

1 Nanoscale zero-valent iron particles for the remediation of
2 plutonium and uranium contaminated solutions

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20 **Keywords**

21 Plutonium, zero-valent iron, nanoparticles, remediation, uranium

22

23 **Abstract**

24 In the current work the uptake of plutonium onto nanoscale zero-valent iron
25 nanoparticles (nZVI) under anoxic conditions has been investigated. A uranyl solution
26 was also studied under similar geochemical conditions to provide a comparative dataset.
27 Following nZVI addition, a rapid and significant decrease in aqueous actinide
28 concentration was recorded for both systems. The removal rate recorded for plutonium
29 was slower, with 77 % removal recorded after 1 hour of reaction, compared to 99 %
30 recorded for uranium. Low aqueous contaminant concentrations (<25 %) were then
31 recorded for both systems until the end of the 7 day reaction period. XPS confirmed
32 contaminant uptake onto the nZVI. For the plutonium system, the recorded photoelectron
33 spectra exhibited Pu 4f lines centred at ~439 eV and ~427 eV, characteristic of Pu⁴⁺ and
34 implying that chemical reduction of the sorbed plutonium had occurred, ascribed to the
35 formation of PuO₂. Similarly, with the U-system, the recorded U 4f photoelectron peaks
36 were centred at energies of ~380 eV and ~391 eV, characteristic of U⁴⁺ in UO₂. Results
37 provide clear evidence that nZVI may be used as an effective material for the removal of
38 plutonium from contaminated waters.

39

40 1. Introduction

41 To date, a principal environmental legacy of mankind's military and civil nuclear
42 activities has been the discharge, either authorised or accidental, of many long-lived
43 radionuclides. Actinides and other radionuclides present a considerable long-term
44 environmental concern and have a strong bearing on the potential for site redevelopment.
45 In addition, the contamination of groundwater by more soluble radionuclides can
46 compromise drinking water sources and spread contamination over significant distances.

47 Within most civil nuclear reactors uranium dioxide (UO_2) is the primary fuel. However,
48 transmutation of non-fissile ^{238}U also generates plutonium which contributes
49 significantly to the overall energy output. This has been estimated to be up to 30 % from
50 a pressurised water reactor (PWR) during its lifetime. [1] Furthermore, plutonium present
51 in spent nuclear fuels has, in some countries, been separated for subsequent use in mixed
52 oxide fission fuels or nuclear weapons. [1] Consequently, there exist several sites
53 worldwide where plutonium contamination is a significant problem. Perhaps most
54 notable is the Mayak nuclear reprocessing plant in the Russian Federation where, as a
55 result of several decades of nuclear fuel reprocessing, plutonium storage and the 1957
56 Kyshtym disaster, soil and vegetation activities of up to several MBq m^{-2} have been
57 recorded across the site. [2] The considerable radioactivity of the plutonium isotopes
58 means that inventories of $^{239+240}\text{Pu}$ at Mayak have consistently contributed several kBq
59 m^{-2} , [2],[3] a significant fraction of the total site radiation levels. In the UK, elevated
60 radioactivity has previously been recorded for water samples taken in proximity to the
61 Sellafield nuclear reprocessing plant in Cumbria, England. For example, a study in 1999

62 reported $^{239+240}\text{Pu}$ concentrations in Scottish waters several hundred miles from the site
63 up to 73 mBq m^{-3} . [4]

64 The most important chemical property which governs the behaviour and fate of
65 plutonium in groundwater systems is generally considered to be its oxidation state. In the
66 environment, plutonium can exist as either: Pu^{3+} , Pu^{4+} , Pu^{5+} or Pu^{6+} . Under oxidising
67 conditions, Pu^{5+} and Pu^{6+} are most common whereas, in chemically reducing conditions,
68 Pu^{3+} and Pu^{4+} typically predominate. [5] In reality, the environmental prediction of
69 plutonium valence is far from routine because all four oxidation states can exist in one
70 single groundwater sample. [5] In conditions that typically exist in surface water systems
71 ($\text{pH} > 6.5$ and positive Eh), Pu^{4+} , Pu^{5+} and Pu^{6+} are the most common, [6],[7] with Pu^{4+}
72 the most common valence state when sorbed. [7] Plutonium is also recognised to readily
73 form complexes with various organic ligands, such as acetate, citrate, formate, fulvate,
74 humate, lactate, oxalate and tartrate, with many inorganic ligands, such as hydroxyl,
75 carbonate, nitrate, sulphate, phosphate, chloride, bromide and fluoride, and with many
76 synthetic organic ligands, e.g. EDTA and 8-hydroxyquinoline derivatives. [8] Carbonate
77 and bicarbonate are common anions in many natural water systems and form extremely
78 stable aqua-complexes with plutonium and actinide ions in general. [9] Consequently, in
79 natural waters the bulk of any dissolved plutonium is often comprised of plutonium-
80 carbonate complexes. For example, a typical aerated groundwater sample at $\text{pH} > 6.5$ is
81 likely to be comprised of $\sim 90\%$ $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ species with a minor percentage of
82 $\text{Pu}(\text{OH})_{4(\text{aq})}$, [8] the latter compound tending to polymerise irreversibly. [10],[11] As a
83 consequence, plutonium in the environment can be in aqueous, solid or colloidal forms.
84 [12],[13] For example, Kersting et al., (1999) [14] documented the unexpected
85 appearance of plutonium down-gradient from a known leakage source and showed that
86 plutonium was transported in association with the colloidal fraction consisting of clays

87 (namely illite and smectite) and zeolites (namely mordenite and clinoptilolite/heulandite).
88 Despite such work, there remains significant residual uncertainty with regard to the
89 environmental fate of plutonium in the natural environment and more specifically how
90 plutonium interacts with geologic materials. [15]

91 A new and potentially potent tool for the clean-up of radionuclide contaminated waters is
92 nanoscale zero-valent iron particles (nZVI). Compared to the granular ZVI more
93 commonly used in permeable reactive barriers (ZVI particulates $>1\ \mu\text{m}$ in diameter),
94 nZVI have a significantly greater surface area to volume ratio, and resultantly, a
95 significantly higher rate of chemical reaction (corrosion). [16] The small size also allows
96 the deployment of nZVI via injection for the *in situ* source treatment of contaminant
97 plumes. [16] To date, nZVI have been investigated for the immobilisation of a range of
98 metal and metalloid contaminant species, including transition metals, such as:
99 chromium, [17] cobalt, [18] copper, [19],[20], molybdenum, [20] nickel, [21], silver, [21]
100 technetium [22], vanadium [23] and zinc [21]; post transition metals, such as: cadmium
101 [21] and lead; [21],[24] and metalloids, such as: arsenic [25] and selenium [26].
102 Investigations for the remediation of radionuclides, however, remains less widely
103 researched and includes: barium, [27], pertechnetate [21],[22] and uranium.
104 [20],[28],[29],[30],[31],[32],[33],[34],[35] As demonstrated by Dickinson and Scott,
105 (2010) [30], uranium uptake onto nZVI typically occurs via sorption and then surface-
106 mediated chemical reduction. In comparison to the body of work reported for uranium,
107 the uptake of plutonium by nZVI has not, as far as we are aware, been previously
108 reported.

109 The current study aims to address this gap in research but does not, however, start from a
110 position of complete ignorance with regard to Fe-Pu interactions. Indeed interactions
111 between aqueous plutonium and iron-bearing minerals/materials are well documented,

112 with plutonium known to efficiently sorb to a range of iron (hydr)oxides, including
113 hematite, ferrihydrite and goethite. [36] In addition many forms of plutonium are known
114 to be redox active with regard to the ferrous iron. For example, aqueous Pu(V) has been
115 documented to reduce to Pu(IV) when sorbed to hematite (α -Fe₂O₃) and goethite (α -
116 FeOOH). [37] As a consequence an emerging field of research is the potential utility of
117 engineered iron bearing materials as sorbents for plutonium. Additionally, as plutonium
118 and uranium are often associated, a remediation technology that is effective for both
119 radionuclides would be of great benefit. Correspondingly, this paper presents a
120 preliminary study to assess the feasibility of using nZVI to remediate both plutonium and
121 uranium contaminated solutions.

122

123 **2. Materials and methods**

124 **2.1. Nanoparticle synthesis**

125 nZVI were synthesised following an adaptation of the method first described by Wang
126 and Zhang, 1997 [38], using sodium borohydride to reduce ferrous iron to a metallic
127 state. Briefly, 7.65 g of FeSO₄·7H₂O were dissolved in 50 mL of Milli-Q water
128 (resistivity 18.2 M Ω ·cm at 25°C) and then a 4 M NaOH solution was used to adjust the
129 pH to 6.8. The salts were then reduced to metallic nanoparticles by the addition of 3.0 g
130 of NaBH₄. The nanoparticle product was isolated through centrifugation and then
131 sequentially washed with water, ethanol and acetone (20 mL of each). The nanoparticles
132 were dried in a desiccator under low vacuum ($\sim 10^{-2}$ mbar) for 48 hours and then stored in
133 a nitrogen-filled glovebox until required.

134

135 **2.2. Experimental procedure**

136 All preparation and experimentation was performed in the oxygen-free nitrogen
137 environment of a Saffron Scientific (Alpha series) glovebox under negative pressure. A
138 Pu-solution of 1 ppm was synthesised by adding 0.3 mL of a 1000 ppm IRMM standard
139 material to a 500 mL polypropylene bottle containing 300 mL of Milli-Q water. The U-
140 solution was made by adding 0.3 mL of a 1000 ppm uranyl acetate stock solution into
141 300 mL of Milli-Q water. The pH of each system was measured and then 0.1 M NaOH
142 was added dropwise to adjust both systems to pH 6. The systems were then left to
143 equilibrate for a time period of 48 hours.

144 Prior to nanoparticle addition a 1 mL sample was taken from each batch system (time =
145 0 h) and the DO and Eh was measured and recorded. The 299 mL solutions were then
146 divided into two smaller volumes of 99 mL and 200 mL to act as the experimental
147 control and the sorption experiment, respectively. Two batches of nZVI (0.02 g each)
148 were then added to 1 mL of absolute ethanol (Sigma Aldrich, $\geq 99.5\%$) and dispersed by
149 sonication for 60 seconds using a Fisher Scientific Ultrasonic cleaner. The resultant
150 slurry was then added to the batch systems, which were then gently agitated to disperse
151 the nanoparticles throughout the sample.

152 Both systems were sampled at 1 h, 2 h, 4 h, 24 h, 48 h and 7 d. Prior to sampling, the jars
153 were gently shaken to ensure homogeneity and then a disposable pipette was used to
154 extract a 1 mL volume of liquid/nanoparticle mix which was expelled into a 1.5 mL
155 Eppendorf tube. Two Eppendorfs were filled in this way, the lids closed and the tubes
156 centrifuged for two minutes at 10,000 RPM using an Eppendorf MiniSpin centrifuge.
157 The supernatant was then poured off into a 10 mL beaker and the process was repeated
158 until approximately 10 mL of liquid had been sampled. (The small volume of solution
159 and sample aliquots was determined by the limitations inherent with working within a
160 glovebox and by the safety considerations around handling plutonium and uranium). Half

161 of the liquid was taken for pH and ORP (oxidation reduction potential) measurements,
162 using a Hanna Instruments meter (model HI 8424) with a combination gel electrode pH
163 probe and a platinum ORP electrode (model HI 3230B), respectively. The aqueous
164 samples collected were then filtered through a 0.22 μm cellulose acetate filter and stored
165 with a drop of concentrated HNO_3 prior to further preparation for inductively coupled
166 plasma mass spectrometry (ICP-MS) analysis. The solids were rinsed sequentially in 2
167 mL each of water, acetone and then ethanol to remove any physi-sorbed species and
168 residual water. At each sampling period the water rinse was also prepared for ICP-MS in
169 order to study the physi-sorbed species. Solid samples were prepared by pipetting an
170 acetone suspension of a small volume of material onto a copper stub for X-ray
171 photoelectron spectroscopy (XPS) analysis and allowing them to dry under a vacuum of
172 1×10^{-2} mbar.

173

174 **2.3. Sample analysis methods**

175 **2.3.1. ICP-MS preparation and conditions**

176 Samples were prepared for ICP-MS by a 100 times dilution in 1 % nitric acid (analytical
177 quality concentrated HNO_3 in Milli-Q water). Blanks, plutonium and uranium standards
178 at 0.1, 0.25, 0.5, 1, 5 and 10 ppb were also prepared in 1 % nitric acid. An internal
179 bismuth standard of 10 ppb was also added to all blanks, standards and samples. The
180 ICP-MS instrument used was a VG Thermo Elemental PQ3.

181 **2.3.2. TEM instrument conditions**

182 TEM images were obtained with a JEOL JEM 1200 EX Mk 2 TEM, operating at
183 120 keV. The nZVI samples were mounted on 200 mesh holey carbon coated copper
184 grids.

185 2.3.3. XRD instrument conditions

186 A Phillips Xpert Pro diffractometer with a $\text{CuK}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$) was used
187 for XRD analysis (generator voltage of 40 keV; tube current of 30 mA). XRD spectra
188 were acquired between 2θ angles of $0\text{--}90^\circ$, with a step size of 0.02° and a 2 s dwell time.

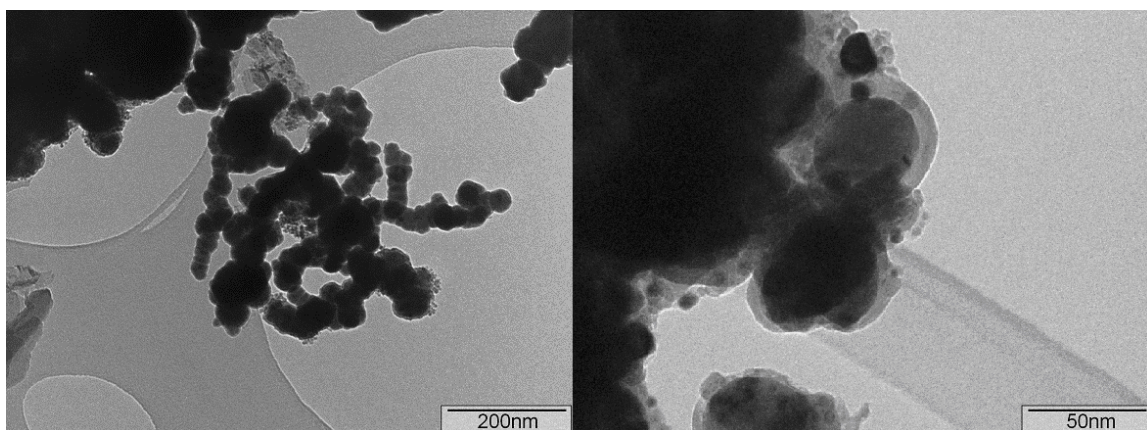
189 2.3.4. XPS instrument conditions

190 A Thermo Fisher Scientific Escascope equipped with a dual anode X-ray source
191 ($\text{AlK}\alpha$ 1486.6 eV and $\text{MgK}\alpha$ 1253.6 eV) was used for XPS analysis. Samples were
192 analysed at $<5 \times 10^{-8}$ mbar with $\text{AlK}\alpha$ radiation of 300 W (15 kV, 20 mA) power. High
193 resolution scans were acquired using 30 eV pass energy and 300 ms dwell time.
194 Following the acquisition of survey spectra over a wide binding energy range, the Fe2p,
195 C1s, O1s, Pu4f and U4f spectral regions were then scanned at a higher energy resolution
196 such that valence state determinations could be made for each element. Data analysis was
197 carried out using Pisces software (Dayta Systems Ltd) with binding energy values of the
198 spectra were referenced to the adventitious hydrocarbon C1s peak at 284.8 eV. In order
199 to determine the relative proportions of Fe^{2+} and Fe^{3+} in the sample analysis volume,
200 curve fitting of the recorded Fe2p photoelectron peaks was performed following the
201 method of Grosvenor et al., 2004. [39] The Fe2p profile was fitted using photoelectron
202 peaks at 706.7, 709.1, 710.6 and 713.4 eV corresponding to Fe^0 , $\text{Fe}^{2+}_{\text{octahedral}}$, $\text{Fe}^{3+}_{\text{octahedral}}$
203 and $\text{Fe}^{3+}_{\text{tetrahedral}}$, respectively. These parameters were selected on the basis that the
204 surface oxide was assumed to be a mixture of wüstite and magnetite, as the oxide Fe^{2+} is
205 in the same coordination with the surrounding oxygen atoms in both forms of oxide.

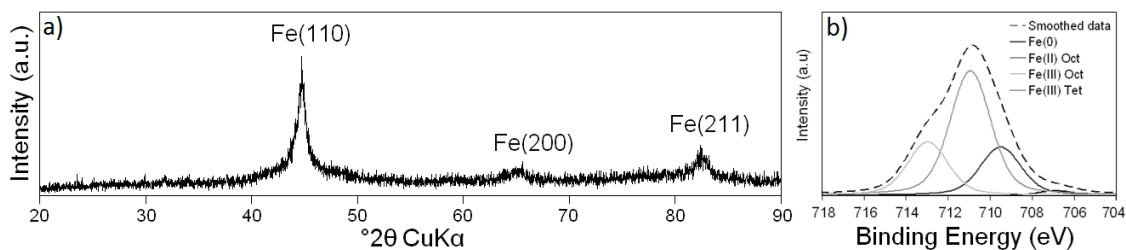
206 3. Results and discussion

207 3.1. Preliminary characterisation of the nZVI

208 Preliminary characterisation of the nZVI was performed using BET surface area analysis,
209 TEM, XRD and XPS. The physical and chemical properties of nZVI has been
210 extensively characterised elsewhere. [40] Briefly, BET surface area recorded the nZVI as
211 exhibiting a specific surface area of $14.8 \text{ m}^2 \text{ g}^{-1}$. TEM analysis (Figure 1) determined that
212 the nZVI are roughly spherical and loosely aggregated into chains and rings (when dry),
213 a feature attributed to electrostatic and/or magnetic attraction forces between individual
214 nanoparticulates. [16] XRD analysis (Figure 2a) confirmed that the nZVI consisted
215 principally of poorly crystalline/amorphous metallic α -Fe with bcc structure. XPS
216 analysis (Figure 2b) recorded a $\text{Fe}^0/\text{Fe}^{2+} + \text{Fe}^{3+}$ ratio of 0.02, indicating that the surface
217 oxide layer of the nZVI extended through the majority of the XPS analysis depth, which
218 is approximately 5nm for Fe oxide materials. [40] Indeed, previous TEM studies have
219 documented the oxide thickness of nZVI to be approximately 3-5 nm. [40] A $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of
220 0.38 was also recorded, indicating that the oxide layer is comprised of a ferrous and ferric iron
221 mixture, with a stoichiometry similar to magnetite (Fe_3O_4). A summary of the experimental
222 results is presented in Table 1.



223
224 *Figure 1. Transmission electron microscopy (TEM) images of the nZVI used in this study.*



225

226 *Figure 2. X-ray diffraction (XRD) spectra for the range 20-90° 2θ (a); and X-ray photoelectron*
 227 *spectroscopy (XPS) Fe 2p_{3/2} photoelectron spectra of the nZVI.*

228

Particle size distribution (%)	0-50 nm	85
	50-100 nm	8
	>100 nm	7
Oxide thickness (nm)		3-4
Surface area (m ² g ⁻¹)		14.8
Surface composition (at. %)	Fe	30.5
	O	32.1
	C	14.5*
	B	22.9
Iron stoichiometry	Fe ⁰ /(Fe ²⁺ + Fe ³⁺)	0.02
	Fe ²⁺ /Fe ³⁺	0.38

229 *Table 1. A summary of the experimental results regarding the bulk and surface*
 230 *properties of the nZVI. * It is likely that a high proportion of this is adventitious carbon.*

231 **3.2. Analysis of liquids**

232 **3.2.1. Changes in actinide concentration**

233 The plutonium and uranium concentrations, shown as percentages of the initial
 234 concentrations, at different reaction times are shown in Figure 3. For the Pu-system the
 235 initial concentration was significantly lower than the intended value of ~1 ppm; it was
 236 measured at 64 ppb. This significantly reduced aqueous plutonium concentration was
 237 ascribed to the adsorption of plutonium onto the clean walls of the reaction vessels and
 238 glassware used for sample preparation. Following the study of Anderson et al., 2007,

239 [41] this was not an unexpected result. This previous study showed that up to 14% of
240 total-Pu had sorbed to their reaction vessels. However, in the current work plutonium
241 'loss' was significantly greater than expected.

242 For the subsequent nZVI uptake experiments, the plutonium control systems indicated a
243 similar adsorption phenomenon over the reaction period, with aqueous plutonium
244 concentrations decreased to 53 % of initial values during the first two hours. This initial
245 significant decrease is attributed to the transfer of the initial 300 mL of plutonium
246 solution into the two smaller reaction vessels (a 200 mL nanoparticle experiment and 100
247 mL control) and the consequential sorption of plutonium onto the new vessels. After this
248 period there was a slight, but less significant, decrease of plutonium concentration over
249 the remaining time period implying that sorption to the vessel walls, or precipitation out
250 of solution, continues to occur slowly over time. Correspondingly, in order to present the
251 nZVI uptake results for plutonium more accurately, the initial decrease in plutonium
252 concentration observed in the control system has been used to adjust the 0 h plutonium
253 concentration in the nZVI sorption experiments, e.g. the initial 64 ppb plutonium
254 concentration has been reduced by 53 % to become a more accurate initial aqueous value
255 of 34 ppb.

256 Figure 3 displays the aqueous plutonium and uranium concentrations as a function of
257 time for the 7 d reaction period. Following the addition of nZVI the concentration of both
258 contaminants was recorded to decrease rapidly, with 77 and 99 % removal recorded for
259 plutonium and uranium respectively at the 1 h sampling point. A further decrease in
260 plutonium concentrations was then recorded throughout the 7 d reaction period. This
261 occurred most rapidly during the initial stages, with 85 and 86 % removal recorded at the
262 2 and 4 h sampling points respectively. At the 24 h sampling point a relative plateau was
263 reached with 90 % removal recorded, increasing to 91 % by the end of the 7 d sampling

264 period. In comparison, uranium removal was recorded to decrease slightly to 97 and 95
265 % respectively for sampling points at 2 and 4 hours respectively. A further gradual
266 increase was then recorded with 84 % uptake recorded for the 7 d sampling point. It can
267 therefore be concluded that both contaminants exhibited similar trends, in general, for
268 their removal onto nZVI, with rapid and significant initial uptake (sampling periods \leq 4
269 h), followed by significant retention of the sorbed actinides. It can also be noted,
270 however, that the kinetics of plutonium uptake was much slower than uranium, and also
271 no re-release was recorded for the former actinide specie whilst some re-release was
272 recorded for the latter specie. With the surface area of nZVI assumed as the same for
273 both systems this behaviour could be attributed to the aforementioned significantly
274 higher starting concentration of uranium in comparison to plutonium. One further
275 explanation could be related to any differential sorption affinities of the two actinides.
276 For example, it is likely that for the starting redox conditions and pH tested in the current
277 work ($E_h = 185$, $pH = 6$) plutonium and uranium would have been present predominantly
278 as $Pu(OH)_3^+$ and UO_2^{2+} respectively, [42] with a lower sorption affinity likely to have
279 been exhibited by the former species since it is a singly charged ion. [43] In addition, the
280 partial re-release of uranium in comparison to the full plutonium retention recorded could
281 also be related to differential chemical transformation (once sorbed) of the actinides. For
282 example, uncomplexed pentavalent and hexavalent plutonium species are typically more
283 easily chemically reduced than uranyl (UO_2^{2+}), and would therefore be more easily
284 transformed into a more stable surface-bound state. [44]

285 A final consideration is that during the 7 day reaction period, the surface area of the nZVI
286 would have changed due to progressive corrosion of the particles to form iron oxy-
287 hydroxide products. This is assumed to have resulted in a progressive increase in the

288 available reactive surface area, which would in turn have encouraged further Pu
289 adsorption.

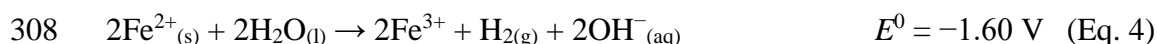
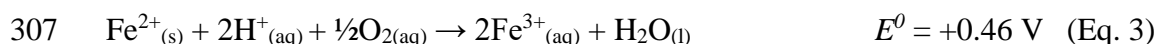
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291 3.2.2. Changes in pH and Eh

292 Prior to nanoparticle addition, the pH of both systems was measured as 6.0. The Eh and
293 dissolved oxygen content were also measured as 185 mV and 3.18 mg L⁻¹, for the Pu-
294 system and 186 mV and 4.43 mg L⁻¹ for the U-system. Following the addition of the
295 nZVI, an increase in solution pH was recorded, reaching a maximum of pH 10.5 and pH
296 9.35 in the Pu- and U-systems, respectively, Figure 3. Concurrent with this was a
297 decrease in solution Eh, reaching minimum values of -233 mV after 1 h for the Pu-
298 system and -294 mV after 2 h for the U-system, Figure 3. This behaviour is attributed to
299 the rapid aqueous oxidation of the surface of the metallic iron nanoparticles (Eq. 1-4).
300 The primary components available for corrosion reactions would have likely been
301 dissolved oxygen (DO) and water itself, with the former being strongly
302 thermodynamically favoured (Eq. 1).

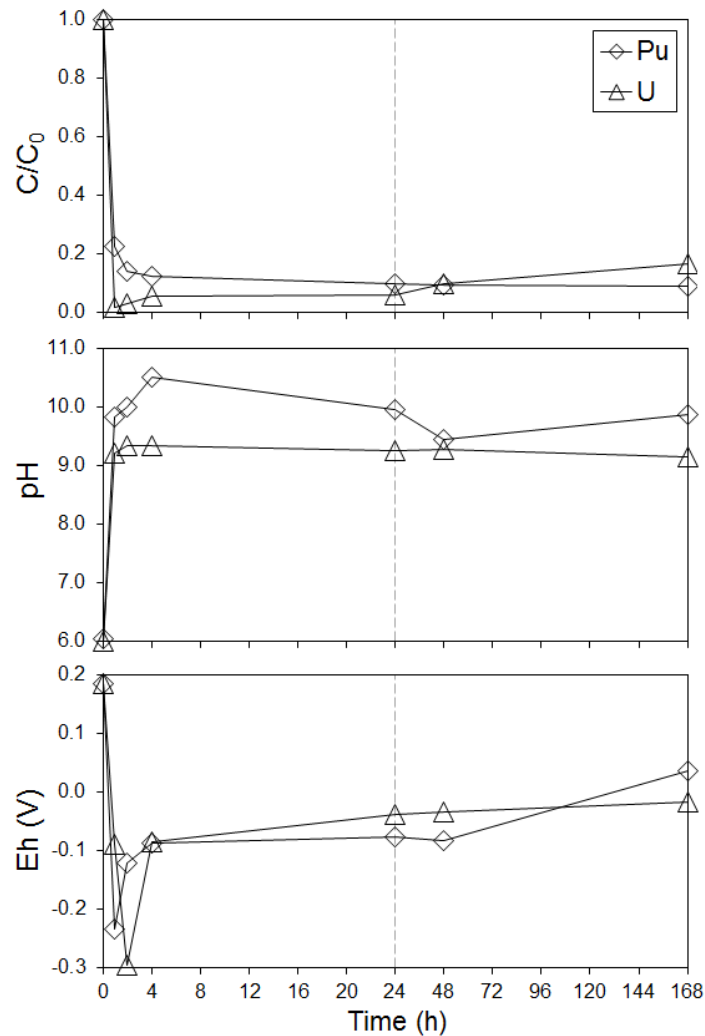


305 Ferrous iron (Fe²⁺) is the primary product from these reactions and, in turn, can undergo
306 further oxidative transformation (Eq. 3 and 4).



309 As a result of these corrosion mechanisms the nZVI would have been an active and
310 dynamic source of various corrosion products, which may have included Fe(OH)₂,

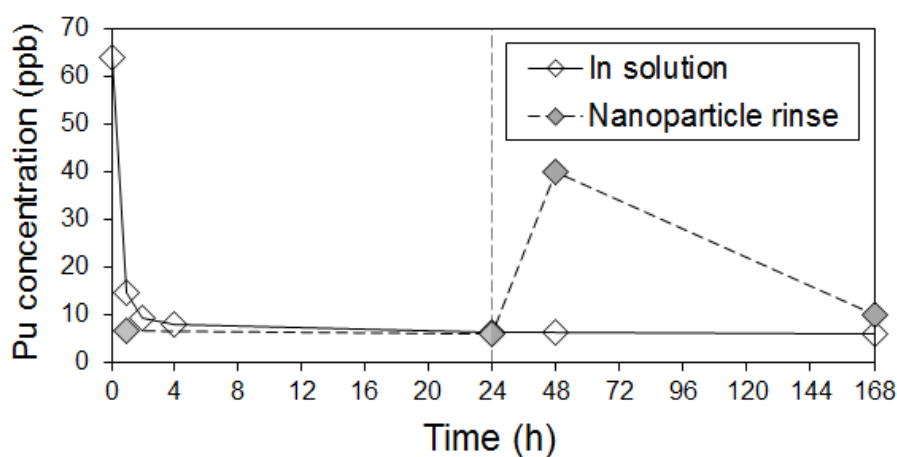
311 $\text{Fe}(\text{OH})_3$, Fe_3O_4 , Fe_2O_3 , FeOOH , $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ and green rusts. It is likely that the
312 formation of these corrosion product(s) and the aforementioned chemically reducing
313 conditions would have been responsible for the physical removal (sorption or
314 enmeshment) and in some instances chemical reduction of the exposed aqueous
315 plutonium and uranium species. It must be noted that whilst Eq. 1 and 2 are useful for
316 illustrative purposes that it would have been highly unlikely that quantitative removal of
317 either plutonium or uranium would have occurred directly on Fe^0 surfaces due to its
318 extremely low aqueous stability. Instead it is likely that the contaminants would have
319 been sorbed onto structural and/or precipitate ferrous or ferric iron species. [16]



321 *Figure 3. Actinide concentration, pH and Eh for the batch systems containing Pu- and U-*
322 *systems at reaction times of 0h, 1h, 2h, 4h, 24h, 48h and 168h.*

323

324 Analysis of the Milli-Q water used to rinse the nanoparticles from the Pu-system is
325 shown in Figure 4. The low concentration typically recorded suggests that the majority of
326 the sorbed Pu was chemi-sorbed (in a chemically reduced state) upon the nanoparticle
327 surfaces.



328

329 *Figure 4. Plutonium concentration (ppb) in solution and in the nanoparticle rinse water.*

330

331 **3.3. Analysis of reacted nanoparticulate solids**

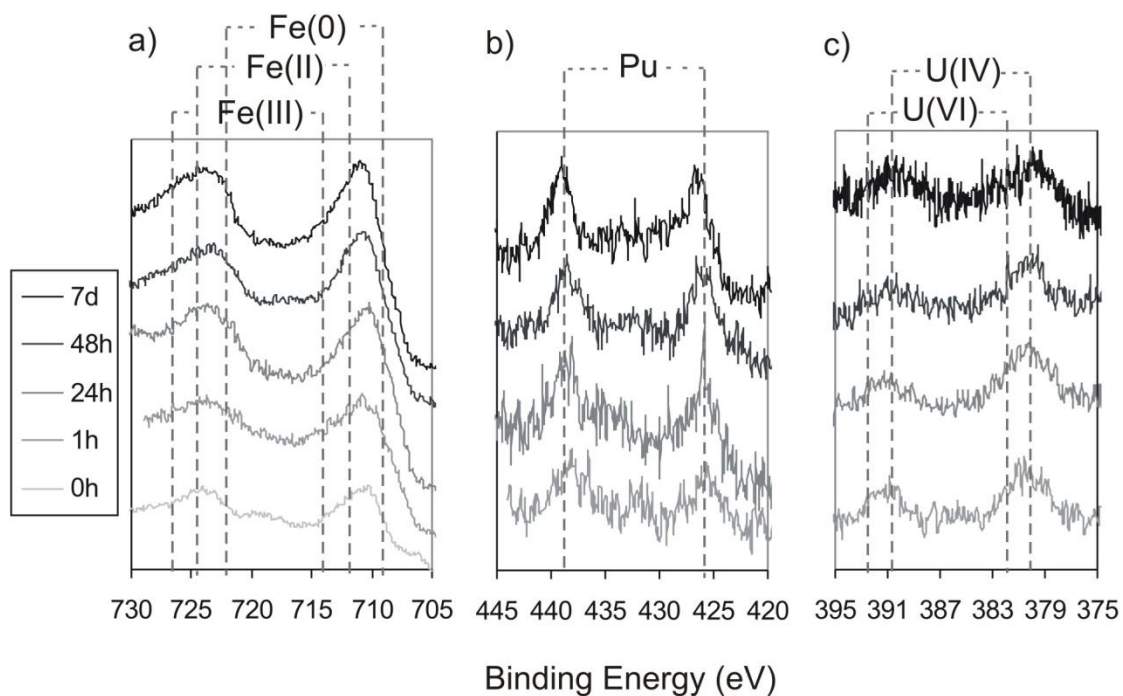
332 XPS Fe 2p_{3/2} spectra of the unreacted nZVI and extracted samples taken at periodic
333 intervals (1 h, 24 h, 48 h and 7 d) during the experiment is displayed in Figure 5.

334 Analysis of the unreacted nanopowder using XPS recorded a Fe 2p_{3/2} photoelectron peak,
335 centred at 710.3 eV (± 0.3 eV), characteristic of a mixed-valence iron oxide (such as
336 magnetite). A shoulder was also recorded on the low energy side of the primary peak,
337 centred at 706.9 eV (± 0.3 eV) indicating the presence of metallic iron, Fe⁰. XPS analysis
338 of the nanopowder extracted during the sorption experiment from both systems recorded

339 an increase in the binding energies of the Fe_{2p_{3/2}} profiles throughout the 7 day reaction
340 period, which is ascribed to the oxidation of the surface oxide from Fe²⁺ to Fe³⁺. Analysis
341 of the O1s photoelectron peak for the standard (unreacted) nanopowder recorded a broad
342 peak centred at ~530.2 eV, indicating the presence of chemi-sorbed OH⁻ groups on the
343 surface of the nZVI prior to reaction. A shoulder peak was also recorded on the lower
344 binding energy side (~529.8 eV), representing O within the surface iron oxide layer.
345 Analysis of nanoparticulate solids taken during the reaction from both systems recorded
346 an increase in the contribution of the sorbed OH⁻ concurrent with a decrease in the iron
347 oxide contribution, with a shift in the O1s peak to ~530.9 eV recorded for both systems,
348 confirming the oxidation of the nanoparticle surfaces during the experiment.

349 For the nanoparticulate solids taken from the solution containing aqueous plutonium, the
350 binding energy region between 420 eV and 445 eV was scanned to determine whether
351 plutonium could be detected to confirm that was present on the nanoparticles. Although
352 the intensity of the photoelectron signal was often quite low, plutonium was identified on
353 all nanoparticulate samples from the sampled time periods. The central peaks were
354 located at ~439 eV and ~427 eV but the signal intensities were insufficient to permit
355 reliable curve-fitting. Larson, (1980) [45] reported the XPS binding energy of plutonium
356 within PuO₂ as between 426.1eV and 426.7eV. Consequently, the recorded peak energies
357 in the present study are typical of those previously reported for PuO₂. This provides
358 direct evidence to indicate that a considerable proportion of the plutonium removed on
359 the nanoparticle surfaces was in a tetravalent state. Furthermore, this implies that a
360 chemical reduction of the sorbed plutonium has occurred, which is ascribed to a coupled
361 redox reaction with Fe²⁺ at the nanoparticle surfaces, similar to the reaction mechanism
362 previously observed for aqueous uranium [46],[44]. For the nanoparticulate solids taken
363 from the solution containing aqueous uranium, the binding energy region between 374

364 eV and 396 eV was scanned to determine the presence and valence state of any uranium
 365 present on the nanoparticle surfaces. Again, uranium was identified on all nanoparticulate
 366 samples from the sampled time periods. The central peaks were located at ~ 380.1 eV
 367 (± 0.2 eV) and ~ 391.2 eV (± 0.2 eV), comparing well with values previously reported for
 368 non-stoichiometric UO_2 , commonly referred to as UO_{2+x} , where $x \leq 2$. [47] Results from
 369 curve fitting following the method of Scott et al., (2008) [47] recorded a $\text{U}^{4+}/\text{U}^{6+}$ ratio of
 370 0.64 after 1 hour reaction, 0.61 after two hours of reaction, 0.74 after 24 hours of reaction
 371 and 0.79 after 7 days reaction. This provides clear evidence of rapid and sustained
 372 chemical reduction of U^{6+} to U^{4+} on the surface of the nZVI throughout the 7 day
 373 reaction period.



374

375 *Figure 5. Photoelectron spectra acquired from nZVI taken from the batch systems after*
 376 *0h, 1h, 24h, 48h and 168h: a) Fe2p from the Pu system; b) Pu4f from the Pu-system; and*
 377 *c) U4f from the U-system.*

378

379 The results displayed here provide an indication the nZVI may be successfully utilised as
380 a material for scavenging actinides from water. However, significant further research and
381 development is required in order to achieve a technology that may be simply and reliably
382 deployed and then subsequently recovered. One specific avenue for investigation is the
383 development of composite filter materials in which nZVI may be incorporated as a
384 reactive material, potentially alongside others. In such a structure the nZVI would be
385 trapped or anchored such that the reactive properties are still exploited but the particles
386 are immobilised. In this way the scavenged actinides may be efficiently recovered after
387 being concentrated on the filter surfaces.

388 **3.4. Potential utility of nZVI as a sorbent for plutonium and uranium**

389 To date a wide array of sorbent materials have been investigated for the removal of
390 plutonium and uranium from waste water, including titania microspheres [48], silica gel
391 [49], transitional metal oxides [50], [51] and activated carbon [51]. The results presented
392 in the current work demonstrate nZVI as effective for both plutonium and uranium
393 removal; however, a direct comparison with the aforementioned conventional actinide
394 sorbent materials cannot be drawn due to differences in experimental setup between the
395 studies. It is clear, however, that a key advantage of nZVI is their ability to be suspended
396 in solution as a colloid for maximum actinide scavenging and then recovered via
397 magnetic attraction. This unique deployment and recovery mechanism could prove of
398 considerable benefit for the treatment of radionuclide bearing waste streams where the
399 magnetic nanoparticles (and sorbed radionuclides) can be efficiently recovered in a one-
400 step and automated process, and then directly vitrified or stripped for re-use. Their reuse
401 efficacy, however, will depend on the concentration of dissolved oxygen in the batch
402 treatment solutions. Time periods in the order of hours (approximately <48 hours) are
403 typical for the transformation of nZVI into non paramagnetic (hydr)oxides in oxygenated

404 water compared to significantly longer time periods (e.g. >28 days) for anoxic systems.
405 [52]

406 **4. Conclusions**

407 The current work has provided a preliminary investigation of the mechanisms and
408 kinetics of the uptake of aqueous plutonium and uranium onto nanoscale zero-valent iron
409 particles. Following the addition of the nZVI to separate batch systems containing
410 plutonium and uranium, a rapid and significant decrease in aqueous concentrations were
411 recorded for both actinide species. Low aqueous contaminant concentrations (<25 %)
412 were then recorded for both systems until the end of the 7 day reaction period. Analysis
413 of extracted nanoparticulate solids using XPS confirmed the uptake of the contaminants
414 onto the nZVI. For the plutonium system, the recorded photoelectron spectra exhibited
415 Pu4f lines centred at ~439 eV and ~427 eV, characteristic of PuO₂. Similarly, with the U-
416 system U4f photoelectron peaks were recorded centred at energies of ~380 eV and ~391
417 eV, characteristic of UO₂. Results therefore indicate a removal mechanism for both
418 actinide species of sorption followed by chemical reduction on nZVI surfaces. Further
419 work will be aimed at determining the extent of chemical reduction more precisely.

420 **6. Acknowledgements**

421 The authors would further like to thank Mr Philip Purdie and Dr Sean Amos at the AWE
422 for facilitating the project. Research was funded by AWE plc under contract no.
423 CDK0534/30002873 and the Engineering and Physical Sciences Research Council.

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