CORROSION STUDY
December 2019
Investigating Liquid Admixtures that Provide a Dual Protection to Steel Reinforcement Corrosion in Concrete

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ABSTRACT

Nearly every man-made structure contains metal that is susceptible to corrosion, a chemical process that causes costly and dangerous damage. A majority of those structures are Reinforced (Structural) Concrete being prone to deleterious materials entering into the concrete matrix, causing rapid corrosion and drastically limiting the "Life Cycle" and necessitating costly and continual repairs of those structures. This problem has a number of alternatives in the marketplace regarding the "metals side"; exotic metal alternatives, coatings, cathodic devices, etc. This study examines and reviews strategies that will address corrosion of embedded metals in concrete from purely the concrete side of things; although the combination of both is thought to be highly effective. This study utilizes several test methods to measure and differentiate the performance of reinforcing steel corrosion mitigating technologies involving concrete admixtures and other pozzolanic alternatives. Ultimately, we are looking for strategies in drastically retarding the Initiation (breakdown of passive layer of steel protection) and Propagation (the active, worsening of corrosive product; resulting in repair and ultimate failure) phases of steel corrosion in concrete.

BACKGROUND

This corrosion study contains four basic "pillars" (testing protocols that illustrate key concrete/cement characteristics) that support the basic technology that encompasses Nano/Micro Silica Integral Concrete Admixture (NMSICA) technology and systems.

I. **<u>Nano Computed Tomography (nCT); Penetration with Iodide</u>** (protocols by Ley et all) **-** Standardized test method using Iodide ion solution (similar characteristics to chloride ions) to penetrate concrete and use an X-Ray machine at different time intervals to plot the results. This is considered acceptable Modifications to **ASTM C1152 – Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete.**

II. **ASTM C876 –** Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete. A protocol that uses a Half Cell instrument to measure resistance between a rebar connection and the surface of the concrete with a measuring probe. This is considered one the most effective and accurate gauges of a concrete's "resistivity", or the ability to withstand deleterious materials from moving through it.

III. **ASTM G109 –** Standard Test Method for Determining Effects of Chemical Admixtures on Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments. A modified approach to visual/destructive autopsy of actual steel encased in concrete specimens following systematic and severe sodium chloride ponding.

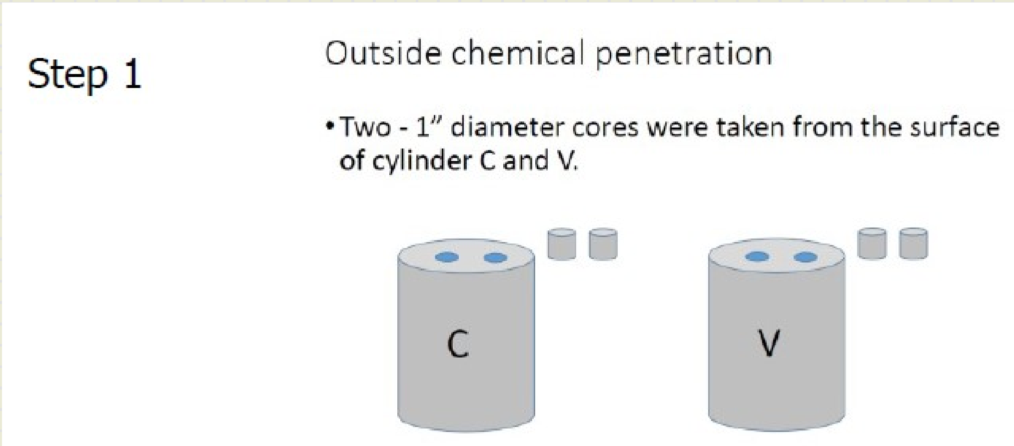
IV. **ASTM D5084 – Coefficient of Permeability tests**; As part of the warranty/insurance component of the Vapor Lock admixture system over the last 10 years, there has been literally 1,000s of test performed to date; non higher than 0.174 US Perms and usually in the 0.02 US Perm range. A rigorous, 23-page ASTM protocol that uses "head pressures" to measure the movement of a fluid, over time, through a sealed concrete specimen (cut from a prepared 4" x 8" cylinder). These tests are randomly performed throughout North America (USA & Canada) and can be supplied under separate copy. They are not required to meet ASTMs C494 and/or C1582 and are not included in this study.

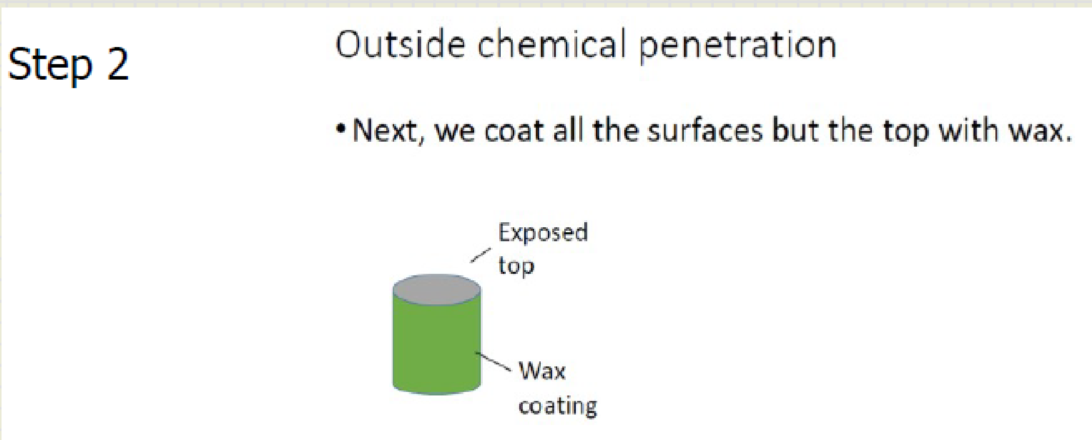
These protocols used in the study, are direct and/or modified versions performed previously by the nation's top leading experts on structural and durability assessments of concrete structures, and the development of repair and service-life extension strategies. The performance and scope of these tests are directly relevant to ASTM protocols (C494 & C1582) that are to be used as corrosion inhibiting admixtures in concrete and were finalized by the nation's leading and most current University Engineering programs; all influenced by the most recent work of ACI, ASTM, and RILEM committee research. The concrete mixes were provided by leading commercial ready-mix companies in Southern California, the Hawaiian Islands and the Western US. Sample specimens were provided by the same ready-mix companies and/or leading commercial labs in those areas. ***The first three ASTMs are submitted in an effort to meet and exceed portions of ASTM C1582 - Standard Specification for Admixtures to Inhibit Chloride-Induced Corrosion of Concrete Reinforcing Steel in Concrete and supplemental to ASTM C494, Type S Admixture – Standard Specification for Chemical Admixtures for Concrete.***

Nano Computed Tomography (nCT); Penetration with Iodide

The first protocol to address the *Initiation Phase* of corrosion, is Nano/Micro Computed Tomography; as proposed and executed by Dr. Tyler Ley at the Oklahoma State University. Instead of grinding away small layers of mortar/concrete, conditioning the sample and physically inspecting it for chemical composition of chlorides – ASTM C1152 and C1218. These protocols (acid and water based, respectfully) show total chloride levels present, when a better measurement would be of only "free chlorides". Research has shown chlorides contained in aggregates and bound by cement hydration have little to no effect on the corrosion process. Our goal with nCT testing, is to illustrate a *highly disrupted capillary system* in concrete is highly desirable in lowering the overall transport mechanism that allows deleterious materials to move through it. *This is considered an acceptable modification to ASTM C1152; and meets and exceeds portions of ASTM C1582.*

nCT protocol is such –



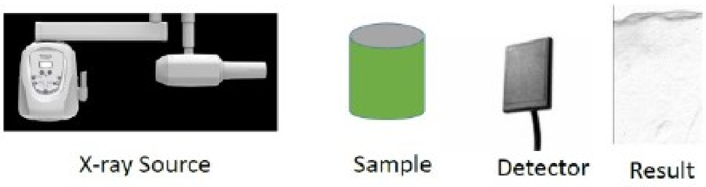


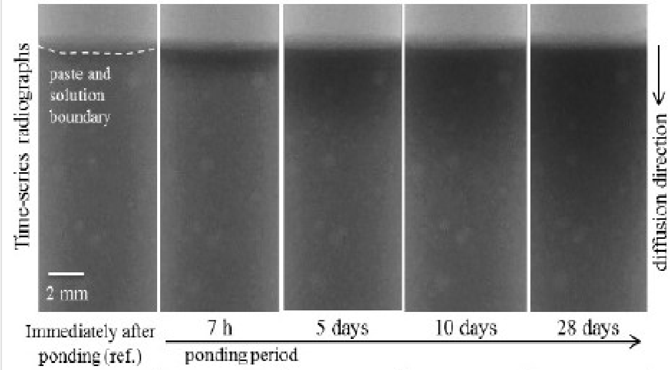
Step 3 Outside chemical penetration

- Place the material in potassium iodide solution.
- Since all sides but the surface are coated with wax then the chemicals will only penetrate from the surface.
- Take X-ray image at 0,1,5,10 days.

Outside chemical penetration

- Take an X-ray image of the sample from two different angles.

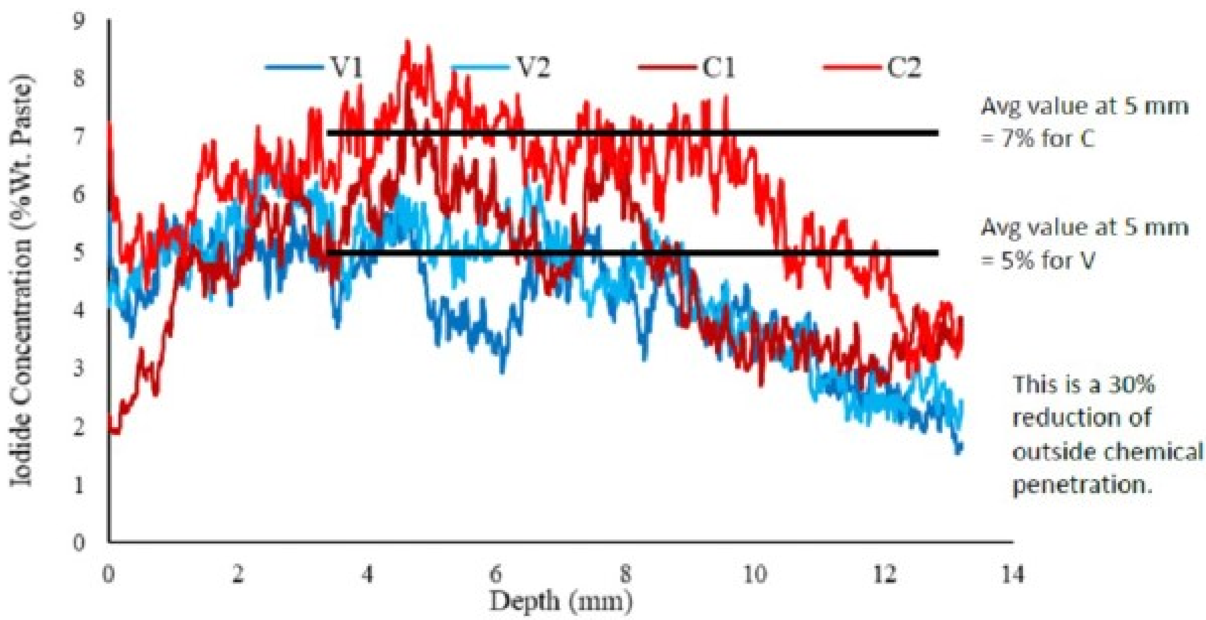




The more time elapsed, the greater the penetration.

Overall Comparison

Concentration profiles of all the samples after 10 days of ponding.



Summary

- Two cores were tested from each cylinder.
- Both cores showed good agreement with each other for sample C and V.
- There is a 30% reduction at 10 days of exposure for sample V when compared to C. Similar results were found at 5 days of exposure.

*Test mix was a pump mix; 1” top size agg., 0.45 w/c ratio, with MasterPozz 322, for pre-job testing in Hawaii. Compressive strengths came in approximately 6,320 psi at 28-days. Mix contained Orca sand and Pacific Northwest cement. Control mix contained Cortec MCI.

ASTM C876 – Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete

The second protocol presented is Half Cell testing that illustrates "resistivity" within the concrete matrix ***and*** any effectiveness of components that deter induced corrosion in a harsh, corrosive environment. A basic Half Cell instrument (a Miller LC-4.5 voltmeter & wide head copper sulfate probe able to measure 360 degrees) is used to ascertain "resistance" between a rebar connection and the surface of the concrete. *This test was performed in tandem (same samples and schedule) as the G109 Cracked Beam/Ponding Tests, to follow. It lends directly to illustrating effectiveness at both the Initiation and Propagation phases of steel corrosion in concrete. This protocol moves above and beyond the portion of measuring Macrocell current required in the G109 Cracked Beam/Ponding protocol, and is considered the bell weather in determining chloride transport properties in concrete.*

Half Cell protocol is such –

The Mix Design tested; and six industry accepted variations are below –

0.45 w/c Ratio, with a 4" (+/- 1") Slump Mix Design (comp. strengths @ 28 days = 5,300psi)

Cement; Type II & V – 658 lbs.

Water – 300.4 lbs. (36 gallons)

1" Agg. (#4) – 1392 lbs.

3/8" Agg. (#8) – 310 lbs.

Washed Con Sand – 1393 lbs.

WR-91, Type A water reducer – 26.32 ounces/yd^3

Air – 1%, 149.8 lbs./ft^3 Plastic Weight, 4045 lbs., 27.0 ft^3

(Aggregate Gradations available upon request)

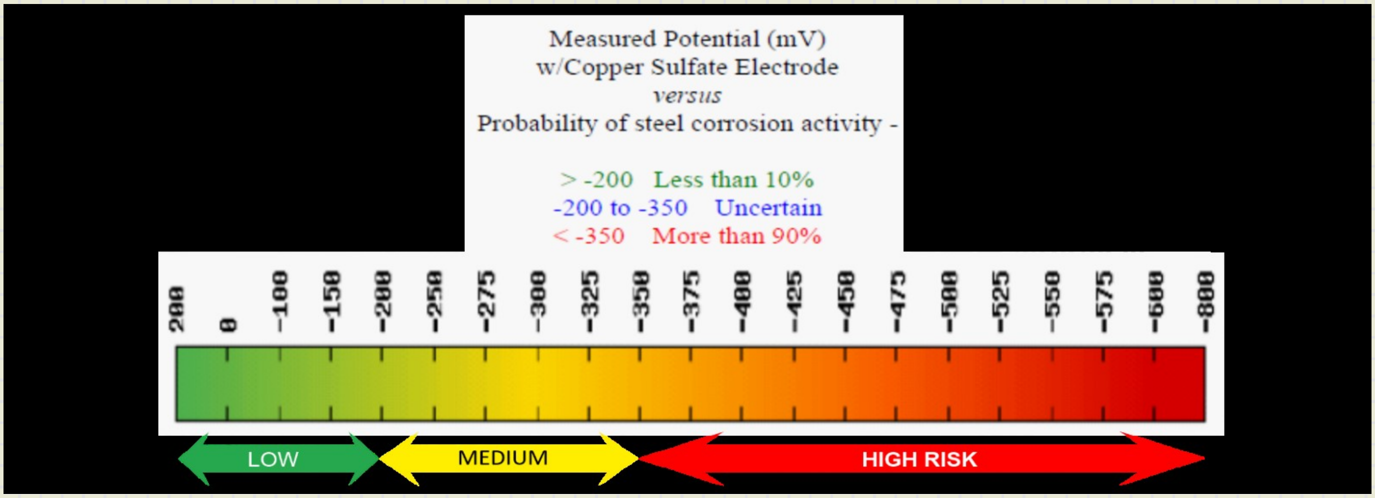
Specimen V – Vapor Lock 40/40 mix; 10 ounces per hundred lbs. of cement = 65.8 ozs. per cu. yard.

Specimen C – Plain Control; straight mix, above.

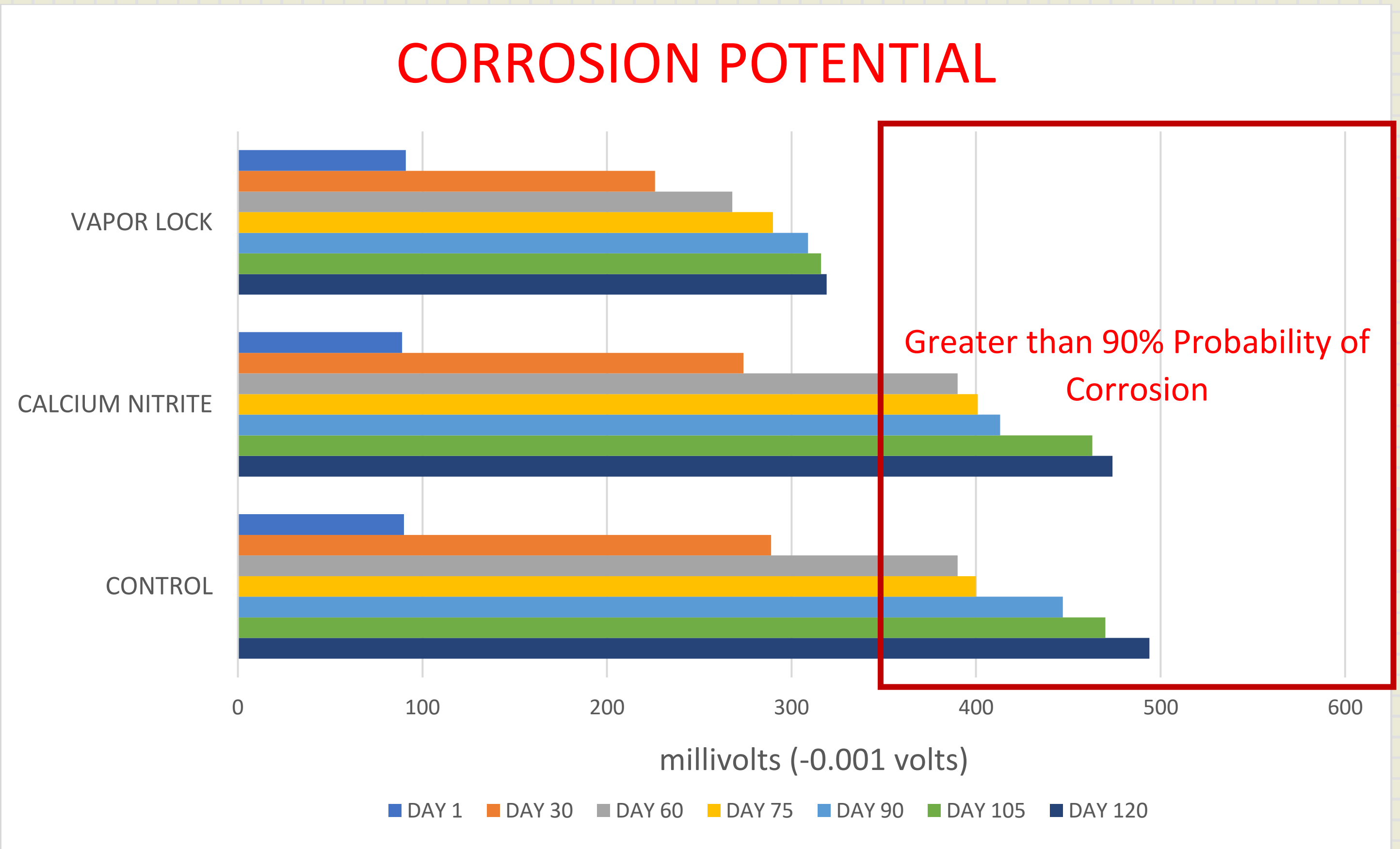
Specimen D – calcium nitrite (min. 30%) dosed at 5.5 gallons per cu. yard. There was 4.61 gallons of water removed (7 lbs. or water per gallon of DCI, 38.5 lbs.); per manufacturer's recommendations to maintain w/c ratio.

Half Cell Readings

(average of 3 readings, - 0.001 volts)	Day 1	Day 30	Day 60	Day 75	Day 90	Day 105	Day 120
D (calcium nitrite)	89	274	390	401	413	463	474
V (Vapor Lock)	91	226	268	290	309	316	319
C (Control, Plain mix)	90	289	390	400	447	470	494



ASTM C876 – Performance Criteria; Potential.



Half-Cell Readings; milliVolts (falling, negative) plotted by time.

Half-Cell readings were taken up to Day 120. Significant corrosion product was apparent on all protruding rebar specimens by Day 90. The 24" length specimens promote interreference and dis-allow correct internal slab readings. Readings were taken within the plexiglass ponding areas within 30 minutes after the addition of weekly salt baths; specimens were considered saturated. All readings were within -0.002 millivolts (less than .2%).

ASTM G109 – Standard Test Method for Determining Effects of Chemical Admixtures on Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments

This protocol is widely accepted to determine and rank SCMs, inhibiting admixtures and exotic rebar materials of steel in concrete samples. We modified our protocol to reflect the most realistic construction conditions and by NOT using any electrical charge (current flow) between the two layers of rebar. Instead, we rely on the previous Half Cell readings to illustrate concrete's "resistivity" and/or "transportability" of chloride ions through concrete and "de-passivity" of reinforcement steel. The only performance portion of these tests, is a final autopsy to subjectively judge the amount of corrosion product formed relative to the same mix design with various admixtures and SCM options.

Cracked Beam/Ponding protocol is such –

To expedite the process (while eliminating microcell current) and show rapid chloride corrosion, we utilized a roughly 20% sodium chloride ponding solution (instead of 3-5% solution).

The specimens were created to accommodate this Cracked Beam/Ponding protocol and the previous ASTM C876 protocol, and include:

The Mix Design tested; and six industry accepted variations are below –

<u>0.45 w/c Ratio, with a 4" (+/- 1") Slump Mix Design (comp. strengths @ 28 days = 5,300psi)</u>

Cement; Type II & V – 658 lbs.

Water – 300.4 lbs. (36 gallons)

1" Agg. (#4) – 1392 lbs.

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(Aggregate Gradations available upon request)

Specimen V – Vapor Lock 40/40 mix; 10 ounces per hundred lbs. of cement = 65.8 ozs. per cu. yard.

Specimen C – Plain Control; straight mix, above.

- Using "off-the-shelf" #4 rebar (1/2", not cleaned or conditioned in any way), positioned into a standard triangle pattern, with the top bar having exactly 1" of concrete cover. Forms are standard 2" x 6" wood and fastened at each corner with two screws. *No form release/oils were used. Specimen size was a nominal 5.5" deep, 24" long, and 8" wide (this gives a 3:1 geometry that would also promote a mid-point crack).

- That 1” of concrete cover was compromised (to simulate an acceptable crack) with a 0.030” metal shim, left mid-point on the top rebar for 4 hours and then removed.

- Mixes were placed into the specimens, vibrated in two spots with a stinger, screeded with a wood float, then hit with a mag float, and finally a steel edger. *There was no ability to use a power trowel, which should be taken into consideration. After the beams were cast, that evening a 3-mil black poly was laid over the specimens and weighted down with wet sand for 7 days to provide a “wet cure”.

- After seven days of common curing (wet cure), the specimens were stripped of forms and air dried for 24 hours. At Day 9, four-inch-high plexi-glass reservoirs were adhered to the surfaces with silicon; 6” wide and 16” long. This was to produce ponding at roughly half the surface area of the specimens.

- At Day 10 a 20% salt solution was added to an approximate depth of 1” for each specimen. The tap water was heated to approximately 115 degrees Fahrenheit. 20% (by weight) fine salt crystals are added and agitated/stirred for approximately 5-7 minutes. It is thought that the increase in water temperature should allow for the highest saturation levels possible.

- Salt water was added every Monday morning at 8am. Specimens were out in the open and have semi to direct sun on them, with full thermal night and day cycles. With April weather in Southern California, they were getting about a 30 to 35-degree swing in temperature; which held constant throughout the year. Wind and rain are sporadic. Monday mornings, a new 20% salt solution is added to a depth of 1” for each specimen. Some weeks, it took all week to evaporate (April, May) and later in the year it took a day and half to evaporate (July, August). Once a month, the inside of the reservoirs were rinsed out with water to remove the salt build-up and their order was rearranged once on the raised bench during the protocol. The reservoirs were repaired once after the first month as well; additional silicone was added to the corners to fix leaks.

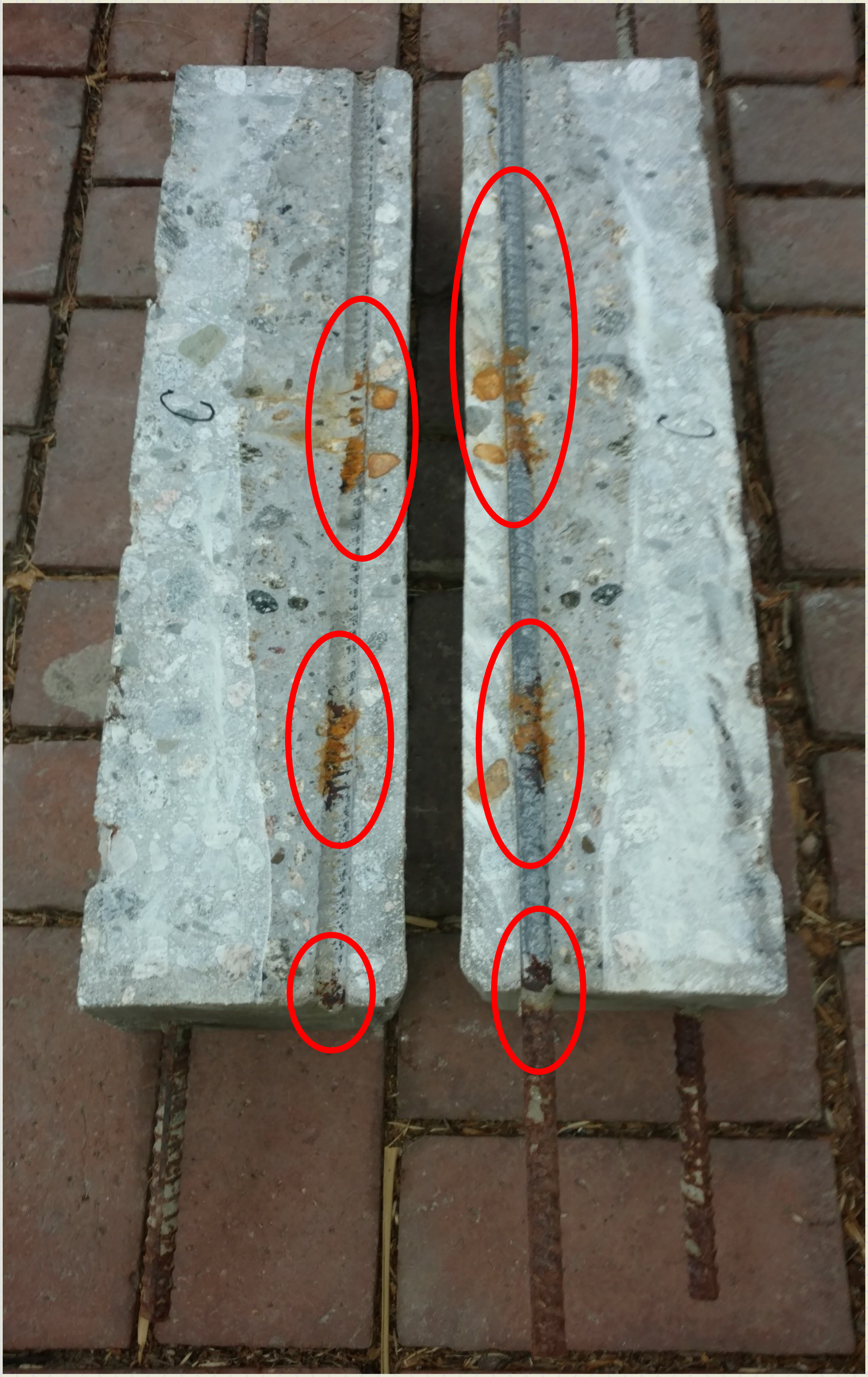
- After 140 days of the ponding protocol (20 weeks), specimens were stripped of their plexi-glass reservoirs, cleaned with water and air-dried for 24 hours. *The two Vapor Lock specimens were more difficult to strip and clean the silicon adhesive off of them.

- Day before autopsy; Physical corrosion product evident on the Control specimen. All specimens had substantial product on protruding rebar, with one side (the side that was accessed) being noticeably worse than the other.

- The conclusion of this protocol is to perform an autopsy to physically inspect the damage to the rebar; pictures supplied to base ratings on. A dry saw-cut was directly over and under the top rebar. The final “split” was accomplished with a hammer and narrow chisel.

- Specimens were laid out in the open for 48 hours (August, SoCal) and photographed.

Control Specimen –



Vapor Lock Specimen –

AKNOWLEDGEMENTS

Without the help of certain individuals and groups, this study would not have been possible. We would like to thank National Ready Mix Concrete's technical and sales department in their support. Also, Ron Pickering at CEL and the local commercial ready-mix producers on Oahu, Hawaii, with which this study would not be possible. And the unique insight of Dr. Tyler Ley and his group at Oklahoma State for their work on nCT technology. Indirectly, we would like to thank the years of work both Dr. David Trejo (Oregon State University) and Dr. Jason Weiss (Oregon State & Purdue University) have offered to the science and direction of past and present Durable concrete design. Finally, the initial foundation of knowledge and study supplied by Drs. Jeffrey Thomas (Northwestern University/GCP) and Hamlin Jennings (Northwestern University/MIT-Concrete Sustainability Hub), with which this technology would go unrealized.

CONCLUSIONS

This study took every step in "reproducing" real-world concrete and construction practice in an effort to bridge-the-gap between "labcrete" and real-world concrete installations. Except for the use of a power trowel during finishing, we feel we provided every-day mixes, with established corrosion inhibiting options (Western United States) and practical rebar options. This study started with the intent of;

1. Proving and ranking the ability to quickly and permanently illustrate a Disrupted Capillary System in OPC Concrete.
2. Illustrate the Additional Advantages of a Migrating Ferrous Coating provided by a NMSICA.
3. Provide these characteristics in a form that satisfies both ASTM C494, Type S admixture and ASTM C1582 - Standard Specification for Admixtures to Inhibit Chloride-Induced Corrosion of Concrete Reinforcing Steel in Concrete; modified or neat.

The literally thousands of Coefficient of Permeability (ASTM D5084) that have consistently produced results in the 0.02 US Perm level and below, consistently throughout North America, illustrate the Ultra Low Permeability level of concrete mixes enhanced with Vapor Lock admixtures. In effect, giving standard mixes (0.42 thru 0.52 water:cementitious ratio) the similar characteristics (i.e. shrinkage/creep, permeability, resistivity, etc.) as concrete mixes in the 0.36 w/cm range on almost a daily basis.

This Ultra Low Permeability of Vapor Lock enhanced concrete is confirmed by the Modified ASTM C1152 – Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete, with nCT - Nano Computed Tomography; Penetration with Iodide. This modified version which provides for a quick, scientific method of measuring surface penetration of potassium iodide with an X-Ray machine, showed a 30% reduction of Vapor Lock enhanced samples over control samples; with all samples showing good agreement (5 and 10 day measurements). The specimens made from a relatively HPC mixes (all 28-day compressive strengths were beyond 7,000 psi); with high modulus of elasticity fine aggregate and some of the highest quality cement available in the United States, were tested around Day 75. Further testing with more pedestrian mixes (~ 5,000 psi), at earlier stages in the production of cement/product development (first 7-28 days), should reveal greater reductions in penetration over control specimens.

In regards to testing solely for the migrating ferrous coating film provided by the Vapor Lock admixture, it's difficult to separate from the severely disrupted capillary system characteristics also provided. If there is technology that can separate and measure this characteristic, we would be pleased to be introduced to it, and incorporate that testing/protocol in the future.

The portions of ASTM C1582 that move beyond just testing for "benign" properties of that admixture, rely on ASTM G109 protocols. Beyond the nCT; Penetration with Iodide showing superior reduction in chloride penetration by the Vapor Lock enhanced specimens, both the ASTM C876 – Half Cell testing and visual inspection of the rebar and concrete specimens (after destructive autopsy) become relevant. The objective Half-Cell results showed at Day-90 a 21% decrease over the control specimen readings, and a 25% decrease over the calcium nitrite specimen readings. As well, the Vapor Lock enhanced specimen readings never left the "uncertain level" of corrosion potential (-200mV to -350mV), with both the control and calcium nitrite specimens entering the "high risk" area of probability (<-350mV) by Day-60 and only progressively getting worse (lower, falling millivolt readings).

The more subjective visual inspections showed very little corrosive product on the Vapor Lock specimen's ends and only slight product just starting to develop mid-way on the encased rebar. With the worst end showing medium product just below 1" into the specimen. Alternatively, the control showed slightly greater product at about the same depth into the specimen's worst end and then substantial product about two inches further into the specimen. As well, substantial product developed over about 3 inches close to the mid-point of the specimen's weakened plane. The "worst end" was apparent, as the samples were accessed mainly from one side; sodium chloride was dumped from a bucket with little care as to splashing and protecting the protruding rebar. In fact, both ends of the protruding rebar for all the specimens showed medium product development with one side consistently showing noticeably more product.

For purposes of meeting and exceeding those standards laid out by both ASTMs C494 & C1582, a Vapor Lock enhanced sample was set against a plain, control mix. For research and marketing purposes, additional specimens including available admixtures and pozzolanic alternatives were included to show both performance, cost and preferable concrete rheology/handling characteristics. Our hope here is to lend flexibility in owners, agencies and managements decisions on the most favorable systems; given the performance in testing ***and*** ultimate handling characteristics of the concrete mix.

Beyond meeting and/or exceeding the ASTMs above, I believe the definition of ACI Committee 222 – Corrosion of Metals in Concrete definition for corrosion inhibitors are "admixtures that will either extend the time of corrosion initiation or significantly reduce the corrosion rate of embedded metal, or both, in concrete containing chlorides in excess of the accepted corrosion threshold value for the metal in untreated concrete" is applicable as well. We feel the drastically disrupted capillary system provided by Vapor Lock (smaller and disconnected pores) and migrating ferrous film coating would satisfy both of the committee's requirement of a true corrosion inhibitor.

*****This Corrosion Study report is intended to give the abbreviated summary of tests conducted. All three tests/protocols (nCT, ASTM C876, and G109) can be viewed in their entirety at – www.DurabilityConsultants.com/downloads *****