Redefining Role of Fluoride ions (F^-) in Metal Recovery: Mechanistic Insights into Electrodeposition Kinetics and Crystallographic Evolution

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Summary

Supporting Information: Additional experimental and analytical details, including reactor and chemicals information, modelling equations and parameters, and calculations were listed. Additional tables and figures, such as COMSOL Multiphysics simulations, CV plots information, *in situ* Raman spectra, EIS fitting values, EDS data, and the current efficiency for Ni electrodeposition under different conditions, are also included.

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Text S1. Reactor information

A 200 mL single-chamber reactor equipped with a conventional three-electrode system was used for electrochemical testing, which consisted of a saturated calomel electrode (SCE) (0.245 V vs. standard hydrogen electrode) as the reference electrode, a 2 × 2 cm piece of DSA (Ti/IrO_2-Ta_2O_5) as the counter electrode, and a 2 × 2 cm piece of 304 stainless steel as the working electrode. Before every experiment, the 304 stainless steel electrode was mechanically polished with sandpaper of decreasing grit size (500, 1000, 1200, and 1500 mesh) and then with alumina power of decreasing particle size (1.5, 0.5, and 0.3 μm), followed by ultrasonic cleaning in deionized water and ethanol three times, and finally dried.

Text S2. Simulations

Finite element modeling:

The nickel (Ni) electrodeposition process was simulated using COMSOL Multiphysic 6.1. A secondary current distribution module was employed to study the distribution of electrode current density and the concentration of Ni(II) species near the electrode.

In the electrolyte, the transport of Ni(II) species, driven by both concentration gradient and electromigration, is described by the following equation:

$$J_i = -D_i \nabla C_i - z_i u_{m,i} F D_i C_i \nabla \varphi \qquad (2)$$

where J_i (mol/(m^2·s)) is Ni^{2+} flux, D_i (m^2/s) is the diffusion coefficient of Ni(II), ∇C_i (mol/m^3) is the concentration gradient of Ni(II), z_i is the charge number of Ni(II), F (96485 C/mol) is Faraday's constant, $u_{m,i}$ (s·mol/kg) is migration rate, ∇φ (V) is the electrolyte potential gradient.

The Ni(II) species in the electrolytes obey the mass conservation and charge conservation equations:

$$\frac{\partial Ci}{\partial t} + \nabla \times J_i = 0 \quad (3)$$

$$\sum_i Z_i C_i = 0 \quad (4)$$

At the interface between the electrolyte and the electrode, the electrodeposition reaction of Ni(II) can be described by:

$$Ni^{2+} + 2e^- \rightleftharpoons Ni \quad (5)$$

The electrochemical kinetics of Ni(II) reduction at the cathode is described by the local current density, which follows the Butler-Volmer equation:

$$J_i = -\frac{i_0}{2F}\left[\exp\left(\frac{\alpha_a F\eta}{RT}\right) - \frac{C}{C_0} exp(\frac{\alpha_c F\eta}{RT})\right] \quad (6)$$

where J_i (A/m^2) is local current density, i_0 (A/m^2) is the exchange current density, η (V) is overpotential, α_a and α_c are the anodic and cathodic charge transfer coefficients, respectively, and C (mol/m^3) is the local Ni(II) concentration in the interface, and C_0 (mol/m^3) is the bulk Ni(II) concentration.

During the simulation, the anodic and cathodic charge transfer coefficients were set to 0.23 and 0.77, respectively. The temperature was fixed at 303 K, and the applied cathodic voltage was set to –1.2 V (vs. SCE).

Text S3. Calculations for current efficiency (CE)

The CE is calculated using the following expression:

$$CE=[(m_e-m_0)nF]/(ItM) \times 100\% \quad (1)$$

Where CE (%) is the current efficiency, m_e (g) is the final mass of the electrode , m_0 (g) is the initial mass of the electrode, n is the number of electrons transferred, F (96485 C/mol) is the Faraday's constant, I (A) is the applied current, t (s) is the electrolysis time, and M (g/mol) is the molar mass of the deposited metal.

Table S1

The information of chemicals employed in this work.

Chemicals	Formula	CAS number	Mass fraction	Sources
Nickel sulfate hexahydrate	$NiSO_4 \cdot 6H_2O$	10101-97-0	⩾98.5%	Chengdu Kelong Chemical Co., Ltd.
Sodium fluoride	NaF	7681-49-4	⩾98.0%	Chengdu Kelong Chemical Co., Ltd.
Sodium hydroxide	NaOH	1310-73-2	⩾98.0%	Chengdu Kelong Chemical Co., Ltd.
Sulfuric acid	H_2SO_4	7664-93-9	95.0%–98.0%	Chengdu Kelong Chemical Co., Ltd.

Table S2

Overpotential and nucleation potentials for Ni electrodeposition in electrolytes with varying F^- concentrations.

F^- concentration (mg/L)	Overpotential (V)	Nucleation potential (V)
0	0.16	–0.81
100	0.26	–0.88
500	0.29	–0.93
1000	0.31	–0.96
1500	0.33	–0.98
2000	0.38	–1.00

Table S3

Electrochemical impedance spectroscopy fitting values of Ni electrodeposition in the electrolytes with different concentrations of F^-.

F^- concentration (mg/L)	R_s/Ω	R_{ct}/Ω
0	24.47	7.34
100	21.46	6.27
500	15.31	3.13
1000	11.23	2.30
1500	8.91	1.88
2000	4.24	1.69

R_s represents the resistance of the solution;

R_{ct} represents the resistance of electron transfer.

Table S4

EDS data of Ni deposits obtained from different concentrations of F^-.

Samples	F^- concentration (mg/L)	Ni	O	F
1	0	99.46	0.54	/
2	100	98.58	0.89	0.53
3	500	99.34	0.28	0.38
4	1000	99.53	0.27	0.21
5	1500	99.43	0.27	0.3
6	2000	99.33	0.23	0.44

Table S5

The composition and properties of actual steel pickling wastewater from a steel processing plant.

Ion species	Concentrations (g/L)
Ni	16.0
TFe	50.0
TCr	28.3
Zn	1.9
Co	0.4
Mn	0.9
F^-	56.0
SO_4^{2-}	43.6

Other parameters: pH 1.89, conductivity 16.25 mS/cm, temperature 25°C.

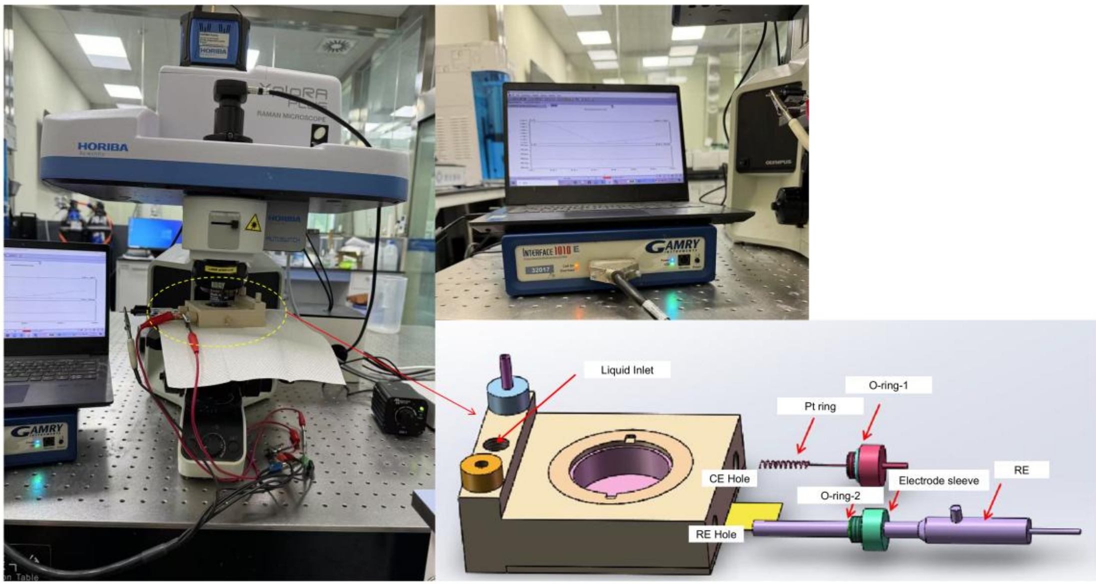

Fig. S1. Schematic of the *in situ* Raman setup: Raman microscope, electrochemical workstation, and Teflon cell.

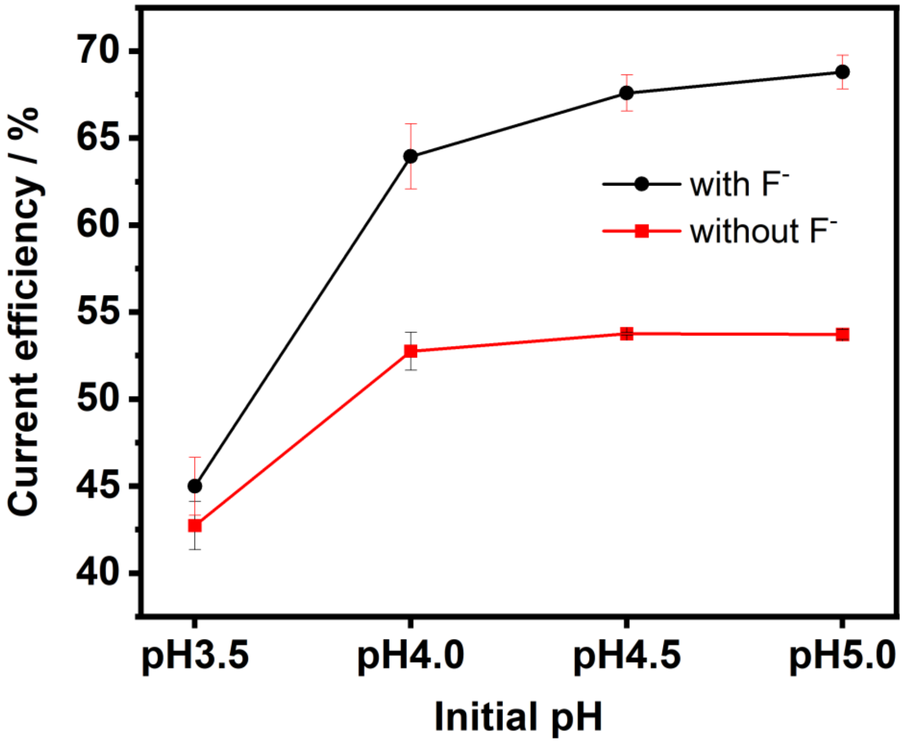

Fig. S2. Current efficiency (CE) of Ni electrodeposition in F^--containing and F^--free electrolytes under varied pH conditions. Conditions: 2000 mg/L Ni^{2+} and 1000 mg/L F^-.

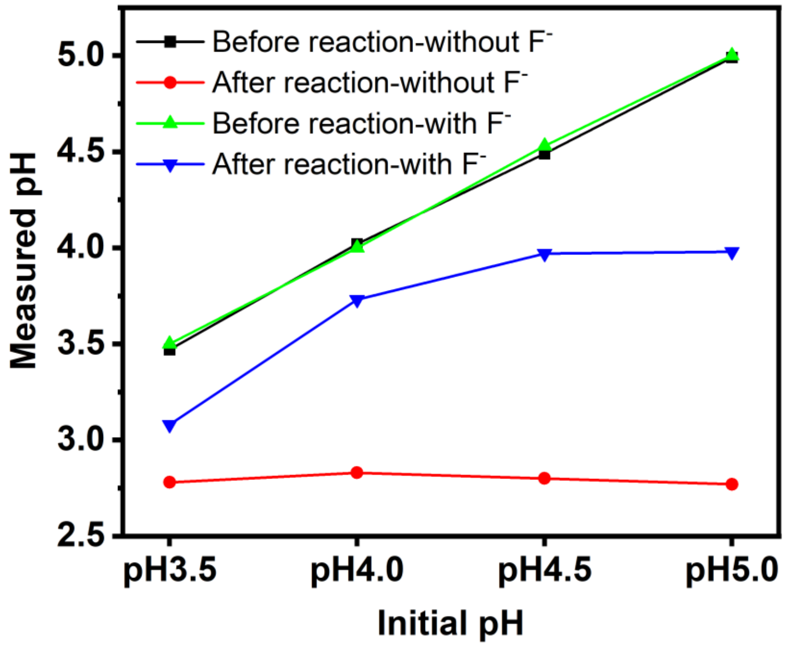

Fig. S3. pH variation before and after Ni electrodeposition in F^{-}-containing and F^{-}-free solutions under varied initial pH conditions. Conditions: 2000 mg/L Ni^{2+} and 1000 mg/L F^{-}.

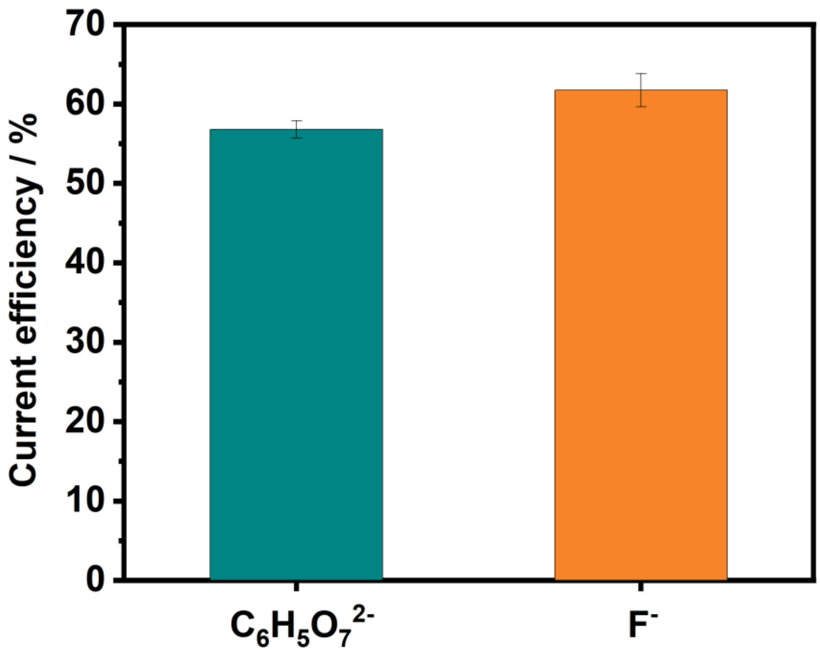

Fig. S4. CE in $C_6H_5O_7^{2-}$-containing and F^{-}-containing electrolytes. Conditions: 2000 mg/L Ni^{2+} and 2000mg/L $C_6H_5O_7^{2-}$ or 500 mg/L F^{-}.

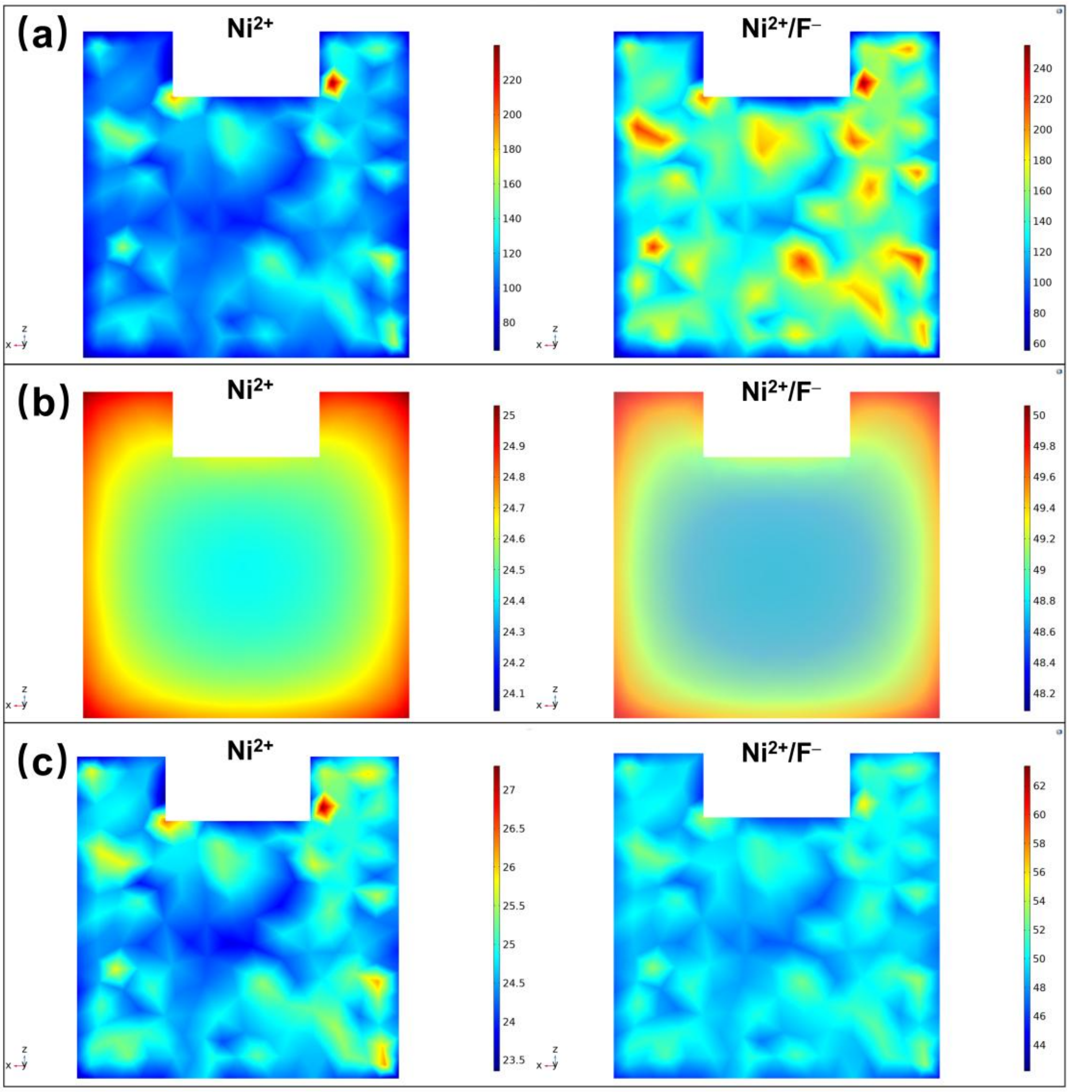

Fig. S5. (a) Distribution of Ni(II) concentration (mol/m^3) near the cathodic electrode surface, (b) current density (A/m^2) at the cathodic electrode surface, and (c) current density (A/m^2) at the cathodic electrode surface coupling with Ni^{2+} in the electrolytes with Ni^{2+} and Ni^{2+}/F^{-}.

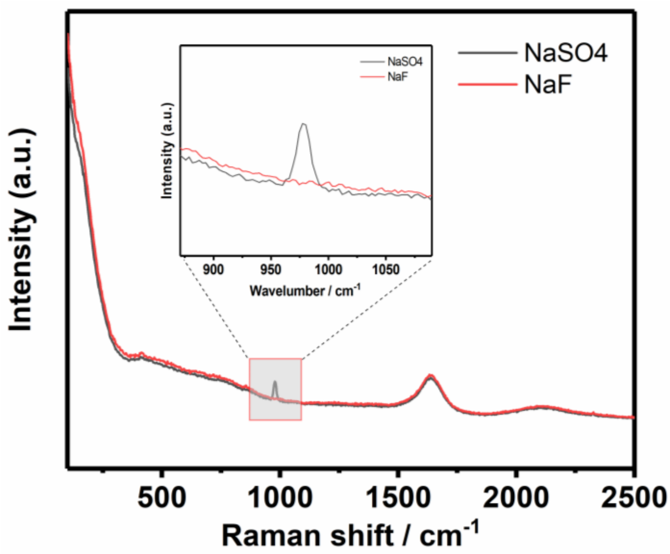

Fig. S6. *In situ* Raman spectra of species bonded to the electrode at open circuit potential in different electrolytes of 2000 mg/L SO_4^{2-} and 2000 mg/L F^-.

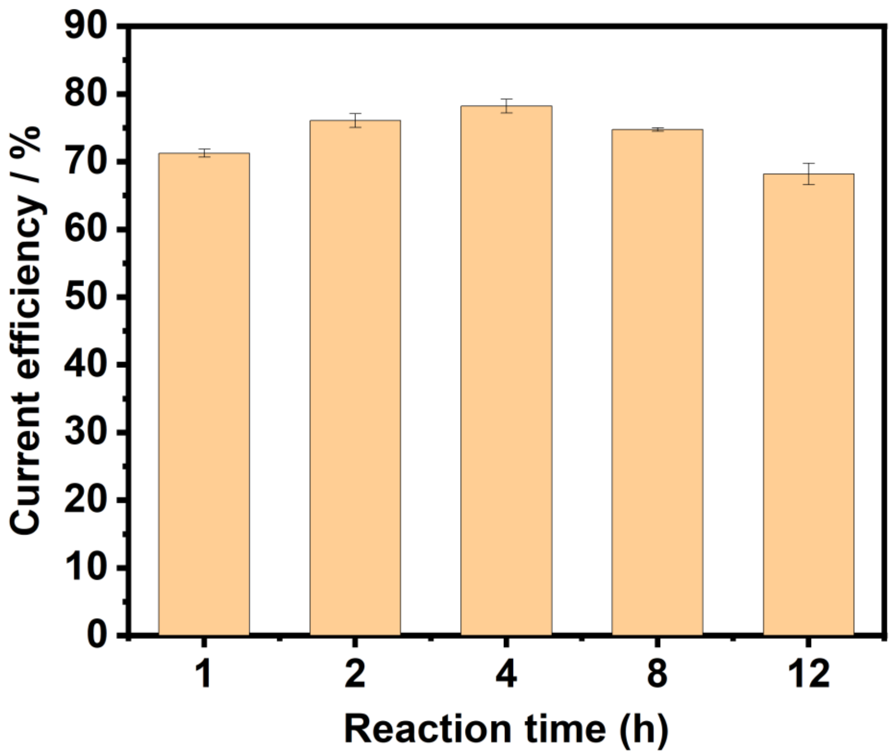

Fig. S7. CE for Ni electrodeposition under different reaction periods (1, 2, 4, 8, 12 hours). (Conditions: 2000 mg/L of Ni^{2+} and 2000 mg/L of F^-, pH 4.0, –1.2 V)

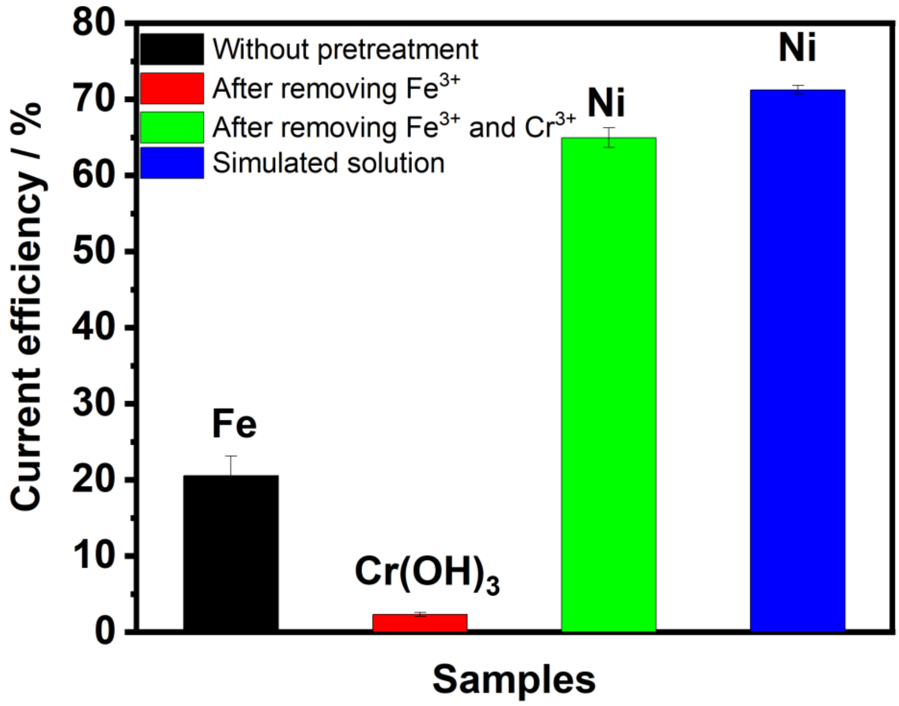

Fig. S8. CE for metal recovery via electrodeposition from simulated wastewater and actual wastewater under three pretreatment conditions of without pretreatment, after removing Fe^{3+}, and after removing Fe^{3+}/Cr^{3+}. (Operational conditions: –1.2 V, 1 hour)

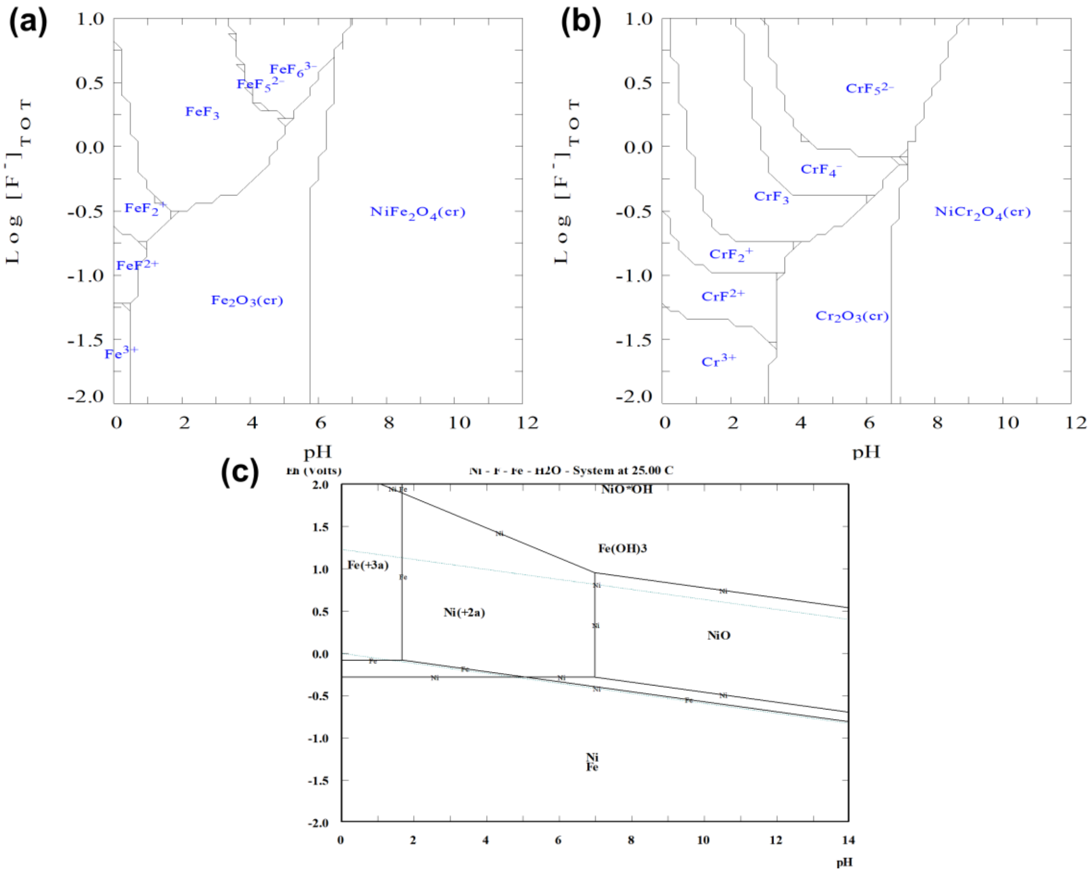

Fig. S9. The dependence of phase and dominant species in solution on F^- concentration and pH: (a) species of Fe(III) (6.25 g/L of Fe^{3+}), and (b) species of Cr(III) (3.5 g/L of Cr^{3+}); (c) Eh-pH diagram of a Ni-Fe-F-H_2O system (2.0 g/L of Ni^{2+}, 6.25 g/L of Fe^{3+}, and 7.0 g/L of F^-).

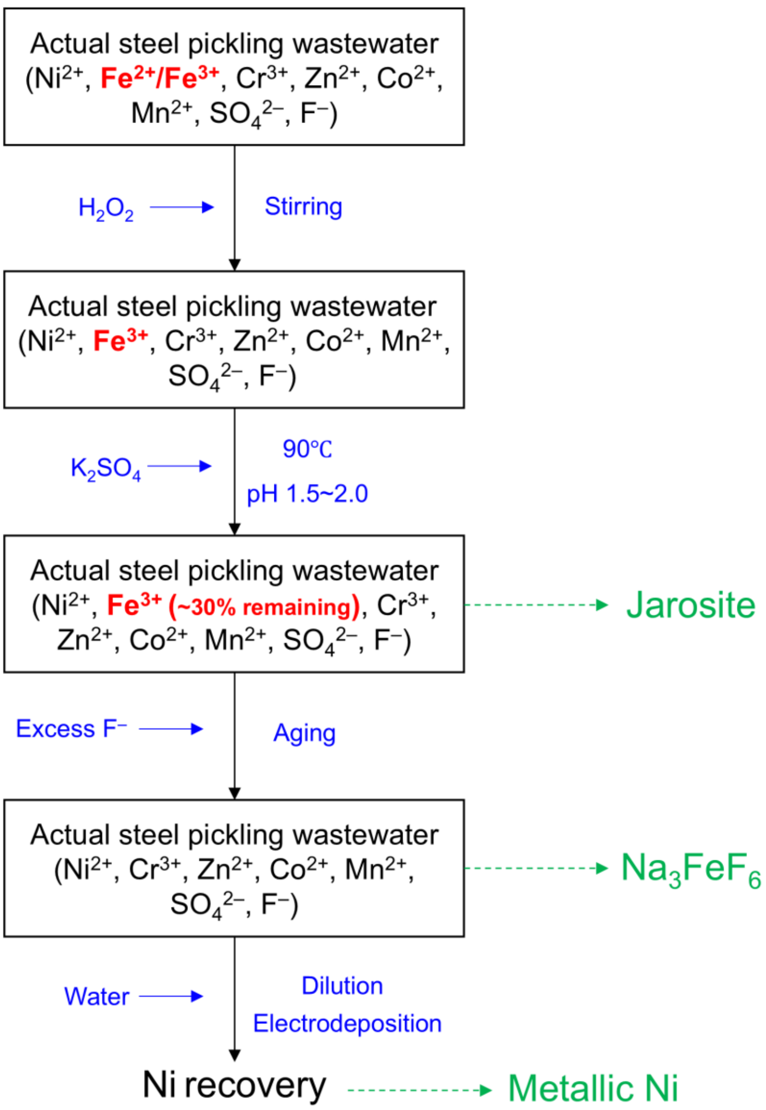

Fig. S10. Flowchart of the pretreatment process for Ni recovery from actual steel pickling wastewater.

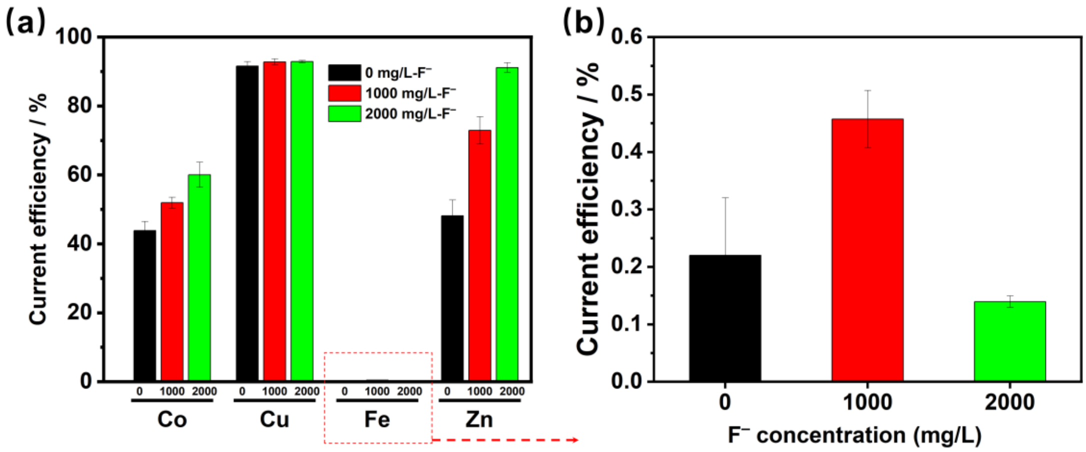

Fig. S11. (a) CE for various metal electrodeposition in F^--containing electrolytes with different F^- concentrations under applied voltages of –1.2 V for Co, –0.8 V for Cu, –1.2 V for Fe, –1.5 V for Zn. (b) Magnified view of the CE for Fe electrodeposition. Conditions: 2000 mg/L metal ions (Co^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}), 0–2000 mg/L F^-.