Characterization and evaluation of microbiologically induced corrosion on water heating networks

Ernesto S. Zumelzu and Ricardo Silva

ABSTRACT: *Microbiologically induced corrosion (MIC) is significant because of the important effects microorganisms have on metal surfaces. MIC produces changes in microstructure and on the electrochemical reactions of corrosion processes. This work examines bacterial populations from a boiler water supply on galvanized iron, stainless steel, and copper. It also analyzes the influence of bacteria on deterioration of such materials. Laboratory conditions simulate actual operations to evaluate MIC of cultures using scanning electron microscopy, transmission electron microscopy, and X-ray dispersive energy microanalyses.*

KEYWORDS: *Bacteria, copper, corrosion, corrosion mechanisms, crevice corrosion, electrochemistry, electrolytes, iron, metals, microorganism control, oxygen, pH, pitting, simulation, steel, water supply.*

Microbiologically induced corrosion (MIC) results from the presence of microorganisms on a metal surface. MIC can produce changes in the velocities and sometimes in the type of electrochemical reactions involved in corrosion *(1)*. Several studies *(2)* suggest that the presence of microorganisms on metal surfaces often produces highly localized changes in the concentration of some constituent electrolytes. There can also be an effect on pH and oxygen levels. For passive metals, any such changes could induce localized corrosion evidenced as pitting and crevice corrosion.

Some common organisms in water distribution systems are *Pseudomones*, *Flavobacterium*, *Proteus*, *Klebsiella*, etc. *(3)*. Bacteria that can oxidize iron and magnesium are *Gallionella*, *Hyphomicrobium*, and related bacteria. These can occur on the nodule and sulfide bacterial formation surface. They are heterotrophic and anaerobic sulfate reducers. There are also iron bacteria such as *Thiobacillus ferroxidans* and *Ferrobacillus ferroxidans* that are autotrophic and bacillary.

This study characterizes and evaluates MIC under simulated conditions in a medium derived from a water heating network of a forestry processing plant. It uses observations by electron microscopy to assess bacterial populations.

The study is relevant to any industry lacking an abundance of water. Such a lack can increase retention times in the water network. An increased concentration of organic acids, sulfides, and metabolic products can consequently promote MIC.

Materials and methods

The detection of MIC in water heating networks is more complex *(4)* than making simple bacterial counts in water samples. Although a bacterial count indicates the microbiological population level, it does not reflect the MIC situation in the circuit. This work therefore used an open experimental circuit of water that mimics the composition of makeup water with water condensed from a boiler water supply tank. Temperature was 32± 1°C with control of fluid speed and agitation. Metal samples placed in this circuit for 72 h had an exposure area of 2 cm^2. Assessment of the formation of

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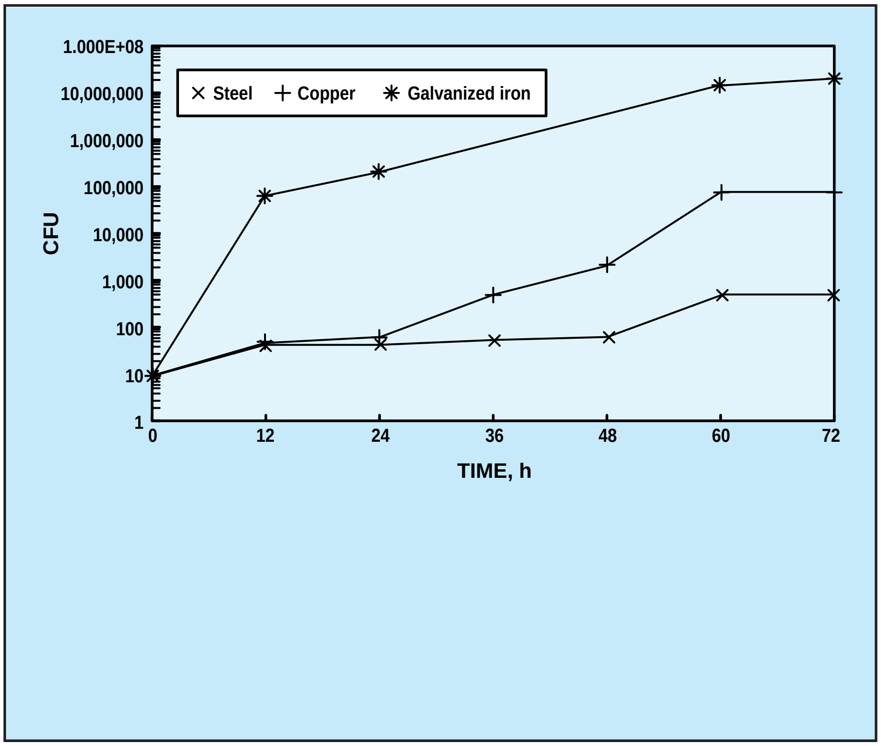
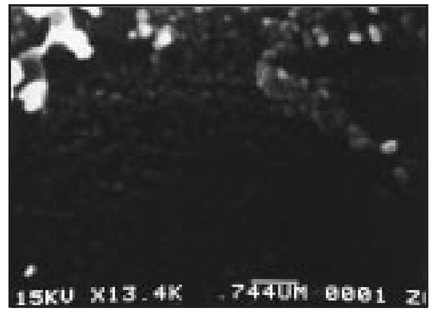
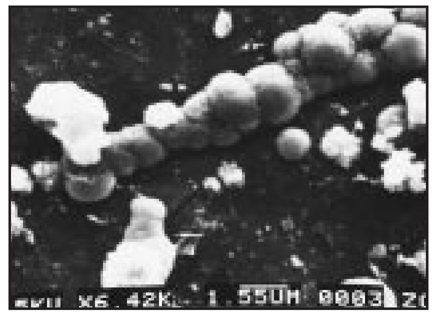
1. Bacterial growth over time on galvanized iron, copper, and steel



2. Spherical bacterial colony over nodules, 13,400X SEM



3. Morphology of bacterial forming rods in the surface, 6420X SEM



nodules and the bacterial growth occurred at different intervals *(5)*. The information derived from the microbiological population assessment techniques and the metallographic observations provided a clear indication of the MIC effects.

Table I shows the characteristics of the materials analyzed in this study. **Table II** presents the characteristics of the electrolyte that is makeup water passed through a filter and an ion exchange water softener resin. It resides in a mixing tank where regular addition of sodium sulfite provides the electrolyte concentration shown in the table. Our study also incorporated a typical quaternary ammonium bactericide commonly used in a boiler.

Microstructural observations and evaluation of MIC used scanning electron microscopy (SEM) and transmission electron microscopy (TEM) supported by a commercially available detector.

I. Characteristics of materials

Material	*Characteristics*	*Composition*
Galvanized iron	Zinc lining 270 g/m^2	Steel: 0.15% C, 0.07% P and S, 0.60% Mn
Steel AISI 316	Stainless	0.08% C, 17.0% Cr, 0.20% Mn, 11.50% Ni, 0.75% Si, 2.25% Mo
Copper DHP	UNS 12200 deoxidized in phosphorus	99.9% Cu

Results and discussion

Figure 1 shows the growth of the total bacterial population in water measured as a colony forming unit per mL per unit of time (CFU) for the immersed materials. The amount of biofilm and superficial tubercles observed by SEM show that the galvanized iron had a higher and faster bacteriological growth than copper and stainless steel.

Microstructural characterization of the MIC

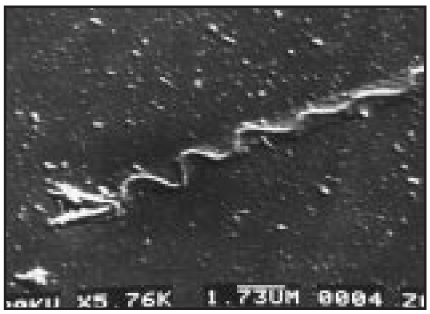
Some microorganisms can survive traditional treatments of water. Under certain conditions, the appearance of discrete deposits or nodules and the formation of continuous biofilms or slime over a metal surface are possible. This formation is responsible for the development of incrustations or tunnels under which corrosion can occur. **Figures 2 through 7** show the size and mor-

4. Shape of a single bacterium between the nodule layers, 22,000X TEM

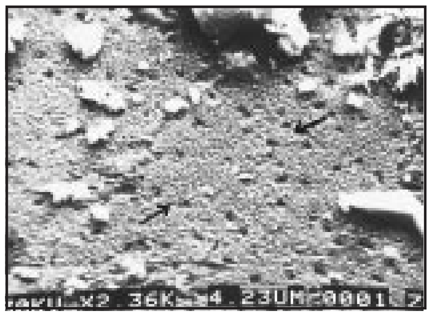
5. Filamentous bacteria over the nodule surface, 1660X SEM

6. Curve-shaped organisms on the nodule surface, 8300X SEM

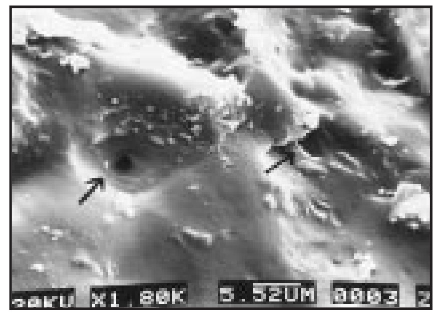
7. Morphology of a spherical-shape bacteria on the nodule surface, 5760X SEM



8. Tunnel formation in nodules over galvanized iron, 2360X SEM



9. Tunnel detail in nodule over stainless steel, 1800X SEM



II. Chemical analysis of water

Parameters	*Specified range*	*Water values in this study*
Alkalinity, P, ppm	100–400	175
Alkalinity, M, ppm	150–600	175
Free OH, ppm	50–200	175
Chloride, ppm	125 maximum	100
Phosphate, ppm	20–40	20–30
Sulfite, ppm	15–30	38.5
Residual hardness, ppm	< 6	< 6
pH	8.2–11.5	8.7

P = Phenolic
M = Medium

phological characterization of different types of bacteria found on the surface of the assayed samples.

The microorganisms shown in these figures comprise the tubercle surface. Incrustation from the water interphase, oxygen, and nutrients constantly occurs. Any incrusted microorganisms receive protection from the action of the residual disinfectants.

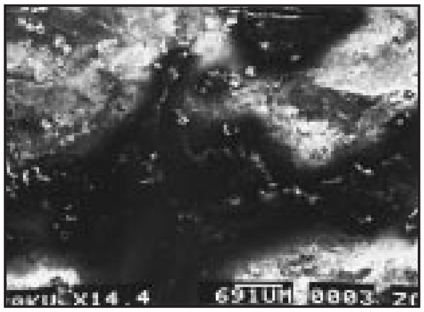
Galvanized iron was more sensitive to the formation of nodules and to the existence of bacteria. X-ray dispersive energy microanalysis of the nodule layer showed Ca, Cu, Fe, Si, Mg, S, and P in small amounts.

Formation of cracks in the nodules

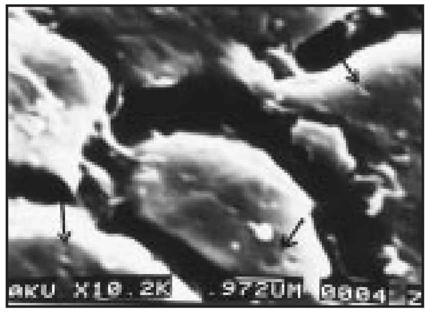
Once a nodule forms on the surface, a defect having the shape of a crack or a tunnel starts to develop from the interphase of electrolyte and tubercle until it reaches the metal surface. The associated nodules and bacteria deplete the oxygen that tries to enter the tunnel region under the nodule. In an oxidized microenvironment, this would induce the development of oxygen concentrated cells where the area outside the nodule was rich in oxygen.

Figure 8 shows the formation of cracks in the surface of nodules with average diameters of 1 μm (dark spots) covering galvanized iron and the colonized bacteria under it. **Figure 9** provides the details of a superficial tunnel in the stainless steel nodules (middle left area). This phenomenon occurs with localized metabolic processes that induce concomitant corrosion processes. The iron oxidizing bacteria can apparently detect the presence of ferrous ions formed from the corrosion of steel. They catalyze the reaction of ferrous ions with water-dissolved oxygen to form ferric oxide. The Fe_3O_4 that they excrete is insoluble in water. It combines with organic matter to form a layer or tubercle over the source of ferrous ions. This tubercle is a deposit that favors cor-

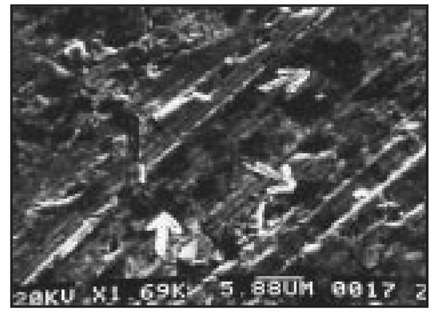
10. Surface morphology of galvanized iron, 14.4X SEM



11. Details of small pits (round spot) in grains under nodules, 10,200X SEM



12. Surface morphology of nodule-free copper, 1690X SEM



rosion under it by increasing the reaction rate of Eq. 1:

$$O_2 + 4e^- + 2H_2O = 4OH^- \qquad (1)$$

This reaction removes electrons from the metal and causes the electrochemical potential to become more positive.

Evaluation of superficial damage under the nodules

The samples having nodules or slime formation with bacteria present underwent cleaning with ultrasound to characterize and evaluate the superficial damage of the material by SEM. **Figure 10** shows the galvanized iron surface free of tubercles. There are different states of iron oxidation and selective damage (dark zone). This occurs because the nodules and the associated microbiological activities create conditions for the ions to concentrate mainly in or under the nodules. Such conditions can promote the oxidation of ferrous iron to ferric iron. Then the need for neutralizing charges results in the accumulation of chloride ion in the nodule or crevice region.

Figure 11 shows the MIC effect on the surface of the stainless steel after removal of the nodule deposit to evaluate the presence of micropitting. The nodules showed small entrance points. These led to a large cavity under the surface. The austenite phase had more severe attack than the ferric one. In addition, the X-ray dispersive energy microanalysis suggested the formation of iron sulfide layers that are responsible for the formation of the tubercle.

For copper samples, **Fig. 12** shows the presence of localized attack (dark areas) to the surface morphology. This remains after the removal of the tubercle or nodule.

The most frequent attack produced by MIC in copper is type I *(6)*. A characteristic of this attack is a shallow cavity with green precipitate. This is similar to the action of medium and high hardness water containing a high concentration of sulfate—the electrolyte in this study. The type I mechanism is pitting corrosion that always has a green or bluish green covering of corrosion products that are mostly malachite *(6)*. A copper oxide layer acting as a membrane completely covers the area of superficial attack.

Although the literature mentions various types of microorganisms in water *(3)*, this work only assessed the presence of bacteria and characterized their habitats. There was no further identification of the bacteria, since this requires additional metabolic processes not within the scope of this study.

Conclusions

Based on our work, it is possible to draw the following conclusions:

- Only microorganism influence can explain the superficial damage to the materials studied using the electrolyte of a water supply circuit.
- A metal and tubercle interphase contains a high population of bacteria. These occur under incrustations protected from the action of the disinfectants. They therefore accelerate the pitting and differential aeration corrosion processes.
- The formation of tubercles is not necessarily a consequence of inadequate treatment or the type of water disinfectants, since the bacterial population constantly adapts to changing environments. TJ

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