MIC MYTHS - DOES PITTING CAUSE MIC?

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ABSTRACT

It is widely accepted that sulfate reducers, acid producers, metal oxidizers and certain other bacteria can contribute to corrosion. However, it is far from clear how biological activity influences corrosion processes, how much metal loss is caused by bacteria, and most importantly, how microbial attack can be differentiated from other corrosion mechanisms. Confusion between Microbiologically Influenced Corrosion (MIC) and other corrosion mechanisms is common. Criteria such as pit “tunneling”, “tiger striping”, pit “terracing”, “high” biological counts, tuberculation and preferential weld attack have frequently been used as diagnostic Rosetta stones solely identifying MIC. Unfortunately, many commonly accepted diagnostic criteria are not unique to MIC, but can also result from numerous corrosion processes unrelated to biological activity. Diagnosis of corrosion mechanisms, whether involving MIC or not, requires critical evaluation of all data, a thorough understanding of fundamental corrosion processes and consistency of both phenomenological observations and theoretical information.

Keywords: MIC, tuberculation, tunneling, tiger striping, weld, weld attack, pit terracing, cooling water, failure analysis, pitting

INTRODUCTION

Interest in microbiologically influenced corrosion (MIC) has exploded in the last two decades. More than 800 works discussing MIC have been collected recently in MIC AB2.01. A variety of quantitative techniques have been used to characterize bacterial contributions to corrosion processes, including electrochemistry, surface analysis and microbiological analysis2. Laboratory studies, despite their sophistication, have proven to be of limited value in either predicting wastage morphologies or in quantifying metal loss in the field. It has been suggested that dichotomous corrosion behavior between laboratory and field studies is an inherent property of biofilm complexity; biological diversity and chemical dynamics of biofilms can make extrapolation from one location to another difficult3. Laboratory investigations may demonstrate that certain organisms may cause corrosion, but do not guarantee that attack will occur in the field or that attack morphologies will be similar. Corrosion unrelated to biological processes may produce attack similar to MIC wastage. Thus, although laboratory studies can be beneficial in understanding fundamental microbial corrosion processes, the diagnosis of MIC in the field remains primarily a correlation process involving phenomenological observation and experience.

It has been assumed that MIC does not produce any unique type of corrosion and that there are no definitive tests or specific observations that can be used to detect MIC4. These seemingly provocative opinions are primarily based upon the assumption that certain bacteria cause wastage such as pitting, crevice corrosion, dealloying, differential concentration cells, “enhanced” galvanic attack and “enhanced” erosion corrosion which are apparently indistinguishable from damage produced by processes unrelated to biological processes. It has been further asserted that spatial correlation of organisms with corrosion is unreliable, at least partially because bacteria can be attracted to both...

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anodes and cathodes. It would appear that if MIC produces no unique identifying signature, that any corrosion in the presence of bacteria could potentially involve microbes. Paradoxically, while the above observations and opinions appear well founded, nevertheless, MIC diagnosis in the field is possible. Diagnosis requires a fundamental understanding of failure analysis.

Many forms of wastage caused by different corrosion mechanisms resemble one another. In this sense MIC identification is no different than diagnosis of any other damage for which some characteristic or characteristics appear in more than one corrosion mechanism. For example, pit morphologies produced by oxygen corrosion, acid attack, cavitation processes and some forms of MIC may closely resemble one another. Taken in an isolated context, without knowledge of metallurgy, corrosion products, operating history, chemical treatment, deposit analysis, manufacturing processes, microscopic examinations, biological analysis and numerous other factors, it may be quite difficult, or even impossible to uniquely identify the failure mechanism or mechanisms. Field diagnosis lacks the certitude of a laboratory study because field analysis is necessarily performed differentially. The diagnosis accuracy is based on all measurements and observations being consistent with only one explanation; self consistency is undoubtedly the single most important principle of failure analysis. Thus, it is not the type of the damage considered in isolation that allows diagnosis, but rather the self consistency of all the data with a single corrosion mechanism or set of mechanisms. Misdiagnosis and confusion occur primarily when a single characteristic is incorrectly assumed to be unique to MIC and other possible mechanisms ignored. MIC misdiagnosis is rife in the literature, and surprisingly much of the difficulty stems not so much from a lack of knowledge concerning the microbial mechanisms, poorly understood as they might be, but rather from a misunderstanding of what and how failure analysis is done.

It is the avowed purpose of this paper to disabuse the reader of the uniqueness of many of the diagnostic criteria currently used to diagnosis MIC.

**TUBERCULATION**

**General description:**

Tubercles are structurally complex corrosion cells in which accumulations of metal oxides, deposits and corrosion products cap localized regions of metal loss. Attack occurs on steel, cast iron, and rarely, on stainless steels. Tubercles may be smooth, nodular or take the form of fluted cones (Figures 1, 2). Morphology depends on water chemistry, dissolved oxygen concentration, temperature, flow and corrosion rates. Tuberculation is fundamentally caused by differential aeration cells. Oxygen deficient regions below the accumulated corrosion products and deposit masses produce anodic sites, while areas atop and surrounding the magnetite shell are cathodic.

Corrosion products and deposits:

Five processes cause tubercular growth. Tubercles grow both internally and externally. Ferrous ions generated internally form ferrous hydroxide in the core as in equation (3) below or are expelled through tubercular fractures and are quickly oxidized to ferric hydroxide upon exposure to oxygenated water outside as in equation (1). The tubercular crust consists of large amounts of precipitated ferric hydroxide. Compounds with normal pH solubility such as carbonates, deposit atop the shell, and previously precipitated and solid materials may also settle atop the crust. Internal reactions within the core, the fluid filled cavity or on the corroding floor may also contribute to tubercular growth, but are usually less important in producing the bulk of the tubercular mass than the previously described processes.

All tubercles have five structural features in common:

- outer crust
- inner shell
- core material
- fluid cavity
- corroding floor

Obviously, even if the structure superficially resembles a tubercle, if these features are absent, the structure is not a tubercle, but rather may simply be an accumulation of deposited iron oxides and other material. A typical tubercle schematic with chemical compounds and structures is shown in Figure 3. Reactions occur as follows:

\[
\text{(outer crust)} \quad \text{Fe(OH)$_2$}^+ + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{4}\text{O}_2 \quad \rightarrow \quad \text{Fe(OH)$_3$} \quad \text{(1)}
\]

\[
\text{(inner shell)} \quad e^- + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \quad \rightarrow \quad 2\text{OH}^- \quad \text{(2)}
\]

\[
\text{(core material)} \quad \text{Fe}^{++} + 2\text{OH}^- \quad \rightarrow \quad \text{Fe(OH)$_2$} \quad \text{(3)}
\]
(fluid cavity) \[ \text{Fe}^- + \text{Cl}^- + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+ + \text{Cl}^- \] (4)

\[ 2\text{H}^+ + \text{Fe}^{++} \rightarrow \text{Fe}^{2+} + 2\text{H}^+ \] (5)

(corroding floor) \[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \] (6)

Many other reactions can occur below the tubercular cap, some involving bacteria, producing siderite, pyrrhotite as well as other compounds (Figures 4, 5, 6). Additionally, atop the tubercle, hydroxide is generated, increasing pH locally and inducing precipitation of compounds with normal pH solubility such as carbonates.

Wastage morphologies:

Corroded areas beneath tubercles in the absence of significant MIC are usually broad, irregular depressions. Corroded floors may be highly striated (Figure 7). Striations are usually associated with rapid corrosion, locally exceeding 10-20 mpy. The striations are caused by preferential attack along longitudinally oriented microstructural features caused by forming or alloy manufacture. Striations can follow pearlite stringers, coring and stressed regions. Striations are known to occur when water pH is highly acidic and can be seen clearly after acid cleanings, but are never produced beneath a tubercle after an acid cleaning (Figure 8). Additionally, circumferentially oriented, concentric ledges sometime called bulls eyes may form if corrosion rates abruptly vary and continue for extended periods at the new rate.

MIC involvement

Many tubercles form in environments in which bacteria would likely be absent. There are some studies which suggest that tubercular masses may be caused by iron depositing bacteria. Tubercles may form in boilers if oxygen is dissolved in the boiler water at high pressures and at temperatures exceeding 100 degrees Centigrade(212 F) and in sulfuric acid baths. But in many cooling water environments, bacteria are almost always present and bacteria can almost always be found in tubercles. Ford et al. have indicated that core materials are the principal sites for colonization of potentially corrosive anaerobes. However the bacteria are clearly not the sole cause of tubercular development, nor should bacteria be considered a significant accelerant of tubercular growth a priori. Features that have frequently been associated with bacterial acceleration of corrosion rates beneath tubercles are the following:

- presence of iron sulfides—especially pyrrhotite crystals near the corroded floor (usually sulfate reducers)
- presence of low molecular weight organic acid salts, e.g., acetic, propionic etc. (usually acid producers)
- deep, hemispherical, clustered pitting superimposed upon the larger dish-shaped depression (usually sulfate reducers)
- striated pit interiors and large fluid filled cavities (usually acid producers) (Figure 7)
- biological counts of core materials exceeding 10,000 for sulfate reducers and 1,000 for acid producers (clostridia)
- absence of high core material chloride concentration (exceeding one percent)
- filamentous structures in core material (attributed to Gallionella)
"TIGER STRIPING"

General description

The term "tiger striping" describes predominantly vertically oriented rust streaks originating at pit sites. A colorful imagination might see a superficial resemblance to the broad vertically oriented stripes on a tiger. Stripes usually grow from pits and tend to originate on surfaces continuously submerged beneath water. Often the pits are found at corroded stainless steel welds.

Corrosion products and deposits

The stripes are predominantly precipitated ferric hydroxide; small amounts of chloride and other anions also tend to accumulate in the stripes. Fluids within pits are usually acidic, both stimulating attack and preventing corrosion product precipitation within the pits (see equations 4 and 5). Eventually, convection and diffusion cause pit contents to be ejected into the oxygenated, higher pH waters outside the pits. The ejected ferrous ions are rapidly oxidized to insoluble ferric hydroxide (see equation 1), and the resulting rust deposits on adjacent surfaces. If pits are on vertically oriented walls, and waters are fairly quiescent, gravitational settling of precipitated material causes rust streaks in the direction of gravity below pits. It is surmised that the settling processes may also contribute directly to some striping on nonstainless steels.

Wastage morphologies

On horizontally oriented surfaces, rust rings may surround pits (Figure 9); regions immediately around the rings may be devoid of significant precipitated rust, it is surmised, because the water near the leaking pits is too acidic to allow rust precipitation. Secondary pitting may occur below primary pit sites due to the leaking chloride, low pH and/or secondary colonization by anaerobic bacteria in the deposited areas. Figures 10 and 11 show secondary pits fanning out below the original pit site on a vertically oriented 316L stainless steel tank wall exposed to waters containing high chlorides and a moderately acidic pH.

MIC involvement

Stripes are sometimes associated with the presence of anaerobic bacteria including acid producers and sulfate reducers. However often the stripes occur in environments essentially devoid of any bacteria, and frequently are found in environments containing chloride and acidic fluids. Striping has occurred at a weld in a 316L stainless steel tank which contained an acidic biocide containing several thousand parts per million of chloride. Further, welds containing defects and some more egregious flaws predispose the welds to preferential attack, whether bacteria are involved or not. Signs of bacterial involvement include:

- gelatinous bacterial accumulations intermixed with red or brown mounds of oxides and hydroxides

- seemingly defect-free weldments

- chloride concentrations in and near pits less than about one percent

PIT "TUNNELING"

General description:

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Pitting is an extremely complex subject and is well beyond the scope of this paper. However, the nature and causes of pit undercutting and tunneling can be reduced to rather simple and general principles. Severe undercutting and subsurface tunneling are fundamentally caused by higher local corrosion rates inside pits than on adjacent surfaces. Any process which increases the aggressiveness of the environment within the pit interior stimulates tunneling and undercutting. Subsurface cavities can interlink to form large, extended voids (Figures 12, 13, 14). Also, the alloy microstructure frequently has a very important influence on tunneling. Coring, twinning, sensitization and other microstructural features have been shown to stimulate preferential attack, and consequently, pit undercutting in 18-8 stainless steels. Often the pits are almost invisible to the naked eye and can be revealed only by probing with a sharp pick; the underlying pit is revealed by peeling back a thin overlying skin of intact metal.

The autocatalytic nature of chloride pitting has been described by Evans as long ago as 1951 and Fontana and Greene in 1967. The pitting process accelerates with time due to the necessary and stimulating conditions of the autocatalytic corrosion mechanism. For example, in an 18-8 stainless steel submerged in sea water, spontaneous concentration of chloride and associated hydrolysis may produce pH of 2 or less within pits, even though the sea water pH may be about 7.8. Additionally, surfaces around the developing pit usually become stable cathodes, the cathodic oxygen reduction decreasing corrosion on adjacent surfaces outside pits.

Corrosion products and deposits:

In stainless steels it is common for pit interiors to be essentially devoid of significant corrosion products and deposits. This is often explained by the highly acidic fluids and the low dissolved oxygen concentrations within the pits, both stimulating metal dissolution and preventing the precipitation of oxides and hydroxides within pits. Reactions in equations 1 and 4-6 describe the chloride pitting mechanism. Frequently, chlorides are found within pits. The failure to find chlorides within pits is often erroneously assumed to rule out chloride involvement. In fact, the highly soluble nature of chlorides makes detection difficult in many cases. Further, it is often the case that the pit contents are either flushed out during sample handling or metallurgical preparation. It is often the case however that the chlorides can either be detected by examination of the pit ejaculate and other debris atop and immediately surrounding the pit site. Occasionally the highly acidic nature of the pit contents can be inferred indirectly by associated attack. Figures 7, 9 show secondary pits nucleating from acidic fluids leaking from the pit above.

Wastage morphology:

Undercutting on 18-8 stainless steels is quite common in a variety of acids and is especially pronounced in acidic chloride containing waters in which autocatalytic processes are favored. Obviously undercutting is the predominant phenomenological feature which differentiates this attack from other pitting. Chloride attack may cause preferential corrosion along twin boundaries, Figure 14. Multiple pit sites may interlink to extend and deepen existing pits, the original pits apparently acting as nucleation sites for new attack (Figure 12).

It is comparatively rare to observe severe undercutting on non stainless steels in the absence of severe acid exposure. However, tunneling can occur in special instances. Figure 15 shows preferential, attack along a weld backing ring on a carbon steel service water pipe in a nuclear service water pipe.

MIC involvement:

Perhaps no single subject is as controversial as is the nature of MIC pitting (hence, the tongue-in-cheek title of this paper). It is extremely difficult to determine if the tunneling, indeed if the pitting, is caused by MIC from a simple visual examination alone. However, characteristics of bacterial involvement include:

- hemispherical pits containing substantial sulfides-only slight undercutting (sulfate reducers-Figures 16 and 17)
- pits clustering beneath deposit, which in turn contain "high" bacterial counts (sulfate reducers)
- tunneling and undercutting (acid producers and possibly metal oxidizers)
- significant biofouling
"HIGH" BIOLOGICAL COUNTS

General description:

It is often stated and written that a corroded component was "loaded with bugs". Such statements while dramatic should not be viewed as self-evident proof of MIC. The presence of bacteria is required for MIC. The amount of bacteria and the location of the organisms can only be used as a loose diagnostic tool for several reasons.

First, Little et al. have shown that some bacteria are apparently attracted to preexisting pit sites. The implications of this deceptively unassuming study are quite clear and quite startling. If organisms are attracted to a pit or corrosion site, the organisms as a fundamental cause of the pit is open to question. It is speculated that "high" numbers of bacteria at corroded welds as a cause of the weld attack may similarly be open to question. Indeed, these observations may call into question whether biological counts are of significant value at any corrosion site.

Secondly, it has been reported that numbers of corrosive bacteria can actually be higher away from corrosion sites than in actively wasting areas. In particular, sulfate reducer counts can be as much as an order of magnitude greater in material removed from between tubercles than in tubercle core material. The higher anaerobic counts between tubercles may of course be to some extent an artifact of poor sampling technique. Higher aerobic counts between tubercles might be expected because of the greater surface area to volume ratio between the relatively flat corrosion products and deposits between tubercles (aerobes would likely favor oxygenated sites near the oxide-water interface).

MIC involvement:

To the best of this observer's knowledge, no systematic, controlled study of biological counts and corrosion have been done. Phenomenological studies have indicated a correlation of increased corrosion rates below tubercles when sulfate reducer counts exceed 10,000 and certain acid producer counts exceed 1,000 colony forming units per gram of wet material.

WELD ATTACK

General description:

Welds are formed by a fusion of metals at their interface. Many problems predispose welds to preferential corrosion and failure. A significant number of problems involve weld defects. A weld defect is a structural or metallurgical interruption in the weldment that significantly degrades the property of the weld with respect to its intended use. Specific weld defects include burnthrough, galvanic corrosion, incomplete fusion, incomplete penetration, porosity, slag inclusions, weld decay, severe heat tint, weld-root cracking and high welding stresses. Often defects are ignored or not understood to be a major contributing cause of failure. The subject of welding is indeed a complex one and is discussed thoroughly elsewhere.

By their very nature, welds tend to be more susceptible to corrosion than most other alloy sites. In many environments corrosion may occur at welds first and with greater severity than elsewhere whatever the source of corrosion. Additionally, it is often the case that the weld may be the only site where corrosion is significant. Very often weld attack has been attributed to MIC when other alternative explanations involving other corrosion mechanisms have been overlooked.

Wastage morphologies:

Preferential attack at dendritic or interdendritic phases in autogenous welds often occurs in 18-8 stainless steels, (Figures 18 and 19). Preferential phase attack is caused by a galvanic effect between the two compositionally different phases in the weld. Upon alloy solidification, solute rejection occurs at the kinetically undercooled dendrite-liquid interface causing a chromium enriched interdendritic phase to form. The less noble phase is preferentially corroded, leaving behind the skeletal remains of the other phase, (Figure 20). As in all galvanically driven processes, the relative areas of the phases may materially change the corrosion process. The greater the relative amount of noble phase, the greater the corrosion of the less noble phase. The relative areas of the noble and less noble phases are affected by the physical orientation of the dendrites in the weld, which in turn, can be affected by the solidification rate and heat input.
Long continuous, more noble, surface lying dendrites tend to increase the relative galvanic effect, and hence, the corrosion\textsuperscript{20,21,22}. Preferential phase attack may also be influenced by the relative oxidizing power of the environment.

Sensitization of stainless steel welds occurs when chromium reacts with dissolved carbon in the weld zone to form chromium carbides. The chromium depleted zones are less noble than the surrounding metal, and consequently, are predisposed to attack\textsuperscript{16}.

Severe heat tint or oxidation of the weld can materially reduce weld corrosion resistance. Much of the cleaning done in stainless equipment is designed to reduce or eliminate the deleterious effects of heat tint.

MIC involvement:

Much of the literature purporting to show that MIC has occurred at welds relies on the topics discussed previously in this paper. Tuberculation, tunneling pits, high biological counts and tiger striping are usually assumed sufficient to warrant a diagnosis of MIC. It is indeed true that such criteria are often associated with weld corrosion. However, similar appearing attack (with the exception of high biological counts) can also be produced by high dissolved halide concentrations, acidic waters and defective welds (Figures 18, 19 and 20). It is clear enough when attack occurs in biocide tanks or immediately after an acid cleaning that attack is likely not MIC. However, often it is assumed that the mere presence of bacteria is enough to warrant MIC. Causality at a minimum should be reinforced by:

- corrosion products consistent with MIC (e.g. sulfides for sulfate reducers, organic acid salts for certain acid producers etc.)
- exclusion of all significant weld defects
- "significant" bacteria counts
- absence of potential corrosives not related to bacteria
- a thorough understanding of operating history and past system treatment (including acid excursions and chemical cleanings)

CONCLUSIONS

There are a variety of ways microorganisms may contribute to corrosion. However, many of the characteristics used to differentiate MIC from other corrosion processes may appear in more than one corrosion mechanism. Major characteristics of MIC include:

SRBs - hemispherical pits
- sulfides and metal oxide corrosion products
- pits clustered in groups
- tubercular corrosion is increased when counts exceed about 10,000 in core material
- preferential weld attack in some steels
- pit terracing

Acid producers (some anaerobic)
- undercut pits
- striated pit interiors
- organic acid salt corrosion products
- tubercular corrosion is increased when clostridia counts exceed about 1,000 in core material
- preferential weld attack in some steels
- Tiger striping
- pit tunneling

All of the above characteristics may be present in other corrosion processes.
MIC can be recognized. Yet, there is no single test which uniquely identifies MIC. Numerous anecdotal factors such as tiger striping, tuberculation, tunnel pitting, high biological counts and preferential weld attack have been used as MIC diagnostic tools. And indeed, some of these criteria do seem to occur in some MIC. However, many descriptions of MIC based upon these factors alone are incorrect. Erroneous identification frequently is caused by a fundamental misunderstanding of the failure analysis process and the mistaken belief that a single factor taken in isolation, and ignoring other data, is sufficient to warrant a correct diagnosis.

MIC diagnosis can be made if and only if all data, observations and system history are consistent with biological attack. If even a single factor is inconsistent with a given failure mechanism, diagnosis cannot be made. If two or more explanations are consistent with the known information, both explanations must be proposed as possible explanations. The explanation requiring the fewest assumptions is usually more probable.

REFERENCES


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FIGURE 1 - Heavily tuberculated carbon steel service water pipe interior.

FIGURE 2 - Cone-shaped tubercles. The tubercles form by precipitation of ferric hydroxide blown away from corrosion sites by water flow.
**FIGURE 3** - Tubercle schematic showing locations of the crust, shell, core, fluid-filled cavity and corroding floor.

**FIGURE 4** - Possible and usual tubercle reactions at specific locations within the tubercular structures.
FIGURE 6 - Hexagonal, flat, pseudomorphically oxidized pyrrhotite crystals near a tubercle floor. Such crystals are often associated with sulfate reducers.
FIGURE 7 - Heavily striated surfaces beneath tubercles suggesting the presence of acid producers.

FIGURE 8 - Striations on a carbon steel pipe interior after acid cleaning. Compare with Figure 7.
FIGURE 9 - Rust ring on 304 stainless steel shaft caused by precipitation of ferric hydroxide ejected from central pit.

FIGURE 10 - Pits caused by exposure to a strong acid on a large diameter 304 stainless pipe. Note the vertically oriented secondary secondary grooves caused by leakage of acidic pit contents above.
FIGURE 11 - As in Figure 10. Note the parallel striations within the pits and grooves. compare with Figures 7 and 8.
FIGURE 12 - Scalloped, partially undercut pits in cross section on a 316 stainless condenser tube. Note the multiple pit origins.

FIGURE 13 - Tunneling pit in a 304 stainless steel tube wall caused by low pH and high chlorides.
FIGURE 14 - Tunnel pits following twin boundaries and emanating from chloride stress corrosion cracks in a 304 condenser.

FIGURE 15 - Deep sulfate reducer pit below a tubercle at a carbon steel weld backing ring.
FIGURE 16 - Aluminum heat exchanger tube severely pitted by sulfate reducers.

FIGURE 17 - Small hemispherical sulfate reducer pits on a 316 stainless steel plate. Light areas pit clusters mark ghost images of deposits.
FIGURE 18 - Weld showing an apparently small surface defect in a 316 stainless steel service water pipe.

FIGURE 19 - As in Figure 18, but showing severe interdendritic attack.
FIGURE 20 - Skeletal remnants of the interdendritic phase shown in Figures 18 and 19.