

Corrosion at the Steel–Medium Interface

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Contributor: Robert E. Melchers

Corrosion on the interface between a metal alloy, such as steel, and a wet, permeable non-metallic medium is of considerable practical interest. Examples include the interface between steel and water, the atmosphere or concrete, as for steel reinforcement bars; between metal and soil, as for buried cast iron or steel pipes; deposits of some type, as in under-deposit corrosion; and the interface with insulation, protective coatings, or macro- or micro-biological agents. In all cases, corrosion initiation depends on the characteristics of the interfacial zone, both of the metal and the medium, and the spatial variability. For (near-)homogeneous semi-infinite media with good interfacial contact, the pitting, crevices and general corrosion of the metal will be largely controlled by the metal (micro-)characteristics, including its inclusions, imperfections and surface roughness.

Keywords: steel ; soil ; concrete ; deposits ; homogeneity ; long-term

1. Introduction

Corrosion is usually considered a process that involves the properties and characteristics of the interface between, on the one side, a metal or alloy and, on the other side, some external environment, such as the atmosphere; water; other fluid; or some, perhaps permeable, solid material, either of finite thickness or approximated as semi-infinite. The latter may be collectively classed as examples of different ‘media’ in interfacial contact with a metal or alloy. For simplicity, the discussion herein is limited to steel and non-metallic media. The latter includes water, the atmosphere or concrete, as for steel reinforcement bars; soil, as for buried cast iron or steel pipes; deposits of some type, as in under-deposit corrosion; insulation, as in corrosion under insulation or protective coatings; or macro- or micro-biological agents in contact with the steel. Galvanic corrosion between the medium and the steel is not considered, nor is cathodic protection for which modern perspectives have become available ^{[1][2]}. In passing, some remarks are also made about alloys other than steel and metallic media.

As might be expected, the interface between the steel and the medium plays a critical role in the initiation and subsequent development of corrosion. That role changes somewhat with the development of corrosion products on the interface and the change from oxygen reduction to hydrogen evolution as the main cathodic reaction. It will become evident that there is a degree of duality in the roles played by the steel and the medium for corrosion at the interface. Noting that the common forms of corrosion, such as ‘uniform, general, pitting, crevice and under-deposit’, ultimately all have the same underlying mechanism—a difference in potential—it is shown that the differences between the steel and the medium, at least for shorter-term corrosion, are the result of local circumstances and scale. These may drive the total amount of corrosion in the early stages, with carry-over effects to later times, but as the corrosion progresses, these earlier influences become less important, and the longer-term rates of corrosion are barely affected by them. Improved understanding of these relationships exposes a degree of unity and will contribute to improving the modelling of the development of the longer-term corrosion behaviour relevant to many infrastructure applications. It also should shed new light on the mechanisms involved in specific industry-related corrosion problems, such as corrosion in soils, under protective coatings and under insulation.

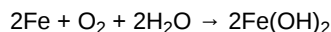
2. Classical Models for Corrosion Initiation and Early Development

2.1. ‘Pure’ Metal in Contact with a Wet Homogeneous (Pure) Medium

For a pure metal in pure water, the possibility of whether corrosion of a metal will occur depends, in the terminology of physical chemistry, on the net (Gibbs) free energy (ΔG) of the reactants potentially involved—in other words, there must be a release of energy for the reaction to proceed. Conventionally, this is denoted by $\Delta G < 0$, indicating the reaction, as written and for which ΔG was derived, is thermodynamically feasible. This condition on equilibrium thermodynamics provides no information about what happens immediately after the reaction commences or the speed of the reaction. It

also provides no information about the destination or fate of the reaction products. As will be seen, the latter is probably the most important aspect of practical infrastructure-related corrosion problems.

For ferrous corrosion, the reaction of interest is that for (pure) iron in (pure oxygenated) water at neutral pH:



As it stands, this is simply a chemical reaction. There can be a transfer of electrons from iron as the electron donor ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$) to oxygen as the electron acceptor ($\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$). This takes place across the interface, with the electrons being transferred from one substance to the other without a specific electron flow, that is, without a corrosion current. It is facilitated by the intimate contact between the components in (1). Further, for ideal materials, implying a perfect interface, there should be no preferential location for Reaction (1)—thus the reaction should, in theory, occur all over the metal surface exposed everywhere to water and oxygen. Thus, the possibility of localized effects is excluded.

As soon as Reaction (1) proceeds, however, the situation changes since the corrosion products are likely to form a barrier at the interface, reducing the access of O_2 and H_2O to the metal surface. For the reaction to continue, it is necessary for these to diffuse through the corrosion products while electron transfer continues by direct contact at the (slowly changing) interface. Except in an ideal situation, it is likely that the corrosion products that form will not do so in an ideal manner but instead form a spatially imperfect, non-uniform and inhomogeneous layer. In an advanced form, this can be seen, for example, in atmospheric rusts [3] (p. 408). It follows that it is likely that the diffusion processes required for the continuation of Reaction (1) will also be non-uniform across the surface. While in the early stages, concentration polarization (or control) is the likely rate-controlling step [3] (p. 84) rather than diffusion, it does mean that the necessary conditions for corrosion as conventionally understood arise very quickly, even before attention is turned to the non-homogeneities of the materials.

It is useful to note that the estimation of ΔG for a particular reaction requires the form of that reaction to be known and to be stoichiometrically correct. In general, the estimation of ΔG requires knowledge of the entropy and the enthalpy (of formation) of each of the potential components in the reaction, as well as the temperature T at which the reaction is expected to operate. For a wide variety of substances (solids, liquids, gases, solutions, elements, compounds), the values for entropy, enthalpy and free energy are available [4]. These values are based on experimental observations for what are assumed to be pure substances, i.e., they contain no alloying elements or inclusions or defects, such as cracks.

For corrosion work, it is more conventional to work with electrochemical potential E . These have also been tabulated [3]. Theoretically, E is related to ΔG by $\Delta G = -nFE$, where n is the number of electrons (or equivalents) exchanged in the reaction and F is Faraday's constant (96,500 coulombs per equivalent). It follows from the relationship between E and ΔG that the same limitations apply to E as apply to ΔG , including that it applies to a uniform interface surface and that it applies to pure substances. Thus, the well-known Pourbaix diagrams, such as for ferrous iron in water, in principle are for pure Fe in pure H_2O , although in practice, these diagrams are based directly on experimental results [3][5].

While pure or triply distilled water (TDW) is readily obtainable and has been used for various experiments to observe the corrosion and corrosion pitting of steel [6], it is not typical of practical applications. Similarly, pure iron is not typical for most infrastructure, although it does have certain industrial applications. It is difficult to obtain and it is expensive. For example, so-called 'Abiko' ultra high pure (UHP) iron has 99.99997 wt% purity [7][8] and is obtained using vacuum-refining of conventional electrolytic iron that is typically 99.9 wt% pure. (UHP iron is expensive—around AUD 4000/tonne for 99.95 wt% pure iron and AUD 100,000–200,000/tonne for 99.9997 wt% [9]). Besides their low content of impurities, these UHP irons typically have very small grain sizes ($<1\text{ }\mu\text{m}$) and are very smooth with shiny exterior surfaces, which is attributed to the slow solidification during manufacture. However, highly inhomogeneous grain structures also have been noted, with, in some cases, grain sizes reaching up to 1–2 mm in diameter and up to 10 mm in length [10]. Despite their many grain boundaries and their wide diversity in grain size, very low rates of corrosion, including pitting corrosion, were observed for UHP irons, even in low-pH environments, such as hydrochloric acid [9][11]. The immediate conclusion is that grain size and grain complexity are not, in themselves, drivers for corrosion, which is likely attributable to the very slight differences in the electrochemical potential that would be associated with grain boundaries.

The electrochemical potential E (or ΔG) provides information only about whether the reaction as postulated is thermodynamically feasible—it tells nothing about whether it will actually occur and, if so, at what rate. This is well known, but sometimes forgotten is that as soon as the reaction(s) occurs, the environment at the corrosion interface changes—there are now corrosion products. In principle, these need to be considered for a (thermodynamic) assessment of the possibility of any further reaction. Thus, the reaction itself changes the conditions from the initial state immediately upon commencement of the corrosion process.

2.2. Practical Metals and a Wet Homogeneous (Pure) Medium

The ideal system described above will reach equilibrium very quickly unless the corrosion products are carried away, such as by diffusion away from the metal surface; by a current; or, for one reason or another, they are deposited somewhere else. This latter possibility leads directly to the notion of conventional electrochemical corrosion, with corrosion products depositing at cathodic regions and not depositing at other regions—the anodic regions. They can come about only through some sufficiently large perturbation(s) ΔE of local electrochemical potential over the corrosion interface (**Figure 1**). This immediately implies non-uniform interfacial surface conditions. Given the comments above, the grain size per se is not an obvious issue—other aspects, such as inclusions and metal surface topology, are relevant.

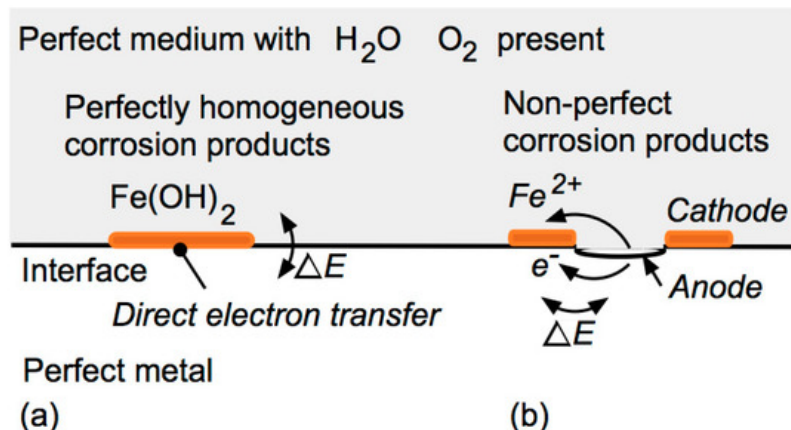


Figure 1. Perfect metal and perfect medium with H₂O and O₂ available: (a) physical-chemical reaction with direct electron transfer at interface and (b) electrochemical reaction set up by imperfect corrosion products, potential perturbation(s) ΔE , and electron flow between anode and cathode.

Practical irons (and steels) typically contain inclusions (or impurities) as a result of the normal commercial iron-making processes [12]. Most often associated with the pitting of commercial steels are MnS inclusions, which were at one time present at a relatively high proportion, but in modern steels at much lower concentrations and typically smaller in size. The corrosion mechanism involved is essentially galvanic with, for mild steels, the MnS being slightly cathodic to the surrounding iron that corrodes (ideally) in an annular region around the inclusion and within the inclusion for stainless steels [13].

Topographical differences across surfaces, such as geometrical imperfections and patchy rust or other deposits, including biofilms, can have the same basic effect—they can set up local potential perturbation(s) ΔE in what is conventionally termed a 'differential aeration' effect, although strictly speaking, this implies differences in oxygen as the electron acceptor. More generally oxygen need not be involved. It can be any situation or reaction that sets up conditions to enable electron transfer from one part of the metal surface to another. One example is electron acceptance in the hydrogen evolution reaction, which is the usual cathodic reaction under acidic pH conditions [3] (pp. 6–8).

Early work on iron and zinc surfaces, as summarized by Evans [14] (pp. 108–113), noted that geometrical defects and scratch lines are sources for the initiation of localized corrosion, even though the potential differences involved are almost certainly small. The effect carries on for longer-term exposures (years) and also at a larger scale (i.e., as 'surface roughness'), as shown experimentally for commercially rolled mild and low alloy steels exposed to natural coastal seawater [15].

2.3. Effect of Chlorides in a Wet Homogeneous Medium

One important aspect of the controlled experimental observations reported by Mercer and Lombard [6] (1995) is that steel corrosion in several different immersion environments was investigated. Contrary to the often-stated proposition that pitting requires a chloride or a sulphate salt to help lower the pH under a rust blister or at an inclusion sufficient for pitting initiation to occur [14] (pp. 118–120) [16], for mild steels, Mercer and Lombard [6] also reported pitting initiation (and subsequent development) in fresh water. In all cases, pitting corrosion continued to occur and increased in depth with longer exposures. Importantly, in near-stagnant conditions, the concentration of chlorides had little or no effect on the overall corrosion. Also, the severity of corrosion, both pitting and mass loss, increased with increased stirring of the solution. These findings imply that for corrosion interfaces that are in some way protected, such as under built-up rusts or within pits, the chloride concentration has little or no effect, confirming an earlier proposition by Foley [17][18] and confirming what were once hotly disputed experimental results for the corrosion loss of steels in different salt solutions

published in 1908 by Heyn and Bauer ^[19]. A theoretical explanation was offered in terms of competition between chloride and other ions ^[20]. As will be considered further below, a stationary 'medium' is an important part of many practical corrosion systems. On the other hand, for steels exposed to moving or turbulent waters typical of natural seawaters or as part of pipes conveying, for example, seawater or chlorinated freshwaters, non-stationary conditions can have significant corrosion effects. Such conditions are also likely to inhibit protruding rusts, such as tubercles ^[21] or rusticles ^[22] forming over pits. Smaller-sized tubercle formations were proposed as the reason for the observed higher concentration of chlorides within pits ^[14] (p. 120) ^[21]. These early observations are consistent with the classical theory of the formation of pits under conditions that are overall aerobic ^[23], even if within the pits themselves, anaerobic conditions are developing, eventually leading to the formation of low-pH ferrous chloride (FeCl_2) inside the pits ^[24]. This is consistent with Wranglen's ^[25] pitting theory and his conclusion that it is possible for water-soluble corrosive ferrous chlorides to form well inside deeper pits if chlorides are available from the external environment, even though they are fundamentally not essential for pit formation and development ^[26]. In this context, it is noted that the Pourbaix diagrams that were presented with the inclusion of chlorides (or other salts) were derived from experimental observations that extend, for entirely practical reasons, somewhat past the ideal of initiation only, with the metals exposed in electrochemical tests for the equivalent of non-negligible periods ^[27].

3. Corrosion Initiation for Non-Homogeneous Media

3.1. Overview

So far, consideration has been given to situations in which an (imperfect) metal (steel) is exposed to a perfect, homogeneous, isotropic medium, such as water or seawater or some other material that can diffuse water (and perhaps oxygen) to the metal–medium interface. Consider now the mirror-image scenario of a (near-)perfect metal (e.g., (almost) pure iron) in contact with an imperfect medium (**Figure 2**). The imperfections in the medium might include inclusions of a material different from the bulk of the medium material, surface geometrical imperfections and voids in the medium where in contact with the metal, and the medium might be patchy in its contact with the metal surface, leaving pockets or wet air voids. If the medium is a layer of finite but not necessarily uniform thickness located between the metal and an external environment, for example, like a protective coating, rust layer, biofilm or marine growth, it is spatially non-uniform in thickness or permeability. All these scenarios are likely to produce differences in local electrochemical potentials on the metal surface in contact with the medium. This scenario will extend to electron flows within the metal, noting that the conductivity of metals is typically very much greater than any conductivity of the medium. The potentials and current flow will result in localized corrosion in the metal, provided a cathodic reaction can occur somewhere on the metal. Also, at the very least, water must be present at the interface with the metal. Examples of some idealized cases are shown in **Figure 5**. These are made more specific in the following examples.

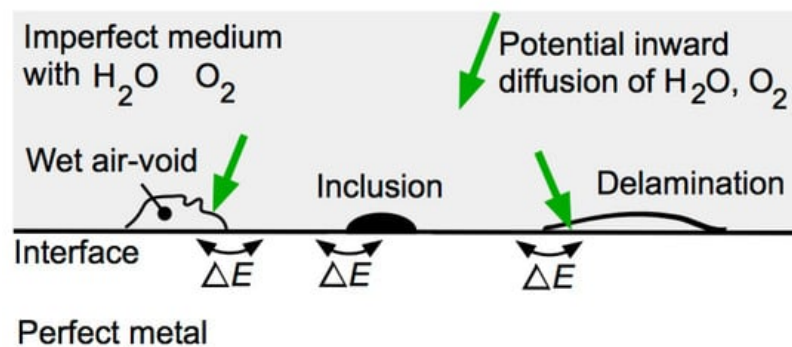


Figure 2. Schematic view of imperfect medium with voids, inclusions and delamination (non-contact regions) showing differential potentials.

3.2. Corrosion Initiation for Ferrous Metals in Contact with Soils

The first case is the important classical example of cast iron pipes buried in and surrounded by backfilled soil. Attempting to understand the drivers for the corrosion of cast iron in various soils has a long history ^{[28][29][30][31]}. Despite classical and repeated attempts to attribute field observations of the sometimes very severe corrosion to microbiological influences ^[32], as recently as 2011, it was admitted that no reasonable explanation for the various observations was available ^[33]. Only quite recently has it become clear, after extensive inspections of many actual field cases (rather than laboratory or experimental field specimens), that the crucial issue is the degree of contact of the soil around the whole of each pipe, including along the bottom and at the joints ^[34]. Deducing the importance of high degrees of contact all around the pipes is not new—it had been noted already in the 1930s for wet clay soils ^[35] but rather forcefully dismissed ^[32] on what can

now be seen to be rather flimsy scientific evidence and, it would seem, the preconceived notion that (the at that time recently discovered) sulphate-reducing bacteria (SRB), and therefore, microbiologically influenced corrosion (MIC) was the main culprit. While MIC can be an important contributor to marine corrosion, a key issue is the identification of the conditions under which it can occur rather than simply assuming it does occur [36][37]. This is illustrated in the following more modern example.

3.3. Corrosion Initiation for Reinforcing Steel in Concrete

The high alkalinity of freshly made concrete (pH usually > 13) is widely held as the critical inhibitor against the initiation of reinforcement corrosion [38]. This notion is, of course, consistent with thermodynamics, as represented in the Pourbaix diagram for pure iron in water. It indicates that corrosion may initiate if the pH adjacent to the steel is lowered (to below about 9) or the electrochemical potential is raised (or both). For a long time, it was proposed that an increased electrochemical potential is caused by the presence of a sufficient concentration of chlorides next to or around the reinforcement steel. However, what that concentration should be has been in dispute for many years (even though the FIB—Federation Internationale du Beton, for example, is still pursuing the setting of such a criterion). The fundamental problem is reflected in published experimental results, of which there is a plethora, that show a very high degree of scatter in the so-called 'critical chloride concentration', as summarized, for example, by Angst et al. [39]. Almost certainly, this means that the phenomena being considered are not completely understood and that other factors are involved. One reason for the scatter in the results is that many data were derived from electrochemical tests in so-called simulated pore waters that in most cases were stirred. These are not the conditions inside real concretes—concretes ensure stagnant pore water conditions and concretes are not merely porewaters—they have a very considerable solid, if not necessarily homogeneous, component. Thus, the conditions inside most concretes are not uniform, homogeneous and isotropic. The inevitable porosity of real concretes will ensure that the solid components of the concrete will have a metal-medium contact effect roughly similar to that of soils. Moreover, as shown experimentally, under stagnant conditions, chlorides essentially have no effect on corrosion loss, even for high concentrations [6][20], and thus, are largely irrelevant. In practical terms, this is consistent with field observations over many years, which are reported mainly in the practical literature, as summarized by Wakeman et al. (1958), Melchers and Li (2009), Angst et al. (2009), and Melchers and Chaves (2017) [40][41][42][43]. The modern research-based version of the role of chlorides is rather more subtle and harks back to classical understanding—it is that chlorides facilitate corrosion *pitting*, even when the surrounding concrete environment has an elevated pH. The relevant conditions, as evident in the Pourbaix diagram with chlorides included [27], are seldom noted in scientific papers or textbooks dealing with reinforcement corrosion.

3.4. Corrosion Initiation under Protective Coatings

Protective coatings, such as multi-layer spray paints, proprietary wraps and powder coatings, separating the external environment from the metal are usually considered to act primarily as (relatively thin) diffusion barriers. For this reason, there is strong industry reference to dry film thickness (DFT) for a given type of coating (implying a certain (low) degree of permeability) as a key component in long-term durability [44][45]. This is also the reason for attention to local differences in thickness, such as from coatings applied around sharp corners of the substrate or over surface deposits, lack of local coating adhesion to the substrate, or so-called 'holidays' in the spatial coverage provided by a coating, which typically arise from poor execution of the application process. All these are likely to permit differences in the rate of inward oxygen diffusion, leading to differences in the electrochemical surface potential, and hence, corrosion initiation.

In terms of corrosion initiation, these coatings may be considered a 'medium' in the sense introduced above. Thus imperfections, inclusions in the medium, surface deposits on the metal, and poor adhesion between the metal and the coating are all issues for initiation. This is reflected in the industry's recognition of the need for good surface preparation [45].

Similarly, the cracking of coatings, or severe defects, such as scratch lines, through to the substrate can cause severe local corrosion, particularly in marine environments. In parallel with the situation for reinforced concrete (see above), where the external environment is saline, any cracks in the coatings that extend to the underlying steel, or similar scratch lines can permit the entry of chlorides. Under conditions leading to oxygen exhaustion in those localized regions, the formation of ferrous chlorides may then occur, with likely severe localized corrosion.

4. Development of Corrosion and Pitting with Continued Exposure

For a variety of metals and alloys and a range of exposure environments, it was demonstrated, using field and laboratory data, that corrosion in general and also corrosion pitting both develop according to the so-called bi-modal trend [46]

(Figure 3). This trend applies to metals and alloys for which both the cathodic oxygen reduction reaction (ORR) and the cathodic hydrogen evolution reaction (HER) are thermodynamically feasible.

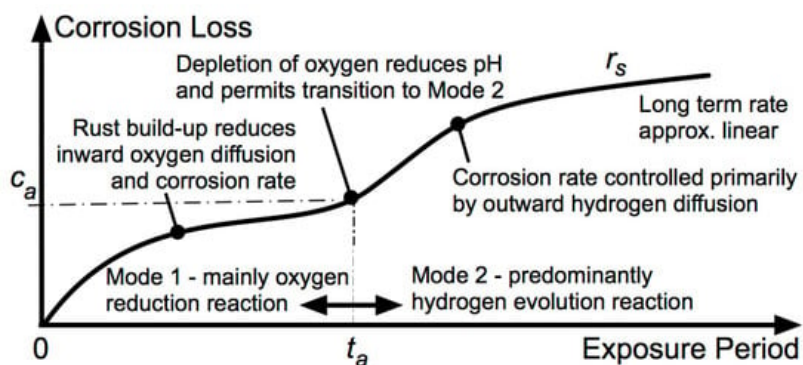


Figure 3. Schematic bi-modal corrosion loss trend showing modes 1 and 2, cathodic reactions and corrosion rate controlling diffusion mechanisms. Note the requirement for a drop in pH to permit the cathodic hydrogen evolution reaction to act in mode 2.

In the bi-modal model, corrosion commences in phase 1 of mode 1, with the principal reaction being the oxygen reduction reaction (ORR) and the rate controlled by the diffusion of oxygen out of the water (concentration control), but by the time phase 2 is reached, the corrosion is rate-controlled by the inward diffusion rate of oxygen from the available water through the corrosion product layer. This rate declines as the corrosion products build up and decrease in permeability with increasing corrosion, noting that the permeability of rust layers is mainly controlled by the presence and thickness of a magnetite layer in the corrosion product layer [47]. The externally visible FeOOH-type corrosion products are relatively permeable and have much less influence. The reduced availability of oxygen leads to lower pH and increased pitting at the interface, and these then allow mode 2 to take over [48]. The principal corrosion reaction in mode 2 is the hydrogen evolution reaction (HER) that operates only under acidic conditions, but the actual rate of corrosion is controlled by the rate of outward gaseous hydrogen diffusion through the increasing thickness of the rust layers. Eventually, with further development of the rust layers and some potential oxidation of their outer layers [49], an almost steady-state long-term corrosion rate r_s will be reached (Figure 3).

The influence of the condition of the metal surface on corrosion loss is reflected by the parameter c_a (Figure 3). It represents the corrosion loss at the end of mode 1. Some of this carries through to subsequent corrosion into phase 3, which itself may be under the influence of similar factors. The overall effect for longer-term corrosion is indicated, somewhat indirectly, by the parameter c_s (Figure 3). For steels exposed to seawater, the values of c_a are available as a function of the seawater mean temperature T , and for seawaters with various concentrations of dissolved inorganic nitrogen (DIN) [50], which is a critical nutrient for microbiologically influenced corrosion (MIC). These and other effects were summarized elsewhere [46].

Turning now to the influence of continued exposure for a system consisting of (a non-perfect) steel with an adjacent non-homogeneous medium of the types outlined above, the question arises regarding how the various local imperfections and impurities affect longer-term corrosion. This can be illustrated with the example of steel reinforcing bars with the surrounding concrete as the medium. When exposed to seawater, the combined effect of local corrosion in one or more (wet) air voids on overall corrosion behaviour is shown in Figure 4 [51]. It shows that there is increased early corrosion with larger air voids but also that the corrosion rate then declines very considerably. The latter is the direct result of (near-)exhaustion of the oxygen in the air voids in the medium (concrete) next to the metal surface. The overall, approximately linear, trend is indicated as rate r_s , also using the parameter c_s obtained via the backprojection of the longer-term rate r_s . The bi-modal trend component is shown in each case as conservatively linearized, as shown in the early stages of longer-term corrosion. Figure 4 also shows that after t_i , the trend for reinforcement corrosion is initially bi-modal and then reverts for extended exposures to mode 2 (cf. Figure 3). This is the long-term reinforcement corrosion trend that is relevant for high-quality well-compacted concretes.

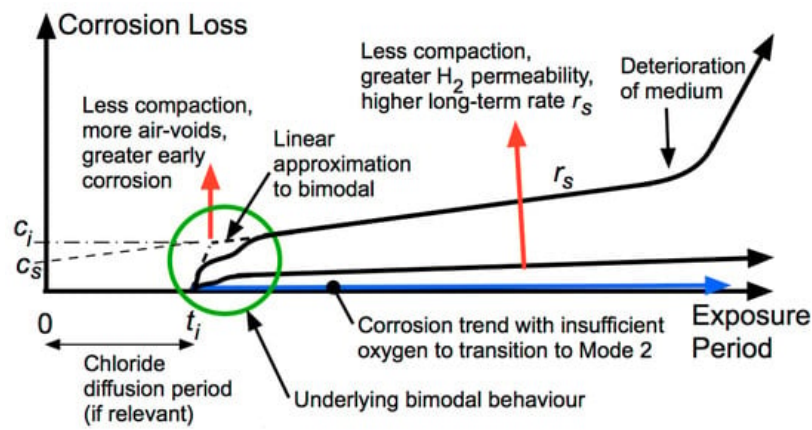


Figure 4. Schematic representation of corrosion loss as a function of exposure period for steel encased in concrete and for steel in soils. For steel in marine concretes, the period $0-t_i$ allows for the inward diffusion of chlorides that may aid corrosion initiation (through pitting) at t_i . For soils at around neutral pH, the period $0-t_i \rightarrow 0$. For highly impermeable concretes and soils, the transition to mode 2 does not occur and the very low corrosion loss (blue line) is relevant. For more permeable media, the long-term corrosion rate r_s increases slightly with permeability.

5. Long-Term Corrosion

As corrosion progresses after t_i (**Figure 12**), the build-up of the corrosion product layer occurs between the steel surface and the medium. This build-up of corrosion product renders the precise condition of the (already corroded) steel surface and that of the medium surface increasingly less relevant as corrosion progresses. Since long-term corrosion relies primarily on the rate of outward diffusion of hydrogen generated by the HER (i.e., as in mode 2, **Figure 3**), it follows that the factor of most importance for long-term corrosion is the permeability and thickness of the rust layers, together with the permeability and thickness of the medium (as a finite-thickness layer). This is consistent with observations from practical experience that show that for high-permeability media, the long-term corrosion rate r_s is higher than for low-permeability media, with $r_s \rightarrow 0$ as the permeability approaches zero (**Figure 4**). This applies both to reinforced concrete and to soils of various types.

The right-hand side of **Figure 4** shows that for extended exposures, it is possible for the deterioration of the medium to permit reinforcement corrosion. For reinforced concrete, for example, such deterioration can be brought about by the (slow, long-term) action of chlorides on the calcium hydroxide component of the concrete matrix ^[52], resulting in the loss and leaching out of ferrous chlorides, as seen, for example, at poorly made construction joints after many decades of ‘at sea’ marine exposures ^[53]. Long-term deterioration of the concrete itself, and its consequential inability to provide effective ‘cover’ protection to the steel reinforcement, can also be caused by alkali–aggregate reactivity within the concrete. This is a much-overlooked deterioration mechanism ^[54]. All in all, a holistic perspective based on a sound understanding of the possibilities involved and the need to meet corrosion science principles is necessary ^[55].

On the basis that interface conditions important for initiation are much less relevant for the rate of long-term corrosion, it might be expected that there would be a high degree of consistency for r_s across various metal–media combinations for similar media properties. Indeed, for metals (not just steels) immersed in seawater, the long-term rate r_s is remarkably consistent at around 2.7 mil/y (0.07 mm/y) for seawaters in the 27 °C temperature range. This also applies to the long-term rate of pit depth progression ^[56].

6. Conclusions

- Both local differences in electrochemical potential due to inhomogeneities of the steel and inhomogeneities of the surface of the medium interfacing with the steel can be sources of initiation of corrosion for the steel, although, for many practical applications, the inhomogeneities of the medium are of greater importance due to their greater physical scale.
- Corrosion of steel in water and the atmosphere may be considered specialized cases of corrosion in homogeneous media extending over semi-infinite spaces.
- As corrosion at the interface progresses, the instantaneous corrosion rate is increasingly governed by the properties of the corrosion products at the interface and less by the properties of the steel or the medium, with corrosion progressing eventually to and then through the hydrogen evolution as the principal long-term cathodic reaction in all cases.

- The same mechanisms are likely to hold for other media of types similar to those considered herein when in contact with alloys and metals other than steel and for which the hydrogen evolution reaction is feasible.
- Breakdown of the medium itself may lead to steel corrosion—it is not always the case that the corrosion of the steel causes damage to, and possibly breakdown of, the medium.

References

1. Ackland, B.G.; Dylejko, K.P. Critical questions and answers about cathodic protection. *Corros. Eng. Sci. Technol.* 2019, 54, 688–697.
2. Coogan, C. *Marine Corrosion and Cathodic Protection*; CRC Press: Boca Raton, FL, USA, 2022.
3. Jones, D.A. *Principles and Prevention of Corrosion*, 2nd ed.; Prentice Hall: Upper Saddle River, NJ, USA, 1996.
4. Garrels, R.M.; Christ, C.L. *Solutions, Minerals and Equilibria*; Harper & Row: New York, NY, USA, 1965.
5. Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*; NACE Int.: Houston, TX, USA, 1974.
6. Mercer, A.D.; Lumbard, E.A. Corrosion of mild steel in water. *Br. Corros. J.* 1995, 30, 43–55.
7. Abiko, K.; Nakajima, T.; Harima, N.; Takaki, S. Preparation of 10 kg ingot of ultra-pure iron. *Phys. Status Solidi* 1998, 167, 347–355.
8. Abiko, K. Why do we study ultra-pure base metals? *Mater. Trans. JIM* 2000, 41, 233–237.
9. Khan, L.; Sato, K.; Okuyama, S.; Kobayashi, T.; Ohashi, K.; Hirasaka, K.; Nikawa, T.; Takada, K.; Higashitani, A.; Abiko, K. Ultra-high purity iron is a novel and very compatible biomaterial. *J. Mech. Behav. Biomed. Mater.* 2020, 106, 103744.
10. Ferrara, E.; Olivetti, E.; Fiorillo, F.; Forton, R.; Martino, L.; Rocchino, L. Microstructure and magnetic properties of pure iron for cyclotron electromagnets. *J. Alloys Compd.* 2014, 615, S291–S295.
11. Li, S.; Hihara, L.H. The comparison of the corrosion of ultrapure iron and low-carbon steel under NaCl-electrolyte droplets. *Corros. Sci.* 2016, 108, 200–204.
12. van der Voort, G.F. *Metallurgy: Principles and Practice*; McGraw-Hill: New York, NY, USA, 1984.
13. Wranglen, G. Review article on the influence of sulphide inclusions on the corrodibility of Fe and steel. *Corros. Sci.* 1969, 9, 585–602.
14. Evans, U.R. *The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications*; Edward Arnold: London, UK, 1960.
15. Melchers, R.E.; Jeffrey, R. Surface roughness effect on marine immersion corrosion of mild steel. *Corrosion* 2004, 60, 697–703.
16. Burstein, G.T.; Pistorius, P.C.; Mattin, S.P. The nucleation and growth of corrosion pits on stainless steels. *Corros. Sci.* 1993, 35, 57–62.
17. Foley, R.T. Role of the chloride ion in iron corrosion. *Corrosion* 1970, 26, 58–70.
18. Foley, R.T. Complex ions and corrosion. *J. Electrochem. Soc.* 1975, 11, 1493–1994.
19. Heyn, E.; Bauer, O. Ueber den Angriff des Eisens durch Wasser und wässrige Lösungen. *Stahl. Eisen* 1908, 28, 1564–1573.
20. Brasher, D. Stability of the oxide film on metals in relation to inhibition of corrosion. I. Mild steel in the presence of aggressive ions. *Brit. Corr. J.* 1967, 2, 95–103.
21. Baylis, J.R. Factors other than dissolved oxygen influencing the corrosion of iron pipes. *Ind. Engrg. Chem.* 1926, 18, 370–380.
22. Little, B.J.; Gerke, T.L.; Lee, J.S. Mini-review: The morphology, mineralogy and microbiology of accumulated iron corrosion products. *Biofouling* 2014, 30, 941–948.
23. Greene, N.D.; Fontana, M.G. A critical analysis of pitting corrosion. *Corrosion* 1959, 15, 41–47.
24. Sharland, S.M.; Tasker, P.W. A mathematical model of crevice and pitting corrosion—I. The physical model. *Corros. Sci.* 1988, 28, 603–620.
25. Wranglen, G. Pitting and sulphide inclusions in steel. *Corros. Sci.* 1974, 14, 331–349.
26. Butler, G.; Stretton, P.; Beynon, J.G. Initiation and growth of pits on high-purity iron and its alloys with chromium and copper in neutral chloride solutions. *Br. Corros. J.* 1972, 7, 168–173.

27. Pourbaix, M. Significance of protection potential in pitting and intergranular corrosion. *Corrosion* 1970, 26, 31–438.
28. Romanoff, M. *Underground Corrosion*, National Bureau of Standards Circular 579; US Government Printing Office: Washington, DC, USA, 1957.
29. Rajani, B.; Kleiner, Y. Comprehensive review of structural deterioration of water mains: Physically based models. *Urban. Water* 2001, 3, 151–164.
30. Cole, I.S.; Marney, D. The science of pipe corrosion: A review of the literature on the corrosion of ferrous metals in soils. *Corros. Sci.* 2012, 56, 5–16.
31. Kleiner, Y.; Rajani, B.; Kryz, D. Performance of ductile iron pipes. I: Characterization of exterior corrosion patterns. *J. Infrastruct. Syst. ASCE* 2013, 19, 108–119.
32. von Wolzogen Kuhr, C.A.H.; van der Vlugt, L.S. Graphitization of cast iron as an electrochemical process in anaerobic soils, *Water (den Haag)*, 18: 147–165 (in Dutch). *Transl. Corros.* 1971 1934, 17, 293–299.
33. Ricker, R.E. Analysis of pipeline steel corrosion data from NBS (NIST) studies conducted between 1922–1940 and relevance to pipeline management. *J. Res. Nat. Inst. Stand. Technol.* 2011, 115, 373–392.
34. Melchers, R.E. Models for prediction of long-term corrosion of cast iron water mains. *Corrosion* 2020, 76, 441–450.
35. Wichers, C.M. Korrosion asphaltierter eiserner Rohre. *Das. Gas. Wasserfach* 1934, 77, 131–132.
36. Liengen, T.; Feron, D.; Basseguy, R.; Beech, I.B. (Eds.) *Understanding Biocorrosion*, European Federation of Corrosion Publications; Number 66; Woodhead Publishing in Materials: Cambridge, UK, 2014.
37. Skovhus, T.L.; Eckert, R.B. (Eds.) *Failure Analysis of Microbiologically Influenced Corrosion*; CRC Press: Boca Raton, FL, USA, 2021.
38. Richardson, M.G. *Fundamentals of Durable Reinforced Concrete*; Spon Press: London, UK, 2002.
39. Angst, U.M.; Geiker, M.R.; Michel, A.; Gehlen, C.; Wong, H.; Isgor, O.B.; Elsener, B.; Hansson, C.M.; François, R.; Hornbostel, K.; et al. The steel-concrete interface. *Mater. Struct.* 2017, 50, 1–24.
40. Melchers, R.E.; Chaves, I.A. A comparative study of chlorides and longer-term reinforcement corrosion. *Mater. Corros.* 2017, 68, 613–621.
41. Wakeman, C.M.; Dockweiler, E.V.; Stover, H.E.; Whiteneck, L.L. Use of concrete in marine environments. *Proc. ACI* 1958, 54, 841–856.
42. Melchers, R.E.; Li, C.Q. Reinforcement corrosion initiation and activation times in concrete structures exposed to severe marine environments. *Cem. Concr. Res.* 2009, 39, 1068–1076.
43. Angst, U.M.; Elsener, B.; Larsen, C.K.; Vennesland, O. Critical chloride content in reinforced concrete—A review. *Cem. Concr. Res.* 2009, 39, 1122–1138.
44. Berensen, A.M. *Marine Painting Manual*; Springer-Science & Business Media BV: Dordrecht, The Netherlands, 1989.
45. Hare, C.H. *Corrosion Control of Steel by Organic Coatings*; Revie, R.W., Ed.; Wiley: New York, NY, USA, 2011; pp. 971–983.
46. Melchers, R.E. A review of trends for corrosion loss and pit depth in longer-term exposures. *Corros. Mater. Degrad.* 2018, 1, 4.
47. Refait, P.H.; Grolleau, A.-M.; Jeannin, M.; Rémazeilles, C.; Sabot, R. Corrosion of carbon steel in marine environments: Role of the corrosionproduct layer. *Corros. Mater. Degrad.* 2020, 1, 198–218.
48. Melchers, R.E.; Jeffrey, R. The transition from short- to long-term marine corrosion of mild steel—1. experimental observations—2. parameterization and modeling. *Corrosion* 2022, 78, 415–436.
49. Stratmann, M.; Bohnenkamp, K.; Engell, H.J. An electrochemical study of phase-transitions in rust layers. *Corros. Sci.* 1983, 23, 969–985.
50. Melchers, R.E. Long-term immersion corrosion of steels in seawaters with elevated nutrient concentration. *Corros. Sci.* 2014, 81, 110–116.
51. Melchers, R.E. Long-term durability of marine reinforced concrete structures. *J. Mar. Sci. Eng.* 2020, 8, 290.
52. Melchers, R.E.; Chaves, I.A. Reinforcement corrosion in marine concretes—2. Long-term effects. *ACI Mater. J.* 2020, 117, 217–228.
53. Melchers, R.E.; Howlett, C.M. Reinforcement corrosion of the Phoenix caissons after 75 years of marine exposure. *Proc. Inst. Civ. Eng.-Marit. Eng.* 2020, 174, 19–30.

54. Melchers, R.E.; Humphrey, H. Concrete alkali-aggregate reactivity and initiation of steel reinforcement corrosion. *Corros. Mater. Degrad.* 2023, 4, 428–444.
55. Melchers, R.E. Mechanisms in long-term marine corrosion of steel reinforcement in concrete. *Corrosion* 2023, 79, 380–387.
56. Southwell, C.R.; Bultman, J.D.; Alexander, A.L. Corrosion of metals in Tropical environments—Final report of 16 years exposures. *Mater. Perform.* 1976, 15, 9–25.

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