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NICKEL INCORPORATION IN Fe(II, III) HYDROXYSULFATE GREEN RUST: EFFECT ON CRYSTAL LATTICE SPACING AND OXIDATION PRODUCTS[1]

Lucia Helena Garófalo Chaves[2], Joan Elizabeth Curry[3], David Andrew Stone[4], Michael D. Carducci[5] & Jon Chorover[6]

SUMMARY

Ni(II)-Fe(II)-Fe(III) layered double hydroxides (LDH) or Ni-containing sulfate green rust (GR2) samples were prepared from Ni(II), Fe(II) and Fe(III) sulfate salts and analyzed with X ray diffraction. Nickel is readily incorporated in the GR2 structure and forms a solid solution between GR2 and a Ni(II)-Fe(III) LDH. There is a correlation between the unit cell *a*-value and the fraction of Ni(II) incorporated into the Ni(II)-GR2 structure. Since there is strong evidence that the divalent/trivalent cation ratio in GR2 is fixed at 2, it is possible in principle to determine the extent of divalent cation substitution for Fe(II) in GR2 from the unit cell *a*-value. Oxidation forms a mixture of minerals but the LDH structure is retained if at least 20 % of the divalent cations in the initial solution are Ni(II). It appears that Ni(II) is incorporated in a stable LDH structure. This may be important for two reasons, first for understanding the formation of LDHs, which are anion exchangers, in the natural environment. Secondly, this is important for understanding the fate of transition metals in the environment, particularly in the presence of reduced Fe compounds.

Index terms: isomorphous substitution, layered double hydroxide, LDH, X ray diffraction

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RESUMO: *INCORPORAÇÃO DE NÍQUEL EM Fe (II-III) GRENN RUST HIDROXISULFATO: EFEITO SOBRE A ESTRUTURA CRISTALINA E PRODUTOS DE OXIDAÇÃO*

Amostras de hidróxidos de dupla camada (HDC), ou "sulfate green rust" (GR2), contendo Ni foram preparadas utilizando-se sulfatos de Ni(II), Fe(II) e Fe(III) e analisadas por difração de raios X. O Ni está incorporado na estrutura do GR2 e forma um sólido entre GR2 e um HDC contendo Ni(II)-Fe(III). Há correlação entre os valores de "a" da célula unitária e os da fração de Ni(II) incorporado na estrutura do Ni(II)-GR2. Desde que haja forte evidência de que a razão entre os cátions divalente/trivalente no GR2 seja igual a 2, é possível, a princípio, determinar a extensão da substituição do cátion divalente por Fe(II) no GR2 a partir dos valores de "a" da célula unitária do cristal. Sob o efeito da oxidação, é formada uma mistura de minerais, porém a estrutura do HDC não é alterada se pelo menos 20 % dos cátions divalentes na solução inicial forem de Ni(II). Isso parece indicar que o Ni(II) está incorporado à estrutura estável do HDC, o que é importante por duas razões: para entender a formação dos HDC, os quais são trocadores aniônicos em condições naturais no meio ambiente; e para entender o destino dos metais de transição no ambiente, particularmente na presença de compostos de Fe na forma reduzida.

Termos de indexação: substituição isomórfica, hidróxido de dupla camada , HDC, difração de raios X.

INTRODUCTION

The substitution of Ni in reduced and poorly crystalline Fe oxides can alter the transformation rate and ultimately the specific end products formed during transformation of these minerals into more stable phases (Cornell et al., 1992; Chung et al., 2002). For instance, Ni substitution retards the transformation of ferrihydrite to more stable Fe oxides such as goethite and hematite (Ford et al., 1999). It has been shown that Ni readily substitutes Fe(III) in goethite due to the similarity in cation size but this produces a local distortion in the structure (Manceau et al., 2000, Carvalho e Silva et al., 2003) which is thought to limit the substitution to ~ 5 mol % (Singh et al., 2002). Nickel is an important alloying element in austenitic stainless steel that reportedly contributes to corrosion resistance (Wambach et al., 2002).

Nickel also can be incorporated in the structure of reduced Fe oxides such as green rust. This has implications for the fate of transition metals in the environment. For instance, Parmar et al. (2001) have shown that Ni in solution is immobilized in the green rust that forms as a result of microbially mediated Fe(III) reduction. Inoue et al. (2008) have shown that Ni enhances the formation of goethite in the oxidation of green rust in aqueous solution. Nickel is also associated with the green rust formed during Fe oxidation in permeable reactive barriers (Bartzas et al., 2006). Chaves et al. (2007) showed that green rust is probably more efficient in removing Ni from the environment by coprecipitation during mineral formation than by adsorption to already formed green rust. Green rust is a Fe(II)-Fe(III) hydroxide that consists of positively charged brucite-like layers, alternating with anions and water molecules. The general composition is $[Fe(II)_{(6-x)}Fe(III)_x(OH)_{12}]^{x+}[(A)_{x/n}.yH_2O]^{x-}$ where x = 0.9–4.2, A is an n-valent anion, e.g., CO_3^{2-}, Cl^- or SO_4^{2-} and y denotes the varying amounts of interlayer water. Two types of green rust can be distinguished: green rust one (GR1), with a rhombohedral unit cell, and green rust two (GR2) with a hexagonal cell. GR2 contains sulfate or other tetrahedral anions such as selenate and perchlorate in the interlayer spaces. The sulfate GR2 structure has been studied in detail and it is known that a long range order exists among the Fe(III) ions in the brucite-like sheet and SO_4^{2-} anions in the interlayer spaces (Génin, 2004). In pure GR2, each Fe(III) is surrounded by six Fe(II) ions, so the ratio of divalent/trivalent ions equal to 2.

More generally, green rust is a member of the family of minerals called "layered double hydroxides (LDH)", which have been the subject of much interest due to potential applications as anion exchangers (Rives, 2001). Known as anionic clays, LDHs are, in general, brucite-like sheets containing a mixture of divalent (e.g. Mg, Mn, Fe, Co, Ni, Cu, Zn) and trivalent (e.g. Al, Mn, Fe, Co, Ni, Cr, Ga) cations. There is wide variety in the potential composition and application of LDHs.

Green rusts are found naturally as corrosion products of Fe metal (Refait et al., 2003a) and as minerals in hydromorphic soils (Génin et al., 2001). They can be synthesized in the laboratory by partial oxidation of Fe(II) or by reactions of Fe(II) and Fe(III) salts in aqueous solutions (Géhin et al., 2002). Green rusts, unlike most Fe oxides, have a large internal surface area and consequently great reactivity. They represent reactive ion exchangers and sorbents (Hansen et al., 2001). The amphoteric surface hydroxyl groups lead to the sorption of heavy metals

(cations) as well as of inorganic anions, e.g. silicate, arsenate and selenate. In addition, cations such as Cu(II), Ni(II), Zn(II), Cd(II), Co(II) and Mg(II) may substitute Fe(II) isomorphically during green rust formation. It has been shown that Ni(II) can substitute Fe(II) in both GR1(Cl$^-$) (Refait & Génin, 1993, 1997; Refait et al., 1994, 1998) and GR2 (Refait et al., 1990, 2005). Oxidation, depending on the extent of Ni incorporation, Ni(II)-Fe(III) produces LDHs stable against further oxidation. While green rust would probably not be used as an agent to decontaminate soil, this incorporation of cationic inorganic contaminants into the structure of reduced green rust and LDHs could provide an effective means to sequester contaminants in the subsurface under appropriate conditions. It is therefore important to understand the potential of green rust to incorporate cations such as Ni during formation as well as the potential to release these same cations as the Fe(II) is converted to Fe(III) on exposure to oxidizing conditions in the environment.

Green rusts are unstable in oxidizing conditions and their rapid reaction with atmospheric O_2 results in the formation of ferrihydrite ($Fe_5HO_8.4H_2O$), goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), hematite (α-Fe_2O_3) maghemite (γ-Fe_2O_3) or magnetite (Fe_3O_4), depending on pH, solution composition, oxidant, oxidation rate, and the dehydration degree and rate (Lin et al., 1996; Loyaux-Lawniczak et al., 2000). Refait & Génin (1997) prepared Ni(II)-Fe(II)-Fe(III) hydroxychloride LDHs by aerial oxidation of mixed Ni(II)-Fe(II)-hydroxides. They found that the final oxidation products depended on the initial Fe/Ni ratio. In the absence of Ni, green rust oxidized to lepidocrocite and the LDH structure was lost. For Fe/Ni > 5/3 both lepidocrocite and some Ni(II)-Fe(III) hydroxychloride were detected by X ray diffraction. For Fe/Ni between 1/3 and 5/3, only the hydroxychloride LDH was obtained. Since LDHs contain a mixture of divalent and trivalent cations in a brucite-like sheet, if enough Ni is present in divalent sites, the LDH structure is preserved on oxidation of structural Fe(II). In the current study we further investigated substitution of Ni(II) in sulfate GR2 and the oxidation products from exposure to air. The specific research objective is to determine the effect of Ni(II) incorporation on the GR2 crystal structure and to determine how Ni(II) affects the oxidation products by directly precipitating nickelous-GR2 from a mixture of Fe(II), Ni(II) and Fe(III) sulfate salts in anoxic conditions followed by aerial oxidation of the dried samples.

MATERIALS AND METHODS

GR2 is very sensitive to air oxidation, and was therefore synthesized in an anoxic chamber (glove box). Sulfate GR2, hereafter referred to as GR2, was prepared by coprecipitating a mixture of Fe(II), Ni(II) and Fe(III) sulfate salts with Na hydroxide, following the method described by Géhin et al. (2002).

Briefly, ferrous sulfate heptahydrate $FeSO_4.7H_2O$, Ni sulfate hexahydrate $NiSO_4.6H_2O$ and ferric sulfate pentahydrate $Fe_2(SO_4)_3.5H_2O$ were dissolved in 100 mL of N_2-purged deionized water. A [(Fe(II) + Ni(II))]/[Fe(III)] ratio of 3 was used with {[Fe(II)] + [Ni(II)] + [Fe(III)]} = 0.2 mol L^{-1}. The ratio P = [Fe(II)]/[Ni(II)] varied from 100 % Fe(II) to 100 % Ni(II).

Samples were prepared with P equal to 100/0, 90/10, 80/20, 70/30, 60/40, 30/70, 20/80, 10/90, and 0/100. The samples 50/50 and 40/60 were not prepared. The initial concentration of Fe(III) in all samples was 0.05 mol L^{-1}. Magnetic stirring ensured fast and complete dissolution. Then, 100 mL of 0.6 mol L^{-1} NaOH, corresponding to a final [OH$^-$]/{[Fe(II) + [Ni(II)] + [Fe(III)]} ratio of 3/2, was added to the solution under continuous stirring. After one hour, the pH was measured (6.36–6.85), stirring was stopped and the sample aged in the flask for 24 h. The sample was then centrifuged and the supernatant decanted and stored for further analysis. The precipitate was subsequently washed twice with N_2-purged deionized water. The decanted solutions from the washing process were also collected and stored for further analysis. A small amount of nitric acid was then added to the decanted supernatant solutions in order to avoid the precipitation of Fe(III) oxyhydroxides. The decanted supernatants were analyzed for Fe(II) after reaction with ferrozine according to Stookey (1970) using an UV-Vis recording spectrophotometer (Shimadzu UV 3101 PC).

Total Fe was determined by inductively coupled plasma mass spectrometry (ICP-MS) and Fe(III) was then calculated by difference. The Ni(II) concentration was determined using an atomic absorption spectrophotometer. The GR2 precipitate was dried and ground to powder in the glove box. X ray diffraction (XRD) was used to characterize the dried samples. XRD analysis was performed on a Philips X'Pert Pro MPD Instrument using CuKα (1.5418 Å) radiation and an X'Celerator RTMS array detector. The samples were placed in air-tight glass vials prior to removal from the glove box. For each sample, the air-tight vial was opened and approximately 0.5 g sample material was backloaded into a round 15 mm diameter sample holder (depth 5 mm), which was immediately placed on the XRD facility and scanned for 11 min. Air exposure during this transfer was less than 5 min.

Preliminary tests showed that GR2 samples had identical patterns when prepared as described and then dispersed in deoxygenated glycerin and smeared on glass plates. Only minor color changes, if any, were observed in both cases. The goniometer calibration was checked daily by comparison of a standard Si powder disk (mounted similarly) to known values. The scan performed covered 5 to 75° 2θ using unfiltered Cu radiation, with interpolated step sizes of 0.017°,

and 20 s/step counting time. The sample was spun at a rate of 1 revolution per 4 s. A fixed divergence slit of 1/4° was used.

After an initial XRD characterization the samples were stored in weigh boats, open to the atmosphere to observe the role of Ni in the transformation of the GR2 samples. The sample was repacked for further scans. XRD was then repeated several times over a period of 7 to 45 days.

RESULTS AND DISCUSSION

Nickel-substituted GR2 (Ni(II)-GR2) samples with varying Ni amounts were prepared and analyzed with XRD. In the studies of Refait & Génin (1993, 1997) and Refait et al. (1990, 1994, 1998, 2005) the green rust samples were prepared by partially oxidizing mixed Fe(II) and Ni(II) salt solutions. In this resdearch the samples were prepared without oxidation by directly mixing Fe(II), Fe(III) and Ni(II) salts in an anoxic environment. All fresh Ni(II)-GR2 samples appeared homogeneous and green in color, except for the sample containing Ni and Fe(III) only, which was yellow, the characteristic color of the Ni(II)-Fe(III) LDH, hydrohonessite (Nickel & Wildman, 1981). The cation composition of the samples was inferred indirectly from the difference between the cation concentrations in the initial solutions and the solution (including washing solutions) unvaried after precipitation of the solid material. The relative molar amounts of Fe(II), Ni(II) and Fe(III) in the samples normalized by Fe(III) are given in table 1.

Even though the divalent/trivalent cation ratio in the initial solution was fixed at 3, with the exception of sample P = 80/20, the ratio in the precipitated samples from P = 100/0 to 20/80 was closer to 2 which is the value for GR2. It is suspected that the anomalously high value for the P = 80/20 sample is due to an error in measuring the Fe(II) concentration in the supernatant. The ratio decreases at high Ni contents (P = 10/90 and 0/100) which could indicate the formation of a separate Fe(III) phase in addition to the LDH.

Figure 1 shows the XRD patterns for all fresh Ni(II)-GR2 samples as a function of the initial solution Fe(II)/Ni(II) ratio. The interplanar distances (c), the size of the unit cell along the a-axis (a), the volume of the unit cell (V) and the size of the particles along the c axis, D_c, for each sample are listed in table 2. The errors noted in table 2 are due to least squares refinement of observed peak positions to the cell given for the GR2 structure.

The XRD plot for GR2 with no Ni (P = 100/0) is shown at the bottom of figure 1 as reference. Six peaks were observed that matched those reported for GR2. These are 2θ = 8.05°, 16.21°, 24.35°, 32.55°, 33.57° and 36.54°. One peak for magnetite was also identified at 2θ = 35.4°. The GR2 c-value was 1.0974 ± 0.0007 nm and the a-value 0.3173 ± 0.0001 nm in excellent agreement with the values reported by Bernal et al. (1959) for GR2. Even as Ni was added in increasing amounts, the characteristic green rust peaks persisted suggesting that Ni is incorporated into the brucite layer structure. Most likely Fe(II) was replaced by Ni(II) resulting in Ni(II)-GR2, which is isomorphous to GR2 (Refait et al., 1994). The divalent

Table 1. Relative molar amounts of Fe(II), Ni(II) and Fe(III) and the divalent/trivalent ratio in the Ni(II)-GR2 samples as a function of the divalent ion ratio Fe(II)/Ni(II) in the starting solution

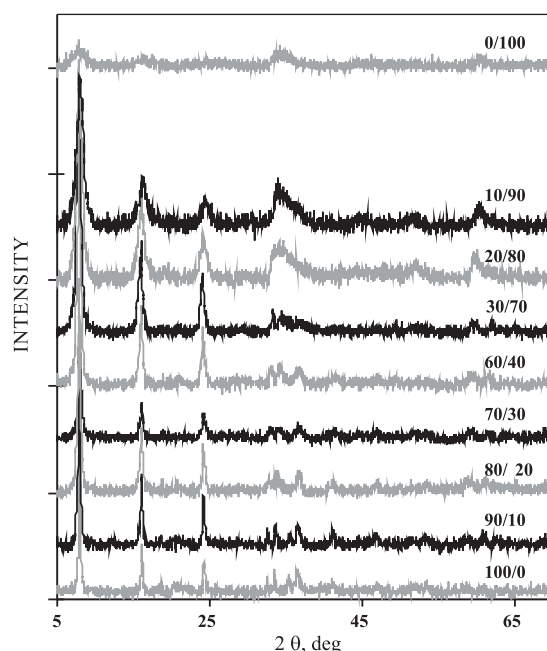| Fe(II)/Ni(II)	Fe(II)	Ni(II)	Fe(III)	(Fe(II) + Ni(II))/Fe(III)
100/0	1.95	0	1.00	1.95
90/10	1.70	0.249	1.00	1.95
80/20	1.88	0.570	1.00	2.45
70/30	1.27	0.720	1.00	1.99
60/40	1.01	0.867	1.00	1.88
30/70	0.727	1.17	1.00	1.90
20/80	0.530	1.32	1.00	1.85
10/90	0.280	1.39	1.00	1.67
0/100	0	1.45	1.00	1.45

Figure 1. X ray diffraction patterns of the initial Ni(II)-GR2 products obtained in anoxic conditions as a function of the Fe(II)/Ni(II) ratio of the starting solution.

mole fraction in the solid as a function of the divalent mole fraction or divalent fraction in solution is plotted in figure 2.

The 001, 002 and 003 peaks at 8°, 16° and 24° 2θ are easily identified for all samples that contain Fe(II). Peak broadening indicates a decrease in crystallinity with increasing incorporation of Ni. In the sample containing only Ni and Fe(III) the three characteristic peaks nearly disappear suggesting a role for Fe(II) in promoting the crystallinity of the brucite-layer structure under these conditions.

Table 2 shows the lattice values of all samples in this study as calculated from the XRD patterns with the exception of the sample containing only Ni and Fe(III), which was poorly crystalline.

In all cases the c-value was near the value of 1.097 nm, for pure GR2. While there is some variation there is no apparent correlation with the Fe(II)/Ni(II) initial ratio, indicating that in this case either the

accuracy was insufficient to distinguish a trend or the c-value was not sensitive to substitution of Fe(II) by Ni(II). In contrast, the variation in the lateral dimension of the brucite-like sheet, given by the a-value, decreased systematically with increasing Ni content. This is consistent with the fact that Fe(II) is larger than Ni(II). More quantitatively, the a-value for $Ni(OH)_2$, which is the pure Ni brucite sheet, was 0.3126 nm (Greaves & Thomas, 1986) whereas the a-value for the pure ferrous brucite sheet, $Fe(OH)_2$, was larger at 0.3262 nm (Bernal et al., 1959). The substitution of Fe(II) by Ni(II) in any brucite-like compound should therefore result in a decrease in the lateral dimension of the unit cell.

It appears that these samples represent a solid solution with the end members GR2 and a Ni(II)-Fe(III) LDH with formula $Ni_4Fe_2(OH)_{12} SO_4 nH_2O$. With the exception of the P = 80/20 sample, the calculated divalent/trivalent ratios for samples P = 100/0 through P = 20/80 were near 2, which is the value for GR2. However, the divalent/trivalent cation ratio decreased for samples containing higher Ni amounts. One possibility is that the divalent/trivalent cation ratio is 2 for the LDH and another Fe oxide phase forms. However, no discrete Fe oxide phase is detectable by XRD. Another possibility is that the ratio decreased to ~ 1.5 for the poorly crystalline Ni(II)-Fe(III) LDH. It is known that the divalent/trivalent cation ratio in LDHs can vary widely with values typically being between 2 and 3 (Drits & Bookin, 2001). Since XRD was not sufficient to eliminate the possibility that another mineral, e.g., a poorly crystalline Fe oxide is present (Refait et al., 2005) it was not possible to confirm either of these possibilities. However, the trend in the lattice values with increasing Ni content suggested that the lattice parameters for the poorly crystalline Ni(II)-Fe(III) mineral should be c ~ 1.09 nm and a ~ 0.309 nm. This correlates well with the lattice values for hydrohonessite (c = 1.08 nm and a = 0.309 nm), a naturally occurring Ni(II)-Fe(III) LDH
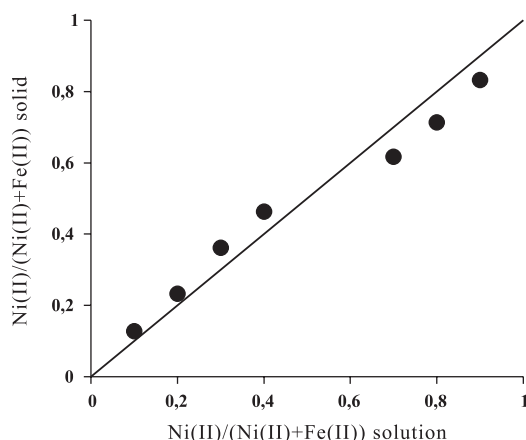

Figure 2. Divalent mole fraction of Ni(II), Ni(II)/(Ni(II)+Fe(II)), in solid vs initial solution phase.

Table 2. Interplanar distances d_{001} (c), size of the unit cell along the a axis (a), volume of the unit cell (V) and thickness (D_c) of crystallites along the c hexagonal axis as determined by the Scherrer formula in the Ni(II)-GR2 samples, as a function of the divalent ion ratio in the starting solution, Fe(II)/Ni(II)

Fe(II)/Ni(II)	c	a	$V/10^6$ pm³	D_c
	nm			nm
100/0	1.0974 (±0.0007)	0.3173 (±0.0001)	95.676	41.96
90/10	1.1003 (±0.0006)	0.3165(±0.0007)	95.470	31.89
80/20	1.1046 (±0.0001)	0.3151(±0.0001)	94.988	26.57
70/30	1.0991(±0.0008)	0.3133(±0.0001)	93.452	20.98
60/40	1.0963 (±0.0002)	0.3134 (±0.0004)	93.243	20.44
30/70	1.1097 (±0.0003)	0.3115 (±0.0001)	93.276	15.94
20/80	1.10 (±0.01)	0.3105 (±0.0005)	92.093	11.07
10/90	1.09 (±0.01)	0.3094 (±0.0007)	90.679	9.60

containing sulfate as the interlayer anion (Nickel & Wildman, 1981). The formula for hydrohonessite is $Ni_6Fe_2(OH)_{16}$ SO_4 nH_2O (Frost et al., 2003) with a divalent/trivalent cation ratio of 3, in contrast to the ratio of 2, which is more consistent with our data for Ni(II)-GR2 up to P = 30/70.

In foundation work used to derive the ideal hydrohonessite formula, Bish & Livingstone (1981) analyzed naturally occurring hydrohonessite samples and found the divalent/trivalent cation ratio to be ~ 2.5. The authors concluded that, analogously to reevesite $(Ni_6Fe_2(OH)_{16}$ CO_3 $4H_2O)$, the Ni(II)/Fe(III) LDH containing carbonate as the interlayer anion, the ideal divalent/trivalent cation ratio for hydrohonessite is most likely also 3, resulting in a formula of $Ni_6Fe_2(OH)_{16}$ SO_4 nH_2O. In contrast, Refait et al. (2005) recently synthesized a Ni(II)-Fe(III) LDH with a Ni(II)/Fe(III) ratio equal to 2 which is isomorphous with GR2, $Ni_4Fe_2(OH)_{12}$ SO_4 nH_2O. The reported lattice values were a = 0.320 ± 0.003 nm and c = 1.094 ± 0.004 nm, which are the same as GR2, indicating that the effect of the substitution of Ni(II) for Fe(II) on the a-value was not detectable in this study. Given that our synthesis method is very similar to that used by Refait et al. (2005) it is likely that the samples synthesized here have a Ni(II)/Fe(III) ratio closer to 2 than to 3 but the a-values are consistent with the end member of the solid solution, being hydrohonessite. Further work is needed to clarify the variation of the Ni(II)/Fe(III) ratio for Ni(II)-Fe(III) LDHs.

The systematic decrease in the lateral unit cell size with increasing Ni content also suggests a quantitative correlation between this parameter and the degree of Ni substitution. Figure 3 shows the a-value determined from the XRD patterns as a function of the Ni fraction in the solid samples calculated based on the molar ratios given in table 1.

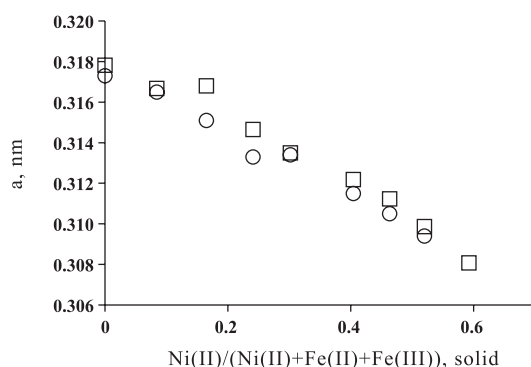There is a linear relationship between the a-value and the Ni fraction in the samples suggesting that

Figure 3. Reduction of the unit cell edge length *a* of the Ni(II)-GR2 samples as a function of Ni(II) content. Circles denote *a*-values determined by XRD measurements. Squares denote *a*-values determined by equation (1).

Vegard's rule (Vegard, 1921) holds for Ni substitution in GR2. Vegard's rule is a long-standing empirical principle in chemical crystallography that has guided structural studies of solid solutions of isomorphous salts. It presumes that the lattice constant varies linearly with the composition of mixed crystals and implies a similarity of structure and symmetry of the mixed crystals and the end members (Gopalan & Kahr, 1993). Vegard's rule has been shown to apply quite generally to substitution in a number of LDHs (Drits & Bookin, 2001; Tichit et al., 2002). Most commonly, allowing the divalent/trivalent cation ratio to vary, the Ni(II)-GR2 can be considered a mixture of three pure end-member brucite-like species, namely $Ni(OH)_2$, $Fe(OH)_2$ and $Fe(OH)_3$ (Bourrié et al., 2004). In this case the Vegard correlation for the ternary mixture can be written as:

$$a_{Ni-GR2} = f_{Fe(II)}\, a_{Fe(OH)_2} + f_{Fe(III)}\, a_{Fe(OH)_3} + f_{Ni}\, a_{Ni(OH)_2} \qquad (1)$$

where $f_{Me} = [Me]/([Fe(II)] + [Fe(III)] + [Ni])$, $f_{Fe(II)} + f_{Fe(III)} + f_{NI} = 1$ and $a_{Me^{+x}\,(OH)_x}$ is the a-value for the pure Me-brucite species. In order to determine the extent of cation substitution in green rust and LDHs in general it is of interest to quantitatively relate lattice values and composition. Using equation (1), the a-value for each sample was calculated using the molar ratios given in table 1 and was plotted as a function of the Ni fraction in the sample in figure 2 (squares) along with the measured XRD values. The a-values for $Ni(OH)_2$ and $Fe(OH)_2$ are assumed to be 0.3126 nm and 0.3262 nm, respectively. The "a-value" for $Fe(OH)_3$ is assumed to be 0.3015 nm which is the Fe(III)-Fe(III) distance in edge-sharing Fe(III) octahedra in α-FeOOH (Bernal et al., 1959). This is very close to the *a*-value (0.3025 nm) for the high-energy ferric green rust prepared by fast oxidation of hydroxychloride green rust (Refait et al., 2003b).

There is good agreement between the calculated and XRD *a*-value suggesting a quantitative relationship between composition and the *a*-value. Note that equation (1) predicts the *a*-value for GR2 at 0.3178 nm, which is very close to the measured value of 0.3174 nm. While it would be desirable to predict composition using only information of the cations present and the a-value, this is only possible in principle for a system consisting of two different cations. For a ternary system such as nickelous green rust, an additional relationship between the molar quantities of the constituents is required. However, in the case of GR2, where the divalent/trivalent cation ratio is generally accepted to be 2:1 (Hansen et al., 1994; Refait et al., 1999, 2005) ($f_{Fe(OH)_2} = 1/3$), the a-value can be used in principle to quantitatively predict the extent of divalent cation substitutions for Fe(II). In the present case this leads to the following relationship between the measured a-value (a_{Ni-GR2}) and the Ni fraction in the GR2 structure.

$$f_{Ni} = \frac{a_{Ni-GR2} - \frac{1}{3} a_{Fe(OH)_3} - \frac{2}{3} a_{Fe(OH)_2}}{a_{Ni(OH)_2} - a_{Fe(OH)_2}} \qquad (2)$$

In principle this relationship could be used to predict the extent of substitution of any divalent cation in the GR2 structure, provided the appropriate a-values are known.

Effect of oxidation

In order to determine the extent to which the LDH structure is retained on oxidation of the structural Fe(II) the samples were exposed to ambient air and then each sample was examined by XRD several times over a period of 7 to 45 days from the time of initial exposure. There was no significant change in the XRD patterns of the oxidized samples in this time interval. Figure 4 shows the XRD results for all samples after one month of exposure to oxidizing conditions; pure GR2 was included at the bottom of the figure as reference.

Samples prepared without Ni (P = 100/0) and the lowest Ni concentration (P = 90/10) oxidized quickly and turned from the initial green color to yellow brown. The LDH structure was lost and goethite and

magnetite were identified based on the XRD pattern. The presence of goethite agrees with Olowe & Genin (1991) who showed that goethite and lepidocrocite are expected GR2 oxidation products, depending on initial conditions. Magnetite was identified in the precipitation of the fresh GR2 sample prior to oxidation. On the contrary, samples with higher Ni content, P = 80/20, 70/30, 60/40 and 30/70, remained greenish. For these samples the three most intense peaks typifying green rust can be easily seen. As was shown for Ni(II)-GR2 (Refait et al., 1990) all Fe(II) is transformed to Fe(III) and the oxidized LDHs contain only Ni(II) and Fe(III). In addition to the reference Ni(II)-Fe(III) LDH isomorphous with green rust (c-value ~ 1.09 nm) additional peaks are seen indicating the presence of other minerals. For P = 80/20 a peak appears at 2θ = 9.85 corresponding to a d-value of 0.926 nm. This peak is still present for P = 70/30 but appears as a shoulder. It was not possible to detect the mineral inducing this peak. For samples P = 60/40 and 30/70 the peak at 2θ = 9.85° was no longer present and three peaks appeared, each of which had shifted to the right of one of the main peaks associated with the reference Ni(II)-Fe(III) LDH with c-value of 1.09 nm. These peaks are marked with asterisks and correspond to an additional LDH with c-value 1.013 nm and a-value 0.3094 nm. The reduction in c-value on exposure to air is probably due to dehydration. This is consistent with the fact that the LDHs honessite (c-value 0.89 nm) and hydrohonessite (c-value 1.09 nm) only differ in the amount of water in the interlayer (Nickel & Wildman, 1981). This suggests the sample is a mixture of two Ni-Fe(III) LDHs which differ in the extent of dehydration. With further increase in Ni content (P = 20/80, 10/90 and 0/100) the oxidized samples become poorly crystalline LDH phases.
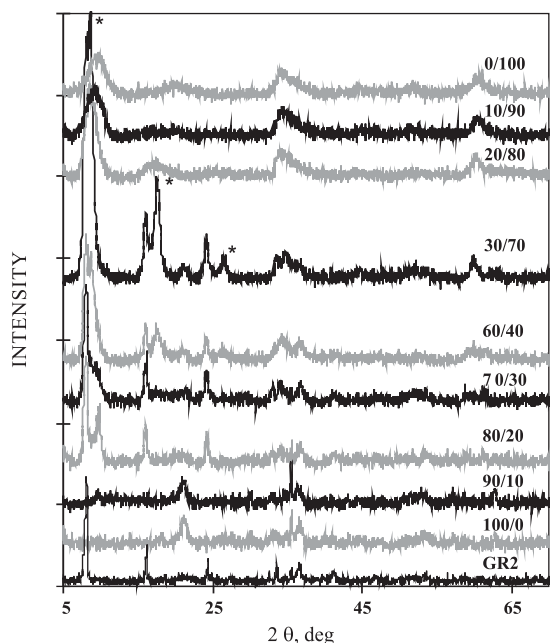

Figure 4. X ray diffraction patterns of the final products from the aerial oxidation of the dry Ni(II)-GR2 samples as a function of the Fe(II)/Ni(II) ratio of the starting solution. Asterisks denote the peak positions for a second LDH with c-value 1.013 nm. Peaks for goethite (2θ = 21°, 33°, 36.6°, 53.2°, 57.0°) and magnetite (2θ = 30.1°, 35.5°, 36.6°, 53.2°, 57.0°, 62.7°) were identified for samples 100/0 and 90/10.

CONCLUSION

Nickel is readily incorporated in the GR2 structure and forms a solid solution between GR2 and a Ni(II)-Fe(III) LDH. There is a correlation between the unit cell a-value and the fraction of Ni(II) incorporated into the Ni(II)-GR2 structure. Since there is strong evidence that the divalent/trivalent cation ratio in GR2 is fixed at 2, it is possible in principle to determine the extent of divalent cation substitution for Fe(II) in GR2 from the unit cell a-value. On oxidation a mixture of minerals are formed but the LDH structure is retained if at least 20 % of the divalent cations in the initial solution are Ni(II). It appears Ni(II) is incorporated in a stable LDH structure. This is important for two reasons, first for understanding the formation of LDHs, which are anion exchangers, in the natural environment. Secondly, this may be important for understanding the fate of transition metals in the environment, particularly in the presence of reduced Fe compounds.

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