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Corrosion behaviour and biocorrosion of galvanized steel water distribution systems

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ABSTRACT

Galvanized steel tubes are a popular mean for water distribution systems but suffer from corrosion despite their zinc or zinc alloy coatings.
First, the quality of hot-dip galvanized (HDG) coatings was studied. Their microstructure, defects, and common types of corrosion were observed. It was shown that many manufactured tubes do not reach European standard (NBN EN 10240), which is the cause of several corrosion problems. The average thickness of zinc layer was found at 41 μm against 55 μm prescribed by the European standard.
However, lack of quality, together with the usual corrosion types known for HDG steel tubes was not sufficient to explain the high corrosion rate (reaching 20 μm per year versus 10 μm/y for common corrosion types).
Electrochemical tests were also performed to understand the corrosion behaviours occurring in galvanized steel tubes. Results have shown that the limiting step was oxygen diffusion, favouring the growth of anaerobic bacteria in steel tubes.
EDS analysis was carried out on corroded coatings and has shown the presence of sulphur inside deposits, suggesting the likely bacterial activity.
Therefore biocorrosion effects have been investigated. Actually sulphate reducing bacteria (SRB) can reduce sulphate contained in water to hydrogen sulphide (H_2S), causing the formation of metal sulphides. Although microbial corrosion is well-known in sea water, it is less investigated in supply water. Thus, an experimental water main was kept in operation for 6 months. SRB were detected by BART tests in the test water main.

1. Introduction

Metals used for water distribution system (cast iron, steel or copper) corrode due to their thermodynamic instability.

To avoid corrosion, steel pipes are covered by a protective layer of zinc or zinc alloy using Hot-Dip Galvanizing (HDG) [1,2]. This process consists in the immersion of steels parts in a molten zinc bath to obtain a coating thickness between 20 and 85 μm depending on quality specifications (NBN EN 10240). The structure of the zinc coating can be predicted by the Fe–Zn diagram. The various phases consist of several layers as shown in Fig. 1 [1–6].

The coating thickness is influenced by various factors, the main being chemical composition of the steel substrate. Actually, solute additions in some substrates, such as silicon and phosphorus, affect the growth rate of the various zinc layers during galvanization, resulting in a thick and brittle coating [1] with a too thick zeta phase (Sandelin effect) [4,5,7]. Bath and annealing temperatures have also major effects on the kinetics of the reactions [1,2].

The zinc coating protects steel against corrosion by the two following effects: a barrier effect due to the continuity of the coating that separates the steel from the corrosive environment and a galvanic protection because zinc acts as a sacrificial anode to protect the underlying steel [1,2]. Usually, a thickness of 55 μm (defined by European standard NBN EN 10240 as 396 g/m^2, obtained by a gravimetric method) is advised for good protection of steel against generalized corrosion in fresh water [8]. However, a coating in which the zeta phase is absent or too thick and presents a columnar morphology [2,4–6] does not protect steel from generalized corrosion. To be efficient, the outer eta layer must represent at least 45% of the thickness of the whole coating [7].

Corrosion can also be accelerated either by high levels of chloride and sulphate in the water, by elevation of the temperature or by the pH of the water [1,3,5,6,8,9].

Various types of corrosion can be found in sanitary plumbing using galvanized steel pipes, due to water composition or temperature, solid particle deposits, galvanic coupling (with copper, brass or stainless steel for examples) or the presence of roaming currents [7,8,10]. Actually, in anaerobic media, the corrosion of zinc proceeds via two partial reactions [11]. The cathodic reaction corresponds to the reduction of dissolved oxygen and leads to a pH increase, and the anodic reaction involves the dissolution of zinc and leads to weight loss.

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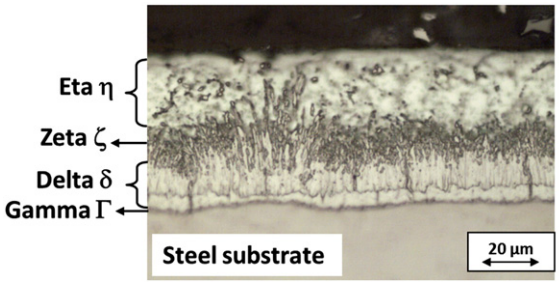

Phase	Composition	HV
η	Zn	37
ζ	$FeZn_{13}$	270
δ	$FeZn_{10}$	450-470
Γ	Fe_3Zn_{10} - Fe_5Zn_{21}	510-550
-	Steel	150

Fig. 1. Optical micrograph of hot-dip galvanized steel (etched with 0.5 vol.% Nital); composition and expected Vickers hardness (HV).

Because corrosion rate of galvanized steel is sometimes too important to be described by common corrosion mechanisms, another type of corrosion has recently been the subject of investigation [12–14]: biocorrosion by sulphate-reducing bacteria (SRB) in oxygen deficient environments, such as plumbing systems, water softeners and water heaters.

Biocorrosion of carbon or stainless steels is a well-known phenomenon occurring in sea medium or in all activities using freshwater sediments and, generally, where bacteria are present and abundant (sea, mud) [15–18]. In the absence of dissolved oxygen as electron acceptor, anaerobic bacteria (like SRB) may reduce sulphate contained in water to sulphite ions, which can be oxidized to hydrogen sulphide H_2S. The electron donor is either H_2 or organic compounds (such as lactate or pyruvate). When H_2 is the electron donor, it is produced by the reduction of hydrogen ion by either zinc (sacrificial anode) or iron which is oxidized to ferrous sulphides [15,19,20]. The organic compounds, on the other hand, are contained and produced by anabolic bacterial cell reactions.

In parallel, the reduction of hydrogen (electron acceptor) is also possible producing adsorbed hydrogen which could be used by bacteria as electron donor. Hydrogen consumption by bacteria still increases corrosion by iron or zinc consumption (electron donor). Moreover, the production of H_2S enhances iron oxidation. This phenomenon could explain corrosion rate in galvanized steel tubes.

Due to the removal of most bacteria from water for drinking, biocorrosion could usually be considered as marginal. Actually, only few studies describe biocorrosion by SRB in potable water means. Seth and Edyvean [21] have noticed frequent occurrences of SRB in drinking water when cast iron pipes are used. They indicated SRB's ability to colonize a new installation quickly, causing an increase of corrosion rate. Ilhan-Sungur and Cotuk [22] highlighted a corrosion rate of 3 µm/y in an abiotic environment against 12 µm/y in a biotic environment for galvanized steel [22]. Moreover, they showed that galvanized steel could be corroded by microorganisms as well as SRB. They assessed that SRB could survive in the mixed species biofilm with very high Zn concentrations. Likewise, a study outlines an increase of corrosion rate from 6 µm per year (µm/y) in abiotic environment to 9.5 µm/y in biotic environment for carbon steel [23]. In some cases, the corrosion rate of galvanized steel can reach 20 µm/y if conditions are favourable to bacterial growth [24].

The object of this paper is to describe microstructures and defects of hot-dip coated galvanized coatings and to present the divergences with optimum structure, as well as to observe various corrosion types in galvanized steel tubes used for sanitary plumbing, and particularly biocorrosion.

2. Materials and methods

2.1. Samples

Various case studies provided us a lot of specimens: (i) new galvanized and new bare steel tubes (16 mm and 22 mm interior diameter galvanized tubes and 16 mm interior diameter steel tubes) and (ii) 16 mm galvanized and bare steel tubes inserted in parallel in an experimental sanitary mean, as shown in Fig. 2, to simulate a potable water distribution system. Water flow in this simulated sanitary mean was maintained at 3.6 l/min.

Samples were studied in the as-received conditions and after use in our experimental sanitary system. Specimens in the as-received conditions were cut axially with a band saw and some were also cut in cross section. They were then prepared for metallographic examination. The mechanical polishing was processed with a water-free lubricant to avoid further corrosion of the galvanized coating. Thickness of the Zn deposit was measured by optical microscopy, with image analysis software. Etching was carried out with 0.5 vol.% Nital for the Zn coating and with 4 vol.% Nital for bare steel tubes to reveal their microstructure.

2.2. Detection and culture of SRB

The presence of SRB was controlled by a BART test (Biological Activity Reaction Test). The BART method evaluates the rate at which bacteria metabolize the substrate and generate an observable reaction as a result of oxidation, reduction, or enzymatic activity. As results of the SRB-BART™ test, the formation of a black precipitate confirms the presence of SRB.

The presence of SRB in our sanitary water main has been checked by a BART test after 6 months of use in our installation. Tests have been realised on the water seeping out of the galvanized steel tube and of the bare steel tube.

The culture medium was prepared as follows: solution A: $MgSO_4$ (5 g/l), sodium citrate (12.5 g/l), $CaSO_4$ (2.5 g/l), NH_4Cl (2.5 g/l), in 400 ml distilled H_2O; solution B: K_2HPO_4 (2.5 g/l) in 200 ml distilled H_2O; and solution C: sodium lactate (8.75 g/l), yeast extract (2.5 g/l) in 400 ml distilled H_2O. The three solutions were mixed after sterilisation in an autoclave at 120 °C during 3 h. Before inoculation, the pH was adjusted to 7.5 with 1 M NaOH.

To favour the development of SRB that could already be present in corroded tubes, tubes were immersed in the culture medium. Reactor temperature was maintained at 37 °C during 2 days. BART tests then were performed on the culture media.

Simultaneously, a culture medium containing SRB was prepared similarly. After sterilisation, a commercial source of SRB (ATCC 7757) was introduced in the culture medium in a reactor under N_2 bubbling (to ensure dissolved oxygen removal and observe effects of bacterial corrosion only) and at 37 °C. Then the tubes were inserted in the reactor

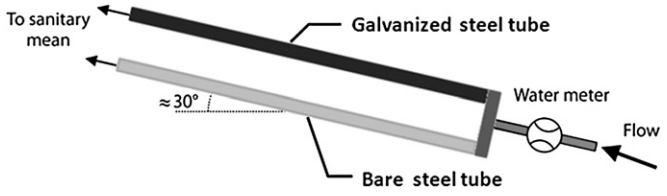

Fig. 2. Bare and galvanized steel tubes installed parallel in laboratory sanitary mean.