



Carbonate and sulphate green rusts—Mechanisms of oxidation and reduction

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ABSTRACT

The oxidation and reduction of carbonate, GR(CO₃), and sulphate, GR(SO₄), green rusts (GR) have been studied through electrochemical techniques, electrochemical quartz crystal microbalance (EQCM), FTIR, XRD and SEM. The used samples were made of thin films electrodeposited on gold substrate. The results from the present work, from our previous studies and from literature were compiled in order to establish a general scheme for the formation and transformation pathways involving carbonate or sulphate green rusts. Depending on experimental conditions, two routes of redox transformations occur. The first one corresponds to reaction via solution and leads to the formation of ferric products such as goethite or lepidocrocite (oxidation) or to the release of Fe^{II} ions into the solution (reduction) with soluble Fe^{II}–Fe^{III} complexes acting as intermediate species. The second way is solid-state reaction that involve conversion of lattice Fe²⁺ into Fe³⁺ and deprotonation of OH groups in octahedra sheets (solid-state oxidation) or conversion of lattice Fe³⁺ into Fe²⁺ and protonation of OH groups (solid-state reduction). The solid-state oxidation implies the complete transformation of GR(CO₃) or GR(SO₄) to ferric oxyhydroxycarbonate exGRc-Fe(III) or ferric oxyhydroxysulphate exGRs-Fe(III), for which the following formulas can be proposed, Fe^{III}₆(OH)_(12–2y)(O)_(2+y)(H₂O)_(y)(CO₃) or Fe^{III}₆(OH)_(12–2z)(O)_(2+z)(H₂O)_(6+z)(SO₄) with 0 ≤ y or z ≤ 2. The solid-state reduction gives ferrous hydroxycarbonate exGRc-Fe(II) or ferrous hydroxysulphate exGRs-Fe(II), which may have the following chemical formulas, [Fe^{II}₆(OH)₁₀(H₂O)₂].[CO₃, 2H₂O] or [Fe^{II}₆(OH)₁₀(H₂O)₂].[SO₄, 8H₂O].

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1. Introduction

Green rusts (GR) are layered Fe^{II}–Fe^{III} hydroxysalts, composed of positively charged Fe(OH)₆ octahedra sheets alternating with interlayers filled with compensating anions and water molecules. Their ferrous–ferric character positions them in the centre of redox processes interfering in corrosion layers and in the biogeochemical cycle of iron, where they could act as both donor and acceptor of electrons.

Green rusts can be formed in some natural slightly reducing environments such as hydromorphic soils, where they control the geochemistry of iron [1]. Their natural occurrence has been suspected since 1905 [2] from the observation of green-blue colour of these water-saturated soils and their colour transitions to red-yellow during draining phenomena (oxidation by air). Their presence has been confirmed only very recently thanks to Mössbauer and Raman spectroscopic analysis [3–5]. On the basis of

these works, green rust was approved as a mineral by the International Association of Mineralogy (IAM 2003-057), under the name “Fougérite”, from the name of the town of Fougères, where it was first found.

Green rusts are also formed during aqueous [6–11], atmospheric [12], and marine [13] corrosion processes of cast iron and steel structures. In some severe marine corrosion damages, the association of green rusts and thiosulfato- or sulfato-reducing bacteria activity was mentioned [14].

The oxidation behaviour of green rusts has been the focus of many studies. Under some conditions (solution composition, oxidation rate, temperature, etc.), this oxidation can imply transformations via solution and can lead to one of the following ferric products: lepidocrocite, goethite or a mixture of these phases [9,15–20]. Some authors [19,21–23], indicate that phosphate or silicate ions can block the dissolution process, therefore hindering the formation of such ferric products.

A solid-state oxidation of green rusts involving the transformation of Fe²⁺ ions into Fe³⁺ ions inside the crystal lattice is also possible. This reaction takes place when high oxidation rate is imposed (use of strong and very soluble oxidants such as H₂O₂, rapid solution stirring), when a previously dried green rust is exposed to air oxidation or when a green rust thin film is elec-

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trochemically oxidised [9,19,24–28]. Génin and Refait [25,26,29], claimed that the resulting ferric compound keeps the same lamellate structure as green rust and used the denomination “ferric green rust”. Legrand et al. [19,24] rather suggested that the oxidation products preserve only relics of lamellate structure and introduced the denomination “ExGR-Fe(III)”. More recently, Génin and co-workers claimed that a $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ solid solution exists between carbonate green rust ($x=0.33$) and its fully oxidised product ($x=1$) [26,29]; a structural model in which the composition of the $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ solid solution is $\text{Fe}^{\text{II}}_{6(1-x)}\text{Fe}^{\text{III}}_{6x}\text{O}_{12}\text{H}_{2(7-3x)}\text{CO}_3$ with $0.33 < x < 1$, was proposed.

Some of our previous studies [19,27] were done with carbonate green rust thin films formed at the surface of iron discs by electrochemical oxidation. For those studies, we assumed that iron substrate did not affect the oxidation/reduction behaviour of green rust thin films.

In the present paper, thin films electrodeposited on inert Au electrodes have been used; we first reinvestigate the oxidation/reduction behaviour of carbonate green rust $\text{GR}(\text{CO}_3)$ and then extend the study to sulphate green rust, $\text{GR}(\text{SO}_4)$. We chose carbonate $\text{GR}(\text{CO}_3)$ and sulphate $\text{GR}(\text{SO}_4)$ green rusts since they are the two most-occurring green rusts in “natural environments” and since they are the typical compounds of the two structural groups, GR1 and GR2, respectively. This paper also examines the reduction behaviour of green rusts, a subject that has not been investigated in any publication to our knowledge. Electrochemical quartz crystal microbalance (EQCM) is widely used and provides information on the redox mechanisms. The results of the present study will complement the literature data on the transformation pathways in order to obtain a better overall understanding of the place of green rusts in environmental or corrosion processes where electron exchange are involved.

2. Experimental

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Aldrich), NaOH (30%, RP normapur, Prolabo), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (ACS Reagent, Aldrich), 1-methyl-imidazole – MetIm – (99%, Aldrich, pH-buffering agent with $\text{pK}_a \sim 7$), *N*-Tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid – TAPS – (Aldrich, pH-buffering agent with $\text{pK}_a \sim 8.4$), were used. The solutions were prepared with $18\text{ M}\Omega\text{ cm}$ nano-pure water and deaerated with argon (U, Air Liquide).

The electrolytes were prepared in a separate closed cell thermostated at 25°C and equipped with a combined pH electrode (WTW SenTix 97/T and WTW Multiline P4 pH-meter), argon inlet and outlet and a rubber cap. 50 mL of a solution containing the relevant species (sodium salt + pH-buffering agent) were introduced into the cell. Dissolved oxygen was removed by bubbling argon for about 15 min. Then, 0.5 mL of 1 M FeCl_2 solution was introduced in the cell through the rubber cap using a syringe and the pH was adjusted with NaOH or HCl . Finally, a volume of the mixture was pumped with a syringe and transferred into the deaerated electrochemical cell just before synthesis.

A gold disc (Goodfellow, 99.95%, laminated, 15 mm diameter) was used as a working electrode. Before each experiment, the Au surface was polished with grade 4000 grit paper (Struers) and rinsed with deionised water. The Au surface in contact with the electrolyte was 0.785 cm^2 in area. Au wire and home-made Ag/AgCl (0.1 M NaCl) electrodes were employed as the counter and reference electrodes, respectively. Electrochemical measurements were conducted with an EG&G PAR 273A potentiostat/galvanostat. The electrochemical cell was thermostated by a circulation of water and argon bubbling was maintained during the electrochemical synthesis. Q_0 , the coulombic charge associated to the electro-

Table 1
Synthesis parameters for the electrodeposition of green rust thin films

	Electrolyte	pH	T ($^\circ\text{C}$)	Electrochemical conditions, E (V)
$\text{GR}(\text{CO}_3)$	0.4 M NaHCO_3 0.02 M MetIm 0.1 M FeCl_2	8.9	25	–0.30
$\text{GR}(\text{SO}_4)$	0.4 M Na_2SO_4 0.02 M MetIm 0.1 M FeCl_2	8.5	25	–0.15

chemical deposition of green rust thin film, was chosen between 12.5 and 100 mC cm^{-2} . Once the film synthesised, the electrode was removed from the solution, quickly rinsed with deaerated deionised water and then transferred to another electrochemical cell in which the oxidation and reduction behaviours of $\text{GR}(\text{CO}_3)$ and $\text{GR}(\text{SO}_4)$ were investigated. For this purpose, 0.4 M NaHCO_3 or 0.4 M $\text{Na}_2\text{SO}_4/0.05\text{ M TAPS}$ solutions at pH 9.5 and $T=25^\circ\text{C}$ were used for $\text{GR}(\text{CO}_3)$ or $\text{GR}(\text{SO}_4)$, respectively. All potentials are referred to Standard Hydrogen Electrode (SHE), after calibration with ferricyanide/ferrocyanide redox system.

Electrochemical quartz crystal microbalance measurements were performed with a Maxtek Inc. RQCM plating monitor coupled to an AUTOLAB PGSTAT30 potentiostat/galvanostat (Eco Chemie). A 5 MHz Au/Ti polished quartz crystal (Maxtek Inc.) with 1.37 cm^2 in surface area was used as a working electrode. Prior to electrodeposition, the Au surface was pretreated by immersion in 1 M HCl ($\sim 0.1\text{ M}$) and subsequently rinsed with copious amounts of $18\text{ M}\Omega\text{ cm}$ nano-pure water.

IR spectra of thin films were recorded on a Bruker IFS28 FTIR spectrometer. A reflection-absorption tool (Grazeby Specac) with variable incidence angle allowed us to analyse the film directly on the disc surface without using any kind of scraping procedure. The incidence angle was fixed at 30° relative to the normal to the film surface. The background measurement was taken with a gold disc that had been mirror-like polished. 20 scans were performed for background and samples. XRD patterns were obtained using a Bruker D8 diffractometer with Cu radiation ($\lambda = 1.540\text{ \AA}$) in θ - 2θ geometry. Surface morphology was observed by a thermal assisted Field Emission Gun Scanning Electron Microscope (FEG-SEM), LEO 1530 Gemini, equipped with a coaxial in-lense secondary detector. The working acceleration voltage was 3 kV.

3. Results and discussion

3.1. Synthesis of green rust thin films

Conditions of synthesis are summarised in Table 1 and complementary information can be found in our previous papers [30]. Fig. 1 shows the current density, I , and the mass variation, Δm , as a function of the deposition time for the potentiostatic oxidation of $\text{Fe}(\text{II})$ into carbonate or sulphate green rusts. The beginning of the I - t transients is consistent with the occurrence of a nucleation/growth process. The difference between the two curves may result from the type of nucleation. After the nucleation stage, the current density does not significantly change. A mass gain is observed throughout the oxidation time for both green rusts. The deposition charge density, Q , was determined by integrating current density. Δm - Q plots are almost linear (such curves will be presented in the next figures). The corresponding experimental slope values are reported in Table 2, as well as the theoretical values deduced from the formula reported in literature [19,31]. For $\text{GR}(\text{SO}_4)$, the experimental values are slightly higher than the theoretical one and this result may arise from the large particle/solution contact surface result-

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