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ABSTRACT

Major field failures due to SRB's are often in the form of localized corrosion, involving hemispherical or shallow pits. In order to address this feature, a small and a large sample of the same carbon steel are preconditioned as an anode and a cathode, using a galvanostat. The stability of the freely corroding cell is then studied with a zero ammeter. This galvanic cell is shown to be stable in the presence of SRB's alone and unstable in sterile conditions, or in the presence of other strains.

1. INTRODUCTION

1.1. Existence and importance of bacterial pitting corrosion

In deaerated oilfield produced waters, the analysis of service failures and corrosion damage induced by sulfate-reducing bacteria (SRB's) shows that the most serious cases always involve localized corrosion (pitting). However, until now, all studies of bacterial corrosion have been based on measurements on carbon steel, expressed in mpy or millimetres per year, which implicitly assume the corrosion to be completely uniform.

Moreover, it has long been considered that the degree of the risk of corrosion should be directly related to the extent of the bacterial contamination, and this is now known not to be true. Indeed, there are cases both in service and in the laboratory (Freiter 1991) where almost negligible uniform corrosion rates are observed in spite of heavy contamination. Conversely, rapidly penetrating pits (1 cm/yr) have been observed for very low levels of bacterial contamination.

It obviously appears that some other factor must be involved in the relation between bacterial contamination and the risk of corrosion. By analogy with CO_2 corrosion in oil and gas wells (Crolet and Bonis 1991), this factor could well be the possibility of stabilizing a mechanism of localized attack, rather than the uniform corrosion process usually studied.

1.2. The nature of pitting corrosion

All forms of localized corrosion are based on the existence of galvanic coupling between the corroded zone and the unaffected surrounding metal (Crolet 1992a). The local depassivation of stainless steels is a well known example (Crolet 1979). However, the existence of a passive layer is by no means necessary. All that is required is the coexistence of two different surface conditions, one of which is significantly more protective than the other.

Furthermore, localized corrosion always involves a "nucleation and growth" type process. The nucleation phase is always due to some random external phenomenon, which temporarily destroys or destabilizes the local protective surface conditions. If mutual stabilization is possible between the galvanic current and the two different surface conditions, the development of local corrosion becomes the most stable process. In effect, the transitory creation of an anode and a cathode engenders a galvanic current, the presence of which can stabilize a difference in electrochemical properties between the two regions. If such a stabilization mechanism exists, then any small anode created by random fluctuations will tend to be maintained permanently in this condition, leading to the formation of a corrosion pit.

Experimentally, the nucleation stage is often very difficult to study in the laboratory, precisely because of its multiple and random character, together with the variable incubation times and the infinite variety of possible causes in service. It is thus perfectly possible that nucleation cannot be reproduced in the laboratory, whereas it must necessarily occur in service. It is therefore much surer to create a galvanic cell artificially between two surfaces, using a potentiostat or a galvanostat, and then to study the variation with time of the free galvanic current, after conversion of the potentiostat to a zero ammeter. This has already been done successfully in the case of CO_2 corrosion (Crolet and Bonis 1984), and was therefore applied to the study of SRB-induced pitting corrosion of plain carbon steel.

2. EXPERIMENTAL TECHNIQUES

The experimental set-up is composed of two metal cylinders of different diameter and surface area, taken from the same bar, separated by a teflon insulator ring. In these preliminary experiments, the metal used was C1020 grade mild steel, the surface areas being 4.37 cm^2 for the cathode and 0.037 cm^2 for the anode, i.e. a current density ratio of 118 between the anode and the cathode.

The anaerobic conditions necessary at the surfaces in the presence of SRB's were assumed to be generated under the biofilm by the presence of *Vibrio natriegens*, and/or by the cathodic protection, with the formation of a calcium and magnesium rich deposit. The low medium renewal rate also favoured the establishment of anaerobic conditions at the surfaces. Future studies could use this same set-up, but with an initially anaerobic medium.

Three populations of bacteria were used for the different experiments;

(a) the heterotrophic aerobic bacterium *Vibrio natriegens*, capable under particular conditions of secreting large amounts of polysaccharides on surfaces, together with organic acids resulting from its metabolism,

(b) the SRB *Desulfovibrio vulgaris*, which survives under aerobic conditions and proliferates in anaerobic environments,

(c) a combination of these two micro-organisms.

Cocultures of *Vibrio natriegens* and *Desulfovibrio vulgaris* have frequently been used in studies of bacterial corrosion, since the first strain generates conditions which promote growth of the second, in particular by creating an anaerobic environment at the metal surface.

In order to avoid excessive initial corrosion of the future anode, the cathodic surface was created by means of an inert auxiliary anode which polarized the large specimen to a potential of - 1.2 V/SCE, for a period of 2 hours. During this time interval, a uniform calcium and magnesium rich deposit, subsequently analyzed by X-ray diffraction, was formed on the surface.

The environment employed for the experiments was the ASTM (D1141) seawater medium, modified by the addition of 20 meq/l of sodium carbonate. After having mounted the specimens and electrodes in the various cells, the whole system was sterilized using ethylene oxide. The cells were then placed in the circulating medium, with a very low liquid renewal rate.

The free corrosion potentials and the galvanic current were monitored with the aid of a high input impedance millivoltmeter and a zero ammeter, both connected to a data logging unit. The current values were converted to anode current densities.

The microbiological analyses were performed by the epifluorescence technique, after scraping and ultrasonic cleaning of the surfaces, separating the anodic and cathodic regions.

3. RESULTS

The strong cathodic polarization of the large surface during the initial two hour period led to the formation of a calcium and magnesium rich deposit, which X-ray diffraction analyses showed to be composed of calcium carbonate in the form of aragonite, and magnesium hydroxide in the form of brucite. Scanning electron microscopy revealed the deposit to be uniform, with complete coverage of the cathode surface. This deposit was a consequence of the cathodic polarization, whose principal aim was to establish a cathode and an anode on the specimen.
The variation of the potentials immediately after interruption of the cathodic polarization indicates that the large surface effectively acts as the cathode and the small surface as the anode, a difference in free potential of about 20 to 40 mV being observed, depending on the specimens and the operating conditions.

3.1. First test series

In the first series of tests, the micro-organisms were injected after interruption of the cathodic polarization, i.e. after establishment of the residual galvanic current engendered by the initial artificial polarization. In the media inoculated with *Vibrio natriegens*, either singly or in combination with *Desulfovibrio vulgaris*, an immediate decrease in the galvanic current was observed, falling virtually to zero in a few hours (Figure 1). This was not the case for media contaminated with an SRB monoculture, for which the initial fall in current was followed by stabilization at a level of about 45 $\mu A/cm^2$ (i.e. an additional corrosion rate of 0.5 mm/yr for the anode).

The bacterial counts made on both the anodes and cathodes also reflect these two types of behaviour. When *Vibrio natriegens* is present, either alone or combined with *Desulfovibrio vulgaris*, the densities of bacteria are essentially identical on the anode and cathode (1×10^8 cells/cm^2 on the cathode and 2.2×10^8 cells/cm^2 on the anode for the monoculture, and 4.7×10^8 cells/cm^2 on the cathode and 3.9×10^8 cells/cm^2 on the anode for the coculture). However, when the SRB is present alone (Table 1A), a higher density of these micro-organisms is observed on the anode (1×10^6 cells/cm^2 on the cathode, compared to 4.7×10^7 cells/cm^2 on the anode).

3.2. Second test series

In the second test series, the micro-organisms were introduced *before* the initial cathodic polarization. The results were similar to those obtained in the previous tests, except that the corrosion current appears to be slightly higher when only SRB's are present, becoming stabilized at about 60 $\mu A/cm^2$ at the end of the experiment (Figure 2). The densities of bacteria are close to those observed in the first test series, with larger SRB concentrations again being observed at the anode in the case of the monoculture (Table 1B).

As in the first test series, in the sterile medium, the initial corrosion current rapidly decreases when the polarization is removed, and subsequently fluctuates slightly to either side of zero (Figure 2).

4. DISCUSSION

The experiments had two different aims :

(a) to demonstrate the feasability of the technique and to design a "prototype" applicable to all future circumstances;

(b) to perform preliminary studies in order to test certain ideas concerning the role of micro-organisms and the associated risk of corrosion.

Two micro-organisms were therefore chosen, including an aerobic bacterium, *Vibrio natriegens*, capable of producing significant quantities of polysaccharides and organic acids, and *Desulfovibrio vulgaris*, a sulfate-reducing bacterium, representing a metabolism whose role in biocorrosion phenomena is widely recognized. Tests were also performed using combinations of the two bacteria, since the production of large quantities of exopolymers and the metabolism of the aerobic strain could create favourable conditions for the growth of the accompanying SRB's.

The oxygen consumption due to rapid growth of the *Vibrio natriegens*, together with the low medium renewal rate, effectively contributed to the promotion of anaerobic conditions, enhancing the growth of SRB's on the metal surfaces. However, the development of the latter micro-organisms under initially aerobic conditions, when inoculated in the form of a monoculture, is more surprising. This rapid growth, indicated by bacterial densities greater than 10^7 cells/cm^2 measured on the metal surfaces, may have been stimulated by the low medium renewal rate and the initial cathodic polarization.

In effect, although the cathodic depolarization theory is now obsolete (Crolet 1992 b), this does not rule out the use by the SRB's of the hydrogen produced during cathodic polarization. Indeed, investigations of this phenomenon have clearly demonstrated the existence of a relation between the growth of these micro-organisms and the use of cathodic protection, which is accompanied by the liberation of hydrogen (Guezennec 1991). It was therefore appropriate to verify this point.

4.1. Effect of the chemistry of the medium

Under sterile conditions, the galvanic current engendered by the strong initial cathodic polarization rapidly falls to practically negligible values. Neither the basic chemistry of the sterile seawater, nor the initial cathodic polarization, nor the presence of calcium and magnesium rich deposits are therefore capable of stabilizing the galvanic coupling necessary for the growth of corrosion pits in a deaerated or partially aerated medium.

4.2. The effect of *Vibrio natriegens*

The results obtained in the two series of tests show that the presence and growth of *Vibrio natriegens* do not enable the initial galvanic coupling to be maintained. This bacterium can therefore only cause uniform corrosion, and can never lead to pitting attack.

The appearance of the specimens at the end of the experiments (heterogeneous corrosion at the anodes and cathodes), together with the essentially identical densities of bacteria observed on the two types of electrode, indicate simply that the initial surface condition of the specimens was irregular. Moreover, in these conditions, the presence of a calcium and magnesium rich deposit is not sufficient to protect the initial cathodic surface, since the bacterial metabolism, particularly the production of organic acids, leads to a partial and random dissolution of this layer. These observations have been verified in more specific experiments designed to study this particular aspect of the relation between cathodic protection and the effects of bacteria (Guezennec *et al.* 1992). Here again, the observation of surface morphologies shows that *Vibrio natriegens* and the mosaic structure of the biofilm lead essentially to uniform corrosion, even if it is not perfectly homogeneous.

4.3. Effect of *Desulfovibrio vulgaris*

When sulfate-reducing bacteria are present alone, the galvanic cell is maintained, and becomes stabilized between 45 and 60 $\mu A/cm^2$ at the end of the test, depending on the conditions. Bacteria counts on the two types of electrode reveal that the population of these micro-organisms is larger on the anode than on the cathode. This observation may be related to differences in the physical-chemical conditions, such as the pH, or the availability of ferrous ions, which is greater at the anode. A similar behaviour has also been noted during studies in the IFREMER laboratory on localized corrosion, biofilms and bacterial microcosms, and remains to be fully explained. The highest current density is obtained when the same SRB's are introduced into the medium before the establishment of cathodic polarization and the formation of calcium and magnesium rich deposits on the cathode. The growth of these anaerobic micro-organisms may then appear surprising, given the aerated nature of the initial medium. However, the SRB's can survive in the initially oxygen-rich medium and can develop significantly when the conditions subsequently become anaerobic.

It can be assumed that the cathodic polarization, even when applied for only a short time (2 to 3 hours), but at a very low potential (-1200 mV/SCE), was sufficient to promote the growth of these bacteria at the metal/solution interface. The presence of higher densities at the anode signifies that the conditions there are more favourable for their growth and survival. The maintenance of a significant galvanic current is therefore related to the higher concentration of SRB's at the anode, contrary to the majority of bacterial corrosion mechanisms proposed until now. The acceleration of the anodic reaction kinetics by sulfidation of the steel surface (Crolet 1992b) and the local acidification of the anodes in the presence of SRB's (Daumas *et al.* 1992), are thus much more satisfactory explanations.

The electrochemistry at the cathode, and the nature of the electrochemical reactions which occur there appear in this case to be much less important than was previously supposed. Indeed, this is not surprising, since the cathode is much larger than the anode, while the geometrical extension of the galvanic coupling is considerably greater at the cathode (Bardal *et al.* 1984). In effect, it is difficult to see how the electrochemistry of the cathode could be different with and without galvanic coupling, since, given the large area of the cathode, the current density is negligible.

Finally, as regards the potential role of hydrogen, it is clear that this must not be interpreted in terms of the impossible cathodic depolarization theory, but should be explained rather on the basis of a chemical specificity of the autotrophic metabolism (Crolet 1992b, Daumas *et al.* 1992).

4.4. The effect of culture combinations

In the presence of combinations of bacteria, a rapid drop in the galvanic current is again observed, the value falling to zero or becoming negligible after a few hours. If the SRB's are assumed to grow due to the initial cathodic polarization and the favourable environment generated by the *Vibrio natriegens*, then the latter micro-organisms appear to play a predominant role under the prevailing conditions, promoting the same more or less uniform corrosion over the whole of the specimen surface. Similar results were obtained whether the bacteria were injected before or after the initial cathodic polarization period.

However, the detailed mechanism involved in the effect of the bacteria combinations is not clear. It may simply be due to dilution, the chemistry of the metabolism of *Vibrio natriegens* overiding that of *Desulfovibrio vulgaris*. It could also be due to an interaction between the two metabolisms, *Vibrio natriegens* preventing the establishment of an autotrophic SRB metabolism, by supplying *Desulfovibrio vulgaris* with the necessary nutrients. The anode acidification process could then be considerably reduced (Daumas *et al.* 1992).

5. CONCLUSIONS

The present work is a very preliminary study, carried out in extremely imperfect conditions. Nevertheless, in spite of its shortcomings, it has led to 4 major results :

- SRB's stabilize pitting corrosion of plain carbon steel in deaerated waters, which is not the case for APB's;
- biofilms composed only of SRB's are more dangerous than mixed flora containing both SRB's and APB's;
- the value of the galvanic current established between the anode and cathode could represent a criterion for evaluating the risk of corrosion associated with bacterial contamination;
- the anode region constitutes the driving force for pitting corrosion, the cathode probably remaining unaffected (or very little changed) relative to the uniform corrosion.

Future work should consider initiation of galvanic coupling by imposing a direct polarization between the future anode and cathode, the use of fully deaerated media, and the evaluation of metabolisms whose chemistry has been recognized as being the most dangerous (Daumas *et al.* 1992). In this way, and in this way only, will it be possible some day to adapt antibacterial treatments to the real risks of biocorrosion.

Table 1 : Evolution of bacterial populations on the anodes and cathodes (cells/cm^2). Inoculation after (A) and before (B) cathodic polarization.

		V. natriegens	**Coculture**	*Desulfovibrio vulgaris*
A	Anode	$2.2\ 10^8$	$3.9\ 10^8$	$4.7\ 10^7$
	Cathode	$1\ 10^8$	$4.7\ 10^8$	$1\ 10^6$
B	Anode	$3.1\ 10^8$	$1.7\ 10^9$	$1.1\ 10^8$
	Cathode	$2.8\ 10^8$	$1.7\ 10^8$	$4.1\ 10^6$

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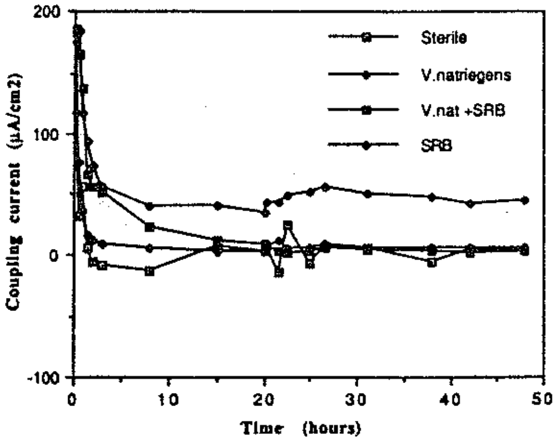

Figure 1: Evolution of the coupling current. Bacterial inoculation after cathodic polarization.

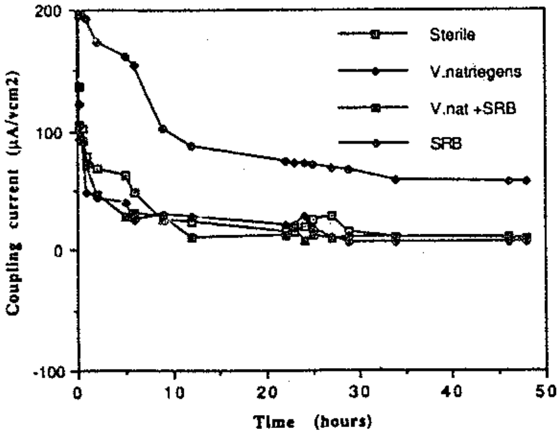

Figure 2: Evolution of the coupling current. Bacterial inoculation prior to cathodic polarization.