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A study of the microbiological-corrosion products of steel and cast iron pipes in fresh water

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Biological corrosion is one of the most common corrosive processes found in steel, cast iron and other metals placed in soil, sea water and fresh water. We have studied this type of corrosion development process in steel and cast iron pipes. This corrosion process shows tubercular morphology on the inside surface of pipes. Resulting corrosion products have been examined by: chemical analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD) and Mössbauer spectroscopy. In all the samples the following iron compounds were found: α-FeOOH (Goethite), γ-FeOOH (Lepidocrocite), non-stoichiometric Fe_3O_4 and colloidal hydrate oxide $Fe(OH)_3 \cdot 0.9H_2O$. Small quantities of α-FeOOH and γ-FeOOH compounds were present as small size grain particles (10–20 nm). These particles may be considered responsible for worsening the organoleptic properties of water.

1. Introduction

Corrosion of cast iron and steel in fresh water involves an electrochemical cycle of reactions resulting in a scale, the composition of which has been thoroughly studied. The phenomena may be largely modified by the presence of micro-organisms.

The first studies involving the microbial acceleration of the localized corrosion in metals were reported by Ellis and Hander in 1919 [1, 2]. Other researchers [3, 4] studied microbially assisted corrosion of metals such as lead, iron, cast iron, etc. placed in soil and aqueous environments by sulphate reducing, sulphur oxidizing and "iron" bacteria. The most common bacteria that normally influence the corrosion of metals are those of the sulphur cycle (*thiobacilli* and *desulphovibrio*), the former have an oxidant action, transforming sulphur to sulphate [5], while the latter catalyze the reduction of SO_4^{2-} to S^{2-}.

Moreover, the presence of micro-organisms with active or non-metabolic processes can generate the formation of aeration cells and other types of concentration cells. Tubercles, which are formed over the corroded area, contain amorphous ferric hydroxides and many typical bacterial sheaths of ferric hydroxide from iron bacteria *gallionella ferruginea.*

In a previous paper [6] we studied a case of biological corrosion in ductile iron pipes in a waterworks in Sardinia, in order to classify the composition of tubercles. In this paper we examine and compare the composition of normal corrosion scale and microbiological tubercles , growing on the inside surface of both ductile iron and steel pipes of these waterworks.

2. Experimental procedure

The water pipes of uncoated nodular cast iron and steel have a diameter ranging from 200 mm (near the reservoir) down to 50 mm. After a few years, the first evidence of water quality alteration was the presence of suspended particles of iron hydroxide, up to 0.2 $g\,l^{-1}$, enough to strongly modify the organoleptic properties of water. In the smallest pipes (50 mm diameter) the presence of large deposits has been observed, having tubercle morphology, in general in the pipes with a lower water flux. After removal of deposits, pipes showed an evident, but not too deep corrosive attack.

An example of corroded water pipe is shown in Fig. 1 (ductile iron pipe). The inside surface appears uniformly coated by a thin brown scale having the same very evident red-brown tubercles. We examined samples of tubercles and uniform scale, taken from ductile iron and steel pipes (500 mm diameter). Chemical analysis of these samples (see Tables I–III) does not show significant differences: iron content was in the range 50–60%, with small amounts of manganese, calcium and magnesium (0.02–0.06%). In the tubercles significant amounts of organic matter were always present (4.43% max). In Tables I–III chemical analysis of iron, cast iron and water are reported, respectively.

In the water, the very low total salinity, the clorides and sulphate content, and the oxygen saturation appear to be significant. The microbial analysis of water revealed the presence of various groups of bacteria both sulphur oxidizing and iron bacteria. Structural characterization of the deposits was performed by X-ray diffraction (CrK_α radiation) and Mössbauer spectroscopy. Mössbaur spectra of deposits were recorded in transmission geometry with constant acceleration movement using a commercial spectrometer, utilizing

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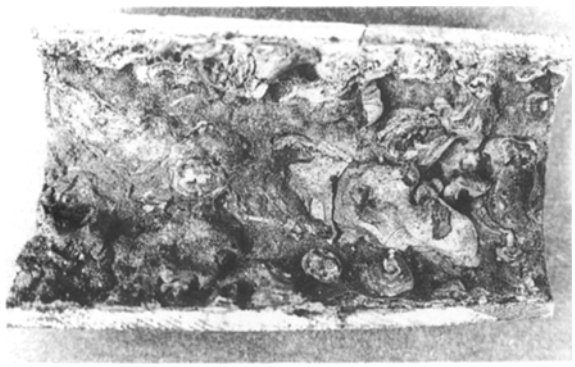

Figure 1 Tubercles in a cast iron tube, of 50 nm diameter.

TABLE I Chemical analysis of corrosion products (wt %)

Fe	Mn	Ca	Mg	SiO_2	Ignition loss
56.8	0.06	0.06	0.02	2.00	4.40

TABLE II Chemical composition of cast iron (A) and steel (B) pipes (wt %)

	C	Si	Mn	S	P
(A)	3.47	2.3	0.45	0.01	0.08
(B)	0.12	0.22	0.35	0.01	0.015

TABLE III Water analysis

pH	Fe^{3+} ($mg\,l^{-1}$)	Mn^{2+} ($mg\,l^{-1}$)	O_2	Hardness ($mg\ CaCO_3\,l^{-1}$)
6.7	0.01	< 0.01	sat.	80

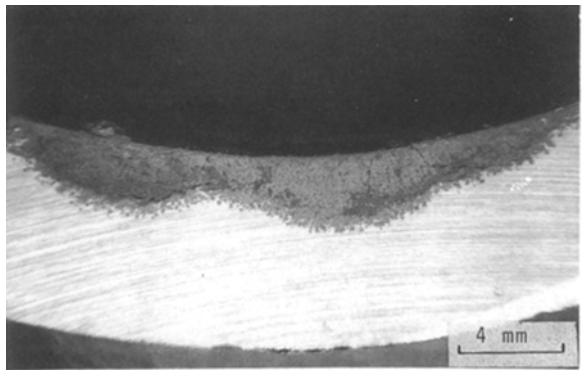

Figure 2 Corrosion phenomena with saucer morphology.

a Co^{57} source, in Rh matrix with nominal activity of 50 mCi. The spectra were analysed with a least-square fit computer program.

3. Results and discussion

In the case we examined the corrosion process generally develops in aerated conditions. Moreover, no

TABLE IV Mössbauer results. H (kG, ± 6) hyperfine field, Δ ($mm\,s^{-1}$, ± 0.2) quadruple splitting, δ ($mm\,s^{-1}$, ± 0.2) isomer shift referred to α-iron, Γ ($mm\,s^{-1}$, ± 0.2) line width, RA% relative area percent, x vacancies concentration in magnetite (Equation 1)

			Cast iron tubercle	surface	Steel tubercle	surface
α-FeOOH		H	286	270	282	—
		δ	0.45	0.37	0.39	
		Γ	2.0	0.6	1.5	
		RA%	44	3	38	
		H	337	318	327	—
		δ	0.44	0.36	0.40	
		Γ	0.86	0.25	0.64	
		RA%	9	5	9	
	total	RA%	53	8	47	
γ-FeOOH		Δ	0.58	0.50	0.50	0.56
		δ	0.37	0.35	0.40	0.38
		Γ	0.40	0.32	0.30	0.6
		RA%	22	23	22	51
Colloidal		Δ	1.0	0.84	0.35	1.0
hydrate		δ	0.43	0.43	0.43	0.42
oxide		Γ	0.60	0.55	0.56	0.50
		RA%	25	60	19	14
Fe_3O_4		H	—	491	484	496
A sites		δ	—	0.30	0.29	0.35
Fe^{3+}		Γ	—	0.5	0.68	0.57
		RA%		7	9	20
B sites		H	—	450	454	461
Fe^{3+}		δ	—	0.60	0.60	0.63
Fe^{2+}		Γ	—	0.97	0.92	0.44
		RA%		2	3	15
	total	RA%	—	9	12	35
		B/A	—	0.28	0.33	0.75
		x	—	0.23	0.21	0.12

significant amounts of sulphur compounds were observed in the water nor in the scale. This is in line with the biological examinations, indicating the predominance of iron bacteria colonies. Such a situation appears more favourable for the formation of differential aeration (and perhaps concentration) cells, due to the uptake of oxygen by the microbiological colonies. This may justify localized corrosion phenomena and tubercular morphology. Even in our case, corrosion phenomena took place under tubercles, not with deep pits but with saucer morphology, in which the metal surface was extremely corrugated (Fig. 2).

Despite the diffusion and growth of tubercles in almost all pipes of the water works, we did not observe any perforation in the pipes. It seems that the above mentioned considerations are important to define this particular case of microbial corrosion and the physical-chemical environments in which the corrosion products we studied were produced.

The X-ray diffraction patterns (Fig. 3) only give preliminary and qualitative information in the composition of the scale and tubercles. Almost the same iron oxides have been found in all the samples examined. In the tubercles, α-FeOOH (Geotheite) is predominant over the γ-FeOOH and the magnetite Fe_3O_4. Instead the patterns of the latter appear more evident in the scales, both in steel and in cast iron, as confirmed by several previous studies [7]. Moreover, in X-ray diffraction patterns of tubercles (in both tubes

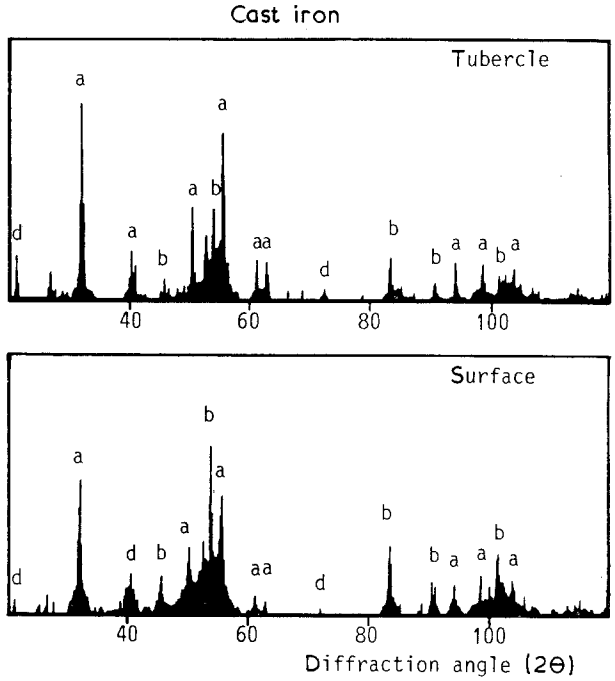

Figure 3 X-ray diffraction patterns (CrK_α), a = α-FeOOH, b = Fe_3O_4, d = γ-FeOOH.

of two different materials) some features, rising from some improperly crystallized phase can be observed.

A more complete characterization of the type of our corrosion products has been obtained by Mössbauer

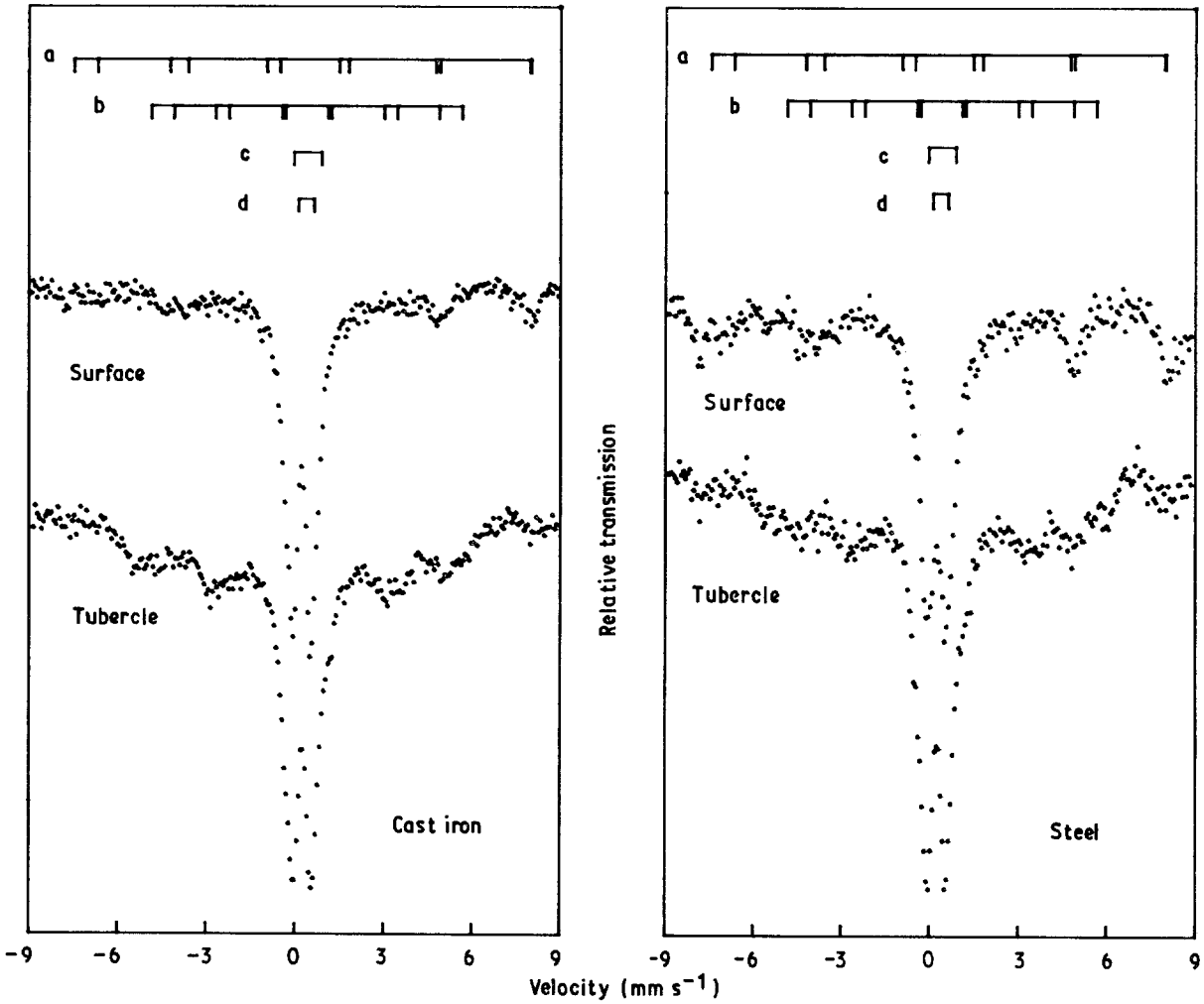

Figure 4 Mössbauer spectra (a = α-FeOOH; b = Fe_3O_4; c = $Fe(OH)_3$ $0.9H_2O$; d = γ-FeOOH).

spectroscopy. Results are shown in Fig. 4 and Table IV. Generally, there is good consistency between the types of iron compounds indicated by X-ray diffraction and Mössbauer. Moreover, Mössbauer spectroscopy confirmed and clarified the presence of a (non crystalline) colloidal phase of hydrate iron oxide $Fe(OH)_3 \cdot 0.9H_2O$ [8], present mainly in the upper area of the tubercles, near the surface, in contact with the flowing water. This colloidal phase appears to be associated with microbial corrosion both in steel and cast iron pipes.

The Mössbauer parameters also give further information on the other types of corrosion products in the tubercles. The α-FeOOH component in the spectra, has been interpreted by two broadened six line patterns (the magnetic component [9]). The broadening may be justified by small particle size. This is consistent with the X-ray diffraction data, indicating a mean apparent crystal size of about 15–23 nm for the Goethite, in our samples.

The more external lines of the Mössbauer spectra, both in tubercles and scale, have to be attributed to the magnetite Fe_3O_4, and consisted of two magnetically split patterns due to Fe^{3+} ions in tetrahedral interstices (A site) and to Fe^{2+} ions in octahedral interstices (B sites) of Fe_3O_4.

The (B/A) spectral area ratio of B site pattern to A site pattern was found to be small compared with the value of 1.88 for the stoichiometric Fe_3O_4. Since the non-stoichiometric magnetite may be represented as [10]

$$Fe^{3+}(Fe^{2+}_{1-3x}\, Fe^{3+}_{1+3x},\, O_x)_x O_4 \qquad (1)$$

the (B/A) ratio, taking into account the difference in the recoilless fraction f (0.94) may be expressed as $2f(1-3x)/(1+5x)$, a function of the vacancies concentration x. Calculated values of x are reported in Table IV.

This lack of stoichiometry can derive from the incorporation of other ions (Mn, Ca, etc.) or from the environmental conditions of oxide formation. In our case, from the chemical analysis, other ions are almost totally absent. Therefore, the structural feature of the magnetite in our sample should be attributed to the environmental conditions, i.e., to the bacterially enhanced corrosion.

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