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Effects of microbial redox cycling of iron on cast iron pipe corrosion in drinking water distribution systems

Haibo Wang, Chun Hu, Lili Zhang, Xiaoxiao Li, Yu Zhang, Min Yang*

Key Laboratory of Aquatic Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 10085, China

ARTICLE INFO

Article history:
Received 28 January 2014
Received in revised form
21 July 2014
Accepted 26 July 2014
Available online 6 August 2014

Keywords:
Bacterial community
Corrosion scales
Nitrate-reducing bacteria
Microbial redox cycling

ABSTRACT

Bacterial characteristics in corrosion products and their effect on the formation of dense corrosion scales on cast iron coupons were studied in drinking water, with sterile water acting as a reference. The corrosion process and corrosion scales were characterized by electrochemical and physico-chemical measurements. The results indicated that the corrosion was more rapidly inhibited and iron release was lower due to formation of more dense protective corrosion scales in drinking water than in sterile water. The microbial community and denitrifying functional genes were analyzed by pyrosequencing and quantitative polymerase chain reactions (qPCR), respectively. Principal component analysis (PCA) showed that the bacteria in corrosion products played an important role in the corrosion process in drinking water. Nitrate-reducing bacteria (NRB) *Acidovorax* and *Hydrogenophaga* enhanced iron corrosion before 6 days. After 20 days, the dominant bacteria became NRB *Dechloromonas* (40.08%) with the protective corrosion layer formation. The *Dechloromonas* exhibited the stronger corrosion inhibition by inducing the redox cycling of iron, to enhance the precipitation of iron oxides and formation of Fe_3O_4. Subsequently, other minor bacteria appeared in the corrosion scales, including iron-respiring bacteria and *Rhizobium* which captured iron by the produced siderophores, having a weaker corrosion-inhibition effect. Therefore, the microbially-driven redox cycling of iron with associated microbial capture of iron caused more compact corrosion scales formation and lower iron release.

1. Introduction

Iron pipes have been used in drinking water distribution systems (DWDSs) for over five centuries (McNeill and Edwards, 2001), and they usually are covered with deposits of corrosion products. The water quality may be deteriorated during transport through DWDSs to the use point due to iron corrosion. For example, corrosion can produce suspensions of iron particles that give the tap water a red, brown, or yellow color, or a dirty appearance (Sarin et al., 2004a).

In the past several years, several serious red water cases occurred in some cities of the United States owing to switching of source water (Imran et al., 2005; Brodeur et al., 2006). In

* *Corresponding author*. Tel.: +86 10 62849628; fax: +86 10 62923541.
E-mail address: huchun@rcees.ac.cn (C. Hu).
http://dx.doi.org/10.1016/j.watres.2014.07.042

October, 2008, red water appeared in some areas in a northern city of China, soon after 80% of the local source water was replaced by source water from a neighboring province. It was noticed that the areas suffering from red water were historically supplied with local groundwater, while the areas without red water were historically supplied with local surface water. Yang et al. (2012) reported that thick corrosion scales or densely distributed corrosion tubercles with higher Fe_3O_4 ratio were mostly found in pipes transporting surface water, but thin corrosion scales and hollow tubercles with higher content of γ-FeOOH and $FeCO_3$ were mostly discovered in pipes transporting groundwater. These indicated that the structure and composition of corrosion scales played important roles in changes of distribution water quality from the interaction of corrosion scales with finished water.

Therefore, study of the formation mechanism of dense and stable corrosion scales on the surface of iron pipes is very useful for controlling the water quality in DWDSs. Sarin et al. (2004a) indicated that corrosion scales growth was a result of continued corrosion followed by a combination of precipitation and oxidation of corrosion products. Typical iron corrosion scales may be composed of goethite (α-FeOOH), lepidocrocite (γ-FeOOH), magnetite (Fe_3O_4), siderite ($FeCO_3$), ferric hydroxide ($Fe(OH)_3$), ferrous hydroxide ($Fe(OH)_2$), and calcium carbonate ($CaCO_3$) (Peng et al., 2010; Sarin et al., 2004a; Tang et al., 2006). Several environmental factors affect the corrosion rates and composition of the corrosion products, such as water quality, flow conditions, and microorganisms (Beech and Slunner, 2004; Gerke et al., 2008; Sarin et al., 2001). Microbiologically influenced corrosion (MIC) has been of interest due to its complicated role in corrosion processes: it can either accelerate or inhibit corrosion. A prevailing theory of MIC holds that biofilms enhance corrosion by inducing the establishment of corrosion cells with microbial aerobic respiratory activity within biofilms (Landoulsi et al., 2008). However, some findings suggested that biofilms can protect the metal from corrosion under certain conditions (Chongdar et al., 2005; Dubiel et al., 2002). For example, corrosion inhibition was caused by the reduction of ferric ions to ferrous ions and enhanced consumption of oxygen, both of which derive from iron-respiring bacteria respiration (Dubiel et al., 2002). Moreover, sulfate-reducing bacteria (SRB) can cause severe corrosion problems of metal pipes. However, nitrate-reducing bacteria (NRB) will overcome SRB, because for a given electron donor, the energy gained from nitrate reduction is greater than the energy obtained from sulfate reduction. Elimination of SRB by NRB can inhibit hydrogen sulfide production and reduce the corrosion rate (Zarasvand and Rai, 2014).

Although a few possible mechanisms involving the effect of biofilms on corrosion were proposed, little research had been reported on the effect of microorganisms in a complicated community on the elemental composition and crystalline phase of corrosion scales. Also, previous researchers mainly focused on the study of corrosion behavior with electrochemical methods, but little importance was attached to the effect of the microbial phase in a complicated environment on the corrosion process and stable dense corrosion scales formation.

The objective of this study was to study bacterial characteristics in corrosion products and their effect on the formation of stable corrosion scales on the surface of cast iron coupons in drinking water, with sterile water acting as a reference. The corrosion process and corrosion scales were characterized by electrochemical and physico-chemical measurements. Quantitative real-time PCR (qPCR) was used to monitor changes in the microbial community of corrosion scales according to specific groups: total bacteria by 16S rRNA gene and denitrifiers by the functional genes *nosZ*, *nirK* and *nirS*. Most probable number enumerations of Fe(III)-reducing and nitrate-dependent Fe(II)-oxidizing microorganisms were detected under different conditions for different corrosion scales biofilms. Pyrosequencing was used to monitor changes in diversity of the microbial community, including bacteria related to iron redox cycling.

2. Materials and methods

2.1. The tested water and water quality

Three kinds of water samples were used in the experiments. The drinking water was collected from a drinking water treatment plant in the north of China, which was treated by coagulation, flocculation, sedimentation, sand filtration, and biologically-activated carbon filtration (prior to entering the chlorine contact tanks). The sterile water was obtained by sterilizing the above drinking water at 120 °C and 1 bar for 20 min. In addition, the third tested water was obtained by the addition of a given amount of $Ca(HCO_3)_2$ to the sterile water to obtain the same water parameters as the drinking water.

Water quality parameters were measured according to standard methods (EPA of China, 2002) for the three tested waters (Table S1 and Table S2). The calculation methods for Langelier saturation index (LSI) and Ryznar stability index (RSI) are given in the supporting information. Differences of water quality were measured using analysis of variance (ANOVA) with a significance threshold of $\alpha = 0.05$.

2.2. Coupon preparation and experiment design

Cast iron coupons were used in this study. The elemental composition of the cast iron coupons was C 19.08%, O 6.09%, Si 2.06%, Ca 0.58%, P 0.65%, S 1.60%, Fe 65%, Cu 1.98%, Mn 0.92%, Zn 2.04%. The surface of each coupon was polished with 1200-grit emery paper, and each coupon was rinsed with sterile deionized water thrice, degreased in acetone, followed by sterilizing in 70% ethanol for 8 h, and then dried aseptically in a laminar flow cabinet. The coupons were exposed to UV light for 30 min prior to use.

In the experiments, ten cast iron coupons, 80 × 15 × 5 mm, were immersed in covered 1.5 L glass fiber-reinforced plastic bottles filled with each of the three waters containing chlorine disinfection, respectively. For the effect of biofilms, the collected drinking water from water utilities was used without any treatment, and the chlorine residual was controlled at 0.5 mg/L with sodium hypochlorite solution. In the sterile experiment, the drinking water sterilized at 120 °C was used with chlorine residual 0.5 mg/L. In the control experiment, the