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Enhanced immobilization of sorbed Pb and Cr during the Fe(II)-catalyzed transformation of ferrihydrite†

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The secondary mineralization of metastable iron (oxyhydr)oxides into thermodynamically stable ones occurring in soil–water interface and sediment mediates the transport of pre-associated trace metal elements (and of other pollutants) in surficial environments. However, the fate of these associated metals and their impact during/on this mineralogical process remain incompletely understood. To address this question, we investigated the transformation of typical trace metal cation [Pb(II)] or anion [Cr(VI)O₄^{2−}] sorbed nanoscale ferrihydrite upon exposure to aqueous Fe(II). After 14 days of interaction, pre-sorbed Pb(II) modified marginally the extent of ferrihydrite conversion (~93% vs. ~94%), but did retard the formation of goethite (~9% vs. ~29%) by incorporating it into intermediates. In contrast, the transformation of Cr(VI)O₄^{2−} pre-sorbed ferrihydrite was essentially hindered (~11%) owing to the formation of (FeO)₂CrO₂[−] complex and less conductive Fe_xCr_{1−x}(OH)₃ at the ferrihydrite surface. In all cases, the secondary mineralization of ferrihydrite significantly enhanced immobilization of sorbed metals (Pb/Cr release rate constant decreased by 99%/37%) owing to the formation of more stable iron (oxyhydr)oxides (*i.e.*, hematite, goethite, and lepidocrocite) partially incorporating pre-sorbed Pb(II) (>24%), or to the formation of Fe_xCr_{1−x}(OH)₃ and Cr₂O₃ that are more resistant to acid corrosion than sorbed species. These findings offer valuable insights into the fate of typical trace metal elements during ferrihydrite transformation and contribute to the development of remediation strategies for metal contaminants.

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Environmental significance

The secondary mineralization of nanoscale ferrihydrite represents a prevalent process that frequently takes place within the supergene environment. This process not only modifies the types of iron-bearing minerals present in environments such as soils and sediments but also exerts a profound influence on the speciation and bioavailability of heavy metal elements and nutrients. This study has unveiled that the presence of two pre-adsorbed ions, namely CrO₄^{2−} and Pb²⁺, effectively impedes the Fe²⁺-catalyzed ferrihydrite transformation process or alters its pathway by hindering the formation of goethite, respectively. Moreover, after the secondary mineralization of ferrihydrite, the two metals bind more tightly to the newly formed iron minerals *via* structural incorporation or forming more stable phases, significantly reducing their migration and bioavailability. The work highlights the environmental significance of adsorption-modulated mineral transformations in controlling pollutant fate, with implications for remediation technologies in soils, sediments, and wastewater treatment systems.

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1. Introduction

Trace metal elements (TMEs) generated by anthropogenic activities and natural processes are of great concern because of their persistent toxicity and bioaccumulation potential in ecological systems. Among these, lead (Pb) and chromium (Cr) deserve special attention.^{1,2} Exposure to Pb can impede children's intellectual development and inflict harm on adults' nervous systems and hematopoiesis.^{3–5} Cr(VI) is categorized as carcinogenic and detrimental to plants, animals, and microorganisms.^{6,7} In subsurface environments, nanosized iron (oxyhydr)oxides (collectively referred to as FeOx) are both abundant and ubiquitous and serve as primary reservoirs for TMEs,⁸ including Pb(II) and

Cr(vi).^{6,9} Accordingly, FeOx play a pivotal role in regulating the mobility and bioavailability of these elements in aquatic and terrestrial ecosystems. Deciphering the intricate interplay between TMEs and FeOx at molecular scales is thus key to unraveling the mechanisms ruling TME mobility in subsurface environments, thereby facilitating the development of effective strategies for remediating contaminated soils and waters.

Ferrihydrite (Fhy) is a poorly ordered and nanoparticulate (<10 nm)^{8,10} FeOx that serves as the initial precipitate^{8,10} in diverse environmental settings and is ubiquitously distributed in soils,¹¹ sediments,^{8,10,12} and even deep-sea ferromanganese nodules.^{13,14} Its high surface area makes it an excellent sorbent, able to trap both cations [e.g., Pb(II)]^{15,16} and anions [e.g., CrO₄²⁻]^{17–19} up to several percents. As a thermodynamically metastable phase with highly disordered atomic structure^{10,11,20} Fhy undergoes structural transformation into more crystalline Fe-rich phases (e.g., goethite) upon aging,^{8,21} or exposure to aqueous Fe(II)^{20,22–25} or other dissolved ions [e.g., S(II),^{26,27} Mn(II)²⁸]. The Fe(II)-induced transformation of Fhy into lepidocrocite, goethite, and other FeOx under anoxic conditions is common in aquifers and sediments,^{22,24,30–34} where Fe(II) and Fhy commonly coexist in anoxic non-sulfidic conditions.²² The transformation initiates with Fe(II) sorption onto Fhy surface and proceeds with electron transfer from sorbed Fe(II) to bulk Fe(III), leading to the formation of secondary FeOx *via* dissolution–recrystallization or Fe atom redistribution within solids.^{8,29} Mechanisms responsible for this complex structural transformation have been unveiled and the influence of factors like pH, ligand type, temperature, and organic matter on Fe(II)-induced secondary mineralization of Fhy determined.^{20,30} However, the effects of associated TMEs and their fate during this process have attracted much less attention. Both isomorphically substituted metals [e.g., Al(III)²⁴ and Zn(II)³¹] and adsorbed divalent [e.g., Ni(II) and Zn(II)]³² or trivalent [Al(III),²⁴ La(III), and Ho(III)³³] cations negatively influence the Fe(II)-induced transformation of Fhy and modify the secondary mineralization pathways. Interestingly, both the above adsorbed divalent cations and rare earth elements appear to be incorporated in the crystal structure of the newly formed FeOx during this secondary mineralization process.^{32,33}

Pb(II) and Cr(vi)O₄²⁻ readily form monodentate or bidentate surface complexes on the surface of Fhy under weakly acidic conditions (pH ≤ 6.5)¹⁶ or over a broad pH range (4.0–9.5),^{17,34} respectively. The formation of surface complexes, whether for Pb(II) or Cr(vi)O₄²⁻, leads to the depletion of surface hydroxyl groups or to a modification of the mineral surface charge,¹⁸ respectively, which in turn impedes further adsorption of other ions.^{1,35} Despite Pb(II)'s significance as a priority contaminant, the effect of pre-sorbed Pb(II) and its behavior on/during the Fe(II)-induced transformation of Fhy has not been systematically investigated. This effect is expected to differ from that reported for the aforementioned ions owing to the stronger

binding ability of Pb(II) to Fhy compared to other metals,³⁶ and to the larger ionic radius of Pb(II) (1.19 Å) compared to Fe(III) (0.645 Å) and other cations [Ni(II): 0.690 Å, Zn(II): 0.740 Å, La(III): 1.032 Å, Ho(III): 0.901 Å].³⁷ Few studies have explored the Fe(II)-induced transformation of Cr-sorbed Fhy,³⁸ without addressing fully the impact of Cr on this process, however. In particular the rapid redox reaction between Cr(vi)O₄²⁻ and Fe(II) leads to the deposition of less conductive Fe_xCr_{1–x}(OH)₃ on Fhy surface,^{38–42} thus passivating the mineral surface,⁴³ and altering the kinetics and pathways of the mineralogical transformation.

The present study thus investigates the transformation of Pb(II)- and Cr(vi)O₄²⁻-sorbed 2-line Fhy in the presence of Fe(II). This work aims at unraveling the impact of the two TMEs on the dynamics and pathways of this Fe(II)-induced mineralogical transformation, and at evaluating the mobility of the two ions along this process. The mineralogical evolution along this process is comprehensively characterized, both qualitatively or quantitatively, from the combination of X-ray diffraction (XRD), Fe K-edge X-ray absorption spectroscopy (XAS), thermogravimetric analysis (TGA) and scanning/transmission electron microscopy (SEM/TEM). The association between Pb/Cr and Fe in reaction products is also assessed by combining high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and acid washing.

2. Experimental methods

2.1 Ferrihydrite preparation

Ferrihydrite was prepared according to the protocol of Cornell and Schwertmann.⁸ In brief, 40.4 g of Fe(NO₃)₃·9H₂O was dissolved in 500 mL of ultrapure water (18.2 MΩ cm), yielding a 0.2 M Fe(NO₃)₃ solution. Subsequently, 330 mL of 1 M KOH was added at the rate of 1 mL min^{–1} into the Fe(NO₃)₃ solution, and the final pH was adjusted to 7.3 ± 0.1. Following this, the mixture underwent vigorous stirring for 2 h. The resulting suspension was then diluted with ultrapure water to 2 L and allowed to stand undisturbed overnight. To eliminate remaining ions and amorphous phases, the supernatant was poured away and the dilution-standing-supernatant removal process was repeated three times. The suspension was then dialyzed against ultrapure water until the conductivity fell below 20 μS cm^{–1}. The dialyzed suspension was centrifuged, freeze-dried, ground, and passed through a 100-mesh sieve. The obtained solid is hereafter designated as Fh₀.

Pb- or Cr-sorbed Fhy samples were prepared by equilibrating Fh₀ into Pb- or Cr-containing solutions. These solutions were prepared by dissolving 0.9930 g Pb(NO₃)₂ or 1.9400 g K₂CrO₄, respectively, into 1.00 L of ultrapure water with 0.04 M Na⁺ (NaNO₃) as a background ion. Then, 2.00 g of Fh₀ were introduced in these solutions and stirred for 48 h to reach equilibrium (maximum Pb/Cr sorption). The resulting suspensions were then centrifuged, and freeze-dried, dry samples being ground and sieved at 100-mesh. The

final solids are hereafter referred to as FhPb_{1.0} and FhCr_{1.0}. In addition, two samples equilibrated in the same conditions for ~40 min and hosting approximately half of the maximum Pb/Cr content were prepared following the same protocol, and are hereafter referred to as FhPb_{0.5} and FhCr_{0.5}. Pb- and Cr-bearing Fhy are hereafter referred to collectively as FhPb and FhCr, respectively.

Fe, Pb, and Cr contents in Fh₀, FhPb, and FhCr were determined *via* acid digestion and flame atomic absorption spectrometry (AAS) (Table 1). Specifically, 10 mg of each solid sample was dissolved in 10 mL of 6 M HCl, and the resulting solution was subsequently diluted with ultrapure water to achieve the target analytical concentration. Measurements were performed in duplicate.

2.2 Fe(II)-induced transformation of ferrihydrite

Fe(II)-induced secondary mineralization experiments were performed in an Ar-filled glove box (MIKROUNA, O₂ < 0.1 ppm). Prior to its use in the experiments, ultrapure water was rigorously purged with N₂ for over 3 h, to effectively eliminate dissolved O₂. Subsequently, 1.00 g of solids (Fh₀, FhPb, and FhCr) were each dispersed in 0.50 L of deoxygenated ultrapure water, generating mineral suspensions used to initiate the reaction. The pH of the mineral suspension was adjusted to 7.00 ± 0.05 *via* dropwise addition of HCl and allowed to stabilize for 12 hours. Subsequently, 0.200 g of FeCl₂·4H₂O solid was added to the suspension, and magnetic stirring was applied to facilitate rapid dissolution, resulting in a 2.00 mM Fe(II) solution. The reaction was deemed to have commenced at this moment. Each sample was then magnetically stirred, and the pH was maintained to 7.00 ± 0.05 with deoxygenated HCl or NaOH solution.

At certain time intervals, aliquots were withdrawn for analysis of aqueous and solid fractions. Aqueous samples were filtered through a 0.22 µm nylon membrane whereas solids were collected from the filter, washed twice using deoxygenated water, and dried in the glove box for further characterization. Fe, Pb, and Cr contents in solution were determined using AAS, the concentration of Fe(II) and Cr(VI) in solution being determined using phenanthroline and diphenylcarbazide colorimetric methods, respectively.

The HCl dissolution experiments were conducted with 0.1000 g of solid [*i.e.*, Fh₀, FhPb_{1.0}, and FhCr_{1.0} and reaction products after 14 days interaction with aqueous Fe(II)] into 100 mL of 2 M HCl at room temperature with stirring.

Solution aliquots were extracted until no solid could be observed, and dissolved Fe, Pb, and Cr contents were measured using AAS.

2.3 Characterization of ferrihydrites and their reaction products

X-ray diffraction (XRD) data was collected on a Rigaku Miniflex 600 X-ray diffractometer equipped with a Cu Kα source (voltage 40 kV, current 15 mA). Data was collected at a 2° min⁻¹ rate with 0.02° steps. Thermogravimetric analysis data (TGA) was recorded from room temperature (~25 °C) to 800 °C at a heating rate of 10 °C min⁻¹ and under a continuous N₂ flow of 20 mL min⁻¹ using a Mettler TGA/DSC 3+ instrument. Scanning electron microscopy (SEM) images were obtained with a Zeiss Sigma300 microscope, a 3 kV accelerating voltage, and a 6.5 mm working distance.

X-ray absorption fine structure (XAFS) spectra were recorded at both Fe K- and Cr K-edges on the 4B9A beamline (Beijing Synchrotron Radiation Facility). Before data collection, Fe and Cr metallic foils were used for energy calibration (*E*₀ = 7112 eV and *E*₀ = 5989 eV, respectively). Data was collected at ambient temperature, with Fe K-edge spectra being collected in transmission mode spanning the 6920–7920 eV energy range, and Cr K-edge spectra being collected in fluorescence mode over 5800–6400 eV. Data reduction was performed using the Athena interface of the IFFEFIT software package.⁴⁴ Fourier transform (FT) of *k*³-weighted $\chi(k)$ data was performed over the 3.0–10.6 Å⁻¹ *k*-range to obtain radial distribution functions (RDF) $\chi(r)$ in real space. The linear combination fitting (LCF) method was employed to determine the proportion of FeOx within reacted samples by fitting the data in *k*-space over 3–12 Å⁻¹ using ferrihydrite, lepidocrocite, hematite, and goethite as standards.

3. Results

3.1 Mineralogical analysis

XRD pattern of Fh₀ displayed two prominent broad peaks centered at ~35° and ~63° (2θ) (Fig. 1), typical for 2-line Fhy nanoparticles,^{8,10} without any other discernible diffraction peaks. Adsorption of Pb(II) and Cr(VI) did not generate extra XRD peaks and XRD patterns of FhPb and FhCr samples were essentially alike those of Fh₀. After one day of exposure to aqueous Fe(II) under anoxic conditions, XRD patterns of all five samples remained largely unchanged (Fig. S1†). After 3 days of interaction, XRD patterns of FhCr samples remain

Table 1 Fe, Pb, and Cr contents (*C*_{Fe/Me}) in synthesized Fh₀, FhPb, and FhCr

Samples	<i>C</i> _{Fe} (mg g ⁻¹)	<i>C</i> _{Me} (mg g ⁻¹)	Me/(Me + Fe) wt%	<i>N</i> _{Me} /g (mmol g ⁻¹)
Fh ₀	540.1 ± 2.4	—	—	—
FhPb _{0.5}	502.0 ± 5.3	18.2 ± 0.1	3.6	0.09
FhPb _{1.0}	489.2 ± 1.8	38.1 ± 0.4	7.8	0.18
FhCr _{0.5}	513.1 ± 1.4	10.1 ± 0.2	2.0	0.19
FhCr _{1.0}	505.1 ± 1.5	16.2 ± 0.2	3.2	0.31

Note: *N*_{Me} denotes the amount of Pb/Cr (in mmol) adsorbed on per gram of ferrihydrite.

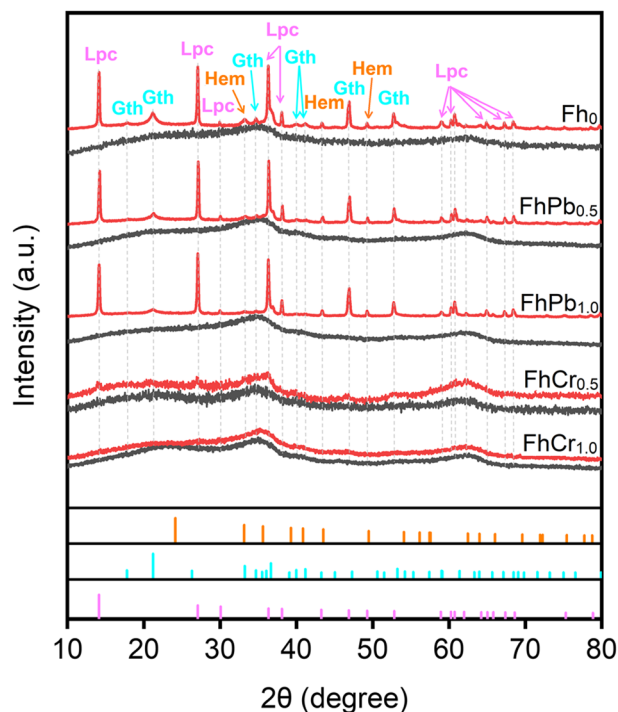


Fig. 1 Comparison of XRD patterns of unreacted Fh_0 , $\text{FhPb}_{0.5}$, $\text{FhPb}_{1.0}$, $\text{FhCr}_{0.5}$, and $\text{FhCr}_{1.0}$ (black) with those of samples exposed to $\text{Fe}(\text{II})$ for 14 days (red). Lpc, Gth, and Hem indicate peaks of lepidocrocite, goethite, and hematite, respectively. Color lines at the bottom of the figure indicate peak positions of diffraction lines from these three FeOx : magenta for lepidocrocite (ICDD#08-0098), cyan for goethite (ICDD#29-0713) and orange for hematite (ICDD#33-0664).

unchanged, whereas those of Fh_0 and FhPb showed marked transformations, with sharp peaks at $\sim 14.1^\circ$, $\sim 27.1^\circ$, $\sim 36.3^\circ$, and $\sim 46.9^\circ$ (2θ), corresponding to lepidocrocite 020, 120, 031, and 200 reflections (ICDD#08-0098), and weak peaks at $\sim 21.2^\circ$ and $\sim 33.2^\circ$ (2θ), typical of goethite 110 and 130 reflections (ICDD#29-0713). Additional faint peaks at $\sim 33.1^\circ$ and $\sim 54.1^\circ$ (2θ), that may be ascribed to hematite 104 and 116 reflections (ICDD#33-0664 – Fig. S1†), were visible for Fh_0 and $\text{FhPb}_{1.0}$. After ~ 14 days of interaction with $\text{Fe}(\text{II})$, XRD patterns of FhCr remained essentially unchanged, however with the presence of weak lepidocrocite peaks in $\text{FhCr}_{0.5}$ XRD pattern (Fig. 1 and S1†), indicating limited transformation of FhCr during the 14 days of interaction with aqueous $\text{Fe}(\text{II})$. On the other hand, 2-line Fhy contributions at $\sim 35^\circ$ and $\sim 63^\circ$ (2θ) essentially vanished in XRD patterns of Fh_0 and FhPb samples whereas peaks indicative of newly-formed FeOx became more intense (Fig. 1 and S1†). The predominant FeOx diffraction peaks indicated the presence of lepidocrocite and goethite, with minor contributions from hematite and magnetite, consistent with previous reports.^{20,22–24,29,31} Intensity of goethite peaks was negatively correlated with initial Pb loading, suggesting that $\text{Pb}(\text{II})$ sorption prevented Fhy conversion to goethite. Moreover, XRD analysis revealed no detectable reflections beyond those corresponding to the phases identified in reacted Fh_0 , indicating that crystalline impurities [such as chromium,

lead, or other iron (oxyhydr)oxides] were either absent or present below detection limits during $\text{Fe}(\text{II})$ -mediated transformation of FhPb and FhCr samples.

3.2 Thermogravimetric analysis

The adsorption of $\text{Pb}(\text{II})$ or $\text{Cr}(\text{VI})$ onto the surface of Fhy induced a significant reduction in weight loss (from $\sim 25^\circ\text{C}$ to 180°C : $\text{FhPb}_{1.0}$ – 15.4%, $\text{FhCr}_{1.0}$ – 16.8%, and Fh_0 – 20.3%; Fig. 2a), indicating that their adsorption involved a ligand exchange process with surface hydroxyl groups. For unreacted Fh_0 and $\text{FhPb}_{1.0}$, the first weight loss, attributed to removal of adsorbed water, occurred from room temperature to $\sim 180^\circ\text{C}$ with a maximum at $\sim 72^\circ\text{C}/\sim 66^\circ\text{C}$, respectively.^{8,45} The second weight loss occurred from $\sim 180^\circ\text{C}$ to $\sim 280^\circ\text{C}$ peaking at $\sim 226^\circ\text{C}/\sim 220^\circ\text{C}$ and was linked to dehydroxylation of Fhy (Fig. 2b).^{8,46} After interaction with $\text{Fe}(\text{II})$, TGA data of reacted $\text{FhPb}_{1.0}$ and corresponding first derivatives differed from that of the unreacted sample (Fig. 2c), consistent with sample mineralogical evolution. Notably, the overall weight loss of $\text{FhPb}_{1.0}$ decreased as reaction with aqueous $\text{Fe}(\text{II})$ proceeded (Fig. 2c, pristine: 24.0%, 3d: 21.8%, and 14d: 16.6%). Both reacted $\text{FhPb}_{1.0}$ samples displayed similar weight loss features but different temperature ranges (Fig. 2c and d). Specifically, maximum removal of adsorbed water occurred at lower temperatures with increasing reaction duration, whereas dehydroxylation of structural OH occurred at higher temperature (Fig. 2d). The latter shift was consistent with Fhy transformation to goethite and lepidocrocite.⁸ Compared to $\text{FhPb}_{1.0}$, newly formed goethite and lepidocrocite contained less adsorbed water that was released at lower temperature, most likely because of their large particle size, whereas loss of their structural OH to form hematite was expected to occur at $>250^\circ\text{C}$.⁸ Finally, unreacted Fh_0 and $\text{FhPb}_{1.0}$ exhibited a third, weight loss at $\sim 320\text{--}400^\circ\text{C}$ peaking at $\sim 370^\circ\text{C}$, which could be ascribed to the formation of hematite.^{47,48}

On the other hand, TGA curves of $\text{FhCr}_{1.0}$ and of its reacted counterparts essentially overlapped (Fig. 2e), thus indicating mineralogical stability of $\text{FhCr}_{1.0}$ upon interaction with $\text{Fe}(\text{II})$. Two minor maxima, undetected in unreacted $\text{FhCr}_{1.0}$, were observed however at $\sim 120^\circ\text{C}$ and $\sim 250^\circ\text{C}$ after reaction with $\text{Fe}(\text{II})$ (Fig. 2b and f). The latter weight loss resulted from goethite and/or lepidocrocite dehydroxylation, as in reacted Fh_0 and $\text{FhPb}_{1.0}$, whereas the former weight loss, absent in all other samples, may be due to the decomposition of $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$, a common and usually amorphous, reaction product in $\text{Fe}(\text{II})\text{--Cr}(\text{VI})$ systems.^{38–40,42}

3.3 Fe K-edge XAFS

Fe K-edge EXAFS spectra (Fig. 3a) and their Fourier transforms (FTs) (Fig. 3b) were used to monitor the evolution of Fe local environment in solids during Fhy reaction with aqueous $\text{Fe}(\text{II})$. Consistent with XRD analysis (Fig. 1 and S1†) and the observed mineralogical stability,

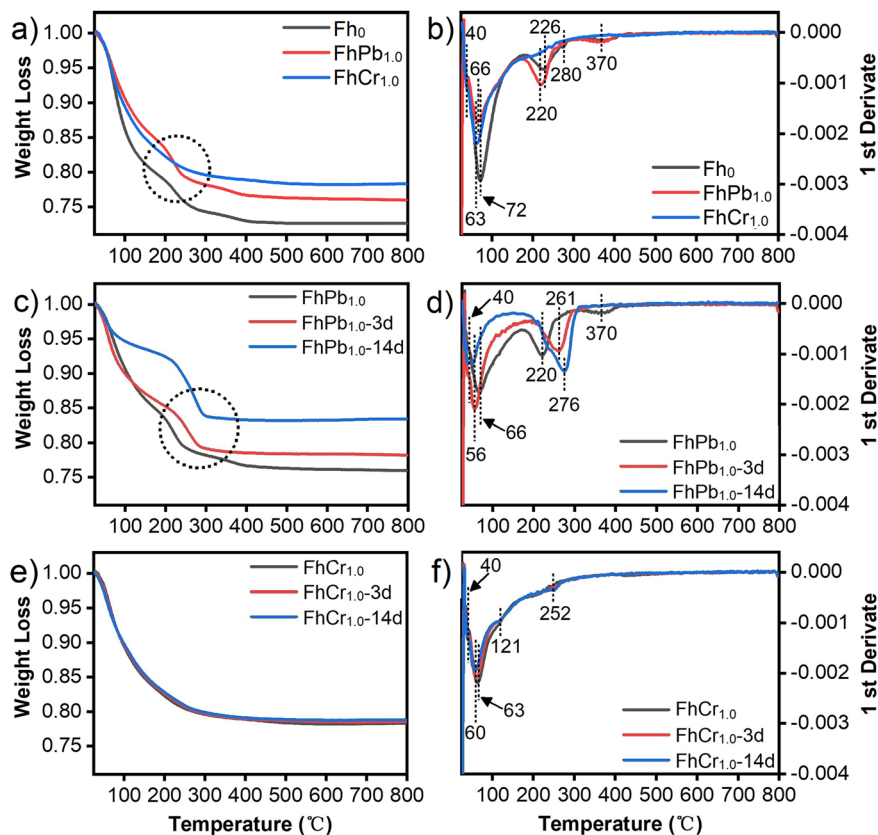


Fig. 2 Comparison of thermogravimetric curves (TG, left) and corresponding first derivatives (right) for unreacted Fh₀, FhPb_{1.0}, and FhCr_{1.0} (a and b), and for Pb-/Cr-bearing samples further reacted with aqueous Fe(II) for 3 or 14 days (c–f).

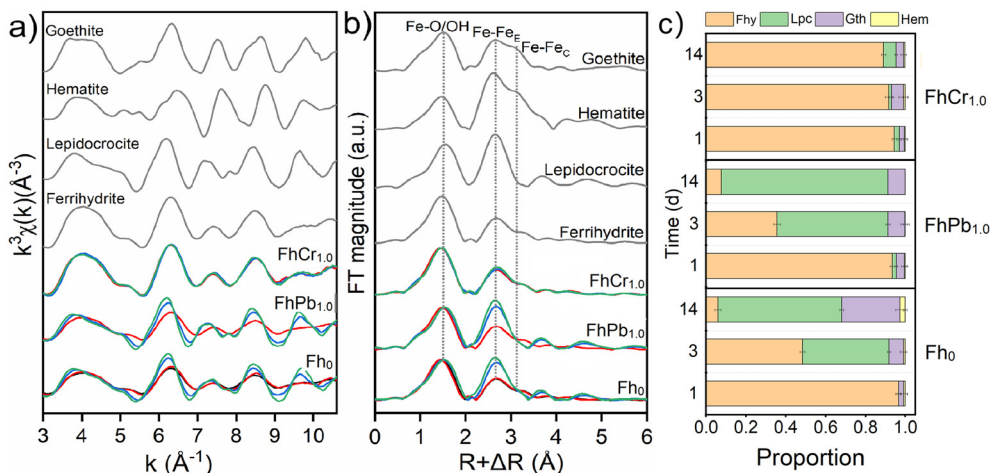


Fig. 3 Comparison of Fe K-edge EXAFS spectra (a) and of their Fourier transforms (FTs – b) of unreacted (black), and reacted Fh₀, FhPb_{1.0}, and FhCr_{1.0} (1 d: red, 3 d: blue, 14 d: green), with those of iron (oxyhydr)oxide standards (gray). The relative abundance of ferrihydrite (Fhy), lepidocrocite (Lpc), goethite (Gth), and hematite (Hem) in reacted solids (c) are derived from linear combination fitting of Fe K-edge EXAFS spectra. Note: the intensity of FT is normalized to the first shell ($R + \Delta R \sim 1.5$ Å) to emphasize the evolution of Fe local environment during the reaction.

EXAFS spectra obtained for reacted FhCr_{1.0} samples were similar to those of the starting materials both in *k*- and *r*-space, and resembled that of pristine Fh₀ regardless of the reaction duration. EXAFS spectra obtained from Fh₀ and FhPb_{1.0} samples reacted for 1 day were also similar to those obtained from pristine Fhy, whereas significant

differences appeared after 3 days. In the *k*-space, these differences were a pronounced shift towards lower *k* values, compared to unreacted Fh₀, and the enhancement of peaks centered at 4.0 Å⁻¹, 6.3 Å⁻¹, 7.5 Å⁻¹, and 8.6 Å⁻¹ (Fig. 3a). In FTs, the first peak at ~ 1.5 Å ($R + \Delta R$), typical for the first Fe–O/OH shell, shifted to higher values after

3 days of reaction (Fig. 3b), to match that of lepidocrocite. Intensity of the first Fe–Fe shell at ~ 2.6 Å ($R + \Delta R$) also increased as reaction proceeded, indicating the increased contribution from FeO₆–FeO₆ edge-sharing octahedra. The shoulder at ~ 3.2 Å originating from the FeO₆–FeO₆ corner-sharing octahedra present in goethite and hematite was absent in the FTs of lepidocrocite and reacted Fh₀ and FhPb_{1.0} for more than ~ 3 days, consistent with lepidocrocite prevalence in Fh₀ and FhPb reaction products (Fig. 3c, Table S1†).

Consistently, linear combination fitting (LCF) of Fe K-edge EXAFS data showed that reaction products contained mainly Fhy and three newly formed FeOx: lepidocrocite, goethite, and hematite to a minor extent (Fig. 3c and S2, Table S1†), consistent with XRD results (Fig. 1) and previous studies.^{20,22,24,30,49} LCF analysis confirmed the minor amounts of newly formed FeOx (total <6%) after ~ 1 day of the reaction for the three systems, whereas XRD overlooked them due to their low abundance and/or to their nanocrystalline nature. After 14 days, transformation of Fh₀ and FhPb_{1.0} was essentially complete, with $\sim 6\%$ (Fh₀) and $\sim 7\%$ (FhPb_{1.0}) of unreacted Fhy, respectively. LCF analysis of reacted Fh₀ and FhPb_{1.0} confirmed the formation of both lepidocrocite and goethite, and the higher proportion of lepidocrocite in FhPb_{1.0} ($\sim 84\%$ vs. $\sim 62\%$ in Fh₀) at the expense of goethite ($\sim 9\%$ vs. $\sim 29\%$ in Fh₀), consistent with relative intensity of XRD peaks in FhPb_{1.0} and Fh₀ reaction products (Fig. 1). LCF analysis also confirmed the very limited character of the mineralogical transformation affecting FhCr_{1.0} as $\sim 89\%$ of Fhy remained even after 14 days of interaction with Fe(II) (Table S1†).

3.4 Electron microscopy

Pb(II) and Cr(VI) adsorption did not alter significantly the morphology of Fhy compared to that of pristine Fh₀, with the predominance of irregularly shaped nanoparticles and of particles with rough surfaces (Fig. 4).^{8,21} Upon interaction with Fe(II), morphologies of all three samples underwent notable modifications. After 3 to 14 days of interaction, reacted Fh₀ and FhPb_{1.0} were dominated by large (>500 nm) irregularly shaped plates having smooth surfaces (Fig. 4 and S3†), typical for lepidocrocite,^{8,49} and, to a lower extent, by clusters of needle-like particles, suggesting the presence of goethite in reaction products.⁵⁰ Selected area electron diffraction patterns and lattice fringe images confirmed the morphological identification of lepidocrocite and goethite (Fig. S4b–d†). Although XRD data and LCF analysis of Fe K-edge EXAFS spectra indicated that FhCr_{1.0} transformation was largely impeded, SEM (Fig. 4 and S3†) and TEM (Fig. S4f and h†) images revealed the presence of nano-plates (~ 100 nm) and minute needles at the surface of unreacted Fhy particles, indicative of a minor lepidocrocite and goethite formation, respectively. Notably, a clear boundary distinguishing pristine Fhy and newly formed lepidocrocite was observed in the reacted FhCr_{1.0} for ~ 3 days (Fig. 4). Fhy, in its irregularly shaped habit, prevailed however in reacted FhCr_{1.0} samples (Fig. S3†).

3.5 Evolution of dissolved Fe(II)

Upon contact with Fhy suspension, Fe(II) concentration [$c_{\text{Fe(II)}}$] decreased steadily over the first 3 days for both Fh₀ and FhPb_{1.0} groups, indicative of Fe(II) adsorption onto Fhy

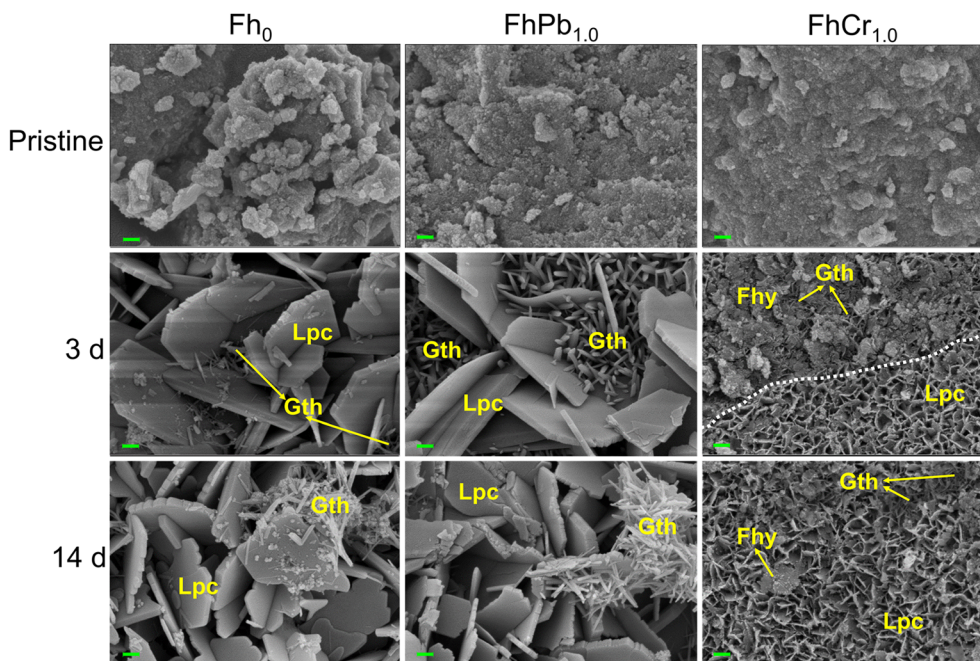


Fig. 4 SEM images of unreacted and reacted Fh₀, FhPb_{1.0}, and FhCr_{1.0} after 3 & 14 days of interaction with Fe(II). Fhy, Lpc, and Gth indicate ferrihydrite, lepidocrocite, and goethite, respectively. The white dotted line represents the boundary between the ferrihydrite region and the lepidocrocite region. The scale bar in the lower-left corner of images indicates 100 nm.

mineral surfaces (Fig. 5).⁵¹ Following this initial stage, $c_{\text{Fe(II)}}$ remained stable at ~ 1.5 mM until the end of the interaction, with a marginal decrease over the last three days, however. Adsorption of Pb(II) on Fhy surface didn't modify significantly the temporal evolution of $c_{\text{Fe(II)}}$ upon contact with Fe(II), albeit the slightly lower adsorption of Fe(II) onto FhPb most likely reflected the competitive interplay of Fe(II) and Pb(II) for adsorption sites.^{8,52} In contrast, $c_{\text{Fe(II)}}$ in FhCr groups exhibited a pronounced initial decrease with $\sim 62\%$ (FhCr_{0.5}) and 92% (FhCr_{1.0}) of the Fe(II) introduced being removed from solution over the first 3 days. This quick depletion of Fe(II) when in contact with FhCr most likely stemmed both from Fe(II) adsorption onto Fhy and from the induced reduction of Cr(VI) to Cr(III) by Fe(II) (Fig. S5†) leading to the formation of amorphous $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$.^{38,41,53} Within ~ 5 days, $c_{\text{Fe(II)}}$ decreased further for reacting FhCr_{1.0} to concentrations below or close to the detection limit. Concurrently, the $c_{\text{Fe(II)}}$ levels in the FhCr_{0.5} system exhibited a distinct biphasic decline pattern, characterized by a gradual decrease spanning from approximately day 3 to day 8, followed by a more rapid decrease from day 8 to day 11, suggesting the involvement of distinct mechanisms of Fe(II) sequestration during these respective phases. In all experiments, Pb and Cr dissolved species were systematically below the detection limit of AAS (data not shown).

3.6 Acid dissolution experiments

Reaction products displayed distinct Fe and Pb/Cr release kinetics upon hydrochloric acid treatment, all being significantly lower compared to those of the corresponding initial materials (Fig. 6 and S6, Table S2†). Notably, initial materials rapidly released a significant amount of Fe (27–40%) within the first ~ 2 min of treatment, and achieved complete dissolution within ~ 5 h (rate constant K : 13.78–20.51 d^{-1} , Fig. S6a and Table S2†). In contrast, reacted samples demonstrated markedly enhanced HCl resistance, showing 66.0–99.6% reduction in Fe leaching

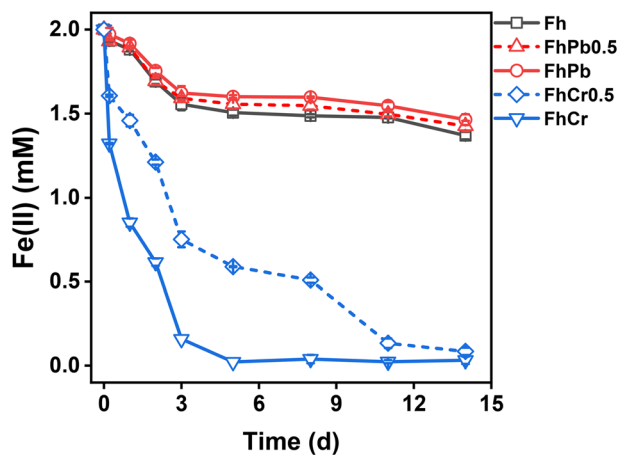


Fig. 5 Evolution of Fe(II) concentration in solution upon reaction of Fh₀, FhPb, and FhCr with Fe(II).

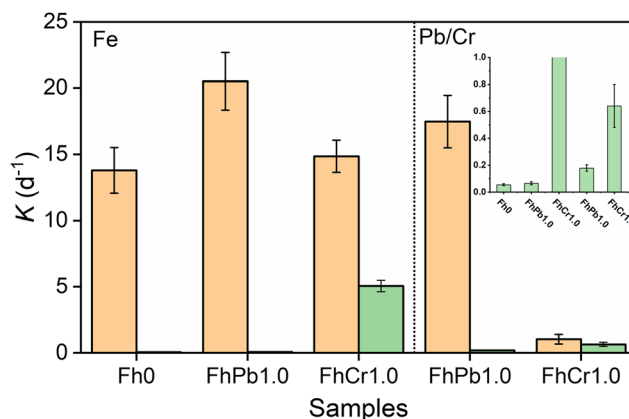


Fig. 6 Comparison of dissolution rate constants [K (d^{-1})] for Fe, Pb, and Cr released from unreacted Fh₀, FhPb_{1.0}, and FhCr_{1.0} (yellowish-brown bars) and their reacted counterparts (green bars) upon HCl treatment. K values were derived by simulating the experimental data using one-phase exponential decay function. The insert figure shows the K values for metals released from reacted samples at a smaller scale.

rates. Particularly, reacted Fh₀ and FhPb_{1.0} showed minimal early-stage Fe release ($\sim 2\%$ for Fh₀ and $\sim 8\%$ for FhPb_{1.0} after ~ 2 min) with prolonged dissolution durations (>100 h; $K = 0.06$ – 0.07 d^{-1} – Table S2†). Among reacted samples, FhCr_{1.0} exhibited the fastest dissolution kinetics (K : 5.05 d^{-1} , Table S2†), due to minor conversion and retention of Fhy during the reaction.

On the other hand, most Pb and Cr sorbed to initial materials were swiftly released upon acid treatment ($\sim 96\%$ of Pb and $\sim 80\%$ of Cr after ~ 2 min), the complete removal of Pb from Fhy surface taking ~ 20 min and Cr removal taking ~ 9 h (K_{Pb} : 17.47 d^{-1} and K_{Cr} : 1.03 d^{-1}) (Fig. S6b†). In contrast, reacted samples displayed reduced initial release of Pb and Cr ($\sim 67\%$ of Pb and $\sim 20\%$ of Cr after ~ 2 min). Following the initial release, both metals experienced a fast release stage with $\sim 76\%$ of Pb and $\sim 62\%$ of Cr being released after ~ 1 h. Pb and Cr release then slowed down, reaching a maximum after ~ 48 h and ~ 54 h (Fig. S6d†), respectively. Notably, the overall release rate constants for Pb or Cr from reacted solids (K_{Pb} : 0.18 d^{-1} , K_{Cr} : 0.64 d^{-1}) decreased by 99.0% and 37.3%, respectively, compared to initial materials. In particular, during the final dissolution stage of reacted FhCr (from ~ 12 h to ~ 54 h), Cr release was decoupled from Fe release, suggesting the presence of Cr (hydr)oxides more resistant to HCl than $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$ and newly formed FeOx.

4. Discussion

4.1 Impact of sorbed Pb(II) or Cr(VI)O₄²⁻ on the Fe(II)-induced ferrihydrite transformation

In the present experiments, Fe(II)-induced transformation of Fhy yielded lepidocrocite, goethite, and hematite after ~ 14 days of reaction. In addition, sorption of Pb(II) or Cr(VI)O₄²⁻ onto Fhy surface either impeded Fhy transformation [Cr(VI)O_4^{2-} – 89% of unaltered Fhy after 14

days] or modified its transformation pathway with a limited formation of goethite [Pb(II)] compared to Fh₀.⁵⁴

Despite similar conversion levels of Fh₀ and FhPb_{1.0} after 14 days, relative proportions of the two main reaction products (goethite and lepidocrocite) were quite different in the two systems. LCF analysis showed that Fh₀ yielded more goethite (~29%) and less lepidocrocite (~62%) compared to FhPb_{1.0} (~9% – goethite and ~84% – lepidocrocite; Fig. 3c and Table S1†). Lepidocrocite is commonly regarded as the initial product during Fhy Fe(II)-induced transformation, and is hypothesized to form from the direct precipitation of dissolved Fe(III) species.²⁵ As a metastable phase, lepidocrocite exhibits higher solubility compared to goethite,^{8,20} and previous studies have reported goethite formation from lepidocrocite precursor in the presence of aqueous Fe(II).^{20,55} Although prior research demonstrates that high-density Fe(II) loading on solid surfaces can facilitate goethite formation,⁵⁵ our experimental results reveal that Pb(II) adsorption (0.09–0.18 mmol g⁻¹ – Table 1) did not significantly alter the surface Fe(II) density of particles [0.19–0.20 mmol g⁻¹ for FhPb vs. 0.22 mmol g⁻¹ for Fh₀, assuming the decrease being caused by Fe(II) sorption]. This observation suggests, on one hand, that no significant competitive effect for adsorption sites [or redox reactions, $E_{\text{Pb(II)/Pb(0)}}^0 = -0.126$ V, $E_{\text{Fe(III)/Fe(II)}}^0 = 0.771$ V] between Pb(II) and Fe(II), implying that the two ions are adsorbed at distinct sites on the Fhy surface. Thus, electron transfer between sorbed Fe(II) and bulk Fe(III) remained feasible upon Pb(II) sorption, allowing comparable conversion of FhPb and Fh₀. On the other hand, it suggests that Fe(II) loading is not the primary factor driving the reduced goethite formation in FhPb groups compared to Fh₀. Notably, Pb(II) loading exhibited an excellent linear correlation ($r^2 > 0.99$) with the increase in lepidocrocite and decrease in goethite within the final products (Fig. S7†), indicating that Pb(II) may substantially participate in the mineral transformation. Specifically, Fe(III) and Pb(II) released from FhPb co-precipitated to form Fe(III)–Pb(II) intermediates, which preferentially transform into lepidocrocite rather than goethite. Finally, pH conditions (~7.0) and room temperature used in the present study likely constrained hematite or magnetite formation in both Fh₀ and FhPb_{1.0} groups.^{21,25}

Meanwhile, the presence of pre-sorbed Cr(VI)O₄²⁻ essentially inhibited Fhy secondary mineralization most likely owing to the formation of bidentate complexes [(FeO)₂CrO₂]¹⁹ and to the subsequent formation of Fe_xCr_{1-x}(OH)₃ (Fig. S5†). TGA revealed enhanced weight loss in FhCr_{1.0} compared to Fh₀ and FhPb_{1.0} (Fig. 2a), indicating the removal significant amount of OH and H₂O from FhCr_{1.0} and the replacement of reactive ≡Fe–OH and ≡Fe–OH₂ sites by (FeO)₂CrO₂⁻ complexes.¹⁹ This not only reduces the point of zero charge (PZC) of FhCr_{1.0} particles, potentially hindering Fe(II) adsorption due to electrostatic repulsion, but also diminishes their reactivity by altering surface chemistry, as evidenced by the absence of the weight loss at ~220 °C related to Fhy

dehydroxylation and new FeOx formation (Fig. 2d), in contrast to unreacted Fh₀ and FhPb_{1.0}. Furthermore, once Fe(II) is adsorbed onto the surface of FhCr_{1.0} particles, Cr(VI) preferentially acquires electrons from Fe(II) over structural Fe(III) due to the redox potential disparity [$E_{\text{Cr(VI)/Cr(III)}}^0 = 1.33$ V], thereby undergoing reduction to form Cr(III) [3Fe(II) + Cr(VI) → 3Fe(III) + Cr(III)]. Consequently, Fe(III) and Cr(III) undergo rapid hydrolysis, leading to the formation of amorphous Fe_xCr_{1-x}(OH)₃. In addition, the deposition of Fe_xCr_{1-x}(OH)₃ resulted in the rapid consumption of most dissolved Fe(II) [~0.80 mmol (0.31 × 0.86 × 3); Fig. S5,† Table 1].⁴² Although Fe(II) was still present in solution after this stage, it scarcely catalyzed Fhy conversion. This phenomenon primarily stems from the formation of Fe_xCr_{1-x}(OH)₃ on the surface, which i) physically impeded the contact and electron transfer between sorbed Fe(II) and structural Fe(III),⁴³ and ii) enhanced particle stability, thereby hindering the dissolution of structural Fe(III). As a consequence, atom exchange or release of newly formed Fe(II) and induced FhCr_{1.0} transformation were also hindered.^{24,29,33} Freeze-drying of chromate-sorbed Fhy possibly impacted its reactivity, as a complete conversion of Cr(VI)-sorbed Fhy was reported after ~1 week in a study in which aqueous Fe(II) was added directly to the pre-equilibrated Cr(VI)-sorbed Fhy suspension (pH = 5.75 and 7.00).⁴¹ In comparison to Cr(VI), arsenate (AsO₄³⁻) sorption imposed minimal influence on the extent of Fe(II)-induced Fhy transformation but altered product distribution, reducing goethite proportion.⁵¹ The ~20% decrease in solution Fe(II) resulted from the competitive sorption at Fhy surface sites rather than from arsenate reduction or non-conductive phase formation. For selenite (SeO₃²⁻), an oxyanion that could be reduced by Fe(II), its influence on Fhy transformation was concentration-dependent, as significant effects occur only at Se/Fe ratios ≥5%, primarily due to competitive adsorption that decreases Fe(II) uptake.⁵⁶ These observations are rooted in Fhy's surface charge properties: with a PZC >7.5,^{8,10} Fhy surfaces carry positive charges at neutral to weakly acidic pH, enabling preferential oxyanion adsorption over Fe(II) *via* electrostatic attraction. This electrostatic dominance explains why arsenate and selenite primarily compete for adsorption sites rather than undergo redox reactions, distinguishing their impacts from Cr(VI)'s redox-driven passivation.

4.2 Fate of Pb and Cr during the secondary mineralization of ferrihydrite

Pb or Cr was trapped by forming bidentate inner-sphere complexes [(FeO)₂CrO₂⁻ and (FeOH)₂Pb⁺] on Fhy surface.¹⁹ During the secondary mineralization of Pb(II)/Cr(VI)O₄²⁻-sorbed Fhy, neither metal was detected in the solution, suggesting that this process wouldn't release the two elements, which were evenly distributed in reaction products (Fig. S8†), into aquatic systems. In addition, HCl dissolution experiments showed that Fe(II)-induced transformation of Fhy promoted immobilization of the two elements (Fig. 6 and S6†) by incorporating them into reaction products more

stable than Fhy (Pb – Fig. S6 and Table S3†) or forming more stable species (Cr – Fig. S5†).

During HCl treatment, after an initial fast Pb release (~1 h) from the reacted FhPb_{1.0} originating from adsorbed species, Pb was released at a much slower rate from those incorporated into newly formed FeOx (~1–48 h, Fig. S6d†). Sorbed and incorporated Pb accounted for ~76% and ~24% of total Pb, respectively. This Fe(II)-induced conversion to crystalline FeOx provides a more stable structural matrix for both Pb species, thereby reducing its mobility and enhancing sequestration efficiency. For sorbed Pb, the immobilization was enhanced as the host phase converted to lepidocrocite and goethite, which are thermodynamically more stable than Fhy. Furthermore, Pb incorporation in newly-formed FeOx was confirmed by elongated unit-cell parameters of goethite (*b*: 9.968 Å in reaction products vs. 9.956 Å in “ideal” goethite)⁸ and hematite (*c*: 13.830 Å in reaction products vs. 13.749 Å in “ideal” hematite)⁵⁷ (Table S3†). Previous studies showed that cations initially sorbed to Fhy, such as Ni(II), Zn(II),³² La(III), and Ho(III),³³ can be incorporated into FeOx during Fe(II)-induced Fhy transformation. Incorporation of foreign cations occurred along the dissolution-recrystallization process of this reaction. In contrast, lepidocrocite unit-cell parameters determined in reaction products were close to ideal ones, consistent with previous studies indicating little Pb incorporation into lepidocrocite,^{58,59} and formation of minute Pb-bearing lepidocrocite crystallites (<6 nm).⁵⁹ Nanocrystalline lepidocrocite may thus more readily endure further transformation to goethite and hematite compared to the large Pb-free lepidocrocite crystals (>500 nm) observed in the present study (Fig. S3†).

Although most Cr(VI) (~86%) was reduced to Cr(III) in the presence of Fe(II) as expected,^{2,7,38,40,43} a minor part of Cr remained hexavalent (~14% – Fig. S5†) and was readily desorbed from reacted FhCr_{1.0}, contributing to initial fast Cr release. In addition, dissolution of Fe_xCr_{1-x}(OH)₃ likely contributed to both the initial fast and subsequent slower release of Cr. As Fe_xCr_{1-x}(OH)₃ with higher Cr content exhibits greater solubility,⁶⁰ meaning Cr-rich phases dissolved first, followed by Cr-poor phases. The exclusive release of Cr (without Fe release) after ~12 h of the treatment could be attributed to dissolution of Cr(III) oxides (*e.g.*, Cr₂O₃) other than hydroxides,^{61,62} as the latter are more soluble than Fe_xCr_{1-x}(OH)₃. Furthermore, the LCF analysis of Cr K-edge 1st derivative of normalized XANES data for FhCr_{1.0} revealed that Cr₂O₃ accounts for ~7% of total Cr in reaction products (Fig. S5†), likely representing the only residual Cr-bearing phase.

5. Conclusions

Ferrihydrite (Fhy), a nanoparticulate iron oxyhydroxide prevalent in subsurface environments, rapidly transforms into stable FeOx phases but persists in soils, sediments, and deep-sea nodules. This study reveals that adsorbed cations/

anions critically influence Fhy's structural evolution *via* distinct mechanisms. Cr(VI) adsorption inhibits Fhy transformation *via* replacement of reactive sites and formation of the less conductive Fe_xCr_{1-x}(OH)₃ surface precipitates, while Pb adsorption minimally affects transformation extent but alters reaction kinetics and product composition by incorporating it into intermediates. As a major sink for TMEs through surface complexation and isomorphous substitution, Fhy governs TME bioavailability in environmental systems. Fe(II)-catalyzed Fhy transformation enhances immobilization of pre-sorbed Pb and Cr, reducing their mobility by 99% and 37%, respectively. For Pb, stability arises from adsorption onto or incorporation into crystalline FeOx phases (lepidocrocite, goethite, and hematite), whereas Cr forms dissolution-resistant amorphous (Fe,Cr) (oxyhydr) oxides. Both mechanisms reduce metal mobility more effectively than Fhy alone. These findings demonstrate that anoxic Fe(II)–Fhy interactions represent a promising strategy for mitigating TME contamination risks.

Data availability

Data for this article, including XRD, TGA, XAS solution chemistry, and acid treatment results for pristine ferrihydrite or that reacted with Fe(II) are available at Mendeley Data at <https://doi.org/10.17632/v7mct8r6jf.1>.

Author contributions

Zhongkuan Wu: writing – original draft, data curation, conceptualization, formal analysis. Chaojun Wang: methodology, writing – original draft, data curation. Bruno Lanson: data curation, methodology, writing – review & editing. Wenbo Dong: data curation, investigation, methodology. Jiarui Jian: data curation, investigation, methodology. Feiting Yu: data curation, investigation, methodology. Binbin Wang: writing – review & editing. Haowen Zou: writing – review & editing. Bo Chen: writing – review & editing. Rui Sun: writing – review & editing. Feng He: formal analysis, funding acquisition, project administration, writing – review & editing.

Conflicts of interest

The authors declare no competing financial interest.

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Supplementary Information for:

Enhanced Sequestration of Sorbed Pb and Cr During the Fe(II)-Catalyzed Transformation of Ferrihydrite

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Text S1 Transmission electron microscope images acquisition

A FEI Tecnai G2 F30 microscope operated at 300 kV was used to obtain Transmission electron microscopy (TEM) images. Interplanar spacing analysis was performed with Digital Micrograph. The images of TEM mapping were obtained from Bruker Nano GmbH (Germany).

Text S2. Cr species determination

Relative proportions of Cr species in reaction products were determined through linear combination fitting (LCF) of 1st derivative of Cr K-edge X-ray absorption near-edge structure (XANES) spectra using K_2CrO_4 , $\text{Cr}(\text{OH})_3$,¹ and Cr_2O_3 as references, respectively, in Athena.

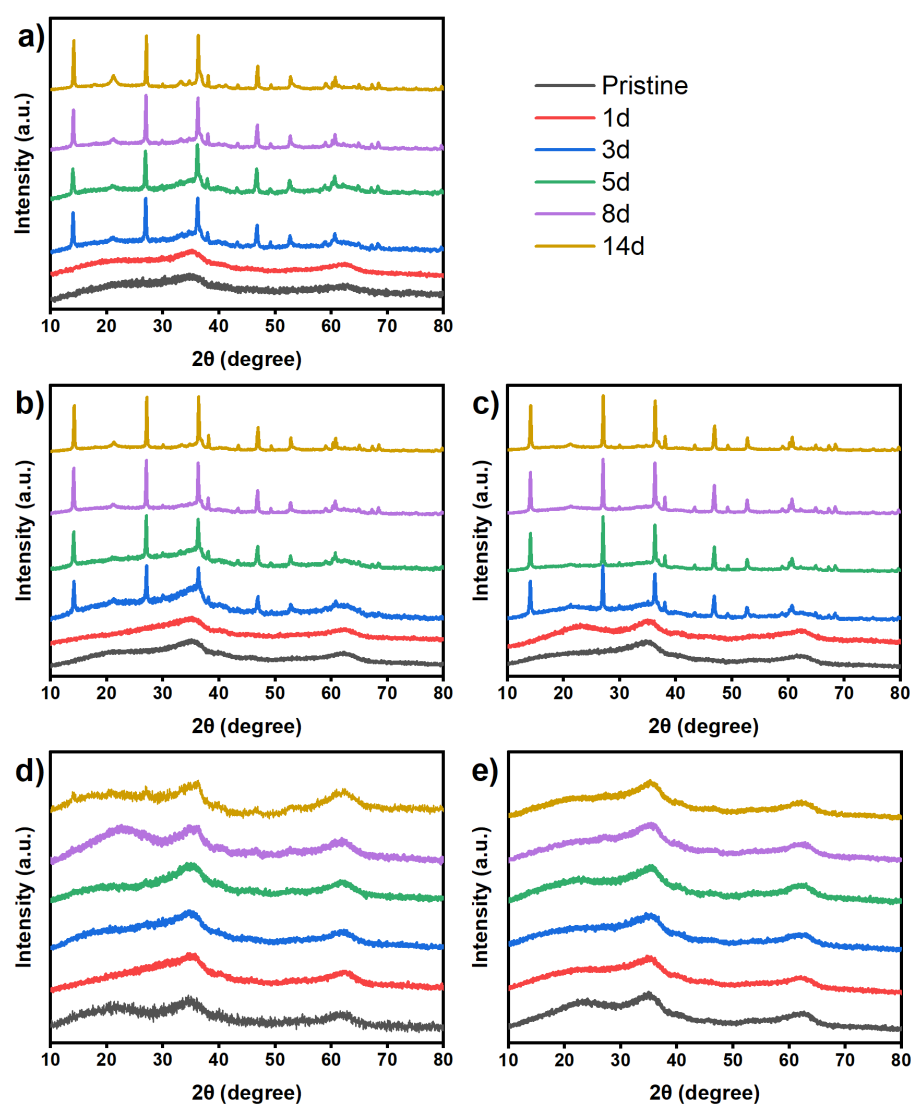


Fig. S1 Evolution of XRD patterns of Fh_0 (a), $\text{FhPb}_{0.5}$ (b), $\text{FhPb}_{1.0}$ (c), $\text{FhCr}_{0.5}$ (d), and $\text{FhCr}_{1.0}$ (e) as a function of reaction duration.

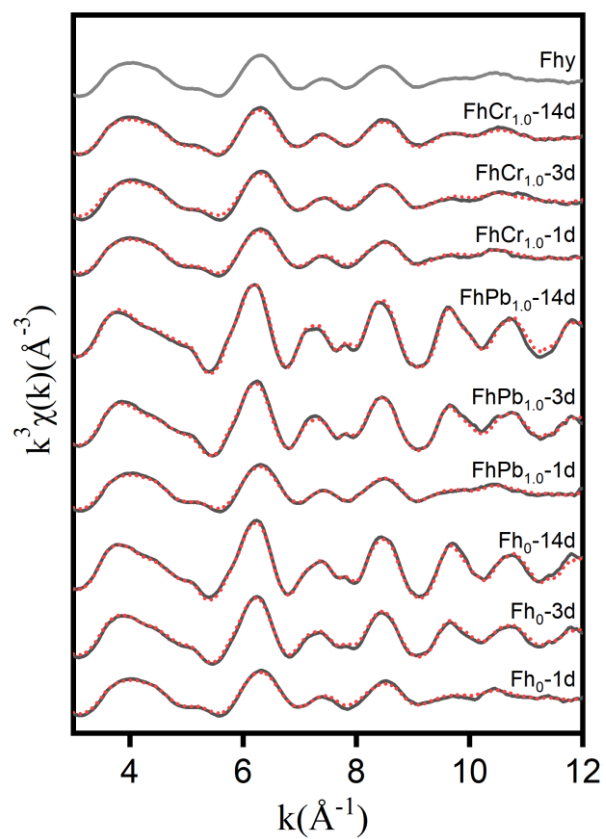


Fig. S2 Linear combination fitting of k^3 -weighted Fe K-edge EXAFS spectra for from reacted Fh_0 , $\text{FhPb}_{1.0}$, and $\text{FhCr}_{1.0}$. Gray lines indicate raw data, and red dotted lines are best fits.

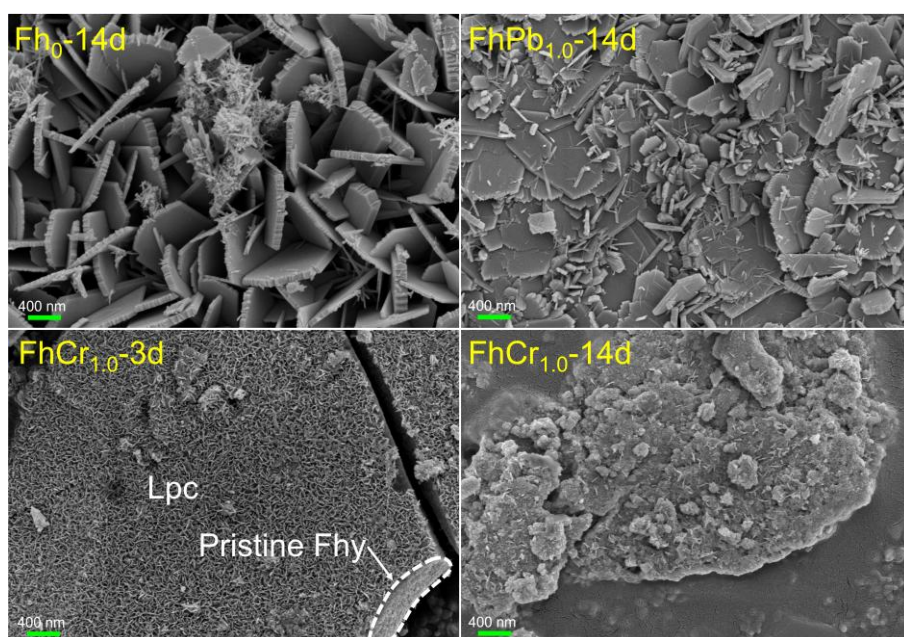


Fig. S3 Low-resolution SEM images of Fh_0 , $FhPb_{1.0}$, and $FhCr_{1.0}$ reacted for 14 days with Fe(II).

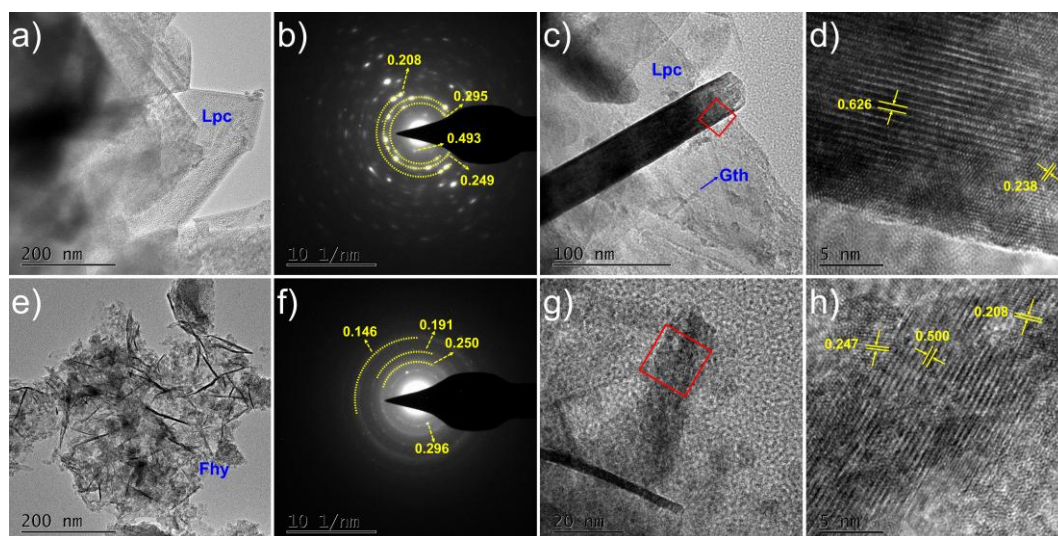


Fig. S4 HRTEM images with low- (a, e) and high- magnification (c, d, g, h) and corresponding selected area electron diffraction (SAED) patterns (b, f) of reacted FhPb_{1.0}-14d (a, b, c, and d) and FhCr_{1.0}-14d (e, f, g, and h). Note: d and h were obtained by magnifying red box areas in c and g, respectively. Lpc and Fhy indicate lepidocrocite and ferrihydrite, respectively. Yellow numbers in b, d, f, and h indicate the interplanar spacings (in nm). The SAED of (a), which was dominated by polygonal plates, displayed bright spots at 0.208 nm, 0.249 nm, and 0.295/0.296 nm, corresponding to 060, 031, and 011 reflections of lepidocrocite (ICDD#08-0098), respectively. The two weak spots in symmetrical positions on either sides of the direct beam indicate the lattice spacing of 0.493 nm, matching the 020 reflection of goethite (ICDD#29-0713). Lattice fringes in (d) with widths of 0.238 nm and 0.626 nm corresponded to the characteristic 111 and 020 planes of lepidocrocite, respectively. The SAED of (e) showed rings at 0.146 nm and 0.250 nm, and spots at 0.296 nm, confirming the dominance of ferrihydrite and the occurrence of lepidocrocite, respectively. A lath with a width of ~20 nm and length of ~50 nm in (g) showed dominated lattice fringes of 0.500 nm, typical for goethite.

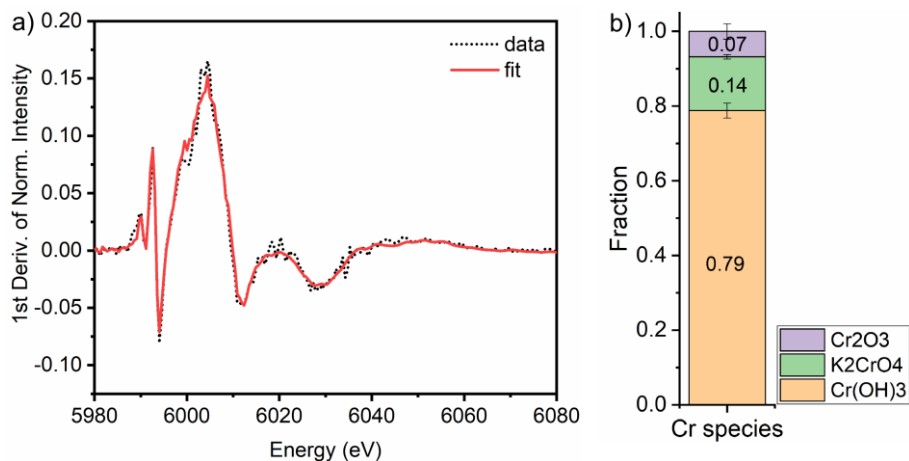


Fig. S5 Linear combination fitting of Cr K-edge 1st derivative of FhCr_{1.0}-14d normalized XANES spectrum (a) and derived composition of Cr species (b).

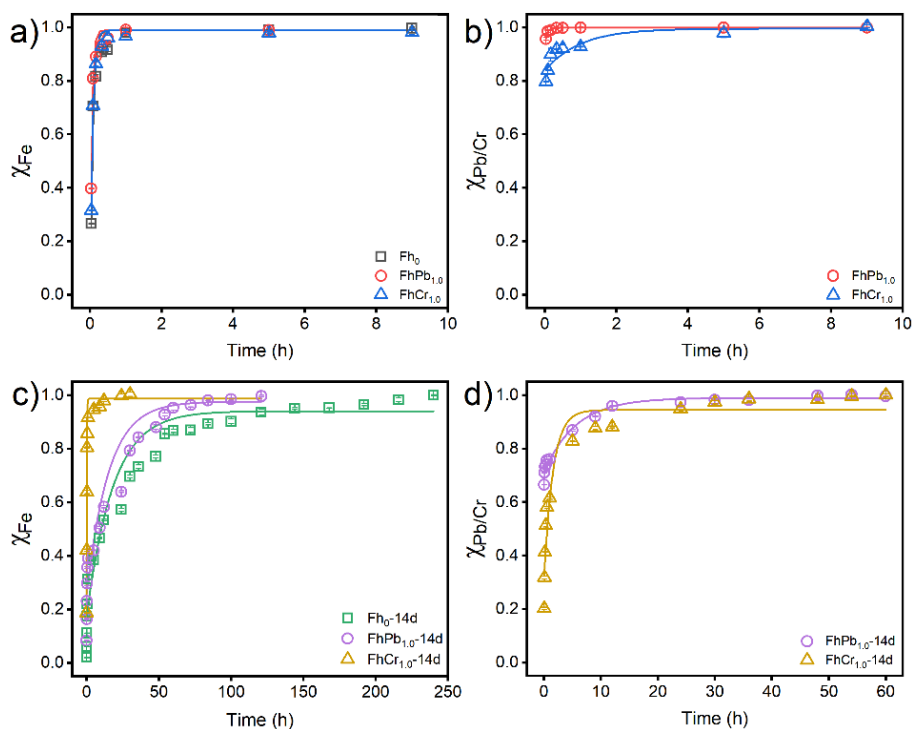


Fig. S6 Fraction of Fe (χ_{Fe}) and Pb/Cr ($\chi_{Pb/Cr}$) released as a function of time upon hydrochloric acid treatment of unreacted Fh₀, FhPb_{1.0}, and FhCr_{1.0} (a, b) and their reacted counterparts (c, d). Symbols represent the data and lines correspond to the fitted model. Note: χ_{Me} is calculated by dividing the real-time concentration of a specific metal by the final (or maximum) release concentration.

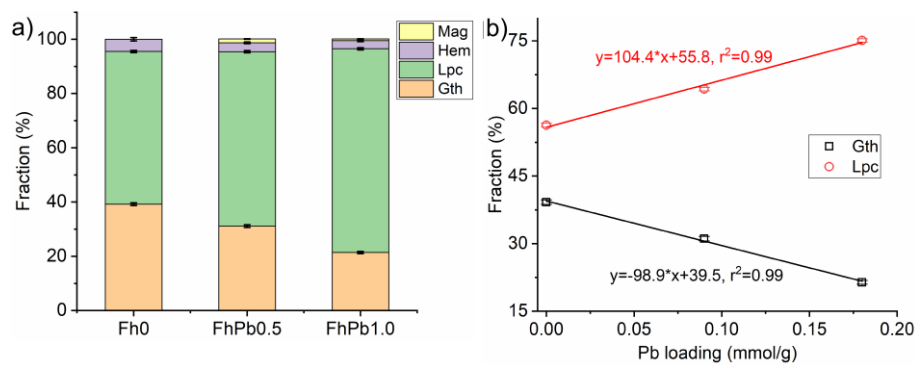


Fig. S7 (a) Product patterns of Fh₀, FhPb_{0.5}, and FhPb_{1.0} reacted with dissolved Fe(II) for 14 days determined via the Rietveld refinement of XRD data using Profex.^{2,3} (b) The correlation between Pb loading vs. the fraction of goethite/lepidocrocite in reacted solids for 14 days.

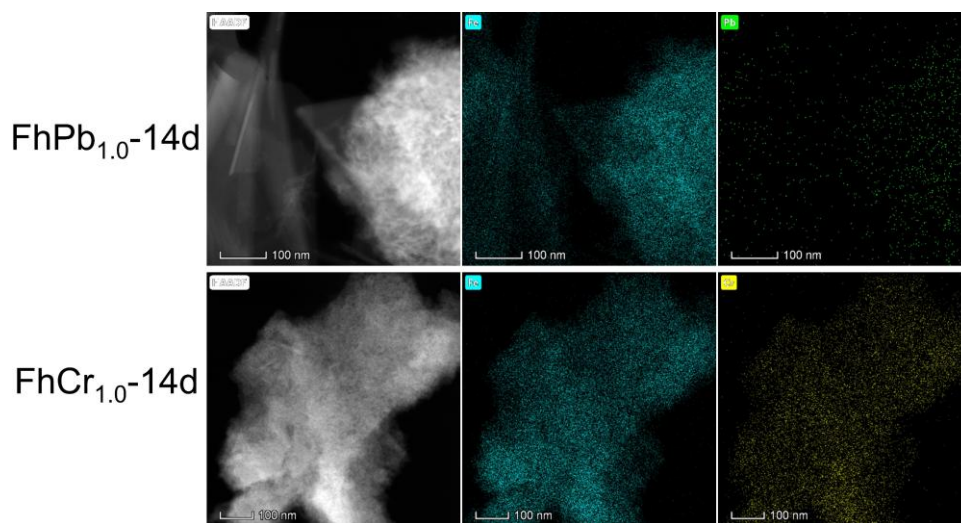


Fig. S8 STEM-EDS maps of reacted FhCr_{1.0} and FhCr_{1.0} showing the distributions of Fe and Pb/Cr within reaction products.

Table S1. Relative proportions of the different FeOx present in reaction products of Fh₀, FhPb_{1.0}, and FhCr_{1.0} as determined from the linear combination fit (LCF) analysis of XAS data by Athena software.

Samples	χ^2	Ferrihydrite/%	Lepidocrocite/%	Goethite/%	Hematite/%	
Fh ₀	1d	0.023	97±1	0	3±2	1±1
	3d	0.010	48±1	43±1	7±2	1±1
	14d	0.011	6±2	62±1	29±2	3±1
FhPb _{1.0}	1d	0.017	94±1	2±1	4±2	0
	3d	0.014	36±2	56±1	9±2	0
	14d	0.017	8±0	84±0	9±0	0
FhCr _{1.0}	1d	0.018	95±1	3±1	2±2	1±1
	3d	0.035	92±2	1±1	6±2	1±1
	14d	0.013	89±1	6±1	4±1	1±1

Table S2. Kinetic parameters of metal release from pristine and reacted solids upon HCl treatment derived from the fit of the chemical data using one-phase exponential decay function.

Sample		y_0	A_1	t_1	K	r^2	Expression ($y=A_1*e^{-t/t_1}+y_0$)
Fh ₀	Fe	0.989±0.009	-1.103±0.097	0.073±0.009	13.783±1.720	0.96	$y=-1.103*e^{-t/0.073}+0.989$
	Pb	0.988±0.006	-1.148±0.105	0.049±0.005	20.505±2.179	0.97	$y=-1.148*e^{-t/0.049}+0.988$
FhPb _{1.0}	Fe	0.999±0.000	-0.073±0.006	0.057±0.006	17.469±1.971	0.98	$y=-0.073*e^{-t/0.057}+0.999$
	Pb	0.988±0.005	-1.081±0.064	0.067±0.006	14.840±1.212	0.98	$y=-1.081*e^{-t/0.067}+0.988$
FhCr _{1.0}	Fe	0.995±0.008	-0.157±0.019	0.973±0.346	1.028±0.366	0.87	$y=-0.157*e^{-t/0.973}+0.995$
	Cr	0.940±0.023	-0.770±0.034	18.176±2.752	0.055±0.008	0.96	$y=-0.770*e^{-t/18.176}+0.940$
Fh ₀ -14d	Fe	0.976±0.027	-0.725±0.034	15.100±2.473	0.066±0.011	0.96	$y=-0.725*e^{-t/15.100}+0.976$
	Pb	0.990±0.007	-0.278±0.010	5.577±0.737	0.179±0.024	0.98	$y=-0.278*e^{-t/5.577}+0.990$
FhPb _{1.0} -14d	Fe	0.987±0.007	-0.905±0.038	0.198±0.017	5.050±0.424	0.98	$y=-0.905*e^{-t/0.198}+0.987$
	Cr	0.945±0.024	-0.632±0.048	1.563±0.391	0.640±0.160	0.94	$y=-0.632*e^{-t/1.563}+0.945$

Note:

A_1 - Initial Amplitude;

t_1 - Decay Time Constant, and $K = 1/t_1$, represents the rate constant;

y_0 - Baseline Offset or Equilibrium Concentration.

Table S3. Mineralogical composition of Fh₀, FhPb_{0.5}, and FhPb_{1.0} reacted for 14 days and those structural parameters derived from the Rietveld refinement of XRD data using Profex.^{2, 3}

Sample		Fh ₀ -14d	FhPb _{0.5} -14d	FhPb _{1.0} -14d
R _{WP}		1.83	2.05	2.02
χ^2		0.89	1.01	1.03
Goethite	wt%	39.2(5)	31.1(5)	21.4(4)
	A	4.618(1)	4.616(2)	4.614(3)
	B	9.957(2)	9.967(4)	9.968(4)
	C	3.023(0)	3.021(0)	3.021(0)
Lepidocrocite	wt%	56.3(4)	64.3(4)	75.1(4)
	A	3.871(0)	3.871(0)	3.871(0)
	B	12.523(0)	12.525(1)	12.526(1)
	C	3.070(0)	3.070(0)	3.070(0)
Hematite	wt%	4.5(6)	3.3(3)	3.0(4)
	A	5.070	5.052(2)	5.070
	C	13.700	13.700	13.830
Magnetite	wt%	n.d.	1.4(1)	0.6(1)
	A	n.d.	8.361(2)	8.347(3)

Note: a, b, and c represent of unit-cell parameters (Å); n.d.: not detected.

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