

Stainless steel corrosion scale formed in reclaimed water: Characteristics, model for scale growth and metal element release

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ABSTRACT

Stainless steels generally have extremely good corrosion resistance, but are still susceptible to pitting corrosion. As a result, corrosion scales can form on the surface of stainless steel after extended exposure to aggressive aqueous environments. Corrosion scales play an important role in affecting water quality. These research results showed that interior regions of stainless steel corrosion scales have a high percentage of chromium phases. We reveal the morphology, micro-structure and physicochemical characteristics of stainless steel corrosion scales. Stainless steel corrosion scale is identified as a podiform chromite deposit according to these characteristics, which is unlike deposit formed during iron corrosion. A conceptual model to explain the formation and growth of stainless steel corrosion scale is proposed based on its composition and structure. The scale growth process involves pitting corrosion on the stainless steel surface and the consecutive generation and homogeneous deposition of corrosion products, which is governed by a series of chemical and electrochemical reactions. This model shows the role of corrosion scales in the mechanism of iron and chromium release from pitting corroded stainless steel materials. The formation of corrosion scale is strongly related to water quality parameters. The presence of HClO results in higher ferric content inside the scales. Cl⁻ and SO₄⁻ ions in reclaimed water play an important role in corrosion pitting of stainless steel and promote the formation of scales.

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Introduction

Stainless steels have diverse applications in water treatment plants, such as delivery pipes, valves, and water treatment equipment, due to their remarkable corrosion resistance and durability (Ryan et al. 2002). These iron alloys contain a minimum of approximately 11% chromium, which prevents the formation of rust in aqueous conditions (Punckt et al. 2004; Sedriks 1979). Pitting corrosion caused by localized electro-dissolution of metal at surface defects and inclusions is a critical corrosion behavior of stainless steel (Alkire and Lott 1989; Frankel 1998; Lott and Alkire 1989). Once microscopic pits are initiated, they grow continuously by a self-sustaining mechanism (Punckt et al. 2004; Sedriks 1979).

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The passive film is damaged, and corrosion products form on the surface of the alloy by electrochemical corrosion and oxidation reactions (Olsson and Landolt 2001; Son et al. 2001). Massive corrosion scales have occurred as a result of long-term accumulation of corrosion products (Benjamin et al. 1996; Sarin et al. 2004b). These result in the failure of stainless steels and have some effect on water quality.

Most studies have focused on corrosion scales on iron and steel in water (Benjamin et al. 1996; Ma et al. 2009; McNeill and Edwards 2001; Sander et al. 1996; Sarin 2004a, 2001, 2004b; Yang et al. 2012). The composition and structure of corrosion scales in iron and steel have been investigated comprehensively. The major chemical compositions of corrosion scales are oxides and hydroxides of iron, including magnetite (Fe₃O₄), hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃), ferrous oxide (FeO), goethite (α -FeOOH), lepidocrocite (γ -FeOOH), ferrous hydroxide (Fe(OH)₂) and ferric hydroxide (Fe(OH)₃). Minor substances like siderite (FeCO₃), green rust I (Cl⁻) (GR1) and green rust $II(SO_4^{2-})$ (GR2) have been found in iron corrosion scales. Iron corrosion scales are usually composed of a corroded floor, a porous core, a shell-like layer and a top surface layer (Sarin et al. 2001, 2004b; Yang et al. 2012). According to the structural features of iron corrosion scales, a hypothesis of their formation mechanism has been proposed to demonstrate the corrosion process of iron in water. The formation mechanism and process of iron corrosion scales are related to many factors. Material and water quality are the main causes. The effect of different water quality parameters including pH, residual chlorine, total organic carbon, conductivity, dissolved oxygen and alkalinity is coupled to mechanisms for metallic material corrosion and corrosion scale formation (Sarin et al. 2001, 2004b; Yang et al. 2012). However, the formation mechanism of iron corrosion scales is unsuited to interpretation of the growth process of stainless steel corrosion scales due to the different composition and structure. Previous research has focused on why stainless steel corrodes, but has not identified the process of how this corrosion scale forms (Frankel 1998; Punckt et al. 2004; Ryan et al. 2002; Sedriks 1979). Therefore, a reasonable hypothesis for the formation and growth mechanism of this corrosion should be developed based on the composition and structure of stainless steel corrosion scales. Meanwhile, the role of corrosion scales in the mechanism of iron and chromium release from corroded stainless steel materials should be clarified.

To resolve this issue, we focus on stainless steel corrosion scales formed in reclaimed water. They were sampled from several type 304 valves that were in service for a long time. The valves were installed on the delivery pipes leading to the clear well in Tianjin Water Recycling Plant. The fundamental objective of this work was to qualitatively and quantitatively examine the stainless steel corrosion scale, and identify its morphological and physicochemical characteristics. We propose a hypothesis for the formation and growth mechanism of this corrosion based on the composition and structure of the corrosion scales. Meanwhile, the water quality parameters relevant to the formation of corrosion scales were analyzed in our study. The research results are expected to be useful for understanding the process for the formation and growth of stainless steel corrosion scale in water and provide guidance for further research on how iron and chromium are released from corroded stainless steel materials.

1. Methods

1.1. Stainless steel corrosion scale sample collection and preparation

Stainless steel corrosion scales were sampled from several butterfly valves. Rubber-seated butterfly valves of different ages were obtained from a reclaimed water plant. This plant was one of the earliest reclaimed water plants in China and was built as a demonstration project in 2002. They were in service for more than 5 and 12 years. The sampled valves were positioned in the advanced water treatment process as shown in Fig. 1. The valves had a diameter of 600 mm and were taken from different delivery pipes that led to the clear well. In order to control bacteria, finished water with 5 mg/L chlorine concentration was diverted to the clear well through the stainless steel pipeline. Valves A and B were located downstream of the chlorine injection, and valves A' and B' were located upstream of the chlorine injection. Though they were always in contact with finished water undergoing chlorination, the chlorine concentrations of positions A and B were higher than positions A' and B'. Corrosion scales on valves A and B were more numerous and larger than those on valves A' and B', as shown in Fig. 2. They were removed after the water plant ceased operations in that location and relocated. The bodies of the valves are made of type 304 stainless steel. The parameters of finished reclaimed water and the treatment processes of the reclaimed water plant are presented in Table 1. The corrosion scales were easily removed from the stainless steel valve plates and stored in an airtight plastic bag for identification. All of the stainless steel corrosion scales had a hemispherical pod-shape. They were different sizes, with the biggest scales measuring more than 50 mm and the smallest scales measuring less than 1 mm. Before scale formation, the corrosion product spread over the surface of the stainless steel, with the corrosion pit as the center. Before the pretreatment procedures, photos were taken using a Canon SX600 HS digital camera. Fine scale powders were prepared by grinding samples after vacuumfreeze-drying pretreatment.

1.2. Scanning electron microscopy-energy dispersive spectrometry (SEM-EDS)

The bottom surface, top surface and cross-section of samples were examined using SEM (Zeiss MERLIN VP Compact, Germany) techniques. The elemental composition of the corrosion scales surface was measured by coupled EDS.

1.3. Powder X-ray diffraction (XRD)

The powders of samples were studied using a RIGAKU (D-Max II) X-ray powder diffractometer with a Cu K α source operated at 200 mA and 40 kV. The 2 θ scan was in the range of 10–85 with a 0.02° step size and each step was separated by a 0.5 sec count time. The Jade 5.0 software was used to retrieve information on the crystalline phases.

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