

THE INFLUENCE OF TEMPERATURE ON THE CORROSION OF STEEL IN CONCRETE

F. PRUCKNER

Institute of Physical Chemistry, University of Vienna, Austria

Abstract

Corrosion rate measurements are already established to determine the state of steel in concrete. Various criteria have been suggested in different standards to assess the corrosion condition of the embedded reinforcement bars in concrete constructions. The recorded corrosion rates, however, are affected by several environmental factors. The present study focus on the effect of temperature across 0° - 50°C on the corrosion rate of mild steel in Ordinary Portland Cement (OPC) concrete containing chloride as an admixture

Keywords: Temperature, corrosion of reinforcement, permeability.

1. Introduction

Corrosion of steel reinforcement in concrete is a major cause of failure in concrete constructions. The enormous amount of money required for repair measures results in need of determining and limiting the zones that require maintenance and restoration of the damaged sections.

An efficient and reliable approach for solving this problem is based on the monitoring of the state of corrosion activity of the reinforcement using electrochemical methods. Common electrochemical non-destructive tests are electrochemical impedance (EIS), linear polarisation resistance measurements (LPR), Tafel- and galvanostatic pulse measurements.

Using those methods it is possible to determine corrosion current densities who are direct proportional to corrosion rates of the in concrete embedded reinforcement steel.

The corrosion rate of steel in concrete depends upon several factors such as humidity, porosity, cement type, cover thickness and mortar resistivity. One important factor regarding corrosion rate is the temperature. The corrosion reaction needs according to

the kinetic theory an activation energy (E_A) which in ideal case can be determined by applying the Arrhenius relation of chemical kinetics to electrochemical kinetics [1]:

$$i_{\text{corr}} = A \cdot \exp\left[-\frac{E_A}{RT}\right] \quad (1)$$

Determining the i_{corr} from Tafel measurements at varied temperatures and plotting $\log(i_{\text{corr}})$ against $1/T$ delivers the quoted value from the slope. From the above equation (1) it is easily understood that a higher temperatures will result in a higher corrosion reaction speed for a given energy of activation.

This work was undertaken to examine the electrochemical behaviour of iron in OPC concrete with chloride as additive examining particularly the effect of temperature. Three different electrochemical techniques, namely EIS-, LPR- and Tafel measurements were used for this purpose.

The temperature dependence of other important factors with respect to rebar corrosion like the concrete resistivity were also investigated in this work.

2. Experimental

2.1. Materials

Concrete prisms of $4.5 \times 8 \times 20$ cm size and $w/c = 0.5$ and $c/ag = 1/3$ were cast from ordinary Portland cement (OPC). The maximum aggregate size used was 9mm. Reinforcing steel bars (ordinary building steel) with a diameter of 8 mm were axially positioned within the prisms giving a minimum of 2 cm cover of concrete. 0 or 3% Cl as NaCl by weight of cement was added to the mix. The concrete/air/steel interface was coated with epoxy resin to avoid any side effects. Graphite rods in parallel to the steel bar were embedded into the concrete samples serving as reference electrodes. As counter electrode an embedded Ti-mesh was used. The specimens were cured at 90% RH and ambient room temperature for 28 days, followed by one year at 80% RH and ambient room temperature. The samples were put into a polyethylene box at either 80% RH or totally submerged in water. Temperature was controlled in a thermostatic water bath and increased in 5°C steps with a hold of > 2 hours (until sample temperature was constant) before measurements were carried out.

2.2. Tafel measurements

For an activation controlled corrosion process with one oxidation process (e.g., metal dissolution) and one reduction reaction, the Tafel equation is:

$$i_{\text{app}} = i_0 \cdot \left(10^{\frac{\pi}{b_c}} - 10^{\frac{\pi}{b_a}} \right) \quad \begin{array}{l} i_{\text{app}} \dots \text{apparent current} \\ \pi \dots \text{polarisation} \\ b_a, b_c \dots \text{anodic, cathodic Tafel constant} \\ i_0 \dots \text{corrosion current} \end{array} \quad (2)$$

The measurements were carried out as described elsewhere [2]. The corrosion current densities at the corrosion potentials were calculated using equation (2).

2.3. LPR measurements

Measurements were performed as described earlier [2]. The R_p (polarisation resistance) values were calculated using Stern's equation (3). For the Stern-Geary constant B a value of 26 mV for active and 52 mV for passive steel is reported in the literature [3].

$$i_{\text{corr}} = \frac{B}{R_p}, \quad \frac{1}{R_p} = \left[\frac{di}{dE} \right]_{E_{\text{corr}}} \quad B = \frac{b_a \cdot b_c}{2.3 \cdot (b_a + b_c)} \quad (3)$$

(Stern-Geary constant)

2.4. Impedance measurements

Impedance measurements were performed on a FFT-based system. Data manipulation was done using Boukamp's impedance software [4]. A peak to peak amplitude of 20 mV in the frequency range from 25 mHz to 5.125 kHz was applied and the response evaluated in each run. Detailed information about the measurement procedure is reported elsewhere [2].

3 Results and discussion

On one specific sample (3% chloride/cement weight, 80% RH) the temperature dependence of the investigated parameters is discussed below. Results on other samples are presented in a table at the end of this paragraph.

The effect of temperature on the corrosion current density calculated from Tafel measurements in the investigated temperature range is presented in Fig. 1. The corrosion rate increases with temperature showing a linear relationship between the logarithm of i_{corr} and the reciprocal temperature (electrochemical Arrhenius plot). The activation energy for the corrosion reaction according to equation (1) is 29 kJ/mol which is a reasonable value for an activation controlled process. Other authors only found 10 kJ/mol for the activation energy for corroding steel in concrete [5].

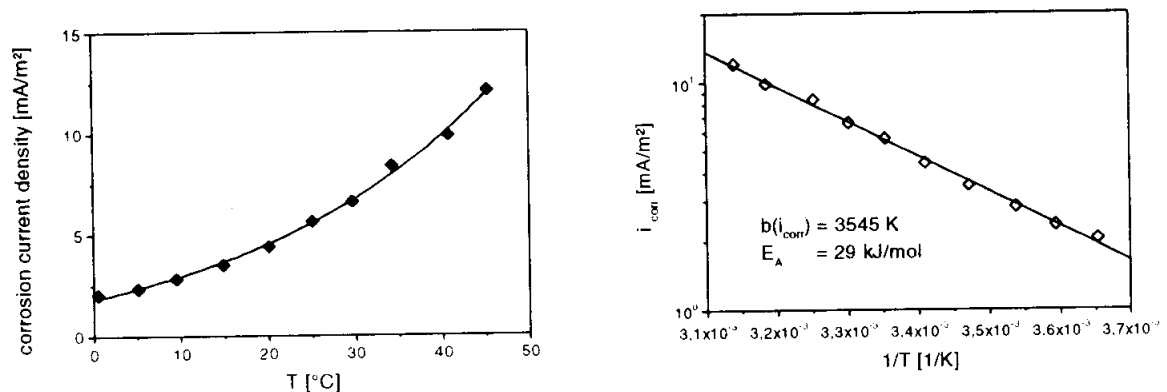


Fig. 1. Corrosion current densities on a sample containing 3% chloride of cement weight at RH = 80% as a function of temperature.

In Fig. 2. the dependence of the polarisation resistance R_p (derived from LPR measurements) and the charge transfer resistance R_{ct} (derived from EIS measurements) are shown.

Tafel-, LPR- and EIS-measurements deliver comparable values for the corrosion rate. Fig. 3. shows the experimental Stern-Geary constant B using equation (2) where i_{corr} values from Tafel measurements and R_p values from LPR measurements were taken. The same procedure was performed using R_{ct} from EIS measurements. The experimental values for B are in good agreement with the in the literature reported value for an active corroding system (26 mV) [3]. A slight dependence on Temperature is expectable for B since the Tafel constants b_a and b_c are dependent on temperature, but the experimental error is obviously too high to show this clearly.

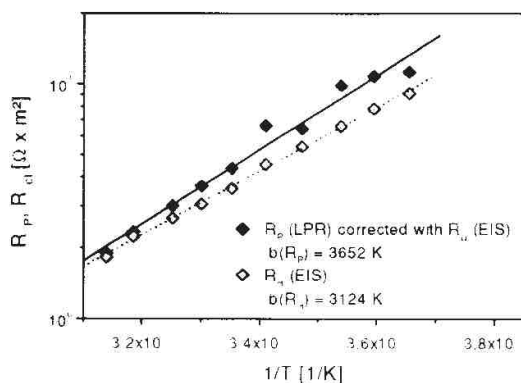


Fig 2. R_p and R_{ct} as a function of temperature.

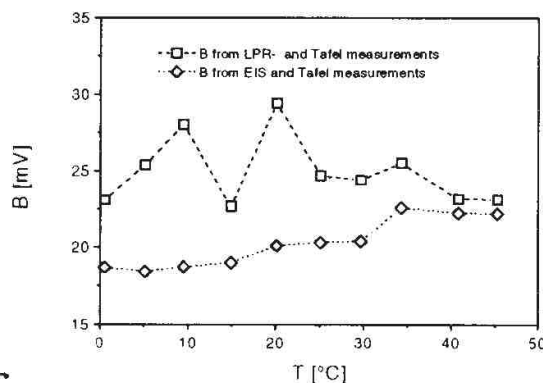


Fig. 3. experimental values for the Stern-Geary constant B .

For the evaluation of the impedance diagrams the in Fig. 4. proposed equivalent circuit was taken. The charge transfer resistance, R_{ct} , corresponds to the resistance in the second RC-element (low frequency part in an impedance diagram), while the first RC-element high frequency part) represents the dielectric film effect which is likely to be solid calcium hydroxide precipitated as a thin film on the steel[6]. A CPE (constant phase element) means a non ideal capacitance.

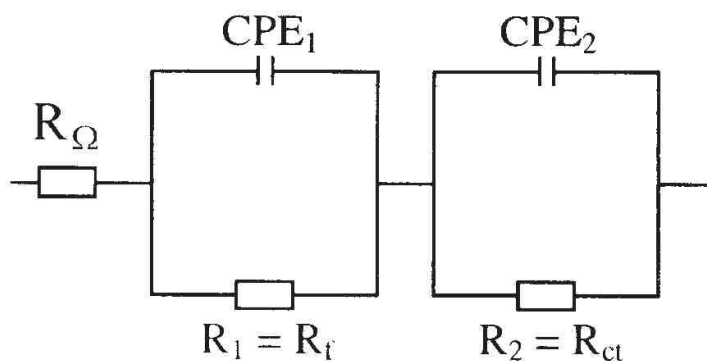


Fig. 4. Equivalent circuit used for evaluation of the impedance spectra of rebars in concrete.

CPE: constant phase element, $R_Ω$: ohmic (concrete) resistance, R_f : $\text{Ca}(\text{OH})_2$ -film resistance (observed in the HF-range), R_{ct} : charge transfer resistance

Fig. 5. shows the impedance elements R_{Ω} (concrete resistance) R_f ($\text{Ca}(\text{OH})_2$ -film resistance) and R_{ct} (charge transfer resistance) as a function of temperature. All these elements are dependent on temperature following the general formula

$$R_i(T) = C_i \cdot \exp\left(\frac{b(R_i)}{T}\right) \quad (4)$$

where $R_i(T)$ is the impedance element for the given temperature, C_i a constant with the unit of a resistance and $b(R_i)$ a constant with the unit [K].

The value $b(R_{\Omega})$ (concrete resistance) is 3224 K in the discussed case. Values for $b(R_{\Omega})$ between 2100 and 5500 K are reported in the literature [7].

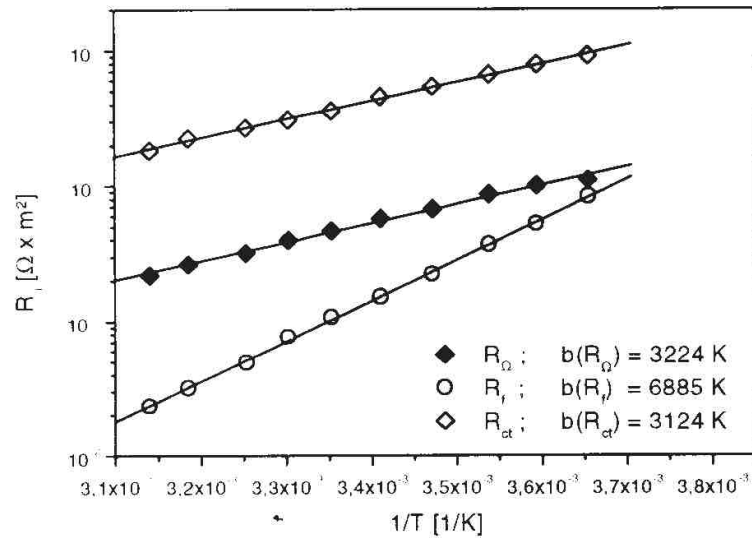


Fig. 5. Temperature dependence of the impedance elements R_{Ω} (concrete resistance), R_f (film resistance) and R_{ct} (charge transfer resistance).

The influence of the temperature on the concrete resistance can at least qualitatively be explained using the electrochemical theory for ion conductivity of an electrolyte.

The conductivity of an electrolyte Λ is described by the formula below:

$$\Lambda = \sum_i |z_i| \cdot c_i \cdot u_i \cdot F, \quad \text{where} \quad u_i = \frac{|z_i| \cdot e_0}{6 \cdot \pi \cdot \eta \cdot r_i} \quad (5)$$

z_i is the charge c_i the concentration u_i the mobility of the ion i . e_0 means the elementary charge and η the solutions viscosity. The solutions viscosity η in the above equation (5) is the only term (in ideal case) which is temperature dependent. This dependency can be described by equation (6)

$$\eta(T) = C \cdot \exp\left(\frac{E_{A_{\text{visc}}}}{R \cdot T}\right) \quad (6)$$

where C is a constant in Pa·s and $E_{A_{\text{visc}}}$ the activation energy for the viscous flow. This would explain the exponential relationship between R_{Ω} and $1/T$. Fig. 6. shows the temperature dependence of the viscosity of water in the range between 0 - 50°C [8]. Applying equation (6) an activation energy for the viscous flow of 17 kJ/mol is found. $b(R_{\Omega})$ therefor will be 2072 K. The discrepancy in the values derived from concrete resistance measurements and derived from the literature values of viscosity is obviously a result of the use of the *ideal* theory for electrolytic conductivity.

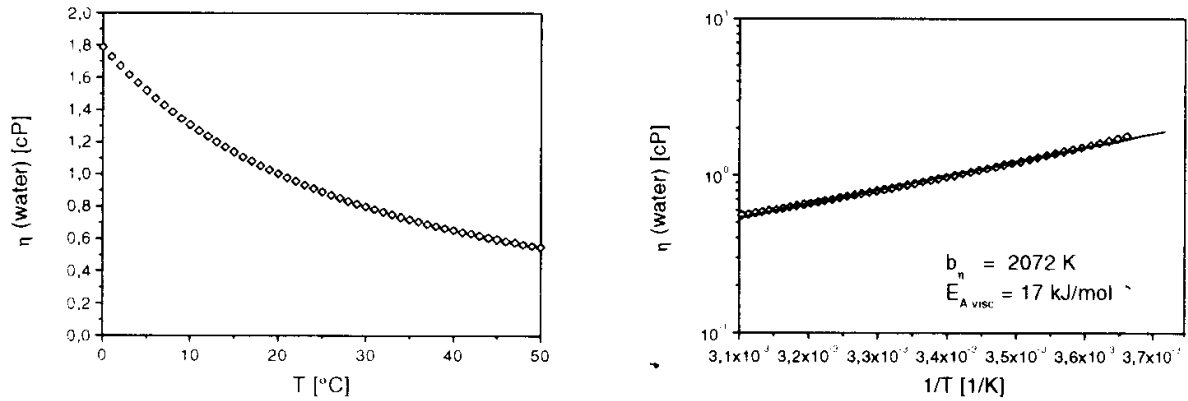


Fig. 6. Temperature dependence of viscosity of water in the range between 0 - 50°C, (1cP = 0.001 Pa·s)

It is possible to determine diffusion coefficients for chlorides in concrete by simple resistance measurements [9] according to the Nernst-Einstein equation (7).

$$\frac{1}{R_{\Omega}} = \sum_i \frac{z_i^2 \cdot F^2 \cdot D_i}{R \cdot T} \quad D_i \dots\dots \text{Diffusion coefficient for the ion } i \quad (7)$$

Taking a value of 3500 K for $b(R_{\Omega})$ the Diffusion coefficient D increases by more than a factor of 5 between 10 and 50°C.

Therefore, it can be concluded that the permeability of concrete for aggressive ions like chlorides becomes higher with increasing temperature.

The temperature dependence of the capacitive elements CPE1 (representing the capacitive effect of the $\text{Ca}(\text{OH})_2$ film precipitated on the steel and CPE2 (representing the double layer capacitance) was also investigated, but their behaviour is not clearly understood. While CPE1 is falling with temperature CPE2 is increasing at the same time which is shown in Fig. 7.

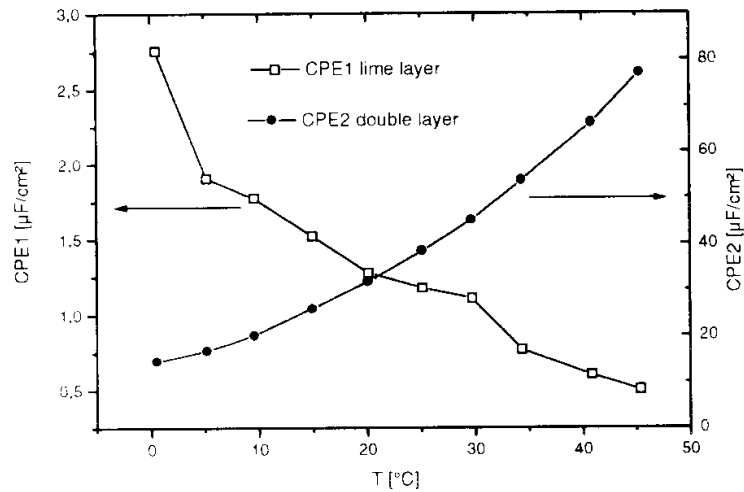


Fig. 7. Temperature dependence of the impedance elements CPE1 (lime layer) and CPE2 (double layer)-

An explanation for the temperature dependence of the capacitances would be very speculative and was therefore not undertaken in this work.

Investigations as described above, have been performed for various samples at two different ambient relative humidities. The final results are shown in table 1.

sample	$b(i_{corr})$ (Tafel) [K]	$b(R_p)$ (LPR) [K]	$b(R_{ct})$ (EIS) [K]	$b(R_{\Omega})$ (EIS) [K]	$b(R_f)$ (EIS) [K]	E_a (Tafel) [kJ/mol]	B (Tafel-LPR) [mV]	B (Tafel-EIS) [mV]
0% Cl ⁻ RH = 80%	1231	2574	1708	3392	6700	10	25.7	31.5
0% Cl ⁻ totally submerged	3667	3648		1525	3813	30	24.6	
3% Cl ⁻ RH = 80%	3549	3652	3124	3224	6885	29	24.9	20.4
3% Cl ⁻ totally submerged	3061	3624		3609	6060	25	24.3	

Table 1.: Parameters, describing the temperature dependence of i_{corr} , R_p , R_{Ω} , R_f and R_{ct} and the average value B for different samples and different relative humidities

Table 1. shows a reproducible value for B for active corroding steel close to the reported value. The reported value of B for passive samples could not be verified. The activation energy for the corrosion rate is about 25 - 30 kJ/mol which seems to be independent from other environmental parameters. The temperature dependence of the concrete resistivity was also comparable for most of the investigated cases and is in good agreement with reported values for $b(R_{\Omega})$.

For non-saturated samples, it can be confirmed that the corrosion process is controlled anodically due to high availability of oxygen [2], while for totally submerged concrete

the corrosion process is diffusion controlled. This is indicated by impedance measurements where for totally submerged samples only Warburg-like behaviour is observed in the low-frequency regime.

4. Conclusions

- Based on electrochemical measurements the corrosion rate of reinforcement in concrete is a function of temperature and *increases approximately by a factor of 2 for a raise in the temperature of 20°C. This has to be considered for judging the corrosiveness of climatic zones around the globe.*
- The concrete resistance falls with temperature. The observed behaviour can qualitatively be explained by the temperature dependence of the viscosity of water.
- The diffusion coefficient increases with temperature (by more than a factor 5 between 10 and 50°C) leading to an increased permeability of concrete for aggressive ions.
- The reported value for the Stern-Geary constant **B** for active corroding reinforcement steel was found to be about 26 mV, while for passive steel the value of 52 mV could not really be confirmed.
- The other impedance elements for the system steel in concrete are also temperature dependent, but a reasonable explanation for those dependencies cannot be given at this moment.

5. Acknowledgement

Financial support for this work by Coating Int. a/s, Norway is gratefully acknowledged.

6. References

1. Bockris, J. O'M (1979) *Quantum Electrochemistry*, Plenum Press, New York
2. Schwarz, W., Gerdes, A., Wittmann, F.H., Pruckner, F. and Nauer, G.E. (1996) Repassivating Effects induced by Cathodic Protection of Rebars in Concrete, *Fourth International Colloquium Materials Science and Restoration, Technische Akademie Esslingen*, Dec. 17th - 19th., 1457-1492
3. Andrade, C. and Gonzalez, J.A. (1978) Quantitative measurements of corrosion rate of reinforcing steels embedded in concrete using polarization resistance measurements *Werkstoffe und Korrosion*, Vol. 29, pp. 515-19.
4. Boukamp, B.A. (1993) Computer program *EQUIVALENT CIRCUIT v. 4.51*, University of Twente (NL)
5. Benjamin, S.E. and Sykes J.M. (1995) Effect of Mix Proportions on Corrosion of Swedish Iron in Ordinary Portland Cement Mortars at elevated Temperatures *The Arabian Journal for Science and Engineering*, Vol. 20, pp. 269-278

6. Wenger, F (1987) Etude de la corrosion de l'acier doux dans le béton par des méthodes électrochimiques Application au contrôle des ouvrages de génie civil, Thesis, published in *Metaux, Corrosion, Industrie*, Vols. 742, 745 and 746
7. Hunkeler, F. (1992) Untersuchungen zum kathodischen Korrosionsschutz von Stahlbeton im Tunnel San Bernadino *Schweizerische Gesellschaft für Korrosionsschutz*, Zürich
8. Lobo, V.M.M. and Quaresma J.L. (1989) *handbook of electrolyte solutions, Part B*, Elsevier Amsterdam - Oxford - New York - Tokyo
9. Andrade, C., Castellote, M., Cervigón, D. and Alonso, C. (1995) Chloride migration in concrete: theory and modelling
Intern. Zeitschr. Bauinstandsetzen, Vol. 1, pp. 485-507