

GREEN RUST: ITS ELECTROCHEMICAL GENERATION, CHARACTERIZATION, AND IMPLICATIONS

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Abstract

Green rust is an important intermediate in oxidative transformation of Fe(II) phase. This unstable compound contains a mixture of ferrous and ferric hydroxides that belong to a family of minerals known as layered double hydroxides (LDH). Its general formula is $[\text{Fe}^{\text{II}}_{(6-x)}\text{Fe}^{\text{III}}_x(\text{OH})_{12}]^{x+}[\text{A}_{x/n}\cdot y\text{H}_2\text{O}]^{x-}$, where A is an n-valent anion mainly Cl^- , CO_3^{2-} and SO_4^{2-} , and in which either the bivalent or the trivalent iron can be replaced for other trivalent or bivalent metal ions. It was first identified as corrosion product, later in soils as a product of interactions between microbes and metals in soils. Due to its high reactivity, it is used in the reduction of organic and inorganic compounds, As removal, and the treatment of acid mine drainage. In this paper, we described the method of electrochemical generation of green rust, its characterization by XRD, SEM and FT-IR, and its implications to electrocoagulation.

Introduction

Green Rust (GR) plays a vital role in soil and aquatic environment chemistry. It is formed by a number of abiotic and biotic processes under circumneutral to alkaline conditions in suboxic environments. It is also considered as an intermediate phase in the corrosion of metallic iron. GR are layered Fe(II)-Fe(III) hydroxides having a pyroaurite-type structure consisting of alternating positively charged hydroxide layers and hydrated anion layers. In the structure, some of the Fe(II) of the octahedral sheets of $\text{Fe}(\text{OH})_2$ are replaced by Fe(III). This results in positive layers of charge that are balanced by the inclusion of anions between the layers (1). Its exact nature depends on the interlayer anion. Various forms have been synthesized and studied. Results of many studies have shown that GR conforms to a general chemical composition and stoichiometry that can be represented with the following general formula:

$[\text{Fe}^{\text{II}}_{(6-x)}\text{Fe}^{\text{III}}_x(\text{OH})_{12}]^{x+}[(\text{A})_{x/n}\cdot y\text{H}_2\text{O}]^{x-}$, where x ranges from 0.9 to 4.2, A is an n-valent anion (typically CO_3^{2-} , Cl^- or SO_4^{2-} and y denotes the varying amounts of interlayer water (typically y ranges from 2 to 4 for most GRs (2)). The literature distinguishes between GRI ($\text{A}^n = \text{F}^-$, Cl^- , Br^- , I^-), GR II ($\text{A}^n = \text{SO}_4^{2-}$) and GR-CO_3 ($\text{A}^n = \text{CO}_3^{2-}$). This division is due to a crystallographic classification of the mineral structures by which GRI is described as rhombic obtained with "planar" anions such as chlorides, carbonate etc, while GR II and GR-CO_3 are hexagonal obtained with three-dimensional tetrahedral anions such as sulfate or selenate (3).

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GR, unlike most iron oxides in whatever form, has an internal surface area; so these minerals have both large specific surface areas and reactivity. Most of the work reported to date has focused on the reactivity of sulfate GR rather than the chloride or carbonate forms (4). They represent reactive ion exchangers and sorbents (5). The amphoteric surface hydroxyl groups lead to both sorption of heavy metals (cations) as well as organic anions, e.g. linear alkyl benzene sulfonates (LAS), the major synthetic surfactant used in laundry detergents and cleaning products worldwide, and inorganic anions, e.g. silicate, arsenate and selenate. Furthermore, polar non-charged compounds are sorbed into the interlayer. Cations as Cu(II), Ni(II), Zn(II), Cd(II), Co(II) and Mg(II), may isomorphically substitute for Fe(II) during GR formation (coprecipitation). For example, nickelous-ferric GRs, the end products obtained by substitution of Fe(II) ions by Ni(II) ions, have been demonstrated (6). This incorporation of cationic inorganic contaminants into the structures of GR could provide an effective means of sequestering contaminants in the subsurface.

The oxidation of the Fe^{2+} ions in GR results in the formation of ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), goethite ($\alpha\text{-FeOOH}$), akaganeite ($\beta\text{-FeOOH}$), and lepidocrocite ($\gamma\text{-FeOOH}$) in well-aerated systems, and hematite ($\alpha\text{-Fe}_2\text{O}_3$) maghemite ($\delta\text{-Fe}_2\text{O}_3$) or magnetite (Fe_3O_4) in oxygen-depleted systems. Conversion depends on pH, solution composition, oxidant, rate of oxidation, and the degree and rate of dehydration (7). Rust composition, therefore, changes with time (and metal composition). On pure iron, $\gamma\text{-FeOOH}$ transforms to the more stable goethite ($\alpha\text{-FeOOH}$) and some spinel. With increasing time, goethite converts to either maghemite or hematite. Conversion to hematite usually requires higher temperatures.

Various processes have been developed to synthesize GR in the laboratory. Two primary procedures were discussed: the first one by partial oxidation of Fe(II) hydroxides or Fe(II) solutions, and the second one by mixing Fe(II) and Fe(III) aqueous solutions or suspensions (coprecipitation). The anion associated with Fe(II) or Fe(III) in the salt is thus present in solution and induces the formation of the corresponding GR, e.g. using FeSO_4 leads to GR- SO_4 . An article by Legrand et al. (1) was devoted to new carbonate green rust obtained electrochemically. GR can be also produced with EC. Composition of pollutants in water or wastewater affects both the generation and the type of GR formed. (8).

Electrocoagulation (EC); which is considered as an accelerated corrosion process, is being used for water and wastewater treatment for more than one century. There are many similarities in reactions that can be achieved, and pollutants that can be removed with GR and EC. The goal of this paper is to discuss to generate green rust using electrocoagulation, and to characterize them using conventional x-ray and IR techniques.

Electrocoagulation

EC is a complex process involving many chemical and physical mechanisms that operate synergistically to remove pollutants from water. EC works through the interactions of electrochemistry, coagulation and flotation. EC is currently experiencing both increased popularity and technical improvements; however, it is empirical and largely heuristic. In this process, the coagulants are produced "in situ". EC in its simplest form uses an electrochemical cell where a DC electric field is applied to the electrodes, usually made of iron or aluminum and the electrolyte is the water or wastewater. The anode is corroded releasing active coagulant agents (Al or Fe ions), while accompanying electrolytic reactions evolve gases. EC involves three stages: formation of coagulants, destabilization of the contaminants, particulate suspensions

and breaking of emulsions, and aggregation of the destabilized particles to form flocs. The mixture separates into a floating layer, a mineral rich sediment and water, which can be extracted by conventional methods (9-10). The factors that influence EC are applied voltage and current, electrolytes, pH, electrode materials, reactor design, and residence time. In some cases, EC can replace primary, secondary and tertiary water treatment. The formation of a dark green floc is often empirically used to visually determine the success of pollutant(s) removal with EC.

Experimental

Three sets of experiments were conducted for the electrochemical generation of GR using EC. The first set of experiments was performed to study the effect of composition of electrolytes on GR generation. It was carried out using 0.02 M solutions of different acids (acetic, nitric, hydrochloric, sulfuric, carbonic, and phosphoric). 0.5 g of NaCl / L was also added to ensure the conductivity of the media. To perform those tests the following equipment and materials were used: a KASELCO EC bench unit (Figure 1). The unit essentially consists of a flow-through cell, the electrode assembly, the feed pump and the DC power supply unit. The volume of the reactor was 450 mL. After each half pass, 100 ml of sample was taken out. After the treatment, 1000 ml were placed in a graduated cylinder, and after 40 minutes the amount of generated sludge was measured. The rest of the solution was filtered. Finally the sludge from the filter was analyzed with XRD and SEM-EDS to identify its end products. Each sample was run for four passes.

Since the first experiment revealed that the combination of sulfuric acid and sodium chloride had the best results, the second set of experiments was performed by using different proportions of those compounds and to observe the influence of sulfate ions. The same equipment and conditions of experiment 1 were used.

A third set of experiments was conducted to see the influence of different ions on the electrochemical generation of green rust. Substances used were sodium chloride, potassium chloride, sodium hydroxide, sodium carbonate, sodium sulfate, sodium bicarbonate and sodium phosphate. For these tests a 400 ml beaker-size reactor was used. Iron electrodes with dimensions for the submerged area of 30x40x2 mm, with 9 VDC applied to the electrodes. The current was 300 mA. The green rust was characterized using Bruker XRD (D4 Endeavor), Nicolet Nexus 470 FTIR, and SEM-EDS (Hitachi S-3400N, EDAX).

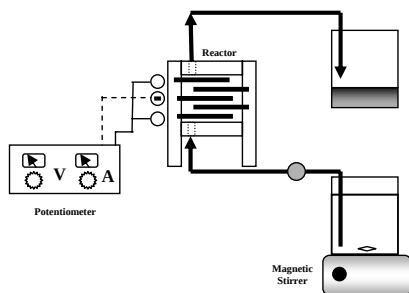


Figure 1. Schematic diagram of Kaselco bench reactor

Results and Discussion

Six different kinds of green rust were prepared with nitrate, acetate, phosphate, chloride, carbonate, and sulfate anions. It was found that pH of the precursor solutions increases as expected during the generation of the GRs using EC. pH increments and final pH are different for each product. X-ray diffraction patterns for these GRs were taken and presented in Figures 2-7.

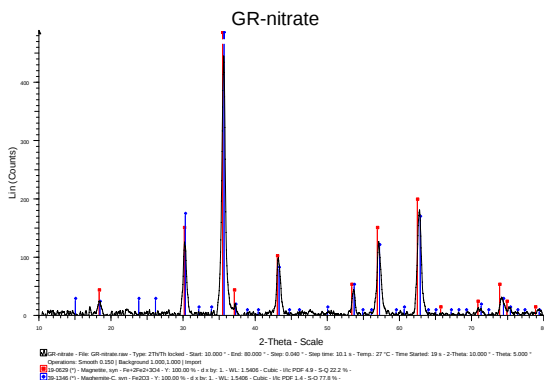


Figure 2. XRD pattern of nitrate GR

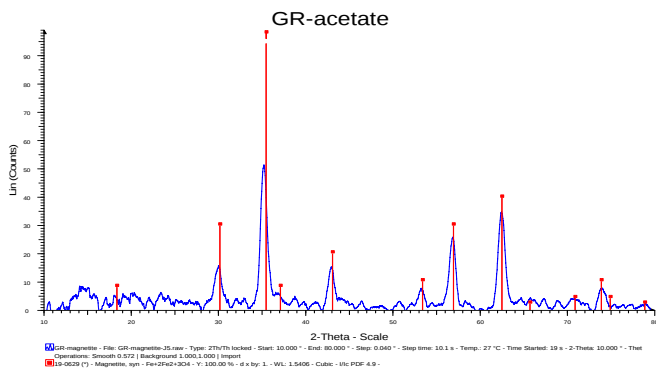


Figure 3. XRD pattern of acetate GR

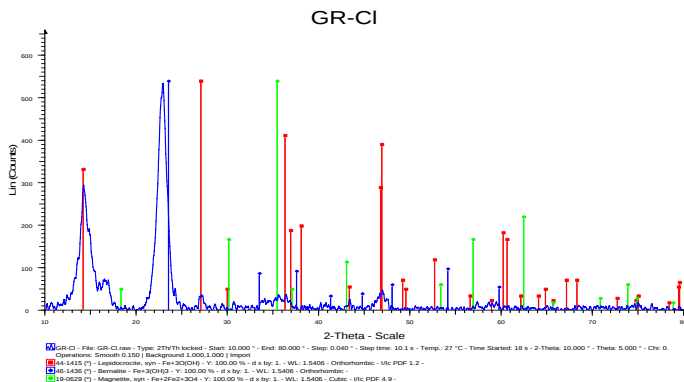


Figure 4. XRD pattern of chloride GR

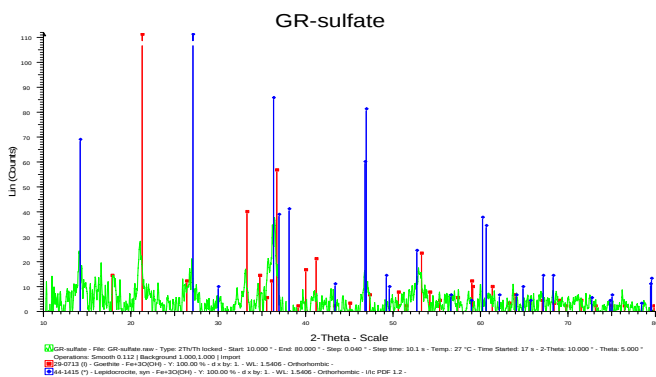


Figure 5. XRD pattern of sulfate GR

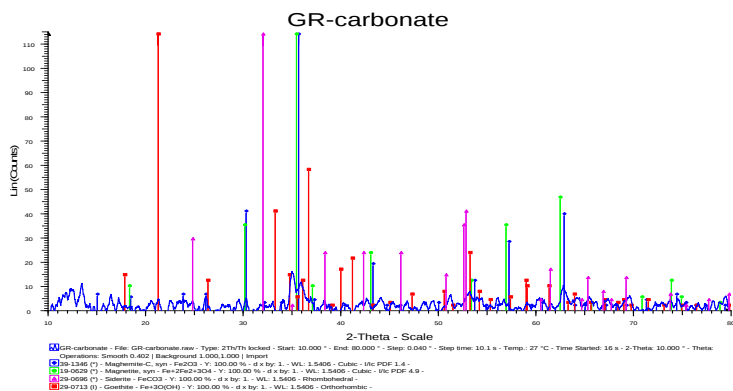


Figure 6. XRD pattern of carbonate GR

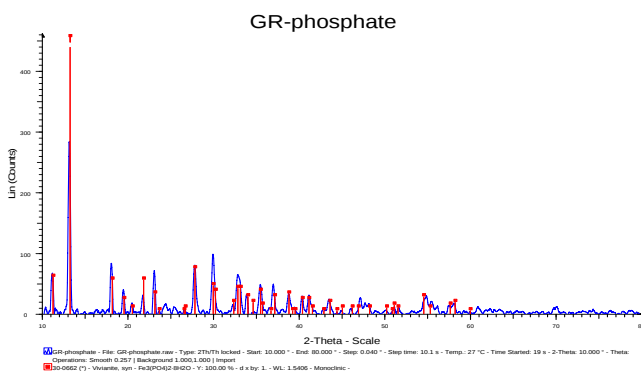


Figure 7. XRD patterns of phosphate GR.

XRD Analysis

XRD results indicate that the prepared acetate, nitrate, chloride, and carbonate GRs mainly contain magnetite. On the other hand, sulfate GR contains goethite and lepidocrocite, and phosphate GR exclusively vivianite. This denotes that for most of the case, the products are in the category of Iron oxides, hydroxides, and oxyhydroxides. With these experiments all three types of GR, i.e., the ones formed with Cl^- (also F^- and Br^-), SO_4^{2-} and CO_3^{2-} ions, all three types were obtained as mentioned in the scientific literature. A scheme was built up to show the relationship among different GR-precursors, GRS, and EC-products as presented in Figure 8. It gives a summarized view about different GRs and the composition of the end-products.

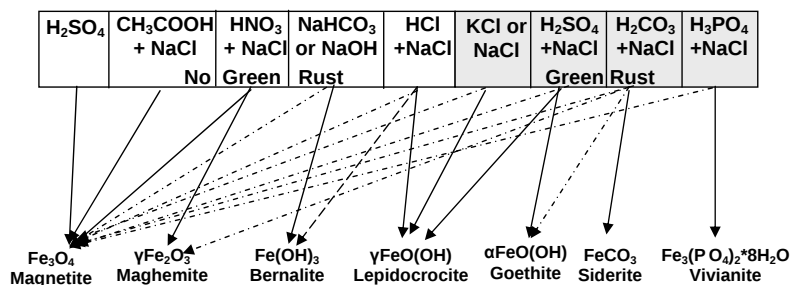


Figure 8. Relationship among different GR-precursors, GRs, and EC products

FTIR Analysis

ATR-FTIR was also performed for different GRs. As expected, it showed the presence of hydroxyl group, Fe-O, and oxyhydroxide vibrations.

SEM-EDS

SEM and EDS were also performed on the generated GRs. In general, they indicate the amorphocity and crystallinity of different sizes in the GRs. Figure 9 shows exemplary the SEM-image of phosphate-GR. Analysis of EDS data confirms the elemental composition of different GRs.

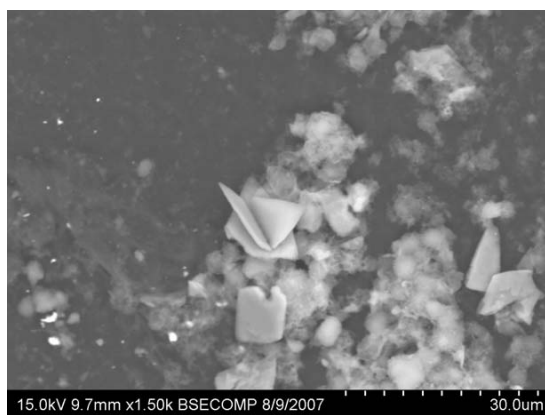


Figure 9. SEM image of phosphate-GR.

Conclusion

Reactions that lead to Green Rust generation, take place at the cathode of the EC reactor. GR formation is an intermediate step during EC reactions and all three types of GR (GRI ($\text{An}^- = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$), GRII ($\text{A}^{n-} = \text{SO}_4^{2-}$) and $\text{GR-CO}_3(\text{A}^{n-} = \text{CO}_3^{2-}$ and GR-PO_4^{3-}) can be generated with EC. Presence of chloride ions is essential for electrochemical generation of GR. A

combination of H₂SO₄ and NaCl leads to sinking GR and maximum production of sulfate-GR. At low pH, combination of HCl and NaCl does not lead to green rust. Combinations of monovalent acids, such as acetic, nitric and hydrochloric, with NaCl promote magnetite formation as end products.

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