Supporting information

Aqueous nickel sequestration and release during structural Fe(II) hydroxides remediation:

the roles of coprecipitation, reduction and substitution

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Table S1: pH variations of SFH-Ni^{2+} mixture in the presence and absence of anions

Text S1: Comparison of the K_{sp} of $Ni_xFe_{(1-x)}(OH)_2$ and $Fe^{III}_{(1+2x/3)}Fe^{II}_{(1-x)}(OH)_5$ precipitations

Text S2: Determination of $E(Ni^{2+}/Ni)$ and $E(NO_3^-/NO)$ based on the conditions of the corresponding system

Fig. S1: SEM images of solid phases of (a) SFH(1:1) (b) SFH(1:2) (c) SFH(1:3)

Fig. S2: Adsorption of Ni(II) on SFH under anoxic conditions (SFH = 0.1 g/L; initial Ni^{2+} concentration = 2.0−250 mg/L; contact time = 20 min; at 25 °C)

Fig. S3: Effect of (dissolved oxygen) DO on Ni(II) removal by SFH(1:2)

(Initial Ni^{2+}=100 mg/L, SFH = 2 mM)

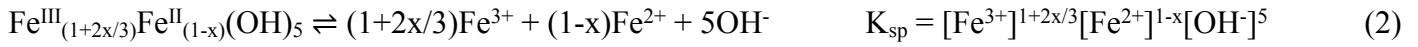**Fig. S4**: XRD pattern of oxidized solid product of SFH(1:2) with NO_3^-(SFH= 2 mM, NO_3^-/Fe^{2+}=10:1)

Fig. S5: FT-IR spectra of SFH(1:2) and PO_4^{3-} or CO_3^{2-} loaded SFH(1:2)

Table S1 pH variations of SFH-Ni^{2+} mixture in the presence and absence of anions

Conditions		Initial pH	End pH (60 min)
SFH(2:1)-Ni^{2+}		6.6	5.8
SFH(1:1)-Ni^{2+}		7.9	6.2
SFH(1:2)-Ni^{2+}		9.1	6.7
SFH(1:3)-Ni^{2+}		11.2	10.2
SFH(1:4)-Ni^{2+}		11.6	10.8
Ni(OH)$_2$-Fe^{2+}		10.5	10.2
Ni(OH)$_2$-Fe^{3+}		10.5	9.3
CO$_3^{2-}$/ SFH(1:2)	1:10	9.2	8.1
	1:1	9.9	8.6
	10:1	10.5	9.1
PO$_4^{3-}$/ SFH(1:2)	1:10	9.1	8.0
	1:1	9.6	8.4
	10:1	10.9	9.6
NO$_3^-$/ SFH(1:2)	1:10	9.0	6.5
	1:1	8.9	5.8
	10:1	8.7	5.1

Text S1. Comparison of the K_{sp} of $Ni_xFe_{(1-x)}(OH)_2$ and $Fe^{III}_{(1+2x/3)}Fe^{II}_{(1-x)}(OH)_5$ precipitations

For the two precipitates, the precipitation-dissolution equilibrium could be described as:

$$Ni_xFe_{(1-x)}(OH)_2 \rightleftharpoons xNi^{2+} + (1-x)Fe^{2+} + 2OH^- \qquad K_{sp} = [Ni^{2+}]^x[Fe^{2+}]^{1-x}[OH^-]^2 \qquad (1)$$

$$Fe^{III}_{(1+2x/3)}Fe^{II}_{(1-x)}(OH)_5 \rightleftharpoons (1+2x/3)Fe^{3+} + (1-x)Fe^{2+} + 5OH^- \qquad K_{sp} = [Fe^{3+}]^{1+2x/3}[Fe^{2+}]^{1-x}[OH^-]^5 \qquad (2)$$

where $[Ni^{2+}]$, $[Fe^{2+}]$, $[Fe^{3+}]$ and $[OH^-]$ are the concentrations of dissolved Ni^{2+}, Fe^{2+}, Fe^{3+} and OH^-, respectively, and K_{sp} is the solubility product. Based on the K_{sp} of $Fe(OH)_2$, $Ni(OH)_2$ and $Fe(OH)_3$,

$$K_{sp}[Fe(OH)_2] = [Fe^{2+}][OH^-]^2 = 8.0\times10^{-16} \qquad (3)$$

$$K_{sp}[Ni(OH)_2] = [Ni^{2+}][OH^-]^2 = 2.0\times10^{-15} \qquad (4)$$

$$K_{sp}[Fe(OH)_3] = [Fe^{3+}][OH^-]^3 = 4.0\times10^{-38} \qquad (5)$$

eq 1 could be rewritten as eq 6.

$$K_{sp}[Ni_xFe_{(1-x)}(OH)_2] = [Ni^{2+}]^x[Fe^{2+}]^{1-x}[OH^-]^2$$

$$= \textbf{Error!} = (K_{sp}[Fe(OH)_2])\cdot \textbf{Error!} \qquad \left(\quad (6) \qquad \right)^X$$

Note that $0<x<1$ and **Error!**$= 2.5>1$, thus

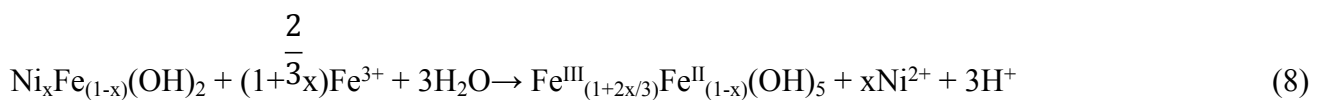$$\mathbf{8.0\times10^{-16} < K_{sp}[Ni_xFe_{(1-x)}(OH)_2] < 2.0\times10^{-15}.}$$

Similarly, eq 2 could be rewritten as eq 7.

$$K_{sp}[Fe^{III}_{(1+2x/3)}Fe^{II}_{(1-x)}(OH)_5] = [Fe^{3+}]^{1+2x/3}[Fe^{2+}]^{1-x}[OH^-]^5$$

$$= \textbf{Error!}$$

$$= (K_{sp}[Fe(OH)_3])\cdot(K_{sp}[Fe(OH)_2])\cdot \left[\textbf{Error!} \quad \right]^X \qquad (7)$$

Note that $-1.5<x<1$ and **Error!**$= 1.5\times10^{-10}<1$, thus

$$\mathbf{4.7\times10^{-63} < K_{sp}[Fe^{III}_{(1+2x/3)}Fe^{II}_{(1-x)}(OH)_5] < 1.7\times10^{-38}.}$$

Based on the calculations: $\mathbf{K_{sp}[Fe^{III}_{(1+2x/3)}Fe^{II}_{(1-x)}(OH)_5] << K_{sp}[Ni_xFe_{(1-x)}(OH)_2]}$, thus the substitution of Ni^{2+} in $\mathbf{Ni_xFe_{(1-x)}(OH)_2}$ by Fe^{3+} is favorable:

$$Ni_xFe_{(1-x)}(OH)_2 + (1+\tfrac{2}{3}x)Fe^{3+} + 3H_2O \rightarrow Fe^{III}_{(1+2x/3)}Fe^{II}_{(1-x)}(OH)_5 + xNi^{2+} + 3H^+ \qquad (8)$$

Text S2. Determination of E(Ni²⁺/Ni) and E(NO₃⁻/NO) based on the conditions of the corresponding system

The electrode reaction for Ni^{2+} reduction could be described as:

$$Ni^{2+} + 2e^- \leftrightarrows Ni, \qquad E^\theta(Ni^{2+}/Ni) = -0.257 \text{ V}.$$

Under alkaline circumstance, E(Ni²⁺/Ni) could be expressed as follows using Nernst equation,

$$E(Ni^{2+}/Ni) = E^\theta(Ni^{2+}/Ni) + \frac{0.059 \text{ V}}{2} \lg[Ni^{2+}]$$

$$= E^\theta(Ni^{2+}/Ni) + \frac{0.059 \text{ V}}{2} \lg\textbf{Error!}.$$

Note that the initial solution pH of Ni^{2+} with SFH(1:2) is 9.05, thus the concentration of OH^- is $10^{-4.95}$ M.

Therefore,

$$E(Ni^{2+}/Ni) = -0.257 \text{ V} + \frac{0.059 \text{ V}}{2} \lg \frac{2.0 \times 10^{-15}}{10^{-9.9}} = -0.398 \text{ V}.$$

The reduction of NO_3^- by structural Fe(II) could generate NO_2^- and subsequent various products, including NO_2^-, NO, NO_2 and NH_4^+. Our previous study showed that NO_x were the predominant products at initial pH ~8 and Fe/N of 10:1. The conditions are similar to that in present study. Here, we take NO as a product of NO_3^- reduction. Under alkaline circumstance, The electrode reaction for NO_3^- reduction could be described as:

$$NO_3^- + 2H_2O + 3e^- \leftrightarrows NO + 4OH^-, \qquad E^\theta(NO_3^-/NO) = -0.14 \text{ V}$$
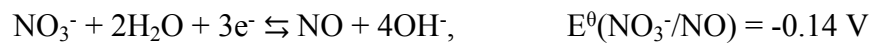
E(NO₃⁻/NO) could be expressed as follows using Nernst equation,

$$E(NO_3^-/NO) = E^\theta(NO_3^-/NO) + \frac{0.059 \text{ V}}{3} \lg\textbf{Error!}$$

$$= E^\theta(NO_3^-/NO) + \frac{0.059 \text{ V}}{3} \lg\frac{[NO3^-]}{[OH^-]4} - \frac{0.059 \text{ V}}{3} \lg(p(NO)/p^\theta).$$

Note that the concentration of NO_3^- and OH^- are 0.02 M and $10^{-4.95}$ M, respectively. Thereby,

$$E(NO_3^-/NO) = 0.216 \text{ V} - \frac{0.059 \text{ V}}{3} \lg(p(NO)/p^\theta).$$

Assuming that the concentration of NO is equal to that of initial NO_3^- (0.02 M), then $p(NO) = nRT/V = 0.02 \times 8.3145 \times 273 / (0.1 \times 10^{-4}) = 4540$ kpa. (The parameters of T and V could be seen in *section 2.2*, and $p^\theta = 100$ kpa). Thus,

$$\frac{0.059 \text{ V}}{3} \lg(p(NO)/p^\theta) = 0.032 \text{ V},$$

which is much less than 0.216 V. So it is determined that

$$E(NO_3^-/NO) \approx 0.216 \text{ V}.$$

By correcting $E(Ni^{2+}/Ni)$ and $E(NO_3^-/NO)$ to the corresponding system, we find that $E(NO_3^-/NO)$ is higher than $E(Ni^{2+}/Ni)$. It indicates that NO_3^- would be easier than Ni^{2+} to be reduced by SFH.
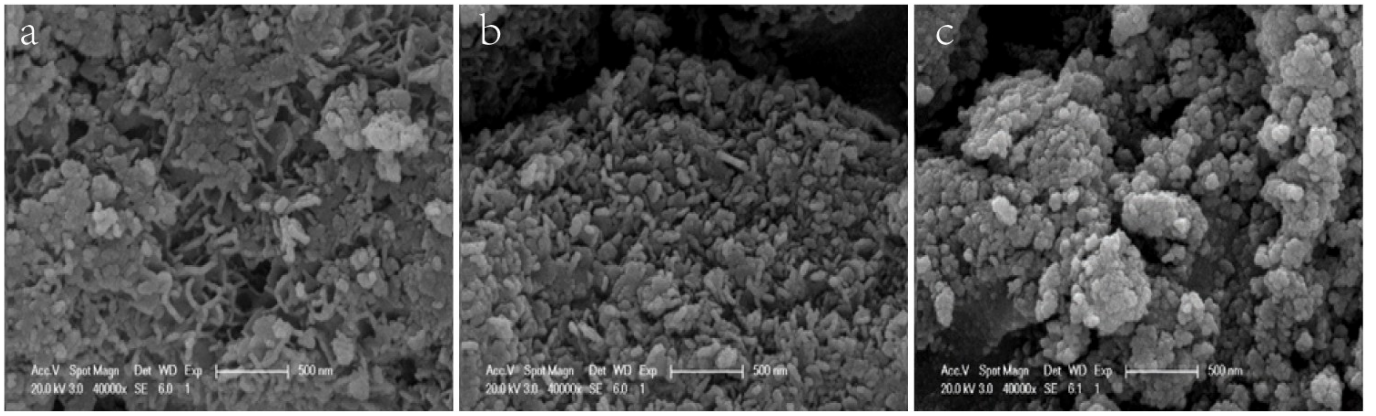
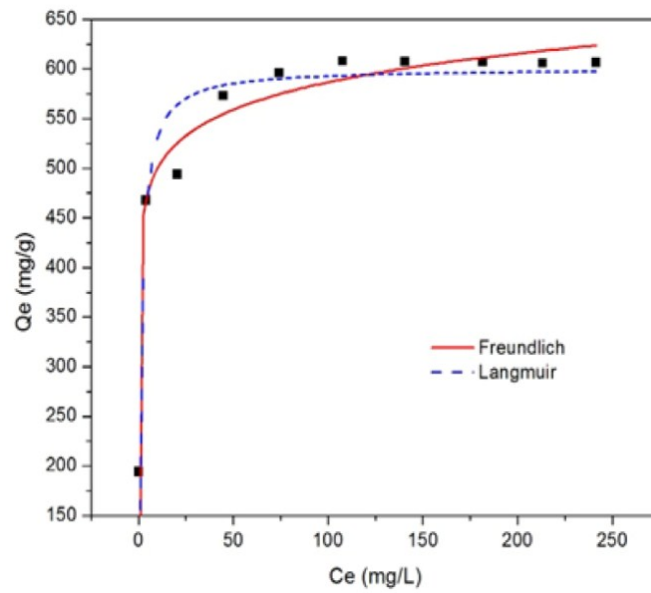**Fig. S1** SEM images of solid phases of (a) SFH(1:1) (b) SFH(1:2) (c) SFH(1:3)

Fig. S2 Adsorption of Ni(II) on SFH under anoxic conditions (SFH = 0.1 g/L; initial Ni^{2+} concentration = 2.0−250 mg/L;
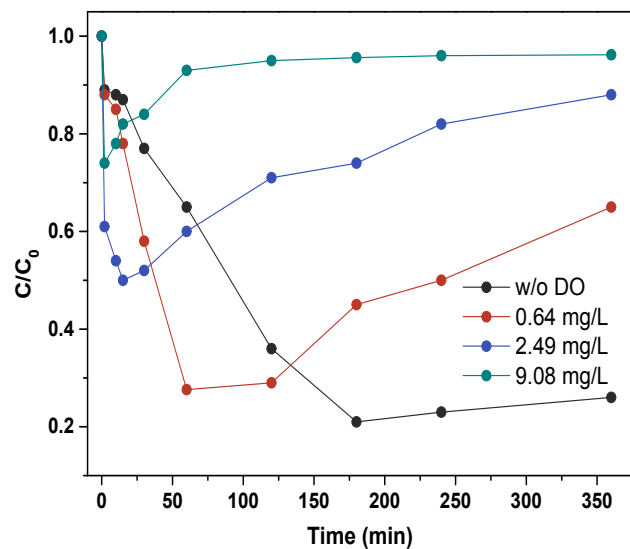
contact time = 20 min; at 25 °C).

Fig. S3 Effect of dissolved oxygen (DO) on Ni(II) removal by SFH(1:2) ((Initial Ni^{2+}=100 mg/L, SFH = 2.0 mM)
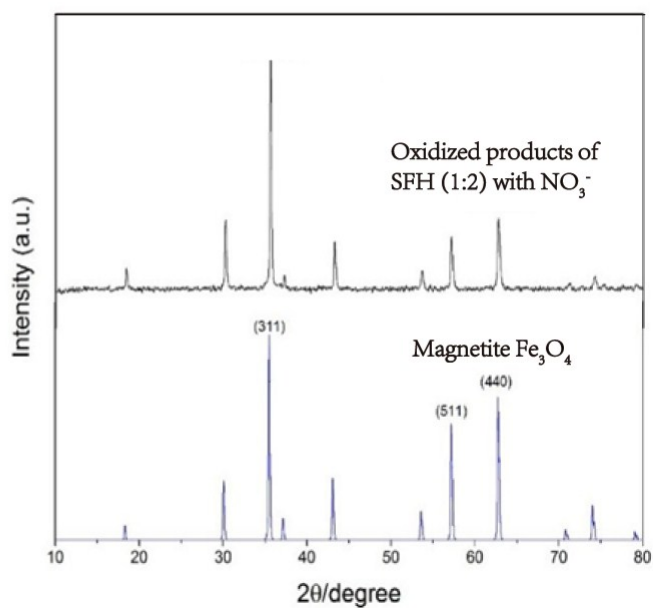

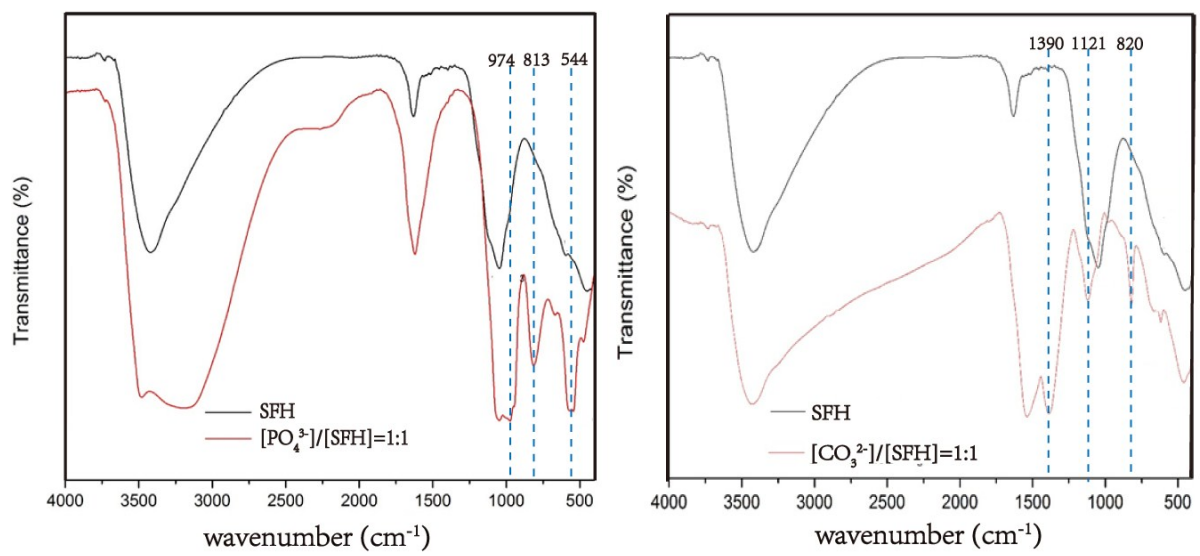**Fig. S4** XRD pattern of oxidized solid product of SFH(1:2) with NO_3^-(SFH=0.11 g/L, NO_3^-/Fe^{2+}=10:1)

Fig. S5 FT-IR spectra of SFH(1:2) and PO_4^{3-} or CO_3^{2-} loaded SFH(1:2)