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Use of the time constant to detect corrosion speed in reinforced concrete structures

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Abstract

The relatively simple to measure 'time constant' is presented as an index for characterizing the level of corrosion experienced by steel in concrete. This communication, largely in the form of a technical note, explicitly illustrates that the time constant determined from electrochemical testing has significant merit for monitoring corrosion of steel in concrete, and appears to be insensitive to the area of electrode being probed. In this work, the time constant, κ, is determined following a galvanostatic excitation signal, revealing a good correlation between the value of κ and corrosion status across specimens of widely varying geometry. Although this notion has been suggested in the past, this work presents both a survey and consolidated review to indicate the utility of the parameter as an index to corrosion rate on-site.

Keywords: Concrete; Steel reinforced concrete; Corrosion; Monitoring; Time constant; Corrosion potential

1. Introduction

The accurate monitoring of corrosion processes occurring upon steel embedded in concrete has long been a challenge [1–4]. Tests conducted in the laboratory cannot easily be mimicked on-site in terms of both geometrical control of sections, and the ability to use advanced electrochemical methods owing to portability of equipment and test times [5]. Of principle interest however, is that the main difficulty in quantitative electrochemical methods applied to steel in concrete is the inability to accurately determine the surface area affected by the polarizing signal [6]. For steel in concrete, estimation of corrosion rate, i_{corr}, expressed as current density is nominally done via use of Stern–Geary equation [7], where

$$i_{\text{corr}} = \frac{B}{R_{\text{P}}} \tag{1}$$

where B is a constant (26–52 mV [8,9]) and R_{P} represents the (measured) polarization resistance per unit surface area of reinforcement (i.e. with the units of $\Omega\,\text{cm}^2$). Measuring R_{P} per unit of surface area is difficult owing to the highly asymmetric geometry of the reinforced sections [10], and the use of a counter electrode whose surface area is necessarily much smaller than that of the reinforced concrete structure to be tested [11].

As noted by Glass [1,12] and recently by others [2,13], corrosion rates are theoretically expected to be related to the time constant describing the corrosion potential fluctuation induced by the application of a small current; since the time constant is related to the polarization resistance through the interfacial capacitance. As the units of the time constant are seconds (s) and the practice of monitoring potentials is expected to be insensitive to steel area, the field determination of the time constant should provide quantitative information regarding the 'speed' at which corrosion is proceeding [14]. The term 'speed' is used since we are not

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evaluating corrosion rate, but an area independent index directly proportional to corrosion rate. Although known theoretically for some time, the utility of the time constant alone has not formed the basis of any dedicated studies. We attempt to experimentally show that the time constant is indeed useful for comparing the level of corrosion being experienced across several parts of a structure that vary in geometry (e.g. a bridge and all its elements). This is done by presenting laboratory and field data, together with a review of prior works that have permitted for evaluation and presentation of an accurate time constant. As a result, this may lead to tentative criteria for use of the time constant as a routine monitoring tool, which does not presently exist in the field. We do not suggest the use of the time constant as a replacement to R_P measurements for determination of precise corrosion rate; instead we show the merit of using the technique illustrated upon various case studies of widely varying, and ultimately unknown, geometry. Furthermore, changes in the time constant over a period of time should provide information regarding deterioration at a particular location, or conversely, the efficacy of any remedial treatments should they be required.

1.1. Evaluation of the time constant

Galvanostatically (viz. current) induced potential–time transients are analyzed in this instance, since they are easier to resolve than those obtained potentiostatically [15].

A typical representation of the data associated with such a test may be seen in Fig. 1. Application of a square pulse of current to the reinforcing steel leads to a charging and discharging transient of potential, together with an ohmic contribution (denoted as $\Delta I \cdot R_\Omega$). This response is best interpreted by the equivalent circuit seen in Fig. 2; which defines a system represented by a non-ideal interfacial capacitance (C_{NI}) associated with the polarization resistance (R_P), and in series with an ohmic/electrolyte resistance (R_Ω).

During the application of a current step (ΔI) to the system depicted in Fig. 2, the ensuing potential–time transient ($\Delta E(t)$) may be given as [2]

$$\Delta E(t) = \Delta I \cdot R_\Omega + \Delta I \cdot R_P(1 - \exp(-(t/\kappa)^\beta)) \quad 0 < \beta \leqslant 1 \tag{2}$$

where $\Delta E(t)$ is the potential shift with time, ΔI the applied current, R_Ω the electrolyte/concrete resistance, R_P the polarization resistance, t the time, C_{NI} the non-ideal interfacial capacitance, and β is the non-ideality exponent. A so-called non-ideal capacitance is used to incorporate a provision that the capacitance may be non-Debye in its response (i.e. behaves is a non-exponential manner owing to both geometrical and current distribution heterogeneities [2,16,17]).

Given that the ohmic component, $\Delta I \cdot R_\Omega$, of the potential response may be subtracted [2,6], as seen visually in Fig. 1, Eq. (2) may be modified for investigation of the charging due to an applied current, to yield,

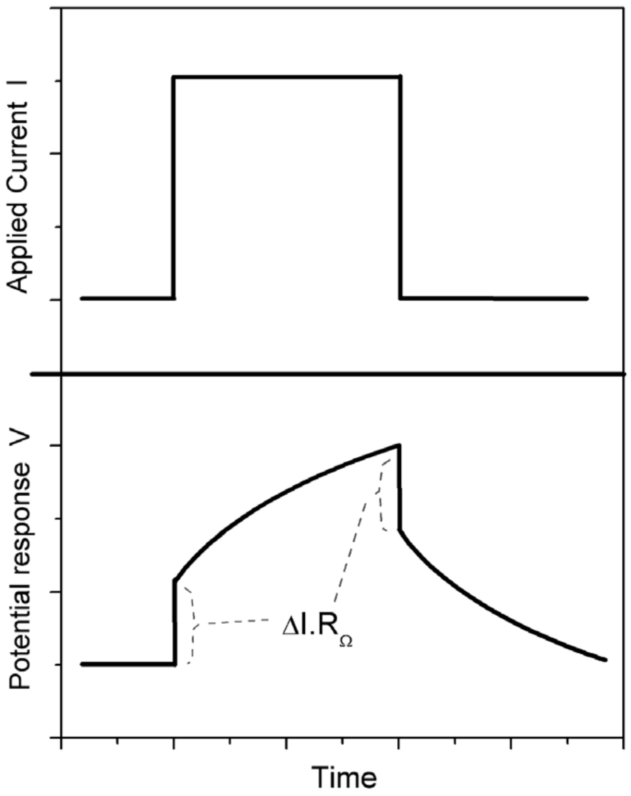

Fig. 1. Idealized schematic showing the principals of the galvanostatic pulse method. A square wave of current is applied to the steel and a transient response ensues, incorporating a charging transient (when current is ON) and a discharging transient (when current is OFF, i.e. in open-circuit conditions).

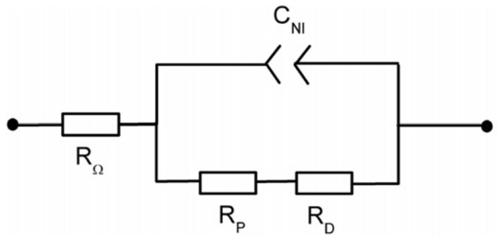

Fig. 2. Equivalent circuit analog used to represent electrochemical response of steel in concrete. R_Ω represents the concrete resistance, R_P the polarization resistance and C_{NI} the interfacial capacitance. In this figure, the element R_D has been included to indicate where an additional resistance term would be placed if the influence of diffusion/mass-transport was prevalent; this is assumed not to be the case in this work such that $R_D = 0$.

$$\Delta E(t)_{\text{charge}} = P1 - \{P1(\exp[-(t/P2)^\beta])\} \quad 0 < \beta \leqslant 1 \tag{3}$$

where $P1 = (\Delta I \cdot R_P)$ and $P2 = (R_P \cdot C_{NI})$. Alternatively for discharging (i.e. the potential decay following applied current) we may use [2]:

$$\Delta E(t)_{\text{discharge}} = P1 \exp[-((t + \varpi)/P2)^\beta] \quad 0 < \beta \leqslant 1 \tag{4}$$

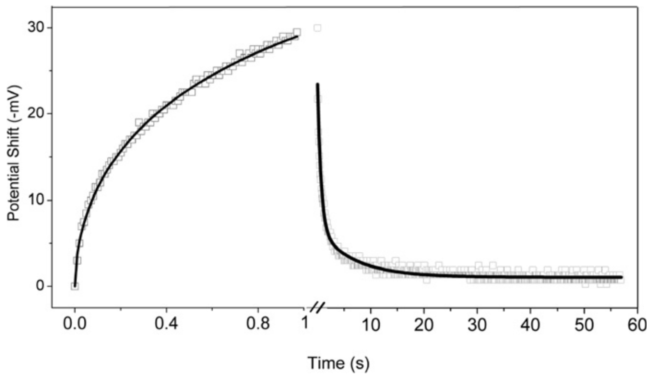

Fig. 3. Potential shift in response to galvanostatic pulse (i.e. square wave of fixed current) for an actively corroding reinforced concrete prism. Actual data for charging and discharging corrected for ohmic contribution (π) and presented along with calculated fit (—) according to Eqs. (3) and (4).

where ϖ is a time shift parameter [2], such that the expression is not confined to perceive the potential following current interruption as the maximum obtainable potential shift, which would occur as $t_{(\Delta I)} \to \infty$.

Iterative curve fitting of Eq. (3) and/or (4) to actual data yields values for $P1$, $P2$ and β; such a fit is shown in Fig. 3.

These equations are valid in the absence of diffusion effects, shown to be a largely valid assumption when small and short polarizations are used [2,18], viz. applied $Q < 100\ \mu\text{C/cm}^2$, where $Q = It$. In the case described above, the time constant of the system is defined as

$$\kappa = R_P C_{NI} \tag{5}$$

where κ represents the time constant of a process which is non-exponential [19]; usually the case for the electrochemical response of steel in concrete [20]. It is this fluctuation, more specifically non-ideality, in the potential–time transient behavior that can frustrate extraction of the time constant [12] when using the 37% decay criterion [6,21]. Therefore κ may be considered a dispersed time constant representing a distribution of charging/relaxation times, centered about a most probable value [19,22]. The magnitude of this level of disparity from the most probable value can be estimated via the value of β. The exponent β characterizes the non-ideality of the process; $\beta = 1$ corresponds to exponential behavior, and $0 < \beta < 1$ corresponds to a 'stretched' exponential (which may correspond to non-ideal capacitance). Therefore an accurate κ value can be directly evaluated from the fit to Eq. (3) or (4) and corresponds to the fitting parameter denoted as $P2$. In this work we use the above-described method for determination for determination of κ. We acknowledge that there are alternative approaches recently summarized in [23], including modifications to expressions which accommodate situations when diffusion may influence the potential response of the steel [21]. All approaches are equally valid and fundamentally linked, hence the selection of a particular procedure or expression is not necessarily critical provided κ can be accurately determined.

The assumption that significant diffusion effects are avoided may be considered appropriate, since the time constant can still be evaluated in the absence of a steady state response, hence allowing for the use of very rapid polarizations (which at the lower limit may correspond to those of coulostatic testing) and the ability to analyze the discharging transient, which is measured in open-circuit conditions. Furthermore, the ability to yield results in the absence of steady state is not possible for more traditional methods such as Linear Polarization Resistance.

Consequently in the absence of significant diffusion effects and neglecting any reactions other than the corrosion reaction, κ may be used as an index of the corrosion status of reinforced concrete. In this paper we present the results of κ for samples of various corrosion activities and geometry.

2. Experimental

A variable current generator connected in series with a current interrupter was used to produce the galvanostatic pulses. Current was passed between the counter (Ti-based) and working electrodes (reinforcing steel) such that the steel was polarized cathodically. The potential response of the reinforcement was monitored via an Ag/AgCl (sat.) reference electrode, with readings logged digitally. The extent of polarization is defined by the current stimulus. Polarization is therefore not strictly controlled, but maintained within a window of 10–30 mV from E_{corr}. To do this, current, I, stimuli used here are between 1 and 100 μA, in order to generate a potential transient of sufficient clarity in the target potential range and with the requirement that charged passed, Q, be less than 100 μC to avoid electrode perturbation (hence small current stimuli may be sustained for longer periods that larger ones). Such aspects were discussed in [17]. Curve fitting for determination of κ was carried out using a commercial program. A typical schematic of such a three-electrode setup for electrochemical testing of steel in concrete may be seen in Fig. 4. In this case Fig. 4 represents our laboratory specimens as described in detail in [29]. We see that the reinforcing steel had its ends coated in Epirez® a distance into the concrete equal to the concrete cover depth, in order to

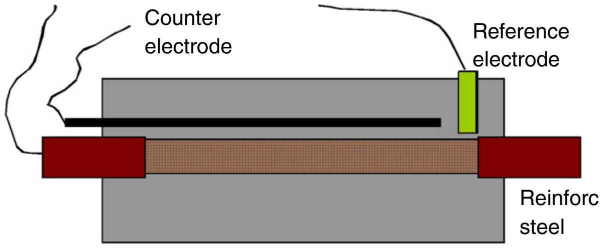

Fig. 4. Schematic of reinforced concrete specimen arranged as a three-electrode electrochemical cell including a counter electrode, reference electrode and working electrode (viz. reinforcing steel). Reinforcing steel ends coated in Epirez®.

Table 1
Properties of reinforced concrete samples tested in this study

Sample name	Housed at	Steel surface area (cm^2)	Counter electrode size (cm^2)	Concrete mix C/W/S/A[a]	Described in reference
Prism	Monash University, Melbourne, Australia	100	100	4/2/8/8	[2]
Cylinder	Heriot-Watt University, Edinburgh, Scotland	25	5	4/2/–/10	[29]
Slab	CENIM, Madrid, Spain	Semi-infinite	7	4/2/–/12	[6]
Jetty	Crib Point, Victoria, Australia	Unknown	5	Shotcrete repairs[b]	[30]

[a] C = ordinary portland cement, W = water, S = sand, A = coarse aggregate (5 mm).

[b] W/C ratio < 0.4, no coarse aggregate (Shotcrete supplied by MBT Australia).

prevent crevice corrosion, to prevent accelerated ingress of aggressive species (i.e. chlorides) and also to allow accurate definition of steel/electrode area.

In order to test the hypothesis that the value of κ can be a worthy index of corrosion status independent of electrode area, various reinforced concrete specimens were studied in this work. The specimens used are described in Table 1, and were exposed to various environments within the laboratory in order to stimulate different degrees of corrosion; these environments included: ponding in brine (0.6 M NaCl), intermittent wetting with brine, wetting with water and leaving specimens to dry out. One set of tests was also conducted 'on-site' upon a jetty (marine structure) continually exposed to the natural environment. The jetty was located in Westernport Bay (Crib Point), Victoria, Australia. The elements investigated in this study include the soffits of the jetty deck and the top of pile muffs; both elements are in the 'splash zone' approximately 1 m above the maximum height of the tidal zone.

3. Results and discussion

3.1. Laboratory evaluations and testing

For the prism samples (see Table 1 and Fig. 4), the logarithm of the measured κ values were plotted versus E_{corr} (Fig. 5), the significance of such a form of data representation is discussed in greater detail in [24], where the value of E_{corr} is commonly used as a qualitative criterion for corrosion risk [25]. Typically, the more negative the value of E_{corr}, the greater the risk that corrosion processes are occurring upon the steel surface [26]. We note that the E_{corr} value is only qualitative not representing corrosion kinetics but corrosion 'risk', whilst prone to various forms of error [14,27], however we acknowledge this and emphasize in this specific example that it is being used as a second parameter of which results may be plotted against. E_{corr} has been previously shown to be very useful in this regard [24].

A distinct relationship is observed between κ and E_{corr}, with κ values increasing as E_{corr} increases and as prisms tend to values indicating increased nobility. The type of exposure experienced by the prism samples (for the 24 months prior to reported testing) has been included in Fig. 5, in order to show that κ is indeed related to the corrosion condition of the samples tested. Fig. 5 also includes reference to specific data points (denoted as A–E) of which their complete fitting parameters have been given in Table 2, which shows rather clearly that the value of κ correlates with associated polarization resistance, R_P, value. The theoretical basis as to why a logarithmic relationship appears to exist between E_{corr} and κ has not been studied, however it has been previously shown that E_{corr} and R_P display a logarithmic relationship [24] arising as a result of the multitude of physical factors that link the two parameters fundamentally, such as Tafel slopes, which may carry a logarithmic dependence.

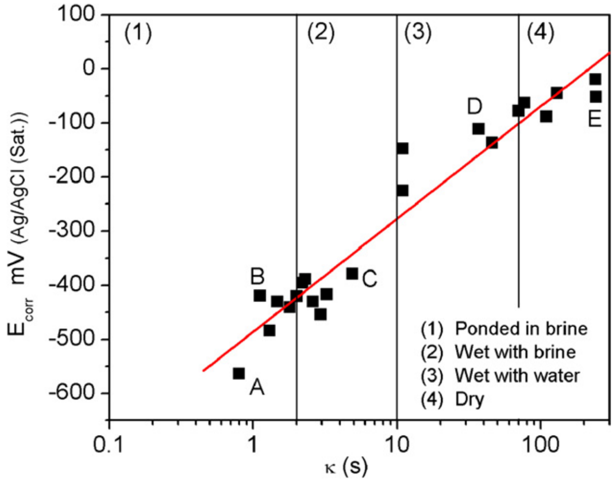

Fig. 5. Corrosion potential (E_{corr}) versus the logarithm of the time constant (κ) for reinforced concrete prisms defined in Table 1. The letters A–E denote individual data points for which the full range of evaluated parameters are given in Table 2.

Table 2
Electrochemical parameters evaluated for various reinforced concrete prism samples

Test	κ (s)	R_P (kΩ cm^2)	C_{NI} (μF/cm^2)	β
A	0.8	2.8	290	0.57
B	1.1	4.0	275	0.58
C	4.9	24.5	200	0.62
D	37.1	1160	32	0.92
E	244	7870	31	0.95

The letters A–E correspond to specific individual tests as denoted in Fig. 5.

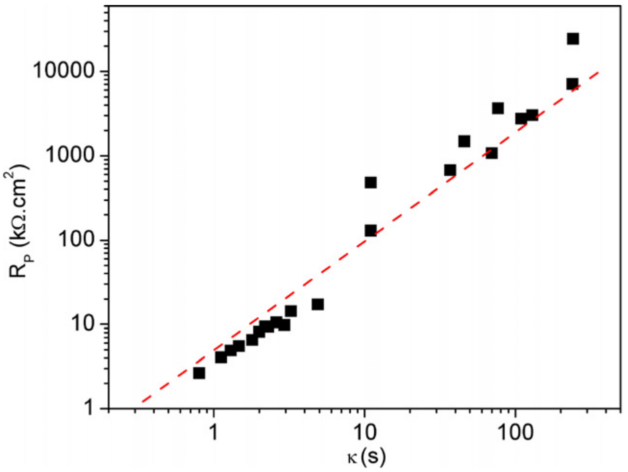

Fig. 6. Polarization resistance (R_P) versus the time constant (κ) for reinforced concrete prisms. Dataset corresponds to that of Fig. 5.

More importantly however, Fig. 6 reveals within close confidence that κ maintains a linear relationship with R_P. In this case we emphasize that we could get an accurate value for R_P via the iterative fitting of Eqs. (3) and (4), since we deliberately know electrode area our laboratory samples [2]. This relationship seen in Fig. 6 is of particular significance to this study. If such a relationship is reserved for κ and R_P, then this suggests that the value of κ is predominantly dominated by the value of R_P, rather than C_{NI} (cf. Eq. (5)). Although not explicitly shown in this form before, this observation is not entirely surprising; since previous laboratory experiments have shown that the value of the interfacial capacitance for steel in concrete varies over a rather narrow window (e.g. between about 30 and 300 μF/cm^2) for samples ranging from passive to actively corroding [17,28]. Whereas under identical circumstances, values of R_P may vary over many orders of magnitude [27] depending on the level of corrosion being experienced by the steel. The above is also evident from inspection of the results given in Fig. 6, where a variation in R_P over four orders of magnitude, corresponds to a variation in κ over 3 orders of magnitude. Thus, at this point we do note that even though C_{NI} may vary within an order of magnitude for steel in concrete as the transition from passive to active condition occurs; we reinstate that the goal of this paper is to introduce κ as a geometry independent index to corrosion, since variations in κ predominantly correspond to variations in the actual rate of corrosion (as judged by R_P). This is distinctly seen in Fig. 6 where R_P was accurately determined since the effective electrode area was known for the prism samples; whilst further examples are also presented in the following section. Consequently, smaller time constants are resolved in cases where corrosion currents are higher, since the time constant drops, concomitant with a fall in the associated R_P.

We do not advocate the use of κ as a means for accurate determining R_P by assuming a typical value of C_{NI}, however the utility of κ itself as an index to corrosion is overwhelmingly apparent.

3.2. Evaluation and assessment of κ in practice

In order to investigate the utility of κ as a geometry independent index to corrosion activity, which has not been systematically done previously, the results from a number of samples with widely varying properties (Table 1) are given in Fig. 7.

Fig. 7 shows that in spite of the various sample types tested, the results tend to fit a simple relationship, within an envelope allowing for some disparity in results. This disparity is expected to a degree, and could be due to a number of factors such as; moisture content, concrete composition, dispersion of anodic/cathodic sites upon the steel surface, and also due to the sensitivity of measured potentials to the thickness of the concrete cover which varies from sample to sample. Again, we emphasize that for illustrative purposes alone we plotted κ versus E_{corr}, since in this case geometry is deliberately treated as unknown and hence there is no attempt to quantify R_P. However for analysis purposes, we suggest the use of κ alone, since this gives a deeper insight than that of corrosion risk which is offered by potential measurements (as per ASTM-C876 [26]). For example, large κ values may be concomitant with very negative E_{corr} values for submerged structures (owing to anaerobic conditions), with the reverse being true in cases where carbonation is occurring (i.e. small κ and less negative E_{corr}); furthermore chemical treatments such as corrosion inhibitors or silane treatments may also led to misleading shifts in E_{corr} that will not impact κ. Hence in such cases κ will be useful, whereas E_{corr} may not.

Nevertheless, the data correlate well allowing one to suggest that the value of κ may be considered independent of the geometry of the sample being tested, with the presentation of results in the manner seen in Fig. 7 lending strong support to the notion that the value of is a useful index related to the rate of corrosion, which we further attempt to highlight further below via Fig. 8.

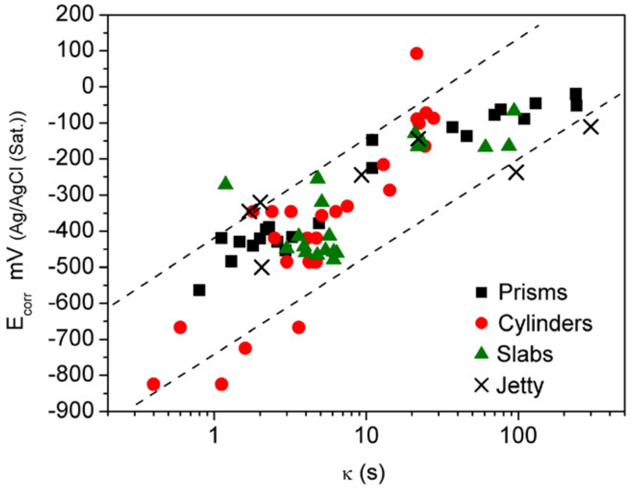

Fig. 7. Corrosion potential (E_{corr}) versus the logarithm of the time constant (κ) for reinforced concrete samples of various geometries as described in Table 1.

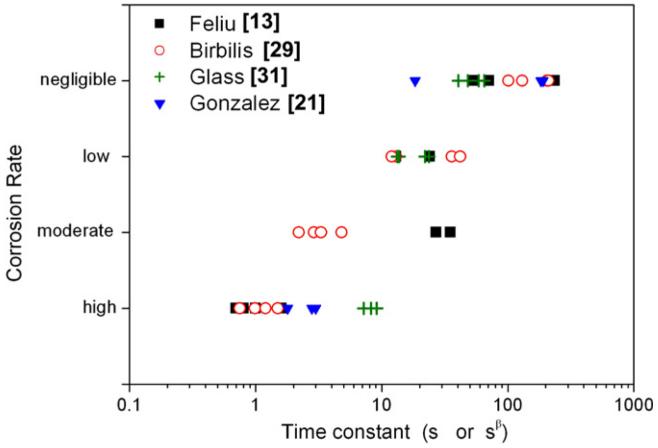

Fig. 8. Time constant versus corrosion rate. Data sampled from for literature according to independent tests in [13,21,29,31]. In this case sample geometries varied, but were known in each case, allowing for accurate electrochemical assessment.

In a review of prior studies in the literature, although there is only very limited data available, those applying the electrochemical approaches refereed to herein for accurate determination of the corrosion related parameters (as defined in part by the analog in Fig. 2) have also tended to present the associated time constant data. Although these tests have been conducted independently, there seems to be generally a very good agreement with the data collected on a number of widely varying samples with various concrete mixtures, exposure regimes and cover depths. This data is presented in Fig. 8 and has been collated incorporating data from various sources in the literature, whilst it may be considered analogous to Fig. 6 but for samples of varying geometry. In order to present the data, results have been grouped according to the corrosion state of the sample which has been determined independently and varies from very active (high corrosion rate) to passive (negligible corrosion rate). In Fig. 8, samples defined as high posses an $R_P < 10\ \mathrm{k\Omega\,cm^2}$, moderate possess $10\ \mathrm{k\Omega\,cm^2} < R_P < 100\ \mathrm{k\Omega\,cm^2}$, low possess $100\ \mathrm{k\Omega\,cm^2} < R_P < 1000\ \mathrm{k\Omega\,cm^2}$, and negligible posses moderate possess $R_P > 1000\ \mathrm{k\Omega\,cm^2}$. What is observed, is that within a range of scatter, the time constant nominally increases by up to three orders of magnitude as corrosion rates range from passive to active (negligible to high). The key point to note is that these results represent vastly varying cell geometries (at times unknown) and concrete chemistries, whilst results were collected and presented independently, by various authors in the literature.

3.3. General

The results and discussion presented above may therefore lead to the development of a broad tentative criteria for condition assessment, in terms of actual corrosion kinetics, of reinforced concrete structures based on the value of the time constant. An example of this is seen in Table 3, representing a tentative criterion based on empirical data in this study and in the literature. We note and emphasize that the interpretation offered in Table 3 corresponds very well with the study of Feliu et al. [13], who recently lists a table of sample history (viz. whether or not reinforced concrete samples were chloride containing, wet, etc.) along with E_{corr}, R_P and time constant values. The criteria as defined herein is more powerful than E_{corr}, representing kinetic information whilst being less open to interpretation (viz. shifts that may be misleading as those observed in E_{corr} when pH alters as a result of either concrete carbonation or excessive corrosion). Clearly however, further investigations into benchmarking κ are required in the future.

Table 3
Value of dispersed time constant (κ) versus corrosion speed, based upon empirical data discussed in this study

κ	Corrosion speed
<5	High
5–10	Moderate
10–40	Low
>40	Negligible

It ought to be emphasized at this point that the experiments mentioned herein are not particularly arduous, whilst the associated equipment is by no means complex. These methods adopt the use of a galvanostatic signal, i.e. a relatively simple and cheap current source, along with a method for logging voltage (i.e. the potential) of the working electrode. One associated benefit is the portability of such equipment, and the ability to integrate automation of the monitoring and the associated data analysis. As infrastructures inexorably age and as the sophistication of reinforced concrete structures increases to exploit slender design and more modern concrete mixtures (e.g. low W/C ratio or the use of admixtures, chemical or natural), the associated condition assessment of reinforcement will demand a more accurate treatise. If kinetic information regarding corrosion 'speed', as opposed to a qualitative and ambiguous measure of 'risk', may be gained within an apposite confidence limit without the need for knowledge of steel area, then (in cases where area confinement is not readily possible) this is advantageous. We indubitably suggest that the collection of κ be carried out in preference to potential measurements, whilst possibly extending this notion to collection of time constant maps for condition assessment over large elements of a structure.

4. Conclusions

- It was shown how a time constant, κ, can be determined via fitting of potential transient data.
- The value of κ correlates with the level of corrosion being experienced by steel in concrete. This was determined theoretically based on an electrical analog of the steel–concrete system, and empirically based on complementary R_P measurements and knowledge of sample exposure.

- κ values were shown to be largely independent of the geometry of the sample under examination, making it particularly useful in cases where area confinement of the electrical signal is difficult or impossible, and an evaluation of corrosion "speed" is required. This is nominally the case on-site whereby area confinement is not readily possible, and the use of E_{corr} alone may not offer any unique information with respect to the rate of change of protection or deterioration processes.
- This method has been utilized on-site to determine corrosion behavior of certain elements of a field structure, and it was shown that results obtained correlate with those of the laboratory samples, lying within a broad tentative criteria developed for interpretation of κ values.

Acknowledgements

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