



Local electrochemistry of reinforcement steel – Distribution of open circuit and pitting potentials on steels with different surface condition



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ABSTRACT

Local electrochemical measurements (open circuit potential (OCP), cathodic and anodic polarization curves, pitting potentials) were performed at random locations on 1 m long ribbed steel bars with different surface conditions. The results show that the local OCP values are statistically distributed. The standard deviation was found to be 45 mV for “as received” surface condition, decreasing to 10 mV only after prolonged immersion in sat. Ca(OH)₂. A model based on local variations of the reduction current density could explain the variations in local OCP and allowed predicting the overall global OCP of the long bars when completely immersed in solution.

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1. Introduction

Electrochemical methods such as half-cell potential measurements allow characterizing a system metal/electrolyte in a rapid and non-destructive way and monitoring changes over time [1–3]. The system under test is characterized by a single potential value E_{corr} , the so-called corrosion or open-circuit potential. The effect of small variations arising from the metal (e.g. composition, surface condition) and the electrolyte (e.g. pH, oxygen content) is typically taken into account by performing several replicate tests. In such an approach however important variables, especially variations of the surface conditions and thus spatial variation of the electrochemical behavior in a range smaller than the sample size are not detected as only mixed potentials, determined by all electrochemical reactions occurring on the sample, are measured. An important example documented in the literature [4–7] is the influence of sample size on the pitting potential. For stainless steel in acidic or neutral solutions [4,5], the pitting potential decreased with increasing sample size [4,5]. Correspondingly the survival probability (thus no occurrence of pitting) was higher for small sample size [6]. For ordinary

steel in alkaline, chloride containing solutions a decrease in pitting potential with increasing specimen size was found [7]. Similarly, increasing sample size (from 0.007 to 0.78 cm²) was reported to require lower chloride concentrations for occurrence of pitting corrosion of mild steel in alkaline solutions [8]. It is well established that pitting initiation is associated with inclusions or other imperfections [10,11], which both are statistically distributed features of the microstructure. The probability of finding such preferential initiation sites on a certain specimen increases with the size of the exposed surface area and consequently the scatter of pitting potentials decreases at larger sample size [5–9].

Similar to the pitting potential also the open-circuit potential of a system metal/electrolyte is expected to show a distribution due to surface inhomogeneity that may also be reflected by local differences in the anodic or cathodic polarization behavior (exchange current densities). Spatial variations were typically studied mainly with the scope to detect localized corrosion phenomena or material inhomogeneities; variations in the OCP only might have been recorded but not reported. The different techniques for studying local electrochemistry were reviewed [12,13] and are briefly presented below.

1.1. Scanning measuring techniques

Moving a very small reference electrode over a large sample surface immersed in an electrolyte allows, in principle, to detect local

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potential differences. However, when exposing a sample surface in an electrolyte, polarization effects occur that homogenize possible potential differences. Only in poorly conducting electrolytes and/or at very small distance between reference electrode and sample surface differences in potential can be measured. Such techniques are SRET (scanning reference electrode technique [12]), SVET (scanning vibrating electrode technique [14]) and LEIS (local electrochemical impedance spectroscopy [15]). Scanning techniques are rapid but usually do not allow gathering information about the polarization behavior of the surface area under test. In order to polarize the sample surface beneath the electrode a counter electrode has to be present.

1.2. Point measuring techniques

Point measurement techniques allow to avoid effects related to mutual polarization of different zones on a metal (leading to homogenization of the potential). One approach is termed “micro-electrochemistry” where electrochemical experiments can be performed on small-scale areas with diameter from 1 to 1000 μm [16]. In this case, a small capillary filled with an electrolyte is placed on the sample surface with the junction between the end of the capillary and the metal under study sealed with silicon rubber in order to avoid lateral loss of electrolyte. This approach has the advantage of a well-defined surface area under test. However, the application is restricted to relatively smooth and flat surfaces, since otherwise, it becomes difficult to achieve tight conditions. Another, similar electrochemical device, the capillary-based droplet cell [17] is a technique which confines a liquid in contact with a sample surface in order to measure electrochemical and corrosion reactions over a limited region where the droplet is actually in contact with the sample.

These experimental techniques [16,17] allow very high local resolution but involve significant experimental effort. Lateral variations in electrochemical properties of the surface are of interest also for industrial applications, e.g. quality control or inspection. Hence the so-called “ec-pen,” a small, portable sensor with integrated reference and counter electrode, was developed by the Swiss Society for Corrosion Protection [18] that provides fast access to electrochemical information. The sensor does not require any sealing to avoid leaking of the electrolyte as the electrolytic contact is established with a porous polymer body. Easy handling, no surface preparation time and the possibility to run the ec-pen on virtually any metallic surface and in any inclination are the advantages.

This sensor (ec-pen) was used in this work to measure local corrosion potentials, cathodic and anodic polarization curves on 1 m long reinforcing steel bars with different surface condition. In this way, the distribution of the local open circuit potentials on a large surface could be assessed. According to the surface state, the results show significant variations of the OCP on different bars. A simple model is presented that allows predicting the corrosion potential of the whole bar when immersed into solution (global potential) based on the local measurements.

2. Experimental

2.1. Materials

Different types of ribbed steel bars, each 1 m long with diameter 10 mm, were used for the experiments:

- (1) Three mild steel bars, with different degree of pre-existing rust. One bar without rust with only mill-scale (Fig. 1a), one only slightly rusted (Fig. 1b) and one bar severely rusted (Fig. 1c).

Their different initial condition was due to different storage histories.

- (2) One 18/8 CrNi stainless steel bar (Fig. 1d)
- (3) Three mild steel bars passivated in a saturated $\text{Ca}(\text{OH})_2$ solution for >1 year (Fig. 1e).

All these bars were tested in “as received” conditions, thus without any pre-treatment prior to the electrochemical measurements.

2.2. Electrochemical sensor for local measurements

To measure local differences along the bars, electrochemical measurements were performed using the ec-pen [18]. This commercial instrument (Fig. 2b) is a small cylindrical container (volume ca. 20 mL) that can be filled with the test solution. The sensor contains a very small Ag/AgCl reference electrode and a platinum counter electrode (Fig. 2a) that allows the classical three-electrode electrochemical measurements. The electrolytic contact to the surface under test is established with a pen like porous diaphragm with a diameter of ca. 1 mm. The sensor does not require any sealing to avoid leaking of the electrolyte as the electrolytic contact is established with a porous polymer body. This diaphragm avoids leaking of the solution and defines the measurement area.

2.2.1. Reference electrode potential of the sensor

The reference potential of the Ag/AgCl reference electrode incorporated in the ec-pen is defined by the chloride concentration in the electrolyte in the pen. The potential of this reference electrode was measured for each test solution used versus a saturated calomel electrode (SCE). All potentials in this paper are given vs. SCE.

For the measurements the ec-pen (Fig. 2b) was positioned every 5 cm along the different bars (ca. 20 measuring spots per rebar). The measurements were performed in the sequence as they are described in the following paragraph.

2.3. Measurements

2.3.1. Open circuit potential

The open circuit potential was measured on each spot after 120 s of contact of the ec-pen with the surface. For the measurements on the three mild steel bars and on the stainless steel bar, alkaline chloride containing solutions (0.1 M NaOH, pH 13, with 0.01 M NaCl) were used as electrolyte in the corrosion pen.

For the bars passivated in sat. $\text{Ca}(\text{OH})_2$, the same electrolyte of sat. $\text{Ca}(\text{OH})_2$, pH 12.5, with 0.001 M NaCl was used. The solution in the ec-pen was the same as the storage solution, so the potential measured was rapidly constant and measuring time was maximum 30 s per point.

2.3.2. Cathodic polarization curve

Cathodic polarization curves were measured on 5–6 randomly selected spots per rebar. They were recorded immediately after the open circuit equilibration, starting from +50 mV to –500 mV vs OCP with the same solutions employed as for the OCP measurements. Measurements were carried out at room temperature using a scan rate of 1 mV/s and without IR drop compensation.

2.3.3. Anodic polarization curves

The anodic polarization curves were recorded in the same conditions as for the cathodic polarizations, starting from –50 mV vs OCP until oxygen evolution or pitting occurred. In order to reach the pitting potential these tests were performed in the same solution with a relatively high chloride content for all the bars (0.1 M NaOH, pH 13, 0.1 M NaCl).

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