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Reductive immobilization of ⁹⁹Tc(VII) by FeS₂: the effect of marcasite

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13

14 ABSTRACT

15

Reductive immobilization of ⁹⁹Tc by a synthetic FeS₂ mixture, i.e. marcasite-pyrite 60:40, was studied 16 17 by a combined approach of batch experiments and powder X-ray diffraction, X-ray photoelectron 18 spectroscopy as well as Raman microscopy. It was found that the FeS₂ mixture removes 100% of Tc from 19 the suspension after 7 days in contact at $6.0 < pH \le 9.0$. The retention outside that pH range was slower and incomplete. Spectroscopic analysis showed that the redox active species at pH 6.0 is Fe²⁺ as expected 20 from previous works with pyrite. However, at pH 10.0 the surprising oxidation of S^{2-} to SO_4^{2-} was found 21 22 responsible for Tc immobilization. This was explained by the high reactivity of marcasite that is easily 23 oxidized to produce H₂SO₄. Our work provides new molecular insights into the reductive mobilization 24 of Tc(VII) by oxidative formation of sulfate. The assigned molecular reactions may also be relevant for 25 the assessment of other redox reactive contaminants. Technetium re-oxidation experiments showed that 26 the fast oxidation of marcasite is associated to the reduction of the remaining Tc(VII) in solution, which 27 gives marcasite the potential of Tc natural remediation since it delays the re-oxidation of Tc(IV).

28

29 KEYWORDS: Technetium removal, iron sulfide, iron sulfate, pyrite, remediation

31 1. INTRODUCTION

32

Technetium (Tc, Z=43) was discovered in Italy by Perrier and Sagré in 1937.¹ Its application as a clinical 33 34 tracer element was first published in the early 60's.² Since then, the metastable ^{99m}Tc (half-life of 6.007 h) has been used for the detection of tumors, as well as for the imaging of several organs like the brain or 35 36 the liver. Despite its relevance in medicine, technetium is very problematic from the environmental point of view. The primary isotope, i.e. ⁹⁹Tc, a pure β^- emitter with a half-life of 2.14×10⁵ years, is produced 37 with a high yield of 6% during the fission of ²³⁵U and ²³⁹Pu.³ Even though it may be naturally formed in 38 trace amounts through the spontaneous fission of ²³⁸U or the interaction of cosmic rays with 39 40 molybdenum, ruthenium and niobium present in the Earth crust, the vast majority of the technetium 41 present on our planet originates from human activities, like nuclear power production.^{3,4}

42

In addition to its long half-life, complex ⁹⁹Tc speciation adds to its high environmental risk. Under 43 44 oxidizing conditions it is mainly occurring as pertechnetate, $Tc(VII)O_4^-$, an anion that is practically not 45 sorbed by minerals or sediments, and also does not form insoluble compounds.⁵ Thus, it freely migrates 46 within ground water.^{3,4} If Tc reaches the biosphere, it will be rapidly incorporated into the food chain 47 and when Tc dose exceeds 0.04 mSv per year (equivalent to the intake of 182 µg of Tc), it can increase 48 the risk of cancer as well as other health problems related to radiation exposure.⁶ Therefore, establishing 49 strategies for pertechnetate immobilization and remediation is of great importance for the nuclear waste 50 management and environmental protection. The most stable species under reducing conditions is 51 $Tc(IV)O_2$, a scarcely soluble oxide with a very low mobility. Consequently, a reduction of TcO_4^- to TcO_2 is the most viable strategy for technetium immobilization.^{3,7,8} Several minerals containing different 52 reducing moieties like $Sn(II)^{9,10}$ or $Fe(II)^{11-15}$ have been proven to effectively scavenge Tc from solution 53 54 through the formation of Tc(IV) and its consecutive precipitation, sorption and/or incorporation.

55

Pyrite, cubic iron sulfide (FeS₂), has shown a remarkable ability for the remediation of pollutants such as mercury,¹⁶ chromium^{17,18} and molybdenum.¹⁹ In a recent study, we have found that it removes almost 100% of Tc(VII) from solution after one day in contact at $5.5 \le pH \le 10.5$.²⁰ X-ray absorption spectroscopy, XAS, showed that after the reduction from Tc(VII), Tc(IV) was either sorbed onto hematite (α -Fe(III)₂O₃) at pH 6.0 or incorporated into magnetite (Fe(II)Fe(III)₂O₄) at pH 10.0, with both hematite and magnetite being oxidation products of pyrite. Based on these results, we concluded that natural attenuation of Tc is expected in nuclear waste repositories with clays (namely bentonite) used as backfill

materials, where pyrite is a very common accessory mineral.^{21–23} This is in particular relevant in sites 63 like the Onkalo spent nuclear fuel repository, where pyrite is abundant per se.²⁴ However, these natural 64 65 attenuation effects clearly depend on the interaction between technetium and other minerals present, possibly changing the retention of Tc. Thus, more realistic scenarios like the presence of marcasite, a 66 FeS_2 polymorph commonly found along with pyrite in the environment,²⁵ should be taken into account. 67 Even though both minerals crystallize in different crystal systems, i.e. orthorhombic (marcasite) and 68 69 cubic (pyrite) and have different space groups (marcasite: Pnnm; pyrite: $Pa\overline{3}$), they are commonly 70 misidentified and confused based on mere crystal habit. For example, acicular pyrite crystals are 71 considered marcasite while in applications like jewelry it is very frequent that pyrite is sold as marcasite.²⁶ 72

73

74 It has been proven that polymorphism, i.e. the existence of a solid phase in different crystalline structures, 75 has a significant effect on the retention of pollutants by minerals. One example is europium sorption that 76 is faster on γ -alumina (γ -Al₂O₃) than on corundum (α -Al₂O₃) because the reaction rates are influenced by the crystallographic features of the mineral.²⁷. The same effect has been observed for plutonium 77 sorption on hematite and maghemite $(\gamma$ -Fe₂O₃).²⁸ Thus, it is quite probable that the retention of pollutants 78 79 by natural pyrite is affected by the presence of marcasite; however, no studies addressed this so far. More 80 specifically for technetium, retained Tc(IV) might get re-mobilized after the decomposition of marcasite, 81 that is unstable with respect to pyrite and whose main oxidation product, H₂SO₄, is a potential re-82 oxidation agent for Tc(IV). Therefore, in order to design an efficient remediation strategy for Tc, a basic 83 understanding of the effect of marcasite on Tc immobilization by pyrite is needed.

84

85 In this work, we have studied the retention of Tc(VII) by a well characterized synthetic mixture of 86 marcasite-pyrite 60:40 using a combined approach of batch experiments with spectroscopic and 87 diffraction measures. The batch contact experiments were carried out at pH ranging from 4.0 to 10.5, 88 contact times from 1 to 45 days, and Tc concentrations varying from 0.1 µM to 1 mM. X-ray 89 photoelectron spectroscopy (XPS), Raman microscopy and powder X-ray diffraction (XRD) were 90 applied to the Tc loaded solids to determine oxidation states and the mineralogical changes after the 91 interaction with technetium. Additionally, re-oxidation experiments were performed at pH 6.0 and 10.0 92 for 90 days, where Raman microscopy and XRD identified the reaction products.

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- 94

95 2. MATERIALS AND METHODS

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Radiation safety. ⁹⁹Tc is a β-particle emitter and should be handled only in a dedicated radiochemistry
laboratory with specific radiation safety protocols in place.

99

100 **General notes.** Unless indicated otherwise, all preparations were performed under N_2 atmosphere inside 101 a glovebox (GS Glovebox-System GS050912; < 1 ppm O₂) at 21°C. The Milli-Q water (resistivity of 102 18.2 MΩ·cm, Water Purified[®]) used for the experiments was boiled for two hours for degassing, sealed 103 and cooled down to room temperature before its placement into the glovebox.

104

The Eh was measured with an Eh electrode (Inlab redox micro 51343203, Mettler Toledo) calibrated
with a redox buffer solution (220 mV / pH 7). The pH was measured by using a pH meter (pH3110,
WTW) with a pH electrode (SI Analytics Blue Line) calibrated with standard pH buffers 4.006, 6.865
and 9.180 (WTW).

109

110 **2.1 Mineral synthesis and characterization**

111 Iron sulfide, FeS₂, was synthesized in a Schlenk line following the procedure described by Huo et 112 al.²⁹ Briefly, 200 mL of 0.1 M FeCl₃ and 200 mL of 0.2 M NaHS were prepared and purged with N₂ 113 for 30 minutes. Then, the solutions were mixed in a round flask of 500 mL and left under N₂ 114 atmosphere and constant stirring for another 30 minutes. Lastly, the mixture was sealed and aged 115 for 24 hours in a stove at 60°C. The black powder obtained was separated by ultracentrifugation 116 (Optima XPN-80 Ultracentrifuge, Beckman Coulter at $2.4 \times 10^5 \times g$ for 1 hour, these conditions apply 117 for all centrifugations) and dried by lyophilization.

118

119 The characterization of the mineral is presented in the Supporting Information (Figure S1). It was 120 done by powder XRD (MiniFlex 600 powder XRD, Rigaku) using Cu K α ($\lambda = 1.54184$ Å) as X-ray 121 source with an X-ray generation of 40 kV / 15 mA (600 W) and a D/teX Ultra 1D silicon strip 122 detector in the Bragg-Brentano θ -2 θ geometry at a scanning speed of 0.02 deg per min. The samples 123 were prepared inside the glovebox, using an agate mortar to homogenize the solid and placing it into 124 a Kapton tape capped low-background airtight sample holders (Rigaku) to ensure inert N₂ conditions. The Brunauer-Emmett-Teller specific surface area was determined as $5.3 \pm 0.4 \text{ m}^2 \text{ g}^{-1}$, 125 126 using isotherm experiments with N₂ at 77 K (Multipoint Beckman Coulter surface analyzer SA 127 3100). The isoelectric point of the mineral (pH_{IEP}) was determined by zeta potential experiments

128 (Zetasizer Nano Series Nano-ZS, Malvern Instruments) of 0.05 g L⁻¹ mineral suspensions in 0.1 M 129 NaCl at pH values between 3.0 and 10.5. Each sample was scanned for 30 seconds; the data 130 presented here are averages of five independent scans. Scanning electron microscopy (SEM) was 131 used to analyze the mineral morphology. The sample was prepared inside the anoxic glovebox and 132 moved by a shuttle (Leica VCT) under inert conditions into the environmental scanning electron 133 microscope (FEI Quanta 650 FEG, now Thermo Fisher Inc.). The operating voltage was 30 kV and 134 the pressure in the analysis chamber 2.8×10^{-4} Pa.

135

136 **2.2 Batch sorption experiments**

137 All batch experiments started with the preparation of suspensions of the mixture marcasite-pyrite 138 60:40, from now on simply referred to synthesized FeS_2 . In general, 42.6 mg of synthesized FeS_2 139 were suspended in water or 0.1 M NaCl (NaCl_(s) from Merck, purity \geq 99%) depending on the experiment. Afterwards, the indicated amount of a 9.22×10⁻³ M K⁹⁹TcO₄ stock solution (Institute of 140 Radiopharmaceutical Cancer Research, HZDR) was added. The final volume of the sample was 141 142 32 mL (final solid to liquid ratio = 1.3 ± 0.2 g L⁻¹). The pH of the samples was adjusted with solutions from 1 to 0.02 M of HCl or NaOH. Due to the oxidation of FeS₂,³⁰ the pH was adjusted 143 144 regularly every 3 to 4 days adding small amounts of HCl or NaOH if required. Such additions never 145 exceeded 10 µL to ensure constant Tc concentration and ionic strength in the sample.

146

147 Once the pH was adjusted, the samples were placed on a horizontal shaker for agitation for the 148 required contact time. After this, the stirring was stopped and the pH and Eh were measured 149 (equilibrium time for Eh measure: 30 minutes). Table S1 in the supporting information (SI) 150 summarizes the conditions for the batch experiments.

151

152 The samples were then ultracentrifuged and 250 μ L aliquots from the supernatant were taken to 153 measure the remaining Tc concentration by liquid scintillation counting, LSC (1414 LSC 154 Winspectral α/β Wallac, Perkin Elmer; detection limit: 0.42 Bq; measuring time: 10 minutes).

155

The amount of Tc retained by the synthesized FeS₂ (%Tc_{removed}) was calculated as follows:

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158
$$\% Tc_{removed} = \frac{([Tc]_0 - [Tc]_t)}{[Tc]_0} \times 100$$
 Eq.1

where $[Tc]_0$ is the initial Tc concentration in the system (in Bq mL⁻¹), measured in a blank solution without the solid, and $[Tc]_t$ is the concentration of Tc remaining in solution after contact with the synthesized FeS₂ (in Bq mL⁻¹) after certain time (*t*) of contact.

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164 **2.3 X-ray photoelectron spectroscopy (XPS)**

0.140 g of the synthesized FeS₂ were transferred into 50 mL of water and the required amount of 165 K^{99} TcO₄ was added to obtain ≈ 1000 ppm of Tc load in the final solid (Tc initial concentration = 166 0.048 mM). Such concentration was necessary achieve at least 4 Tc atoms nm⁻², which is the value 167 needed to perform measurements. The pH was adjusted to 6.0 and 10.0 and the samples were left 168 169 for equilibration for a month on a horizontal shaker (the pH was also adjusted twice a week during 170 this month). Afterwards, the solid was separated by ultracentrifugation and the supernatant was 171 removed. The wet paste was re-dissolved in $\approx 1 \text{ mL}$ of water. Two blanks of synthesized FeS₂ 172 suspensions in water (1.3 g L⁻¹) were prepared at pH 6.0 and 10.0, left in horizontal stirring for one 173 month adjusting the pH occasionally. They were measured at the same conditions as the ⁹⁹Tc-loaded 174 samples. The samples were always transported and measured under inert gas atmosphere (N₂ and 175 Ar).

176

177 A drop of the suspension was applied on indium foil and left to dry. Afterwards, the samples were 178 moved into the XPS (PHI 5000 VersaProbe II, ULVAC-PHI Inc.) using an airtight transfer vessel. 179 The XPS is equipped with a scanning microprobe X-ray source (monochromatic Al Ka (1486.7 eV) 180 X-rays). X-ray source power of 32 W and pass energy of the analyzer of 187.85 eV were used to 181 perform survey scans of the conductive samples. Narrow scans of the elemental lines were recorded 182 at 23.5 eV pass energy, yielding an energy resolution of 0.67 eV FWHM at the Ag 3d_{5/2} elemental line of pure silver. The binding energies of elemental lines of pure metals (monochromatic Al K_{α} : 183 Cu $2p_{3/2}$ at 932.62 eV. Au $4f_{7/2}$ at 83.96 eV)³¹ were used for the calibration of the binding energy 184 185 scale of the spectrometer, obtaining an estimated error of ± 0.2 eV.

186

187 2.4 Raman microscopy

188 Two suspensions of 1.3 ± 0.2 g L⁻¹ of the synthesized FeS₂ were prepared in water and their pH was 189 adjusted to 6.0 and 10.0. The required amount of K⁹⁹TcO₄ was added to obtain \approx 100 ppm of Tc 190 load in the final solid (Tc initial concentration = 5µM). Tc and the samples were placed on the

- 191 horizontal shaker for two weeks with regular pH adjustments. Afterwards, the solids were separated
- 192 by ultracentrifugation and distributed for Raman microscopy and powder XRD.
- 193

194 The wet paste was deposited on a cell containing two CaF_2 Raman quality windows.¹² Once the solid 195 was dry, the cell was sealed to ensure inert atmosphere during the measure. Raman microscopy 196 (Aramis, Horiba) was performed using a He – Ne laser (wavelength: 532 nm) with a 10-fold 197 objective with a D 0.3 filter, a pin-hole of 500 µm and a slit of 600 µm.

198

199 **2.5 Re-oxidation**

Two suspensions of the synthesized FeS₂ in water $(1.3 \pm 0.2 \text{ g L}^{-1})$ were prepared inside the glovebox at pH 6.0 and 10.0, both containing 5 μ M K⁹⁹TcO₄ (50 mL polypropylene tubes yielding a final volume of 35 mL). They were agitated for 14 days during which the pH was regularly adjusted as in the batch experiments (section 2.2). Subsequently, 3 mL aliquots of each sample were ultracentrifuged and the supernatant was sampled for determination of Tc concentration remaining in solution by LSC (section 2.2).

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The tubes were opened outside the glovebox (under ambient atmosphere) and left with constant stirring for one hour. Afterwards they were closed and placed on a horizontal shaker outside the glovebox for 64 days. Identically to the batch experiments, we tried to adjust the pH, but this was not possible as it always dropped to ~3 due to the production of H_2SO_4 after the oxidation of the mineral³⁰ independent of the initial pH (6.0 or 10.0). Therefore, after two weeks adjusting every day, we decided not to adjust the pH anymore but leave it at the stable value reached after the interaction with oxygen (pH = 3.0 instead of 6.0 and pH = 2.8 instead of 10.0).

214

The suspensions were regularly sampled by taking 3 mL aliquots to measure the Tc remaining in the supernatant by LSC (section 2.2). The solids obtained after 60 days of the re-oxidation experiments were studied by powder XRD and Raman microscopy (sections 2.1 and 2.4).

- 218
- 219 **2.6 Speciation calculations**

220 Calculations were performed using the code Chess V2.4.³² The most recent Nuclear Energy Agency 221 thermodynamic databases for $Fe^{33,34}$ and Tc^{35} and their recommended S thermodynamic data were 222 used.

- The reduction of 5 μ M Tc(VII) by either S²⁻ or Fe²⁺ was studied as a function of pH. All calculations assumed that the Tc(VII) reduction was promoted by either dissolved Fe²⁺ or S²⁻ at 25°C with no gas dissolution. It was considered that 1% of 1.3 g L⁻¹ FeS₂ was dissolved, i.e. 0.1 mM Fe²⁺ and 0.2 mM S²⁻. However, it has to be kept in mind that this assumption might not represent a realistic scenario since Tc(VII) reduction is promoted by the structural S²⁻ or Fe²⁺, whose redox potentials differ from the dissolved ones when they form part of a mineral structure.^{36,37}
- 230

231 3. RESULTS AND DISCUSSION

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233 **3.1 Batch sorption experiments**

- Figure 1 shows the results of the batch experiments performed to study the 99 Tc(VII) uptake by the synthesized FeS₂ as a function of Tc concentration, time and pH.
- 236



Figure 1. Batch experiments of ⁹⁹Tc(VII) removal by synthetic FeS₂. a) Isotherm at pH 6.5 in water after 14 days of contact b) Scavenging kinetics at pH 6.5 in water. Tc removal by pure pyrite at pH 6.0 in water was added for comparison.¹⁵ c) Impact of ionic strength: water vs 0.1 M NaCl after 14 days in contact. Tc removal by pure pyrite in water for 14 days was added for comparison.¹⁵ d) Pourbaix diagram of the samples of c. Dashed lines in b and c are shown to guide the eve.

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The isotherm at pH 6.5 (Figure 1a) shows that the lower the Tc concentration in suspension, the better its removal by the synthesized FeS₂. These results are especially important because, due to technical reasons, for analyzing the kinetics of the removal process as well as the pH effect, we have used a Tc concentration of 5 μ M, which is three orders of magnitude higher than the typical technetium concentration in the environment (1×10⁻⁹ M). ^{38,39} Therefore, the isotherm serves as a proof-of-concept of our experiments. Additionally, the isotherm shows a slope of 0.5 suggesting a single reaction mechanism, i.e. sorption on one site. This slope value indicates either that the affinity

of the mineral for the technetium is low,⁴⁰ or that the mechanism of removal could be the precipitation of Tc(IV), most probably as TcO₂ or a TcS_x species.⁴¹

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263

The kinetics of the Tc uptake at pH 6.5 are represented in Figure 1b. It can be seen that Tc removal increases with time, with 50% of the initial technetium removed after one day in contact with the synthesized FeS₂. 100% of Tc(VII) uptake was reached after 7 days. The experiment was carried out for 45 days and the percentage of Tc(VII) scavenged was constant, showing no re-mobilization of the radionuclei. Compared with the Tc immobilization by pure pyrite,²⁰ the presence of marcasite slows down the process, since pure pyrite removed 100% of Tc already after one day of contact under the same conditions.

264 Figure 1c shows that the removal of Tc(VII) from water at $6.0 < pH \le 9.0$ is close to 100%. Under 265 more acidic conditions, the scavenging of technetium by the synthesized FeS₂ is less effective because the solubility of FeS₂ increases as the pH decreases.⁴² It has been found that the 266 267 heterogeneous reduction of Tc(VII) by Fe(II) is more effective than the homogenous reduction (i.e. in solution) since when Fe²⁺ as reducing agent is in solution the formation of Tc(IV) is kinetically 268 hindered.⁴³ In contrast, the reduction becomes more prominent when the Fe(II) takes part of a 269 mineral structure, $^{29,43-45}$ or when it is pre-sorbed on a reactive mineral surface like on alumina.¹² In 270 271 our work, Tc removal at pH < 6.0 decreases due to FeS₂ dissolution, which hinders Tc(VII) 272 reduction.

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274 The Tc uptake by the synthesized FeS₂ also becomes lower at pH 10.0, which might be a result of an increased solubility of TcO_2 .^{11,46} or the formation of TcS_x -like compounds on the surface that 275 would passivate the mineral, preventing a further Tc reduction.⁴⁷ It has been reported that technetium 276 can passivate iron containing materials by forming layers of technetium oxides,^{48,49} however, in our 277 previous study of Tc retention by pure pyrite²⁰ such effect was not observed at pH 10.0 when 278 279 technetium interacted solely with oxygen, which lead us to conclude that if passivation is indeed 280 taking place, it would be most likely due to the formation of TcS_x and not TcO_2 . The Pourbaix 281 diagram (Figure 1d) confirms the reduction from Tc(VII) to Tc(IV) in the whole pH range studied, 282 making the formation of both TcO_2 or TcS_x equally possible. One additional hint for a molecular 283 process understanding is given by the addition of 0.1 M NaCl to the retention system (Figure 1c). 284 As a consequence, the Tc removal at $6.0 < pH \le 9.0$ does not significantly change, meaning that inner-sphere complexation is likely taking place.⁵⁰ The difference on the Tc scavenging at pH < 6.0285

- 286 between the system in water and 0.1 M NaCl can be explained either by outer-sphere complexation or by the increase on Tc(IV) solubility as the ionic strength increases.^{11,51} In case that Tc(IV) is in 287 solution, its interaction with the synthesized FeS₂ would be hindered due to their charge repulsion. 288 289 Although batch experiments provided important macroscopic information, a combined approach of 290 spectroscopic and diffraction methods is needed for conclusions on the chemical identity of the Tc 291 species formed at the synthetic FeS_2 – water interface.
- 292

293 3.2 Molecular analysis of Tc loaded solids

294 To gain understanding on the retention on a molecular level, Raman microscopy and XPS were 295 performed on the solid samples after the interaction with technetium. The Raman spectra of the 296 solids at pH 6.0 and 10.0 are presented in Figure 2. At pH 6.0 the formation of hematite as the 297 resulting iron phase after the FeS₂ oxidation is confirmed by comparison of the spectra with the reference R050300 of the RRUFF database.⁵² This result is in good agreement with our previous 298 findings with pyrite,²⁰ where the inner-sphere complexation of Tc(IV)-Tc(IV) dimers with hematite 299 was responsible of the Tc removal from solution at pH 6.0. 300







Unlike the removal with pure pyrite,²⁰ the Raman spectra of the solid at pH 10.0 presents a band at 306 993 cm⁻¹ typical for the sulfate group of several Fe(II)-sulfate-hydrate minerals. As a reference 307 308 rozenite (Fe(II)SO₄×4H₂O) is shown in Figure 2. This band would indicate that the oxidation 309 reaction at this pH value is not that of iron, as expected for the Tc(VII) reductive immobilization, 310 but of sulfur. This is supported by the high spectral similarity of the Raman spectra of the Tc loaded FeS₂ at pH 10.0 with the pure synthetic FeS₂. The band around 478 cm⁻¹ present in the synthesized 311 FeS_2 before and after the interaction with technetium can be assigned to the Fe(III) moieties⁵³ 312 313 described in the mineral characterization presented in the Supporting Information.

314

315 Figure 3 shows the XPS spectra evaluated for Fe 2p, S 2p, O 1s, and Tc 3d. Figure 3a illustrates the 316 formation of Fe(III) at pH 6.0. In contrast, there is no significant change indicating the oxidation of 317 iron at pH 10.0. This supports the interpretation of Raman spectra (Figure 2) and confirms that at 318 pH 10.0 the main redox sensitive element of the synthesized FeS₂ is sulfur. However, the S 2p spectra 319 (Figure 3b) at pH 10.0 show no signal for sulfate, expected around 168 eV, whereas the binding 320 energies of Fe $2p_{3/2}$ (707.2 eV) and $S 2p_{3/2}$ (162.5 eV) can be unequivocally assigned to FeS₂. This 321 can be explained by a significantly lower sulfate concentration below the XPS detection limit 322 concentration as result of the incomplete reduction of 5 μ M Tc. Whereas XPS analyzes the sample 323 as a whole, the Raman microscope records spectra from different regions of interest of the mineral, 324 being able to detect minor components. As the formation of sulfate is the result of the 325 heteroreduction of technetium, it becomes clear why it could be detected by Raman microscopy in 326 specific spots of the sample but not by XPS. Moreover, the small intensity of the band at 993 cm⁻¹ in Figure 2 portrays the low concentration of sulfate present in the sample. 327

329 The O 1s spectra (Figure 3c) of the pure synthetic FeS₂ presents a signal around 532.3 eV that could be assigned to adsorbed water, which has already been reported in literature for FeS₂.⁵⁴ After the 330 interaction with technetium, the samples at both pH 6.0 and 10.0 display the formation of similar 331 proportions of OH^- and O^{2-} . The Tc 3d spectra of the solids at pH 6.0 and 10.0 are presented in 332 333 Figure 3d. Due to the low concentration of Tc in the experiments the speciation by XPS can only be performed by the Tc 3d main lines. The presence of TcO₂ at both pH values is indicated by the Tc 334 $3d_{5/2}$ peak at 256.5 eV, which is close to the reference value 256.8 eV.⁵⁵ The peak intensity suggests 335 336 that formation of TcO_2 is favored at pH 6.0.

337

338	More intriguing are the Tc $3d_{5/2}$ peaks around 254 eV, whose binding energy is close to the reference
339	binding energy for Tc(0) (253.9 eV 56). But it is preferably assigned to TcSx or Tc-S-Fe bonding
340	because the complete reduction to metallic technetium is not probable, as can be seen in the next
341	paragraphs with the speciation calculations. A similar situation is noted in the Fe $2p$ spectra, where
342	the binding energy of Fe $2p_{3/2}$ at 707.2 eV (Figure 3a) is close to the reference values of FeS ₂ at
343	707.3 eV 47 and Fe(0) at 707.0 eV 57 but it is assigned FeS $_2$ as it makes more $% 10^{10}$ chemical sense
344	according to the sample. Although a reference of the Tc $3d$ binding energy for TcS ₂ could not be
345	found, the Tc $3d_{5/2}$ line of Tc ₂ S ₇ has a binding energy of around 254.8 eV, ⁵⁸ which is close to that of
346	the peaks around 254 eV in Figure 3c. In consequence, the peaks at 254 eV were assigned to the
347	formation of TcS_x -like species that seem to be more abundant as the pH becomes more alkaline.
348	Such species were not detected by the S $2p$ spectra due to the low concentration of technetium. In
349	section 3.1, it was suggested that TcS_x species could passivate the mineral making the Tc reduction
350	slower. Surface complexes might be formed, too, working as transient phases in the total redox
351	process. Further studies are needed to gain deeper insight.
352	



Figure 3. XPS spectra of the synthetic FeS₂ after the reaction with Tc(VII) ([Tc] = 1000 ppm) at pH 6.0 and 10.0. a) Fe 2p. b) S 2p. c) O 1s. d) Tc 3d. Tc 3d elemental lines are superimposed by the broad loss line of S 2s.

Figure S2 in the SI shows the speciation diagrams of Tc reduction in presence of Fe²⁺ and/or S²⁻. The performed calculations predict a quantitative Tc(VII) reduction to TcO₂ from pH 4.5 to pH 10.5. The Tc(VII) reduction by Fe²⁺ shows that main Fe(II) species in solution are Fe²⁺ at pH < 7.0 and for pH > 7.0 Fe(OH)⁺ and Fe(OH)₂. For Fe(III) the main species formed are hematite at pH < 6.5 and magnetite at pH > 6.5 (SI Figure S2a). In the case of the Tc reduction promoted by S²⁻, the main S(⁻II) species are HS⁻ throughout the entire pH range evaluated and the sulfur oxidation products are S_(cr) at pH < 5.0 and SO₄²⁻ for pH > 5.0 (SI Figure S2b).

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In contrast, when the reduction of Tc(VII) is calculated in presence of both Fe^{2+} and S^{2-} (SI Figure S2c), the formation of two solids, i.e. pyrite and mackinawite, and the presence of $Fe^{2+}_{(aq)}$, FeOH⁺_(aq) and HS⁻_(aq) are favored while the amount of Fe(III) and oxidized sulfur species represent a minority.

- This is related to the fact that Fe^{2+} and S^{2-} concentration are respectively 20 and 40 times higher than Tc and thus the main species found are Fe(II) and S(-II), whereas the formation of Fe and S oxidized products is low in comparison. These set up conditions might not be representative for a realistic scenario. However, when Fe^{2+} and SO_4^{2-} are in solution at pH > 7.0 the formation of FeSO₄ is favored.⁵⁹ Even though these calculations need to be evaluated carefully since Tc homoreduction (i.e. in solution) by Fe²⁺ and S²⁻ coming from an assumed 1% FeS₂ dissolution is assumed, they support the Raman spectra obtained for the solids after interaction with Tc.
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- In summary, there is a clear effect of the marcasite on the technetium immobilization when compared with the previous results obtained with pure pyrite.²⁰ Not only the overall process is slower but also the Tc retention is incomplete at pH 10.0, which is a result of the change of the predominant redox active element (sulfur instead of iron).
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383 **3.3 Re-oxidation experiments**

384 The initial concentration of Tc was 5 μ M and the systems were left to interact for 14 days, after 385 which the concentration of Tc in solution became 0.28 µM at pH 6.0 and 1.13 µM at pH 10.0. In order to estimate the amount of oxygen necessary to oxidize the synthetic FeS₂, the oxidation rates 386 previously published for marcasite⁶⁰ and pyrite⁶¹ were used. Assuming that the mineral was entirely 387 marcasite, the 0.065 g used for the re-oxidation experiments would need around 10 s to be fully 388 389 oxidized whereas if the sample was constituted only by pyrite, it would need around 6 days. Even 390 though these calculated times should be carefully considered as the FeS₂ oxidation rate should be 391 affected by the presence of Tc(VII) as an oxidizing agent, they allow us to conclude that the time of 392 the experiment was appropriate to observe Tc(IV) re-oxidation. Moreover, the concentration of 393 oxygen required was rapidly reached since the opened tubes were shaken for one hour, then closed 394 and left under constant agitation for the entire experiment and they were opened several times for 395 pH adjusting on the first days and for sampling during the following two months.

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Figure 4 shows the results of the re-oxidation experiments. The batch experiments from Figure 4a depict the interesting fact that after the suspension at pH 10.0 was in contact with ambient atmosphere, the technetium concentration in solution was significantly lower (0.48 μ M) than before the opening of the tube (1.13 μ M). It is important to bear in mind that marcasite is much more reactive than pyrite and when it is exposed to oxidizing conditions, it rapidly generates H₂SO₄.²⁶ This does not only explain the impossibility of maintaining the pH at 6.0 or 10.0 (section 2.5), but is also responsible for the further reduction of the Tc(VII) that was still in the suspension before the entry of oxygen at pH 10.0. The concentration of technetium in both suspensions remained below $1 \mu M$ for 50 days. In the last point of the re-oxidation experiments (64 days in figure 4a), it is apparent that the re-oxidation begins and it is more favorable in the suspension initially set at pH 6.0 than at pH 10.0. This behavior is very similar to the one found for pure pyrite.²⁰ The slower reoxidation at pH 10.0 indicates that the Tc(IV)-species bond with the mineral is stronger, suggesting surface complexation at pH 6.0 and incorporation or co-precipitation at pH 10.0.

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Figure 4b shows the Raman spectra of the two Tc loaded-solids after 50 days under ambient atmosphere. The two solids have the same chemical identity, consisting of a mixture of the initial mineral (marcasite-pyrite 60:40) and sulfur in solid state, whose presence was confirmed by XRD of both solids (Figure 4c) and supported by the speciation calculations (SI Figure S2). This means that the initial pH does not play a role on the speciation after the system interacts with oxygen, most likely due to H_2SO_4 production.

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The results presented here show that the presence of marcasite along with pyrite in a nuclear waste repository will prevent the re-mobilization of technetium due to the production of H_2SO_4 triggered by the presence of O_2 and the subsequent formation of elemental sulfur. The oxidation of marcasite is associated to the reduction of the Tc(VII) remaining in solution. Our results suggest that Tc will be immobilized as Tc(IV) until all the marcasite has been consumed, which would considerably limit a technetium distribution within the repository near and far field even if Tc(VII) reduction is not complete.



Figure 4. Evaluation of Tc re-oxidation (re-ox) experiments at different pH values (pH_{initial} = 6.0 and 10.0; pH_{air} = 3.0 and 2.8, respectively). a) Tc concentration in suspension for 70 days in ambient atmosphere. Dashed lines are shown to guide the eye. b) Raman spectra of the solids at pH_{initial} 6.0 and 10.0 after 60 days of exposition to ambient atmosphere. The Raman spectra of the

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pure synthetic FeS_2 and sulfur (reference R040135) are shown as reference.³⁰ c) XRD of the solids at pH_{initial} 6.0 and 10.0 after 60 days of exposition to ambient atmosphere. The XRD of sulfur (reference R040135) are shown as reference.³⁰

436

437 4. CONCLUSIONS

The immobilization of ⁹⁹Tc(VII) by a synthesized FeS₂, presenting a mixture of marcasite and pyrite 438 439 (60:40) was studied. It was found that 100% of Tc(VII) is removed from solution after 7 days of 440 interaction at $6.0 < pH \le 9.0$. The Pourbaix diagram confirms that the initial step of the 441 immobilization is the reduction of Tc(VII) to Tc(IV) at all the working pH values. At pH< 6.0 the Tc 442 removal is incomplete due to the solubility of the synthesized FeS₂, as the reduction of Tc(VII) is less efficient when Fe²⁺ is in solution. The spectroscopic analysis revealed that Fe(II) acts as the reducing 443 444 agent at pH 6.0, producing hematite on which Tc(IV) sorption is feasible. These results are comparable to pure pyrite.²⁰ The behavior of the synthesized FeS₂ at pH 10.0 is different to pure 445 pyrite and very surprising. Here, the Raman spectra indicated the formation of a Fe(II)SO₄ like 446 mineral, implying that the reducing agent in that case was S^{2-} , which is a consequence of the higher 447 reactivity of marcasite and might be an explanation for the incomplete Tc removal at this pH. 448 Previous works with mackinawite, FeS,⁶² and in the presence of microorganisms⁴⁷ have shown that, 449 in general, after the reduction of Tc(VII) the formation of TcS_x compounds and polysulfides is 450 451 observed. To our knowledge, our work provides new insights into the formation of sulfate minerals 452 after the reduction of Tc(VII), highlighting the importance of further studies of the interaction of technetium with sulfur and other sulfur minerals like galena or chalcopyrite. 453

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Even though the presence of marcasite makes the overall Tc retention less efficient when compared with pure pyrite, the re-oxidation experiments showed that the production of H_2SO_4 under ambient atmosphere leads to the immobilization of the technetium that was not retained by the synthesized FeS₂. In a realistic scenario, the oxidation of marcasite will promote the Tc(VII) reduction, which will favor Tc retardation due to the formation of less mobile Tc(IV) species.

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As stated before, pyrite and marcasite are commonly misidentified and confused. This is a significant problem for the modeling of their ability to immobilize contaminants in the environment, which is especially important for most prominent redox-sensitive actinides and fission products in the context of a nuclear waste repository. This study shows the crucial role of the crystalline structure in the retention mechanism of technetium and opens the door to further comparisons of the scavenging

466 ability of other polymorphs, like hematite and maghemite. Likely, data sets of other environmental pollutants, e.g. Se, As, Cd need a careful revision with respect to polymorphism. 467

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469 **Supporting Information.** Conditions of the batch sorption experiments. Mineral characterization. 470 Speciations calculated as a function of pH.

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472 **CRediT** authorship contribution statement

473 Diana M. Rodríguez: Formal analysis, Investigation, Writing - Original Draft. Natalia Mayordomo 474 Herranz: Formal analysis, Investigation, Writing - Review & Editing. Dieter Schild: Formal analysis, Writing - Review & Editing. Salim Shams: Formal analysis, Writing - Review & Editing. Vinzenz 475 476 Brendler: Conceptualization, Writing - Review & Editing, Supervision, Project administration. Katharina Müller: Conceptualization, Writing - Review & Editing, Supervision, Project administration. 477 478 Thorsten Stumpf: Conceptualization, Writing - Review & Editing, Supervision.

479

480 **Declaration of competing interest**

481 The authors declare that they have no known competing financial interests or personal relationships that 482 could have appeared to influence the work reported in this paper.

483

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