Characterization of Formation and Oxidation of Green Rust (Cl^-) Suspension

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(Received on April 30, 2009; accepted on July 3, 2009)

Green rust (GR) containing both ferrous (Fe(II)) and ferric (Fe(III)) ions is formed in an aqueous solution with a relatively low electrochemical potential. In this study, in order to understand the formation and oxidation of GR, a suspension of GR containing chloride ions ($\text{GR(Cl}^-)$) was synthesized and subsequently oxidized by injecting nitrogen gas containing oxygen under different conditions. X-ray diffraction (XRD) measurements were performed for identifying the solid particles formed under different conditions. The results show that the $\text{GR(Cl}^-)$ suspension was formed from specific concentrations of hydroxyl, ferrous, and ferric ions. The pH values and oxidation-reduction potential (ORP) of the aqueous solution were measured during oxidation of the $\text{GR(Cl}^-)$ suspension. It was observed that because of oxygen injection, $\text{GR(Cl}^-)$ was transformed into iron oxides such as $\alpha\text{-FeOOH}$, $\gamma\text{-FeOOH}$, and Fe_3O_4 . These iron oxide and oxyhydroxide species formed by oxidation were dependent on the oxidation conditions such as temperature. This suggested that conditions of aqueous solution are crucial for the transformation of $\text{GR(Cl}^-)$ into different iron oxides and oxyhydroxides.

KEY WORDS: oxidation; reduction; green rust; iron oxyhydroxide; copper; X-ray diffraction; X-ray absorption spectroscopy.

1. Introduction

Iron oxyhydroxides such as goethite ($\alpha\text{-FeOOH}$), akaganeite ($\beta\text{-FeOOH}$), and lepidocrocite ($\gamma\text{-FeOOH}$) and iron oxides such as magnetite (Fe_3O_4) have different structures and morphologies; further, they provide corrosion resistance to steel.^{1–4)} Although these iron oxides and oxyhydroxides are formed by oxidation of ferric (Fe(III)) and ferrous (Fe(II)) ions in an aqueous solution, it is difficult to characterize the formation process of these iron oxides. This is because Fe(II) ions in the aqueous solution are easily oxidized to Fe(III) ions by dissolved oxygen. In addition, the formation of iron oxides is also affected by foreign cations and anions present in the solution. Therefore, the formation conditions of different iron oxides and oxyhydroxides in aqueous solution remain to be clarified. Since iron oxyhydroxides such as $\alpha\text{-FeOOH}$, $\beta\text{-FeOOH}$, and $\gamma\text{-FeOOH}$ are likely to be formed in aqueous solution by oxidation of precursor oxides containing Fe(II) ions, a suitable method for synthesizing these precursor oxides must be developed. If the formation conditions of different iron oxides from the corresponding precursor oxides containing Fe(II) ions are clarified, the formation processes of the iron oxides can be easily understood.

Green rust (GR) containing Fe(II) and Fe(III) ions are known to be typical oxides that can be oxidized to iron oxides containing Fe(III) ions in aqueous solutions.^{5–11)} GR is composed of alternate layers of positively charged hydrox-

ide layers and negatively charged interlayers composed of anions and water molecules; the GR species depends on the negatively charged interlayers and water molecules.^{7,8)} As GR is observed in a lower layer between the upper layer of the corrosion products and the metallic iron substrate,^{3,4)} GR is formed in aqueous solutions with a relatively low electrochemical potential. Thus, GR is considered to be transformed into iron oxides and oxyhydroxides through dissolution and precipitation of Fe(II) and Fe(III) ions in an aqueous solution by atmospheric oxygen.^{10–14)} Therefore, GR is considered to be an important precursor oxide that would help to understand the reaction conditions in the transformation of GR into different iron oxides in aqueous solution.

A chemical method for synthesizing $\text{GR(SO}_4^{2-})$ has already been established.¹²⁾ $\text{GR(SO}_4^{2-})$ is synthesized by adding sodium hydroxide (NaOH) to a solution containing ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) and ferrous sulfate (FeSO_4), where the ratio of ferrous to ferric ions ($[\text{Fe(II)}]/[\text{Fe(III)}]$) is 3. An aqueous NaOH solution is added to the iron sulfate solution under Ar bubbling at 278 K. Upon the addition of aqueous NaOH solution to the iron sulfate solution, precipitation of $\text{GR(SO}_4^{2-})$ ($\text{Fe(II)}_4\text{Fe(III)}_2(\text{OH})_{12}\text{SO}_4$) continues to occur until the ratio of the hydroxyl ions to the total number of iron ions ($[\text{OH}^-]/\{[\text{Fe(II)}]+[\text{Fe(III)}]\}$) becomes 1.5. Aerial oxidation of $\text{GR(SO}_4^{2-})$ to iron oxides and oxyhydroxides has been studied.^{12–14)} The results show that the oxidation of $\text{GR(SO}_4^{2-})$ to different iron oxides is sensitive

to the reaction temperature, oxidation rate, and the existence of foreign cations and anions, although the actual oxidation mechanism has not yet been clarified.

GR(Cl⁻) is another important precursor that can be oxidized to iron oxides in aqueous solutions, since metallic iron is easily oxidized in a solution containing Cl⁻. The objective of this study is to elucidate the formation conditions of GR(Cl⁻) by carrying out co-precipitation of different amounts of Fe(II) and Fe(III) chlorides/hydroxides in aqueous solution and to clarify the reaction conditions under which GR(Cl⁻) is oxidized to different iron oxides. The oxidation of GR(Cl⁻) was studied by oxidation-reduction potential (ORP) measurements of the aqueous solution and structural analysis of the precipitated particles. In particular, the influence of the partial pressure of oxygen ($P(O_2)$) and temperature on the oxidation of GR(Cl⁻) were focused on, since the conditions of an aqueous solution are thought to affect the formation of different iron oxides.

2. Experimental

2.1. Sample Preparation

The GR(Cl⁻) suspension was synthesized by adding NaOH to a solution containing ferric chloride (FeCl₃) and ferrous chloride (FeCl₂). The total concentration of iron in the solution was 0.25 mol/L. At first, an iron chloride solution, in which the [Fe(II)]/[Fe(III)] ratio was 4.5, was prepared. Subsequently, an aqueous NaOH solution was added to the iron chloride solution in a reaction vessel under magnetic agitation under Ar bubbling at 278 K. This procedure is similar to that employed for the preparation of GR(SO₄²⁻).¹²⁾ The addition of aqueous NaOH was continued until the $[OH^-]/\{[Fe(II)]+[Fe(III)]\}$ ratio was in the range of 1.3–2.5. GR(Cl⁻) precipitated from the GR(Cl⁻) suspension when $[OH^-]/\{[Fe(II)]+[Fe(III)]\}$ was in the abovementioned range.

A portion of the GR(Cl⁻) precipitate was rinsed with Ar-bubbled water in order to remove unwanted ions that may be present in it. A part of the GR(Cl⁻) precipitate was kept unwashed in order to reduce the effect of water on iron oxide formation. For the oxidation of GR(Cl⁻), a reaction vessel consisting of a 500-mL glass beaker and an airtight acrylic lid with openings for inserting pH and Pt electrodes, gas inlet/outlet ports, a stirrer port, and a sampling port were used. The GR(Cl⁻) suspensions were reacted with oxygen in a water bath maintained in the temperature range of 278–308 K. The GR(Cl⁻) suspensions were oxidized by passing nitrogen gas containing oxygen with different $P(O_2)$ in the range of 5–100% at a flow rate of 200 mL/min. The suspensions were sampled at a regular time intervals. Then, Ar was injected into the suspensions in order to arrest the oxidation reaction. The oxidized solid particles were separated from the suspensions by centrifugation. Fully oxidized particles were obtained by freeze-drying for more than 400 min.

2.2. Measurements

In order to monitor conditions of the aqueous solution during the formation of different iron oxides, the pH and ORP of the aqueous solution were measured. A TOA DKK IM-55G ion meter was used for automatically measuring

the pH and ORP of the GR suspensions as a function of the oxidation time. The amount of dissolved oxygen in the aqueous solution was also measured using an oxygen meter in a few experiments.

X-ray diffraction (XRD) patterns of the solid particles formed in the aqueous solution were measured for identifying the oxide components present in them. Samples for the XRD measurements were carefully prepared in a glove box by mixing the solid particles separated from the suspension with glycerol in order to avoid air oxidation. XRD measurements were performed on a Rigaku RINT-2200 diffractometer using Mo $K\alpha$ radiation (17.447 keV).

3. Results and Discussion

3.1. Formation of GR(Cl⁻) under Different Conditions

Figure 1 shows the XRD patterns of the solid particles precipitated from solutions with a constant [Fe(II)]/[Fe(III)] ratio of 4.5 and different $[OH^-]/[Fe]$ ratios. The reference peaks for GR(Cl⁻), Fe₃O₄, and Fe(OH)₂ provided in the JCPDS database are also shown. Samples for which the XRD patterns were measured were extracted from the as-prepared suspensions. Most of the diffraction peaks in the obtained XRD patterns were assigned to GR(Cl⁻), although small diffraction peaks attributed to Fe(OH)₂ and Fe₃O₄ were also detected. The formation of Fe₃O₄ may be attributed to the unintentional oxidation of GR caused by rinsing in Ar-bubbled water, as will be explained later. The intensity of the Fe(OH)₂ peak (appearing at approximately 9°) in the XRD patterns increased with the $[OH^-]/[Fe]$ ratio. These results clearly indicate that under the present reaction conditions, the formation of GR containing Fe(II) and Fe(III) ions and Fe(OH)₂ containing Fe(II) ions depends on

Fig. 1. XRD patterns of particles precipitated from solutions in which [Fe(II)]/[Fe(III)]=4.5 and (a) $[OH^-]/[Fe]=1.3$, (b) $[OH^-]/[Fe]=1.5$, (c) $[OH^-]/[Fe]=1.6$, (d) $[OH^-]/[Fe]=1.8$, (e) $[OH^-]/[Fe]=2.0$, and (f) $[OH^-]/[Fe]=2.5$. Reference diffraction peaks for GR(Cl⁻), Fe₃O₄, and Fe(OH)₂ provided in the JCPDS database are also given.

Fig. 2. XRD patterns of (a) particles precipitated from solutions in which $[\text{Fe(II)}]/[\text{Fe(III)}]=4.5$ and $[\text{OH}^-]/[\text{Fe}]=1.5$, (b) particles subsequently rinsed with water, and (c) particles exposed to air.

the $[\text{OH}^-]/[\text{Fe}]$ ratio.

In order to suppress the oxidation of the $\text{GR}(\text{Cl}^-)$ precipitate caused by rinsing it in water, unrinsed precipitates from solutions in which the $[\text{Fe(II)}]/[\text{Fe(III)}]$ and $[\text{OH}^-]/[\text{Fe}]$ ratios were 4.5 and 1.5, respectively, were prepared. XRD patterns of the particles rinsed in water and those not rinsed in water are shown in Figs. 2(a) and 2(b), respectively. Small diffraction peaks assigned to Fe_3O_4 were detected in the XRD patterns of the particles rinsed in water. This indicated that the formation of Fe_3O_4 was probably induced by rinsing the $\text{GR}(\text{Cl}^-)$ suspension in water, which had a slightly high electrochemical potential. Thus, the $\text{GR}(\text{Cl}^-)$ suspension that was not rinsed in water was used as the starting sample for the oxidation experiments. Prior to systematic oxidation of the $\text{GR}(\text{Cl}^-)$ suspension, the XRD pattern of the particles formed by exposing the $\text{GR}(\text{Cl}^-)$ precipitate that was not rinsed in water to air was recorded. Figure 2(c) shows the XRD patterns of the particles formed by exposure to air, indicating that $\text{GR}(\text{Cl}^-)$ was transformed into $\alpha\text{-FeOOH}$, $\beta\text{-FeOOH}$, and Fe_3O_4 by air exposure. Cl^- present in $\beta\text{-FeOOH}$ was thought to have been supplied by $\text{GR}(\text{Cl}^-)$ during the oxidation process. Although $\beta\text{-FeOOH}$ was present in the particles exposed to air, it was not detected in the particles prepared for the experiments that are described in the following sections. This implied that $\beta\text{-FeOOH}$ may be formed from concentrated $\text{GR}(\text{Cl}^-)$ containing a high concentration of Cl^- .

3.2. Oxidation of $\text{GR}(\text{Cl}^-)$ under Different $P(\text{O}_2)$

In order to investigate the oxidation of $\text{GR}(\text{Cl}^-)$ in aqueous solution, nitrogen gas containing oxygen with different $P(\text{O}_2)$ was injected into the $\text{GR}(\text{Cl}^-)$ suspension, and the ORP and pH values of the aqueous solution and the structures of the particles were analyzed. Nitrogen gas containing oxygen with different $P(\text{O}_2)$ was injected into the

Fig. 3. Plot of ORP and pH of the aqueous solution vs. oxidation time after injecting nitrogen gas containing oxygen with $P(\text{O}_2)$ of (a) 5%, (b) 20%, and (c) 100% into the $\text{GR}(\text{Cl}^-)$ suspension at 278 K.

Fig. 4. XRD patterns of fully oxidized particles. XRD patterns are obtained after injecting nitrogen gas containing oxygen with $P(\text{O}_2)$ of (a) 5%, (b) 20%, and (c) 100% into the $\text{GR}(\text{Cl}^-)$ suspension at 278 K.

$\text{GR}(\text{Cl}^-)$ suspension at 278 K. Figure 3 shows the plot of ORP and pH of the aqueous solution versus the oxidation time for different $P(\text{O}_2)$. From the figure, it can be understood that the oxidation rate of the solution increased with increasing $P(\text{O}_2)$, although $P(\text{O}_2)$ was not always proportional to time to the oxidation stage of ORP and pH.

In order to identify the solid particles formed from the $\text{GR}(\text{Cl}^-)$ suspensions at different $P(\text{O}_2)$, the structures of the fully oxidized particles are characterized. **Figure 4** shows the XRD patterns of the freeze-dried particles obtained from $\text{GR}(\text{Cl}^-)$ oxidized by injecting nitrogen gas containing oxygen with $P(\text{O}_2)$ of 5, 21, and 100% into $\text{GR}(\text{Cl}^-)$ at 298 K over 400 min. The reference peaks for α - FeOOH , γ - FeOOH , and NaCl provided in the JCPDS data are also shown in Fig. 4. From Fig. 4, it is apparent that γ - FeOOH particles are mainly formed under the abovementioned conditions, although NaCl particles precipitated from the solution remain. The diffraction peaks are broad for the γ - FeOOH particles formed at high $P(\text{O}_2)$, indicating that the oxyhydroxides are poorly crystallized, and/or their particle size decreases with an increase in $P(\text{O}_2)$. This trend may be attributed to the rapid precipitation of $\text{Fe}(\text{III})$ ions by oxidation in aqueous solutions.

3.3. Oxidation of $\text{GR}(\text{Cl}^-)$ at Different Temperatures

The oxidation of $\text{GR}(\text{Cl}^-)$ is considered to be influenced by temperature and $P(\text{O}_2)$ since the thermally activated process of a reaction and the solubility of oxygen in aqueous solution depend on temperature. In order to investigate the influence of temperature on the oxidation of the $\text{GR}(\text{Cl}^-)$ suspension, the ORP and pH of the solution during oxidation at different temperatures were measured. Nitrogen gas containing oxygen with $P(\text{O}_2)$ of 21% was injected into the $\text{GR}(\text{Cl}^-)$ suspension, and the ORP and pH of the aqueous solution were measured at oxidation temperatures of 278, 298, and 308 K. **Figure 5** shows the plot of ORP and pH values plotted against the oxidation time. The time taken for oxidation of the $\text{GR}(\text{Cl}^-)$ suspension at 278, 298, and 308 K was approximately 30, 60, and 30 min, respectively. The time taken for oxidation at 278 and 308 K was shorter than that for oxidation at 298 K; this suggested that oxidation of the $\text{GR}(\text{Cl}^-)$ suspension was influenced by temperature in a complicated manner.

Since the solubility of oxygen in aqueous solution may depend on temperature, the amount of dissolved oxygen in the solution was measured during each oxidation; corresponding to the results shown in Fig. 5. **Figure 6(a)** shows the plot of the amount of dissolved oxygen in the aqueous solution against oxidation temperatures of 278, 298, and 308 K after injecting nitrogen gas containing oxygen with $P(\text{O}_2)$ of 21% into the $\text{GR}(\text{Cl}^-)$ suspension. An enlarged plot for the initial reaction is shown in Fig. 6(b). From Fig. 6(b), it is understood that some reaction occurs in the $\text{GR}(\text{Cl}^-)$ suspension because of oxygen injection before the main oxidation stage. The amount of dissolved oxygen is approached to a level in equilibrium with the solution in the final oxidation stage.

Figure 7 shows the XRD patterns of the freeze-dried particles obtained from the $\text{GR}(\text{Cl}^-)$ suspension oxidized by injecting nitrogen gas containing oxygen with $P(\text{O}_2)$ of 21% into it at 278, 298, and 308 K for more than 400 min. With an increase in temperature, the concentration of α - FeOOH particles exceeds that of γ - FeOOH , although a residual amount of NaCl remains. The results show that the formation of α - FeOOH and γ - FeOOH by oxygen injection depends on the temperature of the solution.

In order to investigate the sequential formation of differ-

Fig. 5. Plot of ORP and pH of the aqueous solution vs. oxidation time after injecting nitrogen gas containing oxygen with $P(\text{O}_2)$ of 21% into the $\text{GR}(\text{Cl}^-)$ suspension at (a) 278 K, (b) 298 K, and (c) 308 K.

Fig. 6. (a) Plot of concentration of dissolved oxygen in the aqueous solution vs. oxidation time obtained after injecting nitrogen gas containing oxygen with $P(\text{O}_2)$ of 21% into the $\text{GR}(\text{Cl}^-)$ suspension at 278 K, 298 K, and 308 K, and (b) enlarged plot during the initial reaction time.

ent iron oxides, the particles formed through dissolution and precipitation of $\text{GR}(\text{Cl}^-)$ by oxidation were analyzed using XRD. **Figure 8** shows the XRD patterns of the parti-

Fig. 7. XRD patterns of particles fully oxidized. XRD patterns obtained after injecting nitrogen gas containing oxygen with $P(\text{O}_2)$ of (a) 5%, (b) 20%, and (c) 100% into the $\text{GR}(\text{Cl}^-)$ suspension at (a) 278 K, (b) 298 K, and (c) 308 K.

Fig. 8. XRD patterns of particles formed after (a) 0 min, (b) 5 min, (c) 10 min, (d) 30 min, (e) 60 min, and (f) 90 min of injecting nitrogen gas containing oxygen with $P(\text{O}_2)$ of 21% into the $\text{GR}(\text{Cl}^-)$ suspension at 278 K.

cles formed by injecting nitrogen gas containing oxygen with $P(\text{O}_2)$ of 21% into the $\text{GR}(\text{Cl}^-)$ suspension at 278 K for 0, 5, 10, 30, 60 and 90 min. The particles were sampled from the oxidized suspension. α -FeOOH was formed during oxidation at 278 K up to 10 min, and then γ -FeOOH was formed by further oxidation. This implied that α -FeOOH and γ -FeOOH were formed at low and relatively

Fig. 9. XRD patterns of particles formed after (a) 0 min, (b) 5 min, (c) 10 min, (d) 30 min, (e) 60 min, and (f) 90 min of injecting nitrogen gas containing oxygen gas with $P(\text{O}_2)$ of 21% into the $\text{GR}(\text{Cl}^-)$ suspension at 298 K.

Fig. 10. XRD patterns of particles formed after (a) 0 min, (b) 5 min, (c) 10 min, (d) 30 min, (e) 60 min, and (f) 90 min of injecting nitrogen gas containing oxygen gas with $P(\text{O}_2)$ of 21% into the $\text{GR}(\text{Cl}^-)$ suspension at 308 K.

high electrochemical potentials, respectively, although the oxidation of the $\text{GR}(\text{Cl}^-)$ suspension may be affected by various factors such as the concentrations of ions in solution. It should be noted that the XRD patterns of particles formed for long time do not necessarily correspond to the results shown in Fig. 7. This may be because aqueous solution and glycerol are contained in a sample extracted from the suspension, and residual ions are precipitated in a freeze

dried sample. XRD patterns of the particles formed by injecting nitrogen gas containing oxygen gas with $P(\text{O}_2)$ of 21% into the $\text{GR}(\text{Cl}^-)$ suspension at 298 K and 308 K are shown in **Fig. 9** and **Fig. 10**, respectively. The results also show that α -FeOOH was firstly formed during oxidation, and then a small amount of γ -FeOOH was additionally formed by oxidation. These results are also interpreted with the formation of α -FeOOH under low electrochemical potential. In addition, it is remarked that γ -FeOOH seems to be formed at relatively low temperatures, as shown in Fig. 7(a) and Fig. 10. This may be attributed to an increase in the amount of dissolved oxygen that is probably an increase in the oxidation rate during the reaction at 278 K, as shown in Fig. 6.

In order to understand the mechanisms of formation of the GR suspension and its oxidation, the reaction conditions observed in the present study should be discussed on the basis of the electrochemical potentials for Fe(II) and Fe(III) in aqueous solution. The GR suspension is formed at relatively low electrochemical potentials of aqueous solutions. As the electrochemical potential of the aqueous solution increases with the oxidation rate, GR is oxidized to γ -FeOOH or α -FeOOH; however, Fe(II) ions are oxidized in aqueous solutions with high electrochemical potentials. This is responsible for characteristic large stages that appear in the ORP and pH curves, as shown in Figs. 3 and 5. γ -FeOOH is predominantly formed at low temperatures, and the particle size decreases with an increase in $P(\text{O}_2)$, that is, the oxidation rate. On the other hand, α -FeOOH is formed during oxidation at high temperatures, although α -FeOOH is initially formed at a low electrochemical potential. Although GR was not well recognized in previous works on corrosion of iron, the results of this study clearly show that the reaction conditions conducive for the oxidation of GR containing Fe(II) ions are important in controlling the formation of the iron oxides and oxyhydroxides in aqueous solution.

β -FeOOH particles are formed when the Cl^- concentration is high and at a relatively high oxidation rate, as shown in Fig. 2(c). In addition to the electrochemical potential and pH of the solution, the Cl^- concentration present in the $\text{GR}(\text{Cl}^-)$ suspension also influences the formation of β -FeOOH. This is because β -FeOOH contains Cl^- supplied by the decomposition of $\text{GR}(\text{Cl}^-)$. Formation of α -FeOOH or γ -FeOOH is enhanced if the Cl^- concentration is insufficient for the formation of β -FeOOH.

4. Conclusion

In order to study the formation of the $\text{GR}(\text{Cl}^-)$ suspension at a relatively low electrochemical potential and its subsequent oxidation, the $\text{GR}(\text{Cl}^-)$ precipitate formed were characterized by XRD. Changes in the ORP and pH of the solution in the $\text{GR}(\text{Cl}^-)$ suspensions after oxidation were

monitored. The results indicated that $\text{GR}(\text{Cl}^-)$ is formed under specific conditions, and is oxidized to different iron oxides. The relatively low electrochemical potential of the $\text{GR}(\text{Cl}^-)$ suspension was considered to trigger the oxidation reaction. The measured ORP and pH values showed that characteristic stages appeared during oxidation of the $\text{GR}(\text{Cl}^-)$ suspension. These results were consistent with those obtained by analyses of the solid particles formed after oxidation. Therefore, chemical reactions of the $\text{GR}(\text{Cl}^-)$ suspension were thought to be influenced by the electrochemical potential of the ions present in aqueous solution.

The results of the present study have revealed that oxidation and reduction experiments using GR are useful in studying the formation of different iron oxides in aqueous solutions. As GR is formed between an upper layer of corrosion products and a metallic iron substrate, it is likely to be oxidized to different iron oxides under electrochemical conditions. Thus, these experiments are useful in clarifying the roles of reaction factors during the formation of iron oxides or corrosion products of steel.

Acknowledgements

This work was supported by the Grant-in-Aid for Scientific Research Fund from the Japan Society for Promotion of Science.

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