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On quantitative corrosion rate monitoring with ultrasound

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ABSTRACT

Wall-thickness loss rate (WTLR) is an important parameter that defines a corrosion process. The speed at which a WTLR can be determined is directly related to how quickly one can intervene in a process that is heading in the wrong direction. Ultrasonic testing has been widely used as a convenient and efficient technique for online corrosion monitoring. One of the key performance parameters of ultrasonic corrosion monitoring is detection speed. While WTLRs can be determined by fitting linear lines to wall-thickness loss (WTL) measurements, the presence of noise in the measurements makes it difficult to judge the confidence levels of the slopes that are calculated this way. In this paper, a statistics based approach for assessing the detection speeds that are achievable by ultrasonic corrosion monitoring systems is presented. Through the statistical analysis of experimental data, a state-of-the-art laboratory setup is shown to be able to detect both WTLRs and changes in WTLR that are of interest to industry (i.e. 0.1–0.2 mm/year) within 1–2 h.

1. Introduction

In the US alone, corrosion costs the oil and gas industry billions of dollars a year [1]. Corrosion induced component failures have caused devastating environmental, social and financial consequences [2,3]. Online corrosion monitoring helps to improve the safety and the sustainability of assets. Conventional corrosion monitoring techniques, such as linear polarisation resistance measurements [4,5] and weight loss measurements [6–8], are intrusive since they require probes to access the interiors of closed vessels. Also, the estimation of wall-thickness loss rates (WTLRs) by these techniques depends on a number of assumptions (e.g. the chemical reactions that take place and the areas over which they occur) which often lead to loss of accuracy.

Ultrasonic testing (UT) offers a non-intrusive and more direct approach for corrosion monitoring. In the past, UT could only be carried out manually, and due to the uncertainties associated with transducer positioning and coupling, the method suffered from poor measurement repeatability (i.e. 0.1–0.5 mm) [9]. The use of permanently installed transducers has significantly improved the measurement repeatability of the method [10]. Ultrasonic wall-thickness loss (WTL) measurements with micron level precision were subsequently reported [11,12]. Lately, the authors constructed a state-of-the-art laboratory setup that is able to achieve an unprecedented WTL measurement repeatability in the range of 10s of nanometres [13].

The simplest way of determining WTLRs from ultrasonic WTL measurements is by linear least squares regression. When very small WTLRs are to be determined, it is crucial to be able to differentiate genuine WTLs from measurement noise. In this paper, a statistical approach is used to assess the speeds at which corrosion processes and changes in corrosion rate can be detected. The approach quantifies the confidence levels with which WTLRs and changes in WTLR can be estimated by linear line fitting. WTL measurements that were acquired during open-circuit corrosion processes, using the setup constructed by the authors, were quantitatively analysed to demonstrate the state-of-the-art measurement capability of ultrasonic corrosion monitoring. The statistical approach offers a convenient way of evaluating the performances of ultrasonic corrosion monitoring systems.

2. State-of-the-art ultrasonic wall-thickness loss measurements

Fig. 1 shows the ultrasonically measured WTLs of a 10 mm mild steel sample (BS 970:1983:080A15, UNS G10160) during open-circuit corrosion experiments. The experiments were conducted using the ultrasonic monitoring setup constructed by the authors [13] which has a thickness measurement repeatability of ~20 nm over 1 h and that of ~40 nm over 24 h. The measurements were acquired at 1 min intervals. The electrolytes used are distilled water, 0.1 M citric acid and 0.1 M acetic acid. The ultrasonic measurements were validated by optical surface profile scans which were obtained by a white light interferometer (TMS-100 TopMap Metro.Lab, Polytec, Germany) after the corrosion experiments had finished. The procedure for carrying out the optical scans can be found in [13].

As shown in Fig. 1(a), distilled water had not caused any noticeable WTL over the time frame of the experiment. The measurements that

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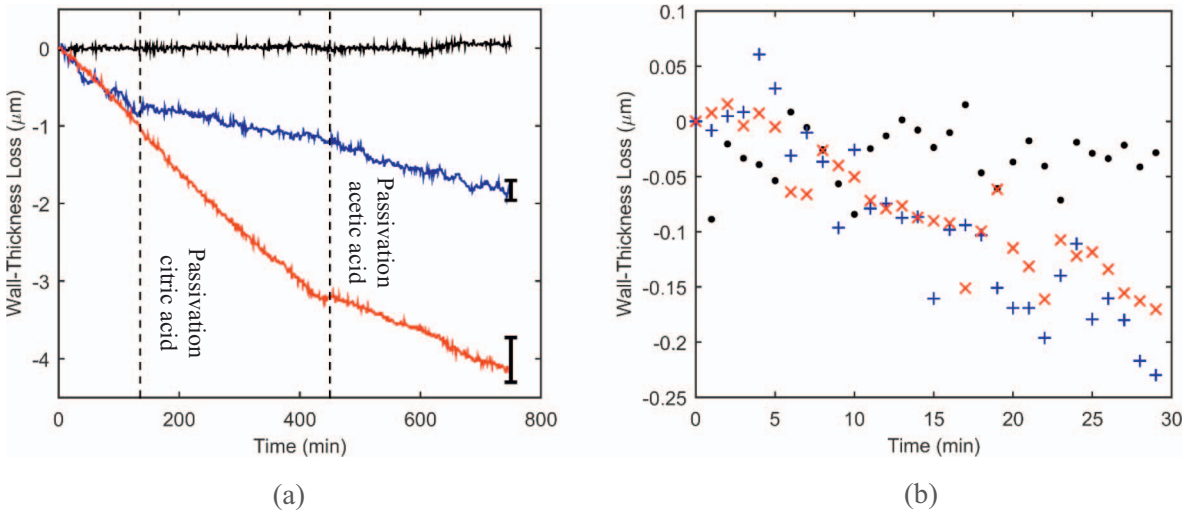

Fig. 1. (a) Ultrasonic measurements of the WTLs of the sample during the experiments with distilled water (black), 0.1 M citric acid (blue) and 0.1 M acetic acid (red). The mean thickness changes calculated from the optical profile scans of the corrosion surfaces are shown as error bars. (b) Measurements that were acquired in the first 30 min. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

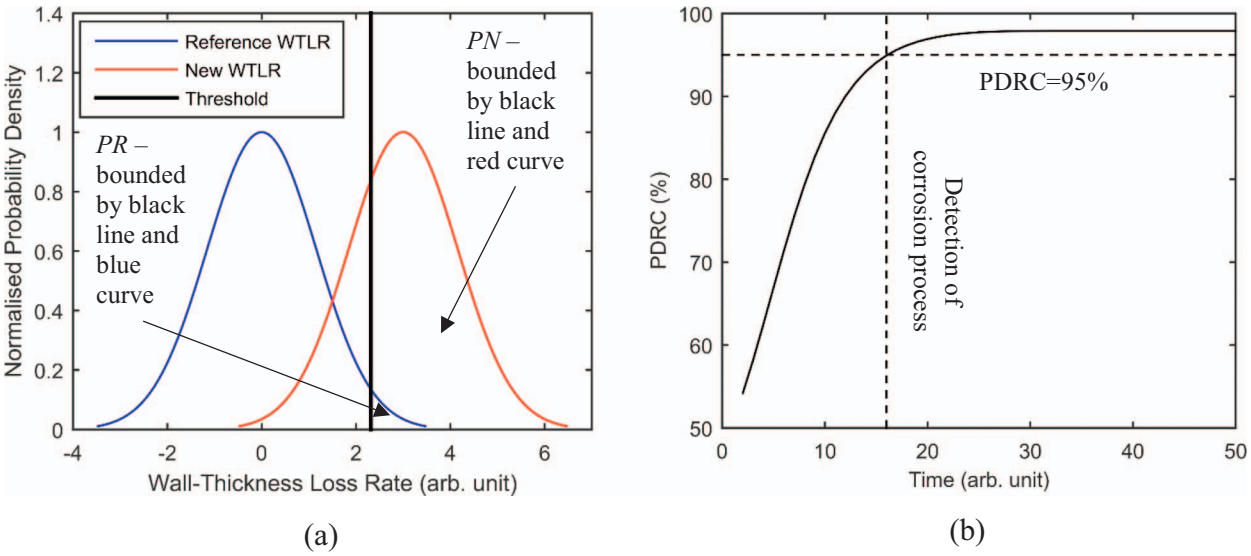

Fig. 2. (a) PDF curves of the reference and the new WTLRs that are determined up until a given time instant. (b) PDRC curve for WTLRs.

were acquired during the experiment with distilled water are therefore indicative of the noise level of the measurement system that was employed. The two acidic solutions, on the other hand, had resulted in micron level WTLs. During the two acidic corrosion processes, the effect of surface passivation, which caused WTLRs to change, was observed at the 2nd and the 7th hour respectively. It is worth mentioning that surface passivation occurs when corrosion products gradually deposit onto the corroding surface. This leads to the formation of a corrosion-inhibiting passivation layer which hinders further diffusion of ions and hence slows down corrosion kinetics.

While it is relatively easy to retrospectively identify the two corrosion processes and calculate the WTLRs from the WTL measurements by linear least squares regression, it is not straightforward to do so at the onsets of the changes (without a large number of a priori measurements) since the presence of noise introduces uncertainty to the linearly fitted WTLRs. As illustrated in Fig. 1(b), the two acidic corrosion processes cannot be clearly identified in the first 15–20 min since the WTL measurements lie within the noise level of the ultrasonic setup. Therefore, in this paper, a statistical approach for confidently determining WTLRs and changes in WTLR is described, and it is through the consideration of confidence levels that automated, on-the-spot detection of corrosion processes and changes in corrosion rate is achieved. The statistical approach is equally applicable to analysing field measurements which expectedly have lower measurement repeatability and hence result in longer detection times. Also, it is capable of making predictions of the response times of ultrasonic corrosion monitoring systems.

3. Detection of statistically significant wall-thickness loss rates

Consider a set of N WTL measurements which have a variance of σ_w^2. The standard deviation (σ_r) of all the WTLRs that can be calculated from these WTL measurements is given by

$$\sigma_r = \sqrt{\frac{\sigma_w^2}{\sum_{i=1}^{N}(t_i - \bar{t})}} \quad (1)$$

where t_i is the sampling time instant of the i^{th} WTL measurement, and $\bar{t}$ is the mean value of all the sampling time instants.

A quantity named the probability of detecting a real change (PDRC)

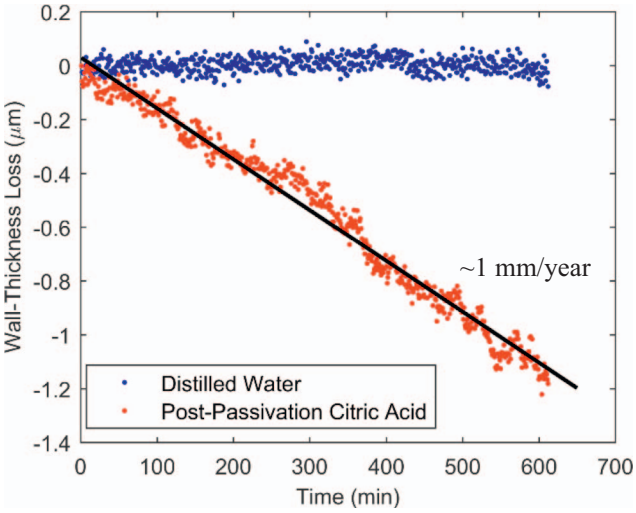

Fig. 3. Illustration of the alignment of the reference and the new measurements that were considered for the detection of corrosion processes.

[14] is introduced to calculate the probability that a WTLR, measured at time *t*, genuinely represents a corrosion process or a change in corrosion rate as opposed to the result of measurement noise. In equation

Table 1
Times of detection for the corrosion processes recorded.

Electrolyte	Corrosion stage	WTLR (mm/year)	Time of detection (min)		
			Experimental	Predicted	
				σ_w = 20 nm	σ_w = 40 nm
Citric acid	Pre-passivation	~3	11	8	13
	Post-passivation	~1	21	17	26
Acetic acid	Pre-passivation	~4	8	7	11
	Post-passivation	~1.8	12	11	18

form, PDRC is expressed as

$$PDRC(t) = \frac{PN(t)}{PR(t) + PN(t)} \quad (2)$$

where, as illustrated in Fig. 2(a), *PN* is the area bounded by a certain threshold and the probability density function (PDF) curve of the WTLRs that are determined from a set of new WTL measurements that are acquired up until time *t*, and *PR* is the area bounded by the same threshold and the PDF curve of the WTLRs that are determined from an

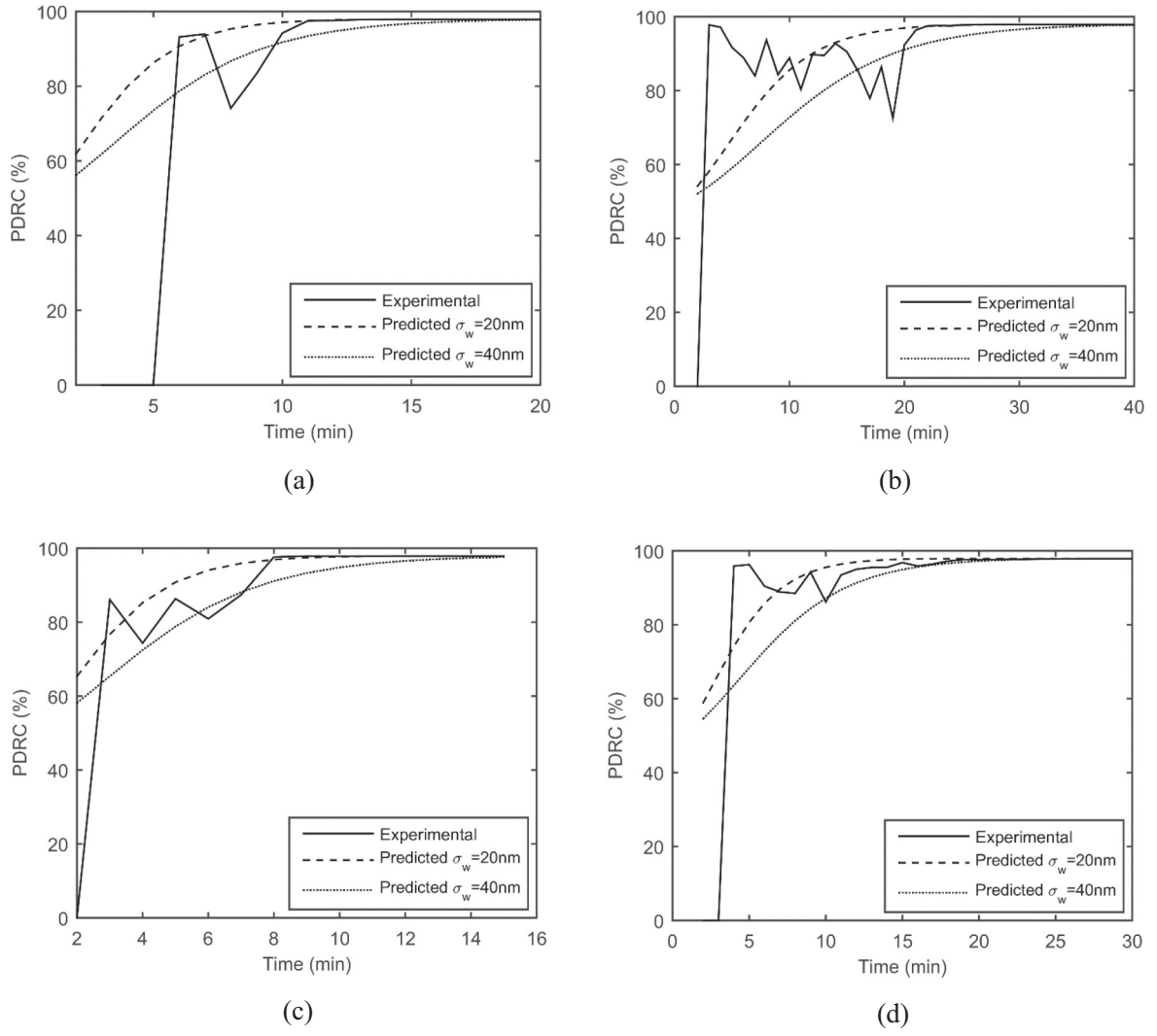

Fig. 4. PDRC curves for (a) pre-passivation and (b) post-passivation corrosion process with citric acid, and (c) pre-passivation and (b) post-passivation corrosion process with acetic acid.

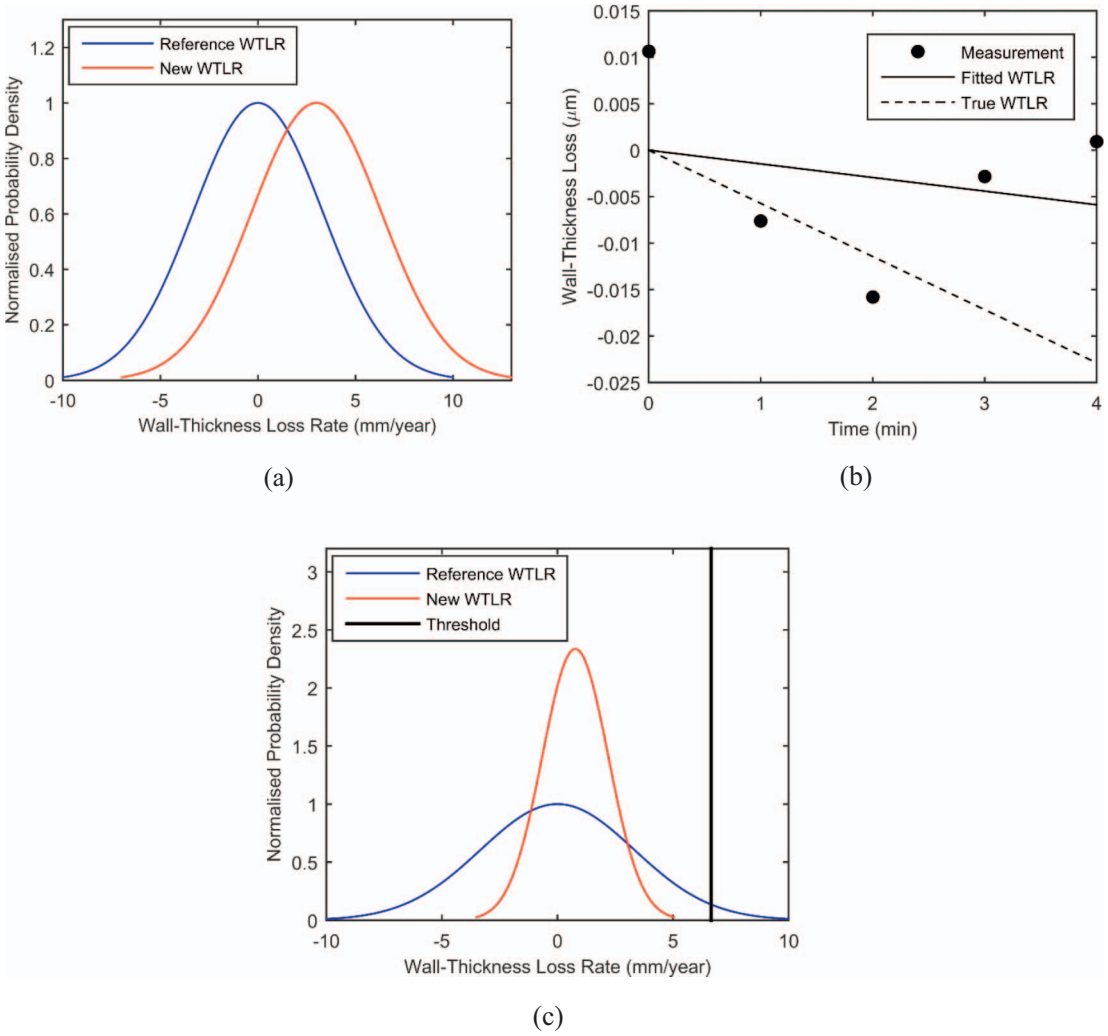

Fig. 5. Illustration of the reason for the mismatch between initial PDRC values. The data makes use of the measurements that were acquired during the pre-passivation corrosion process with citric acid. (a) PDF curves drawn with pre-defined mean WTLRs and measurement repeatability. (b) Comparison of true (pre-defined) and temporarily fitted mean WTLR. (c) PDF curves drawn with temporarily fitted mean WTLRs and measurement repeatability.

equal number of reference WTL measurements. In this work, the threshold was set to two times the standard deviation of the reference WTLRs. As shown in Fig. 2(b), a corrosion process or a change in corrosion rate is defined as detected when the PDRC value is stably > 95%.

It is also possible to use Eqs. (1) and (2) to predict the amount of time that a measurement system will take to detect a given corrosion process. This is done by inputting the pre-determined measurement repeatability of the measurement system, the WTLR of the corrosion process, and the sampling intervals at which measurements are acquired.

4. Application of statistics based detection to state-of-the-art experimental data

The WTL measurements that were acquired during each of the two acidic corrosion processes can be divided into two segments of data by the onset of surface passivation. The mean WTLRs that were calculated by linear least squares regressions are ~3 and ~1 mm/year for the pre- and the post-passivation corrosion process with citric acid, and ~4 and ~1.8 mm/year for those with acetic acid. The speeds at which the four different segments of corrosion processes could be detected were evaluated. The ultrasonic measurements that were acquired during the experiment with distilled water were used as the reference data. The WTL measurements that were acquired during each of the two post-passivation acidic corrosion processes were shifted in time and in space to begin at the origin as demonstrated in Fig. 3.

Fig. 4 shows the predicted and the experimentally obtained PDRC curves for the four different segments of corrosion processes. The predictions were attained using σ_w = [20, 40 *nm*], *WTLR* = 0 for the reference measurements, *WTLR* = [3, 1, 4, 1.8 *mm/year*] for the new measurements, and sampling intervals of 1 min. The times of detection that are determined from the predicted and the experimentally obtained PDRC curves are given in Table 1. The experimental values lie in between the predictions which outline the expected variability.

It is observed from Fig. 4 that while the initial values of the predicted PDRC curves are close to 50%, the experimentally obtained curves begin from 0. The predicted curves were constructed using mean WTLRs and measurement repeatability that were pre-defined. For a given corrosion process, the PDF curves of the new and the reference WTLRs assume the same shape, and for a small number of measurements, they have much overlap (Fig. 5(a)), resulting in *PR* and *PN* being similar and hence PDRC being close to 0.5. On the other hand, the experimentally obtained PDRC curves were constructed in situ using mean WTLRs and measurement repeatability that were determined based on a priori WTL measurements. In this case, when only a small number of measurements are present, the temporarily fitted WTLR is very likely to be different from the true value though its confidence level may be quite high (Fig. 5(b)). The consequence of this is that the

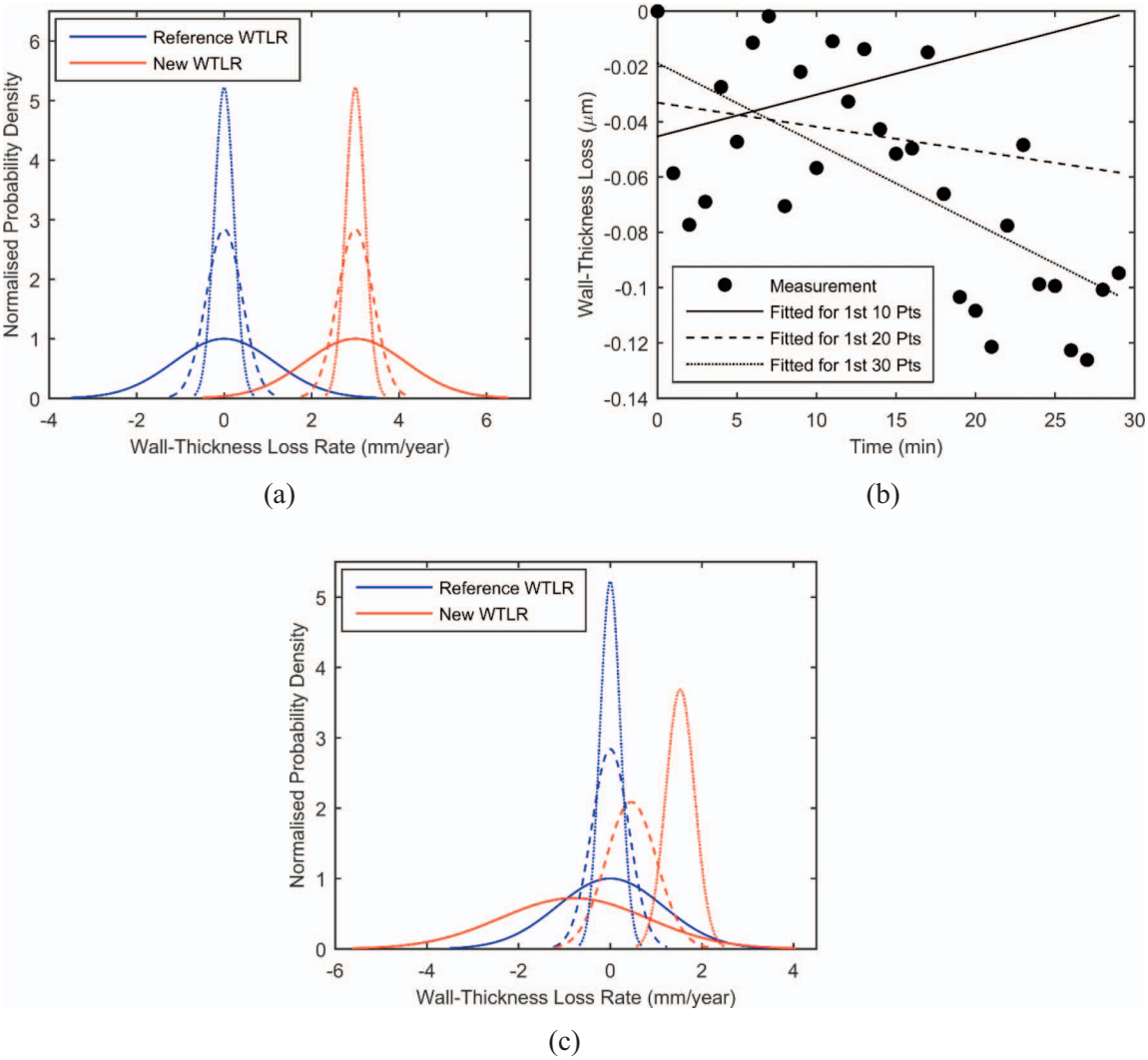

Fig. 6. Illustration of the reason for the fluctuation in experimentally obtained PDRC values. The data makes use of the measurements that were acquired during the post-passivation corrosion process with citric acid. (a) PDF curves drawn with pre-defined mean WTLRs and measurement repeatability. (b) Comparison of the mean WTLRs that were determined in situ using different numbers of WTL measurements. (c) PDF curves drawn with temporarily fitted mean WTLRs and measurement repeatability. For (a) and (c), solid line: based on first 10 measurements, dashed line: based on first 20 measurements, dotted line: based on first 30 measurements.

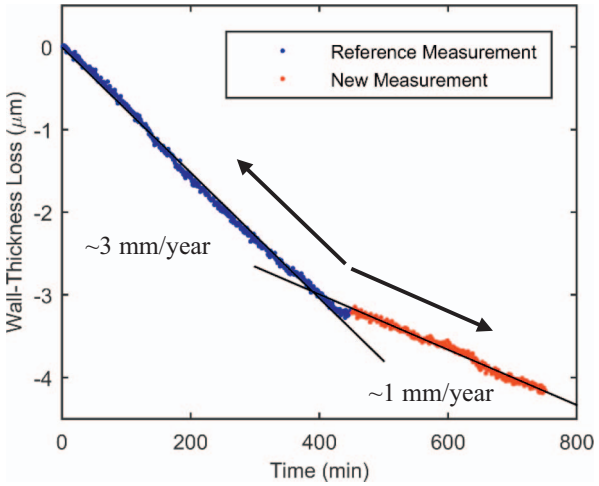

Fig. 7. Illustration of the reference and the new measurements that were considered for the detection of changes in corrosion rate. The data makes use of the measurements that were acquired during the corrosion process with acetic acid.

PDF curve of the new WTLRs falls within that of the reference WTLRs, and hence the threshold (i.e. two times the standard deviation of the reference WTLRs) lies outside the PDF curve of the new WTLRs. This in turn leads to $PN = 0$ and $PDRC = 0$.

Another observation that can be made from Fig. 4 is that the predicted PDRC curves converge smoothly, whereas the experimentally obtained curves fluctuate before arriving at convergence. Since the mean WTLRs and the measurement repeatability that were used to construct the predicted curves were pre-defined, the overlap between the PDF curves of a given pair of reference and new WTLRs decreases gradually with increasing number of measurement (Fig. 6(a)). Consequently, *PR* and *PN* part, and PDRC converges to a value that is close to 1. In contrast, the mean WTLRs and the measurement repeatability that was determined in situ from a small number of experimental WTL measurements exhibit fluctuation (Fig. 6(b)). This gives rise to varying PDF curves (Fig. 6(c)) which then output varying *PN* and PDRC.

One of the key purposes of online corrosion rate monitoring is to identify accelerated component degradations so that appropriate corrosion control strategies can be applied on time to mitigate further excessive structural losses. In order to ensure that the mitigation strategies applied are effective, it is essential to be able to detect the changes in corrosion rate that they will have led to.

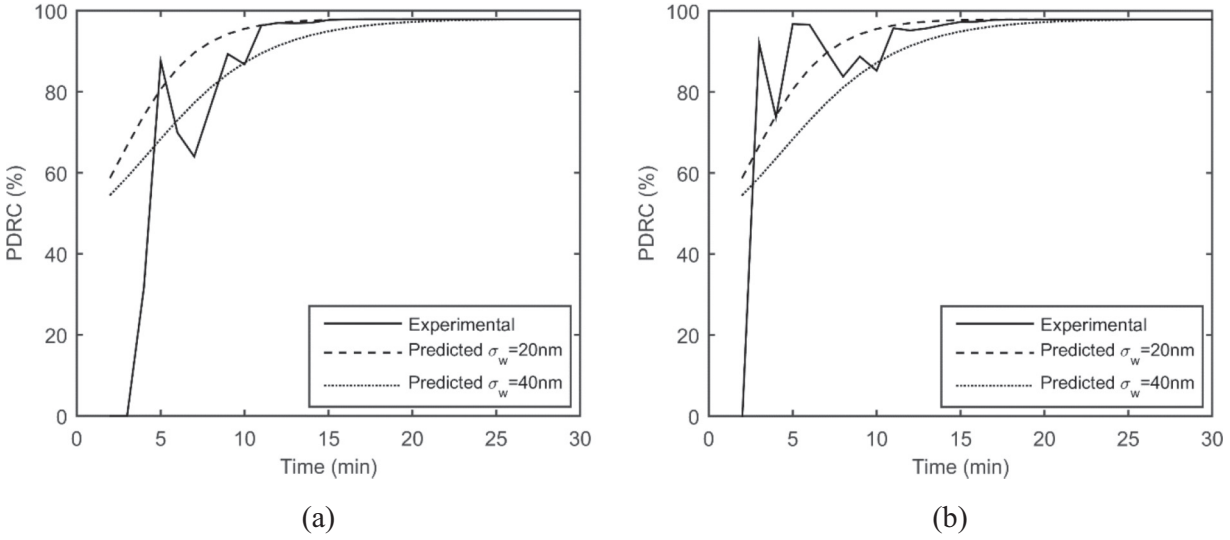

Fig. 8. PDRC curves for the changes in corrosion rate in the corrosion processes with (a) citric acid and (b) acetic acid.

Table 2
Times of detection for the changes in corrosion rate recorded.

Electrolyte	Change in WTLR (mm/year)	Time of detection (min)		
		Experimental	Predicted	
			σ_w = 20 nm	σ_w = 40 nm
Citric acid	~2	13	11	17
Acetic acid	~2.2	11	10	16

The mean WTLRs of the two acidic corrosion processes changed at the 140th and the 455th minute respectively due to surface passivation. Assume that these changes were caused by the application of some corrosion mitigation strategies. In order to construct the PDRC curves of the post-change corrosion processes, the pre-change WTL measurements were used reversely as the reference measurements as demonstrated in Fig. 7. The reversion allowed the measurements that are closer to the onsets of the changes to be contrasted against earlier in the construction of the PDRC curves.

The predicted and the experimentally obtained PDRC curves for the changes in corrosion rate in the two acidic corrosion processes are displayed in Fig. 8. The predicted curves were constructed using σ_w = [20, 40 *nm*], *WTLR* = [3, 4 *mm/year*] for the reference measurements, *WTLR* = [1, 1.8 *mm/year*] for the new measurements, and sampling intervals of 1 min. The discrepancies between the predicted and the experimentally obtained curves can also be attributed to the aforementioned reasons. Table 2 shows that the times of detection that are determined from the experimental results lie within the predicted variability.

5. Evaluation of ultrasonic corrosion monitoring systems

The results presented thus far suggest that the statistics based approach is effective in evaluating the capabilities of ultrasonic corrosion monitoring systems to detect corrosion processes and changes in corrosion rate. It is worth mentioning that the approach is only sensitive to absolute changes in WTLR, meaning that, in theory, a corrosion process that take places at 2 mm/year requires the same amount of time to be detected as a change in corrosion rate from 1 to 3 mm/year does. Therefore, the time that it takes to complete the monitoring of a

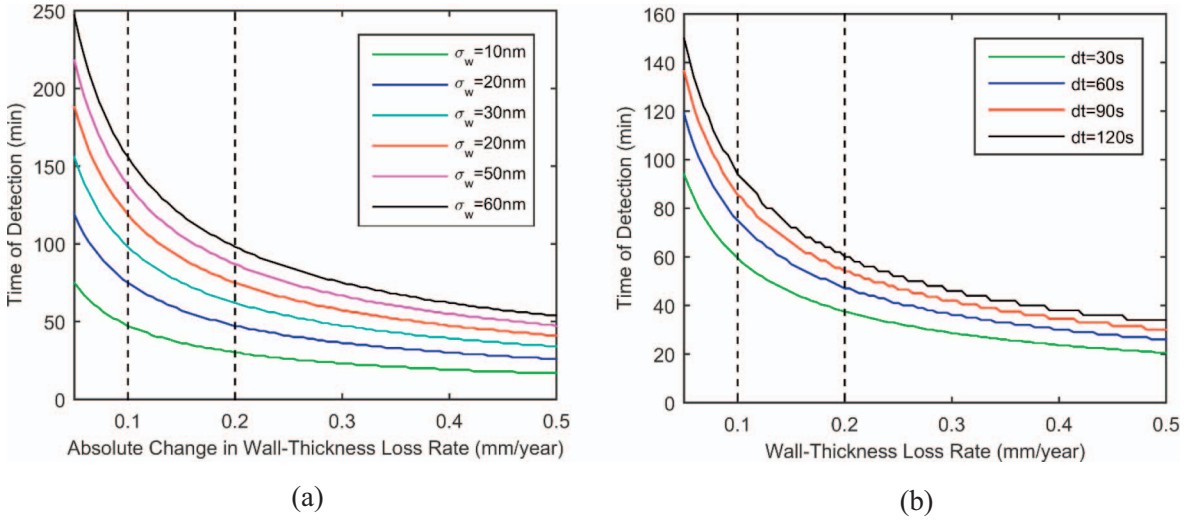

Fig. 9. Detectability of absolute changes in corrosion rate with respect to (a) measurement repeatability (sampling time increment: 1 min) and (b) sampling time increment (measurement repeatability: 20 nm). The variability of the detection speeds that are achievable by the setup constructed by the authors are bounded by the blue and the red curve in (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

corrosion control cycle is essentially equivalent to the sum of the times that it takes to detect all the absolute changes in corrosion rate that are involved.

Fig. 9 shows the detection speeds that can be achieved at different values of measurement repeatability and different sampling intervals. It can be seen that detection speed increases with the reduction of either variable. Such detectability charts provide direct visualisation of the measurement capabilities of ultrasonic corrosion monitoring systems, and hence enable users to make more informed decisions when it comes to choosing the right systems for their applications. Fig. 9(a) indicates that using the current state-of-the-art setup which acquires measurements at 1 min intervals and has a measurement repeatability of 20 to 40 nm, absolute changes in corrosion rate that are of interest to industry (i.e. 0.1–0.2 mm/year) can be confidently detected within approximately 2 h.

6. Conclusion

In this paper, a statistical approach for evaluating the speeds at which corrosion processes and changes in corrosion rate can be detected based on ultrasonic WTL measurements is presented. In order to mitigate the effect of measurement noise, points of detection are determined based on confidences levels of WTLRs and changes in WTLR that are calculated by linear least square regression. The approach was used to analyse the measurement capability of a state-of-the-art ultrasonic corrosion monitoring setup by considering WTL measurements that were acquired during open-circuit corrosion processes. The result suggests that detection times in the range of 1–2 h can be achieved for WTLRs and changes in WTLR that are of interest to industry (i.e. 0.1–0.2 mm/year). It is shown that further improvement in detection speed can be realised through the use of faster data acquisition hardware. The statistical approach presented in this paper can also become a standardised method for quantifying the performances of ultrasonic corrosion monitoring systems.

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