



Influence of tungstate ions on transformation of green rust to ferric oxyhydroxide via aqueous solution investigated by *in situ* X-ray absorption spectroscopy



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ABSTRACT

Influence of tungstate ions on the transformation of chloride-containing green rust (GR(Cl⁻)) to fine goethite (α -FeOOH) particles due to the oxidation reaction via aqueous solution at about 300 K was investigated by *in situ* measurements of X-ray absorption spectra. Results showed that the transformation rate of GR(Cl⁻) in the suspension containing 5 mol% W was lower than that in the suspension without tungstate ions. Almost all tungstate ions in the suspension were adsorbed on GR(Cl⁻) and α -FeOOH. It is probable that the adsorption of tungstate ions reduces the transformation rate of GR(Cl⁻) and also leads to the precipitation of fine particles.

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1. Introduction

Weathering steels are used for various structures such as bridges because of their superior corrosion resistance properties. To elucidate the corrosion resistance mechanism of weathering steels, a number of studies have been performed on the characterization of the oxidation products formed on the weathering steels [1–3]. Results have shown that a dense covering layer composed of fine goethite (α -FeOOH) particles acts as a barrier against oxidation, though the oxidation products formed on weathering steels contain not only α -FeOOH but also akaganeite (β -FeOOH), lepidocrocite (γ -FeOOH), and magnetite (Fe₃O₄) etc. [4,5]. However, the corrosion resistance of weathering steels under a chloride environment is not so high [6]. As chloride contamination is common in various environments, improvement of their corrosion resistance under a chloride environment is industrially desirable. It is important to investigate the formation mechanism of fine α -FeOOH particles under a chloride environment.

Green rusts (GRs) are known as intermediate products when corrosion products are formed on metallic Fe in aqueous solution [7–9]. GRs are classified as iron hydroxides containing ferric (Fe(III)) and ferrous (Fe(II)) ions. By reaction with dissolved oxygen, they are decomposed in aqueous solution and then the iron oxyhydroxides and/or iron oxide such as α -FeOOH, β -FeOOH, γ -FeOOH and/or Fe₃O₄ are precipitated [10]. Such transformation of GRs

due to the oxidation reaction via aqueous solution has been extensively investigated in connection with the aqueous corrosion of iron and steels [10–12]. In the crystal structure of GRs, Fe(II) and Fe(III) ions are bonded octahedrally to six hydroxide ions [13]. The edge-shared Fe(OH)₆ octahedral units form brucite-like iron hydroxide layers, which alternate with interlayers containing anions and water molecules. Though several species of anions, such as SO₄²⁻ and CO₃²⁻, are present in the interlayers [13–16], chloride-containing green rust (GR(Cl⁻)) with the chemical formula Fe(II)₃Fe(III)(OH)₈Cl·2H₂O is of particular interest as it can help elucidate the corrosion process of iron and steels under a chloride environment [13,17,18].

The transformation of GR(Cl⁻) due to the oxidation reaction via aqueous solution sensitively depends on the reaction conditions such as pH, dissolved oxygen (DO), oxidation–reduction potential (ORP), temperature and coexisting ions [17–22]. It has been pointed out that fine α -FeOOH particles of nanometer size are preferentially formed in a GR(Cl⁻) suspension containing tungstate ions by the controlled injection of oxygen gas, though γ -FeOOH particles with a micrometer length are formed in the GR(Cl⁻) suspension without tungstate ions under the same reaction conditions [23]. The results are considered to be useful to promote the formation of fine α -FeOOH particles on weathering steels under a chloride environment. Furthermore, it has been reported that tungstate ions are efficient inhibitors for iron and steels [24,25]. Therefore, the influence of tungstate ions on the transformation of GR(Cl⁻) due to the oxidation reaction via aqueous solution is worth investigating. Already, *in situ* measurements of electrochemical

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properties such as pH, DO and ORP during controlled oxidation have been performed for $\text{GR}(\text{Cl}^-)$ suspensions containing tungstate ions [23]. In addition, X-ray diffraction patterns of solid particles extracted from the $\text{GR}(\text{Cl}^-)$ suspension containing tungstate ions at different oxidation times have also been measured [23]. However, the mechanism of the precipitation of fine α -FeOOH particles in the $\text{GR}(\text{Cl}^-)$ suspension containing tungstate ions is still not completely understood.

In this study, *in situ* measurements of X-ray absorption spectroscopy (XAS) at both Fe K and W L_3 absorption edges of the $\text{GR}(\text{Cl}^-)$ suspension containing tungstate ions were carried out during oxidation. Recently, *in situ* XAS measurements at the Fe K edge of the transformation of $\text{GR}(\text{Cl}^-)$ due to the oxidation reaction via aqueous solution have been performed [26]. By using the above-mentioned technique, in this study, the local structure around Fe atoms and the chemical state of Fe in the $\text{GR}(\text{Cl}^-)$ suspension containing tungstate ions were observed during oxidation. The local structure around W atoms was also characterized. The influence of tungstate ions on the transformation of $\text{GR}(\text{Cl}^-)$ to fine α -FeOOH particles due to the oxidation reaction via aqueous solution was investigated.

2. Experimental

Chemicals such as ferric chloride ($\text{Fe}(\text{III})\text{Cl}_3$) hydrate, ferrous chloride ($\text{Fe}(\text{II})\text{Cl}_2$) hydrate and aqueous sodium hydroxide (NaOH) were used for the synthesis of a $\text{GR}(\text{Cl}^-)$ suspension. First, deaerated water, which was prepared by bubbling of Ar gas, was used to prepare an iron chloride solution with an $[\text{Fe}(\text{II})]/[\text{Fe}(\text{III})]$ ratio of 4.5, in which the total iron concentration was 0.2 mol/L. Subsequently, an aqueous NaOH solution was added to the iron chloride solution in a reaction vessel with continuous bubbling of Ar gas at 278 K. When the addition of aqueous NaOH solution was continued until the $[\text{OH}^-]/([\text{Fe}(\text{II})] + [\text{Fe}(\text{III})])$ ratio equaled 1.5, a $\text{GR}(\text{Cl}^-)$ suspension was obtained.

A tungstate solution was prepared from sodium tungstate (Na_2WO_4) hydrate and deaerated water. To obtain a $\text{GR}(\text{Cl}^-)$ suspension containing 5 mol% W with reference to the total amount of

Fe, deaerated tungstate solution was added to the $\text{GR}(\text{Cl}^-)$ suspension. For comparison, a $\text{GR}(\text{Cl}^-)$ suspension without W was also prepared by the addition of deaerated water blank. These suspensions are hereinafter referred to as $\text{GR}(\text{Cl}^-)$ -5W and $\text{GR}(\text{Cl}^-)$ -0W, respectively.

A specimen holder consisting of cellulose fabric and polyethylene film was used for *in situ* XAS measurements. As cellulose fabric sponged the 0.4-ml $\text{GR}(\text{Cl}^-)$ -5W and $\text{GR}(\text{Cl}^-)$ -0W suspensions, a homogeneous dispersion of $\text{GR}(\text{Cl}^-)$ in aqueous solution was maintained during the *in situ* measurements. Each fabric containing the suspension was packed in 0.02-mm-thick polyethylene film. Note that atmospheric oxygen gas can permeate the polyethylene film. In order to avoid oxidation of the $\text{GR}(\text{Cl}^-)$ suspension prior to *in situ* XAS measurements, the above-mentioned procedures were performed in a glove box, in which the oxygen content was maintained at 0.1%. Then, the $\text{GR}(\text{Cl}^-)$ -5W and $\text{GR}(\text{Cl}^-)$ -0W suspensions placed in the specimen holders were kept in a desiccant box. Immediately before the *in situ* XAS measurements, these suspensions were exposed to air at about 300 K. As a result, the $\text{GR}(\text{Cl}^-)$ -5W and $\text{GR}(\text{Cl}^-)$ -0W suspensions in the specimen holder were oxidized.

The XAS measurements were carried out at the Fe K (7112 eV) and W L_3 absorption edges (10,198 eV) using the synchrotron radiation facility at the beam line station BL14B2 at SPring-8, Japan Synchrotron Radiation Research Institute, Japan. *In situ* measurements of XAS at the Fe K and W L_3 absorption edges were performed in the transmission and fluorescence modes, respectively. The specimens were irradiated with a beam 1 mm \times 5 mm in size. X-ray absorption spectra at the Fe K and W L_3 absorption edges were collected for approximately 4 min and 3 min, respectively, using the quick X-ray absorption fine structure (QXAFS) technique [27]. The measurements were periodically repeated during the oxidation. As later described, the tungstate ions added to the $\text{GR}(\text{Cl}^-)$ -5W suspension are considered to be adsorbed on solid particles such as $\text{GR}(\text{Cl}^-)$ and oxidation products. To obtain the adequate intensity, appropriate amounts of the solid particles were separated from the $\text{GR}(\text{Cl}^-)$ -5W suspension by centrifugation, and then their X-ray absorption spectra at the W L_3 absorption edge were also measured in the transmission mode. All of XAS

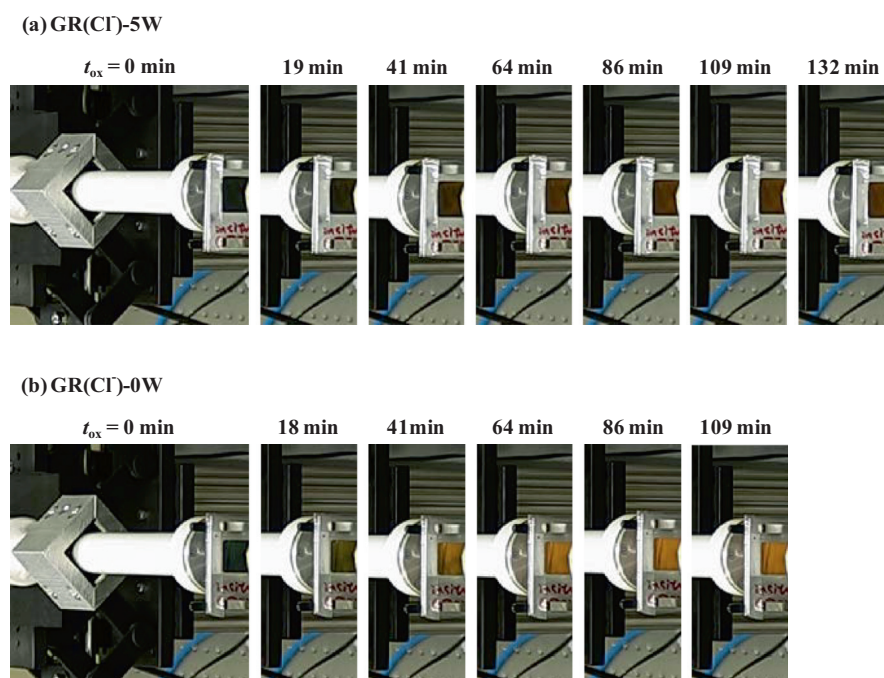


Fig. 1. Aspects of (a) the $\text{GR}(\text{Cl}^-)$ -5W and (b) $\text{GR}(\text{Cl}^-)$ -0W suspensions in the specimen holder, made of transparent polyethylene film, during the *in situ* XAS measurements.

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