

Kinetics of nitrate reduction by green rusts—effects of interlayer anion and Fe(II):Fe(III) ratio

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Abstract

The reaction between the synthetic chloride form of green rust (GR) with an Fe(II):Fe(III) ratio of 3:1 (GR_{Cl}, Fe_{4.5}Fe_{1.5}(OH)₁₂Cl_{1.5}·xH₂O) and nitrate has been studied at GR_{Cl} concentrations up to 2.5 mM and nitrate concentrations from 0.7 to 14.2 mM in non-buffered aqueous suspensions under an argon atmosphere. Nitrate is reduced stoichiometrically to ammonium while GR_{Cl} is oxidized to magnetite with concurrent decrease of pH from 8.2 to 6.1. No nitrate reduction was observed in homogenous Fe(II) solutions at neutral pH. The rates of ammonium formation and consumption of Fe(II) in GR_{Cl} (Fe(II)_{GR}) are well described by first-order reaction kinetics. No clear rate dependence with respect to nitrate was found, but it appears that above a nitrate concentration of approximately 7 mM and at fixed concentrations of Fe(II)_{GR}, the rate of nitrate reduction is almost constant and independent of the nitrate concentration. Under these conditions, the rate law may be given by:

$$\frac{d[\text{NH}_4^+]}{dt} = k[\text{Fe(II)}]_{\text{GR}}$$

where $k = 2.0 \pm 0.5 \times 10^{-5} \text{ s}^{-1}$. Interlayer chloride in GR_{Cl} could be exchanged with sulphate without change in the Fe(II):Fe(III) ratio of the GR. The resulting sulphate GR reduced nitrate six times slower than the original GR_{Cl} but the reaction was five times faster when compared with reduction by sulphate GRs having Fe(II):Fe(III) ratios of 2:1. Thus, the high rate of nitrate reduction by GR_{Cl} can be attributed partly to ready exchange of chloride with nitrate in the GR interlayer and partly to a high proportion of Fe(II) in the octahedral layers of GR. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: green rust; layered double hydroxides; nitrate; ammonia; nitrate reduction; iron(II); Mössbauer spectroscopy

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1. Introduction

The layered iron(II)iron(III)hydroxides known as green rusts (GRs) have been demonstrated to reduce nitrate to ammonium with formation of magnetite (Hansen et al., 1996). The rate of reduction is comparable to the rate of microbial nitrate reduction and the process is thus of special interest in anoxic environments exhibiting low microbial activity. GRs or GR-like substances also have been observed to reduce halogenated alkanes (Erbs et al., 1999; Pecher et al., 1997) and selenite (Myneni et al., 1997) at appreciable rates. Furthermore, GR may act as a collector of heavy metal cations through substitution into the GR hydroxide layers (Shokes and Möller, 1999; Taylor et al., 1998; Tamaura, 1985). Thus, GRs represent interesting substances in studies of natural pollution control. In vivo studies of GRs are still sparse, although the possible activity of GRs are often indicated in investigations of polluted soils, sediments and landfills, and in remediation techniques using Fe(0) (Gu et al., 1999; Scherer et al., 1999; Frederickson et al., 1998). It is known that GRs easily form during corrosion of iron (Kassim et al., 1982). The high reactivity of GR including its extreme sensitivity towards oxidation by oxygen probably explains why GR is not generally identified in standard mineralogical works. However, more recent findings suggest its occurrence in soils, intertidal marsh sediments and ochre (Trollard et al., 1997; Al-Agha et al., 1995; Bender Koch and Mørup, 1991).

GR belong to the pyroaurite-group of compounds (Brindley and Bish, 1976), and are composed of alternating trioctahedral hydroxide layers, $[\text{Fe}_{6-x}^{\text{II}}\text{Fe}_x^{\text{III}}(\text{OH})_{12}]^{x+}$, and anionic interlayers, $[\text{A}_{x/n}^{n-}y\text{H}_2\text{O}]$, where A is an n -valent anion. Previously, we have taken the approach to modify and compare different forms of the GRs in order to elucidate the fundamentals of the reaction (Hansen and Bender Koch, 1998). The reactive sites for nitrate reduction must be located at the iron(II)iron(III) hydroxide layers, and thus the rate of reaction will depend on the layer area, which can be accessed by nitrate. If nitrate can exchange with the interlayer anion (A^{n-}), reaction can take place both at outer and inner surfaces of the GR particles. Apparently, nitrate cannot penetrate the interlayer when carbonate or

sulphate constitutes the interlayer anions (Hansen and Bender Koch, 1998). This agrees with the low affinity of the interlayer for monovalent anions compared with higher-valent anions in analogues layered hydroxides (Miyata, 1983). However, when nitrate was forced into the interlayer by extracting the interlayer sulphate through precipitation of barium sulphate outside the GR particles, the observed 40-fold increase in rate of nitrate reduction almost equaled the increase in exposed surface area of the Fe(II)Fe(III) layers (Hansen and Bender Koch, 1998). From these observations, it is expected that the rate of reaction will depend on the particular anionic form of GR, specifically the ease with which nitrate can exchange with A^{n-} in the GR interlayer, and the crystallite size. Interlayer forms of GR containing easy exchangeable anions like halogenides are expected to show high reaction rates.

In this work, the stoichiometry and the kinetics of the reaction between nitrate and the chloride form of GR (GR_{Cl}) have been investigated. The kinetics are compared with those for the similar reaction with carbonate and sulphate forms of GR (GR_{CO_3} , GR_{SO_4}). In addition, a sulphate GR produced from GR_{Cl} by exchange of interlayer chloride with sulphate ($\text{GR}_{\text{Cl} \rightarrow \text{SO}_4}$) has been used to evaluate how the Fe(II):Fe(III) ratio of the GR and the ease of interlayer anion exchange with nitrate influence the rate of nitrate reduction.

2. Materials and methods

2.1. Synthesis of GR_{Cl} and reaction with nitrate

The chloride form of GR was synthesized by air oxidation of FeCl_2 solutions at constant pH using a titrator, a technique also used for synthesis of GR_{SO_4} s (Hansen et al., 1996). All solutions and suspensions were kept in flasks sealed with rubber septa and flushed with argon (99.9995%, flow $50 \text{ cm}^3 \text{ min}^{-1}$); in- and outlets to/from the flasks were made of 1-mm stainless steel needles or 1-mm Teflon tubes. First, a stock solution of approximately 0.5 M FeCl_2 was prepared by reacting an excess of iron powder (Merck 3819, particle size $10 \mu\text{m}$) with 100 cm^3 of Ar-flushed 1.0 M HCl at 80°C . The synthesis of GR_{Cl} was carried out in a thermostated ($25 \pm 0.1^\circ\text{C}$)

300 cm³ flask equipped with a pH combination electrode, inlets for titrator (0.25 M NaOH), Ar and air, and valves for gas out and sampling. Ten cubic centimeters of the FeCl₂ stock solution was transferred into the synthesis flask containing 190 cm³ of Ar-flushed 0.5 M NaCl, and pH adjusted to 7.5 after which the pH-stat control was switched on. A peristaltic pump introduced CO₂-free air into the solution at a rate of 0.25–5 cm³ min⁻¹ while Ar-flushing the headspace above the solution. The formation rate was controlled at an OH⁻ consumption of 8×10^{-5} mol s⁻¹. The oxidation was stopped when approximately 60% of the initial Fe(II) had been incorporated in the precipitated solids.

After settling of the greenish-blue precipitate, the synthesis flask was transferred into a glove box flushed by Ar (99.9995%). The flask was opened, the supernatant discarded and the remaining slurry filtered on a suction filter (pore diameter 10–16 μm) and washed with 4×10 cm³ of Ar-bubbled water. Now the GR_{Cl} product was transferred to one or more reaction flasks. In one type of experiments, the product was transferred to 100-cm³ crimp seal vials containing 70 cm³ of Ar-bubbled water. In another type of experiments, in which pH was monitored during the reaction, the GR_{Cl} was mixed with 190 cm³ of Ar-bubbled water in a 300-cm³ reaction flask fitted with a pH-electrode and a sampling port both inserted through a rubber septum. After proper sealing and dispersion of the GR_{Cl}, the vials/flask were removed from the glove box. Initial suspension concentrations of Fe(II) in GR_{Cl} were between 3 and 11 mM. The reaction was started when 10 cm³ of Ar-bubbled NaNO₃ solution was added resulting in initial nitrate concentrations of 0.71, 1.78, 3.57, 7.14 and 14.23 mM. The crimp seal vials were placed on a shaking table (50 strokes min⁻¹) whereas suspensions in 300-cm³ reaction flasks were magnetically stirred. At regular time intervals, the reaction mixtures were sampled using Ar-flushed syringes. Filtered samples were taken for determination of Fe(II) in solution (Fe(II)_{sol}), unfiltered samples treated with 0.1 M HCl for determination of Fe(II) in GR + solution (Fe(II)_{sol+GR}), and unfiltered samples quenched by rapid aerial oxidation for determination of ammonium (Hansen et al., 1996). The concentration of Fe(II) in GR (Fe(II)_{GR}) was determined as the difference between Fe(II)_{sol} and Fe(II)_{sol+GR}.

Experiments were also performed in which chloride in GR_{Cl} was exchanged with sulphate (GR_{Cl→SO₄}). The chloride GR was synthesized, separated and washed as described above and subsequently treated with 50 cm³ of Ar-bubbled 0.5 M Na₂SO₄ solution for 24 h. The ion exchanged product was again separated, washed and redispersed, and then used for reaction with sodium nitrate at a starting concentration of 14.23 mM as described above.

Blank experiments in which no NaNO₃ was added to the GR_{Cl} suspensions, were carried out to test for possible leakage of oxygen into the reaction flasks. Furthermore, the possible reaction of nitrate with soluble Fe(II) was tested in control experiments using crimp seal vials containing 15 mM FeCl₂ solutions free of GR buffered at pH 7.25 with HEPES (4-(2-hydroxyethyl)-1-piperazineethansulfonic acid) and kept under an Ar-atmosphere in a glove box. Both during synthesis and reaction, all flasks were wrapped with Al-foil to prevent photochemical reactions.

2.2. Analysis

Iron(II) was determined by the 1,10-phenanthroline method (Fadrus and Maly, 1975). Total dissolved Fe (Fe(II) + Fe(III)) was determined by the same method after reduction with 8% (w/v) ascorbic acid. Ammonium was determined spectrophotometrically in filtrates of the quenched suspensions by flow injection analysis employing reaction of ammonium with an indicator solution (Ramsing et al., 1980). Filtered suspension samples were preserved against oxidation by use of glycerol and examined by X-ray diffraction (XRD) using a Philips PW1050 goniometer (Co Kα radiation). The smears were scanned at a speed of 1° 2θ min⁻¹ (Hansen, 1989). Mössbauer spectra of GR samples were obtained at 80 K using a conventional constant acceleration spectrometer and a source of ⁵⁷Co in Rh. The spectrometer was calibrated using a 12.5-μm foil of α-Fe at room temperature and isomer shifts are given relative to the centroid of this absorber. The spectra were fitted using simple Lorentzian line shape.

All chemicals were p.a. quality. Double deionized or glass distilled water was used throughout, and all glass and plast ware were soaked in 4 M HNO₃ for 1

h and carefully rinsed in double deionized water before use.

3. Results and discussion

3.1. Synthesis of GR_{Cl}

X-ray diffraction of the suspended solids demonstrates that GR_{Cl} and magnetite are the only crystalline solids in the initial and final reaction mixtures, respectively (Fig. 1). Basal reflections are very intense compared with other reflections indicating strong preferred orientation of crystallites in the XRD samples due to a platy morphology of the GR_{Cl} crystallites. The average thickness of the GR_{Cl} crystals determined from the width of the 003 peaks and the Scherrer formula ($k = 0.9$) is 38 ± 6 nm, which is comparable to the thickness of synthetic GR_{SO_4}

particles (Hansen and Bender Koch, 1998). No other oxidation products than magnetite was observed. Lepidocrocite can form as an oxidation product of GRs but normally at higher oxidation rates than were found here and possibly with magnetite as an intermediate phase (Srinivasan et al., 1996).

The Mössbauer spectrum of the GR_{Cl} is shown in Fig. 2A. A two-doublet component fit of the spectrum gives an isomer shift of 1.26 mm s^{-1} and a quadrupole splitting of 2.73 mm s^{-1} for the dominating Fe(II) component and isomer shift of 0.44 and a quadrupole splitting of 0.38 mm s^{-1} for the Fe(III) component. Assuming identical f -factors for the two components, the relative areas of the two components give an Fe(II):Fe(III) ratio of 2.7 ± 0.2 . This ratio close to 3:1 is in good agreement with findings by Lewis (1997) and Refait and Génin (1993). The GR_{Cl} formula is thus close to $Fe_{4.5}^{II}Fe_{1.5}^{III}(OH)_{12}Cl_{1.5}yH_2O$, which will be used in the following. The magnetite produced by the reaction is well crystalline and is assumed to be stoichiometric as found

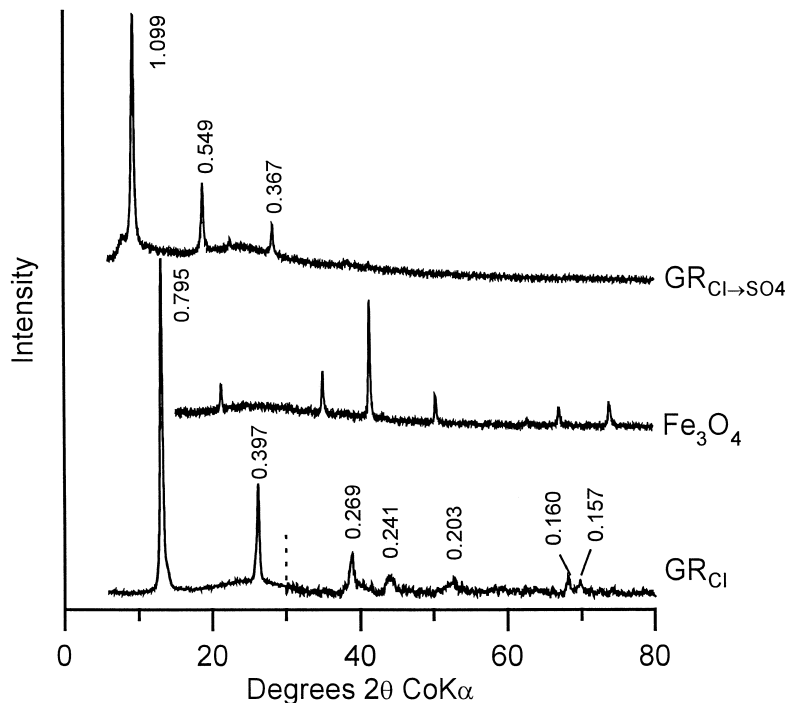


Fig. 1. X-ray traces of the starting material GR_{Cl} , the sulphate-exchanged GR_{Cl} ($GR_{Cl} \rightarrow SO_4$) and the final magnetite oxidation product. The dashed line marks a five-time expansion of the intensity scale (d -spacings in nm).

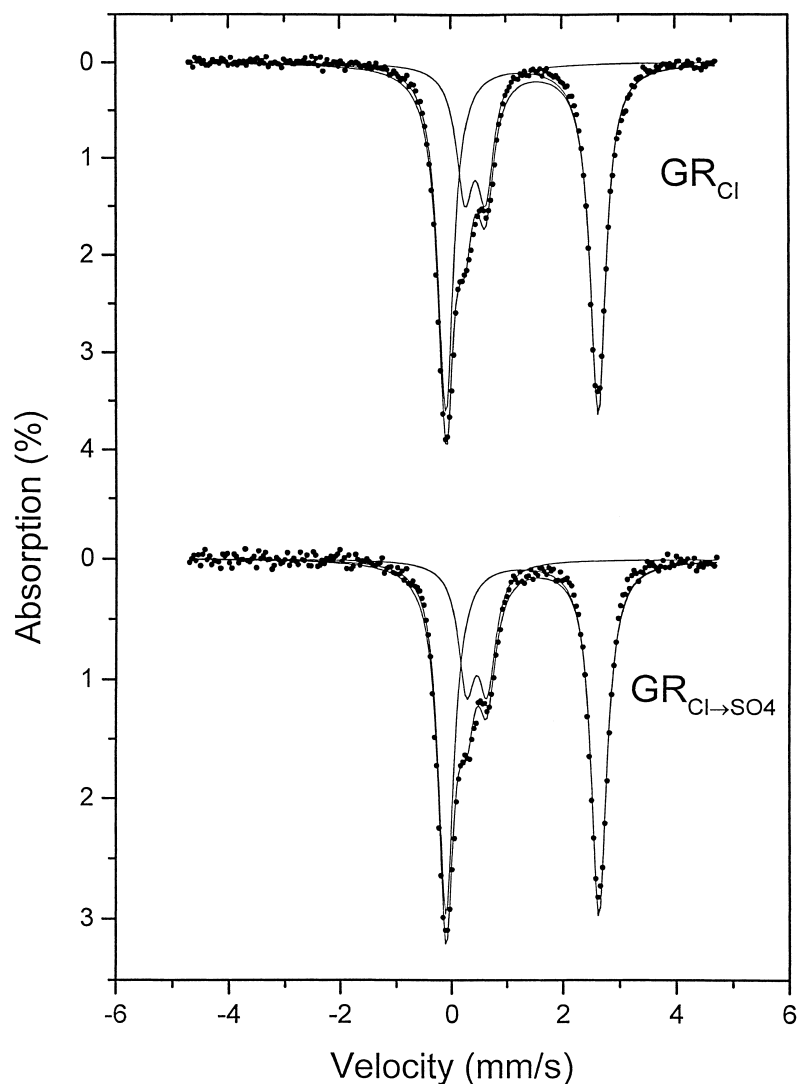


Fig. 2. Mössbauer spectra of GR_{Cl} and after exchange with sulphate ($GR_{Cl \rightarrow SO_4}$) obtained at 80 K.

in a previous analysis of magnetites produced under similar conditions (Hansen et al., 1996).

3.2. Stoichiometry and rate of nitrate reduction by GR_{Cl}

Nitrate is reduced to ammonium by GR_{Cl} , as evidenced by both the formation of ammonium and consumption of $Fe(II)_{GR}$ (Fig. 3). With the applied concentrations of $Fe(II)_{GR}$ and nitrate, the reaction is completed within 300 min, which is much faster than

observed for the reaction between nitrate and GR_{SO_4} (Hansen et al., 1996). Protons generated during reaction cause a pH decrease from 8.2 to 6.1 at the end of reaction, which is followed by a slight increase in the concentration of $Fe(II)_{sol}$ presumably due to dissolution of GR_{Cl} at the lower pH. In control experiments with pure GR_{Cl} but without addition of nitrate minor oxidation of $Fe(II)_{GR}$ took place probably owing to oxygen leakages into the reaction flasks. In these experiments, the concentration of $Fe(II)_{GR}$ in the suspensions decreased only little, and at an

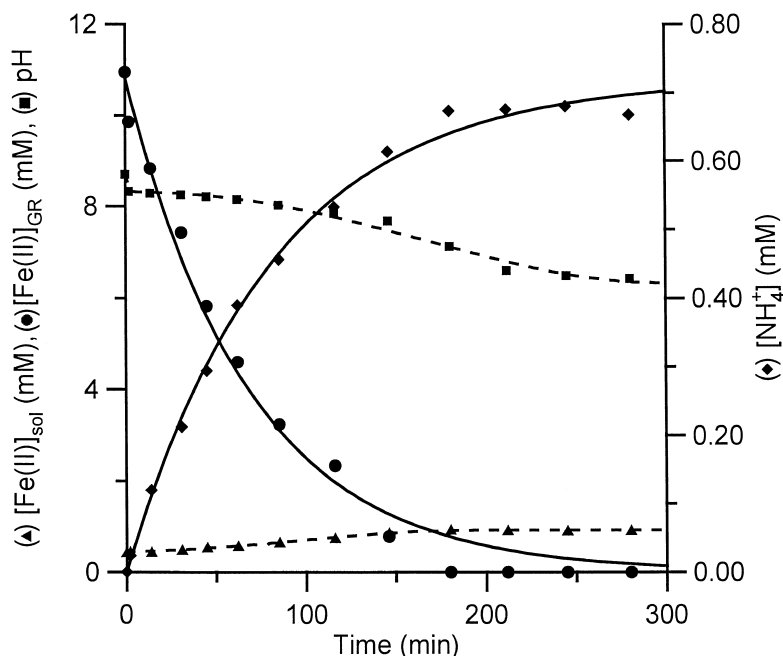
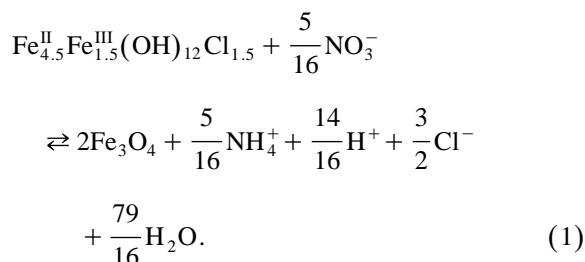


Fig. 3. Rate of formation of ammonium (\blacklozenge) and consumption of $\text{Fe(II)}_{\text{GR}}$ (\bullet) with accompanying first-order fits (full line). Also shown are the concentration of Fe(II) in solution (\blacktriangle) and pH (\blacksquare). Dashed curves are drawn as a guide to the eye. ($[\text{NO}_3^-]_{\text{init}} = 14.28 \text{ mM}$).

average rate of $12.3 \cdot 10^{-8} \text{ M s}^{-1}$, which is 15–20-times less than the oxidation rate when nitrate is added to the GR_{Cl} . It was found that solutions of iron(II) chloride did not reduce nitrate to ammonium at the time scale of the experiments (Table 1), clearly demonstrating that $\text{Fe(II)}_{\text{GR}}$ and not $\text{Fe(II)}_{\text{sol}}$ is the actual reductant in the reactions.

Assuming that ammonium is the only N-containing product of the reaction, the overall redox reaction can be specified by:



For each mol of GR_{Cl} , 2 mol of $\text{Fe(II)}_{\text{GR}}$ pass on unoxidized into magnetite while 2.5 mol of $\text{Fe(II)}_{\text{GR}}$

are consumed for reduction of nitrate. The theoretical ratio between formation of ammonium and consumption of $\text{Fe(II)}_{\text{GR}}$ (r_{ox}) equals $(5/16)/4.5 = (5/72) = 0.0694$. In Fig. 4, the observed maximum production of $\text{Fe(II)}_{\text{GR}}$ for the experiments listed in Table 1. The value of r_{ox} determined by linear regression equals 0.0658, which is not significantly different from the theoretical r_{ox} value of 0.0694 at the 99% level of significance. The slight background oxidation causes oxidation of $\text{Fe(II)}_{\text{GR}}$ without formation of ammonium, and therefore the observed r_{ox} values will be slightly underestimated, especially in experiments with low initial concentrations of $\text{Fe(II)}_{\text{GR}}$ where the relative consumption of $\text{Fe(II)}_{\text{GR}}$ in the background oxidation reaction is highest. It can be concluded that nitrate is almost quantitatively reduced to ammonium on reaction with GR_{Cl} according to Eq. (1). Formation of other N-containing reduction products cannot be excluded, but their concentration will be very low. Stoichiometric reduction of nitrate to ammonium has also been observed in the reaction between GR_{SO_4} and nitrate (Hansen et al., 1996).

Table 1
Reaction and kinetic parameters for the reduction of nitrate by GR

Experiments	[Fe(II)] _{GR,init} ^a (M) × 10 ⁻³	[NO ₃ ⁻] _{init} ^a (M) × 10 ⁻³	Initial rate ^b (M s ⁻¹) × 10 ⁻⁸	k _{obs} ^c (s ⁻¹) × 10 ⁻⁴	r ^{2c}
Control ^d	0	14.28	0	0	na ^e
SG32	5.77	0.71	5.46	1.44	0.9836
SG33	5.43	1.78	6.45	2.12	0.9831
SG21	10.88	3.57	15.51	2.03	0.9784
SG34	3.68	3.57	6.73	3.82	0.9931
SG13	8.58	7.14	14.31	2.46	0.8148
SG23	7.03	7.14	15.61	2.95	0.9747
SG14	8.55	14.28	16.56	2.95	0.9095
SG24	5.26	14.28	14.79	4.18	0.9453
HNK12	10.95	14.28	15.54	2.12	0.9953
ME37 ^f	6.31	14.28	2.18	0.47	0.8723

^aInitial concentration of Fe(II)_{GR} and NO₃⁻, respectively.

^bInitial rate of formation of NH₄⁺.

^cDetermined from NH₄⁺ vs. time data by fitting to [NH₄⁺] = [NH₄⁺]_{max}(1 - exp(-k_{obs}t)) with r² the coefficient of regression.

^dReaction with 15 mM FeCl₂ at pH 7.25.

^eNot applicable.

^fGR_{Cl} exchanged with SO₄²⁻ (GR_{Cl→SO₄}, for details see text); average of two experiments.

Both the rate of disappearance of Fe(II)_{GR} and the rate of ammonium formation can be fitted as first-order reactions (Fig. 3). Tentatively, the rate law for ammonium formation may be expressed by:

$$\frac{d[\text{NH}_4^+]}{dt} = k[\text{Fe(II)}]_{\text{GR}}^1[\text{NO}_3^-]^\beta \quad (2)$$

where β is the reaction order with respect to nitrate. The rate law can also be expressed as the disappearance of nitrate but because ammonium and not nitrate was measured, the rate of ammonium formation is given in Eq. (2). For higher initial concentrations of nitrate (≥ 3.57 mM), the reaction can be treated as a pseudo zero-order reaction with respect to nitrate, and thus the rate equation simplifies to:

$$\begin{aligned} \frac{d[\text{NH}_4^+]}{dt} &= k_{\text{obs}}([\text{NH}_4^+]_{\text{max}} - [\text{NH}_4^+]) \\ &= \frac{5}{72}k_{\text{obs}}[\text{Fe(II)}]_{\text{GR}} \end{aligned} \quad (3)$$

where

$$k_{\text{obs}} = \frac{72}{5}k[\text{NO}_3^-]^\beta \quad (4)$$

and [NH₄⁺]_{max} is the maximum concentration of ammonium produced at completion of reaction. The k_{obs} parameters can be determined from Fe(II)_{GR} or ammonium vs. time data, and similar values are obtained in most cases. The error of determination is smaller for the ammonium than the Fe(II)_{GR} measurement due to the indirect estimation of the latter. Consequently, k_{obs} values have been determined from the ammonium data. Values of k_{obs} vary between 2 and 4 × 10⁻⁴ s⁻¹ for initial concentrations of nitrate varying between 1.78 and 14.28 mM (Table 1). An estimate of the reaction order with respect to nitrate and the rate constant k may be derived from initial rates and concentrations according to the logarithmic form of Eq. (2):

$$\begin{aligned} \log\left(\frac{[\text{NH}_4^+]}{dt}\right)_{\text{init}} - \log([\text{Fe(II)}]_{\text{GR,init}}) \\ = \log(k) + \beta \log([\text{NO}_3^-]_{\text{init}}). \end{aligned} \quad (5)$$

A plot of the left hand side vs. the right hand side of Eq. (5) gives $k = 1.69 \times 10^{-4} \text{ M}^{-0.45} \text{ s}^{-1}$ and $\beta = 0.45$. However, the correlation is not good ($r^2 = 0.5681$) and a *t*-test indicates that the hypothesis:

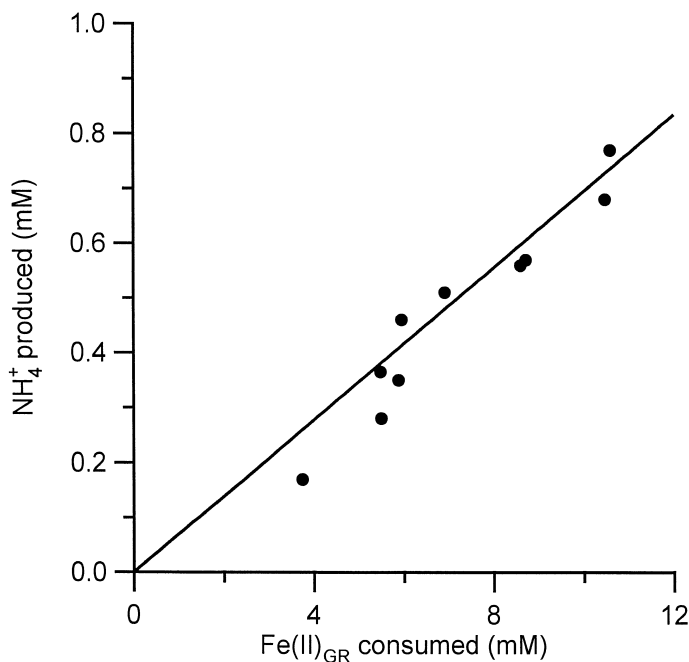


Fig. 4. The observed formation of NH_4^+ vs. consumption of $\text{Fe(II)}_{\text{GR}}$ at completion of reaction in the different experiments (cp. Table 1) and different initial concentrations of nitrate. The straight line ($[\text{NH}_4^+] = (5/72)[\text{Fe(II)}_{\text{GR}}]$) represents the ideal stoichiometric ratio according to Eq. (1).

$\beta = 0$ cannot be excluded. However, the initial rate data indicate that ammonium formation reaches an almost constant rate at nitrate concentrations of 7 mM (Table 1). Thus, there is some evidence that the rate of reaction increases with nitrate concentrations up to some upper limit at 7 mM nitrate after which the reaction becomes “saturated” with respect to nitrate. Variation in particle sizes and hence reactive surface areas of the starting GR_{Cl} reactants between experiments could blur a clear rate dependence of nitrate concentration, but estimated from peak widths in XRD traces of the GRs particle sizes were almost constant.

Assuming that $\beta = 0$ for nitrate concentrations above the “saturation” point, i.e. experiments at nitrate concentrations of 7.14 and 14.28 mM, the rate equation may be given as:

$$\begin{aligned} \frac{d[\text{NH}_4^+]}{dt} &= \frac{72}{5}k([\text{NH}_4^+]_{\text{max}} - [\text{NH}_4^+]) \\ &= k[\text{Fe(II)}]_{\text{GR}} \end{aligned} \quad (6)$$

where $k = 2.0 \pm 0.5 \times 10^{-5} \text{ s}^{-1}$.

To see if any change of the layer thickness of the GR would occur during oxidation by nitrate, XRD traces of the 003 reflection were recorded at different times after mixing with NaNO_3 (Fig. 5). A slight but insignificant decrease in layer thickness from 0.795 nm before addition of NaNO_3 to 0.792 nm after reaction for 80 min was observed. This indicates that a nitrate-exchanged GR is not present as the $d(003)$ -spacing for the nitrate form of GR is about 0.77 nm (Hansen and Bender Koch, 1998). The peak width of the 003 reflection was found to be almost constant with time corresponding to no decrease in GR particle thickness during a major part of the reaction. These observations are consistent with a reaction mechanism where nitrate progressively exchanges with chloride from particle edges and inwards, and where $\text{Fe(II)}\text{--Fe(III)}$ hydroxide layers in contact with nitrate becomes quickly oxidized. Thus, platy GR particles are reduced in size from plate edges and inwards keeping the plate thickness almost constant. Furthermore, no nitrate interlayer form will be detected by XRD as that part of the GR crystal in contact with nitrate becomes oxidized and dissolves.

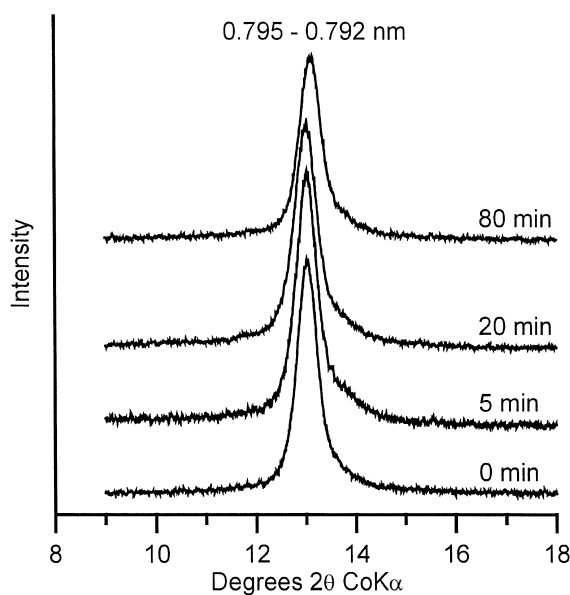


Fig. 5. X-ray traces of the 003 peak of GR_{Cl} just before (0 min) and after reaction with nitrate for 5, 20 and 80 min ($[NO_3^-]_{init} = 14.28$ mM).

The reaction seems to consist of a particle by particle oxidation mechanism rather than a progressing average oxidation of all particles.

3.3. Reaction of nitrate with sulphate-exchanged GR_{Cl}

Interlayer chloride was successfully exchanged with sulphate as demonstrated by the XRD trace of

the $GR_{Cl \rightarrow SO_4}$, which shows basal reflections typical of GR_{SO_4} (Hansen et al., 1996). The widths of the basal reflections did not change during anion exchange and thus the crystal thickness remained almost constant. The Mössbauer parameters of the $GR_{Cl \rightarrow SO_4}$ were almost identical to those of GR_{Cl} and the Fe(II):Fe(III) ratio of the former was 2.8 ± 0.2 (Fig. 2B) demonstrating that the Fe(II):Fe(III) ratio is kept constant during anion exchange. This result indicates that the interlayer anion exhibit only minor influence on the local environment of the cations within the hydroxide layers (Bender Koch, 1998).

The produced sulphate GR ($GR_{Cl \rightarrow SO_4}$) has an Fe(II):Fe(III) ratio of 3:1 whereas GR_{SO_4} s produced by direct synthesis have Fe(II):Fe(III) ratios of 2:1 (Hansen et al., 1996). Nitrate reduction by $GR_{Cl \rightarrow SO_4}$ is about six times slower than reduction of nitrate by GR_{Cl} (Table 1). However, GR_{SO_4} s with Fe(II):Fe(III) ratios of 2:1 show five times slower rate of nitrate reduction compared with the $GR_{Cl \rightarrow SO_4}$ and 30 times slower rate compared with GR_{Cl} (Table 2). The differences in reactivity between traditional GR_{SO_4} (Fe(II):Fe(III) = 2) and $GR_{Cl \rightarrow SO_4}$ (Fe(II):Fe(III) = 3) indicate that the relative amount of Fe(II) in the octahedral layer affects nitrate reduction rates. Variation in rates of reaction could be due to differences in specific surface areas between GR_{Cl} , GR_{SO_4} and $GR_{Cl \rightarrow SO_4}$. However, the crystal thickness along the *c*-axis of the various GRs as determined from the width of the basal reflections does not show substantial differences (cf. Fig. 1, and Hansen and Bender Koch, 1998) indicating that the observed variation in

Table 2
Comparison of rates of nitrate reduction by GR_{SO_4} and GR_{Cl} at an initial nitrate concentration of 14.28 mM and room temperature

GR type	Nitrate salt	Fe(II): Fe(III) ^a	$[Fe(II)]_{GR,init}^b$ (M) $\times 10^{-3}$	k_{obs}^c (s^{-1}) $\times 10^{-5}$	Reference ^d
GR_{Cl}	NaNO ₃	3:1	4–11	30.8 ± 10.4	This work
$GR_{Cl \rightarrow SO_4}$	NaNO ₃	3:1	6–7	4.7	This work
GR_{SO_4}	NaNO ₃	2:1	2–10	0.95 ± 0.38	1
GR_{SO_4}	Ba(NO ₃) ₂	2:1	5–12	32.8 ± 9.2	2

^a Fe(II):Fe(III) ratio of GR.

^b Initial concentration of Fe(II)_{GR}.

^c Determined from NH₄⁺ vs. time data by fitting to $[NH_4^+] = [NH_4^+]_{max}(1 - \exp(-k_{obs}t))$.

^d [1] Hansen et al. (1996), [2] Hansen and Bender Koch (1998).

reactivity is not due to differences in the external surface areas of the GR particles.

The increase in nitrate reduction rates when Fe(II):Fe(III) ratios are increased can be attributed to two effects: an increase in the reducing capacity of the GR, and the lower charge density of the hydroxide layers. The smaller layer charge of the $\text{GR}_{\text{Cl} \rightarrow \text{SO}_4}$ compared with GR_{SO_4} is expected to favour the exchange of sulphate for nitrate thus placing nitrate at the reactive surfaces resulting in higher reaction rates. In case of the GR_{Cl} , the much easier exchange of chloride for nitrate further contributes to the high reduction rates observed for GR_{Cl} . This is similar to the dramatic increase in nitrate reduction rates observed on forced exchange of sulphate with nitrate in GR_{SO_4} (Hansen and Bender Koch, 1998).

A smaller layer charge also implies that fewer Fe(III) reactive centers in the hydroxide layers are present and this partially could lead to lower reduction rates. Mössbauer spectroscopy provides no evidence of charge delocalization in GR at room temperature. Consequently, if Fe(III) in the hydroxide layers constitutes the reactive sites, one reactive site per nitrate may not suffice to provide all eight electrons needed for full reduction of nitrate to ammonia. This suggests that the reactive complex may have to diffuse around at the surface for completion of reaction, which may limit the reaction rate.

The observed “saturation” with respect to the rate of nitrate reduction in the GR_{Cl} system for nitrate concentrations above approximately 7 mM may indicate that at this concentration the interlayer chloride has been fully exchanged with nitrate and that the maximum nitrate reduction rates of hydroxide layers with Fe(II):Fe(III) = 3 have been achieved. Alternatively, the chloride for nitrate exchange may constitute the rate limiting reaction. However, if the activation energies for nitrate reduction are as high as in GR_{SO_4} systems, 84 kJ mol⁻¹ (Hansen and Bender Koch, 1998), ion exchange is probably not the rate limiting reaction as the activation energy for such a reaction is low.

Apparently, the rate of nitrate reduction by GR_{Cl} decreases less than what could be expected if the reaction was first-order with respect to nitrate, and which was observed for the GR_{SO_4} system (Hansen et al., 1996). This means that nitrate reduction rates in the GR_{Cl} system are substantial even at nitrate

concentrations below 1 mM, i.e. the GR_{Cl} is an active reductant also at low concentrations of the oxidant.

4. Conclusions

Nitrate is reduced stoichiometrically to ammonium by synthetic GR_{Cl} ($\text{Fe}_{4.5}^{\text{II}}\text{Fe}_{1.5}^{\text{III}}(\text{OH})_{12} \cdot x\text{H}_2\text{O}$) in an apparent first-order reaction with respect to $\text{Fe(II)}_{\text{GR}}$. Reduction rates increase with increasing nitrate concentrations up to some threshold concentration of nitrate at about 7 mM above which no further increase in reduction rates takes place. Nitrate reduction rates are 30–40 times higher than the rates observed for reduction by GR_{SO_4} , which have Fe(II):Fe(III) ratios of 2:1. Sulphate exchange of GR_{Cl} produced a sulphate-GR with an Fe(II):Fe(III) ratio of 3:1. The resulting GR reduced nitrate six times slower than the GR_{Cl} . Therefore, both the type of interlayer ion, the layer charge and the relative content of Fe(II) in the hydroxide layers influence nitrate reduction rates.

References

- Al-Agha, M.R., Burley, S.D., Curtis, C.D., Esson, J., 1995. Complex cementation textures and authigenic mineral assemblages in recent concretions from the Lincolnshire Wash (east coast, UK) driven by Fe(0) to Fe(II) oxidation. *J. Geol. Soc. (London)* 152, 157–171.
- Bender Koch, C., 1998. Structures and properties of anionic clay minerals. *Hyperfine Interact.* 117, 131–157.
- Bender Koch, C., Mørup, S., 1991. Identification of green rust in an ochre sludge. *Clay Miner.* 26, 577–582.
- Brindley, G.W., Bish, D.L., 1976. Green rust: a pyroaurite type structure. *Nature* 263, 353.
- Erbs, M., Hansen, H.C.B., Olsen, C.E., 1999. Reductive dechlorination of carbon tetrachloride using iron(II)iron(III)-hydroxide-sulphate (green rust). *Environ. Sci. Technol.* 33, 307–311.
- Fadrus, H., Maly, J., 1975. Suppression of iron(III) interference in the determination of iron(II) in water by the 1,10-Phenanthroline method. *Analyst* 100, 549–554.
- Frederickson, J.K., Zachara, J.M., Kennedy, D.W., Dong, H., Onstott, T.C., Hinman, N.W., Li, S.-M., 1998. Biogenic iron mineralization accompanying the dissimilatory reduction of hydrous ferric oxide by a groundwater bacterium. *Geochim. Cosmochim. Acta* 62, 3239–3257.
- Gu, B., Phelps, T.J., Liang, L., Dickey, M.J., Roh, Y., Kinsall,

- B.L., Palumbo, A.V., Jacobs, G.K., 1999. Biogeochemical dynamics in zero-valent iron columns: implications for permeable reactive barriers. *Environ. Sci. Technol.* 33, 2170–2177.
- Hansen, H.C.B., 1989. Composition, stabilization, and light absorption of Fe(II)Fe(III) hydroxy carbonate (Green Rust). *Clay Miner.* 24, 663–669.
- Hansen, H.C.B., Bender Koch, C., 1998. Reduction of nitrate to ammonium by sulphate green rust: activation energy and reaction mechanism. *Clay Miner.* 33, 87–101.
- Hansen, H.C.B., Bender Koch, C., Nancke-Krogh, H., Borggaard, O.K., Sørensen, J., 1996. Abiotic nitrate reduction to ammonium: key role of green rust. *Environ. Sci. Technol.* 30, 2053–2056.
- Kassim, J., Baird, T., Fryer, J.R., 1982. Electron microscope studies of iron corrosion products in water at room temperature. *Corros. Sci.* 22, 147–158.
- Lewis, D.G., 1997. Factors influencing the stability and properties of green rusts. *Adv. GeoEcol.* 30, 345–372.
- Miyata, S., 1983. Anion-exchange properties of hydrotalcite-like compounds. *Clays Clay Miner.* 31, 305–311.
- Myneni, S.C.B., Tokunaga, T.K., Brown, G.E. Jr., 1997. Abiotic selenium redox transformations in the presence of Fe(II,III) oxides. *Science* 278, 1106–1109.
- Pecher, K., Haderlein, S.B., Schwarzenbach, R.P., 1997. Transformation of polyhalogenated alkanes in suspensions of ferrous iron oxides. 213th ACS National Meeting, Division of Environmental Chemistry, Preprints of papers, American Chemical Society, Washington DC, pp. 185–187.
- Ramsing, A., Ruzicka, J., Hansen, E.H., 1980. A new approach to enzymatic assay based on flow injection spectrophotometry with acid–base indicators. *Anal. Chim. Acta* 114, 165–181.
- Refait, P., Génin, J.-M.R., 1993. The oxidation of ferrous hydroxide in chloride-containing aqueous media and Pourbaix diagrams of green rust one. *Corros. Sci.* 34, 797–819.
- Scherer, M.M., Balko, B.A., Tratnyek, P.G., 1999. The role of oxides in reduction reactions at the metal–water interface. In: Grundl, T., Sparks, D. (Eds.), *Kinetics and Mechanism of Reactions at the Mineral/Water Interface*. American Chemical Society, pp. 301–322.
- Shokes, T.E., Möller, G., 1999. Removal of dissolved heavy metals from acid rock drainage using iron metal. *Environ. Sci. Technol.* 33, 282–287.
- Srinivasan, R., Lin, R., Spicer, R.L., Davis, B.H., 1996. Structural features in the formation of the green rust intermediate and γ -FeOOH. *Colloid Surf.* 113, 97–105.
- Tamura, Y., 1985. Ferrite formation from the intermediate, green rust II, in the transformation reaction of γ -FeO(OH) in aqueous suspension. *Inorg. Chem.* 24, 4363–4366.
- Taylor, R.M., Arthur, R.W., Ennis, I.D., Robins, R.G., 1998. Remediation of AMD: The green precipitate process. EPD Congress. The Minerals Metals and Materials Soc., TMS Warrendale PA. pp. 367–379.
- Trollard, F., Génin, J.-M.R., Abdelmoula, M., Bourrié, G., Humbert, B., Herbillon, A., 1997. Identification of a green rust mineral in a reductomorphic soil by Mössbauer and Raman spectroscopies. *Geochim. Cosmochim. Acta* 61, 1107–1111.