Kelvin Probe electrode for contactless potential measurement on concrete – Properties and corrosion profiling application

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ABSTRACT

The practical feasibility of Kelvin Probe measurement of potential of the concrete surface was demonstrated. The measurements require no contact between the reference element and the concrete. Potential readings when placing the probe on dry concrete were nearly instantaneous and highly stable, in contrast with considerable potential drift with a conventional wet-tip electrode. The probe output was only modestly sensitive to the reference element working distance. The shape and range of potential profiles measured with the probe on concrete with locally corroding reinforcement were consistent with those using a conventional wet-tip reference electrode, both identifying the anode location.

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1. Introduction

The electric potential distribution on the external surface of concrete can be indicative of various ongoing processes of interest. For example, surface potential mapping is often conducted to identify the location of corroding reinforcing steel. For that application potential measurements are normally conducted by connecting the positive terminal of a high impedance dc voltmeter to the reinforcing steel assembly, and the other terminal to the metallic terminal of a reference electrode, usually a copper–copper sulfate electrode (CSE). The electrolyte end of the reference electrode is then placed in successive contact with an array of points on the external concrete surface, and the potential for each point is recorded. The resulting potential map provides a diagnostic of the presence and position of regions of the reinforcement assembly with high likelihood of ongoing active corrosion. The method [1–3] relies on the sizable potential transition (e.g. from ~ -150 to ~ -400 mV CSE) that formerly passive steel often experiences upon the onset of active corrosion [4,5]. Thus, regions displaying negative potentials in the order of several hundred mV vs. CSE may be considered suspect of ongoing active corrosion. If active corrosion affects only a portion of the steel, the potential is not uniformly highly negative on the concrete surface because of the finite resistivity of concrete that joins the active and the passive portions of the assembly. The steel in the latter is only partially polarized and potential measurements against nearby concrete remain only mildly negative, so the external potential map

can reveal the location of the corroding zones as well. Because of measurement artifacts described later, the measured potentials may be more or less globally offset from those in an ideal case. Thus, identification of corroding regions often relies more on consideration of potential gradients rather than of the absolute potential values.

Concrete surface potential measurements are also routinely conducted to monitor cathodic protection systems, assess the effectiveness of corrosion repair patches, and as part of electrochemical corrosion rate measurements. The latter are estimated by polarization measurements, where the amount of impressed current needed to achieve a small potential change is determined. The current is impressed by means of an additional external electrode attached to the concrete surface [4] or by means of rebar not in metallic contact with that being tested [6]. Within certain limitations [4,7,8], the ratio of potential change to impressed current density yields the polarization resistance Rp which is related to the corrosion current density i_{corr} through the Stearn–Geary parameter B by the equation $i_{corr} = B/Rp$. The resulting value of i_{corr} can then be related to the corrosion rate of the steel by the usual Faradaic conversion [9].

Surface potential measurements are sensitive to the condition of both the bulk of the concrete and its surface. For example, the presence of a carbonated concrete skin, even if it is very thin, can result in an appreciable potential difference (e.g. as much as 200 mV) between the outer surface and the bulk of the concrete [10–13]. That difference reflects the widely different pH of pore water in the outer and inner regions. A diffusion potential (a general term that includes junction and membrane potentials as well as those resulting from other electrokinetic effects [13]) develops to preserve charge neutrality upon coupled diffusion, across the region joining both zones, of anions (OH^-) and cations (K^+, Na^+) that have significantly different

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diffusivities. Weathering, sulfate attack, and other environmental interactions may cause similar electrochemical potential gradients that may affect the surface potential pattern. A very dry concrete surface may prevent accurate potential determination as the effective contact resistance begins to approach the value of the voltmeter input resistance. The sensitivity of the potential measurements to these phenomena creates both an opportunity for their characterization and a concern as a source of artifacts in corrosion condition determination.

The extent to which potential measurement artifacts are present is obscured by the disruptive nature of the electrochemical reference electrode, which requires a shared electrolyte link between the metallic terminal and the concrete pore water. When the electrolyte tip of the reference electrode touches the concrete surface, a liquid transport process starts that transfers some of the electrode solution into the concrete pores and vice versa. The process may range from mostly interdiffusion if the concrete pores are nearly saturated, to strong convective capillary action if the pores are nearly dry. The latter case may result in appreciable drift in the voltmeter reading as the system slowly approaches a steady state condition, likely involving the evolution of a diffusion potential pattern that includes both junction and membrane potential components [10,13]. Such drift can introduce added uncertainty on the result of the potential measurement, and significant artifacts in electrochemical corrosion rate measurements. Sometimes to partially alleviate those effects a pre-wetting procedure is used for the concrete surface before placing the reference electrode [1], but comparable uncertainty exists as to the potential variation (and its time variation) created by the intrusion of the wetting fluid to the formerly dry concrete.

Use of a Kelvin Probe (KP) electrode offers an alternative to avoid some of the artifacts noted above, by means of a contactless procedure that does not depend on a shared electrolyte, and that is inherently non-disruptive of the region sampled by the probe. To the knowledge of the authors, application of the KP to this end does not seem to have been previously conducted. In this work, macroscopic measurement of concrete surface potentials with a KP is explored. The probe operation, performance, and application to potential mapping is demonstrated.

2. Principle of the KP operation and application to concrete

The KP determines the potential difference E between two surfaces designated as working and reference, respectively. The principle of operation has been described extensively in the literature [14–17] so only a brief review is presented here before addressing the issues specific to measurements on a concrete surface.

In the present case the working surface is a small part of the outer concrete surface, and the reference surface is the surface on one side of a macroscopically small (e.g. ~1 cm diameter) disk of a suitable metallic material, for example, gold or stainless steel with a stable passive film. The disk and the concrete surfaces are a small distance h apart so as to approximate a parallel-plate capacitor configuration. The disk is connected through electronic conductors to the steel bar assembly embedded in the concrete. The steel bar surface is connected to the external surface of the concrete by an electrolytic path provided mainly by the water in the concrete pore network. Consequently the concrete and the reference surfaces are joined through an electronic and electrolytic conductive path with associated interfaces that determine the value of E. The relationship linking electrical charge Q and potential difference E across a capacitor with capacitance C is

$$Q = EC \tag{1}$$

For plates with small gap the capacitance is approximated by

$$C = \varepsilon \, \varepsilon_0 A / h \tag{2}$$

where ε is the dielectric constant of the medium in the gap between the plates (normally air, $\varepsilon \sim 1$), ε_0 is the permittivity of vacuum and A is the one-sided surface area of the smallest of the plates, in this case the reference surface. Since E is fixed by the characteristics of the intervening conducting and interfacial chain, if h is changed from one static position to another the static value of Q needs to change accordingly as well to satisfy Eqs. (1) and (2). In the KP h is varied cyclically with time by attaching the reference disk to the end of an electrically insulating, longitudinally vibrating stem. Consequently Q changes cyclically as well resulting in an alternating current I_A circulating through the conductive path.[1] If a potential source with known potential E' selected at will is inserted in that path (for example, into a break made in the connecting wire to the rebar) the potential between the reference and concrete surface becomes $E + E'$. When $E' = -E$ the potential across the capacitor is zero and the alternating current vanishes. This permits then determining the value of E by varying E' until $I_A = 0$, a condition that can be reached with great sensitivity by adequate electronic amplification. The zeroing process can be made manually or performed automatically and promptly with ordinary control circuitry, yielding an immediate record of the value of E.

With interfaces having well-defined boundaries and locally uniform electric charge profiles, the potential E measured by the KP is the difference between the Volta (outer [15,18]) potential ψ_R of the reference surface and the Volta potential ψ_W of the working surface being examined

$$E = \psi_R - \psi_W \tag{3}$$

The metallic reference disk generally approximates those conditions and may be considered to have a well-defined spatially averaged ψ_R value. The concrete facing it is quite heterogeneous, as is the distribution in its pore network of the electrolyte responsible for much of the electric charge configuration in the material. Hence ψ_W should be considered only as an effective value, that of an ideal conductor that would yield the same experimental results as those obtained with the concrete. Thus ψ_W may be viewed as representing an approximate average of the potential of the surface of the concrete beneath the footprint of the of the reference surface disk. Lateral heterogeneity up to the mm scale (pore space-paste-fine aggregate domain) is expected to be reasonably averaged beneath the disk, but some sensitivity to the distribution of the coarse-aggregate, which is typically >1 cm in size, can be anticipated.

The value of E measured by the KP is determined by the present system as schematically described in Fig. 1. The reader is referred to the treatment by Leng [17] for a thorough discussion on accounting for potentials at multiple interfaces in a KP measurement. For simplicity, only two different metals are assumed to be involved, one for the reference surface (R) and one for the steel bar (S). The respective inner (Galvani [18]) potentials are designated Φ_R and Φ_S with a corresponding interfacial potential difference $X_{SR} = \Phi_R - \Phi_S$. The arrows in the figure indicate that the stated difference of potential is added to the potential at the tail to obtain that at the head. Designations for the medium–air interfacial potential differences are, respectively, $X_{AR} = \Phi_R - \psi_R$ and $X_{AW} = \Phi_W - \psi_W$, and for the metal–electrolyte interfacial potential $X'_{WS} = \Phi_S - \Phi'_W$. Both Φ_W and Φ'_W are effective magnitudes representing a similar idealization as that noted above for ψ_W. The values of Φ_W and Φ'_W are in general not the same because of the ohmic potential drop created by the corrosion macrocell currents in the concrete, and of electrolyte composition gradients within the concrete that cause

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[1] In a dynamic condition E is not exactly constant due to interfacial polarization and ohmic drops caused by I_A, but its small value makes those effects correspondingly small, and they disappear anyway at the zeroing condition.