

Novel Kelvin Probe electrode for non-intrusive corrosion rate evaluation of steel in aged concrete structures

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Abstract: Dynamic polarization measurements of embedded reinforcing steel can be used to estimate corrosion rate in ageing structures. Potential in such tests is commonly measured using a conventional reference electrode but this can yield unstable readings, particularly on aged concrete with high near-surface resistivity. Interaction between the concrete and the electrode introduces time-dependent liquid junction potentials requiring waiting for stabilization. The Kelvin Probe (KP) uses a vibrating-plate capacitor principle to measure potential without contacting the concrete surface thus avoiding complications of electrolyte interaction. This paper extends application of a previously introduced KP-based system to include dynamic Electrochemical Impedance Spectroscopy (EIS) measurements of steel in concrete.

Keywords: corrosion, concrete, reinforcement, contactless, polarization

1 Introduction

Corrosion rate evaluation of reinforcing steel in concrete structures is often conducted by means of steel polarization measurements. A small current density is impressed on the steel-concrete interface and the resulting small (e.g. 10 mV) potential change is measured either in the time domain or in the frequency domain, as in the case of electrochemical impedance spectroscopy (EIS) where impressed alternating currents over a range of frequencies range are used.

In the simplest cases the corrosion rate is found to be proportional to the inverse of the polarization resistance which corresponds with the low-frequency limit of the ratio of the potential change to the impressed current density with appropriate correction for ohmic components. In more complicated cases the measurements require more sophisticated analysis. In both cases, obtaining accurate results requires that the potential, which is measured by means of a reference electrode normally placed on the concrete external surface, is stable in time despite any inherent instability of the reference electrode or changes occurring on the concrete surface during the test. An important source of potential drift stems from the nature of conventional reference electrodes (e.g. Copper/Copper Sulfate electrode), which require electrolytic contact between the internal electrode medium and the pore water near the surface of the concrete. The required contact normally involves a porous tip at the bottom of the electrode body and some intermediate moist body such as a small sponge in contact with the concrete surface. In most cases and especially in the case of dry or aged concrete surfaces, the contact with the sponge results in relatively large electrolyte intrusion to the initially nearly empty surface pore network. The intrusion results in the development of slowly evolving diffusional potential differences across the depth of the near-surface region. The consequent drift in the potential reading can be large (e.g. 200 mV) and continue over a long time (e.g. hours) thus delaying the start, or otherwise compromising the validity, of the corrosion rate derived from polarization measurements.

The Kelvin Probe (KP) uses a vibrating-plate capacitor principle to measure potential without contacting the concrete surface thus avoiding complications of electrolyte interaction. The principle of operation of the KP is well documented in the literature [1-4] so only a brief review is presented here. The KP embodiment in these experiments used a 13 mm diameter austenitic

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stainless steel (Type AISI 302) disk placed ~ 1mm over the concrete surface and made to vibrate perpendicular to the concrete surface at ~150 Hz with ~ 0.5 mm amplitude. An electromagnetic voice coil was used as a driver. The disk is connected through a current-sensing electronic circuit and a variable voltage source to the reinforcing steel that is embedded in the concrete directly beneath the disk. The natural Volta potential difference between the disk and the surface of the concrete, which together form a parallel-plate capacitor, results in a capacitive charge directly proportional to the value of the potential difference (nominally constant due to the interconnection) and the disk-concrete capacitance. Since the capacitance varies with the oscillating gap distance, the charge likewise varies resulting in an alternating current through the disk-steel interconnecting circuit. An automatic zeroing circuit changes the value of the voltage source until the current vanishes. The value of the source voltage at that point is equal but opposite to the natural steel-disk potential difference. That value is then recorded as the probe potential reading for that position on the surface of the concrete.

Since the disk doesn't contact the concrete and because its material properties are not subject to change, KP readings obtained by moving the disk over different parts of the concrete surface effectively constitute a survey of the potential gradients over the concrete surface. That information can be used to identify corroding regions of reinforcement within a concrete body, in the manner of the ASTM C-876 [5] potential mapping procedure but without disturbing the concrete surface.

The authors have recently demonstrated the feasibility of using a novel customized KP as an alternative to a conventional electrode for potential mapping [6]. They also demonstrated the use of the probe for nearly non-intrusive polarization resistance measurements in the time domain that may serve for corrosion rate determination [7]. In this paper, recent advances are presented expanding the use of the KP to include frequency domain polarization measurements of steel in concrete, in the form of Electrochemical Impedance Spectroscopy (EIS) tests. This type of measurement can provide more accurate evaluation of polarization parameters with greater sensitivity, while avoiding any disturbance of the concrete surface at the location of measurement.

2 Materials and Methods

2.1 Kelvin Probe Embodiment for Polarization Measurements of Steel in Concrete

For steel polarization measurements the KP disk was placed at a single location on the concrete surface, with a relatively large (10 x 10 cm square with a 3 cm diameter hole in the centre) external counter electrode (CE) surrounding the sensing disk but not touching it. The CE and disk were separated by a grounded shield (Figure 1). The CE was made of a conductive elastomer (resistivity in the order of 1 ohm-cm) that does not moisten the concrete surface thus minimizing disturbance to the concrete footprint of the counter electrode and surroundings (including the place beneath the sensing disk) and was pressed against the concrete surface with a clamped steel plate. A polarizing current was introduced between the CE and the embedded steel, resulting in a change of the steel-concrete interfacial potential plus an ohmic potential drop due to the electric resistance of the intervening concrete between the surface of the concrete and that of the steel. Given the relatively large size of the counter electrode, the current flow toward the steel was nearly uniform and the KP sensed the combined ohmic and interfacial polarization response to the applied current. The values of the current and the combined potential change were recorded and the results were then, after making appropriate working assumptions of the effective steel area and other system parameters, processed to obtain a nominal polarization resistance and subsequently a nominal corrosion rate for the underlying steel. Calibration of the KP against a conventional electrode is unnecessary since only changes in potential matter. The feasibility of this approach was recently demonstrated by the authors for direct current galvanostatic pulse polarization resistance measurements in laboratory reinforced concrete specimens [7].

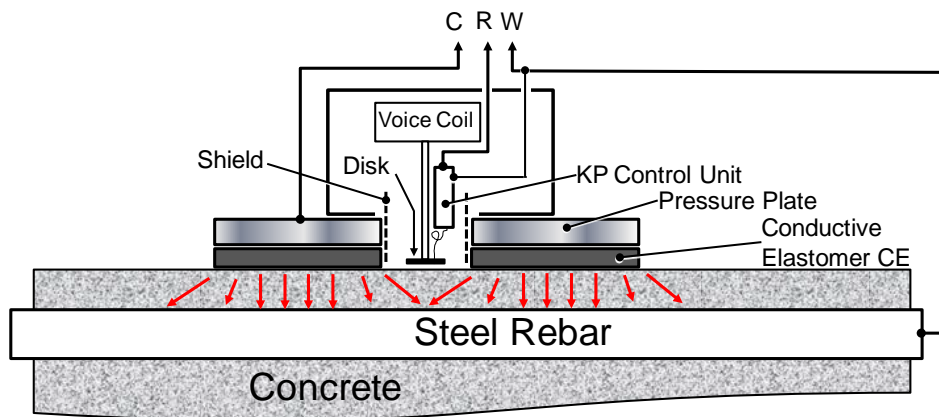


Figure 1 Schematic diagram of combined KP reference (R) plus dry counter electrode (CE) system with the reinforcing steel bar (rebar) as the working electrode (W); red arrows show idealized excitation current path.
Patent Pending

2.2 Electrochemical Impedance Spectroscopy

The extension to alternating current operation for EIS measurements, introduced in this paper, was implemented by connecting the system to the C, R, and W terminals of a Gamry 600 potentiostat and impedance analyzer unit. Because the vibrating disk operated at near 150 Hz and the electronic processing unit had typical settling times in the order of $\frac{1}{2}$ second, EIS measurements were conducted only at frequencies $< \sim 1$ Hz. That constraint does not represent a severe limitation because much of the EIS corrosion rate information for steel in concrete is present at the lower frequencies of the spectrum [8]. The low frequency limit was typically 0.001 Hz. The tests were normally conducted in galvanostatic mode since in that mode the default settings of the impedance analyser resulted in stable operation. That choice is not limiting as potentiostatic operation should be equally feasible with adequate potentiostat response time settings. For comparison purposes, EIS measurements were made also using a conventional reference electrode and the same counter electrode at each measurement location. These tests involved placing the tip of a Saturated Calomel Electrode (SCE) on top of a small ($\sim 13 \times 13$ mm) lightly moistened sponge in contact with the concrete surface.

The reinforced concrete specimens were duplicate beams 5 cm thick, 15 cm wide and 70 cm long, and designated A and B. Each beam had a longitudinally centered #3 (10 mm diameter) plain steel ASTM A-615 reinforcing steel bar with dark mill scale. The central 50 mm of each beam contained 8.4 kg/m^3 Cl^- ion (2.5 wt% of the cement content, exceeding typical corrosion initiation threshold levels [9]) admixed by adding the corresponding proportion of NaCl. Concrete cover on top of the steel was 2 cm. The beams had been cast ~ 3 years before the tests described here and were normally kept in a moist condition. Before conducting the tests the beam surfaces were allowed to dry at least overnight in laboratory air. All tests were conducted at temperatures around 22 °C. EIS measurements were conducted on each beam with the electrodes placed on top of the steel bar on the central, chloride contaminated region ($x = 0$ cm) where the steel surface was in the actively corroding condition, and at a location 20 cm away ($x = 20$ cm) from the center where the steel surface was in the passive condition.

3 Results and Discussion

The steel open circuit potential values were determined using an SCE placed on the concrete surface, as well as by the KP at the same locations (Table 1, average of representative values

during the period of testing). The SCE potentials were comparable in the replicate beams and consistent with the expected active and passive character of each position [7].

Table 1 Baseline steel potential readings (mV)

	Beam A		Beam B	
	Active (x=0 cm)	Passive (x = 20 cm)	Active (x=0 cm)	Passive (x = 20 cm)
Open Circuit Potential, KP [mV]	-425	-227	-334	-175
Open Circuit Potential, SCE [mV]	-365	-169	-298	-163

The potentials recorded by the KP, although offset as expected from the SCE values by an approximately constant amount that depends on the disk material and its surface condition, showed essentially the same active/passive differentiation as those obtained from the SCE, confirming earlier work that demonstrated the feasibility of concrete potential mapping with the KP [6].

Figure 2 shows examples of EIS spectra obtained with the KP used as a reference electrode at the active and passive locations of one of the beams, together with results obtained using the conventional SCE electrode. Functioning as a reference electrode, the KP successfully followed the programmed EIS excitation over the entire frequency range. Results were comparable and reproducible in the replicate beam and in replicate tests. The results for the KP approached closely the overall form of those obtained with the conventional electrode (the small relative resistive offset between the KP and SCE results for x=0 cm may be ascribed to minor differences in placement and would not have a significant effect in corrosion rate estimations). Both sets of results show dramatic differentiation between the active and passive regions.

For quantitative comparison, the results for x=20 cm, which show a well-defined low frequency loop, were fit to those of an equivalent circuit consisting of a solution resistance R_s in series with the parallel combination of a non-ideal interfacial capacitance (Constant Phase Element, CPE [10]) and a polarization resistance R_p . For x=0, the EIS spectrum was not amenable to straightforward interpretation but was indicative of much lower low frequency polarizability (and hence correspondingly greater corrosion rate) than that at x=20. Analysis was thus limited to assigning a nominal solution resistance R_s^* to the real part of the impedance at 1 Hz, and a nominal polarization resistance R_p^* to the modulus of the difference of impedances at 1mHz and 1 Hz.

Comparison of the results of the analysis using the KP and the SCE is shown in Figure 3 for all of the resistive elements. The figure shows overall good agreement, spanning more than one order of magnitude, of the KP results and those of the conventional electrode. The agreement is in the order of, or better than, the usual uncertainty in converting electrochemical corrosion rate determinations to actual metal loss [11]. There was also good agreement in the values of the CPE parameters [10]. The average values for Y_0 and n were $5,3 \text{ S s}^n$ and $4,3 \text{ S s}^n$, and 0,69 and 0,67 for the KP and SCE x=20 cm measurements respectively.

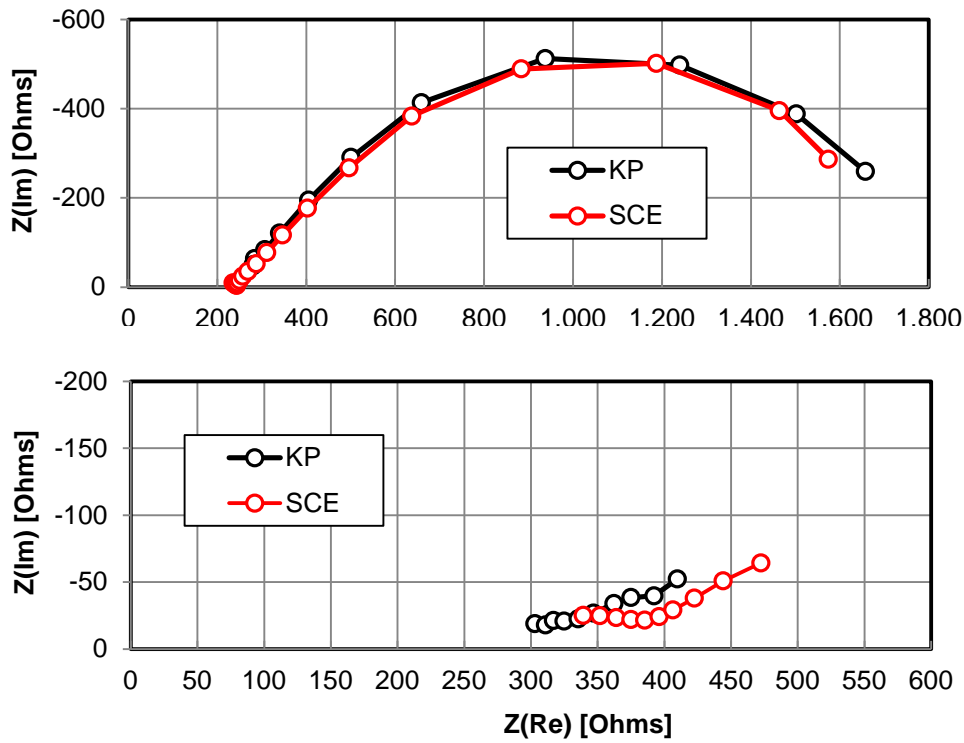


Figure 2 Examples (Beam A) of Nyquist representation of EIS spectra observed at the $x=20\text{cm}$ (top) and $x=0\text{ cm}$ locations with the KP and with a conventional SCE electrode; lowest and highest frequencies were 1 mHz and 1 Hz respectively (3 points per decade)

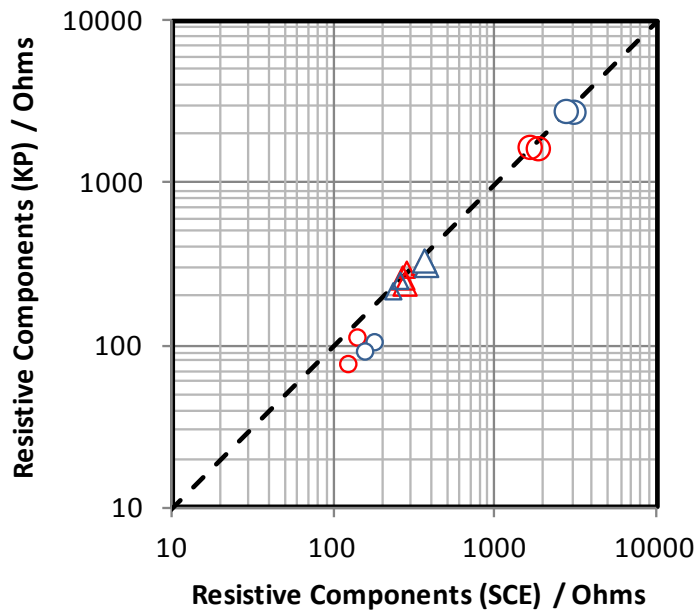


Figure 3 Comparison of R_s (triangles) and R_p (circles) values obtained in repeat tests at the $x=20\text{cm}$ (large symbols) and $x=0\text{ cm}$ (small symbol) locations with the KP and with a conventional SCE electrode, showing overall agreement between results; red: beam A, blue: beam B; The dashed line represents theoretical 1:1 correlation

Since the counter electrode did not include a guard ring [12] the sampled area of steel was uncertain and thus the impedance parameters are not reported in surface area-normalized form. Nevertheless, assuming an approximate Stearn-Geary parameter of 26 mV [11], and for simplicity that the steel area sampled is roughly that beneath the counter electrode footprint (~ 30 cm²), the Rp values for the x=0 cm and x=20 cm locations indicate nominal corrosion current densities in the order of 10 $\mu\text{A}/\text{cm}^2$ and 0.4 $\mu\text{A}/\text{cm}^2$ respectively, which are in the order of values expected for actively corroding and nearly passive steel behaviour.

The absence of a guard ring does not in any way represent a fundamental limitation of KP implementation and the incorporation of an integrated guard ring represents an opportunity for future development. Any negative consequences associated with the uncertainty of the actual area of the sampled region in the experiments described in this paper would apply equally to both the SCE and KP.

The KP's use as an EIS reference electrode shows promise as a means by which fast, automated field corrosion data acquisition can be facilitated in cases where the use of a conventional wet-tip electrode would be disruptive or time-consuming.

4 Conclusions

- The innovative use of a Kelvin probe as a contactless reference electrode in the measurement of EIS spectral data for reinforcing steel in concrete without contacting the concrete surface, and fitted with a novel counter electrode arrangement was successfully demonstrated.
- The results were in good agreement with EIS spectral data measured with a conventional reference electrode, successfully identifying and characterizing a high corrosion rate location.

Acknowledgement

This work was performed with the support and facilities of the University of South Florida. Note that 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.

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