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Redox Interaction between Selenite and Mackinawite in Cement Pore Water

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29 **Abstract**

30 In cement-rich radioactive waste repositories, mackinawite (FeS) could form at the
31 steel corrosion interface within reinforced concrete and potentially retard the transport
32 of redox-sensitive radionuclides (e.g., ⁷⁹Se) in cement porous media. Redox
33 interactions between selenite and mackinawite in hyperalkaline conditions remain
34 unclear and require further investigations. Here, using a comprehensive
35 characterization on both aqueous and solid speciation, we successfully monitored the
36 whole interaction process between selenite and mackinawite in hyperalkaline
37 conditions. Results show similar chemical environments for SeO_3^{2-} and $\text{S}^{2-}/\text{S}_n^{2-}$ at the
38 mackinawite-water interface, verifying an immediate reduction. After 192 h reaction,
39 SeO_3^{2-} was reduced to Se^0 and SeS_2 , accompanied by the oxidation of $\text{S}^{2-}/\text{S}_n^{2-}$ to
40 $\text{S}_2\text{O}_3^{2-}$ and Fe(II) to Fe(III) in mackinawite. Aqueous results showed that ~99 % of
41 aqueous selenium was present as Se_4S nano-particles due to the dissolution of Se from
42 the solid. In parallel, ~62% of $\text{S}^{2-}/\text{S}_n^{2-}$ was released into the solution, with
43 mackinawite transforming to magnetite, $\text{Fe}(\text{OH})_3$ and FeS_2O_3^+ complexed to Cl^- or
44 OH^- species, and magnetite subsequently dispersed in the solution. This study
45 provides valuable data about the retardation mechanisms of redox-sensitive
46 radionuclides by soluble iron sulfides, which is critical to advance our understanding
47 on reactive concrete barriers used in nuclear waste disposal systems.

48 **Synopsis:** The comprehensive investigation of the fate of Se, S and Fe under
49 hyperalkaline conditions promotes a better description of cement-rich radioactive
50 waste repository environments.

51 **Key words:** mackinawite, selenite, cement pore water, interaction mechanism,
52 reactant fate

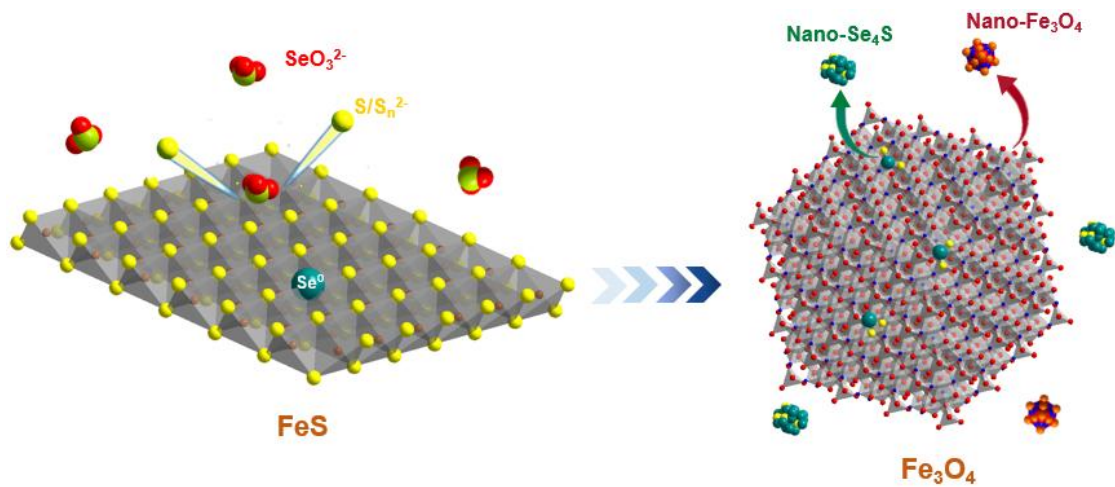
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57 **Table of Contents (TOC)**



58

59 **1. Introduction**

60 The trace element selenium (Se) is essential for human health, but highly toxic when
61 exceeding the appropriate intake range.¹ ⁷⁹Se is one of the ²³⁵U fission products, with
62 a long half-life of 4.8×10^5 years. Its safe disposal is a requisite to the sustainable
63 development of nuclear industry. Oxidized species of selenium are highly mobile,
64 which has stimulated the research on selenium interactions with potential
65 anthropogenic or natural barriers such as clays²⁻⁴, cements⁵⁻⁷ or Fe phases^{4, 8-12}. The
66 various oxidation states of selenium (-II, -I, 0, +IV, +VI) and their complexation
67 ability with inorganic and organic matter make selenium chemistry complex. Under
68 oxidizing conditions, Se often occurs as highly soluble and thus mobile oxyanionic
69 forms, i.e., SeO₃²⁻ and SeO₄²⁻. In contrast, under reducing conditions selenium adopts
70 oxidation states of 0, -I and -II, having much lower solubility and mobility. This
71 makes reductive immobilization an important pathway to decrease Se transport in the
72 environment. Determining the ability of different barrier materials to reduce selenium
73 species is therefore of high importance for the safety assessment of radioactive waste
74 disposal initiatives.

75 The CEM-V/A cement, highly resistant to sulfate corrosion, is being evaluated as an
76 engineered barrier for deep underground radioactive waste disposal in France.
77 Mackinawite (FeS), a precursor of thermodynamically more stable iron sulfides
78 minerals (e.g., greigite and pyrite), can be present naturally in host rocks of claystone
79 and granite, and also in engineered concrete structures, such as at steel corrosion
80 interfaces.¹³ Its high reactivity and large specific surface area lead to a high potential
81 to immobilize soluble ions, e.g., heavy metals and radionuclides¹⁴⁻¹⁸. Previous studies
82 have shown that Se(IV) can be reduced to a tetragonal FeSe-like phase after being in
83 contact with mackinawite under acidic and anoxic conditions. However, red Se(0)
84 nanoparticles could be formed though the reduction of Se(IV) by mackinawite at
85 higher pH.¹⁰ Along with the Se(IV) reduction, mackinawite was oxidized to green rust
86 firstly and then to magnetite or goethite. Besides, both aqueous Fe(II) and S(-II) were
87 able to reduce Se(IV) to Se(0) under highly alkaline conditions (e.g., at pH ~13.29)¹⁹.
88 Meanwhile, other studies observed that Se(IV) could be reduced to elemental Se or
89 Se-S precipitates (e.g. $\text{Se}_n\text{S}_{8-n}$) by aqueous sulfide species.²⁰ However, to the best of
90 our knowledge, little data on selenite sorption on mackinawite in the presence of
91 cement pore water (at high pH) has been reported in literature. More specifically,
92 precise information about the detailed interaction mechanism and the fate of each
93 reactant in abiotic reduction processes by mackinawite under hyperalkaline conditions
94 have not been fully unravelled. Considering that the geochemistry of selenite has
95 close relationship with the chemical cycles of iron and sulfur in cement-rich
96 repositories, a deeper knowledge about the interplay between selenite and
97 mackinawite under the chemical environment of underground concrete structures (i.e.,
98 hyperalkaline and reducing conditions) is strongly required.

99 In this study, we have investigated the interaction mechanism between SeO_3^{2-} and
100 mackinawite in cement pore water (CPW), the solution from the interconnected pore
101 structure produced by cement hydration, using a combination of X-ray absorption
102 spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), transmission electron

103 microscopy (TEM) and wet chemistry methods. This work contributes to advance the
104 understanding on the interaction mechanisms between redox-sensitive radionuclide
105 oxyanions and iron sulfides and to promote our knowledge on redox chemical
106 processes within reactive concrete barriers.

107 **2. Materials and Methods**

108 **2.1 Materials and Chemicals.** All chemicals used for synthesis of mackinawite (FeS)
109 and stock solution (CPW) were analytical reagents. Boiled and N₂-degassed Milli-Q
110 water (18.2 MΩ·cm) was used for all solutions and suspensions. Sodium selenite
111 (Na₂SeO₃·5H₂O) and chemicals used for FeS synthesis and stock solution were
112 purchased from Sigma–Aldrich. Synthetic fresh CPW at pH ~13.5 according to the
113 recipe from CEA²¹ was used as matrix solution in all reactors, with its chemical
114 composition shown in Table S1. All experiments were performed in a 99.99%
115 N₂-filled glovebox (O₂ < 2 ppm, using NaOH as the CO₂ trap) to prevent oxidation
116 and possible CO₂ contamination. The mackinawite suspension was prepared
117 following the method reported previously¹⁰. More details are shown in Text S1 of the
118 Supporting Information. The synthesized mackinawite solid was prepared on a silicon
119 plate, sealed in the air-tight powder holder, and then checked by powder X-ray
120 diffraction (XRD) (Bruker axs, D8 advance) with Vortex-EX detector (Hitachi) under
121 Cu Kα radiation, showing no distinct impurity diffraction peak (Figure S1). The
122 specific surface area of mackinawite was determined to be 102.3 m²/g by the
123 Brunauer–Emmett–Teller (BET) N₂ absorption method. The surface site density was
124 assumed to be 4 site nm⁻² and thus the corresponding surface-site concentration was
125 1.36 mM. The size and shape of the mackinawite particles were further characterized
126 by TEM as illustrated in Figure S2.

127 **2.2 Wet chemistry experiments.** Sorption experiments of SeO₃²⁻ on mackinawite
128 were performed at 25 °C under constant shaking and anoxic conditions (< 2 ppm O₂).
129 The system was tightly closed, except during sampling, to avoid CO₂ contamination.
130 The solid-to-liquid (S/L) ratio in all the reaction suspensions was set to 2 g/L. The

131 initially added concentration of SeO_3^{2-} was 4.70 mM. Prior to introducing SeO_3^{2-} ,
132 mackinawite was equilibrated with CPW for 24 h. The pH of suspension was
133 measured by a combined glass Micro-pH electrode (Metrohm 6.0234.100) during the
134 reaction after its calibration by pH 4.00, 7.01, 10.00 and 12.00 standard solutions. A
135 combined Pt-ring ORP electrode (Metrohm 6.0451.100) was used for the Eh
136 measurement, after being calibrated with Zobell's solution (200 mV at 25 °C).²²
137 Samples of 10 mL of the suspension were filtered by 0.22 μm nitrocellulose
138 membrane by vacuum filtration at reaction times of 1, 17, 24, 50, 73, 96, 138 and 192
139 hours. Extreme care was taken to minimize the potential for sample oxidation during
140 subsequent solid characterizations (see the details in Text S2). Total aqueous
141 concentrations of S, Fe and Se in the filtrates were analyzed by inductively coupled
142 plasma optical emission spectrometry (ICP-OES) with a Varian 720-ES apparatus.
143 The concentrations of SeO_3^{2-} and sulfur species, including $\text{S}^{2-}/\text{S}_n^{2-}$, SO_3^{2-} and SO_4^{2-} ,
144 were analyzed by ion chromatography (Dionex ICS-6000) with an Dionex™
145 IonPac™ AS9-HC IC Columns with 0.8 mL/min Na_2CO_3 (12.5 mM) as eluent. The
146 retention time and calibration curves for SeO_3^{2-} and sulfur species were shown in
147 Figure S3 and the standards of IC were cross-checked by ICP-OES.

148 **2.3 X-ray Absorption Spectroscopy (XAS).** Iron and selenium K-edge X-ray
149 absorption near-edge structure (XANES) and extended X-ray absorption fine structure
150 (EXAFS) spectra were collected at the Core Level Absorption & Emission
151 Spectroscopy (CLÆSS, BL22) beamline at the Spanish synchrotron ALBA-CELLS,
152 Barcelona, Spain. Elemental Se foil and Fe foil were used for energy calibrations in
153 parallel with the measurements at the Se K-edge (12.658 keV) and Fe K-edge (7.112
154 keV), respectively. Si(111) and Si(311) double crystal monochromators were used
155 with approximately 0.3 eV resolution at 2.5 keV. A silicon drift detector (KETEK
156 GmbH AXAS-M with an area of 80 mm²) was employed to collect the fluorescence
157 signal. All the samples for XAS were double-face sealed using polyimide tape,
158 mounted on a sample holder, and measured in fluorescence mode, except for Se and

159 Fe references, which were prepared as pellets with a cellulose matrix and measured in
160 transmission mode. Before being transferred into the vacuum experimental chamber,
161 samples were stored under N₂ atmosphere. For EXAFS signal collection, a liquid N₂
162 cryostat was used to lower the temperature to 77 K, in order to minimize the effects of
163 thermal disorder due to atomic vibrations. The data integration and reduction of
164 XANES and EXAFS spectra were performed by the Demeter software package.²³
165 Linear combination fits (LCF) were applied to identify and quantify the components
166 in samples. Regarding the quantitative EXAFS fit of Se samples, radial distribution
167 functions were obtained by Fourier Transform (FT) of k^3 -weighted EXAFS
168 oscillations (k -range: 3.0–12.0 Å⁻¹) using a Kaiser-Bessel window. FEFF8.4 was used
169 to calculate the theoretical backscattering paths to perform the fits of radial
170 distribution functions.²⁴ Only the first atomic shell ($R+\Delta R$: 1.0–2.7 Å) was fitted
171 considering the quality of the EXAFS data.

172 **2.4 Transmission Electron Microscopy (TEM).** The pristine mackinawite, as well
173 as the solids and nano-sized colloids after reaction, were analyzed by TEM
174 (JEM-2100F) with energy dispersive X-ray spectroscopy (EDS). The solid samples
175 were dispersed in ethanol and sonicated for 5 min, while no treatment was performed
176 for the supernatant. A drop of treated samples was deposited on ultra-thin carbon
177 grids for the measurement. TEM images were collected at 200 keV. Gatan Digital
178 Micrograph software was used to analyze the images.

179 **2.5 X-ray photoelectron spectra (XPS).** XPS was recorded with a Kratos Axis Ultra
180 electron spectrometer equipped with a delay line detector. The reacted solid was
181 collected and dried in the glove box and then brought to the XPS facility using an
182 anaerobic jar. To avoid any oxidation, the samples were quickly transferred to the
183 XPS chamber. A monochromatic Al K α source operated at 150 W, a hybrid lens
184 system with a magnetic lens providing an analysis area of 0.3 mm \times 0.7 mm, and a
185 charge neutralizer were employed for the measurement. The energy step was set to
186 0.1 eV for collecting Fe and S data. The binding energy was always calibrated using

187 C 1s peak (284.8 eV). The XPS spectra of Fe 2p and S 2p were fitted using the
188 CasaXPS software with Gaussian Lorentzian function through
189 background-subtraction corrections using a Shirley-type optimization.

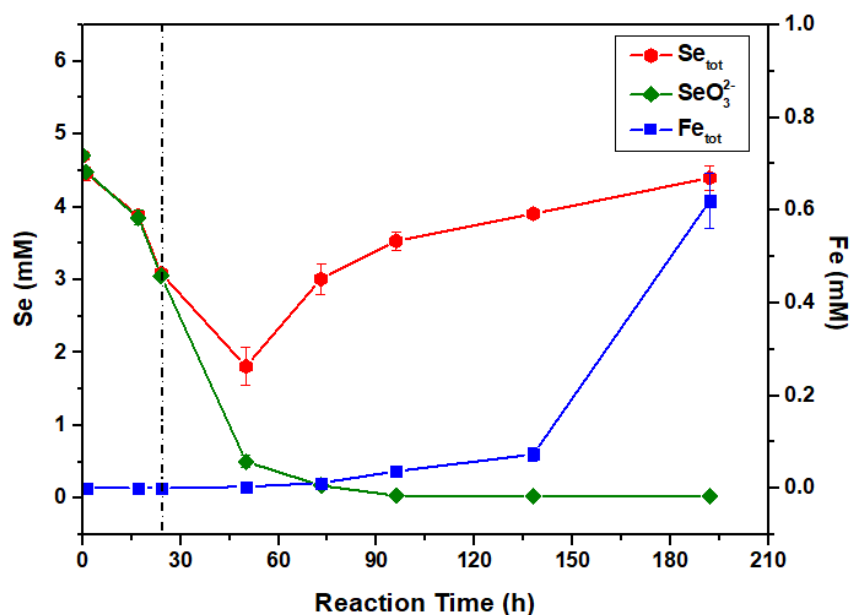
190 **3. Results and Discussion**

191 **3.1 Selenium reduction kinetics**

192 The pH of the suspension stayed constant for the entire duration of the experiment,
193 whereas the Eh decreased during the first 50 h and then remained stable until 192h
194 (Figure S4). The Eh decrease could result from the continuous consumption of
195 oxidants (i.e., Se(IV)), in good accordance with the Se(IV) concentration decrease as
196 shown in Figure 1. Aqueous concentrations of SeO_3^{2-} and total Se during the reaction
197 with mackinawite are shown in Figure 1. Nearly all the aqueous SeO_3^{2-} was removed
198 by mackinawite after 96 h. Specifically, during the first 24 h the aqueous
199 concentration of total Se was equal to that of SeO_3^{2-} , indicating that SeO_3^{2-} was the
200 only species in aqueous phase and that the decreased amount of SeO_3^{2-} was retained in
201 the bulk solid phase. More intriguingly, after reacting for 50 h the aqueous
202 concentration of SeO_3^{2-} continued to decrease while the total concentration of
203 selenium as determined in the filtrate was increasing with reaction time. This suggests
204 that the reduction products of SeO_3^{2-} could be nano-sized, such as nano- Se^0 , resulting
205 in a colloidal dispersion in the suspension, which could not be separated out by the
206 0.22 μm membrane. After reaction for 73 h, the concentration of Se(IV) decreased to
207 0.17 mM but the Se_{tot} concentration was 3.01 mM, which implied a concentration of
208 2.84 mM aqueous Se nanoparticles in the solution. Although previous studies also
209 showed that mackinawite had an extremely strong affinity towards Se(IV), the
210 formation of nano- Se^0 colloids has been rarely reported.^{2,25,26} The distinct reaction
211 kinetics and products observed here could be probably related to the hyperalkaline
212 nature of CPW. The disassociation of nano- Se^0 from the solid adsorbent was likely to
213 be accompanied with a dissolution of mackinawite, which will be discussed afterwards
214 in detail. Meanwhile, the filtrate colors turned yellow after 24 h reaction from

215 transparent (1 h) to orange (50 h), olive (73 h) and black (138 h and 192 h), as shown
216 in Figure S5. The orange color at 50 h might suggest that SeO_3^{2-} was reduced to red
217 Se^0 nanoparticles that were released to the solution afterwards. Han et al and
218 Breynaert et al. also observed that the mackinawite suspension turned red after
219 interacting with Se(IV) regardless of the ratios of Se(IV)/FeS; they speculated that
220 Se(0) particles formed through Fe-mediated Se(IV) reduction.^{2, 25} Therefore, the total
221 Se concentration of the filtrate took into account both aqueous SeO_3^{2-} and dispersed
222 nanosized Se^0 species. At 192 h, the concentrations of Se_{tot} and Se(IV) measured in
223 the filtrate were 4.40 mM and 0.031 mM, respectively, indicating that ~ 0.3 mM (6
224 %) of Se was adsorbed on the solid and ~99 % of aqueous Se was reduced species.
225 The mass balance of Se in the filtrate (measured) and filtered solid (calculated) at
226 different reaction times is listed in Table S4. Moreover, the filtrate color continued to
227 change, and turned olive and black from 73 to 192h, indicating the possible formation
228 of green rust and magnetite. This was due to the oxidation of FeS and the subsequent
229 release of iron nanoparticles into the solution, which caused the increased of
230 measured Fe concentrations (Figure 1). The chemical interactions between
231 mackinawite and SeO_3^{2-} in CPW (pH ~13.5) were simulated by Phreeqc modelling
232 using the Andra THERMOCHEMIE database.²⁷ The experimental aqueous Fe
233 concentration (0.62 mM at 192 h) is comparable with but lower than the calculated
234 values of 1.5 mM $\text{Fe}(\text{OH})_3^-$ and 1.7 mM $\text{Fe}(\text{OH})_4^-$, respectively. This is probably due
235 to the lack of thermodynamic equilibrium. Note that the measured Fe concentrations
236 in the filtrates also include the contributions from nano-sized magnetite as indicated
237 by the dark colour of filtrates in Figure S5. The precise forms of Se-solid species were
238 further explored using XAS.

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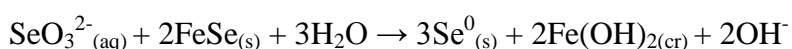


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241 Figure 1. Measured concentration of SeO_3^{2-} by IC, total Se and Fe by ICP-OES in
 242 CPW as a function of the reaction time.

243 In XAS, the XANES region of the probed element can be used as a fingerprint of the
 244 chemical species, which depends both upon the valence state and the coordination
 245 environment. Se K-edge XANES spectra were collected for solid samples at different
 246 reaction times. LCF results of the solids and the references are shown in Figure 2.
 247 After reacting for 1 h, SeO_3^{2-} was mainly reduced into 35.8(3.0)% FeSe_2 , 35.5(9.2)%
 248 FeSe and 19.2(1.0)% SeS_2 , while only 4.9(2.9)% Se^0 and 4.9(1.2)% SeO_3^{2-} could be
 249 identified, indicating that SeO_3^{2-} can be quickly adsorbed on the surface and reduced
 250 to $\text{Se}(0, -I, -II)$. From 24 h to 196 h, all the spectra showed similar features, with
 251 ~63% SeS_2 and 30-32% Se^0 identified to be the primary solid Se species. In contrast,
 252 previous studies at lower pH demonstrated that nano Se^0 was the main reduced Se
 253 product.^{10, 19, 25} Kang et al. found that $\text{Se}(-II)$ was transformed to elemental Se in the
 254 presence of remaining non-reduced selenium oxyanions.²⁹ Therefore, the reduced
 255 species of FeSe and FeSe_2 after reacting for 1 h could be oxidized by the residual
 256 SeO_3^{2-} forming $\text{Se}(0)$ at 24h and the corresponding reaction would be:

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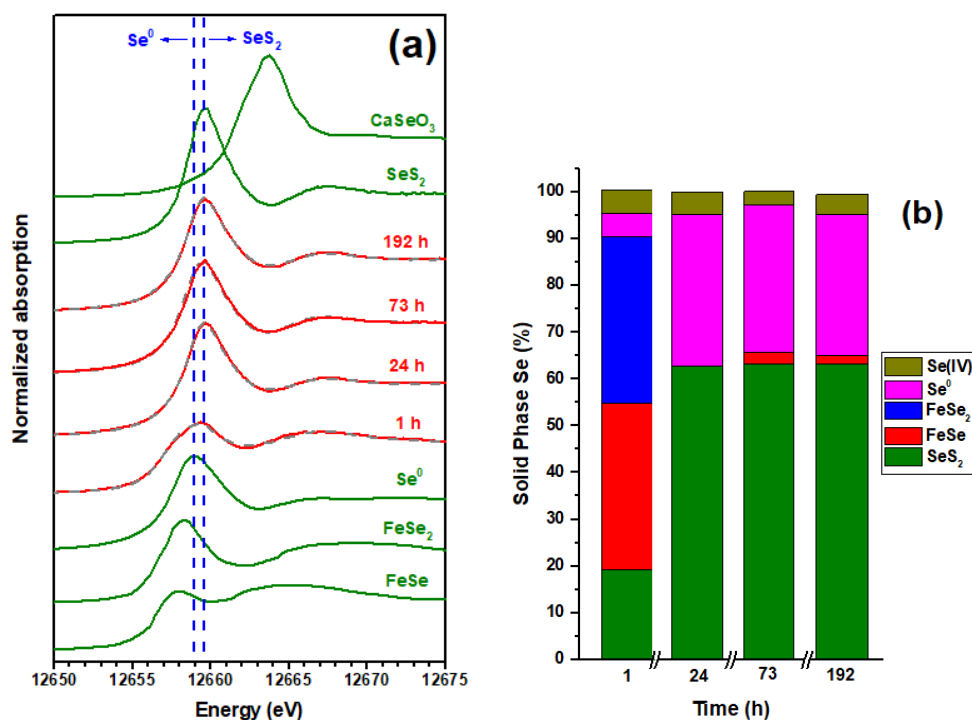


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EXAFS data were fitted to determine the coordination environments of adsorbed

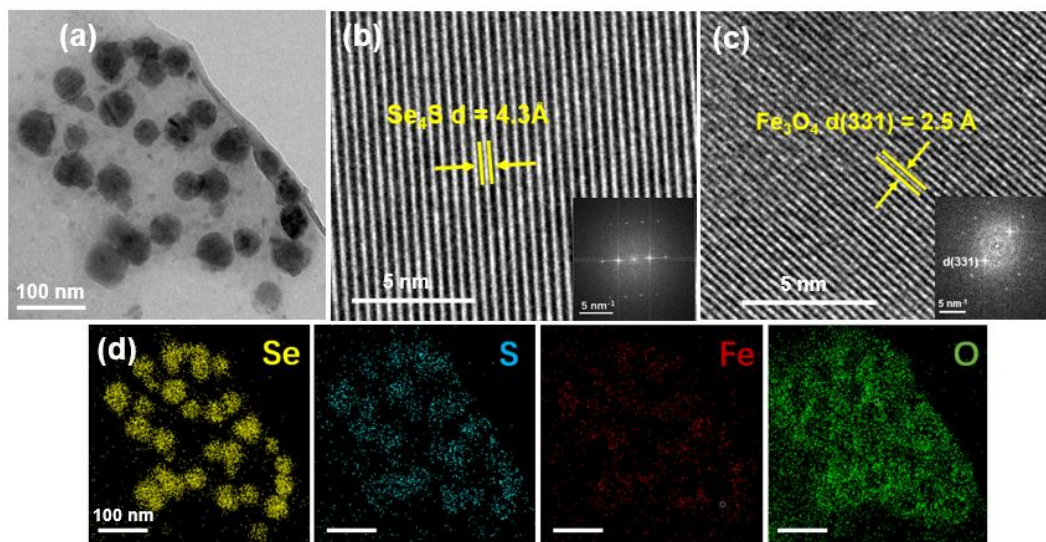
259 selenium, as shown in Figure S6. Fitting the main peak in R space allowed obtaining
260 interatomic distances and coordination numbers (CN) for the first two coordination
261 shells. As shown in Table S2, the spectrum of the 1 h sample yielded a CN ~ 1.7
262 Se-Fe pair at 2.31 Å and CN ~ 1.1 Se-Se pair at 2.61 Å. The Se-Se backscattering path
263 used was the average from the Se-Se paths of FeSe, FeSe₂, SeS₂ and Se⁰. Regarding
264 samples from 24, 73 and 192 h, apart from the Se-Se pair that was fitted at ~ 2.3 Å
265 with a CN ~ 1.5 , a backscattering signal from Se-S pair was also observed, resulting
266 in a CN of $\sim 0.6-0.9$ with $d_{\text{Se-S}} = \sim 2.1$ Å. The EXAFS fits also confirmed the existence
267 of SeS_x species in the solid product. Diener et al. reported that selenium, belonging to
268 the family of chalcophile, can incorporate into the structure of mackinawite and pyrite
269 by replacing S sites and consequently forming zero-valent Se. Also, the decreased
270 coordination number of the neighbour Se atoms around the incorporated Se⁰ site
271 indicated a small cluster size,³⁰ in good agreement with our study. With regard to the
272 SeS_x precipitate, the zero-valence selenium and sulfur are miscible in all proportions
273 and can form cyclic-structures (e.g. Se_nS_{8-n}). Previous studies have showed that
274 Se_nS_{8-n} are susceptible to form and precipitate as a result of Se(IV) reduction by
275 sulfide, though the resulting sulfur-to-selenium ratio varied from 1.7 to 2.3.³¹
276 However, TEM imaging and EDS mapping analysis did not succeed in identifying Se⁰
277 nanoparticles and Se-S precipitates on the surface of solid sample for 192 h (the
278 expected shape of Se-S particles is irregular and the elemental Se can adopt
279 nanospheres and nanorod-like morphologies).^{32,33} Furthermore, no obvious selenium
280 peaks of 50 and 192 h filtered solids were checked by XRD probably due to the poor
281 crystallinity or detection limit (Figure S7). The Se was therefore likely to be present
282 forming very small precipitates or amorphous atomic level cooperation with S (Figure
283 S8). By combining with the information from Se K-edge XANES results, we
284 proposed that SeO₃²⁻ was adsorbed onto surface sites corresponding to the S²⁻/S_n²⁻
285 environment of mackinawite, and it was reduced by neighboring S²⁻/S_n²⁻ or Fe²⁺,
286 forming a very fine Se⁰ phase or amorphous cluster followed by the formation of Se-S
287 through the immediate bonding to Se⁰ and S. The S²⁻/S_n²⁻ that was substituted by

288 SeO_3^{2-} dissolved into the solution (see Section 3.2). The Eh-pH diagrams of Se and Fe
289 species calculated using Andra THERMOCHEM database are shown in Figure S9.
290 It is worth noting that after 192 h zero-valent Se predominated among Se species,
291 even though ferroselite (FeSe_2) was predicted to be more stable under the
292 experimental conditions of pH \sim 13.5 and Eh \sim -0.4 V as indicated in Figure S9(a). The
293 zero-valent Se is therefore a metastable phase, with slow transformation kinetics from
294 Se^0 to Se(-I). These results allow making a hypothesis to explain the fact mentioned
295 above: the total concentration of selenium was higher than that of SeO_3^{2-} after reacting
296 for 24 h. It can be speculated here that $\equiv\text{Fe-S-Se}^0$ could break down to its constituent
297 parts in CPW, i.e. into $\equiv\text{Fe-S}$ and nano- Se^0 , or $\equiv\text{Fe-OH}$ and nano-sized SeS species.
298 After 192 h, the nanoparticles present in the filtrate were characterized by (S)TEM
299 (Figure 3). As it can be seen, the size of nanoparticles was approximately \sim 20 to 60
300 nm (Figure 3a). The nanoparticles formed at 192 h consisted of Se, S, Fe and O with a
301 ratio of Se to S roughly at 4:1 according to EDS analysis (Figure S10). Generally,
302 elemental Se occurs in three forms: trigonal Se (t-Se), monoclinic Se (m-Se) and
303 amorphous Se (a-Se). The interplanar spacings of trigonal Se that is considered as the
304 most stable allotropic form are 4.96 Å and 3.78 Å along and perpendicular to the
305 helicoid growth direction, respectively,³⁴ which was different from that (4.3 Å)
306 observed in nanoparticles in the filtrate as shown in Figure 3b. Taking into account
307 the EDS results, the interplanar spacing may belong to Se_4S crystalline phase,
308 whereas no data is available to identify the lattice plane of Se_4S . Se species in the
309 filtered solids and filtrates at different reaction times are shown in Table S3. The
310 high-resolution transmission electron microscopy (HRTEM) image (Figure 3c)
311 illustrated that the interplanar spacing was \sim 2.5 Å, corresponding to the (331) lattice
312 plane of magnetite (Fe_3O_4).³⁵ This indicates that mackinawite transformed to
313 nanosized magnetite during the reaction, resulting in the increased Fe concentration
314 with time shown in Figure 1.



315

316 Figure 2. (a) Se K-edge normalized XANES spectra of solid samples after reacting for
 317 1, 24, 73 and 192 h, comparing to Se references. (b) The fractions of FeSe, FeSe₂, Se⁰,
 318 SeS₂ and CaSeO₃ components in each Se-solid sample determined by LCF method.



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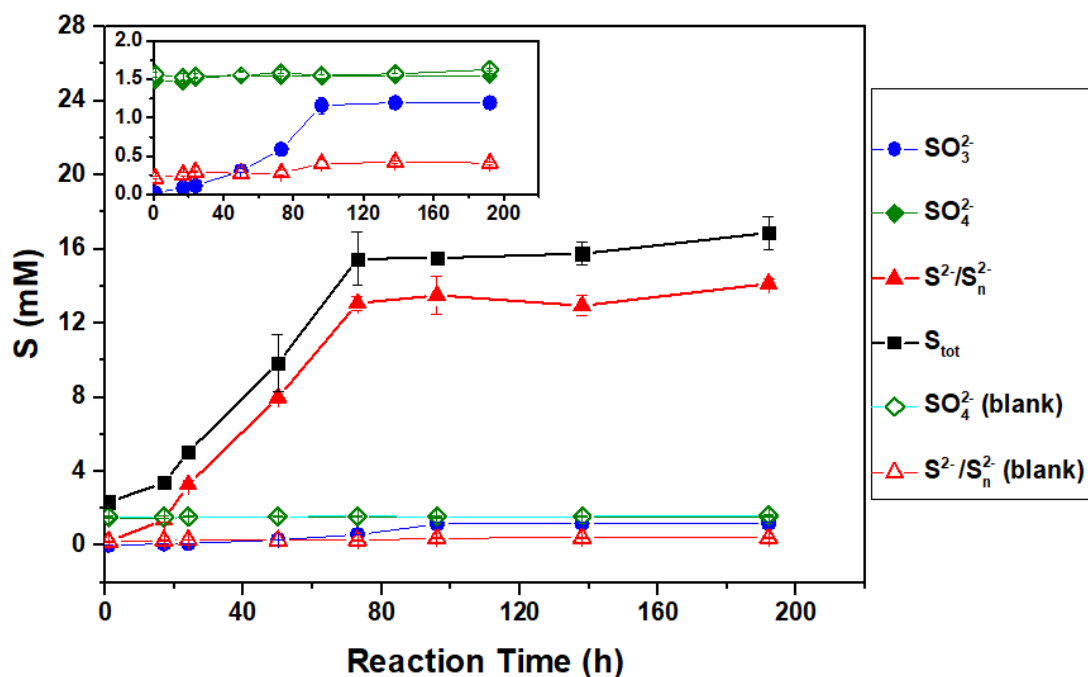
320 Figure 3. Transmission electron micrographs of nanoparticles found in the filtrate
 321 after reaction for 192 h. (a) Transmission electron microscopy image; high resolution
 322 transmission electron microscopy (HR-TEM) image on two spots on a single particle
 323 (b) SeS₄ and (c) Fe₃O₄ with the corresponding Fast Fourier Transform (FFT); (d)

324 Elemental mapping by energy-dispersive X-ray spectroscopy analysis with Se in
325 yellow, S in blue, Fe in red and O in green.

326 **3.2. Dissolution kinetics of mackinawite with/without SeO_3^{2-}**

327 The ion concentrations of CPW equilibrated with mackinawite for 24 hours are shown
328 in Table S4. 1.28 mM Ca^{2+} was removed from the original CPW by mackinawite after
329 24 h equilibration, nearly equal to the value of the mackinawite surface-site
330 concentration of (1.36 mM). The pH value (~ 13.5) of CPW was much higher than the
331 point of zero charge of mackinawite (7.5).³⁶ It is reasonable to think thus that the
332 negatively charged surface of mackinawite favored the adsorption of Ca^{2+} from CPW
333 leading to the formation of $\equiv\text{FeSCa}^{2+}$ surface species. 0.24 mM S^{2-} and almost no Fe
334 were detected after 24 h, suggesting that mackinawite was not congruently dissolved.
335 However, Phreeqc calculations predicted that 0.06 mM of both HS^- and Fe^{2+} should
336 be released once the dissolution reached equilibrium. A plot of S concentration versus
337 reaction time is shown in Figure 4. It can be seen that when no SeO_3^{2-} was added, the
338 $\text{S}^{2-}/\text{S}_n^{2-}$ concentration increased very slowly and aqueous SO_4^{2-} (blank) was kept
339 constant with increasing reaction time. This suggests a limited dissolution of
340 mackinawite and no significant amount of aqueous SO_4^{2-} adsorbed onto mackinawite.
341 The color of filtrate after 192 h was clear and the measured Eh of the suspension was
342 about -0.402 V, which is closed to the Eh value (-0.398 ± 0.005 V) of the suspension
343 with SeO_3^{2-} (Figure S4). In contrast, in the presence of SeO_3^{2-} , a critical threshold of
344 reaction time (73 h) was observed based on the concentration change of $\text{S}^{2-}/\text{S}_n^{2-}$.
345 Dissolved concentration of $\text{S}^{2-}/\text{S}_n^{2-}$ originating from the solid increased quickly during
346 the first 73 h, remaining roughly constant at 13-14 mM thereafter; the same tendency
347 for the total concentration of sulfur was observed. This supports the hypothesis that 2
348 to 3 $\text{S}^{2-}/\text{S}_n^{2-}$ units were substituted by one SeO_3^{2-} atom according to the concentrations
349 of the two species. The measured concentrations of SO_4^{2-} , $\text{S}^{2-}/\text{S}_n^{2-}$, SO_3^{2-} and total S
350 with the addition of SeO_3^{2-} are shown in Table S6. After reaction for 1 h, the
351 summation (1.74 mM) of SO_4^{2-} , $\text{S}^{2-}/\text{S}_n^{2-}$ and SO_3^{2-} concentrations by IC was lower

352 than the total concentration of S (2.34 mM) by ICP. This suggests that other soluble S
 353 species, probably S^0 , existed in solution. However, it is almost the same value
 354 between the total S concentration and the sum from 24 h to 192 h. It means that no
 355 other S species were present in the filtrates. 14.12 mM S^{2-}/S_n^{2-} was detected in the
 356 filtrate and the dissolution efficiency was ~62% after 192h. The mass balance of S in
 357 the filtrate (measured) and filtered solid (calculated) at different reaction times is
 358 listed in Table S4. Han et al. proposed a mechanism by which Se(IV) was reduced to
 359 FeSe or FeSe₂ by mackinawite at pH 8 and the replaced sulfide by Se released into the
 360 solution, with no detection of aqueous sulfide.²⁵ The SO_4^{2-} concentration remained
 361 1.55 ± 0.03 mM during the reaction, which means that no SO_4^{2-} adsorbed on the
 362 surface of the solid during reaction. A considerable amount of aqueous SO_3^{2-} was
 363 observed following the same kinetic tendency of sulfide, resulting in 1.20 mM SO_3^{2-}
 364 after 192 h. SO_3^{2-} can be present as intermediate but stable species at high pH, as the
 365 presence of S^{2-} seems to inhibit further oxidation of SO_3^{2-} .³⁷



366

367 Figure 4. Measured concentration profiles of (poly)sulfide (S^{2-}/S_n^{2-}), sulfate (SO_4^{2-})
 368 and sulfite (SO_3^{2-}) of the experiment with SeO_3^{2-} and S^{2-}/S_n^{2-} (blank), SO_4^{2-} (blank) of

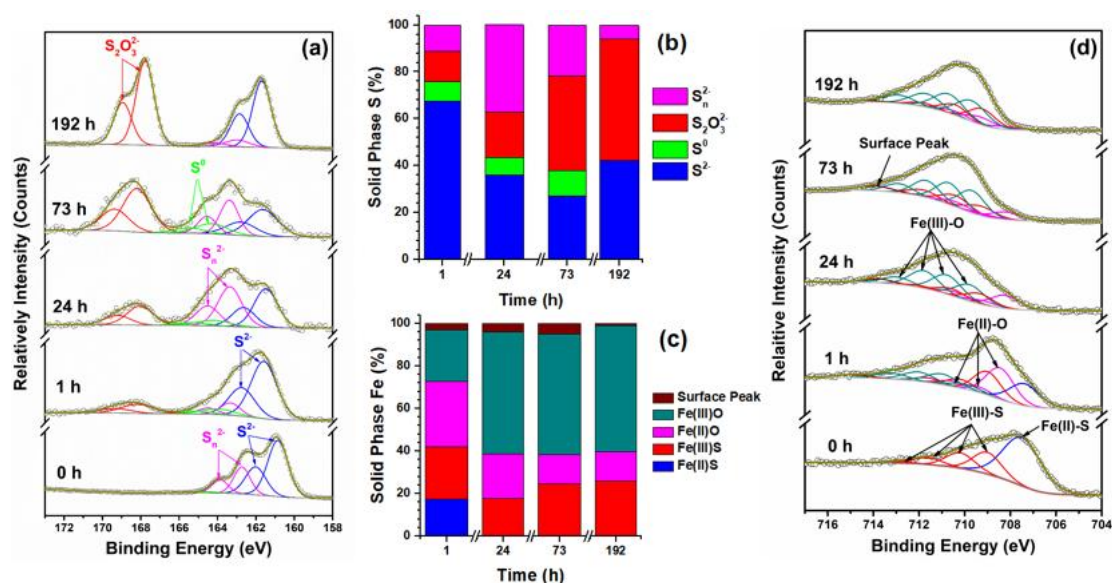
369 experiment without SeO_3^{2-} as a function of reaction time. The inset shows an enlarged
370 view of the less abundant species.

371 **3.3 Possible Reaction Involving Fe, S and Se**

372 S(2p) and Fe(2p_{3/2}) XPS spectra of Se-reacted mackinawite nanoparticles at different
373 reaction times are shown in Figures 5a and 5b. In Figure 5a, to adequately fit the
374 S(2p) spectrum of pure mackinawite (0h), three 2p_{3/2} components at 160.9 eV, 162.7
375 eV and 164.4 eV were required. The one at 160.9 eV, accounting for 71.3% of the
376 total S(2p) signal, was typically attributed to sulfide(S^{2-}); the second component
377 located at 162.7 eV may correspond to polysulfides (S_n^{2-}), taking up 27.3%. The third
378 was fitted to take into account the high energy tail of the S(2p) spectrum, attributed to
379 elemental sulfur S^0 (1.4%) (Table S7).³² The S:Fe ratio of 1.2 derived from TEM-EDS
380 analysis experiments was consistent with the data of previous studies,⁴² and suggests
381 the formation of greigite ($\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{S}_4$) on the surface of mackinawite, although this
382 solid was not identified by XRD.⁴¹ Recently studies revealed the existence of Fe_3S_4
383 species in FeS_{nano} , as a solid-phase precursor of mackinawite, and of edge-sharing
384 FeS_4 species to stabilize FeS structure to form mackinawite.⁴³⁻⁴⁴ In our case, we
385 speculate that Fe_3S_4 , as the representative species of solid S_n^{2-} , reacted with SeO_3^{2-}
386 especially at 1 h. A set of redox and oxidation reactions susceptible to occur between
387 Se couples and the considered solid product couples are listed in Table S8. After
388 reacting with SeO_3^{2-} , the S(2p) spectra exhibited different features, which were
389 characterized by the energy increases (0.6-0.7 eV) of S^{2-} and S_n^{2-} species and probably
390 attributed to surface defects, Ca or Se impact. After 1 h reaction, there is evidence for
391 thiosulfate ($\text{S}_2\text{O}_3^{2-}$) species at 168.0 eV by XPS and an obvious decrease of S_n^{2-} signal
392 of solid coupled to an increase in S^0 and $\text{S}_2\text{O}_3^{2-}$ contributions, indicating that S_n^{2-}
393 (Fe_3S_4) on the surface of mackinawite was oxidized to S^0 and $\text{S}_2\text{O}_3^{2-}$ accompanied
394 with SeO_3^{2-} reduction to FeSe, FeSe_2 and Se^0 (Figure 2). The corresponding half
395 reactions (1)-(5) are listed in Table S8. Oxidation reaction (4) and (5) suggest that
396 S_n^{2-} ($\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{S}_4$) was the active reductant of aqueous SeO_3^{2-} within a short reaction

397 time and was responsible for the formation of FeSe and FeSe₂ at high pH via the
398 formation of Fe(OH)₂ and Fe(OH)₃ species, which was also confirmed in acid
399 solution.⁴⁵ Previous studies showed that SO₃²⁻ reacted with S⁰ to form thiosulfate
400 (S₂O₃²⁻), which is thermodynamically stable and is an excellent complexing agent for
401 metal ions.³⁸ Therefore, the S₂O₃²⁻ species detected in our system were probably
402 formed through the disproportionation reaction. Also, S₂O₃²⁻/S₄O₆²⁻ was observed in
403 the reaction between Se(IV) and pyrite by Han et al.,³⁹ while Scheinost et al. reported
404 that the sulfide in mackinawite was oxidized to elemental sulfur at pH 5.7, coupled to
405 the reduction of Se(IV).⁴⁰ The content of S²⁻ decreased from 67.6% at 1 h to 36.1%
406 after 24 h contact, while an increase of S_n²⁻ and S₂O₃²⁻ content occurred
407 simultaneously. As the oxidation state S within S²⁻ and S_n²⁻ is same, it suggests that
408 S²⁻ was primarily oxidized to S₂O₃²⁻ through the reduction of aqueous SeO₃²⁻ to
409 zero-valent Se (SeS₂ and Se⁰). The increase of solid S_n²⁻ observed in S_{2p} XPS spectra
410 suggests the formation of an intermediate amorphous solid phase Fe₂^{III}Fe^{II}S₄ (later
411 transformed to pyrite), which could account for Fe(III) species in Fe(2p_{3/2}) XPS
412 part.⁴⁶⁻⁴⁸ Finck et al. reported that sulfide, instead of Fe(II), contributed to the
413 reduction of SeO₃²⁻, as indicated by the detection of FeS₂ by XRD.¹⁹ Here, it should
414 be noted as the content of Se-sorbed was quite lower than the mass of solid matrix and
415 the primary Se XPS region is 3d, the interference of Se 3p_{3/2} (161.7 eV) could be
416 neglected. After 73h, the percentage of S₂O₃²⁻ peak area increased to 40.5% and
417 10.8% of S⁰ species were also detected. In contrast, the percentages of S²⁻ and S_n²⁻
418 contributions decreased to 27.1% and 21.5%, respectively, suggesting that S²⁻ and
419 S_n²⁻ were oxidized to S₂O₃²⁻ and S⁰ (equation 5 and 6). From 73h to 192h, more S_n²⁻
420 was oxidized to S₂O₃²⁻, which should be responsible for the reduction of SeO₃²⁻.
421 Usually, the oxidation of S²⁻ followed S²⁻- S_n²⁻ - S⁰ pathway during Se(VI) reduction
422 and more than 90% of S²⁻/S_n²⁻ was oxidized to S⁰ with little amount of S₂O₃²⁻ and
423 SO₄²⁻ at acid or weakly alkaline conditions.^{45,49} In the present study, S₂O₃²⁻ was the
424 only oxidation product after 192 h reaction with Se(IV). The summed concentration
425 of S²⁻/S_n²⁻, SO₃²⁻ and SO₄²⁻ is almost the same value of the total S (Figure 4),

426 indicating that Se(VI)-sorbed onto mackinawite was reduced by solid S^{2-} , not by
 427 aqueous S^{2-} species even though plenty of aqueous S^{2-}/S_n^{2-} were present in solution.
 428 The reduction mechanism is not totally consistent with the one reported for U(VI)
 429 reduction by FeS by Hua et al, who found U(VI)-sorbed to be reduced by either
 430 S^{2-} -solid or dissolved HS^- .⁵⁰ A direct reduction of Se(IV) by aqueous S^{2-} was shown to
 431 be the dominant reaction at low initial pH.¹⁹ Probably aqueous solid S^{2-} was more
 432 reactive for the reduction of Se(IV) than aqueous S^{2-} in CPW. Aqueous S^{2-} was
 433 stable at pH 12.2 under reducing conditions for a long time.⁵¹



434
 435 Figure 5. XPS spectra (a) narrow S(2p) and (d) Fe(2p_{3/2}) (d) XPS scan, and the
 436 fractions of corresponding components of (b) S and (c) Fe species. Circles were
 437 experimental data; bottom solid line was the Shirley background; dashed lines were
 438 the fit to each spectrum and top solid line was the sum of background and fitted
 439 peaks.

440 The broad Fe(2p_{3/2}) spectrum of mackinawite (Figure 5d, 0 h reaction time) could be
 441 fitted by one Fe(II)-S peak at ~707.5 eV and one main peak of Fe(III)-S at 709.1 eV
 442 with three multiple peaks.⁴¹ The area ratio of each multiple peak to the first Fe(III)-S
 443 component is equal to 0.66, 0.31, and 0.10 respectively, in good agreement with other
 444 studies on mackinawite.⁴² The Fe(2p_{3/2}) peaks fitted in the current study are listed in

445 Table S9. Compared with the XPS result of pristine mackinawite, three multiple peaks
446 of Fe(II)-O and four multiple peaks of Fe(III)-O were observed in the Fe 2p spectrum
447 of SeO_3^{2-} -reacted mackinawite at 1 h. This suggests the oxidation of Fe(II) to Fe(III)
448 (equation 7), coupled to SeO_3^{2-} reduction (equation 1). Also, the Fe(II)
449 hydroxyl-complexes are important in alkaline solution and $\text{Fe}(\text{OH})_2$ is probably
450 formed. An increased (33.2%) Fe(III)-O peak intensity and an absence of Fe(II)-S
451 peak are observed after 24 h reaction compared with the 1 h sample, which was
452 probably related to the oxidation of Fe(II) and the further release S^{2-} by the solid. The
453 XPS peak of S^{2-} to be show in Figure 5a at 24 h may be attributed to Fe(III)-S species.
454 Similar results of Fe(II) oxidation to Fe(III) were observed in mackinawite reacted
455 with Se (IV) at different pH values.^{25,40} As reaction time increased to 73 h, the content
456 of Fe(III)-O remained constant, indicating that no more SeO_3^{2-} was reduced by Fe(II).
457 Mixtures of Fe(II)-O and Fe(III)-O observed on the solid surface may imply a
458 formation of multi-valent iron (oxyhydr)oxides such as green rust, magnetite, or other
459 phases containing both ferrous and ferric sites.⁵² Furthermore, the presence of
460 Fe(III)-S species was probably due to the transformation of FeS to amorphous
461 $\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{S}_4$ resulting in the enrichment of S combined with Fe(III) or/and the
462 formation of $\text{Fe}^{\text{III}}\text{S}_2\text{O}_3^+$ species via Se reduction. Lan et al. suggested that Fe_3S_4 was
463 present beneath Fe(III) (hydr)oxide precipitation during FeS transformation at pH 8.⁵³
464 The XRD patterns of 50 and 192 h solid samples show a poor crystallinity and
465 differed from the original mackinawite in Figure S7. The XRD pattern from the 50 h
466 sample probably indicated that the formation of poor crystallized Fe_3S_4 and $\text{Fe}(\text{OH})_3$,
467 in agreement with the XPS results. The very broad XRD reflections in 192 h sample is
468 attributed to magnetite and $\text{Fe}(\text{OH})_3$ with very poor crystallinity. Normalized Fe
469 K-edge XANES spectra of the 192 h solid sample and of the references, including
470 mackinawite, magnetite, and hematite, are shown in Figure S11, together with the
471 LCF result. The result shows that the species present in the solid product was similar
472 to magnetite, in good accordance with black color of the filtrate at 192 h.

473 Furthermore, the ratio of Fe(II)-O/Fe(III)-O identified by XPS at 192 h was 0.23, less
474 than the idea value of 0.5, and the presence of Fe(III)-S species suggested the final
475 solid contained amorphous $\text{Fe}(\text{OH})_3$ and FeS_2O_3^+ complexed to Cl^- or OH^- species
476 except very poor crystallization magnetite. The Eh-pH diagram of Fe species shown
477 in Figure S9b indicated that mackinawite tends to dissolve and to form magnetite. It is
478 well known that $\text{Fe}(\text{OH})_2$, an extremely redox-sensitive phase in solution, could lead
479 via the Shikorr reaction⁵⁴ to a disproportionation reaction to magnetite under anaerobic
480 condition. Furthermore, the interaction of SeO_3^{2-} with Fe(II) could produce Se^0 and
481 metastable green rust (GR), which is know to have the potential to reduce SeO_3^{2-} to
482 Se^0 via being oxidized to magnetite.⁵⁵

483 **4. Environmental relevance**

484 It is critical to waste depository safety to improve our understanding of reductive
485 precipitation of mobile radionuclides in hyperalkaline conditions, and specifically to
486 measure the surface complexes, aqueous speciation and solubility in order to decipher
487 immobilization pathways and the underlying interaction mechanisms when
488 contaminations are in contact with cement media.⁵⁶ Mackinawite, as one of the steel
489 corrosion products and one of the common naturally-occurring iron sulfides, showed
490 an extremely high sorption and reduction ability towards SeO_3^{2-} within a relatively
491 short interaction time (~96 hours). SeO_3^{2-} can be reduced to a mixture of SeS_2 and Se^0
492 solid species, as confirmed by Se K-edge XAS. However, the zero-valent selenium
493 species shows a relatively high solubility and thus mobility in CPW, with ~99% of
494 reduction products released to the solution in the form of Se_4S nanoparticles
495 confirmed by TEM-EDS after 192 hours. The surface chemistry of the mackinawite
496 evolved during the reaction in the following wasy: 2 to 3 $\text{S}^{2-}/\text{S}_n^{2-}$ units were
497 substituted by one SeO_3^{2-} atom. 62% of initial solid $\text{S}^{2-}/\text{S}_n^{2-}$ was released into solution
498 when in presence of SeO_3^{2-} and mackinawite was transformed to magnetite, $\text{Fe}(\text{OH})_3$
499 and FeS_2O_3^+ complexed to Cl^- or OH^- species after 192 h. The current study provides

500 valuable information about the reduction mechanisms of redox-sensitive radionuclides
501 in presence of iron sulfides that have strongly reduction capacity.

502

503 **ASSOCIATED CONTENT**

504 **Supporting Information Available.** Additional materials referenced in the text are
505 available free of charge.

506 The composition of CPW. XRD patterns, and TEM micrograph of synthesized
507 mackinawite. The calibration curves of SO_4^{2-} , SO_3^{2-} , $\text{S}^{2-}/\text{S}_n^{2-}$, SeO_3^{2-} and the relative
508 retention time of the ions. Picture of the filtrate color. Se K-edge EXAFS of solid
509 samples. STEM image and EDS mapping results of solid sample. Se and Fe species
510 Eh-pH diagrams. Aqueous concentration of SO_4^{2-} , SO_3^{2-} , $\text{S}^{2-}/\text{S}_n^{2-}$ in the filtrate.
511 Binding energies (BE), Peak full width at half maximum (FWHM) and peak areas for
512 S(2p) and Fe(2p_{3/2}). Fe K-edge normalized XANES spectra and LCF result of solid
513 samples.

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518 **Notes**

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528

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