History of the Development of Liquid-Applied Coatings for Protection of Reinforced Concrete

Joseph J. Curran
ASRC Aerospace
NASA Corrosion Technology Lab
Kennedy Space Center, FL 32899

Marlin H. Hansen
Cortec Corporation
St. Paul, NM

ABSTRACT

Corrosion of reinforcing steel in concrete is an insidious problem for structures at Kennedy Space Center (KSC). KSC is located on the coast of Florida in a highly corrosive atmosphere. Launch pads, highway bridge infrastructure, and buildings are strongly affected. To mitigate these problems, NASA initiated a development program for a Galvanic Liquid-Applied Coating System (GLACS). A breakthrough in this area would have great commercial value in transportation, marine and construction industry infrastructures.

The patented NASA GLACS system has undergone considerable testing to meet the needs of commercialization. A moisture-cure coating gives excellent adhesion with ease of application compared to existing galvanic products on the market. The latest development, *GalvaCorr*, can be sprayed or hand applied to almost any structure shape. A self-adhesive conductive tape system has been devised to simplify current collection within the coating areas.

In testing programs, millivolt potential and milliamp output per square foot of anode have been closely studied at actual test sites. These two parameters are probably the most challenging items of a resin-based, room-temperature-applied, galvanic coating. Extensive re-formulation has resulted in a system that provides the needed polarization for catholic protection of reinforcing steel in concrete in a variety of structure environments.

The rate of corrosion of rebar in concrete is greatly affected by the environment of the structure. In addition to this, for any given concrete structure; moisture level, carbonization, and chloride contamination influences the rate of rebar corrosion. Similarly, the cathodic protection level of galvanic systems is also dependent on the moisture level of the concrete. GalvaCorr is formulated to maintain galvanic activity as the moisture level of the structure declines. GalvaCorr is available as a three-part kit. The mixing step requires about ten minutes. The viscosity can be easily adjusted to meet the application needs. The pot or working life is four to six hours, depending on the temperature. GalvaCorr can be thought of as a spray-on coating, battery ready to provide up to -1.4 volts (relative to CSE) of cathodic protection (CP) potential.

Key Words: concrete, cathodic-protection, coating, corrosion, rebar

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. In September of 2003 a United States Patent was issued to the inventors. Subsequent to this patent, NASA issued a non-exclusive license to Cortec for the application and marketing of this coating.

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. The KSC coating has metal particles suspended in the paint matrix. The KSC main metallic constituents are zinc, magnesium, and indium in a specified ratio with a silicate binder. The Cortec GalvaCorr coating consists of aluminum and magnesium in a specific ratio mixed in a urethane binder. This aluminum and magnesium mix provides up to -1.4 volts (relative to CSE electrode) of protection.

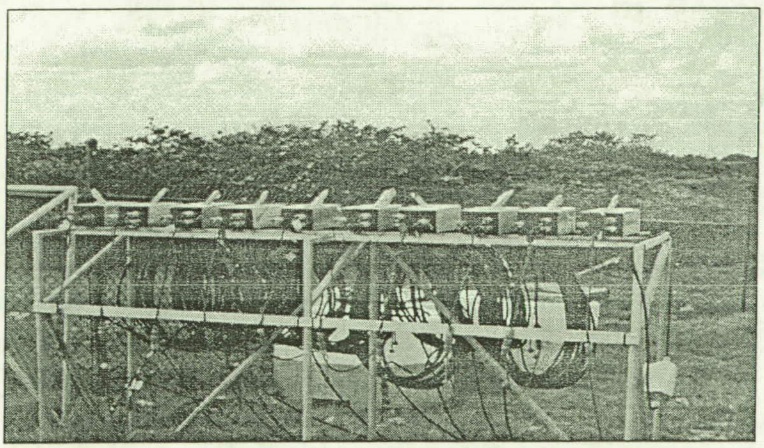

Figure 1. Test Blocks

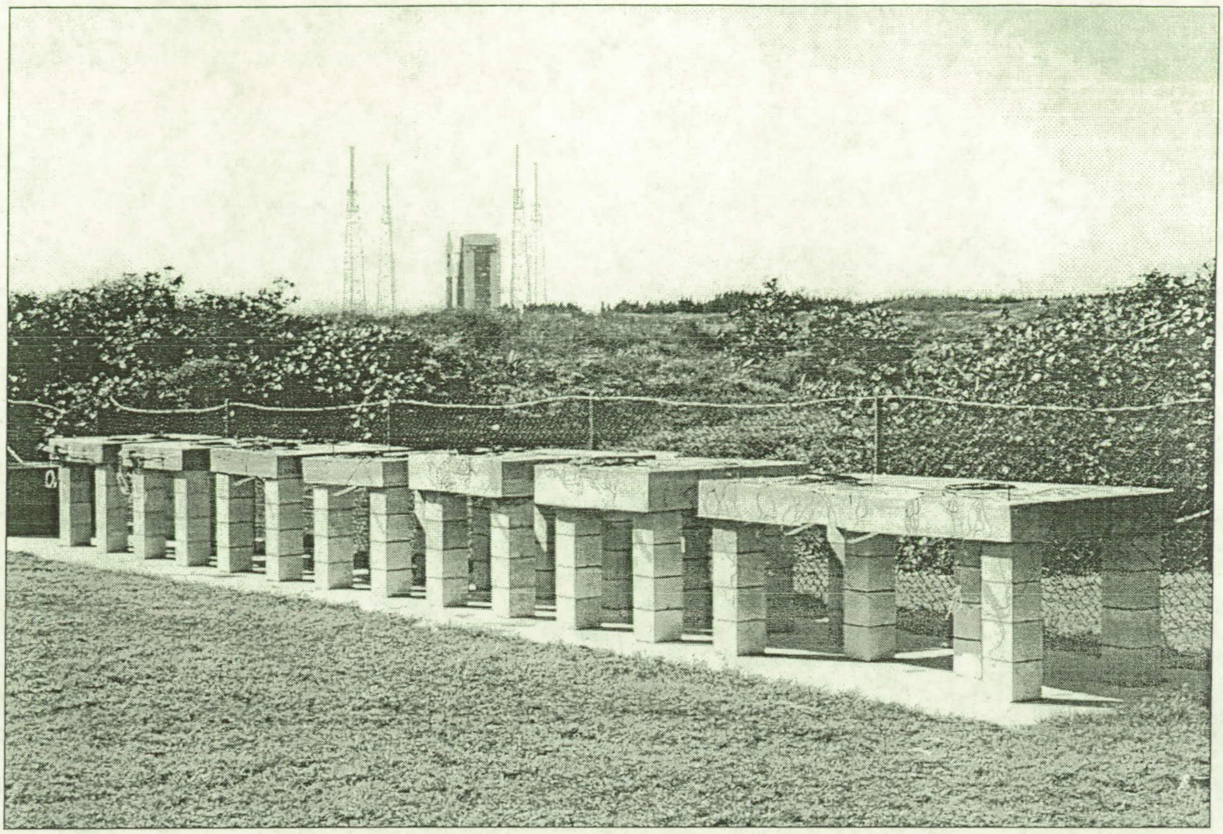

Figure 2. Simulated Reinforced Concrete Structures

EXPERIMENTAL PROCEDURE

The effort was 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, 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 new concrete design mix included chlorides, at 15-lbs/yd^3, to simulate contaminated reinforced concrete structures.

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.

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
4	0	100	Yes	400	-300	700	-350	300	-50[5]	?	Good
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

[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.

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	Block #	Depolarization, mV[1]
25/75	1	156
0/100	4	78
100/0	5	Bad Connection
100/0	6	35
0/100	7	47
50/50	9	28
25/75	10	145
50/50	8	Not measured

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

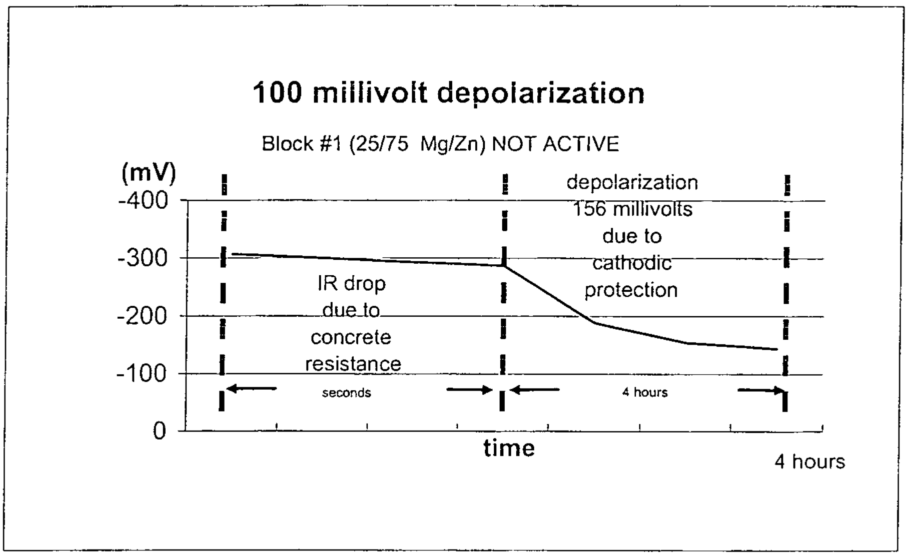

Figure 3. Results of Phase One Depolarization Test

Phase II

<u>Task C. Identify Moisture-Attracting Agents For Incorporation Into The Liquid Applied Coating Formulation.</u> Seven humectants were considered for incorporation into the formula. At this time none were chosen to be incorporated into the present formula.

<u>Task D. Design and Fabricate Test Slabs To Evaluate New Coating Formulation.</u> Test slabs simulating balconies have been designed and were prepared for monitoring. 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.

Phase III

<u>Task E. Monitor Phase II Test Blocks For Effectiveness.</u> 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. 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 3). 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 3.
LAC Test Blocks w/ 75% Zn, 25% Mg Coatings (Jan. 2002)

Loc.	Block ID#	Humectant	Potential, mV vs. Ag/AgCl- Coating	OCP	Polarized	ocp/pol delta	Depol.(4hr.)	IR drop	pol/depol delta (minus ir drop)
1	2	None	-725	-193	-610	-417	-202	78 mV	330 mV
9	20	CuS	-385	-212	-322	-110	-157	22 mV	143 mV

Task F. Refurbish Test Blocks (if needed) Blocks were completely stripped and re-coated on March 7, 2002 with either a Zn/Mg or Zn/Mg/In coating. Potential measurements were recorded before placing on the racks at the beach (see Table 4). 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 4.
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 mV	-610 mV
2	10	75/25/0	38 mil	-213 mV	-1250 mV	-642 mV
3	14	75/25/0	38 mil	-267 mV	-1230 mV	-590 mV
4	15*	75/25/0.2	39.5 mil	-254 mV	-1280 mV	-870 mV
5	16	75/25/0	35 mil	-150 mV	-1230 mV	-615 mV
6	17	75/25/0	38 mil	-282 mV	-1250 mV	-587 mV
7	18*	75/25/0.2	37 mil	-299 mV	-1290 mV	-900 mV
8	19	Uncoated	0	-245 mV	n/a	-255 mV
9	20	75/25/CuS	old	-212 mV	-385 mV	-320 mV
10	24*	75/25/0.2	34.5 mil	-343 mV	-1270 mV	-740 mV

*Indium Added

Task G. 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 5). 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 5.
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 H. Apply LGCS To Test Slabs, Expose To Environment, And Activate System. The slabs were coated in the 4th quarter 2002.

Task I. 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.

Task J. Coating Adhesion. Coating adhesion test were performed, using ASTM D4541-02, on blocks 16 and 24 with dry film thicknesses of 10 mils each. The adhesion tests showed the GLACS coating having a good bond with the substrate. The ASTM D4541-02 Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers was used as a guideline.

RESULTS

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.

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 4).

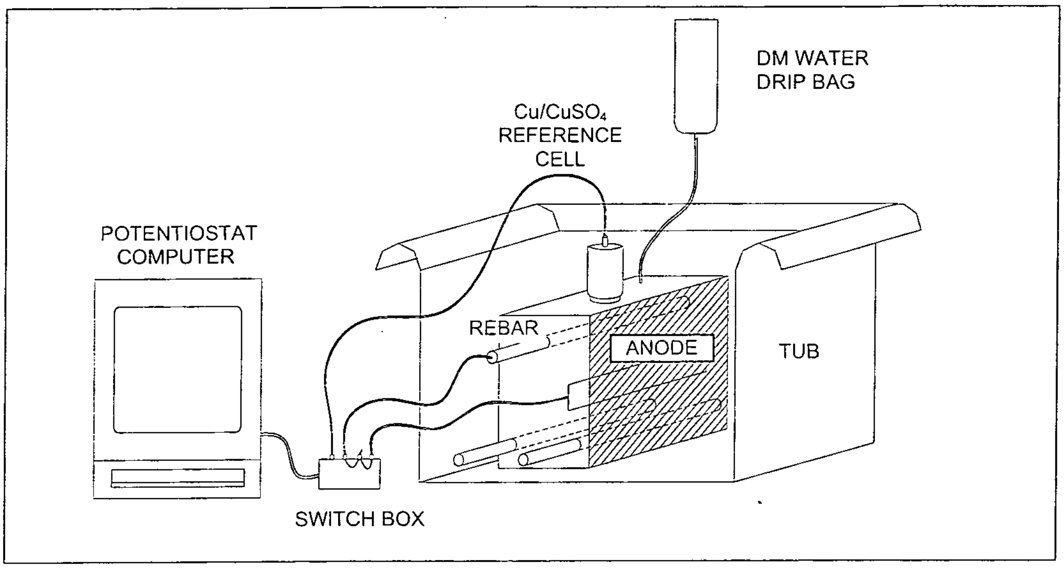

Figure 4. Test Block Experimental Setup

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 6). As shown in Table 6, 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 5). 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 6.
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

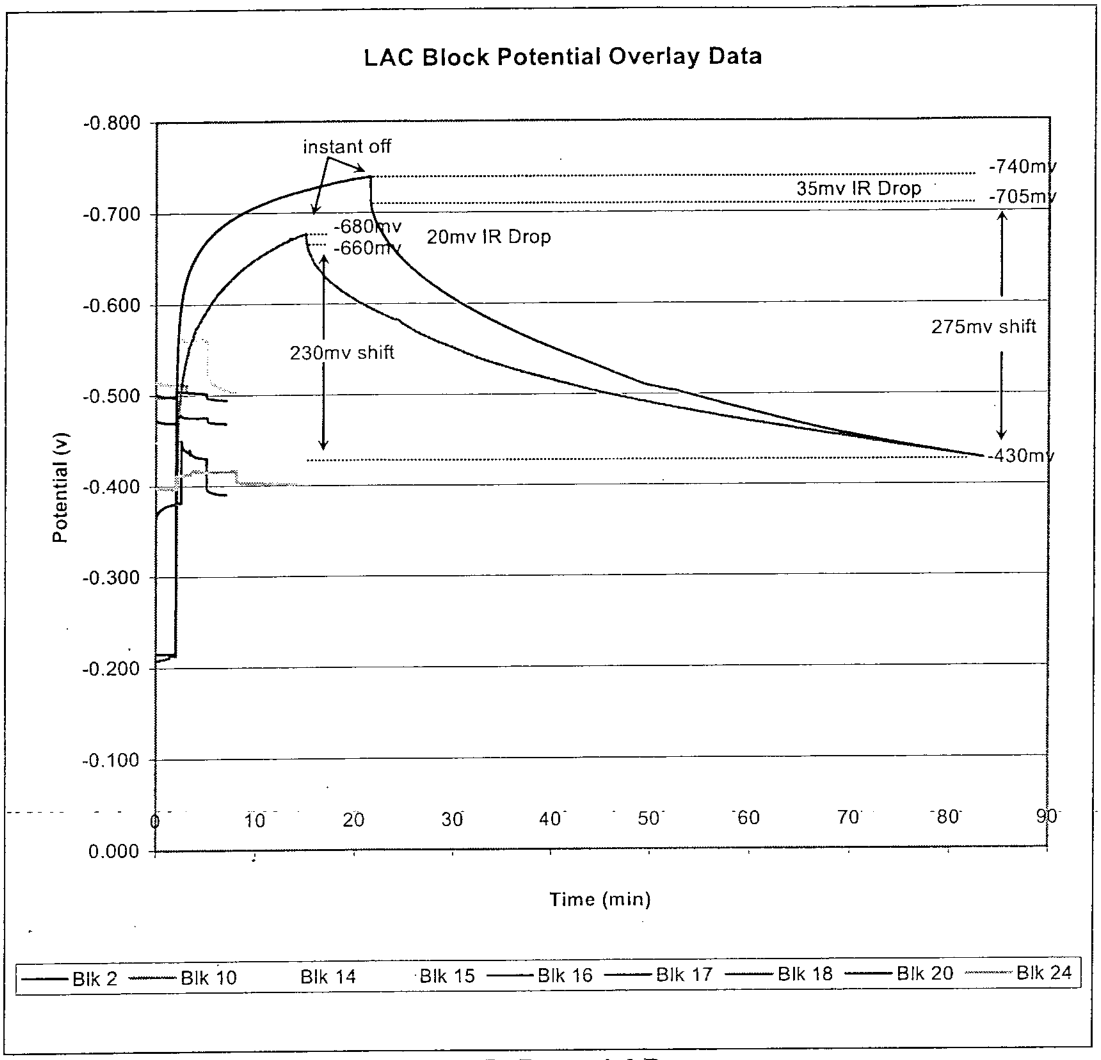

Figure 5. Potential Data

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.

GalvaCorr

GalvaCorr is a three component moisture cured metallic rich coating. This room temperature liquid coating can be applied to structures of many shapes. This new reformulated coating provides galvanic cathodic protection arresting corrosion for steel in concrete at a coverage rate of 180 sq. ft. per gallon.
Galva Corr can be:

- Applied by spray, brush, or roll coating
- Recommended for bridges, decks, ramps, and garages
- Applied to uneven surfaces and to the underside of structures

Experiments at the Cortec labs shows no corrosion of samples when subjected to 6 months in a humidity chamber, whereas, the unprotected control samples gave signs of corrosion. Subsequent to these experiments the underside application to a bridge structure was undertaken by the city of St. Paul.

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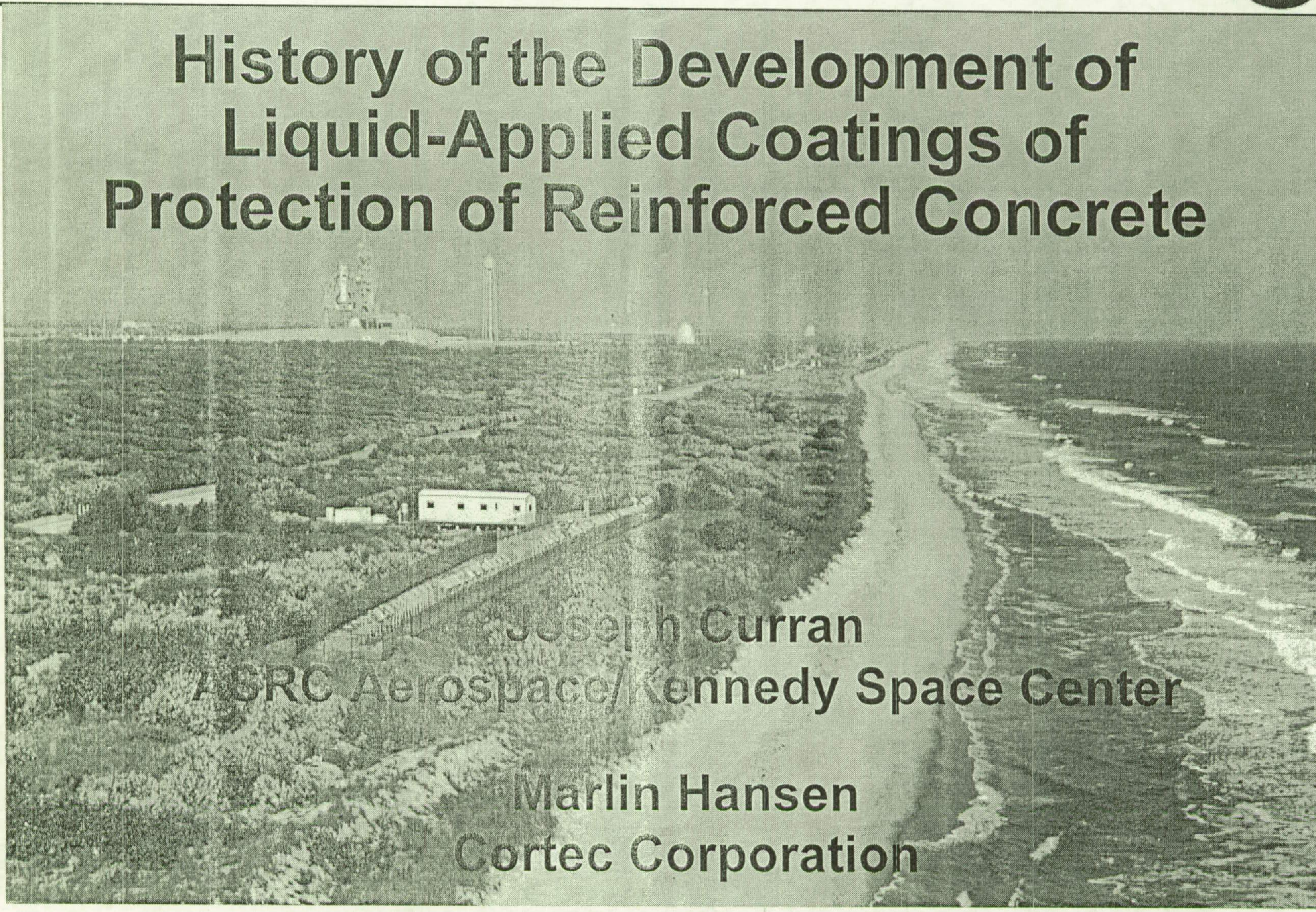

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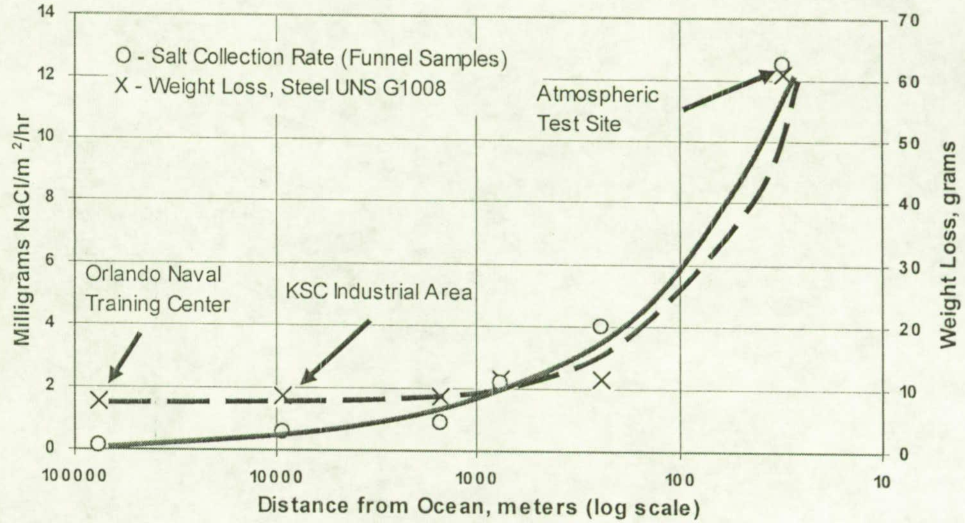
Outline

- Environment at KSC
- Material Evaluations at KSC
- Corrosion of Reinforcing Steel in Concrete
- Galvanic Liquid Applied Coating
- Experimental Design
- Data
- GalvaCorr

Environment at KSC

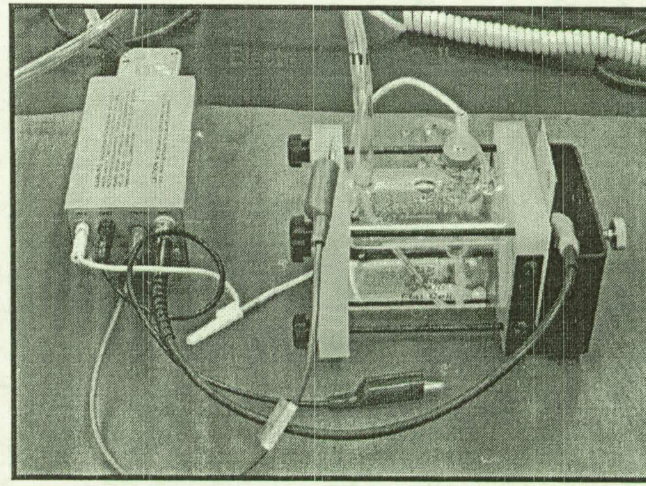
Location	Type Of Environment	µm/yr	Corrosion rate (a) mils/yr
Esquimalt, Vancouver Island, BC, Canada	Rural marine	13	0.5
Pittsburgh, PA	Industrial	30	1.2
Cleveland, OH	Industrial	38	1.5
Limon Bay, Panama, CZ	Tropical marine	61	2.4
East Chicago, IL	Industrial	84	3.3
Brazos River, TX	Industrial marine	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

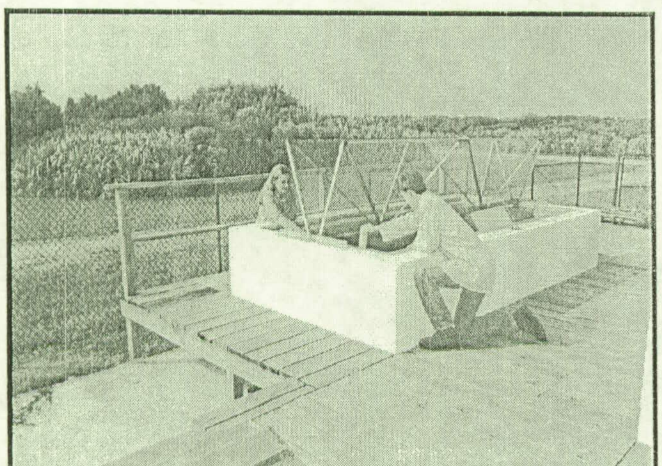


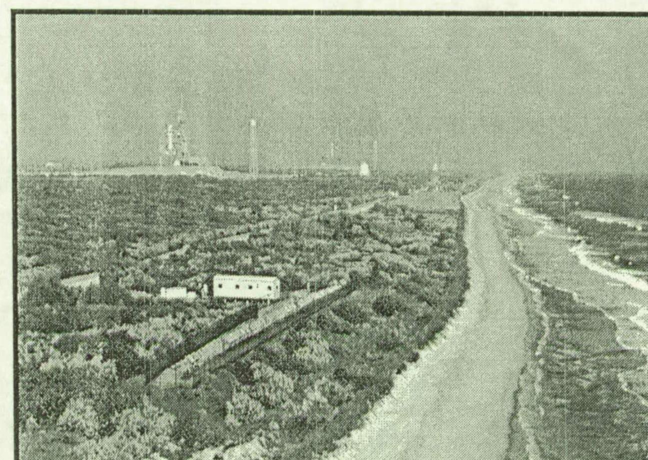
- ASM documented this site as one of the most corrosive naturally occurring environments.

Corrosion Technology Testbed

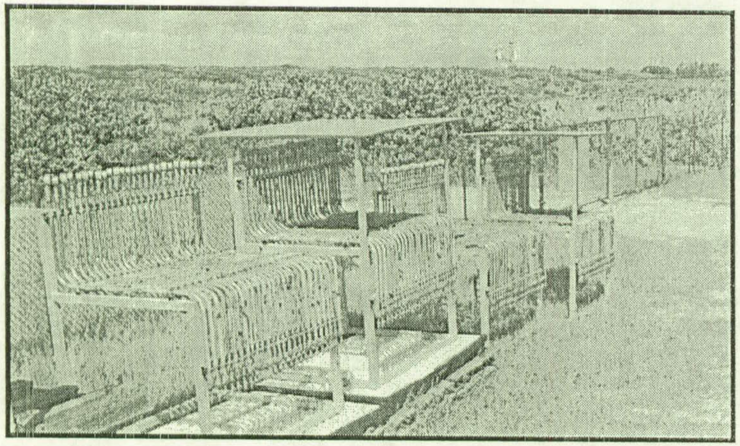
- Electrochemistry laboratory
- Accelerated corrosion equipment
- Coatings application laboratory
- Seawater immersion system
- Atmospheric exposure site

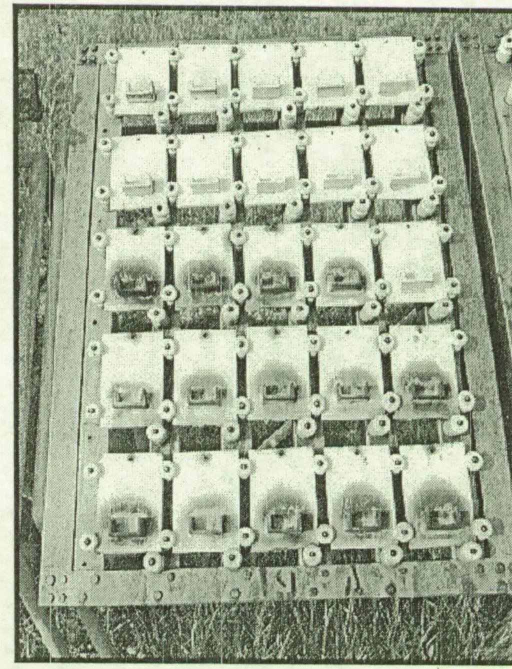


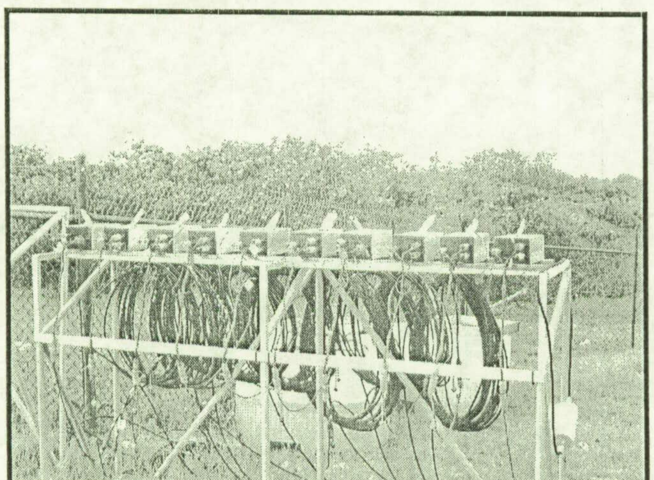




Materials Investigated at the NASA Corrosion Technology Testbed



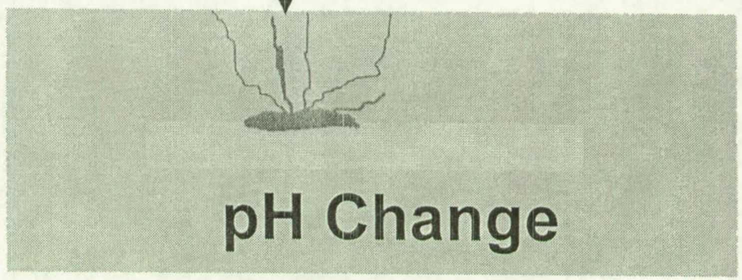




The Corrosion of Steel in Concrete

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

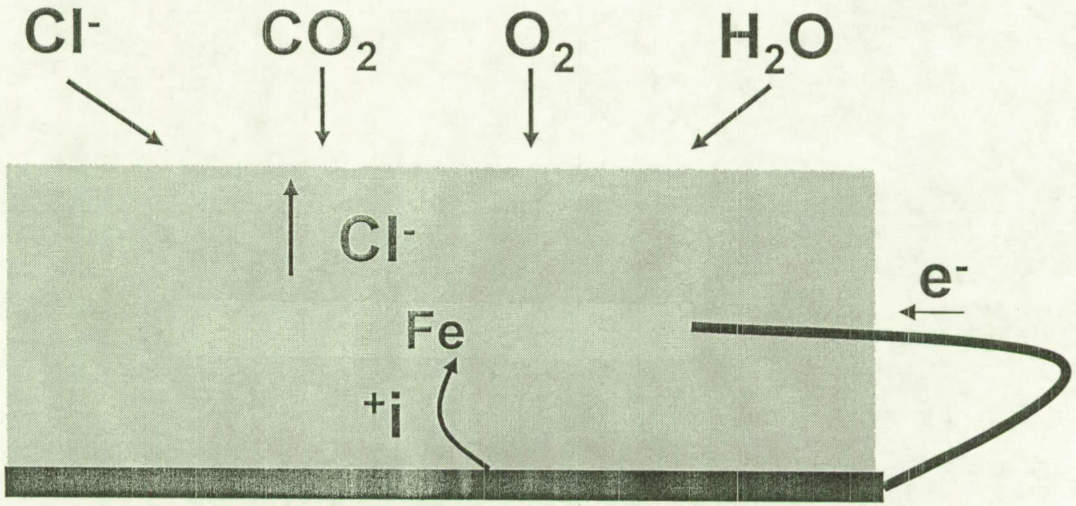
1) Chlorides
2) O_2
3) Moisture
4) CO_2



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

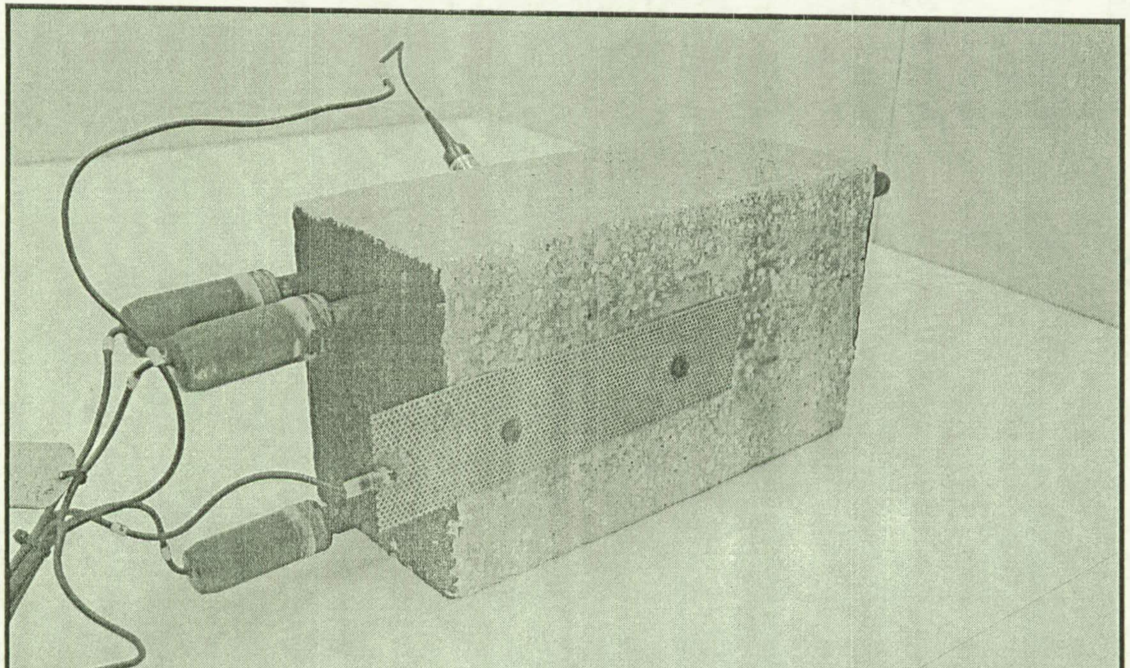
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

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

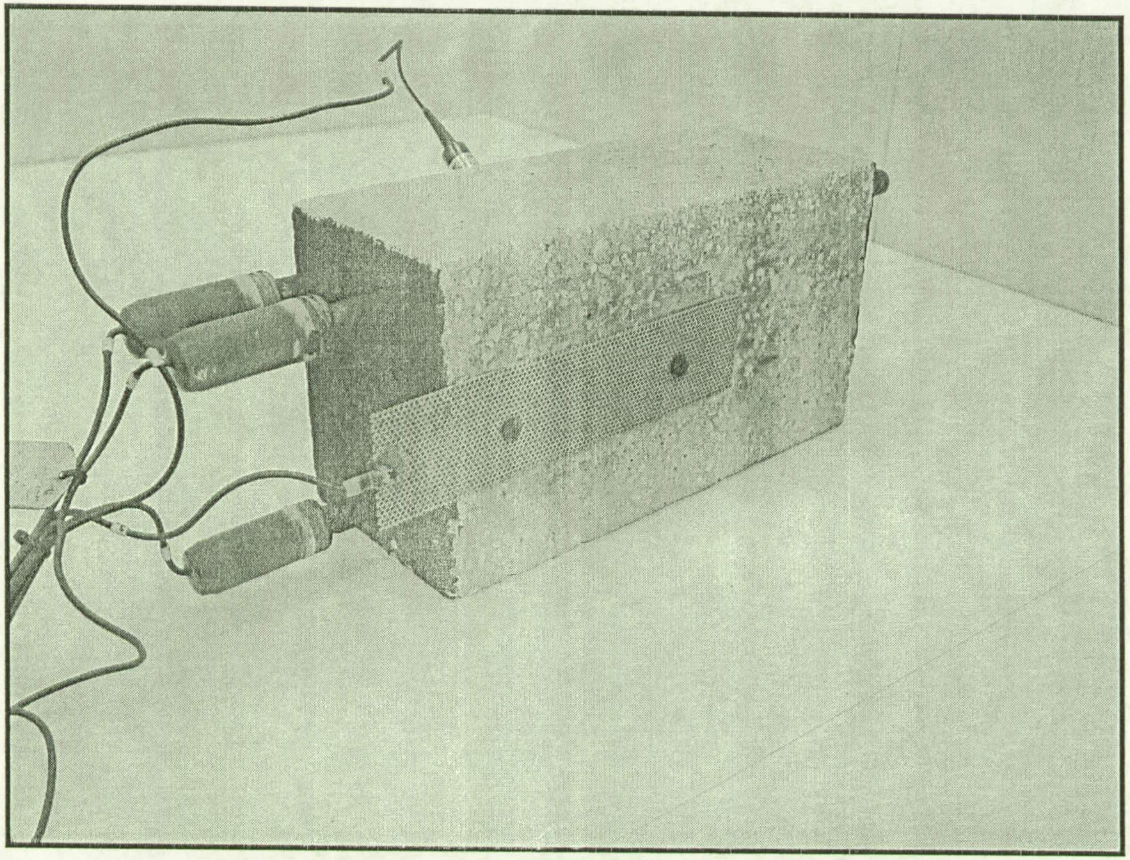


Sacrificial Protective Coating

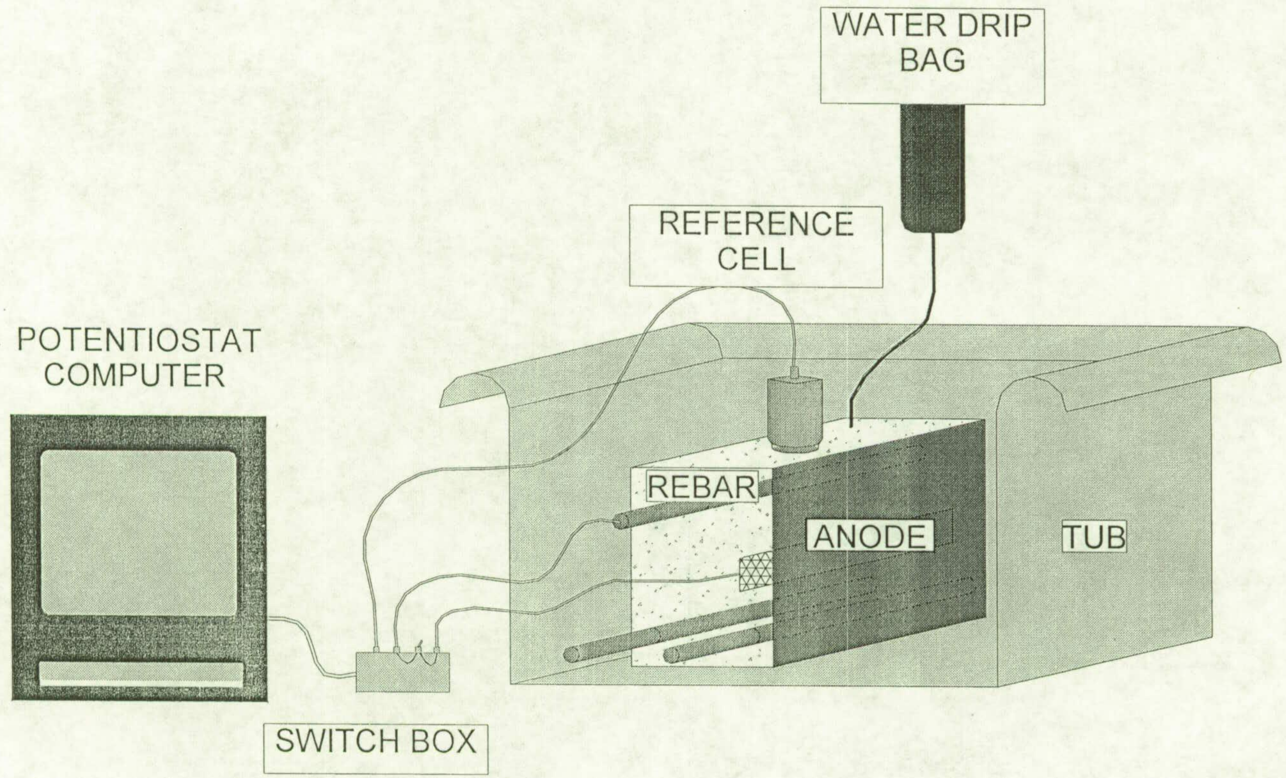
$$M \rightarrow M^{n+} + ne^-$$



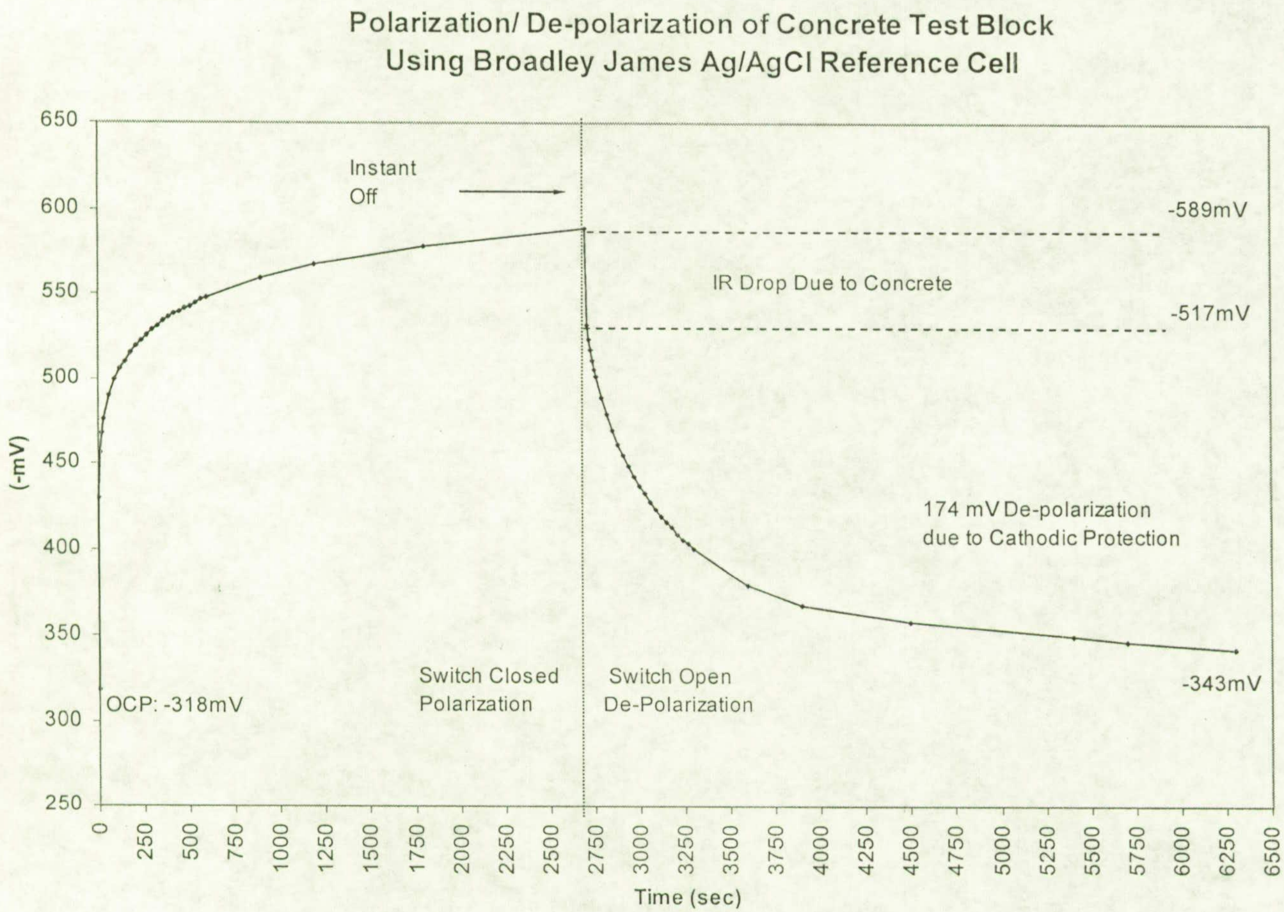
Experimental Test Blocks Modified ASTM G 109



Experimental Apparatus (Laboratory)



Depolarization Testing
(NACE RP0169-96)



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)

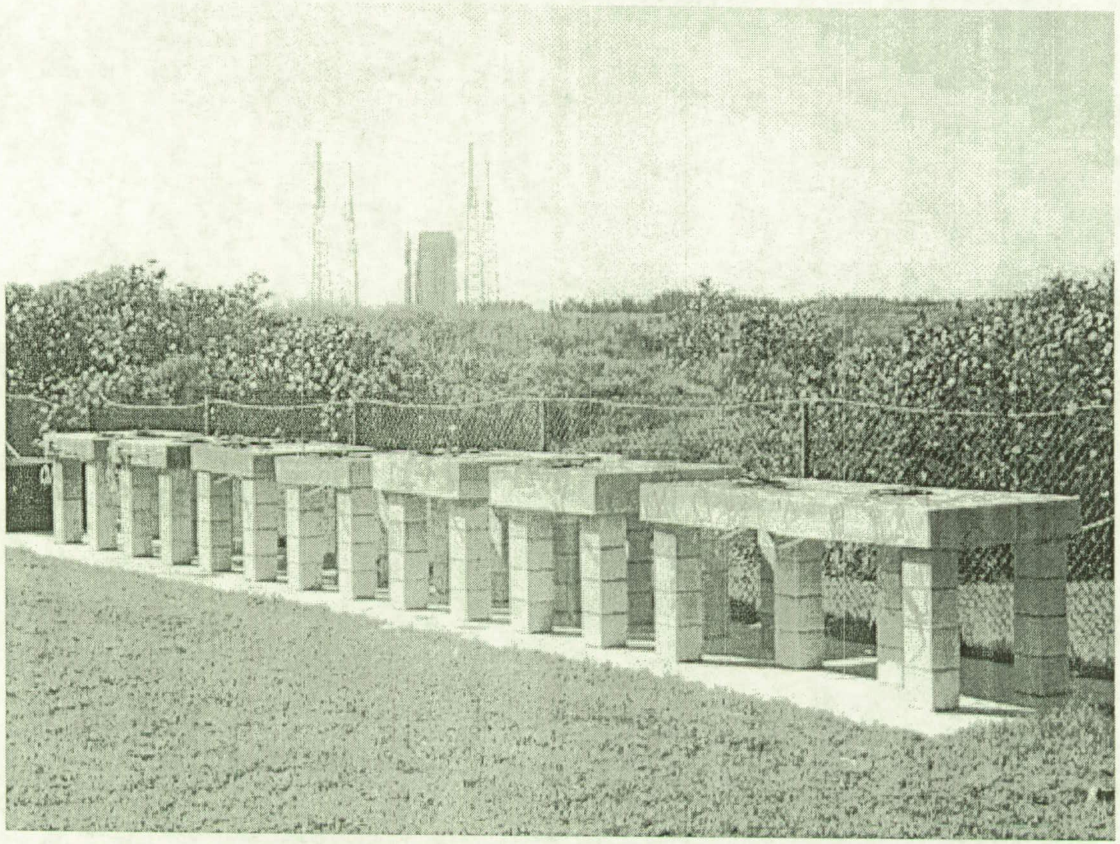
March 2002

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**	**ΔE_{0-35}**	**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.
- U. S. Patent issued
- Cortec has applied GalvaCorr to bridge 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

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