

Do micro-organisms “eat” metal?

Sten B. Axelsen and Trond Rogne, SINTEF Materials Technology

Introduction

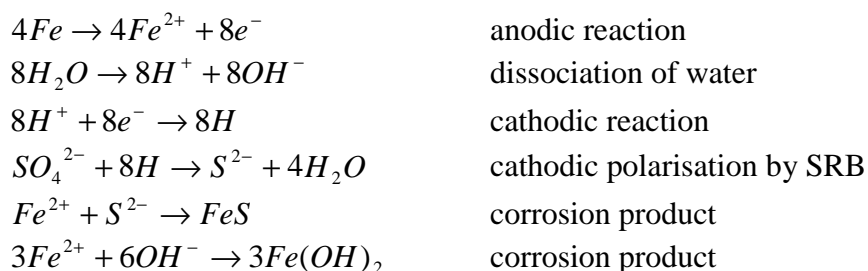
Microbially induced corrosion, MIC, was first recognized on lead (Pb) by J.H. Garrett¹ about a century ago. Over the past years MIC has however become a problem under varied service conditions, and on different materials. According to Yasushi Kikuchi² MIC is often found in weld parts and is now counted as a standard weld defect. Why do these micro-organisms especially like the weld parts, and what role do the bacterial species play in the microbially induced corrosion process? Do micro-organisms “eat” metal? These, and a few other questions are hopefully answered in this memo, as the MIC mechanisms suggested in literature are discussed.

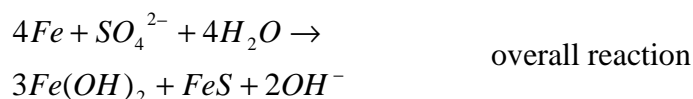
Mechanisms

The term “microbially induced corrosion” are used about corrosion processes where micro-organisms, e.g. bacteria or fungus, are involved in the materials degradation. Which type of micro-organism that is involved differs by type of material and by environment. In environments with high oxygen contents the aerobic bacteria are active, but when the oxygen level is lowered these are replaced by anaerobic bacteria. Aerobic and anaerobic bacteria are two of the general physiological groups of bacteria. The bacteria are also categorised as slime-forming, acid-producing, sulfate-reducing, nitrate-reducing, iron-oxidising and iron-reducing bacteria. Within each of these groups there are hundreds of individual species of bacteria. MIC is almost always due to the action of microbiological communities containing several different types of bacteria.

According to Pope and Morris³ the following mechanisms are potentially involved in cases of MIC:

- *Cathodic depolarisation.* This is the classic mechanism for MIC of steel and iron proposed by Wolzgen Kuhr and Van der Vulgt⁴ in 1934. It is based on the idea that dissociation of hydrogen from the cathodic site is the rate-limiting step in the corrosion process. Further are the sulfate-reducing bacteria (SRB) consuming hydrogen through the action of their hydrogenase enzymes, and thus depolarise the cathode, accelerating corrosion. This theory has however been rejected in several later studies⁵. The following equations are those originally proposed by Wolzgen Kuhr and van der Vulgt to explain the mechanism of cathodic depolarisation:





This mechanism is also illustrated in Figure 1.

- *Formation of occluded area on metal surface.* This mechanism is based on the observation that micro-organisms form colonies in local “community centres”. The location of these centres may be related to metallurgical features such as roughness, corrosion sites, inclusions or surface charge. When a colony has been formed it produces sticky polymers which tend to attract and aggregate other biological and non-biological species. This, in addition to the metabolism of available oxygen, iron, manganese, etc., result in conditions within and under the colonies very different from those of the surrounding material. Crevices, oxygen and ion concentration cells may be formed, allowing corrosion to proceed.
- *Fixing the anodic site.* More than 90% of MIC is seen as pitting-type corrosion. This is due to the fact that most microbiological community usually remains fixed to the colonisation site. Under the colony the presence and activities of the microbes create conditions in which incipient pitting leads to pitting, driven principally by microbiological activities.
- *Underdeposit acid attack.* Most of the final products of MIC community metabolism are short-chain fatty acids, and acetic acid is the most common. Acetic acid is very aggressive to carbon steel when concentrated under a colony or other deposits.

Pope and Morris³ did also propose a general model for the development of MIC (see Figure 2).

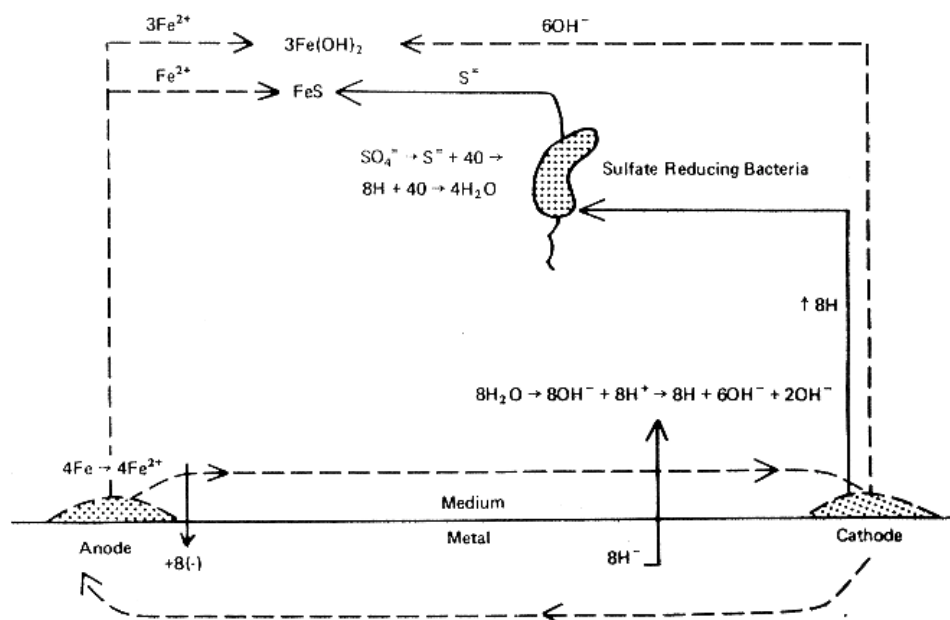


Figure 1 Schematically drawing of cathodic depolarisation⁶.

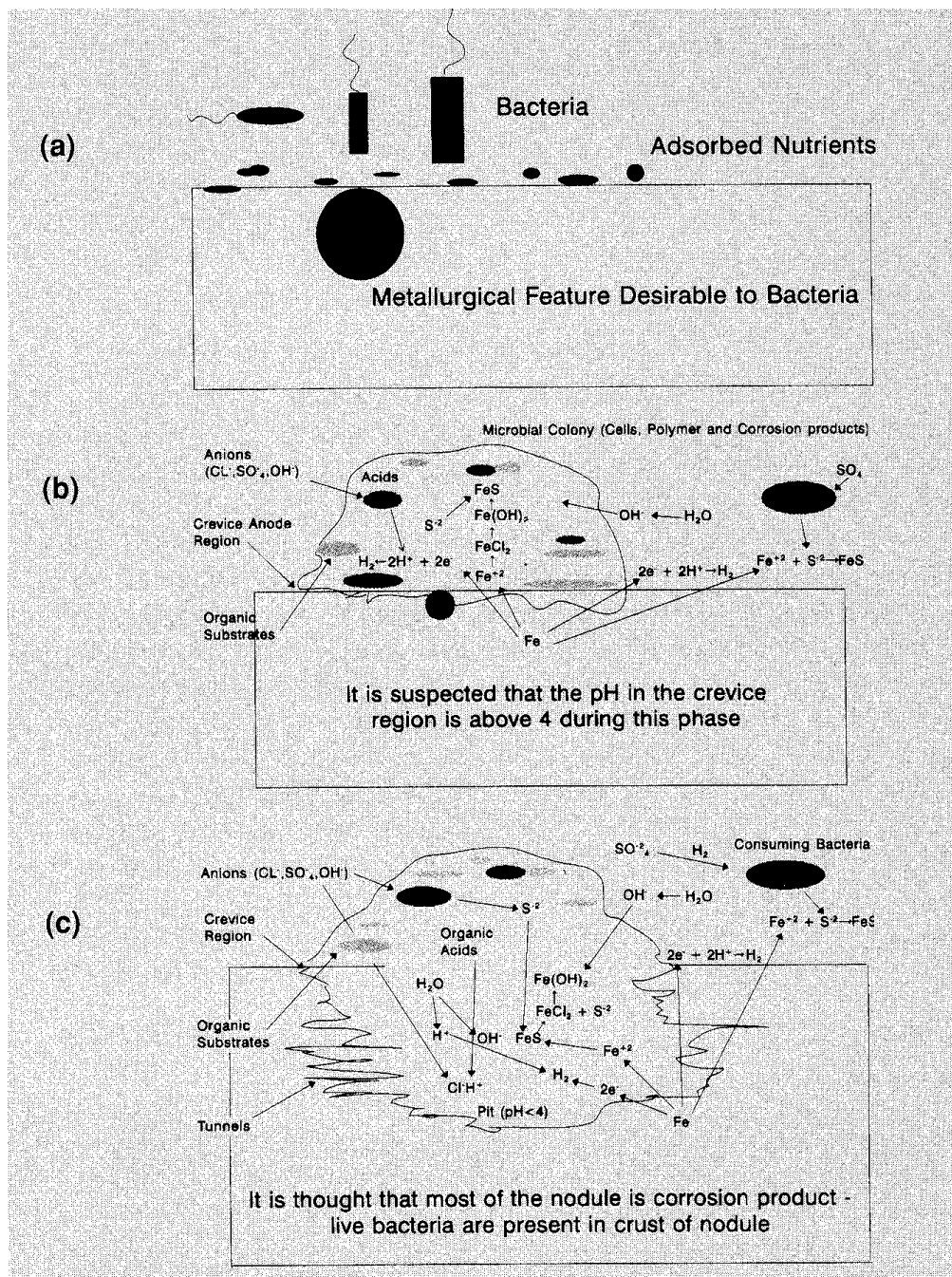


Figure 2 MIC development model³. (a) Recognition of desirable sites. (b) Colony formation and crevice corrosion begins and anode is fixed. (c) Nodule is formed over "mature" pit.

As can be seen, the role of the microbes in the MIC process is to provide aggressive conditions under which the corrosion process is accelerated. The microbes do not "eat" metal themselves. This will be even clearer when we now will look further in detail on some of the bacteria and some of the different materials subject to MIC.

Bacteria

Discussing the different types of bacteria it is important to keep in mind that microbial influenced corrosion results from the activities of microbial communities, not single types microbes⁷. It is the interactive growth activity of bacteria consortia that actually stimulates the corrosion process.

Rodney Towers⁸ has studied MIC in cargo tanks and seen how *acid-producing bacteria (APB)* and *sulfate-reducing bacteria (SRB)* interact. The APB are the principle initiator of MIC. Their nutrient source is oxygen, and they produce low molecular weight organic acids, alcohol and aldehydes. The low molecular weight organic acids are not so corrosive, but they are the primary food source for SRB, which are the best known group of organisms involved in the corrosion of iron and steel. They fall into three main genera: *Desulphovibrio*, *Desulphotomaculum* and *Desulphomonas*. The sulfate-reducing bacteria has by several authors^{8,9,10} been reported as very corrosively aggressive when the environmental conditions are right. This is because SRB convert sulfate into corrosive sulfide. Figure 3 shows Towers' illustration of a SRB corrosion attack. First the APB creates suitable conditions for SRB to grow. Once the SRB begin to proliferate their production of hydrogen sulfide, the environment gets toxic to most aerobes, and eventually they can kill off almost all other organisms. Pit initiation is thought to begin at breaks in the biofilm by SRB sulfide stimulation of the electrochemical corrosion process. The sulfides are cathodic to the steel and attack the surface by consuming anodic iron. Local areas of acidity are created around sources of APB concentration, and SRB use these acids as their nutrient. The SRB-generated sulfides reduces the steel to ferrous compounds, which expand to form "crusty top hats" usually found capping pit craters.

According to Towers⁸ microbial sulfide generation is optimised at 37 – 41°C. Eistrat and Thoren¹⁰ have however reported the optimum to be 25 – 35°C. Optimum pH condition they reported to be 7-8. According to Pope and co-workers¹¹ the sulfate-reducing bacteria tolerate temperatures from 5 to 75°C, pH from 5 to 9.5, a range of osmotic conditions and a hydrostatic pressure of at least 100 MPa. The SRB have been reported to survive, but not grow under aerobic conditions⁸.

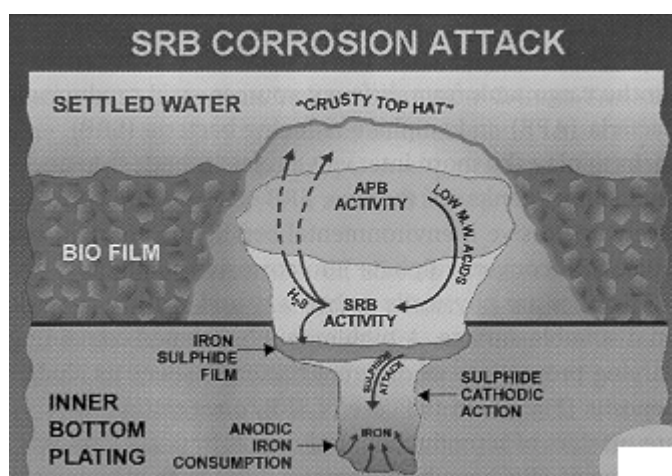


Figure 3 Towers' illustration of a SRB corrosion attack⁸.

Most *iron bacteria* are aerobic, but the necessary oxygen concentration may be very low, ~0.1 ppm. These bacteria are most common in fresh water, and they are active in the pH range from 4 to 10 and in temperatures from 5 to 40°C¹¹.

Slime-forming bacteria are mostly aerobic, and according to Pope and co-workers¹² their ability to attack stainless steels are well documented. Through production of a slime layer they may form crevices in which regular crevice corrosion is initiated. The organisms' oxygen consumption may also prevent the repassivation in areas where the passive film is destructed. The consumption of oxygen does also create suitable conditions for SRB to grow. According to Tatnall¹³ this is the most important contribution of the slime-forming bacteria in the corrosion process. It has also been suggested that slime-forming bacteria promotes corrosion through polarisation of the surface¹². Unpublished data from SINTEF show that in natural seawater from Trondheimsfjorden, an active slime layer may be formed at temperatures below 27-29°C. Féron¹⁴ has however performed tests in France which showed that an active slime layer was built up at 30°C, but not at 40°C. These results indicate that T_{\max} may vary somewhat dependent on where on earth you are located.

Materials

Microbially induced corrosion has been reported on most industrial metals and alloys^{15,16}. The susceptibility to MIC does however differ significantly.

Alloying elements are added to metals to improve material properties. The alloying elements alter the formation, chemical composition, thickness and tenacity of corrosion products, and may increase or decrease susceptibility to MIC.

Stainless steels, SS, are indubitable the material subject to most investigations of MIC. Their corrosion resistance is due to the formation of a thin passive chromium-iron oxide film at additions of chromium in amounts of 12% or more. Metal depositing organisms, important in MIC of SS, may catalyse the oxidation of metals, accumulate abiotically oxidised metal precipitates, or derive energy by oxidising metals¹⁷. Dense deposits create oxygen cells that effectively exclude oxygen from the area under the deposit. Underdeposit corrosion is important because it initiates a series of events that are, individually or collectively, extremely corrosive. In oxygenated environment, the area under the deposit becomes a small anode compared to the large surrounding cathode. Cathodic reduction of oxygen may also result in an increase in pH of the solution in the vicinity of the metal, and metal cations will be formed at anodic sites. One of the most common forms of MIC attack on SS is, as mentioned in the introduction, at or adjacent to welds at the heat-affected zone (HAZ), the fusion line and in the base material. Low grade austenitic stainless steels (304, 316) are particularly susceptible to this form of MIC. According to Borenstein¹⁸ both austenite and delta ferrite phases may be susceptible; and all combinations of filler and base materials have failed, including matching, higher- and lower-alloyed filler combinations. Superaustenitic stainless steels, SS containing more than 6% molybdenum, were once thought to be immune to MIC. However, about ten years ago both Scott *et al.*¹⁹ and Little *et al.*²⁰ showed that they are not. The discussion of MIC of stainless steels would not be complete without some reference to ennoblement. Ennoblement of corrosion potential, E_{CORR} , during exposure to natural seawater has been reported in several studies^{21,22,23,24,25,26}. The practical importance of this

ennoblement is increased probability of localised corrosion as E_{corr} approaches the pitting potential. Motoda and co-workers²⁷ have proposed that the cause for the potential ennoblement of SS in natural seawater is oxygen evolved from the carbonate assimilation process. Dexter and Zhang²⁸, on the other hand, suggested that the potential ennoblement is caused by the reduction in pH due to formation of organic acid through digestion and dissociation processes. However, the extent of potential ennoblement observed appears to be appreciably larger than the levels that might be explained by these two mechanisms. Thus, it is suspected that a certain qualitative change in the steel surface, leading to the promotion of cathodic reactions, might be brought about²⁴.

Aluminium and aluminium alloys. The corrosion resistance of aluminium and its alloys is due to an aluminium oxide passive film. This film may be attacked locally by halide ions, and the susceptibility of aluminium to localised corrosion makes it particularly vulnerable to MIC. There are two mechanisms for MIC that have been documented for aluminium and its alloys: Production of water-soluble organic acids by bacteria and fungi, and formation of differential aeration cells.

Titanium and titanium alloys. No cases describing MIC of titanium have been reported. Schutz²⁹ has reviewed mechanisms for MIC and titanium's corrosion behaviour under a broad range of conditions. He concluded that at temperatures below 100°C, titanium is not vulnerable to iron/sulfur-oxidising bacteria, SRB, acid-producing bacteria, differential aeration cells, chloride concentration cells, and hydrogen embrittlement. Buchanan *et al.*²³ have tested Ti-based weldments, and they actually observed that microbial influence resulted in corrosion inhibition.

Copper- and copper/nickel alloys. Copper alloys are vulnerable to biocorrosion. Differential aeration, selective leaching, underdeposit corrosion and cathodic depolarisation have all been reported as mechanisms for MIC of copper alloys¹⁷. According to Pope *et al.*³⁰ the following microbiological products contribute to acceleration of the localised attacks on copper alloys: carbon dioxide, hydrogen sulfide, ammonia, organic and inorganic acids, metabolites that act as depolarisers, and sulfur compounds. In most investigations of MIC of copper alloys, pitting due to SRB seems to be the problem. MIC-induced pitting is however not necessarily due to SRB. The presence of the biofilm appears to contribute to corrosion by maintaining enhanced local chloride concentrations and differential aeration cells¹⁷. Copper/nickel alloys are superior to predominantly copper alloys because the protective surface film remains intact under turbulent and erosive conditions¹⁷. They are therefore used extensively in highly aerated, high-velocity sea water applications. According to Uhlig and co-workers³¹ the critical nickel concentration required for passivity is 35 percent. If nickel/copper alloys contain less than this amount of nickel they will behave like copper. The alloy 400 (UNS N04400) has been reported to be susceptible MIC-induced pitting and crevice corrosion by several investigators^{30,32,32}.

References

1. F. Kajiyama, *Proc. 100th Corrosion Symposium on Microbial Corrosion (II)*, JSCE, p.55, 1994.
2. Yasushi Kikuchi, Microbially Induced Corrosion and Biodegradation, *Corrosion Engineering*, **47**, p. 909-913, 1998.
3. D.H. Pope and E.A. Morris III, Some Experiences with Microbiologically Influenced Corrosion of Pipelines, *Materials Performance*, p.23-28, May 1995.
4. C.A.H. Von Wozgen Kuhr and L.S. Van der Vulgt, Den Haag, **18**, 1934.
5. A.K. Tiller, A review of the European research effort on microbial corrosion between 1950 and 1984, *Proceedings Biologically Induced Corrosion*, NACE, Houston TX, 1985.
6. G. Kobrin, *Materials Performance*, P. 38-43, July 1976.
7. R.T. Huang, B.L. McFarland and R.Z. Hodgman, Microbial Influenced Corrosion in Cargo Oil Tanks of Crude Oil Tankers, Paper No. 535 presented at *Corrosion 97*, NACE, Houston TX, 1997.
8. R. Towers, Accelerated Corrosion in Cargo Tanks of Large, Double-Hull Ships, Causes and Countermeasures, *Protective Coatings Europe*, p. 30-42, March 2000.
9. R.E. Tatnall, *Corrosion 81*, NACE Conference, Paper NO. 130, 1981.
10. D.E. Hill, B.J. Remus and M.J. Undesser, Control of Microbiological Related Problems in the Kuparuk River Unit Water Flood, *Corrosion 87*, Paper No. 378, NACE, San Fransisco, 1987.
11. K. Eistrat and A. Thoren, Mikrobiell korrosjon – en litteraturoversikt, KI-report, No. 64080 Korrosionsinstitutet, Sweden, 1980 (in Swedish).
12. D.H. Pope, D.J. Duquette, A.H. Johanes and P.C. Wayner, *Corrosion-83*, Paper No. 247, 1983.
13. R.E. Tatnall, *Materials Performance*, p. 32-38, Sept. 1981.
14. D. Féron, Corrosion behaviour of stainless steel in sea water thermally altered, *Proceedings: Sea Water Corrosion of Stainless Steels – Mechanisms and Experiences*, Trondheim, Nov. 1995.
15. D.H. Pope, et al., Microbiologically Influenced Corrosion: A State-of-the-Art Review (Columbus, OH: Materials Technology Institute of the Chemical Process Industries, 1984).
16. D.H. Pope, et al., *Material Performance*, 23, p.14, 1984.
17. P. Wagner and B. Little, Impact of Alloying on Microbiologically Influenced Corrosion – A Review, *Materials Performance*, p. 65, Sept. 1993.
18. S.W. Borenstein, *Materials Performance* 30, 1, p. 52, 1991.
19. P.J.B. Scott, J. Goldie and M. Davies, *Materials Performance* 30, 1, p. 55, 1991.
20. B. Little, P. Wagner and R.Ray, An Experimental Evaluation of Titanium's Resistance to Microbiologically Influenced Corrosion, *Corrosion/92*, Paper No. 173, NACE, Houston TX, 1992.
21. R. Johnsen and E. Bardal, *Corrosion*, **41**, p. 296, 1985.
22. M.H.W. Renner and G.H. Wagner, Microbiologically influenced corrosion of stainless steels, *Stainless Steel World*, p. 36, Nov. 1996.
23. R.A. Buchanan, A.L. Kovacs, C.D. Lundin, K.K. Khan, J.C. Danko, P. Angell and S.C. Dexter, Microbially Influenced Corrosion of Fe-, Ni-, Al-, and Ti-Based Weldments, *Material Performance*, p. 46, June 1997.
24. H. Sasaki, M. Nishimura and The Editorial Staff, Bacteri-induced Corrosion of Stainless Steel Weld Joints, *Corrosion Engineering*, **41**, p. 859-864, 1992.

25. J.P. Audouard, C. Compere, N.J.E. Dowling, D. Feron, D. Festy, A. Mollica, T. Rogne, V. Scotto, U. Steinsmo, C. Taxen and D. Thierry, Effect of marine biofilms on stainless steels: Results from an European exposure program, European Federation of Corrosion Publications, Number 19.
26. R. Holthe, Dissertation, Norwegian University of Science and Technology, Trondheim, Norway, 1988.
27. S. Motoda *et al.*, *Fushoku Boshoku* (Corrosion) '89, *JSCE*, p. 247.
28. S.C. Dexter and H.-J. Zhang, *Proc. of the 11th Int. Corr. Cong.*, 4-333, Florence, 1990.
29. R.W. Schutz, *Material Performance* 30, 1, p. 58, 1991.
30. D.H. Pope, *Microbial Corrosion on Fossil-Fired Power Plants – A Study of Microbiologically Influenced Corrosion and a Practical Guide for its Treatment and Prevention*, Palo Alto, CA: Electrical Power Research Institute, 1987.
31. H.H. Uhlig and W.R. Revie, *Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering*, 3rd Edition, New York, Wiley-Interscience, 1985.
32. M. Schumacher, *Seawater Corrosion Handbook*, Park Ridge, NJ, Noyes Data Corporation, 1979.
33. V. Gouda, I. Banat, W. Riad and S. Mansour, *Corrosion* 49, 1, p. 63, 1993.