

WHITE PAPER
- The Case for a Disrupted Capillary System and its effect
on Steel Corrosion in Concrete
(DRAFT)

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HYPOTHESIS – Structural or Reinforced Concrete (RC), concrete that encases and protects steel reinforcement above and beyond the basic engineering properties of concrete itself, is arguably the most valuable and dynamic system man has ever created. Cement (the main component of concrete) manufacturing is energy dense and leaves a heavy carbon footprint. Today we find our efforts centered around using enough, but not an excess amount of cement (from a structural engineering and sustainability perspective) in combination with technologies that lend superior concrete characteristics. Easily the greatest threat to RC and thus our infrastructure in this country (and the world), has to lie in chloride egress into the concrete matrix, propagating steel corrosion. It is this massive expense and greatest threat to Reinforced Concrete that we will address.

BACKGROUND - Concrete has a capillary system made up of voids, holes, cracks, and tiny capillaries that represent the absence of the constituents that make up concrete; water, cement, and aggregate. This has held true since the beginning of the tandem system of concrete and steel coming together to make RC. Doctors Thomas and Jennings with Northwestern University, Evanston, Illinois, have made some quantifications and measurements of this phenomenon. Dr. Thomas began the MIT Concrete HUB (<https://cshub.mit.edu/>) program in 2010 and passed in 2015. Both have been involved with some of the most important nano-level studies and research performed to date, giving us what is now the foundation of concrete “Durability” principles and practice used by the American Concrete Institute and corresponding building industries today.

Reflected in *The Science of Concrete* portal - <http://iti.northwestern.edu/cement/index.html> In section 5.6 they have broken down the *Phase Composition of Portland Cement Paste* - see Exhibit 1.

In essence, their studies show a common 0.45 w/c ratio mix design, at 28 days, has almost 11% voids in a typical concrete matrix (air in the paste/binder). A 0.50 w/c ratio mix, at the same 28 days, has almost 17% pores – a 55% increase.

Exhibit 1

Table 5.1: Phase data for a Type I OPC paste made with a w/c of 0.45.

Phase	Density (g/cm ³)	Volume %	
		At Mixing	Mature Paste
C ₃ S	3.15	23.40	1.17
C ₂ S	3.28	7.35	0.78
C ₃ A	3.03	4.42	0.00
C ₄ AF	3.73	2.87	1.39
Gypsum (C \bar{S} H ₂)	2.32	3.47	0.00
C-S-H (solid) ^a	2.65	0	29.03
C-S-H (with gel pores) ^b	1.90	0	49.99
Portlandite (CH)	2.24	0	13.96
Ettringite (AFt)	1.78	0	6.87
Monosulfoaluminate (AFm)	2.02	0	15.12
Water	1.00	58.49	31.69
Gel porosity	--	0	20.96
Capillary porosity	--	58.49	10.73

This predictable and constant capillary system in concrete is a product of the way concrete dries, cures, and hydrates; three distinct processes that all have to do with water leaving the cement matrix. This same mechanism allows for the transport of harmful, deleterious elements back into the concrete matrix, attack, break down, and eliminate the structural characteristics of reinforcement steel encased in RC. Since the early 1950s, research has identified and shown that a disrupted capillary system within concrete is most advantageous on a number of levels.¹

“Exposure of reinforced concrete to chloride ions is the primary cause of premature corrosion of steel reinforcement. The intrusion of chloride ions, present in deicing salts and seawater, into reinforced concrete can cause steel corrosion if oxygen and moisture are also available to sustain the reaction. Chlorides dissolved in water can permeate through sound concrete or reach the steel through cracks.”²

Also from the Portland Cement Association – “Corrosion of embedded metals in concrete can be greatly reduced by placing crack-free concrete with low permeability and sufficient concrete cover.” Sufficient concrete cover is prescribed in ACI 318 and local building codes; ultimately dictated by the Structural Engineer of record. Our focus and contribution lie in the “**...crack-free concrete with low permeability...**” arena.³

Noting that “cracking” is a substantial discussion worthy to have, we would make the direct observations, and put that aside for another discussion;

- Synthetic Fibers to lend tensile strength during that first “concrete birthing” period; 5 minutes to 48 hours have shown very good results,
- Proper curing substantially increases compressive and flexural strengths, while inhibiting cracking; physical ponding with membranes, curing compounds, internal curing, etc.
- Shrinkage (both autogenous and physical) in concrete is the greatest long-term predictor of overall concrete cracking; with proper gradation of aggregates being the greatest variable,
- Shrinkage Reducing Admixtures or chemical compensating cements (contains an expansion component) can help combat shrinkage to varying degrees.

We begin with “Low Permeability” concrete. From almost the beginning of kiln-fired (Portland) cement-based concrete, there has been an effort to achieve surface densification by adding various types of silicates. By applying silicates to the surface of concrete within the first 48 hours of concrete placement, we’ve attempted to lower shrinkage, water/damp proof, impart enhanced abrasion and densification characteristics, and improve final surface tolerances, all to varying degrees of success. The majority of these silicates are the product of silicon dioxide manipulation, with the premise being a pozzolanic reaction with calcium hydroxide and water, creates relatively large amounts of additional calcium silicate hydrate (c-s-h) gel. The greatest advancement to this technology has been the careful manipulation of silicon dioxide (temperature and pH level) to create very small (Colloidal) silicate formation. This additional c-s-h is the main vehicle of enhanced concrete characteristics and the impetus to move beyond just surface modification and towards an Integral approach with relevant technology throughout the entire concrete matrix.

For over 11 years, there has been a base of this Integral Admixture Technology that has addressed moisture/vapor issues in floorings, coatings and roofing to good success – Integral Silicate Admixtures or MVRAs. In 1998, the United States EPA issued a nationwide Architectural and Industrial Maintenance (AIM) Coatings rule limiting emissions from volatile organic compounds (VOCs) pursuant with the Clean Air Act. The purpose of this rule was based on the EPA’s determination that VOC emissions from the use of architectural coatings had the potential to contribute to ozone levels. Overnight the VOC content of flooring adhesives and coatings plunged from the tens of thousands of parts per million, to the hundreds parts per million – making them essentially “water-based” products. Concrete that releases relatively small portions of moisture in the form of vapor, re-emulsifies adhesives and coatings, promotes mold and fowls indoor air quality. This was a significant problem, thought to be well past the \$1.4 Billion a year mark, since the inventories of “cut-back” or solvent based adhesive inventories were eliminated. Since 2006 (about the time the actual problem was properly diagnosed), Integral Silicate Admixtures or MVRAs have been efficiently and effectively addressing these problems in a cost-

effective manner, allowing for on-time flooring, coatings, and roofing products, and the intact critical paths of all trades involving concrete and those trades. In 2017 MVRAs were established and recognized by the National Ready Mixed Concrete Association.

As this technology has proven successful in thousands of applications and millions of square feet of flooring and roofing in perfect service to date, the Integral Silicate Admixture technology has been expanded to a number of other applications all with increases in scope and performance. There are several testing protocols that will illustrate a concrete structure with a permanent and severely disrupted capillary system. Through this mechanism, we will illustrate and make logical inferences as to how that will inhibit steel corrosion in concrete. Lastly, we will illustrate a second mechanism (introduced in conjunction with the Integral Silicate Admixture) of a migrating ferrous coating, illustrate the testing and infer how this acts as a second mechanism that physically and actively protects regular steel reinforcement in concrete.

TEST RESULTS

There has been a myriad of tests that claim to address corrosion inhibition, permeability and concrete's "resistivity" to chloride ion penetration with varying degrees of success. With the Background above, we have broken down the levels of testing into two components of steel corrosion in concrete; *Initiation* and *Propagation*.

The focus below is on chloride entry through either sorption and/or hydrostatic functions through the concrete, inwards to the steel, and how to address and discourage that through "Low Permeability" (we're using permeability to denote permeance) concrete with the following protocols/tests;

Coefficient of Permeability – ASTM D5084; soil protocols that involve sealing a concrete specimen and forcing water through it via head pressure. The result is a measurement of distance over time – a very small number. We convert that number (product of a constant) to produce a US Perm value for easy comparison. There are several companies that use this testing/protocol as a quality control measure for the foundation of their moisture vapor reducing admixture (mvra) commercial systems. On average, my personal experience is taking regular concrete from the 5 US Perms through 200 US Perms levels down to the 0.02 US Perm level, consistently and accurately into my 11th year now. This protocol is shortened to Coefficient of Permeability, when it would be more accurate to describe this procedure as Coefficient of Permeance.

*Specimen sampling has never produced a result greater than the base value of 1×10^{-8} cm/second or 0.174 US Perms.

I maintain and manage a list of about 231 projects in the Western US that have utilized ISAs and I've been involved with. I can produce actual permeability testing for each one, upon request.

X-Ray Penetration with Iodide (Dr. Tyler Ley's protocol) - Standardized test method using Iodide ion solution (similar characteristics to chloride ions) to penetrate concrete and at different time intervals take an X-Ray of the Iodide. Fast, easy way to illustrate and quantify liquid penetration into 1" diameter, by 1" deep concrete specimens.

*This protocol is considered a modification of both ***ASTM C1152 & ASTM C1218 – Chloride (Acid & Water Soluble) Testing for Concrete & Mortars***. These standard test methods of taking pulverized sections of concrete (moving your way down a ponding or injected specimen), adding nitric acid or water (respectively), boiling that mixture and measuring the chloride content produce large swings in results, with chlorides pulverized from aggregate being included; which we know have little intent or purpose on the corrosion of steel. Plus, some chlorides are bound by cement hydration product and aren't a factor in steel corrosion either.

The following mix designs were used –

Mix Designs

4500 psi, Pump Mix

1" top size agg., w/c = 0.45

*Sand is a blend of local and Orca (Vancouver/Polaris Materials) sand.

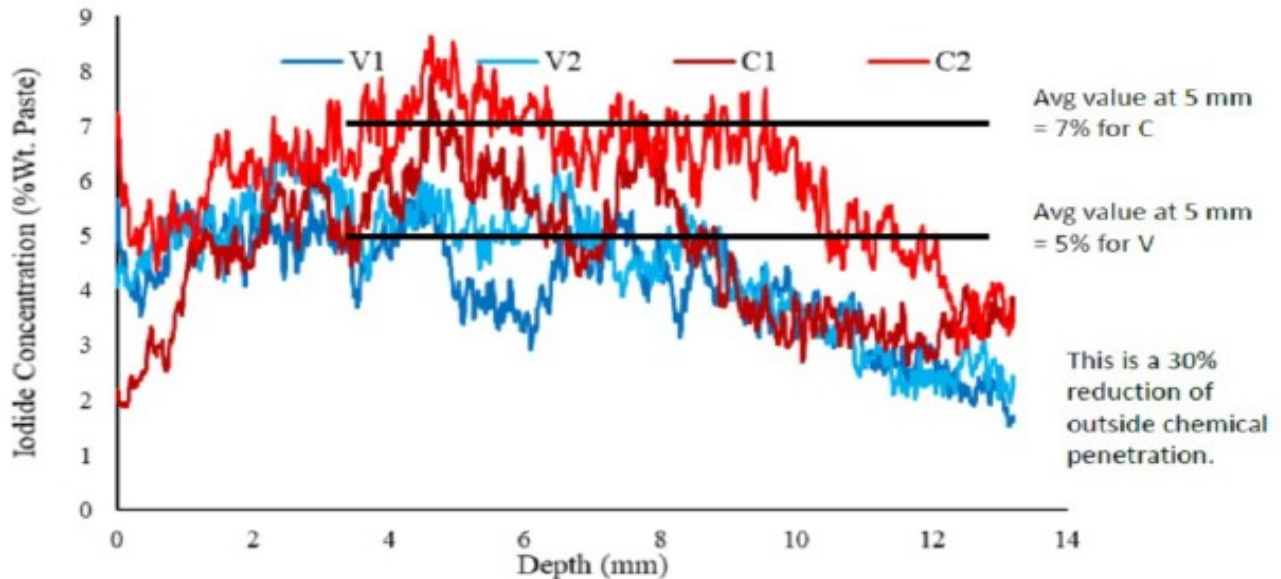
**This was pre-project testing for Kaneohe-Kailua Wastewater Conveyance and Treatment Facilities Project; Oahu, Hawaii.

Materials	Weights
1" Aggregate	1,053 lbs.
3/8" Aggregate	708 lbs.
Sand	1,393 lbs.
Cement	630 lbs.
Water	283 lbs./34.0 gallons
MasterPozz 322 - 4 ounces per hundred weight	25.2 ounces
Control C Mix - amine salts/carboxylic acids admixture	24 ounces
Control V Mix - Vapor Lock 40/40 admixture	63 ounces

* It's important to note this mix utilized imported Polaris/US Concrete's Orca sand blended with local sand. This is the same sand imported to Southern California to meet current MOE specifications in high-rise construction.

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.

**Relatively High Performance Mixes at around 60 days showed a 30% reduction in surface/shallow penetration.

***Complete tests at https://docs.wixstatic.com/ugd/925158_71c25f21c24d4aa3aa0be9b6b1772d66.pdf

We feel this protocol is a logical and practical modification from the standard ASTMs C1152 and C1218 – Chloride (acid & water soluble) Testing for Concrete & Mortars and shows greater agreement and precision consistently. Although not currently readily available from most commercial labs, it can be performed relatively quickly and economically at the University engineering program level.

Per PCAs recommendations of “Low Permeability” concrete, an argument could be made that a disrupted capillary system would significantly inhibit the *Initiation* of chloride corrosion, as well as greatly inhibit the *Propagation*, or continued worsening, of the chloride corrosion process. A second, robust physical film coating, that migrates in the early plastic stage of concrete, attracted by electro-chemical attraction created by anything ferrous would be highly desirable and effective. This secondary component has been commercially attempted several times by several companies with limited success. Either the mix is altered in such a state to drastically lower compressive strengths, add massive, destructive amounts of foam (air), and require low water-to-cement ratios that are constraining to production and installation.

PROTOCOL & RESULTS

There are a number of protocols that strive to illustrate the protective nature of an admixture as outlined in ASTM C1582 - Standard Specification for Admixtures to Inhibit Chloride Induced Corrosion of Reinforcing Steel in Concrete. This is above and beyond the practical “benign” properties of the admixture and how it reacts with a particular mix. The protocols used were all mentioned in G109 testing; including the Cracked Beam test, the Southern Exposure test, and several ponding protocols.

We’ve taken a combination of the above in an attempt to create the most realistic and fast acting corrosion inducing environment with modified “Cracked-Beam” Ponding tests – rapid wetting and drying protocol with 20% sodium chloride solution. With “practical application mixes”, we’ve used beams with three pieces of off-the-shelf number 4 rebar placed in a standing triangle, induced a crack with a 0.03” (1/32 of an inch) shim placed over the top rebar for 4 hours to create a weakened plain; ultimately promoting a small crack. We weekly use a fresh, aggressive sodium chloride bath (water heated to 115 degrees and dissolved salt at a 20% by weight, minimum). Except for a standing “power trowel” machine to aid in finishing (only wood, mag and steel trowels were used), we feel this is as realistic to normal structural concrete installation as is practical and possible. This protocol is finalized by the ultimate autopsy of the reinforced beams to physically inspect each piece of rebar.

Because of the long timeframe for substantial corrosion to take place (even under the harshest constraints), we’ve incorporated ASTM C876 – Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete. In essence, a basic Half Cell instrument to ascertain the resistivity throughout the concrete between the steel and the surface; a determination of corrosion activity.

The Mix design and six industry accepted variations are bellow –

Compressive Strength: 4,500 psi at 28 days, w/cm Ratio: 0.45, Slump: 4.00 +/- 1 inch

Cement Type II/V – 658 lbs.

Water – 300.4 lbs. (36 gallons)

1” x #4 – 1392 lbs.

3/8” x #8 – 310 lbs.

Washed Concrete Sand – 1393 lbs.

WR-91 Type A – 26.32 oz/yd³

Air – 0.27 (1%), 149.8 lbs./ft³ Plastic Unit Weight, 4,045 lbs., 27.0 ft³

(Aggregate Gradations available upon request)

X - Crystalline Growth mix; popular (new) concentrated dry powder added at 1.25% of cement weight.

D - Calcium nitrite mix; popular admixture with 30% calcium nitrites at 5.5 gallons per yard.

F - 20% fly ash mix; a direct 20% reduction in cement.

V - Vapor Lock 40/40 mix; 10 ounces per hundred weight of cement.

VL - Vapor Lock 40/40 with lightweight sand; 10 ozs. per 100 weight of cement plus 22% replacement of regular sand.

C - Plain Control.

We have adopted the following;

1. Specimens made in the shape to simulate common floor/roof deck assemblies; 24" long, by 8" wide (3 to 1 to help promote mid-point cracking) off of 2x6s (5.5" nominal) thickness. *The beams were made with a vibrating stinger, wood strike/float, mag troweled, and steel rounded edges around the entire specimen. There was **no** ability to stand on the specimens with a power-trowel, which would be assumed to be common, representation of finishing; and should be taken into account.
2. Three number 4 bars (1/2" diameter) placed in a standing triangle pattern, with the top bar being 1" from the surface. Steel was purchased from a standard building material center and not cleaned or treated in any way.





Exhibits showing specimen size and rebar layout.

3. A 0.03 inch (1/32") steel shim was placed mid-point (12") across the specimen, laying on the top #4 bar for four hours, and then removed. This is to provide a "weakened" plane to mimic a small, acceptable crack.



Exhibit showing 0.03" (1/32") shim placed mid-point across specimen for 4 hours and removed.

4. Along with the cracked beam specimen, two 4" x 8" cylinders were made with each mix design. One specimen is for Dr. Tyler Ley's Chemical Penetration testing and one for ASTM D5084 – Coefficient of Permeability testing.



5. After the beams were cast, 3-mil black poly was laid over the specimens and weighted down with wet sand for 7 days to provide a “wet cure”.



6. After seven days of common curing (wet cure), the specimens were stripped of forms and air dried for 24 hours.



7. 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.



8. At Day 9, a 20% salt water bath was added to each specimen at approximately $\frac{3}{4}$ ” deep.



9. Ponding Protocol – Specimens are 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 are getting about a 30 to 35 degree swing in temperatures; should hold constant throughout the year. Wind and rain are sporadic. Monday mornings, a new 20% salt solution is added to a depth of $\frac{3}{4}$ " for each specimen. It might take all week to evaporate (April, May) or it might take two days to evaporate (July, August). Once a month, the inside of the reservoirs are rinsed out with water to remove the salt build-up. *The tap water is 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.

At approximately 180 days, specimens should be deconstructed at the mid-point area where the crack was induced. Physical inspection should be enough to properly discern actual damage caused by salt water ponding with most of the damage assumed to be nearest the induced crack (top bar).

ADDITIONAL QUANTITATIVE TESTING

Because of the long timeframe for substantial corrosion to take place (even under the harshest constraints), we've incorporated **ASTM C876 – Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete**. In essence, a basic Half Cell instrument (Miller LC-4.5 voltmeter & wide head copper sulfate probe able to measure 360 degrees) to ascertain the resistivity throughout the concrete between the steel and the surface; a scientific determination of corrosion activity. Every 7 days starting at Day 1 (Day 9 actual) there are three readings taken inside each full reservoir. Because of the relatively small service area being mapped, numbers are usually constant or less than 0.2% change in value. The Scope and Significance of Use are summarized with current results.

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

(Summarized)

1. Scope

1.1 This test method covers the estimation of the electrical corrosion potential of uncoated reinforcing steel in field and laboratory concrete, for the purpose of determining the corrosion activity of the reinforcing steel.

1.2 This test method is limited by electrical circuitry. Concrete surface in building interiors and desert environments lose sufficient moisture so that the concrete resistivity becomes so high that special testing techniques not covered in this test method may be required (see 5.1.4.1). Concrete surfaces that are coated or treated with sealers may not provide an acceptable electrical circuit. The basic configuration of the electrical circuit is shown in Fig. 1.

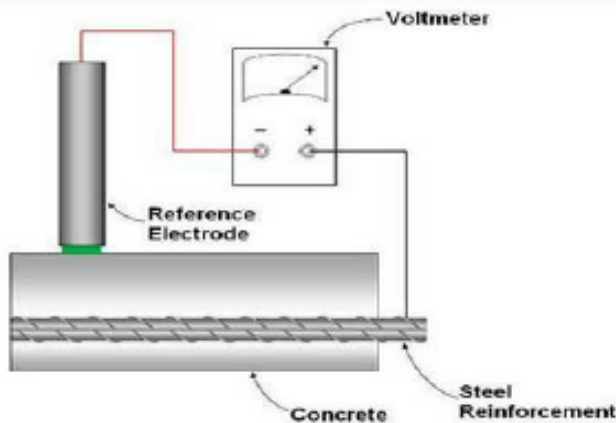


Figure 1

4. Significance and Use

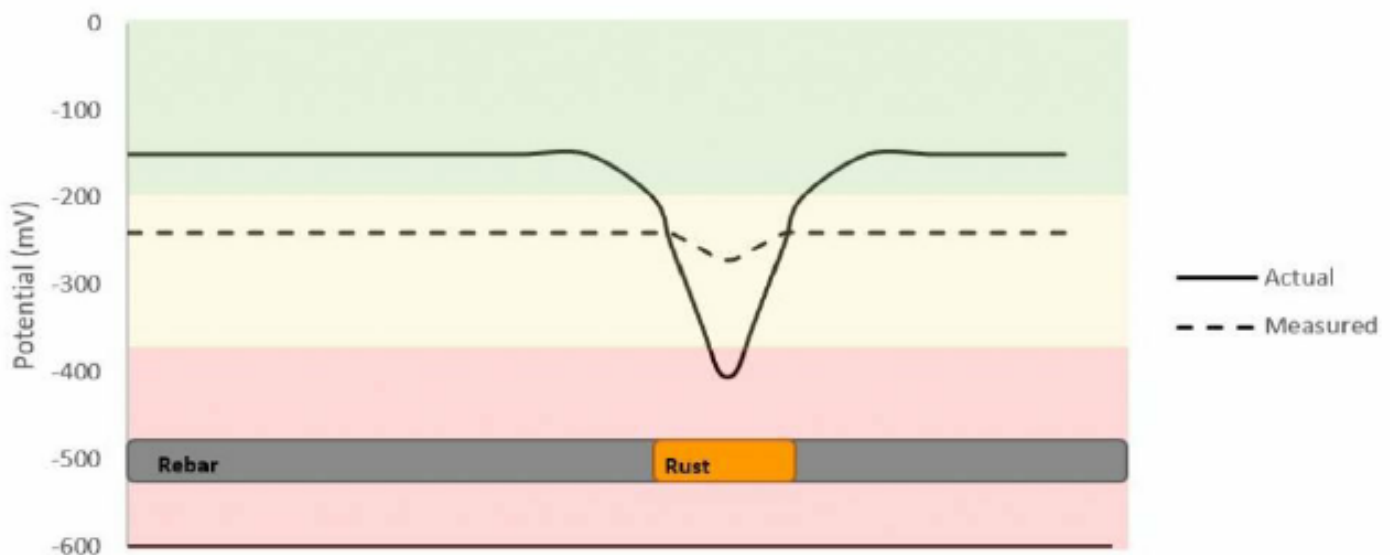
4.1 This test method is suitable for in-service evaluation and for use in research and development work.

4.2 This test method is applicable to members regardless of their size or the depth of concrete cover over the reinforcing steel. Concrete cover in excess of 3 in. (75 mm) can result in an averaging of adjacent reinforcement corrosion potentials that can result in a loss of the ability to discriminate variation in relative corrosion activity.

4.3 This test method may be used at any time during the life of a concrete member.

4.4 The results obtained by the use of this test method shall not be considered as a means for estimating the structural properties of the steel or of the reinforced concrete member.

4.5 The potential measurements should be interpreted by engineers or technical specialists experienced in the fields of concrete materials and corrosion testing. It is often necessary to use other data such as chloride contents, depth of carbonation, delamination survey findings, rate of corrosion results, and environmental exposure conditions, in addition to corrosion potential measurements, to formulate conclusions concerning corrosion activity of embedded steel and its probable effect on the service life of a structure.



Actual corrosion rate is usually greater than half-cell readings.



C = -.90



X = -.91



D = -.89



F = -.91



V = -.091



VL = -.92

DAY 1 OF PONDING

Measured Potential (mV)
w/Copper Sulfate Electrode

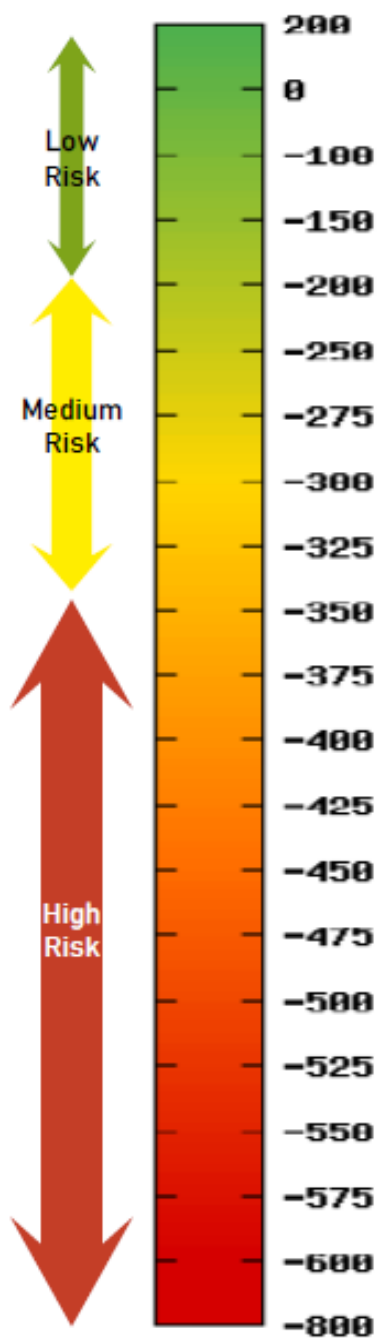
versus

Probability of steel corrosion activity -

> -200 Less than 10%

-200 to -350 Uncertain

< -350 More than 90%



DAY 30 OF PONDING

Measured Potential (mV)
w/Copper Sulfate Electrode
versus

Probability of steel corrosion activity -

> -200 Less than 10%
-200 to -350 Uncertain
< -350 More than 90%



C = -0.289



X = -0.267



D = -0.274



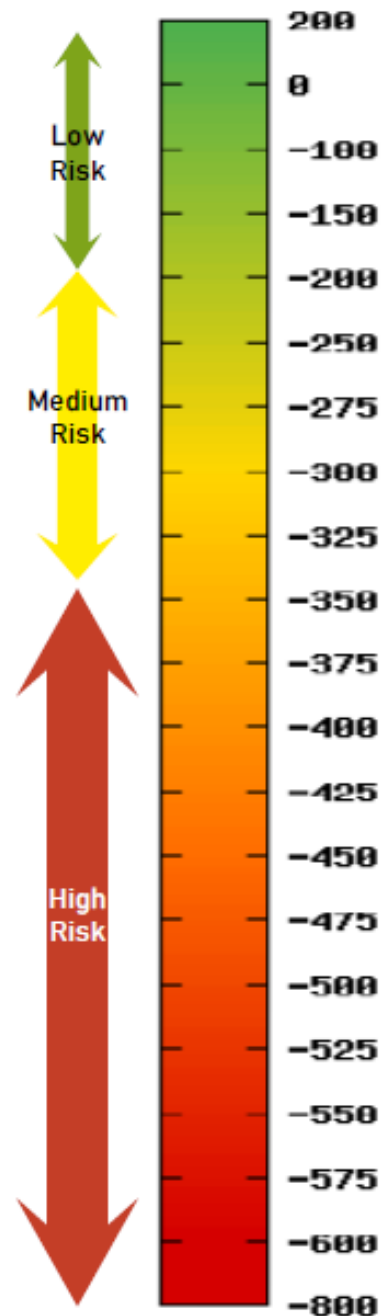
F = -.241



V = -.226



VL = -0.240





C = -.390



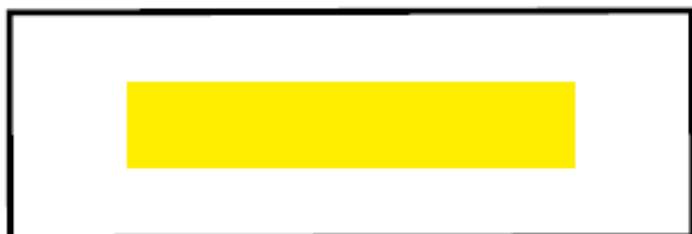
X = -.354



D = -.390



F = -.330



V = -.288



VL = -.330

DAY 60 OF PONDING

Measured Potential (mV)
w/Copper Sulfate Electrode

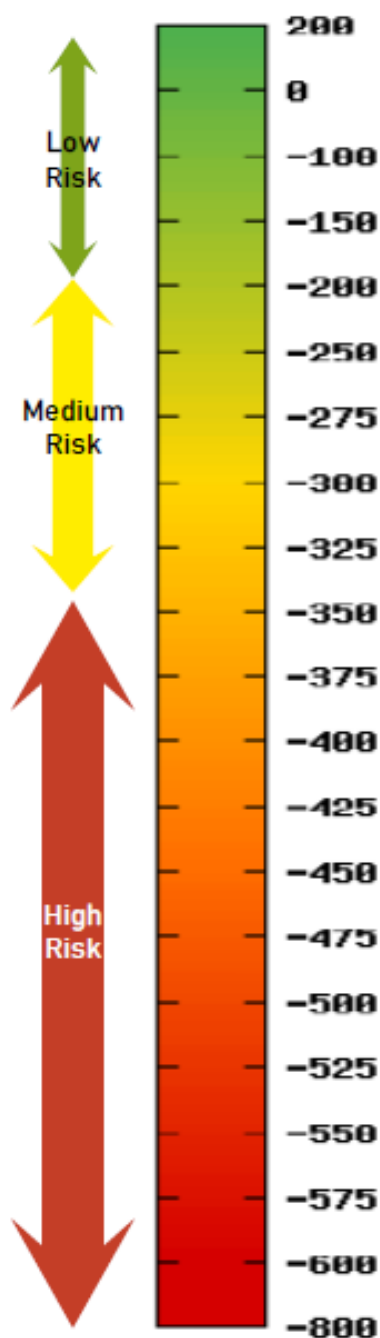
versus

Probability of steel corrosion activity -

> -200 Less than 10%

-200 to -350 Uncertain

< -350 More than 90%



RECOMMENDATIONS & CONCLUSIONS

In respect to PCA's assertion of "proper concrete cover and a low permeability concrete" to combat steel corrosion in concrete, the Chemical Penetration protocol put forth by Dr. Ley works intuitively towards accuracy, speed and the ability to compare specimens with admixtures. In conjunction with the numerous Coefficient of Permeability test results in and around the 0.02 US Perm area, the ability to provide a relatively quick and permanent capillary break (low permeability) seems apparent and can be inferred to drastically slow the *Initiation* period of corrosion.

In regards to the second *Propagation* period, we can infer certain characteristics from the quick movement of all specimens into the 'Medium Risk' zone (yellowish) by Day 30 of aggressive ponding. From there, the specimens move apart in regards to the Probability of Steel Corrosion Activity; with the Vapor Lock enhanced and then the Fly Ash samples showing superior readings. Next 90 Day readings will be telling if the trends continue or not.

In regards to both the "conventionalism" of the test specimens and Half-Cell protocols, we can only look at the latest recommendations from ASTM G01 – Corrosion of Metals, sub-committee 14.02 – in Concrete & Mortar and their latest prescribed changes to G109, including;

- leaving scale on rebar to promote greater cathode activity,
- and using 10 ohms resistance for improved voltmeter sensitivity and more acute low-end resistance.

Both were incorporated in the above protocols; steel was purchased from a local building supply company and not cleaned in any way. Also, the millivolt (one thousand of a volt) measurements above, where all from the 10 ohms resistance setting prescribed in the newest changes of the sub-committee. Beyond the "newest" nuances in corrosion ponding-type testing, as we are only about 30% into the prescribed 180 days, only time and the ultimate inspection will show agreement with the resistance/half-cell results.