dolly 2	200 psi	50% cohesive between layers 1 & 2 50% adhesive bonding to topcoat	2
Dolly 3	300 psi	15% cohesive between layers 1 & 2 85% adhesive bonding to topcoat	3

Loc 10/ Blk 24		Failure Mode:	
Dolly 1	150 psi	20% cohesive between layers 1 & 2 80% adhesive bonding to topcoat	1
Dolly 2	125 psi	1% cohesive between layers 1 & 2 99% adhesive bonding to topcoat	2
Dolly 3	150 psi	40% cohesive between layers 1 & 2 60% adhesive bonding to topcoat	3

Loc 9/ Blk 20		Failure Mode:	
Dolly 1	50 psi	100 % Coating	1
Dolly 2	100 psi	100 % Coating	2
Dolly 3	90 psi	100 % Coating	3



Carbonation Analysis

A carbonation profile was performed on the concrete test slabs and a few of the test blocks in May 2003. Seven core samples of 1" diameter by 1" deep were retrieved from the topside of each test slab numbered 1 –5, A, and B. Samples were also taken from test blocks 19, 20, and 24. The drilling was completed using a dry core bit, so the samples could be tested upon removal without having to wait for the cores to dry. To measure the pH of the cement paste the newly cut out core was split in half, sprayed with a universal indicator, and allowed to dry (Figure 6). The pH was then revealed by colors as illustrated below.

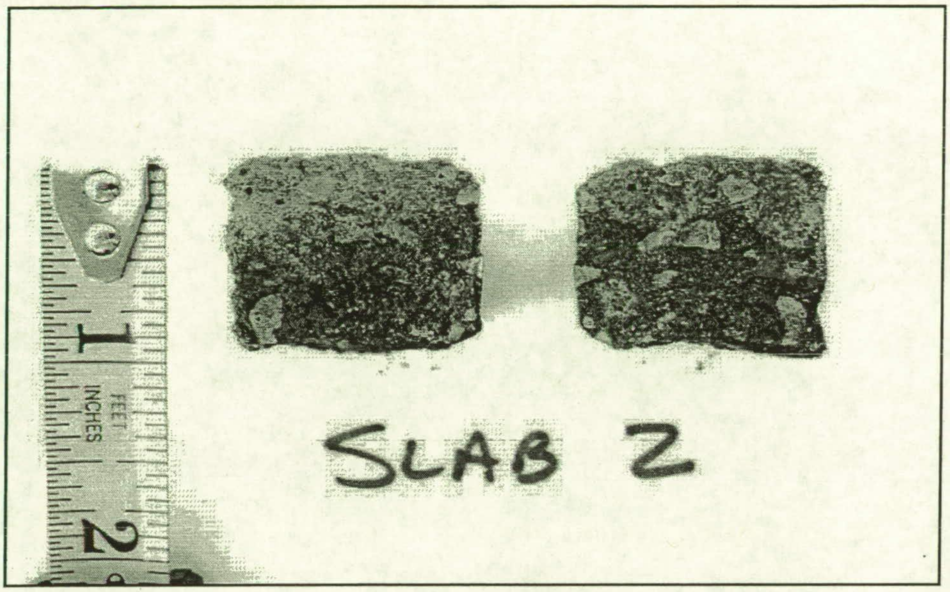


Figure 6. Typical Core Sample with Universal Indicator Applied

pH:	5	7	9	11	13
Color:					

All of the slabs showed some extent of carbonation with pH values between 5 and 7 penetrating from 1/8" to 1/2" deep as summarized in the Figure 7 below.

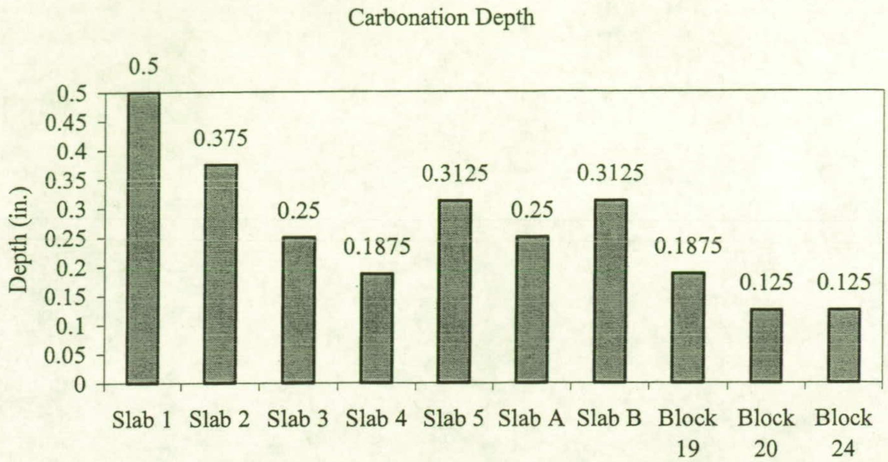


Figure 7. Carbonation Depths of LAC Concrete Samples

Concrete Re-alkalization

The concrete slabs were re-alkalized by ponding a sodium hydroxide solution to the concrete surface. This analysis gives baseline data to use for comparison against the re-alkalized concrete. A dam was set-up on the topside of the slabs using 1" x 2" lumber in August 2003. The final dimensions were 35" x 35" x 1.5", which equates to a volume of 1837.5 in^3 or approximately 30 liters. A 1000ml beaker of sodium hydroxide crystals was added to the water filled dam and stirred. After the mixture was allowed to soak on the slab surface for 60 hrs (over the weekend), the dams were removed and the slab was rinsed off. Once the slabs were dry a core sample of 1" diameter by 1" deep was retrieved from the topside of the test slab. The pH of the newly cut out core was split in half, sprayed with a universal indicator, and allowed to dry. The pH of the re-alkalized concrete core were at least 13 as shown in Figure 8 by the dark blue color of the typical core sample.

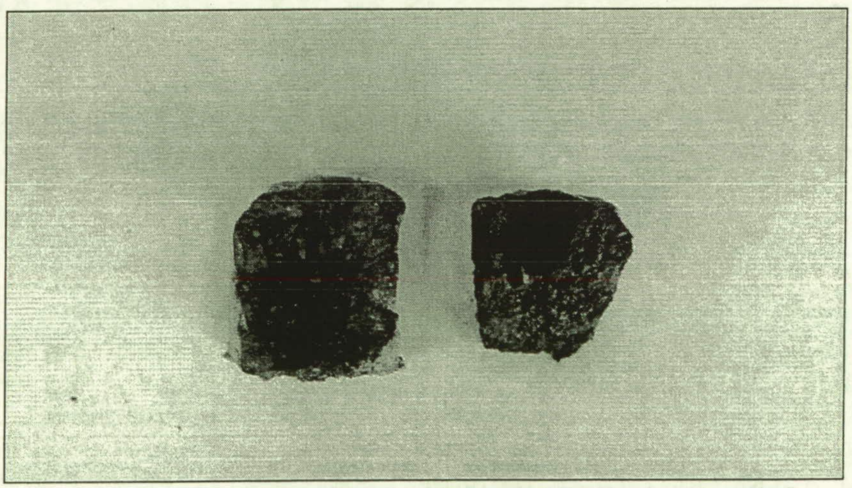


Figure 8. Core Sample with Universal Indicator Applied

pH:	5	7	9	11	13
Color:					

Liquid Applied Coatings Test Blocks-Coating Performance Summary

The LAC test blocks were brought in to the beach laboratory from the exposure racks on May 28, 2003 for coating performance tests. All blocks were allowed to fully depolarize over a 48-hour period. Each block was then soaked in a tub with four liters of DM water for a minimum of 24 hours. After the 24-hour wetting period the coating potentials and embedded $Ag/AgCl^-$ reference electrodes were checked using an external Miller Nelson $Cu/CuSO_4$ and a calibrated Broadley James $Ag/AgCl^-$ reference electrodes. The potential difference between the Miller Nelson and Broadley James reference cells was measured to be -125 mv. The embedded Ag/AgCl reference electrodes were determined to be functioning if their potential readings were within a +/- 20mv tolerance to the external Broadley James and adjusted Miller Nelson measurements. The data collected showed that 50% of the embedded reference cells were malfunctioning and in need of replacement.

Open circuit potential, polarized potential, instant off, and de-polarized measurements of each block were recorded using a Gamry PC-4 Potentiostat. The experimental setup consisted of placing a demineralized water saturated test block in a tub with the rebar of interest upward, placing a Miller Nelson $Cu/CuSO_4$ reference cell on the surface, and positioning a demineralized water drip to wet the top surface (Figure 9).

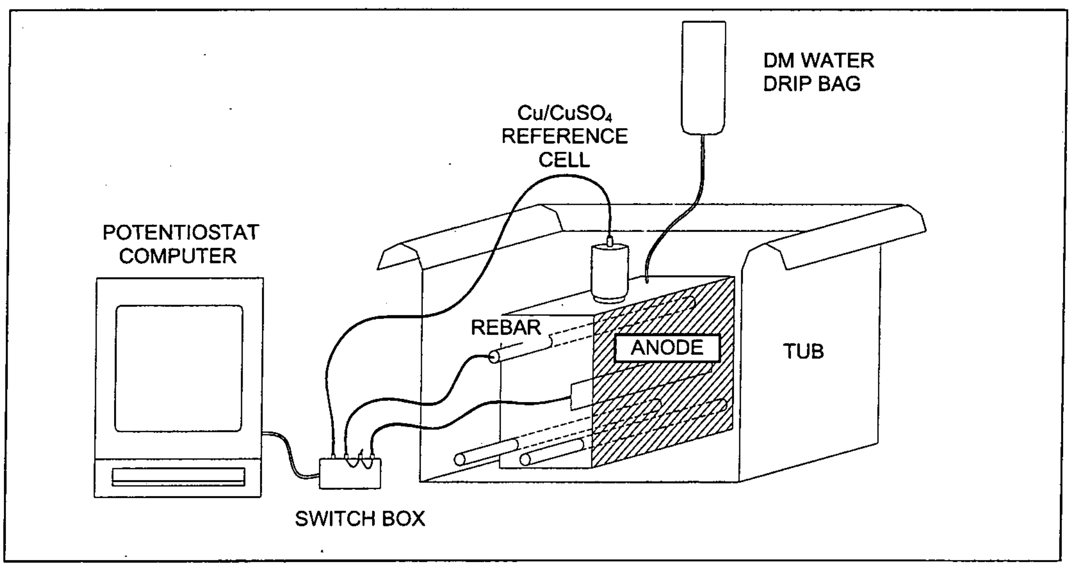


Figure 9. Test Block Experimental Setup

The potential measurements of the internal reinforcing steel were measured using an external Miller Nelson $Cu/CuSO_4$ reference electrode. The blocks were polarized until the potentials stabilized (+/- 5mV) then allowed to depolarize until the "off" potentials stabilized or reached the NACE RP0290 100mv criterion shift (Table 16). As shown in Table 16, blocks 18 and 20 met the NACE RP0290 criteria for sufficient cathodic protection. The potential data was plotted collectively on the same graph to show performance characteristics of the different test blocks (Figure 10). This data confirms the minimum100mv potential shift required to satisfy NACE RP0290 criteria. All values are in millivolts and referenced to Cu/CuSO4 half-cell.

Table 16.
LAC Block Potentials (June 2003)

Block #	Coating % Zn/Mg/In	Coating Potential	OCP- Rebar	Rebar Polarized Potential	Depolarized Potential (1hr))	pol/depol delta
2	75/25/0	-523	-470	-481	-468	<100mv
10	75/25/0	-751	-497	-513	-501	<100mv
14	75/25/0	-676	-447	-463	-447	<100mv
15	75/25/. 2	-781	-514	-566	-502	<100mv
16	75/25/0	-840	-370	-449	-390	<100mv
17	75/25/0	-826	-500	-504	-493	<100mv
18	75/25/. 2	-787	-207	-677	-429	>100mv
19	None	None	-515	N/a	N/a	N/a
20	100% Zn	-1035	-307	-740	-494	>100mv
24	75/25/. 2	-656	-397	-416	-401	<100mv

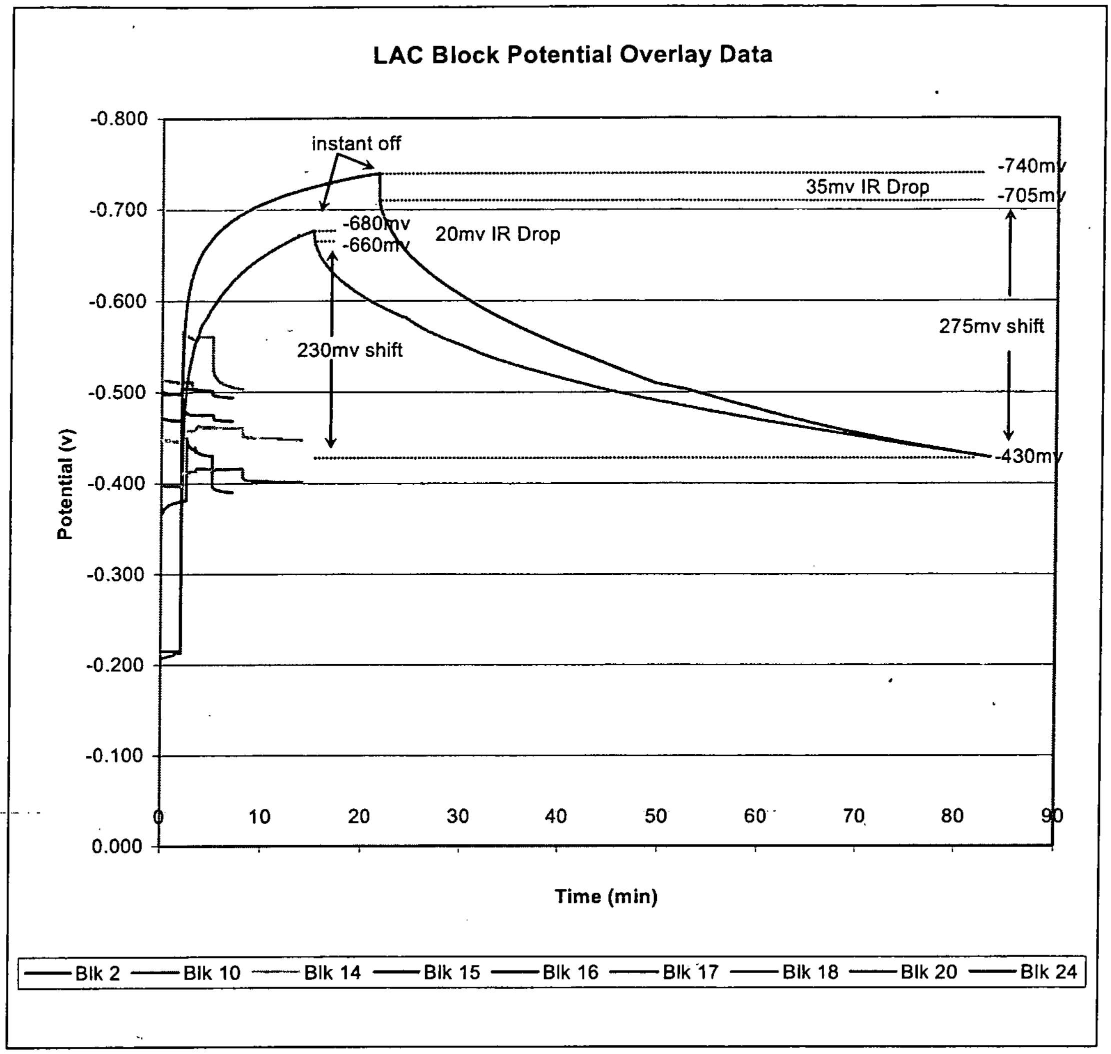


Figure 10. Potential Data

CONCLUSIONS

Half of the embedded reference cells are malfunctioning and need to be replaced. Embedded reference cells are needed for collecting continuous real-time data on the DAS computer. This is an ongoing problem and a suitable embedded reference cell needs to be procured or developed. Blocks 18 and 20 met the criteria for cathodic protection according to NACE RP0290 100mv shift. Further research is needed to discover why these two blocks are performing well while the others have failed. The test blocks were placed back on the exposure stand and reinstalled to the DAS computer system on June 16, 2003.

The Galvanic Liquid Applied Coating works on the smaller test blocks and meets the NACE criteria for protection. Investigation is proceeding in regard to the failure of the coating to protect the reinforcing steel in the larger structures.

SPACEPORT
ENGINEERING &
TECHNOLOGY

National Aeronautics and
Space Administration
John F. Kennedy Space Center

Galvanic Liquid Applied Coatings for the Protection of Steel in Concrete

Joseph Curran and Jerry Curran
ASRC Aerospace/Kennedy Space Center

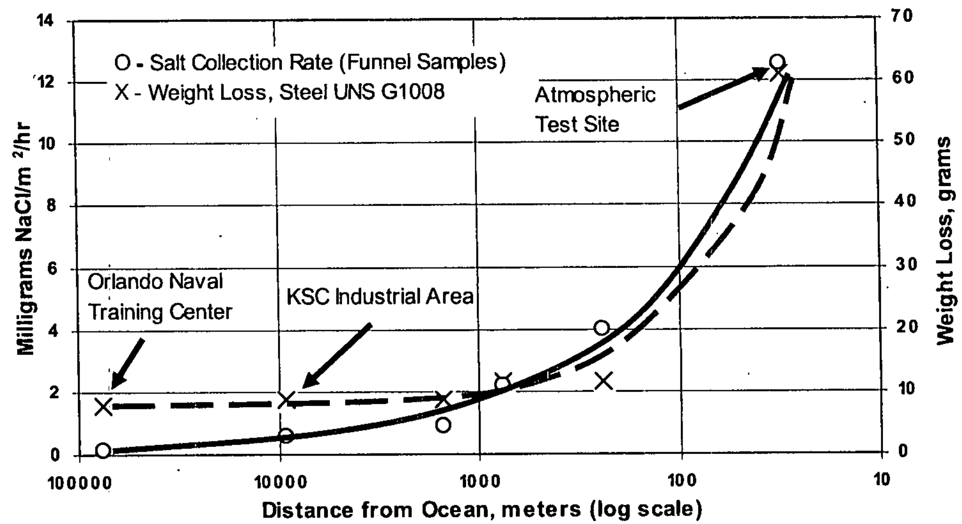
Louis MacDowell
NASA/Kennedy Space Center

Outline

- Environment at KSC
- Material Evaluations at KSC
- Corrosion of Rebar in Concrete
- Functionality of Galvanic Liquid Applied Coating
- Experimental Design
- Data
- Conclusions

Environment at KSC

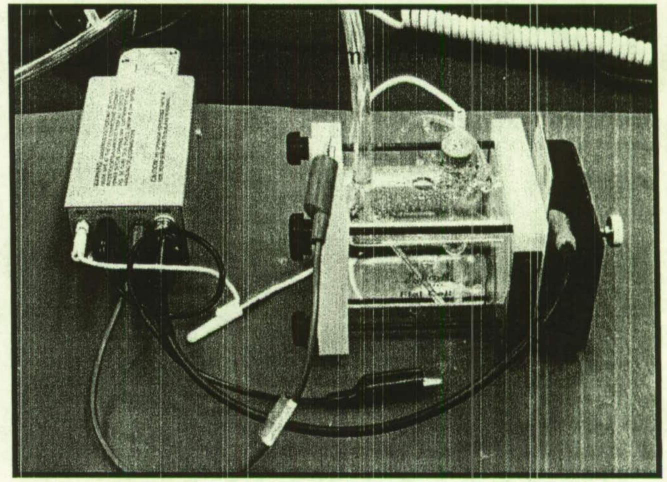
Location	Type Of Environment	µm/yr	Corrosion rate (a) mils/yr
Esquimalt, Vancouver Island, BC, Canada	Rural marine	13	0.5
Pittsburgh, PA	Industrial	30	1.2
Cleveland, OH	Industrial	38	1.5
Limon Bay, Panama, CZ	Tropical marine	61	2.4
East Chicago, IL	Industrial	84	3.3
Brazos River, TX	Industrial marine	94	3.7
Daytona Beach, FL	Marine	295	11.6
Pont Reyes, CA	Marine	500	19.7
Kure Beach, NC (80 ft. from ocean)	Marine	533	21
Galeta Point Beach, Panama CZ	Marine	686	27
Kennedy Space Center, FL (beach)	Marine	1070	42

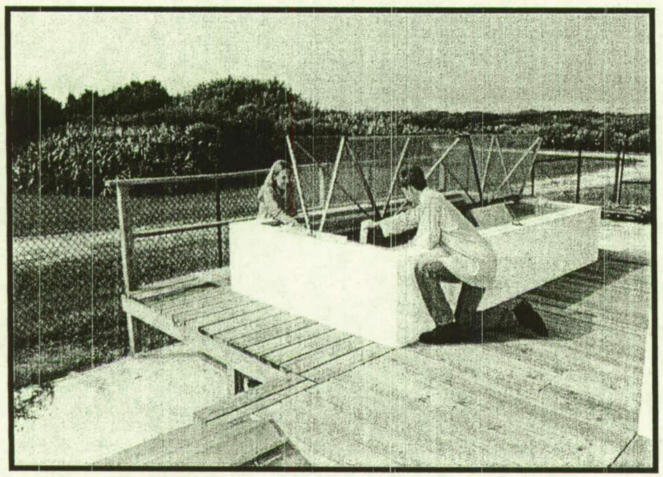


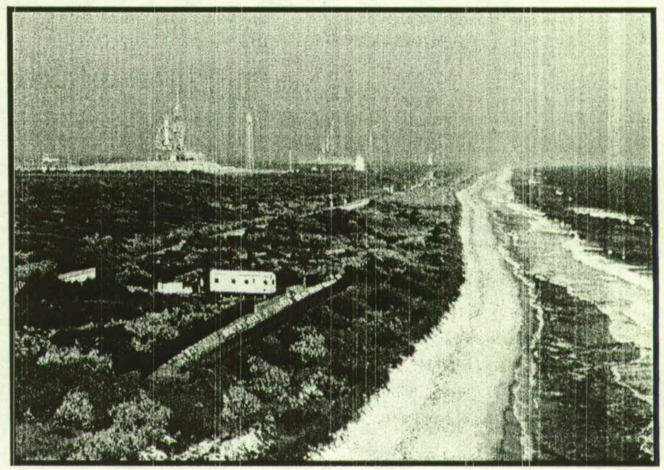
- **ASM documented this site as one of the most corrosive naturally occurring environments.**

Corrosion Technology Testbed

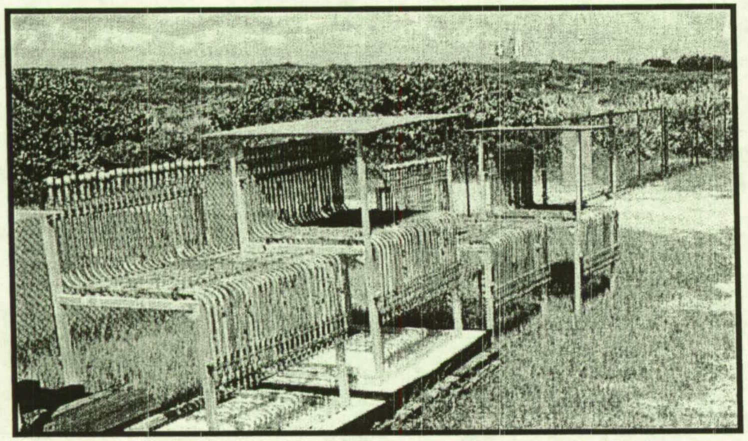
- Electrochemistry laboratory
- Accelerated corrosion equipment
- Coatings application laboratory
- Seawater immersion system
- Atmospheric exposure site

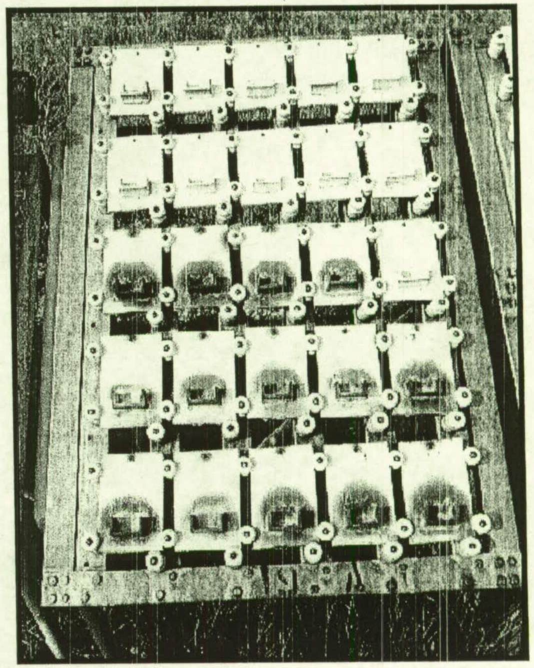


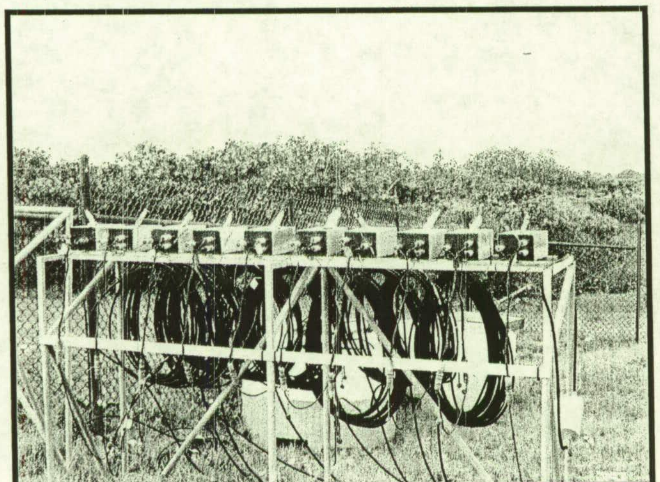




Materials Investigated at the NASA Corrosion Technology Testbed



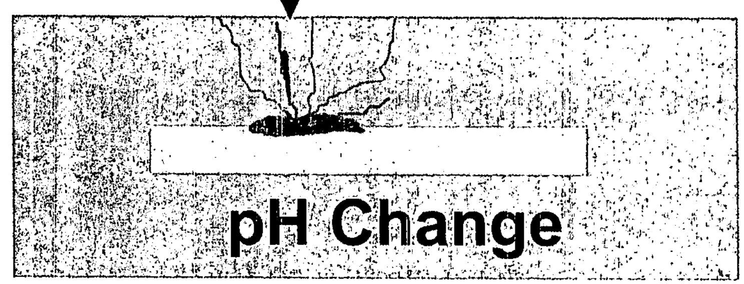




The Corrosion of Steel in Concrete

- A passive film protects rebar from corrosion
- The passive film can be broken down by:
  - Chloride Attack
  - Carbonation of the Concrete
- Corrosion occurs

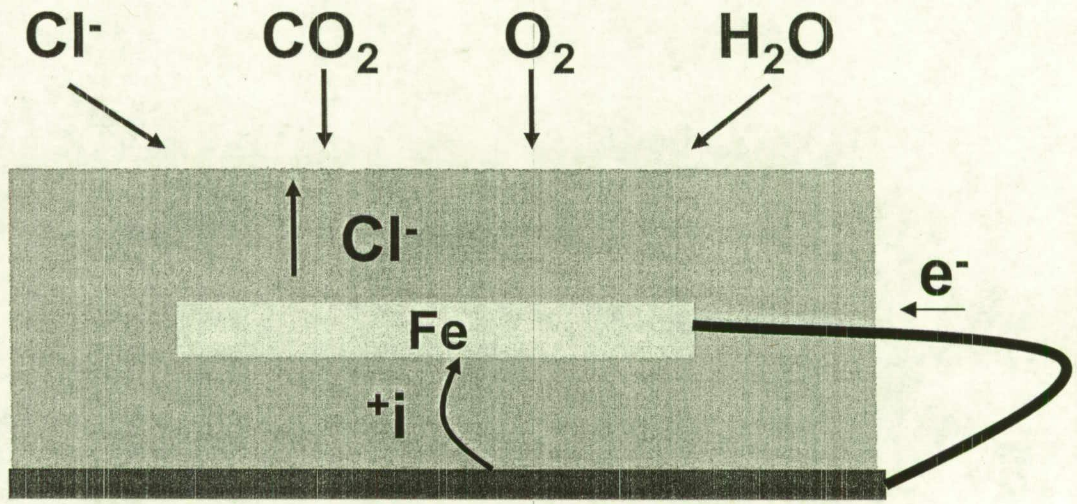
1) Chlorides
2) O_2
3) Moisture
4) CO_2



$$2Fe \rightarrow 2Fe^{+2} + 4e^-$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

The Protection of Steel in Concrete with a Galvanic Liquid Applied Coating



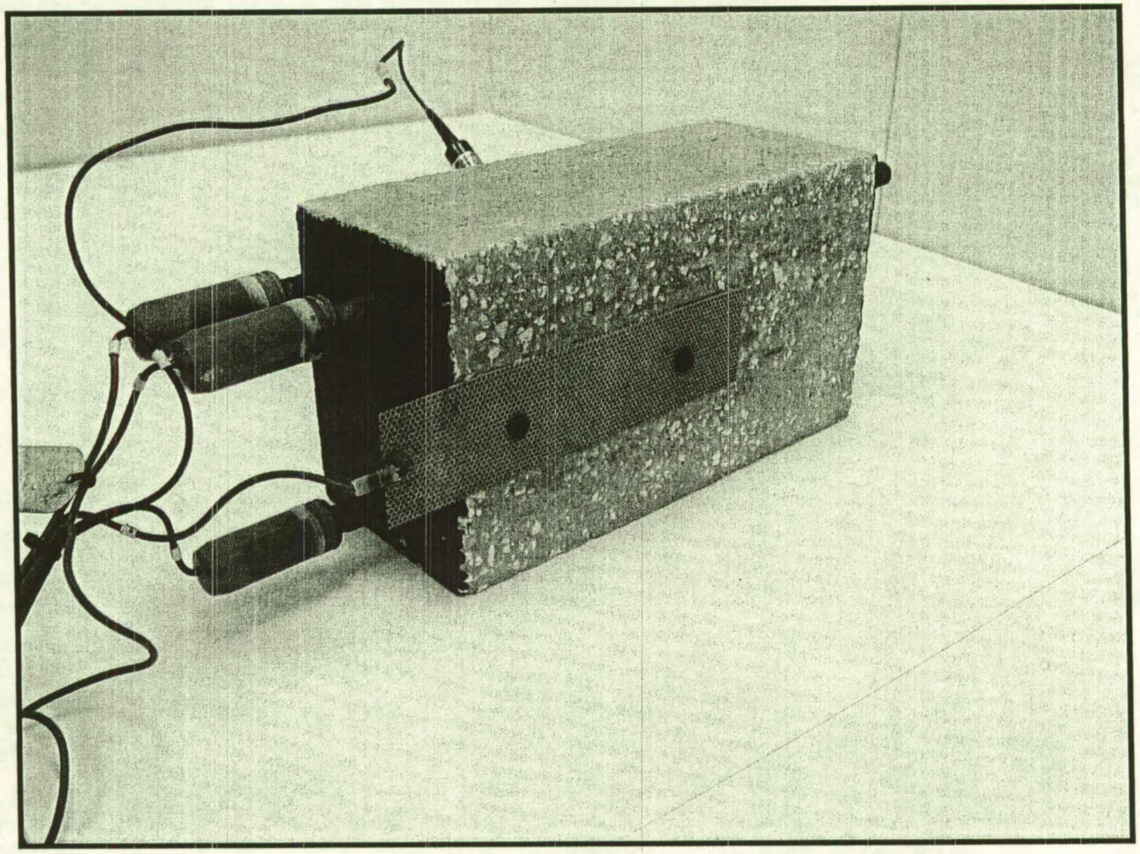
Sacrificial Protective Coating

$$M \rightarrow M^{n+} + ne^-$$

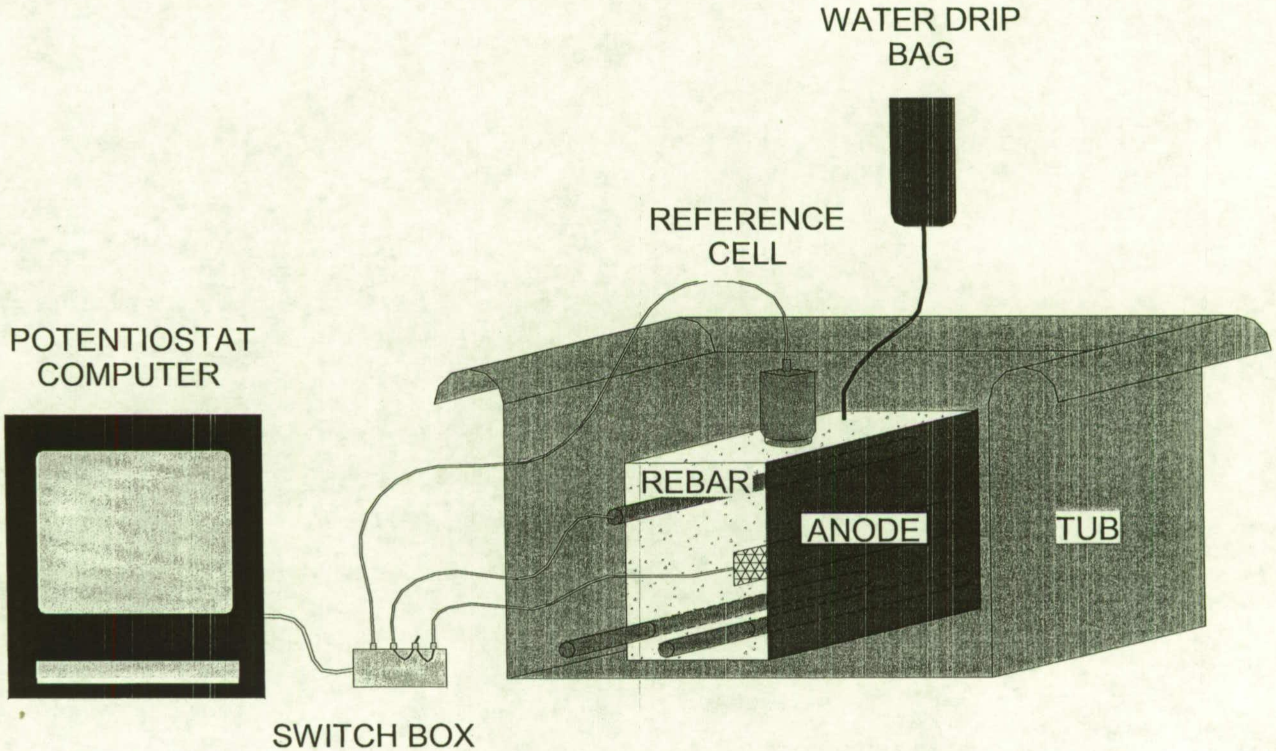
SPACEPORT
ENGINEERING &
TECHNOLOGY

National Aeronautics and
Space Administration
John F. Kennedy Space Center

Experimental Test Blocks
Modified ASTM G 109

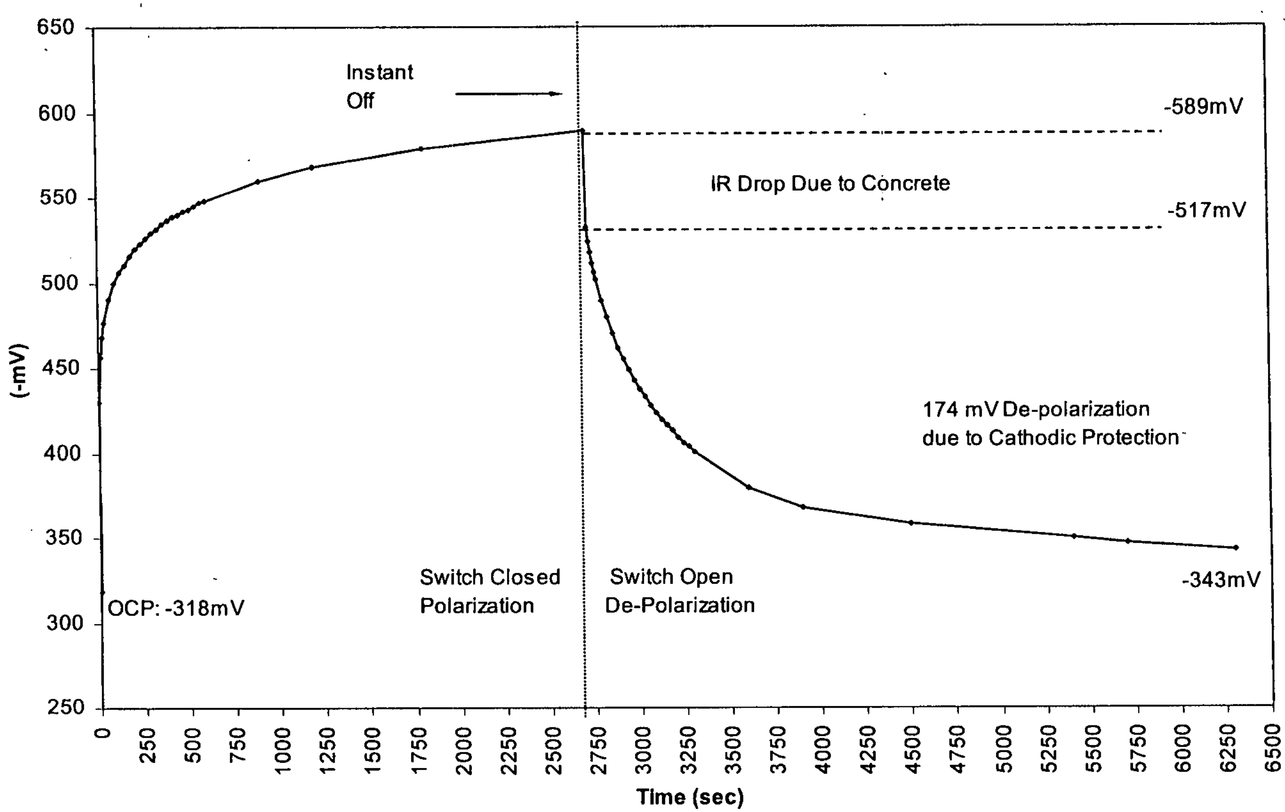


Experimental Apparatus (Laboratory)



Depolarization Testing
(NACE RP0169-96)

Polarization/ De-polarization of Concrete Test Block
Using Broadley James Ag/AgCl Reference Cell



Results of Depolarization Test
(NACE RP0169-96)

Mg/Zn (%)	Active[1]	Depolarization (mV)
0/100	NO	47 mV
0/100	YES	78 mV
25/75	NO	**156 mV**
25/75	YES	**145 mV**
50/50	YES	28 mV
100/0	NO	35 mV

1 "Active" denotes salt-ponding to induce corrosion

Electrochemical Measurements under Atmospheric Conditions

Test Parameters		Before Rain		After Rain		Changes		Protection Summary	
Mg/Zn (%)	Active [3]	Current (uA)	Voltage (mV) [4] (Ag/AgCl-)	Current (uA)	Voltage (mV) [4] (Ag/AgCl-)	Δ uA	Δ mV	Corrosion	Protection
0/100	No	0	-50	5	-130	5	-805	?	Fair
0/100	Yes	Na	-300	na	-330	na	-305	Yes	n/a
0/100	Yes	400	-300	700	-350	300	-505	?	Good
25/75	No	0	-30	270	-260	2705	-2305	?	Good
50/50	No	5	-60	20	-100	15	-405	No	Fair
50/50	Yes	0	-170	350	-350	3505	-1805	No	Good
100/0	No	0	-30	5	-40	5	-10	No	Fair

1 Change in current and voltage occurs from time rain starts to about 0.7 days later.
2 "Protection" denotes a subjective evaluation of the current and voltage at the rebar, whether there is sufficient negative voltage and sufficient current to prevent rebar corrosion. The NACE standard, RP0169-96, was used as a guideline for determining protection (with a sacrificial coating in place) potential of the rebar.
3 "Active" denotes salt-ponded to induce corrosion.
4 Referenced to an Ag/AgCl- half cell (manufactured by Broadley James) at 199 mV vs. standard hydrogen electrode (SHE).
5 Sharp peak occurred after each rain.

Recorded Potentials (New Formulation)

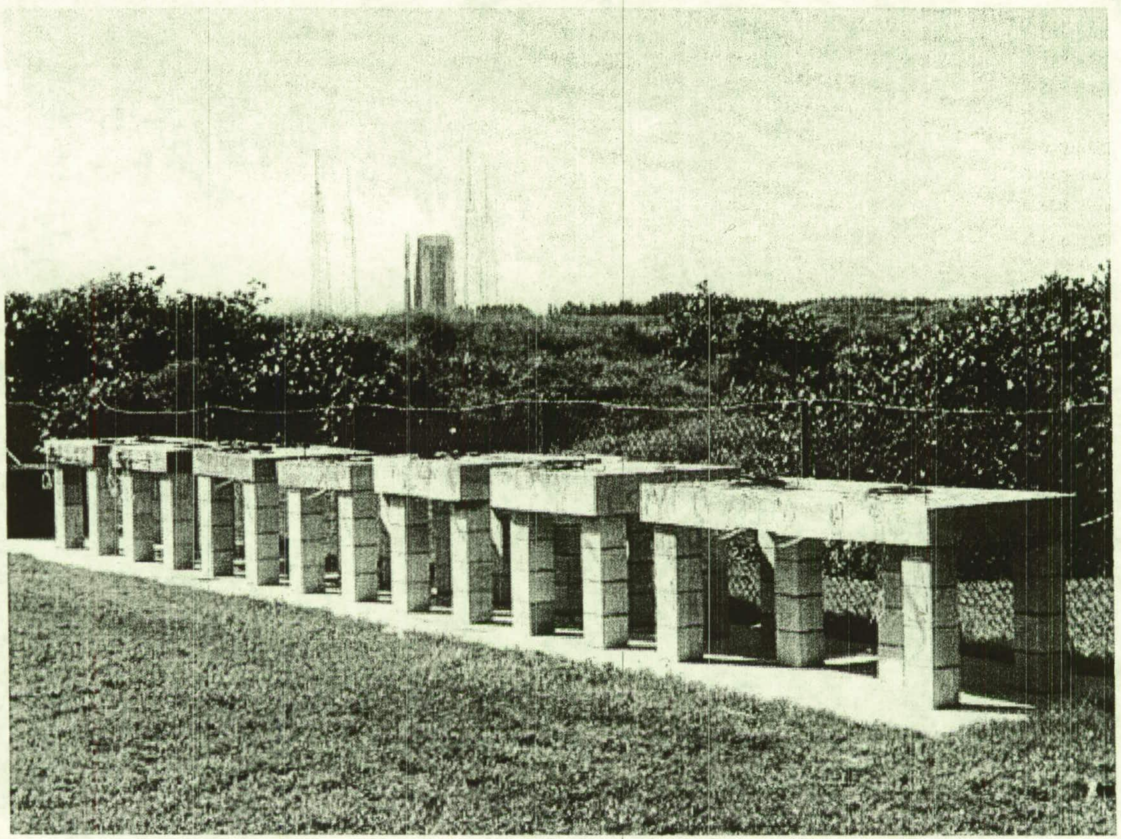
March 2002

Coating % Mg/Zn/In	Coating Dry Thickness	OCP - Rebar ($Ag/AgCl^-$)	Coating Potential ($Ag/AgCl^-$)	Rebar Polarized Potential ($Ag/AgCl^-$)
Uncoated	0 mil	-245 mV	n/a	-255 mV
25/75/0	38 mil	-282 mV	-1250 mV	-587 mV
25/75/0	38 mil	-267 mV	-1230 mV	-590 mV
25/75/0	38 mil	-213 mV	-1250 mV	-642 mV
25/75/0	35 mil	-150 mV	-1230 mV	-615 mV
25/75/0.2	34.5 mil	-343 mV	**-1270 mV**	**-740 mV**
25/75/0.2	37 mil	-299 mV	**-1290 mV**	**-900 mV**
25/75/0.2	39.5 mil	-254 mV	**-1280 mV**	**-870 mV**

Comparison of Measured Potentials

Potential vs. Ag/AgCl$^-$ (mV)					
Coating % Mg/Zn/In	**OCP 7/2000**	**OCP 1/2002**	**OCP 6/2003**	**$\Delta E_{0\text{-}35}$**	**Protection**
Uncoated	-350	-245	-380	30	
25/75/0	-315	-193	-345	-30	Good Init. Perf.
25/75/0	-500	-324	-375	125	Good Init. Perf.
25/75/0	-490	-383	-322	168	Fair
25/75/0	-480	-274	-245	235	Good
25/75/0.2	-270	-200	-82	188	Great
25/75/0.2	-470	-309	-272	198	Fair
25/75/0.2	-345	-390	-390	-45	Corroding

Current / Future Work



Conclusions and Comments

- Two Blocks met the criteria for cathodic protection according to the NACE RP0169 100 mV shift.
- The Galvanic Liquid Applied Coating works on ASTM G109 test blocks and meets the NACE criteria for protection.
- The data suggests that the environment surrounding the rebar has changed to a more protective condition as indicated by the positive shift in OCP on the reinforcing steel for five of the seven test blocks.
- The Coatings have caused a shift in potential of the reinforcing steel greater than 300 mV and as much as 600 mV.
- An investigation is proceeding to determine the effectiveness of the liquid applied coating to protect reinforced steel in larger structures.

NASA Corrosion Technology Testbed

Louis MacDowell
NASA/Kennedy Space Center
321-867-4550
Louis.G.MacDowell@nasa.gov

Luz Marina Calle
NASA/Kennedy Space Center
321-867-3278
Luz.M.Calle@nasa.gov

Joseph Curran
ASRC Aerospace Corporation
321-867-7558
Joseph.Curran-1@ksc.nasa.gov

KSC Web Site
http://corrosion.ksc.nasa.gov

Acknowledgements

- Without the support of many others, this project could not have been possible. Following are people and groups that deserve many thanks:
- Chris Fogarty
- Guy Smith
- Dave Mclaughlin
- Jerry Staub
- Bill Dearing
- Luz Marina Calle
- Rubie Vinje
- Mark Kolody
- ASRC Data Acquisition System Lab personnel
- ASRC Chemical Instrumentation & Processes Lab personnel