Electrochimica Acta 283 (2018) 212–220

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Identifying corrosion of carbon steel buried in iron ore and coal cargoes based on recurrence quantification analysis of electrochemical noise

Y. Hou, C. Aldrich*, K. Lepkova, B. Kinsella

Curtin Corrosion Centre, Western Australian School of Mines, Curtin University, Bentley, WA 6102, Australia

ARTICLE INFO

Article history:
Received 20 April 2018
Received in revised form
19 June 2018
Accepted 19 June 2018
Available online 20 June 2018

Keywords:
Bulk cargo carriers
Corrosion
Electrochemical noise
Recurrence quantification analysis
Corrosion type identification
Random forests

ABSTRACT

The effect of bulk cargo materials - iron ore and coal – on the corrosion of cargo hulls in carriers was investigated using electrochemical noise. Two reference corrosion systems were set up with the steel samples in contact with moist silica sand and immersed in NaCl solution, which generated localised corrosion and general corrosion, respectively. The electrochemical noise was measured and recurrence quantification analysis was used to extract feature variables. A random forest model using these feature variables as predictors was able to discriminate between the two reference corrosion systems. This model was successfully applied to the assessment of carbon steel corrosion in iron ore and coal. The results predicted by the model were in agreement with visual and microscopic observations of the relevant corroded steel samples. This work provides a novel analytical approach to future on-line monitoring of carrier structures in contact with bulk cargoes.

1. Introduction

Steel carriers are commonly used for transportation of cargoes, such as coal and iron ore [1,2]. Corrosion has been identified as one of the major causes of ship structural failures [3–5]. Fortunately, with adequate maintenance and proper protection of the steel structures, the impact of corrosion could be controlled. However, field observations revealed that the maintenance practices were not always sufficient and some areas, such as the lower parts of the bulk coal and iron ore carriers, might not be suitable for the implementation of protection measures [3]. Therefore, an enhanced corrosion monitoring program is called for to guide efficient inspections and timely maintenance plans.

Corrosion can occur in different forms at different positions of the cargo hold of the bulk carrier. The overall thickness of the steel structure could be considerably reduced due to continuous general corrosion. In comparison, localized corrosion may result in little mass loss, but could lead to decrease of the strength of the steel structure and cause crack or penetration of the steel structure without pre-warning [6,7]. Real-time monitoring of the corrosion processes could increase the chance of capturing the fault conditions of the steel structures and reduce unnecessary inspections, thereby decreasing the maintenance cost.

Previous experimental studies on corrosion of steels by bulk cargoes, like coal and iron ore, mainly focused on the factors that influenced general corrosion rates, including particle size, quantity of moisture, pH level as well as chloride and sulphate concentrations in the water phase of the ores [8–10]. To date, little attention has been paid to the real-time monitoring of the corrosion process at steels in contact with bulk cargoes and no studies have been carried out on the identification of different corrosion types.

There are a number of corrosion monitoring techniques that are frequently used in industries to assist the development and implementation of inspection and maintenance programs, such as electrical resistance (ER), linear polarisation resistance (LPR) and electrochemical impedance spectroscopy (EIS). Although these techniques could provide near real-time corrosion rate related to general corrosion process, they are not particularly useful in detecting localised corrosion events [11,12].

It is widely recognized that electrochemical noise (EN) generated from corrosion processes bears valuable information regarding the underlying forms of corrosion [13–16]. Localised corrosion events can be revealed by indicators derived from the collected EN

* Corresponding author.
E-mail address: chris.aldrich@curtin.edu.au (C. Aldrich).

https://doi.org/10.1016/j.electacta.2018.06.129

signals with appropriate analytical approaches. Over the past few decades, a variety of parameters derived from the EN data have been proposed for corrosion monitoring and corrosion type identification, e.g. localisation index or pitting factor [17], characteristic charge and frequency [18], roll-off slope of the power spectral density plot [19], correlation dimension [20], energy distribution plot (EDP) [21], etc. Nevertheless, contradictory results have been observed and no agreement has been reached as to the optimal measures.

More recently, recurrence quantification analysis (RQA) has been employed to interpret EN data [22–24]. It was demonstrated that feature variables extracted from EN data by use of RQA were capable of capturing the characteristics of different types of corrosion processes. Furthermore, in our recent studies [25–27], the combination of RQA and advanced machine learning methods was shown to be capable of distinguishing localised corrosion from general corrosion *in-situ*.

Specifically, the EN data segment was first converted to a so-called recurrence plot, from which twelve variables were then extracted. A recurrence plot is in essence a graphical representation of a square matrix, which is commonly expressed as $R_{i,j} = H(\varepsilon - \|\boldsymbol{x}_i - \boldsymbol{x}_j\|)$. In our studies, $R_{i,j}$ represents the $(i, j)^{\text{th}}$ point in the recurrence plot, ε is a predefined threshold value, $\boldsymbol{x}_i$, $\boldsymbol{x}_j$ are the measured EN values at times i and j, and $\|\cdot\|$ refers to the Euclidean distance between this pair of data points. $\mathrm{H}(\cdot)$ represents the Heaviside function, which gives the value of one, if the distance between $\boldsymbol{x}_i$ and $\boldsymbol{x}_j$ falls within the threshold. Otherwise, it is zero. The quantification of the recurrence plots is termed as recurrence quantification analysis (RQA), by which various feature variables can be derived.

In previous investigations [25,26], twelve variables extracted by RQA method, as shown in Table 1, were used as predictors of a random forest (RF) model to distinguish between uniform, pitting and passivation processes of carbon steel in NaCl solution, $NaHCO_3$ + NaCl solution, and $NaHCO_3$ solution respectively. Furthermore, the RF model was capable of identifying pitting corrosion of carbon steel beneath sand deposit and general corrosion in CO_2-saturated brine [27].

The present study is an extended application of the methodologies and the data analytical procedures proposed earlier [25–27]. The objective is to identify the types of corrosion process that take place at carbon steel exposed to the two bulk cargoes investigated. Two other corrosive systems, which are expected to result in general and localized corrosion, are used to obtain electrochemical noise data for development of the random forest model. Specifically, carbon steel immersed in NaCl solution will be used for general corrosion assessment, and silica sand moist with NaCl solution is used for localized corrosion assessment. Deposits of silica sand at carbon steel have been previously shown to cause pitting [28]. A random forest model will be developed based on recurrence quantification analysis of the EN data generated from these two reference corrosion systems to discriminate between the two types of corrosion. Once established, this model will be applied to identify the corrosion types of specimens buried in iron ore and coal cargoes on the basis of associated EN recordings. This could be accomplished in real time, without having to take the specimens out. It is expected that this work could offer an additional analytical method for corrosion monitoring of bulk cargo carriers.

2. Experimental work

2.1. Materials

Carbon steel specimens (grade 1030) with chemical compositions of (wt.%): C (0.37), Si (0.282), Mn (0.80), P (0.012), S (0.001), Cr (0.089), Ni (0.012), Mo (0.004), Sn (0.004), Al (0.01), and Fe (balance) were used in this study. Two rectangular specimens with the same dimensions of 1.5 cm × 1.4 cm × 0.5 cm were soldered with a conducting wire for electrical connection and then electrocoated using Powercron 6000CX. Afterwards, the two specimens were mounted together in epoxy resin (Epofix), leaving approximately 2 cm^2 for each specimen as a working surface. This assembly, named as EN electrode, was used as working electrode in the electrochemical noise tests. Prior to EN tests, the electrode was ground on silicon carbide paper up to 240 grit, followed by rinsing with ultrapure water and ethanol and finally drying with nitrogen.

Table 1
Recurrence quantification variables.

Number	RQA variable	Equation
1	Recurrence rate	$RR = \frac{1}{N^2}\sum_{i,j=1}^{N} R_{i,j}(\varepsilon)$
2	Determinism	$DET = \frac{\sum_{l=l_{min}}^{N} l\,P(l)}{\sum_{i,j}^{N} R_{i,j}(\varepsilon)}$, $l_{min} = 2P(l)$ − Histogram of the diagonal lines* of length l.
3	Averaged diagonal length	$L_{mean} = \frac{\sum_{l=l_{min}}^{N} lP(l)}{\sum_{l=l_{min}}^{N} P(l)}$
4	Length of longest diagonal line	$L_{max} = \max(\{l_i; i = 1,2,\ldots N_l\})N_l-$ Total number of diagonal lines.
5	Entropy of diagonal length (ENTR1)	$ENTR1 = -\sum_{l=l_{min}}^{N} p(l)\ \ln p(l) p(l)$ − Probability distribution of diagonal lines.
6	Laminarity	$LAM = \frac{\sum_{v=v_{min}}^{N} vP(v)}{\sum_{v=1}^{N} vP(v)}$, $v_{min} = 2P(v)$ − Histogram of vertical lines** of length v.
7	Trapping time	$TT = \frac{\sum_{v=vmin}^{N} vP(v)}{\sum_{v=v_{min}}^{N} P(v)}$
8	Length of longest vertical line	$V_{max} = \max(\{v_i; i = 1,\ 2,\ \ldots,\ N_v\})Nv$ − Total number of vertical lines.
9	Recurrence times of 1st type	$\{RT1(i) = t_i - t_{i-1} \| i = 1,2,\ \ldots\}$
10	Recurrence times of 2nd type	$\{RT2(i) = t_i' - t_{i-1}' \| i = 1,2,\ \ldots\}$
11	Entropy of recurrence period density (ENTR2)	$ENTR2 = -\frac{1}{\ln(t_{max})}\cdot\sum_{t=1}^{t_{max}} P(t)\cdot\ln(P(t))P(t) = R(t)/\sum_{k=1}^{t_{max}} R(k)$ − Recurrence time probability density. $R(t)$ − The histogram of recurrence times. t_{max} − The maximum recurrence time.
12	Transitivity	$TRANS = \frac{\sum_{i,j,k=1}^{N} R_{i,j}\cdot R_{j,k}\cdot R_{k,i}}{\sum_{i,j,k=1}^{N} R_{i,j}\cdot R_{k,i}}$