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Detection of microbiologically influenced corrosion by electrochemical noise transients

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ABSTRACT

This work investigates the electrochemical processes involved in pitting corrosion induced by microbiologically influenced corrosion by using time-resolved instantaneous frequency information of electrochemical current noise (ECN) transients obtained from Hilbert spectra. In addition to the time-frequency analyses, also the open corrosion potential is investigated and microscopic examinations of the specimens are performed after the tests. Hilbert spectra of the ECN signals indicated the development of transients in one of the two electrochemical cells containing sulphate-reducing bacteria with a different instantaneous frequency decomposition as compared to the background ECN signal, which resulted from the anaerobic general corrosion process. After day 13, the transients in the ECN signals developed towards consistent instantaneous frequency decompositions in the Hilbert spectra that are typical for relatively fast pitting corrosion processes. Post-exposure microscopic observations confirmed the existence of pits underneath the attached biofilms at the working electrodes.

1. Introduction

Microbiologically influenced corrosion (MIC) can be described as (the acceleration and/or alteration of) corrosion processes resulting from the presence and activities of microorganisms [1], generating a biofilm at the metal surface [2,3]. It has been documented for metals exposed to seawater, but also to e.g. groundwater and industrial waters [4–6]. MIC therefore is a process that affects systems operating in maritime environments and many other sectors of industry. The process occurs in environments where corrosion with potentially exceptionally high reaction rates would otherwise not be expected, e.g. under anaerobic or low chloride conditions [1,4]. Therefore, MIC can lead to unexpected failure of systems. The process does not produce a unique type of corrosion, but it is usually localized, inducing e.g. pitting corrosion [1,5]. Microorganisms can accelerate the mechanisms of the corrosion processes, for which they require water, nutrients and electron acceptors [4,7,8].

1.1. Biofilm

Bacterial biofilms are most recognized for their influence on corrosion. For example, it was observed already quite some time ago that in the presence of steel, the amount of sulphate reduced to sulphide by sulphate-reducing bacteria (SRB) increases [9]. Bacteria can either exist individually or form colonies [1]. They grow, reproduce and produce extracellular polymers forming a biofilm [1,3]. The morphology of this biofilm depends on the surface material and roughness [10]. Bacteria either perform aerobic or anaerobic respiration [1,4]. These processes are symbiotic in such a way that conditions for the existence of each species within the biofilm are facilitated [1,4]. The bacterial adhesion pattern and its extent depend on many factors, including bacterial characteristics (e.g. their mobility in the electrolyte), substrate properties, available nutrients, temperature and influences of electrolyte flow (which also affects mobility of the bacteria) [1]. Moreover, the (extent of) formation of biofilms is generally not uniform and difficult to predict [1,11]. The presence of a biofilm at a metal substrate can shift the corrosion potential in the noble direction [1,11]. The

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mechanism for this ennoblement is still under discussion, however acceleration of the cathodic oxygen reduction reaction due to microbial activity is a generally accepted cause [1].

1.2. Corrosion mechanism

Although typical biofilm formation involves co-operation between aerobic and anaerobic bacteria, in this work the primary focus is on anaerobic bacteria (i.e. SRB). Under anaerobic conditions in a neutral electrolyte, carbon steel is expected to exhibit a very slow corrosion rate due to the relatively slow cathodic reduction reaction [4]:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1)$$

However, in the presence of SRB, corrosion is enhanced because sulphate acts as terminal electron acceptor due to its reduction by SRB [12–17]:

$$SO_4^{2-} + 8H^+ + 8e^- \rightarrow HS^- + OH^- + 3H_2O \quad (2)$$

On carbon steel, the sulphide typically reacts with the iron ions made available by the anodic reaction and subsequently the anodic site acidifies by the formation of iron sulphide [1,4,12,18]:

$$Fe^{2+} + HS^- \rightarrow FeS + H^+ \quad (3)$$

The conductive iron sulphide precipitates at the metal surface, thus facilitating electron flow from the substrate to the biofilm [17,19]. Indeed, pitting corrosion attack on carbon steel in the presence of SRB is reported to occur under the biofilm [20].

1.3. Investigation of MIC

To investigate MIC effectively, the phenomenon should be treated from a multidisciplinary point of view. This means that electrochemical techniques should be combined with other (surface analysis) techniques [21]. The possibility to distinguish characteristic MIC signatures using electrochemical noise measurements (ENM) is recognized [22,23]. It was found that differences in the type of electrochemical potential noise (EPN) signal could enable differentiation between biological and non-biological corrosion [24]. Investigation of the electrochemical noise (EN) time signal can provide useful information on the type of corrosion process induced by MIC [23,25]. For example, parameters like characteristic charge and frequency of events proved valuable for this purpose [23]. Analysis of the variance of the electrochemical current noise (ECN) and EPN signal has been shown to reveal the moment of transition between general and localized corrosion [26]. In the frequency domain, application of fractional Fourier transform has been reported to give satisfactory results in distinguishing MIC mechanisms, where conventional fast Fourier transform failed [27]. In the time-frequency domain, analysis of EPN transients by using wavelet transform can reveal signal features typical for localized corrosion associated with the presence of a biofilm [22].

In the present work the application of time-frequency analysis of EN data is proposed as an innovative way to detect and characterize pitting corrosion on carbon steel induced by SRB. The identification of ECN transients generated by pitting corrosion through MIC is a difficult task. The specific signal characteristics of the transients should be separated from the background ECN generated by the anaerobic general corrosion process of the carbon steel working electrodes. But once the transients have been identified, the ability to analyse only the contribution of the individual pitting processes, and to omit any instantaneous frequency information that is associated with the anaerobic general corrosion of the carbon steel, will prove to be very useful.

The approach followed in this work is as follows. The principle of transient analysis as introduced in earlier work [28,29] is applied to characterize the pitting corrosion process. To promote the metabolism of the SRB [30], the initial experimental conditions comprise a sterile, anaerobic, nutrient rich condition under elevated temperature, with a bare carbon steel substrate, initially in the absence of corrosion product. This is considered important in the investigation of MIC induced by SRB, since any corrosion product present at the metal surface acts as a diffusion layer [30]. For proper investigation of the development of EN characteristics due to the presence and activity of a bacterial biofilm, in the initial stage the working electrode surfaces should be freely accessible for species from the electrolyte.

In the next section, the experimental setup will be described in more detail, as well as the microscopic investigation and the procedure to analyse the obtained EN signal. Section 3 then discusses the results, where the visual and microscopic observations are related to the transients in the EN signal. Finally, in section 4 some conclusions are drawn.

Table 1
Chemical composition of the carbon steel working electrodes (wt.%).

Element	Carbon steel
C	≤0.17
Si	–
Mn	≤1.40
P	≤0.045
S	≤0.045

2. Experimental

2.1. Electrochemical cell

The four electrochemical cells consist of butyl rubber-stoppered containers with a volume of 500 ml. The measurements were performed in a conventional three-electrode configuration under open-circuit conditions, requiring two nominally identical carbon steel working electrodes and one platinum electrode, acting as reference electrode. The working electrodes consist of round bars, protruding through the butyl rubber sealing at the top to enable electrical connection while maintaining sterility. The chemical composition of the carbon steel working electrodes is provided in Table 1.

The working electrodes were partly coated with araldite glue, which is resistant to the dry sterilization temperature of 190 °C, and acts as a corrosion protective coating. Only a well-defined area of 19,6 mm^2 (corresponding with a diameter of 5 mm) of each working electrode was exposed to the electrolyte. The area of the square platinum mesh used as reference electrode was approximately 100 mm^2. The working electrodes were wet ground using up to 4000-grit SiC paper. The medium used was Postgate C [31], made from demineralised water and analytical grade reagent. NaCl was added to the medium to make the concentration 2,5 wt.% NaCl. After flushing the medium with N_2 for 1 hour, the medium was sterilized by autoclaving. Subsequently, the medium was allowed to cool down in a glovebox under controlled N_2 atmosphere. The electrochemical cells were mounted together and dry sterilized at 190 °C for 2 hours, to prevent the formation of corrosion product at the working electrodes due to autoclaving. After immediate transfer to the glovebox and cooling down, 500 ml of the medium was added to each electrochemical cell. Subsequently, 5 ml of a freshly grown culture of Desulfovibrio Indonesiensis (further denoted as SRB) was added to two of the four electrochemical cells. The other two cells served as sterile controls. The electrochemical cells were stored in an incubator at 28 °C. No additional nutrients were added during the experimental series.