

Contactless Kelvin Probe Electrode for Potential and Polarization Resistance Measurements of Reinforcing Steel in Concrete

Alberto A. Sagüés and Michael T. Walsh
Department of Civil and Environmental Engineering
University of South Florida
4202 East Fowler Ave.
Tampa, FL 33620 U.S.A.

ABSTRACT

The practical feasibility of using a Kelvin Probe as a novel reference electrode in the measurement of both potential and polarization resistance of reinforcing steel in concrete is demonstrated. Duplicate reinforced concrete beam test subjects with well-differentiated centrally corroding rebar segments were analyzed using both the Kelvin Probe (KP) and a conventional Saturated Calomel Electrode (SCE). A combination KP and customized counter electrode applied a small galvanostatic polarizing current and potential variations in both the active and passive regions were recorded using the KP. The observed potential response and recovery curves were consistent in shape and magnitude with curves provided by conventional reference electrodes. The nominal polarization resistance was successfully obtained from the polarization data acquired with the KP.

Keywords: Corrosion, Steel, Reinforcement, Polarization, Mapping

INTRODUCTION

The determination of rebar corrosion presence in reinforced concrete structures often involves measurement of the steel's open circuit potential at the concrete surface. Further polarization measurements can also determine corrosion rate by impressing currents and measuring changes of the potential. Traditional potential measurement procedures typically specify the use of a conventional wet-tip reference electrode. Effective use of a wet-tip electrode however necessitates an electrolytic path from its inner electrode to the concrete pore water. This path is generally formed by a combination of the electrode's own electrolyte and porous plug, and water or conductive solution that is applied to an electrolytic junction device (sponge) that maintains direct contact with the concrete.¹ If the concrete surface is dry prior to making the potential measurement, the pattern of diffusion potential differences across the concrete near the surface can be substantially altered as the electrolyte/solution slowly infiltrates the pore network.²⁻⁵ The alteration can be more significant if the concrete near the surface is carbonated by atmospheric CO₂.² The actual formation of the new pattern

may take several minutes or even a number of hours during which considerable potential drift (up to >200mV) may be observed.² To minimize the uncertainties and consequences of diffusion potential pattern evolution with time, a process of pre-wetting, that is, applying water directly to the surface is often used. Implementing this process, which necessitates delaying the actual potential measurement or polarization process until after the new stable diffusion potential pattern has been established, is not always practical or expedient especially in tightly scheduled field tests.

The Kelvin Probe (KP) is a device that enables contactless measurement of electrical potential, thus offering the possibility of obviating some of the artifacts indicated above. While different manifestations of the Kelvin probe have been used in other technologies, use of the KP for potential measurements of rebar embedded in concrete has only very recently been introduced by the authors, with promising results.⁶ The present work reviews initial application of the KP to open circuit potential mapping, and shows expansion of the method to polarization measurements for corrosion rate estimation with a customized probe design. Results demonstrate functionality and validation by comparison with values independently obtained via use of a conventional wet-tip electrode.

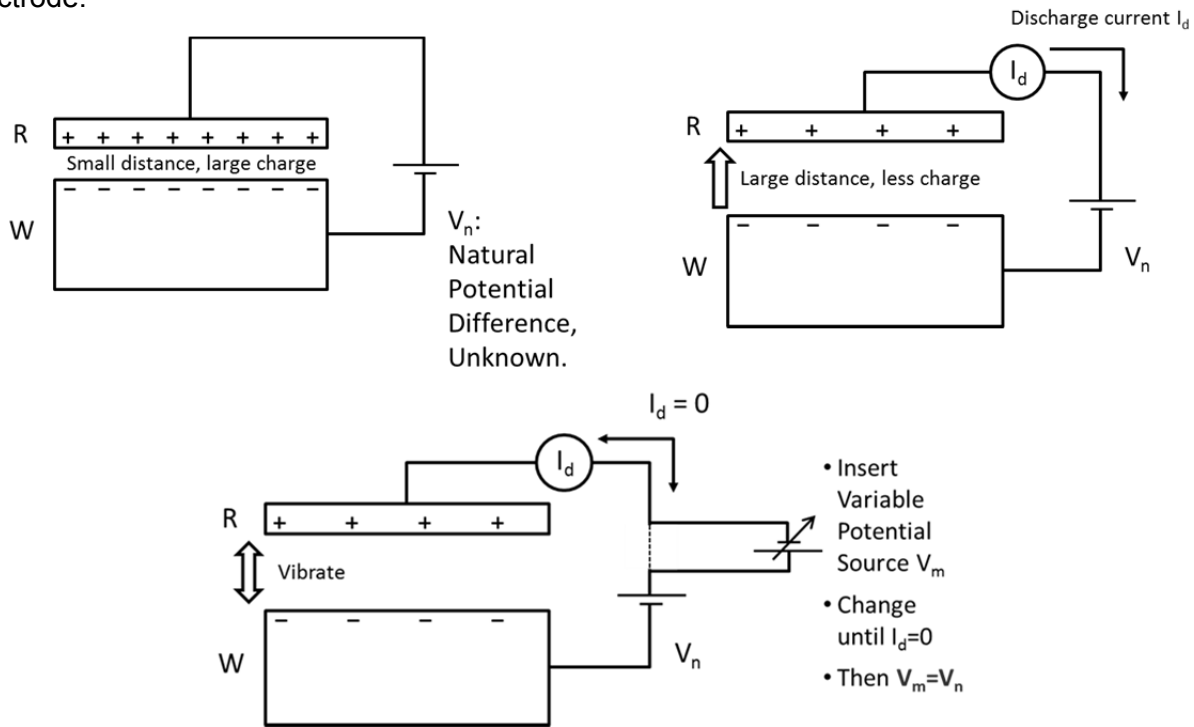


Figure 1: Basic operation of a Kelvin Probe

A detailed presentation of the principles involved has been presented by the authors elsewhere^{7,8,9,10} so only a brief summary will be presented here. In Figure 1, upper left, a metallic reference disk R is placed a short distance above a working surface W, in this case the surface of a concrete component. A metallic conductor joins the disk with the reinforcing steel mat in the concrete (not shown) allowing for the passage of current until the system achieves static electric equilibrium. The difference of potential V_n between the disk and the concrete surface is the algebraic sum of all the potentials (including the steel-concrete interfacial potential) that exist across the various media and interfaces participating in the circuit joining both surfaces. The system acts as a parallel plate capacitor so an electric charge cumulates on the facing sides of the disk and the concrete, proportional to V_n and inversely proportional to the separating distance.

If the disk is now physically elevated to a greater distance over the concrete surface (Figure 1, upper right) and the system allowed to equilibrate again, the value of V_n stays the same but the electric charge is now lower. Hence, part of the charge had to be transported in the form of a discharge current

I_d . If the disk motion is such that it is made to vibrate up and down by a mechanical actuator, I_d becomes an alternating current that could be measured. Consider now that the connecting wire is cut and a variable DC potential source of Value V_m opposing V_n is introduced in the circuit as shown in Figure 1, bottom. The current I_d will now be proportional to the value of $V_m - V_n$. If V_m is made to vary such that I_d vanishes, the corresponding value of V_m is then an exact opposite match to V_n , thus providing a measurement of V_n without needing to touch the concrete surface.

The procedure is implementable with automatic control circuits, and by hovering the probe disk over various parts of a reinforced concrete surface a surface potential map or profile is obtained, without touching the concrete surface. As shown by the authors⁶ the profile thus obtained successfully parallels, through a calibration offset, the profile that can be obtained with a conventional electrode for identifying corroding reinforcement spots. Unlike the conventional electrode method however, the KP measurements are made without touching the external concrete surface thus obviating the need for wetting the surface and waiting for stabilization delays.

This paper presents continuation work whereby the KP is fitted with an additional counter electrode (CE) for polarization measurements in a pulse mode, thus providing values of the nominal polarization resistance of the underlying steel with minimum surface disruption. Consequently, stabilization delays are avoided as well as any disruptions that would have resulting from needing to moisten the concrete surface as is the case of conventional polarization resistance methods. The objective of this work was to demonstrate feasibility of the concept.

METHODOLOGY

Concrete prisms 5 cm (2.0 in) thick, 15 cm (5.9 in) wide and 70 cm (27.6 in) long were made and tested in duplicate. The central 5 cm (2.0 in) of the prism contained 8.4 kg/m³ Cl⁻ ion (2.5 wt% of the cement content, exceeding typical corrosion initiation threshold levels [16a]) admixed by adding the corresponding proportion of NaCl. Each prism had a longitudinally centered #3 (10 mm (0.39 in) diameter) plain steel ASTM A-615 reinforcing steel bar with dark mill scale. Figure 2 shows a simplified view of the steel placement arrangement, which was described in detail in previous work.⁶

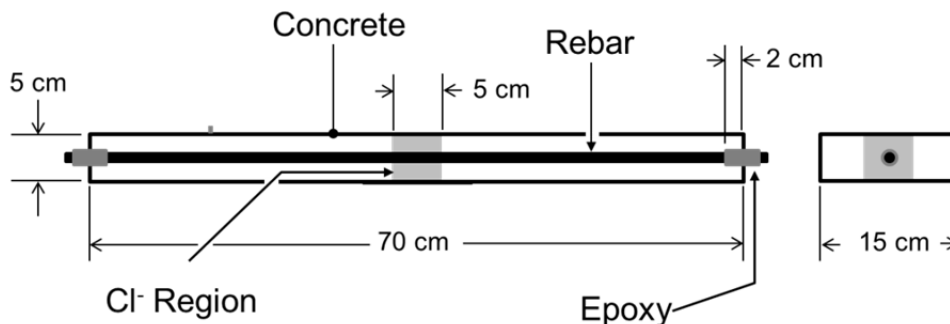


Figure 2: Reinforced concrete test specimen configuration

The arrangement of the KP fitted with a counter electrode is shown in Figure 3. The KP used a 13 mm (0.51 in) diameter austenitic stainless steel (Type AISI 302) reference disk vibrating at ~150 Hz with an amplitude ~0.5 mm (0.20 in) peak-to-peak, driven by a voice coil electromagnetic driver. At rest the disk to concrete surface distance was 1 mm. To minimize disturbance to the concrete surface the 10x10 cm (3.94 in) CE was made with an electrically conductive elastomer (resistivity in the 1 ohm-cm range) pressed against the concrete surface by a steel pressure plate. The KP faced the concrete surface through a 25 mm (0.98 in) diameter central opening that allowed representative sampling of the average surface potential of the CE-concrete interface. An automatic sensing circuit obtained the value

of V_m at a rate of 1 sample per second as it changed upon application of current through the CE-rebar circuit.

For simplicity and to eliminate the need for a potentiostatic control loop in these initial experiments, the tests were conducted in a galvanostatic pulse mode. The pulse was applied by means of an external high impedance current source. The pulse amplitude was selected by trial and error so as to obtain deviations from the pre-pulse-application potential of $\sim < 15$ mV.

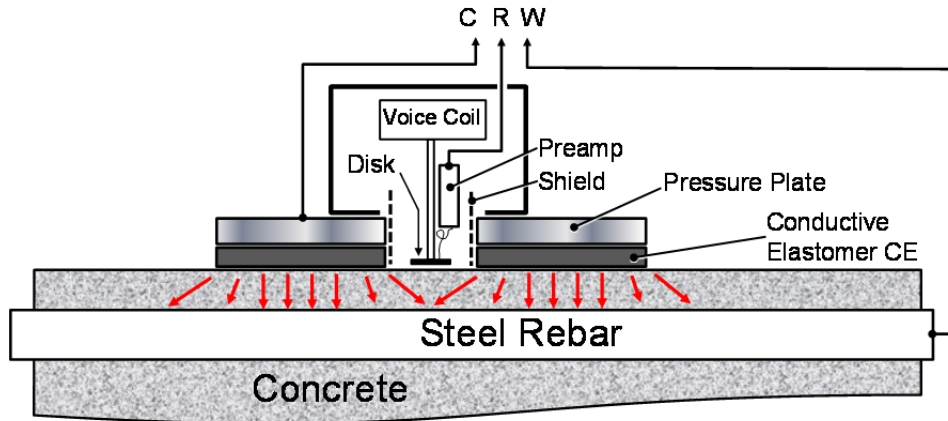


Figure 3: Schematic diagram of Combined KP Reference plus Dry Counter Electrode System. Red arrows show idealized excitation current path. Note: Patent Pending.

The pulse direction was selected to polarize the steel into the cathodic (more negative potentials). The time schedule consisted in monitoring the open circuit potential (OCP) for about 120 seconds, then applying one galvanostatic pulse for 60 seconds, allowing to recover for another 90 seconds, and applying a second 60 second pulse afterwards. The potential was monitored for an additional 90 seconds after the second pulse.

Measurements were conducted on each slab with the probe disk placed centered on the rebar first in the chloride contaminated region, and then on a chloride free region 20 cm away from the center of the slab. The static, pre-test potential indicated by the KP at each of the test locations was recorded prior to the polarization test.

After the KP polarization tests were completed, a comparison set of measurements using a conventional reference electrode was conducted. These tests used the same counter electrode on each spot, but replaced the KP sensing assembly with a small ($\sim 13 \times 13$ mm (0.51 x 0.51 in)) moist sponge in contact with the concrete surface, and placing the tip of a Saturated Calomel Electrode (SCE) on top of the sponge. The galvanostatic pulse sequence was then repeated, this time monitoring the SCE potential. Prior to each test the static OCP potential indicated by the SCE was recorded as well.

RESULTS AND DISCUSSION

Baseline potential measurements.

Table 1 lists the potential values measured with the KP placed on the beam center and at 20 cm (7.87 in) away, in duplicate beams. In each case the steel potential with respect to the concrete surface in the chloride contaminated central region was markedly more negative than the potential on the passive

region, consistent with the expected active vs passive condition of the steel in each region. Table 1 also shows the potentials measured using a conventional SCE electrode in both regions. As indicated previously by the authors the KP potentials are effectively offset, by an amount that may be calibrated, with respect to the conventional electrode. Both the KP and SCE were used to measure the potential difference ΔE between the active and passive regions of each beam and the results were very similar. This effectively reconfirmed the ability of the KP to identify active steel regions by differential measurements in concrete as demonstrated in previous work.⁶

Table 1
Baseline potential measurements.

	Beam A		Beam B	
	Active (x=0)	Passive (x=20cm)	Active (x=0)	Passive (x = 20cm)
Open Circuit Potential, KP [mV]	-408	-207	-314	-189
Open Circuit Potential, SCE [mV]	-369	-158	-294	-175
ΔE , KP [mV]	201		125	
ΔE , SCE [mV]	211		119	

Dynamic polarization measurements.

Dynamic measurements were successfully demonstrated, achieving the objective of this work. The KP was able to produce highly usable results to evaluate the dynamic polarization response of the system, tracking the potential evolution in real time and with noise typically well below 1 mV. That effective resolution was adequate to clearly establish system response when the potential deviations were in the order of several mV, which is a customary potential excursion range in polarization resistance or electrochemical impedance evaluations in concrete. Figure 4 (left side) shows the response to the galvanostatic pulses as measured with the KP. The system behavior revealed by the tests was as expected, with an initial instantaneous change reflecting the effective ohmic potential drop across the solution resistance that exists between the concrete surface and the underlying rebar, followed by a slower potential evolution. The latter results from part of the current satisfying the quasi-capacitive demand of the effective interfacial charge storage process, and the rest of the current polarizing the electrochemical Faradaic reactions of the interface. On first approximation, the overall behavior may then be represented by that of a solution resistance R_s in series with the parallel combination of an interfacial non-ideal capacitance represented by a constant phase element (CPE) and a polarization resistance, R_p .¹¹ That analog circuit responds in the time domain in a manner that essentially replicates that observed in Figure 4.

The behavior in tests of the two replicate beams was comparable, demonstrating consistent outcome of the methodology when switching specimens. Within each beam, the response to the second galvanostatic pulse closely replicated that of the first, showing good immediate reproducibility of results. The slight offset in the second pulse compared with the first is due to the relatively short recovery time in between the pulsed with correspondingly incomplete stabilization of the system before the second pulse. Correspondingly, the length of the pulse (60 seconds) allows for only partial evolution of the system toward a terminal state where the interface would act as the simple series combination $R_T = R_s + R_p$. Nevertheless, ignoring such residual effect a nominal result may be obtained by $R_T \sim -(E_f - E_i)/I_g$ where E_f and E_i are the values of the potential recorded just before and at the end of the applied galvanic pulse. Likewise and following the same approach used in instant-off solution resistance compensation procedures,¹² a nominal value of R_p may be obtained by $R_p \sim -(E_f - E_{io})/I_g$ where E_{io} is

the value of the instant potential obtained immediately following the beginning of the pulse application. For the present introductory tests, E_{io} was taken to be the potential measured 2 seconds after starting application of the pulse.

Table 2 shows the selected values of I_g and the resulting values of E_i , E_{io} , E_f , R_T , R_p and R_s (by difference) for each of the beams and at each of the two locations examined. Only results for the first pulse were used. Any residual potential drift was de-trended by calculating the corresponding linear baseline trend and subtracting from the data. The results are consistent with the appearance of the potential traces in Figure 4, whereby at the central, active steel locations the value of R_p is much smaller in accord with the expectation of high local corrosion rate (and with the more negative static potential noted earlier), while the opposite is observed at the $x=20$ cm (7.87 in), passive steel position. The value of R_s obtained was not very different between the active and passive steel positions. This was consistent with expectation, given that the concrete pore water is highly conductive due to its high ionic content even in the absence of chloride ions, and introduction of the latter in moderate amounts as used here does not create a radical relative increase in conductivity.

Table 2
Summary of dynamic polarization measurements

	Beam A				Beam B			
	KP		SCE		KP		SCE	
	Active (x=0)	Passive (x=20cm)	Active (x=0)	Passive (x=20cm)	Active (x=0)	Passive (x=20cm)	Active (x=0)	Passive (x=20cm)
I_g [μA]	39.7	7.7	39.0	7.6	39.6	7.9	37.5	7.7
E_i [V]	-2.62E-04	5.44E-05	-1.84E-04	2.51E-04	1.28E-04	-1.12E-05	1.16E-04	1.22E-04
E_{io} [V]	9.97E-03	3.18E-03	1.09E-02	3.71E-03	7.60E-03	3.80E-03	1.35E-02	4.81E-03
E_f [V]	1.19E-02	1.05E-02	1.25E-02	1.13E-02	8.92E-03	1.20E-02	1.50E-02	1.32E-02
R_T [Ω]	305	1,351	324	1,451	222	1,514	396	1,701
R_p [Ω]	47	945	39	995	33	1,032	39	1,092
R_s [Ω]	258	406	285	455	189	482	357	609

Note: the E_i and E_{io} values are given with reference to an arbitrarily zeroed condition for instrumentation purposes. Actual E_i values are presented in in Table 1.

Further demonstration of the ability of the KP to conduct useful polarization measurements was provided by comparison with the results in which the SCE was used as the reference electrode. The results are graphically displayed on the right side of Figure 4, showing excellent qualitative and in general, quantitative agreement with the KP results. It is noted that the SCE data were much more prone to drift, which was advantageously much less pronounced when using the KP.⁶ Numerical treatment of the SCE results to obtain resistive parameters was conducted similarly to that for the KP data and the results are listed in Table 2 as well. Graphic comparison of the R_T and R_s values obtained with both methods is shown in Figure 5, showing overall consistent findings and providing comparative validation of the use of the KP for polarization measurements.

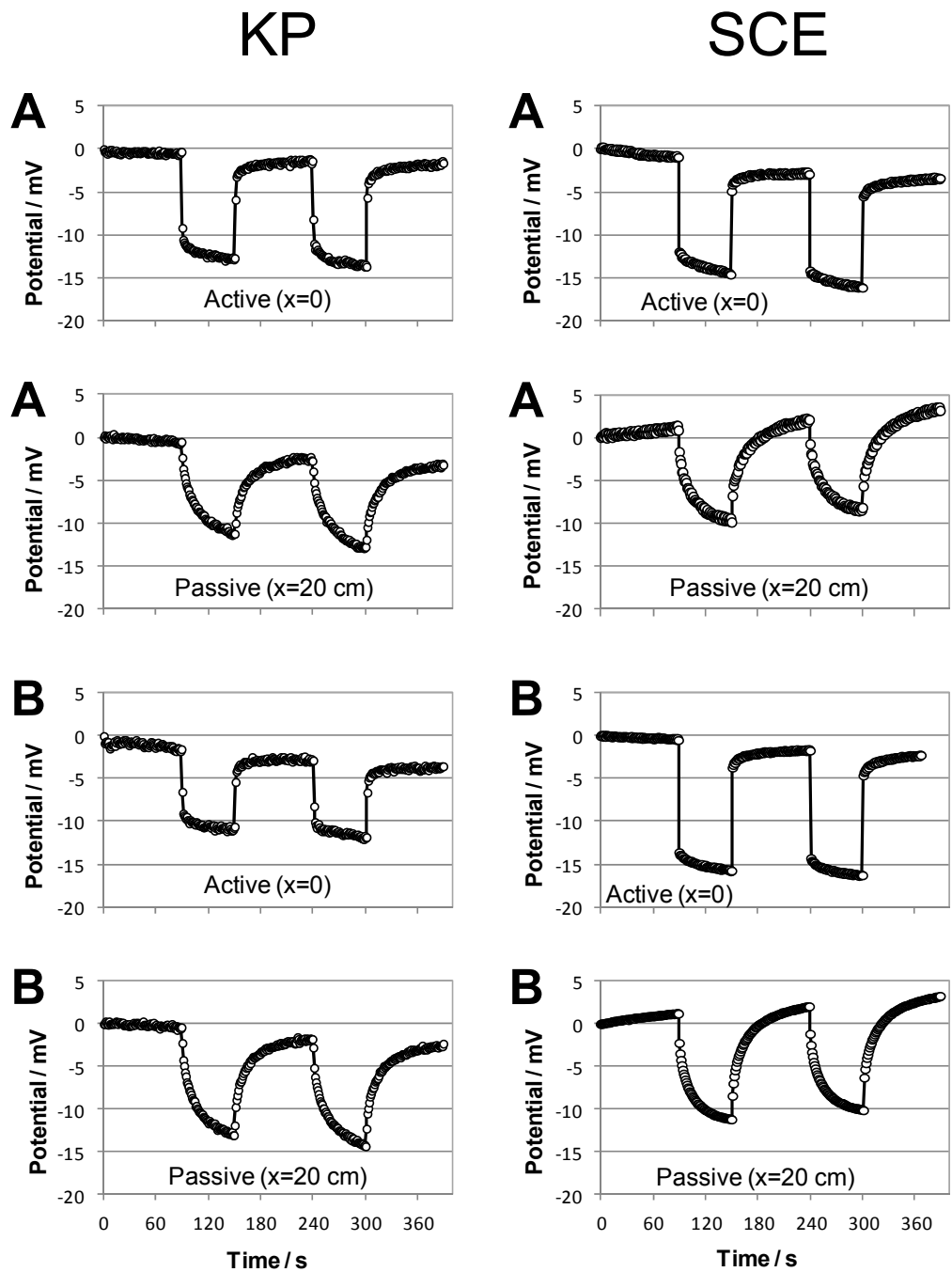


Figure 4: System response to Galvanostatic pulses (see text for amplitude selection) as measured by KP and SCE. Note that the center regions (i.e. $x=0$) of beams A and B contain actively corroding steel while other regions (e.g. $x=20$ cm (7.87 in)) contain steel in the passive state. All potentials have been referred vs. E_i to represent deviations from the starting condition only.

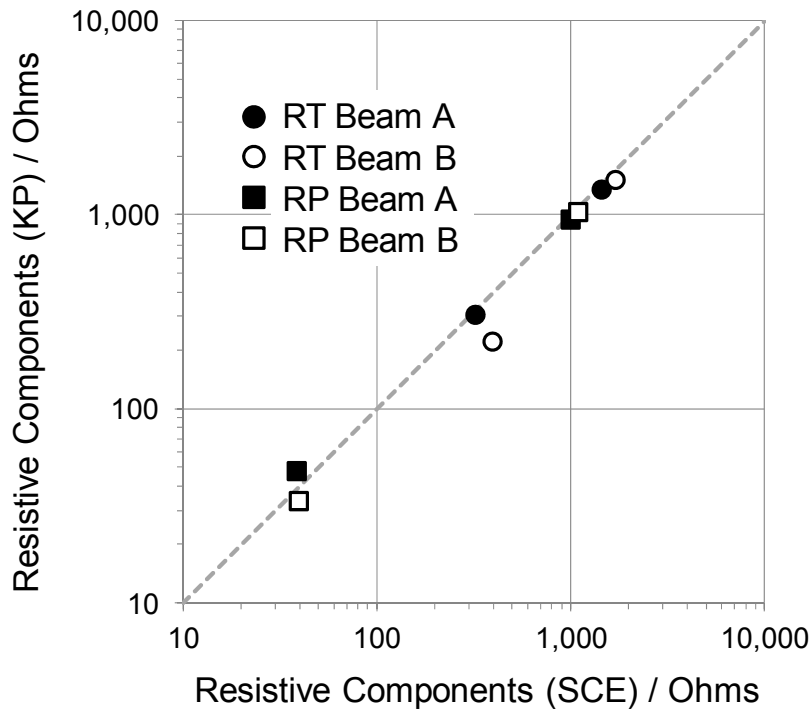


Figure 5: Comparison between KP and SCE galvanostatic pulse polarization results from Table 2, showing overall agreement between results. The dashed line represents theoretical 1:1 correlation.

Closing Observations

The galvanostatic measurement technique was chosen as a convenient means to establish the ability of the KP to perform dynamic polarization tests in concrete. Galvanostatic operation requires initial trial and error to select a current value that does not result in excessive potential excursion during the test, and that approach was used here. However, there is no fundamental limitation of application of the KP to measuring polarization of steel in concrete by other methods relying on automatic potential control, such as commonly used for linear polarization resistance or electrochemical impedance spectroscopy. Initial tests with a full control loop for potential and current using a commercial potentiostat have been performed with promising performance and will be presented in subsequent publication.

The KP's use as a reference electrode shows promise to facilitate fast, automated field corrosion data acquisition in cases where the use of a conventional wet-tip electrode would be disruptive or time consuming. Promising applications include facilitating assessment of corrosion condition of existing systems and related operations such as cathodic protection depolarization measurements.

CONCLUSIONS

- The use of a Kelvin probe was successfully demonstrated for polarization resistance measurements of reinforcing steel in concrete without contacting the concrete surface, and fitted with a novel counter electrode arrangement.
- The results were in good agreement with polarization measurements conducted with a conventional reference electrode.

ACKNOWLEDGEMENT AND NOTICE

This work was performed with the support and facilities of the University of South Florida. The assistance of Kingsley Lau with previous trial tests is greatly appreciated.

A portion of the findings of this paper constitute intellectual property related to a U.S. Utility Patent Application that was filed on May 30, 2013. Accordingly, the declaration "Patent Pending" must be associated with the device and technology associated with the embodiment described herein.

REFERENCES

1. ASTM C876 - 09, "Standard Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete", (West Conshohocken, PA: ASTM).
2. R. Myrdal, Phenomena that Disturb the Measurement of Potentials in Concrete, Corrosion/96, paper no. 339, NACE International, Houston, 1996.
3. R. Myrdal, Potential Gradients in Concrete Caused by Charge Separations in a Complex Electrolyte, Corrosion/97, paper no. 278, NACE International, Houston, 1997.
4. U. Angst, O. Vennesland, and R. Myrdal, "Diffusion Potentials as Source of Error in Electrochemical Measurements in Concrete," *Materials and Structures* 42 (2009) pp. 365-375.
5. U. Angst, B. Elsener, R. Myrdal, and O. Vennesland, "Diffusion Potentials in Porous Mortar in a Moisture State below Saturation," *Electrochimica Acta* 55 (2010) pp. 8,545-8,555.
6. A. Sagüés and M. Walsh, "Kelvin Probe electrode for contactless potential measurement on concrete – Properties and corrosion profiling application," *Corrosion Science*, Vol 56, (2012): pp. 26-35.
7. U. Klein, W. Vollmann, and P.J. Abatti, "Contact Potential Differences Measurement: Short History and Experimental Setup for Classroom Demonstration," *IEEE Transactions on Education* 46 (2003) pp. 338-344.
8. M. Stratmann and H. Strechel, "On the Atmospheric Corrosion of Metals which are Covered with Thin Electrolyte Layers – I. Verification of the Experimental Technique," *Corrosion Science* 30 (1990) pp. 681-696.
9. L. Kronik and Y. Shapira, "Surface photovoltage phenomena: theory, experiment, and applications," *Surface Science Reports* 37 (1999) pp. 1-206.
10. A. Leng, H. Streckel, and M. Stratmann, "The Delamination of Polymeric Coatings from Steel – Part 1: Calibration of the Kelvin probe and Basic Delamination Mechanism," *Corrosion Science* 41 (1999) pp. 547-578.
11. A. Sagues, S. Kranc, and E. Moreno, "Evaluation of Electrochemical Impedance with Constant Phase Angle Component from the Galvanostatic Step Response of Steel in Concrete," *Electrochimica Acta*, Vol 41 Nos. 7/8 (1996) pp. 1,239-1,243
12. H. Hack, P. Moran, and J. Scully, "Influence of Electrolyte Resistance on Electrochemical Measurements and Procedures to Minimize or Compensate for Resistance Errors," *The Measurement and Correction of Electrolyte Resistance in Electrochemical Tests*, ASTM STP 1056, L.L. Scribner and S.R. Taylor, ASTM, Philadelphia (1990) pp. 5-26

©2014 by NACE International.

Requests for permission to publish this manuscript in any form, in part or in whole, must be in writing to NACE International, Publications Division, 1440 South Creek Drive, Houston, Texas 77084.

The material presented and the views expressed in this paper are solely those of the author(s) and are not necessarily endorsed by the Association.