Electrochemical evaluation of under-deposit corrosion and its inhibition using the wire beam electrode method

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1. Introduction

The presence of solid deposits on metal surface can cause a localised form of corrosion, namely under-deposit corrosion (UDC). UDC is often pitting and mesa-type of attack that is frequently observed in cooling water systems where scales and fouling exist and in oil and gas pipelines where sand, debris, biofilm and carbonate deposit are present. In order to control UDC, aggressive pigging programs are used in industry to remove deposits on a regular basis. Unfortunately frequent pigging treatment is troublesome, expensive, and is not suitable for some pipeline systems. Corrosion inhibitor treatment is often applied as an alternative or supplementary means of preventing UDC. Inhibitors are believed to mitigate UDC if applied in sufficient concentrations [1]. However, the effects of inhibitors on UDC have not been effectively assessed in industry because UDC is considered nearly impossible to assess by normal corrosion testing techniques. Currently there is only limited understanding on the efficiency of UDC inhibition. Most of the research and tests conducted in the past have been to explore the effects of inhibitors on carbon dioxide (CO₂) corrosion of bare steel surfaces. Unfortunately corrosion data from bare steel testing cannot be used to determine the behaviour of under-deposit corrosion. It was reported that a crude oil pipeline that was found to have very low corrosion rates by conventional corrosion monitoring in the bulk fluid suffered severe under-deposit pitting corrosion on the bottom of the line where large volume of sediments existed [2].

Understanding the mechanism and factors affecting UDC is obviously critical in determining optimal approaches to UDC problems and in developing effective corrosion inhibitors. Industry experience suggests that complex factors, such as the retention of aggressive species in the deposits, failure of inhibitors to penetrate the deposits, a large cathode to anode surface area ratio and the possible formation of a localised differential concentration cell would affect UDC [1]. Current explanation for UDC is often based on an assumption that the accumulation of deposits on metal surface prevents corrosion inhibitors and biocides from accessing metal surface, leading to insufficient inhibitor concentration and accelerating anaerobic growth underneath deposits. These assumptions need to be verified through corrosion tests that are able to determine local electrochemical parameters from under-deposit areas and that are capable of evaluating all major factors affecting UDC.

An effective UDC test not only needs to effectively simulate complex UDC environmental parameters and diffusion pathways, more importantly it should correctly simulate the mechanism that leads to the initiation and propagation of UDC. Ideally, it should be able to accurately measure local corrosion parameters on an instantaneous basis. During recent years several techniques have been developed in various laboratories [3–9] in order to meet the industry requirements in UDC inhibitor testing and evaluation. For instance de Reus et al. [3] used an experiment device to measure inhibitor performance under solid deposits. The device was made of two sets of three electrode arrays with one set covered with sand and another directly exposed to brine solution. Such device was designed to allow simultaneous electrochemical measurements at both uncovered and covered areas for direct electrochemical comparison. Using this device, de Reus et al. [3] found that a higher concentration of
inhibitor had to be used to prevent UDC than that would be needed to inhibit general corrosion. However, an obvious issue in this experiment is that this device is unable to simulate galvanic corrosion activities associated with UDC. It is well-known that galvanic corrosion due to a large cathode to anode surface area ratio contributes significantly to the UDC mechanism. Obviously failure to measure galvanic currents flowing between covered and uncovered areas would lead to underestimation of UDC.

Pedersen et al. [4] designed a different experiment device that allowed the measurement of galvanic currents flowing between a
large cathode and a small anode. Their experiment device used three specimens with two specimens covered with sand and one directly exposed to brine solution. One of the covered specimens was coupled to the uncovered specimen. Corrosion inhibitors were assessed by detecting galvanic currents flowing between the sand covered and uncovered specimen. It was found that the sand covered specimen was anodically polarised and was under localised corrosion attack. Indeed this device could simulate galvanic effect; however, it may not work in high resistance media such as a multiphase fluid where a high electrolyte resistance would prevent galvanic current flowing between the sand covered and uncovered specimen. Another issue is that the device would not effectively simulate localised chemical changes that could occur over partially covered steel pipeline surfaces.

Another experiment device designed for evaluating UDC is the artificial pit electrode method [5–7] where a pit electrode is coupled through a zero resistance ammeter (ZRA) to a large piece of steel and immersed in a brine solution. In this method, galvanic current is believed to relate to the rate of pit propagation and its change before and after inhibitor addition can be used as an indicator for assessing inhibitor performance. A modified version of the experiment was introduced by Han et al. [8], where the anode and the cathode were kept closer in order to simulate real situation that the pit electrode and the large piece of steel should be parts of a single metal surface. Although the artificial pit electrode method should be able to detect galvanic currents flowing between localised anodes and cathodes over a partially covered metal surface, it has similar limitations to the method by Pedersen et al. [4] in detecting galvanic current in high resistive media. It also has difficulties in simulating ions diffusion and chemical changes over a partially covered metal surface. It would not provide spatial information on localised corrosion. Another critical issue is that this method does not take the fact that UDC can occur by both direct and indirect mechanisms into consideration. In direct UDC attack, for instance corrosion under a bacteria containing deposit, galvanic currents could flow only between anodic and cathodic areas that are both under the deposit. It is well-known that the growth of bacteria, such as sulphate-reducing bacteria and the formation of biofilms may result in direct UDC attack because bacteria activities can generate oxidising substances such as acids under the deposits. Under this situation, no measurable galvanic corrosion could be detected by a ZRA that couples the electrode to a piece of external steel and thus the artificial pit electrode method would be unable to evaluate this type of UDC or its inhibitors. Secondly, even if indirect UDC occurs due to environmental differences inside and outside the deposit the ZRA may still be unable to detect any galvanic current if the deposit has a large resistance or if the electrolyte resistance is high. Under this situation, anodic areas will locate near cathodic areas and galvanic currents flow only between these neighbouring areas without passing through the external ZRA.

Indeed techniques discussed above have some limitations in simulating UDC mechanism and in measuring local electrochemical parameters affecting UDC. Tan et al. [10] reviewed these limitations and concluded that sufficient attention needs to be paid to localised corrosion mechanism and its effect on corrosion testing because the severity and pattern of corrosion is often determined by the corrosion mechanism. If a corrosion test fails to simulate corrosion mechanism such as galvanic effects, it could result in unsuccessful and misleading results [11–15]. Limitations in conventional techniques in measuring local electrochemical parameters are also responsible for difficulties in measuring UDC. Electrochemical techniques, such as linear polarisation resistance and electrochemical impedance spectroscopy can be used to measure the corrosion rates on an instantaneous basis; however, they have limitation in measuring localised corrosion [16–18]. The cyclic polarisation method is probably the only traditional electrochemical method that is used to determine localised corrosion susceptibility [19]; however, it does not determine the rates of localised corrosion. Relatively new methods such as scanning probe techniques have been developed into useful research tools for localised corrosion studies, however, scanning probes are unable to scan corrosion occurring under solid deposits. Electrochemical noise analysis and the wire beam electrode (WBE) method are probably the only techniques that have potential in measuring localised corrosion rates. Although some controversial issues still exist in the interpretation of electrochemical noise data, electrochemical noise has been recognised to be a rich source of information on the corrosion process and localised corrosion [20]. The WBE is a multi-electrode array that has been applied successfully in various localised corrosion testing and research [16–18]. The WBE’s working surface is electrochemically-integrated by coupling all the wire terminals in the solid phase and by closely packing all the wires in the solid/electrolyte interface. This electrochemical integration allows the working surface of a WBE to effectively simulate a conventional one-piece electrode surface in electrochemical behaviour. Indeed research has shown that similar corrosion patterns were produced over WBE and conventional one-piece electrode surfaces when both were
exposed to identical corrosion environments and this has been verified theoretically [16–18].

Two important characteristics of the WBE method that are particularly valuable for UDC testing are, (i) the WBE is applicable to high resistance multi-phase environment, as demonstrated in a previous study [21], and is thus able to simulate UDC under high resistance deposits; (ii) the WBE can map corrosion on an instantaneous and continuous basis, providing unprecedented spatial and temporal information on localised corrosion processes occurring under-deposits. Turnbull et al. [9] used a multi-electrode array to study UDC; however, their electrode array was made of far-spaced and uncoupled multi-electrodes that are not electrochemically integrated to simulate localised corrosion occurring over a continuous metal surface.

2. Experimental

Fig. 1a illustrates a UDC experiment setup using the WBE. The WBE used in this work was made from one hundred identical mild steel (UNS No. G10350) wires embedded in epoxy resin, insulated from each other with a very thin epoxy layer. Each wire had a diameter of 0.19 cm and acted both as a mini-electrode (sensor) and as a corrosion substrate. The working area was abraded with 240, 320 and 1200 grit silicon carbide paper, rinsed with deionised water to remove water-soluble contaminants and by ethanol to remove organic contaminants. As shown in Fig. 1b, the WBE working surface was partially covered with a rubber ‘O’ shaped ring filled with sand to simulate a localised under-deposit corrosion environment. The partially covered WBE surface was then exposed to 3 l of synthetic brine (3% NaCl by weight, 0.01% NaHCO3 by weight) contained in a custom-made electrochemical testing cell at room temperature (approximately 21 °C). During CO2 corrosion testing, CO2 sparging was continued to maintain a virtually oxygen free environment. During corrosion exposure periods, all the wire terminals of the WBE were connected together and, therefore, electrons could move freely between wires, in a similar way as would be the case with larger one-piece electrode. All chemicals used were of analytical grade supplied by Sigma and Aldrich and used without further purification.

UDC processes were monitored by mapping galvanic currents across the multi-electrode array to understand how localised corrosion initiated and propagated under sand and how it changed with the introduction of the inhibitor or oxygen (O2). Galvanic current was measured between a chosen individual electrode and all the other electrodes shorted together using a pre-programmed Autoswitch device and an ACM AutoZRA. Corrosion potentials were also mapped when necessary to help understand the mechanism of UDC. Galvanic current and corrosion potential data were analysed by procedures similar to that described in references [21] and [22] using a custom-designed analysis software. The measurements were taken regularly to determine changes in corrosion processes and patterns.
In this paper, the term ‘galvanic current’ is used to describe currents caused by local potential differences that can be originated from variations in surface metallurgy or in surface chemistry. Measurement of potential is useful for determining the thermodynamics of a corrosion cell; while the measurement of galvanic currents is useful for evaluating corrosion kinetics.

Organic inhibitor imidazoline has been studied because it is the most commonly used inhibitor in oil and gas pipelines. The behaviour of imidazoline in inhibiting general CO₂ corrosion has already been studied previously [23]; however, its behaviour on inhibiting UDC has not yet been reported. The molecular structure of imidazoline is shown in Fig. 2.

3. Results and discussion

The first experiment was carried out to understand the baseline CO₂ corrosion behaviour. Fig. 3 shows a typical baseline galvanic current map that was measured from a bare WBE exposed to CO₂ saturated brine without inhibitor present. The large number of anodic sites shown in Fig. 3 indicates general corrosion occurring over the WBE surface. Another experiment was carried out to evaluate UDC under O₂ containing atmospheric environment where UDC is considered to be similar to conventional crevice corrosion due to the formation of an oxygen differential aeration cell inside and outside the deposit-covered metal surfaces. As shown in Fig. 4, anodic dissolution currents concentrated on areas covered by a rubber ‘O’ ring and sand, while cathodic currents that are mainly due to the oxygen reduction reaction distributed mostly outside the sand deposit. The galvanic current and corrosion potential distribution maps in Fig. 4 are in good agreement. This result is also in agreement with the conventional oxygen differential aeration cell mechanism.

Very different corrosion behaviour was observed from a partially covered WBE surface exposed to a CO₂ saturated brine environment. As shown in Fig. 5a, positive galvanic currents concentrated mainly on areas uncovered by ‘O’ ring and sand, while cathodic currents distributed mainly over areas closer to CO₂ sparging tube. This is in good agreement with corrosion potential distribution map shown in Fig. 5b, which indicates that anodes were located on uncovered areas (more negative potentials). The fact that cathodes were located at areas close to CO₂ sparging tube suggests that nonuniform CO₂ distribution in solution probably played a key role in determining the potential distribution and cathode locations. This result suggests that UDC will not occur under this situation because the...
area under the sand behaved as cathode and thus no or little corrosion would occur. This result seems surprising; however, in fact it is in good agreement with our previous observation of CO₂ corrosion under an artificial crevice [21]. As shown in Fig. 5b, the potential difference between cathodic and anodic areas was relatively small (approximately 29 mV) that was probably insufficient to drive an anodic corrosion current under sand-covered areas because the sand behaved as a barrier to carbonic acid penetration and metal ion diffusion. This phenomenon requires further investigation and better understanding.

When inhibitor imidazoline was added into the brine solution, corrosion anodic and cathodic sites changed immediately. Fig. 6a–c shows typical galvanic current distribution maps obtained from a WBE surface that was partially covered by sand and was exposed to CO₂ saturated brine solution with imidazoline present. When 10 ppm (by weight) of imidazoline was added into the corrosion cell, corrosion anodes and cathodes quickly switched locations. As shown in Fig. 6a, corrosion anodes shifted to areas covered by ‘O’ ring and sand, while cathodes located mainly over the four corners where no sand was present. This is surprising and interesting since this result suggests that the addition of inhibitor initiated the formation of corrosion anode under the sand deposit, in other words, UDC was the result of inhibitor addition. When the concentration of imidazoline increased from 10 to
30 ppm the maximum corrosion anodic current, that indicates the most active anodic dissolution, did not decrease. In fact as shown in Fig. 6a–c the maximum anodic current value increased from 0.022 to 0.034 mA/cm². Anodic currents concentrated at the central areas of the sand deposit, indicating enhanced under-deposit localised corrosion. However, as shown in Fig. 7 the total anodic current, i.e. the sum of all anodic currents measured over the whole WBE surface, decreased significantly after the addition of imidazoline, suggesting that imidazoline reduced overall corrosion. This experiment illustrates the complexity of UDC and the effects of inhibitors.

Corrosion potential distribution map in Fig. 8 confirms that the addition of imidazoline significantly changed corrosion potential and its distribution over the WBE surface. The potential difference between cathodic and anodic areas is more than 250 mV with areas that have easy access to inhibitor as the cathode (−391 mV vs. 3 M Ag/AgCl). This potential difference (250 mV), which is significantly larger than that shown in Fig. 5b (29 mV), should be sufficient for driving galvanic currents to flow between inside and outside of the sand covered areas. The area under-deposit was forced to become anode, initiating UDC. This result was confirmed by weight-loss coupon tests. As shown in Fig. 9, corrosion occurred and focused on under-deposit area after 7 days of exposure of a corrosion coupon to CO₂ UDC conditions with 50 ppm imidazoline inhibitor present. This result appears to question the wisdom of using corrosion inhibitor of the type and concentrations for UDC prevention.

After testing inhibitor in a CO₂ saturated environment, CO₂ purging was stopped and air was allowed to enter the corrosion cell, i.e. O₂ contamination was introduced to the corrosion environment. As shown in Fig. 10, the size of anodic area decreased and corrosion concentrated on a smaller area under the sand deposit, leading to more localised corrosion. This phenomenon requires further investigation. Currently there is still a major lack of understanding on the mechanism of the localised corrosion that proceeds under various forms of deposits.

4. Conclusions

An electrochemically integrated multi-electrode array, namely the wire beam electrode has been successfully applied to measure
corrosion of mild steel under sand deposits. The effects of corrosion inhibitor imidazoline and oxygen contamination on the rates and patterns of under-deposit corrosion were evaluated by analysing the WBE galvanic current and corrosion potential distribution maps. It was found that no under-deposit corrosion occurred in a CO₂ saturated pure brine solution under ambient temperature; however, when inhibitor imidazoline was introduced to the brine or when the environment was contaminated by O₂ under-deposit corrosion initiated. Increase in imidazoline concentration was found to reduce overall corrosion rates; however, it enhanced localised corrosion.

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References

[1] NACE Task Group TG 380, Under Deposit Corrosion testing and mitigation methods, draft report distributed to members for review and comments (March 2009).