From biology and corrosion to biocorrosion

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ABSTRACT

The treatment of certain cases of corrosion in living environments involves the consideration of two quite different disciplines, namely biology and corrosion. Either one or the other will be preponderant, according to the problem and the circumstances, and the two aspects are not necessarily permanently interdependent.

Since the difficulties inherent in any multidisciplinary research are particularly pronounced for two such disparate fields, training and information exchange are of paramount importance. The need to harmonize terminology and concepts signifies, for the biologists, the use of a more chemically precise vocabulary and the abandonment of certain outdated theories, such as the notion of "cathodic depolarization", which are incompatible with modem electrochemical ideas.

Until now, no specific mechanism of biological corrosion has yet been identified, the phenomenon being simply associated with particular local chemistries of living corrosive media. The most useful contribution of the biologists would be accurately to describe this chemistry, in terms that meet the requirements of the corrosion engineer. In particular, the precise quantification of bacterial metabolisms would be especially appreciated.

While the generic term "biocorrosion" has become highly topical, it also incorporates past misunderstandings. The less ambitious expression "corrosion in living media", which conforms more closely to reality, would be certainly more reasonable.


RÉSUMÉ

De biologie et corrosion à biocorrosion

La résolution de certains cas de corrosion en milieux vivants nécessite de prendre en compte deux disciplines tout à fait différentes, à savoir la biologie et la corrosion. Selon les problèmes et les circonstances, l'une ou l'autre sera prépondérante, et les deux aspects ne sont pas nécessairement imbriqués en permanence.

Les difficultés inhérentes à toute approche pluridisciplinaire sont particulièrement marquées dans le cas de domaines aussi séparés. La formation et l'information mutuelle prennent donc ici une importance toute particulière, avec notamment la nécessité d'harmoniser les concepts et la terminologie. Pour les biologistes, ceci implique l'utilisation d'un vocabulaire chimique plus précis, et l'abandon de certaines théories obsolètes, comme la notion de «dépolarisation cathodique», totalement incompatible avec l'électrochimie moderne.

Jusqu'à présent, aucun mécanisme spécifique de corrosion biologique n'a jamais été identifié, et les phénomènes observés sont simplement dus à des modifications de la chimie locale des milieux corrosifs vivants. La meilleure contribution des
biologists would then be able to describe this chemistry with precision, and in the terms necessary for the corrosion engineer. In particular, a quantification precise of the metabolic processes necessary for the corrosion engineer would be very useful.

Moreover, if the term “biocorrosion” is becoming more and more common in recent years, it will remain (Defranoux and Hache, 1974).

In this field, the distinction has long been made between the “sea”, i.e. unadapted to present representations of corrosion mechanisms. The old literature is thus extremely polluted, and as the result of a combination of quotations and bad reading, this pollution has unfortunately been perpetuated up to the present day. For anyone who is not thoroughly versed, not only in the science of corrosion, but also in its history, it is consequently quite difficult to sort the wheat from the chaff. Furthermore, the understanding of corrosion has advanced along parallel paths in many different industries. Thus, knowledge which can be used today to understand certain types of bacterial corrosion has not necessarily been acquired in this explicit area. Such information is then completely inaccessible to modern methods of computer-assisted bibliography.

Finally, neither corrosion nor biology are simple sciences, and this has led to many mysteries that have resisted investigation over the years. Inexplicable interactions between the living and mineral kingdoms have thus exerted an almost metaphysical attraction on generations of research workers. There remains today a permanent temptation to attribute differences in corrosivity observed in living media to corrosion mechanisms specific to this environment (Molica, 1990). In fact, until now, no specific mechanism has ever been detected, but merely an often surprising and paradoxical chemistry particular to living media.

The weight of the problems

Beyond a quite legitimate professional interest, corrosion studies are not undertaken for pleasure, but out of necessity. The manner in which the problems are perceived is therefore not independent of the solutions available, and the latter depend in their turn on the industrial and economic context (the degrees of freedom are not infinite). They also depend on the difficulties and technological limits which may be encountered.

Consequently, the perception of “biocorrosion” is totally different according to whether it must be counteracted via the resistance of a material or through control of the biology of a medium. In the former case, the contribution of biologists will often be small, being strictly conditioned by the needs expressed by the corrosion engineers. On the contrary, in the latter case, the role of the biologists will be decisive, although it will often tend to be focused on toxicological aspects far removed from the original corrosion problem (Magot, 1990).

Past misunderstandings will be dissipated only through an extensive exchange of information between the two spiritual families of corrosion engineers and biologists. It is in this context that the present article aims to illustrate, for the use of biologists, what are the real needs of the corrosion engineers, and what they know today. This will be attempted on the basis of two well known examples, marine corrosion of stainless steels and the corrosion of carbon steels by sulphate-reducing bacteria.
The pollution of ports, the eutrophication of lagoons, and marine sediments lead to the formation of H$_2$S or bacterial sulphides, depending on the local pH.

**Pitting corrosion in sea water**

It is recalled that, in this case, the resistance criterion for stainless steel is the difference between the free potential and a critical "pitting" potential (Crolet, 1976a). The increase in the free potential in living sea water was recognized at an early stage (Defranoux, 1964), and rapidly attributed to the presence of a biofilm. The complex life in the biofilm was not analyzed in detail, this not being considered necessary at the time. While biofilms are perhaps better understood today, corrosion specialists still do not require this information. In effect, it is not the film itself, but the resulting potential which affects the initiation of pits. Indeed, corrosion engineers systematically limit their attention to the oxidizing power of the environments which they encounter, and the resulting free potentials. These electrochemical data have the advantage of being directly and easily measurable. Any phenomena situated upstream of these parameters are often of only a qualitative interest, and are not really necessary to the solution of the problem.

It may even be said that the free potential is not only the sole characteristic of the biofilm which needs to be known, but also the quickest and cheapest to measure. In any case, given the low intrinsic reproducibility of a biofilm, detailed biological characterization would prove to be of no practical service.

**Crevice corrosion under barnacles**

Stainless steels show excellent resistance to marine fouling, with the unfortunate exception of barnacles (Defranoux and Hache, 1974; Crolet et al., 1977a). In effect, the latter promote crevice corrosion, even in such highly alloyed grades as AISI 316.

This phenomenon is due to the change in the composition of the unrenewed medium within interstices (Crolet and Defranoux, 1973). The resistance criterion for stainless steel is its depassivation pH (Crolet, 1976a). The criterion for the severity of a crevice would be its thickness (Crolet and Defranoux, 1973), at least, if this could be defined and inspected. However, even under apparently well defined conditions, as - for example - with a rubber seal, it has never been possible to apply any detailed model to crevice corrosion, let alone for conditions as variable as those associated with a living organism.

In fact, a barnacle is no more than a shelled sucker, and its specific severity can be no more readily defined than that of a real rubber sucker (Oldfield and Sutton, 1980; Watson and Postlethwaite, 1990). Indeed, marine fouling deposits are not reproducible, either from one place to another, or even from one year to the next in a given locality (Crolet et al., 1977a).

**Corrosion in polluted sea water**

The pollution of ports, the eutrophication of lagoons, and marine sediments lead to the formation of H$_2$S or bacterial sulphides, depending on the local pH. The effect of sulphur-containing species on depassivation in chloride-rich media is well known (Crolet et al., 1977b). It is thus normal that the biological generation of H$_2$S should modify the local severity of marine corrosion as regards stainless steels (Molica, 1990), in the same manner as it does for zinc (Mor et al., 1974) or copper (Mor and Beccaria, 1978).

However, the role of sulphur-containing species has been known for only fourteen years and was discovered in a completely different context. Any previous or contemporary publication was therefore justified in seeking, imagining or quoting specific "biocorrosion" mechanisms. Today, the truth is much more prosaic: biological phenomena modify the local chemistry of the corrosive medium. While this H$_2$S pollution can markedly affect the amplitude of the corrosion phenomena, it does not fundamentally change their nature.

**Summary**

In the three examples presented above, independent "biological corrosion" mechanisms are never involved, the observed effects being simply related to biologically-induced variations in the electrochemistry, geometry, or real chemistry of the chloride-bearing corrosive medium. These variations can be analyzed or dissected for each individual case. However, as long as they cannot be accurately and reproducibly defined, their fine biological specificities will be of no avail in the daily struggle against corrosion.

The marine corrosion of stainless steels is therefore likely to remain for a long time a strictly corrosion issue. It will simply be recalled that the sea and living sea water are different from sterile sea water. Biological phenomena will be of no further concern, either for the study of the problem or for the choice of materials.

Conversely, the biological solution of the problem (e.g. chlorination of seawater) in fact has a chemical action on corrosion, by modifying the corrosive medium in the opposite manner. However, the toxicological processes involved and the possible difficulty of treatment are totally independent of the mechanisms of the corrosion itself.

In general, the situation thus comprises either a corrosion problem, involving the choice of stainless steels resistant to marine attack, or a biology problem implying the selection of suitable sterilization procedures. However, in neither case is there any real necessity for technical integration of the two disciplines.

To the extent that such corrosion in living media remains a matter either essentially of corrosion or primarily of biology, it is perhaps overly ambitious to designate it by the term "biocorrosion".

**CORROSION OF CARBON STEELS BY SULPHATE-REDUCING BACTERIA**

**Generic mechanism**

This particular type of bacterial corrosion has been known since the beginning of the century (Guezenec, 1990), but
the corrosion data necessary for its understanding have only been available for some fifteen years. Moreover, since those data were originally published in a company journal (Süry and Weber, 1973), and subsequently in the context of surface physics (Oudar et al., 1974; Marcus et al., 1975) or of pickling and the corrosion resistance of sulphurized stainless steels (Crolet et al., 1977 b; Crolet, 1976 b), their existence and importance completely escaped the attention of biologists preoccupied by bacterial corrosion.

Furthermore, the mystery of corrosion by sulphate-reducing bacteria [SRB (sulphate-reducing bacteria)] was elucidated quite abruptly, with no specific intention on the part of the authors concerned (Süry and Weber, 1973; Oudar et al., 1974; Marcus et al., 1975; Crolet, 1976 b). Indeed, the basic question suddenly became so trivial that no one even bothered to discuss it in writing. The surprising and sudden nature of the solution merely made it a subject of lively anecdotes in the lobbies of several subsequent conferences. This was evidently insufficient, but fortunately the omission was rapidly rectified (Salvarezza and Videla, 1980; Salvarezza et al., 1983).

What then is effectively involved? All SRBs are described by biologists as producing greater or lesser amounts of CO₂, organic acids and H₂S (Donham et al., 1976). Now, in acid media, traces of H₂S are an extraordinary catalyst of all anodic dissolution kinetics (Süry and Weber, 1973; Oudar et al., 1974; Marcus et al., 1975; Crolet, 1976 b). The metal surface beneath a bacterial canker thus constitutes a local anode during galvanic coupling with the surrounding surface. The dissolution rate at this anode is so much higher than in the adjacent regions that there is no reason whatsoever to seek any other explanation of the corrosion phenomena which occur on four different and unrelated scales, viz:

- the macroscopic scale: hole diameter ~ 1 mm;
- the microscopic scale: SRB dimensions ~ μm (= 10⁻³ mm);
- the atomic scale: H⁺ ionic diameter ~ 1 Å (= 10⁻⁷ mm); and
- the quantum scale: electron diameter ~ 10⁻¹ⁱ mm.

The physical laws and concepts are not the same on each scale, and it is important not to mix them together. In particular, the conduction electrons in a metal can no longer be considered as particles, being totally delocalized waves (Fermi cloud). Thus, in the metallic phase, the differences in potential are infinitely small and charge transport is infinitely rapid compared to their equivalents in solution. Indeed, the real effects of current circulation occur in the solution, involving interactions with the drop in resistance or the diffusion of ions (Crolet, 1988). Moreover, it is always in the solution that the difficulty arises in the mathematical modelling of galvanic coupling between two adjacent surfaces (Bardai et al., 1984).

In summary, the Figure is an excellent picture, since it is simple, but a very bad model, because it is simplistic.

"Cathodic depolarization"

The overall reaction for the corrosion of iron in neutral deaerated water is given by:

\[
\text{Fe} + 2 \text{H}_2\text{O} \rightarrow \text{Fe}^{++} + 2 \text{OH}^- + \text{H}_2
\]  

By definition, a corrosion reaction is obviously not an equilibrium phenomenon. It is even profoundly irreversible, in so far as the reverse electrodeposition reaction is totally inaccessible in a conventional corrosive medium. Nevertheless, probably for historical reasons, many corrosion courses still begin with chemical thermodynamics,
and with the study of equilibrium at the two types of electrode. It frequently ensues that the fundamental irreversibility of reaction (1) is not fully grasped, and that Le Chatelier’s equilibrium law is abusively applied to it. However, with the exception of extraneous phenomena such as the precipitation of corrosion deposits, or the elimination of a possible gas layer isolating the metal from the liquid, charging the corrosive medium with ferrous ions will never decrease the corrosion rate of iron, any more than hydrogen stripping will accelerate it.

From a purely pedagogical standpoint, this psychological stumbling block can now easily be avoided by introducing corrosion concepts in terms of the direct physical description of the respective atomic structures of a metal and an electrolyte (Crolet, 1975).

Historically, the theory of cathodic depolarization was introduced for the first time by Von Wolzogen Kuhr (VWK) in 1934 (Von Wolzogen Kuhr and Van der Vlugt, 1934). This theory assumes that, by removing the hydrogen produced in reaction (1), the SRBs could accelerate the corrosion of iron, and the 1934 reference continues to be quoted up to the present day in biology publications, without the slightest hint of criticism.

However, it should be realized that, at the time when this theory was put forward, corrosion studies were steeped in a gigantic historical error, subsequently designated as the “Nernstian hiatus” (Bockris and Reddy, 1970, chapter 1; Defranoux, 1974), which consisted in reasoning in terms of equilibrium on phenomena which in fact were purely kinetic. Errors persist to this day concerning the notion of the intrinsic “nobleness” of materials or of “galvanic series” of standard potentials (Defranoux, 1974; Shreir, 1976).

Historically, VWK (Von Wolzogen Kuhr and Van der Vlugt, 1934) was thus perfectly justified in proposing his explanation of bacterial corrosion by SRBs. In effect, modern kinetic concepts first appeared only in 1925, with the Evans diagram (Evans, 1929), and developed only very slowly up to the Second World War (Wagner and Traud, 1938). With hindsight (Pourbaix, 1974), it can even be said that corrosion emerged from the Nernstian hiatus only in 1949, with the creation of the CITCE (French acronym for “International Committee of Electrochemical Thermodynamics and Kinetics”), which in 1970 became the present-day International Society for Electrochemistry.

In comparison with the case at the time of VWK, the thermodynamics of irreversible phenomena today tells us that polarization is the expression of the “creation of entropy” (Defranoux, 1974), i.e. of the irreversible nature of both the anodic and cathodic reaction kinetics (Bockris and Reddy, 1970; Defranoux, 1974).

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{++} + 2 \text{e}^- \\
2 \text{H}_2\text{O} + 2 \text{e}^- & \rightarrow 2 \text{OH}^- + \text{H}_2 
\end{align*}
\]

(2)

(3)

In effect, an electrochemical reaction can have no net flux at its equilibrium potential. For an electrochemical current to pass, there must be an electrode overpotential, which increases with the strength of the current.

Moreover, in media where the reverse reactions are inaccessible, the very notion of overpotential becomes as fictitious as that of equilibrium potential. It would therefore be more exact to say that, because of the thermal activation of the kinetics, the slope of a polarization curve expressed, for example, in mV per decade (in U-log i coordinates), cannot be equal to zero.

In fact, the relative position of the cathodic polarization curve defines the “oxidizing power” of the corrosive medium (Crolet, 1976 a), but this quantitative concept is not directly related to the qualitative notion of polarization. Furthermore, it is also known today that equation (3) is the overall sum of a series of elementary reactions involving intermediate absorbed species of all kinds. In the steady-state regime, the common rate for this series of reactions is determined by the slowest step in the chain (Bockris and Reddy, 1970; Defranoux, 1974). Anything which happens before this step can thus affect the rate, whereas anything which occurs after it can have no retroactive effect (Bockris and Reddy, 1970, chapter 7). Consequently, neither the polarization of the cathodic reaction, nor the reaction itself, can be modified by eliminating the final reaction product.

Finally, it is known that the anodic and cathodic reactions can be superimposed at all points on both the macro and even microscopic scale (Bockris and Reddy, 1970, chapter 11). The local anodes and cathodes are simply the result of a localized imbalance between the rates of these two types of reaction, but in no way represent a strict geographic separation.

Similarly, it is not necessary to imagine mythical and invisible microcells to explain the uniform corrosion phenomenon.

To conclude, any interpretation of a corrosion phenomenon must be compatible with current knowledge of physics and electrochemistry. In this field, the excellent book by Bockris and Reddy is strongly recommended. As regards our present concerns, the cathodic depolarization theory must consequently be consigned to oblivion, along with all other such “false good ideas”. It could have provided an explanation, but in fact it can’t (Videla, 1988).
**Improper terminology and unbalanced chemical equations**

In chemistry, since Lavoisier and Dalton, unbalanced chemical equations have no great meaning, and any student forgetting this is likely to encounter serious problems at examination time. Moreover, it is usual to designate each chemical species by a precise name. There is even an official international nomenclature, to avoid any error or deviation in vocabulary. For example, acetic acid is a different species from the acetate ion or the sodium acetate salt.

However, in biology, habits are different. In effect, most experiments take place in a medium which is strongly buffered with regard to the production or consumption of acidity. From this viewpoint, bacterial metabolism is not studied in a closed medium, but in one which is open to the buffer. This does not facilitate the study of the matter balances, and necessarily renders the equations more difficult to balance.

Furthermore, biochemistry and physiology are above all concerned with the role of radicals in the metabolism. For instance, experiments will follow the overall outcome of the acid, the salt and the ion. In all the biology journals, this is quite systematic (Gounot, 1990). Habits are even so firmly anchored as to escape the vigilance of a journal such as "Corrosion Science" (Daumas et al., 1988).

Now, it is clear that acidity and pH are fundamental notions in corrosion, particularly in the presence of weak organic acids, or of CO₂ and H₂S (Crolet and Bonis, 1984; Crolet and Bonis, 1990). From this standpoint in particular, acetic acid and acetate are not merely different, but strictly opposite. If acetic acid acidifies, the acetate represents on the contrary an alkalinity. In effect, it buffers the medium, and prevents acidification when H⁺ ions are added. Consequently, for corrosion applications, all biology publications on bacterial metabolisms must be read with the greatest care, and all the information must be deciphered in the light of the prevailing linguistic conventions.

This means that any thorough technical integration of the two disciplines, biology and corrosion, would require prior harmonization of the language and concepts employed, on the basis of official international usage.

**The role of hydrogenase**

On re-reading the original biological publications on the SRBs, or the review articles, the points described in the last paragraph ("The outmoded ideas to be eliminated") are unfailingly encountered [Pankhania (1988) even quite innocently writes equations (2) and (3) with a double arrow]. If it is attempted a posteriori to balance the equations which represent the metabolism, the following general form is obtained:

\[
\text{SRB} \quad \text{SO}_4^{2-} + \text{nutrient} \rightarrow \text{HS}^- + \text{HCO}_3^- + \alpha \text{H}^+ \quad (4)
\]

where \( \alpha \) varies from 0 to 1/3 depending on the strain of SRB and the nutrient. In biological language, equation (4) represents a production of "\( \text{CO}_2 \) and \( \text{H}_2\text{S} \)". In corrosion language, it is simply a question of hydrocarbonate (= bicarbonate) and hydro sulphide.

On the other hand, if the SRBs do not perhaps acidify to the extent assumed up to now, the local precipitation of corrosion product certainly constitutes a powerful acidification mechanism:

\[
\text{Fe}^{++} + \text{HS}^- \rightarrow \text{FeS} + \text{H}^+ \quad (5)
\]

If not only the corrosion facets (see paragraph "The "hole" model") of bacterial corrosion are revised, but also the biochemical aspects (see paragraph "Improper terminology and unbalanced chemical equations"), it is seen that the canker in the Figure is probably not even impregnated by the direct metabolite, but rather by a modified version of it. In fact, the bacterial corrosion canker appears to be essentially composed of acid corrosion products, sulphidized by the SRBs.

In the presence of sulphides and water, the Fe⁺⁺ ions finally lead to the formation of H⁺ ions, exactly like the Cr⁺⁺ ions in the pits on stainless steels (Crolet et al., 1977 c). The analogy between SRB attack and pitting corrosion is therefore even stronger than was already apparent in the paragraph "The "hole" model". At this stage, it is clear that the value of \( \alpha \) in equation (4) plays a decisive role in the initiation of the acidifying chain reaction (Crolet et al., 1977 c). It is equally evident that \( \alpha \) will depend on the manner in which each strain metabolizes the hydrogen.

The well known effect of hydrogenase thus seems to be due rather to an indirect influence on the initiation of acidification, or on the sensitivity of the metabolic activity to the ambient pH; but in this regard, direct corrosion experimentation is difficult to envisage. Indeed, the systematic quantification of the bacterial metabolisms, species by species, would appear to be a much more promising approach, and could be useful for applications other than bacterial corrosion.

**CONCLUSIONS**

Corrosion and biology constitute two different disciplines, with separate developments, but from time to time they must be combined to solve problems of corrosion in living environments. Depending on the type of problem and the circumstances, one or the other will predominate, and a full permanent technical integration is not necessary. Between two such disparate fields, the usual difficulties of multidisciplinarity are especially pronounced, and the need for appropriate training and mutual information is particularly acute. However, such exchanges require prior harmonization of the vocabulary, concepts and literature base. The intended contribution of the present article is to specify the precise chemical nature of the phenomenon, to encourage the abandonment of the outdated "cathodic depolarization" theory and to recommend certain sources of good reading.
If corrosion engineers and biologists endeavour to be honest, they will realize that there are never, in fact, specific biological corrosion mechanisms, i.e. ones in which the life processes intervene directly in one or other of the two basic corrosion reactions. Corrosion in living environments involves exactly the same electrochemical processes as the phenomenon which occurs in sterile media. What happens is simply that the real local chemistry in the presence of living organisms is frequently suprising, or even paradoxical, and often profoundly different from that in the equivalent sterile medium. Moreover, living environments are not the only corrosive media in which the real local chemistry is poorly appreciated. In the chemical industry, certain process reactions can also lead to paradoxical local situations, which are far from being fully understood (Crolet and Robert, 1990).

In these conditions, the most useful contribution of the biologists is certainly not to carry out "biocorrosion" studies in the place of the corrosion specialists, but rather to provide the latter with an accurate description of the chemistry of living corrosive media, in scientifically accurate terms, based on the parameters normally involved in corrosion. In the field of microbiology, a precise quantification of the metabolism of the different species of SRB would be particularly appreciated, and would perhaps lead to a final explanation of the well known role of the hydrogenase.

In this context, while the term "biocorrosion" has become topical and popular, it helps to perpetuate certain unfortunate misunderstandings. The expression "corrosion in living media", which conforms more closely to reality, would certainly be more reasonable.

REFERENCES


