1 **Characterizing the reactivity of metallic iron in Fe^0/U^{VI}/H_2O systems by long-term**

2 **column experiments**

3 C. Noubactep

4 Angewandte Geologie, Universität Göttingen, Goldschmidtstraße 3, D - 37077 Göttingen, Germany.

5 Tel.: +49 551 39 3191, Fax.: +49 551 399379, e-mail: cnoubac@gwdg.de

6

7 **Abstract**

8 Aqueous iron corrosion has been identified as a powerful process for environmental

9 remediation and safe drinking water provision. The intrinsic reactivity of conventional micro-

10 scale metallic iron (Fe^0) has been mostly enhanced by the association of other metals (e.g. Cu,

11 Ni, Pd) or by using nano-scale Fe^0. However, the mechanisms responsible for increased

12 reactivity are yet to be univocally elucidated. Therefore, it appears that basic knowledge on

13 Fe^0 intrinsic reactivity decreases as Fe^0 technology advances. This work was performed to

14 address the intrinsic reactivity of four selected conventional Fe^0 materials in long-term

15 column studies. Five systems were investigated. Each system was made up of two columns in

16 series. The first column contains 5.0 g of a U-bearing rock mixed with sand. The second sand

17 column contained 0.0 or 4.0 g of each Fe^0. The extent of U fixation in the systems was used to

18 characterize the reactivity of the Fe^0 materials. Results showed a clearer differentiation among

19 the three Fe^0 materials which exhibited very closed extents of iron dissolution in 2 mM EDTA

20 under dynamic conditions. The crucial importance of long-term column experiments to test

21 the suitability of Fe^0 for field applications is delineated. A new research trend is presented.

22

25

1   Introduction

25

26   Science and technology have developed various efficient methods for safe drinking water

27   provision, wastewater recycling, and groundwater remediation. These methods can be

28   classified on the basis of biological, chemical, physical, and thermal principles [1]. The most

29   current methods include adsorption, centrifugation, coagulation, crystallization, distillation,

30   evaporation, flotation, ion exchange, oxidation, precipitation, sedimentation (and gravity

31   separation), and reverse osmosis [1-7]. Among these methods, adsorption, ion exchange and

32   reverse osmosis are excellent technologies, adsorption being the most affordable one [6,7].

33   The use of metallic iron (Fe^0) for safe drinking water production has been discussed in the

34   literature during the last 10 to 15 years [8-16]. Actually, detailed concepts for the application

35   of Fe^0 for safe drinking water production at several scales have been presented. In particular,

36   Fe^0 seems to be an ideal safe water production medium in emergency situations, for remote

37   and in low-income communities [12,15]. For the realization of these concepts, a profound

38   knowledge on Fe^0 intrinsic reactivity under field conditions is needed. A purposeful use or

39   modification of Fe^0 for each application can only be based on such a profound knowledge.

40   The present work is a continuation of an effort which objective is to establish a reliable tool to

41   characterize Fe^0 intrinsic reactivity under natural near conditions. Previous works have

42   characterized the reactivity of 18 materials using batch EDTA-test [17,18]. The batch EDTA-

43   test was significantly disturbed by the abundance of atmospheric corrosion products and was

44   not suitable for powdered materials [18]. On the other hand, the long-term EDTA leaching

45   column test could not really differentiate the reactivity of seven granular materials [19]. The

46   shortcoming of the EDTA-test is that Fe^0 materials are characterized by the extent of Fe

47   dissolution which is not necessarily linearly coupled to contaminant removal. Another short

48   term batch test accounting for this shortcoming has been developed [20]. This test is based on

49   the extend of discoloration of a methylene blue solution by Fe^0 in the presence of a well-

50   characterized MnO_2 (MB-test). The MB-test suffers from the lack of a referential MnO_2

51   material but could be satisfactorily used for internal purposes.

52   Filtration on Fe^0 beds is a deep-bed filtration. This means that contaminants are not only

53   removed in the entrance zone or at a reaction front but in the whole bed [15,21]. Accordingly,

54   characterizing the reactivity of Fe^0 in column studies should not be limited to determine the

55   time to contaminant breakthrough, but rather the reactivity of Fe^0 in the beds. Based on this

56   evidence, this work intentionally used small amounts of Fe^0 and characterized the systems by

57   the extent of U fixation in the bed (also see ref. [22]). The other peculiarity is that, not a U

58   solution is piped into the columns, but U was leached in-situ from a natural rock by a natural

59   spring water.

60   The objective of this study was to further differentiate the reactivity of Fe^0 materials from

61   recent works by using near natural systems. For this purpose, U was leached from a natural

62   rock by a spring water and the intrinsic reactivity of Fe^0 materials was characterized as the

63   extent of fixation of leached U. Preliminary works enable the optimisation of experimental

64   conditions. Results delineate the importance of natural near systems for the characterization

65   of Fe^0 materials for practical use. A new experimental trend for laboratory experiments

66   regarding the characterization of the suitability of Fe^0 under natural conditions is introduced.

67   **2   Materials and methods**

68   **2.1   Solid materials**

69   **2.1.1   U-bearing rock**

70   The used U-bearing rock was crushed and sieved at the Helmholtz-Zentrum Dresden-

71   Rossendorf. The fraction 0.200 to 0.500 mm was used without any further pre-treatment. The

72   rock contains around 0.6 % U and is further composed of: 74.16 % SiO_2, 0.19% TiO_2; 7.42 %

73   Al_2O_3, 1.64 % Fe_2O_3, 0.03% MnO; 0.86 % MgO, 12.68 % CaO, 1.53 % Na_2O, 1.45 % K_2O,

74   0.04 % P_2O_5 and 0.18% SO_3. The composition was determined by X-ray fluorescence (XRF)

75   analysis. The EDX analysis (results not shown) revealed that the used rock is a multi-

76 mineralic one containing, among others, uraninite (UO_2), arsenopyrite (FeSAs), and galena

77 (PbS). Associations of U with arsenopyrite was also encountered.

2.1.2 Fe^0 materials

79 One scrap iron (ZVI1), and three commercially available Fe^0 materials have been tested. The

80 main characteristics of these materials are summarized elsewhere [19]. Before being used

81 ZVI4 was crushed and sieved; the size fraction 1.0-2.0 mm was used without any further pre-

82 treatment. The specific surface area of the materials varies between 0.043 and 0.63 m^2 g^{-1}.

83 These data were compiled from the literature (Tab. 1). The materials were compared solely on

84 the basis of the extent of U removal by the same initial mass of Fe^0 (1.2 or 4.0 g) under

85 similar experimental conditions. Apart from ZVI4, all other materials were used as obtained.

86 Crushing and sieving ZVI4 aimed at working with materials of particle size relevant for field

87 applications. The materials differ regarding their characteristics such as iron content, nature

88 and proportion of alloying elements, and shape.

89 The four used materials were selected from nine materials which were recently characterized

90 by leaching with 0.2 M EDTA in column study [19]. In turn, the tested nine materials were

91 selected from eighteen materials after a screening in batch experiments using the EDTA-test

92 [17,18]. Both tests could not really differentiate the reactivity of ZVI1, ZVI3 and ZVI4. The

93 reactivity of these three materials toward U removal from a natural rock was investigated in

94 this study. For comparison the least reactive commercial Fe^0 (ZVI2) was incorporated in this

95 study.

2.1.3 Other materials

97 **Dolomite**: The used dolomite mineral was crushed, sieved and the fraction 0.63 to 1.0 mm

98 was used. The mineralogical composition (XRF) is: SiO_2: 1.2%, TiO_2: 0.03%; Al_2O_3: 0.4%,

99 Fe_2O_3 0.6%, MgO: 20.24%, CaO: 30.94%, Na_2O: 0.04%. Dolomite is a carbonate mineral; its

100 dissolution increases the kinetics of U leaching because of the formation of stable complex

101 with carbonates [23,24]. The dolomite layer was placed after of the rock layer and thus its

102 capacity in retarding U transport is investigated.

103 **Apatite**: The used hydroxyapatite was a natural sample from a private collection (origin

104 unknown). The material was crushed, sieved and the fraction 0.5 to 1.0 mm was used.

105 **Glass beads**: The used glass beads were from Roth (Karlsruhe, Germany). Their particle size

106 was $0.25 < d$ (mm) < 0.50. They were used as filling material. Their adsorption capacity was

107 also tested in using three different volumes of glass beads in columns containing sand.

108 **Sand**: The used sand was a commercial material for aviculture ("Papagaiensand" from RUT –

109 Lehrte/Germany). Papagaiensand was used as received without any further pre-treatment nor

110 characterization. This sand was the operational reference non-adsorbing material.

111 **2.2   Leaching solution**

112 The leaching solution was spring water from the Lausebrunnen in Krebeck (administrative

113 district of Göttingen). Spring water was used as proxy for natural groundwater and was

114 supplied weekly. Its average composition (in mg/l) was: Cl^-: 9.4; NO_3^-: 9.5; SO_4^{2-}: 70.9;

115 HCO_3^-: 95.1; Na^+: 8.4; K^+: 1.0; Mg^{2+}: 5.7; Ca^{2+}: 110.1; and an initial pH 7.8.

116 **2.3   Uranium leaching and immobilization**

117 Laboratory scale glass columns were operated in up-flow mode (Fig. 1). The influent solution

118 was spring water (Lausebrunnen/Krebeck) and was pumped upwards from PE bottles using a

119 peristaltic pump (Ismatec, ICP 24). Tygon tubes were used to connect inlet reservoir, pump,

120 column and outlet. Ten glass columns (40 cm long, 2.6 cm inner diameter) were used in two

121 series of experiments. The columns were mostly packed with sand (Fig. 1). The effective

122 length, the bulk density and the porosity of the packed columns were not characterized as they

123 were not necessary for the discussion of the results. The extent of U dissolution by water and

124 the extent of its removal by selected materials were the sole targets. The experiments were

125 performed at room temperature (22 ± 3 °C) in the ISOLAB at the Department of Physical

126 Chemistry. In individual experiment series, a stable flow rate was maintained throughout the

127 experiment. Samples for analysis were collected at periodic intervals.

128 **2.3.1 One-column experiments**

129 U rock and other materials (including Fe^0) were packed into the same column (Fig. 1 - left).

130 The rock was placed at the inlet, at 5.0 cm from the bottom on a layer of sand. The other

131 material was placed at 5.0 cm from the outlet. 10 parallel experiments were performed with

132 3.0 g of the rock, 1.2 g of Fe^0, 6.0 g of dolomite, 6.0 g of apatite and three different depths of

133 glass beads (5.0, 10.0 and 20.0 cm – mass not measured) . The columns were fed with spring

134 water at a constant flow rate of 19.0 mL/h. The experiments were stopped after 37 days when

135 each column was leached by about 17.0 L of water.

136 **2.3.2 Two-column experiments**

137 Based on the results of the one-column experiments, the two-column experiments were

138 designed to better characterize the reactivity of tested Fe^0 materials (Fig. 1 - right). Five

139 parallel experiments were performed. The same mass of the rock (5.0 g) was placed in a first

140 column and 4.0 g of each tested Fe^0 was placed in the second column. In the reference system,

141 the second column contained only sand (no Fe^0). The experiments were stopped after 84 days

142 when each column was leached by 24.0 L of water. The water flow rate was constant at 12.0

143 mL/h.

144 **2.4 Analytical methods**

145 Analysis for U was performed by inductively coupled plasma mass spectrometry (ICP-MS) at

146 the Department of Geochemistry (University of Göttingen). All chemicals used for

147 experiments and analysis were of analytical grade. The pH value was measured by

148 combination glass electrodes (WTW Co., Germany). The electrodes were calibrated with five

149 standards following a multi-point calibration protocol [25] and in agreement with the new

150 IUPAC recommendation [26].

151 **3   Results and discussion**

152 **3.1 Expression of experimental results**

153 The mass (m) of leached U (mg) at any time (t) is calculated from the concentration of the

154 effluent using Eq. (1):

155 $$m = P.V \qquad\qquad (1)$$

156 Where P is the U concentration (in mg/L) and V the volume (L). At the end of the experiment

157 the total amount of leached U can be calculated by addition and the extent of U leaching by

158 spring water deduced. Knowing the percentage of U in the natural rock (0.6 %), the maximal

159 leachable mass (m_0) of uranium can be calculated. The percentage (P) uranium leaching at

160 each time is given by Eq. (2):

161 $$P = 100 * m/m_0 \qquad\qquad (2)$$

162 At each time the amount of U leached in the reference system (P_{ref}) can be set to 100 and the

163 relative leaching percent (P_{rel}) for all other systems deduced by Eq. (3):

164 $$P^* = P_{rel} = 100 * P/P_{ref} \qquad\qquad (3)$$

165 Finally, the relative percent of U removal (P_{fix}) by each material is given by Eq. (4):

166 $$P_{fix} = 100 - P_{rel} \qquad\qquad (4)$$

167 **3.2   Uranium removal in one-column experiments**

168 Table 2 and Figure 2 summarize the results of U leaching (reference system) and removal by

169 glass beads, apatite, dolomite and the four Fe^0 materials. It can be seen from Tab. 2 that the

170 maximal U leaching corresponds to 10.43 mg of U. This value corresponds to 29 % of the

171 total amount of U contained in the 3.0 g U rock. It is important to note that in all systems, the

172 effluent U concentration after 37 days was larger than 350 µg/L (Fig. 2). That is more than 16

173 times the maximum contaminant level (MCL) of the World Health Organization (WHO MCL

174 = 20 µg/L) [27]. This experimental fact suggests that instead of synthetic solutions, natural

175 rocks and minerals can be leached by natural or relevant synthetic solutions and the leachates

176 used as initial solution for decontamination experiments. The double advantage of this

177 approach is: (i) the leaching process of contaminant from natural phases can be accurately

178 investigated/characterized, and (ii) contaminant removal is investigated with concentration

179 nearer to the real world as with all possible synthetic solutions. Note that the used rock was a

180 multi-mineralic one, making the leachates multi-contaminant systems. Presently, however,

181 multi-contaminant systems have received less attention in the Fe^0 remediation community

182 [28].

183 Fig. 2a shows clearly that the process of contaminant removal under natural near conditions is

184 complex. There is no uniform trend for the evolution of U concentration. The elevated U

185 release at the beginning of the experiment (up to day 12) could be attributed to the presence of

186 fines and very reactive site at the surface. Based on relative steady state after day 20 it was

187 decided at day 30 to stop the reaction. However, prolonged sojourn in the laboratory

188 ("restricted access area") was not possible from day 27 to 37 due to technical problems.

189 Accordingly, the experiments were stopped at day 27 and the peak at day 37 is due to a 10-

190 days-stagnation which resulted in increased U leaching.

191 Table 2 shows no U removal in the systems with 5 cm and 10 cm glass beads. This both

192 systems are very comparable to the reference system showing that the results were

193 reproducible. The 6 % U removal in the column with 20 cm glass beads can be attributed to U

194 precipitation in the glass beads-layer at the beginning of the experiment as the solution are

195 necessarily over-saturated [24]. In fact, given the small size of glass beads, precipitation of U

196 as U(VI) phases (e.g. as schoepite $UO_3.2H_2O$) is very likely. Table 2 also shows that used

197 apatite and dolomite are not suitable for U removal. The suitability of apatite for U removal is

198 well documented [29-31].

199 Fig. 2b shows the cumulative mass of uranium in selected systems representative for all

200 investigated systems. It can be seen that the curves have the same allure and are very closed to

201 each other. Remember that experiments aimed at differentiating materials ZVI1, ZVI3 and

202 ZVI4 for their intrinsic reactivity using less reactive ZVI2 as negative reference. P* values

203   from Tab. 2 confirmed that ZVI2 is less reactive than the three other materials while a slight

204   differentiation between (ZVI1, ZVI3) and ZVI4 was possible. These results are not

205   satisfactorily. Accordingly, the system was modified to exploit the huge potential of this

206   experimental tool. The water flow velocity was reduced from 19 to 12 mL/h, the Fe^0 mass

207   was increased from 1.2 to 4.0 g and the mass of U rock was increased from 3.0 to 5.0 g.

208   Additionally, the Fe^0 and rock were packed in different columns (Fig. 1) and the experimental

209   duration was lengthened.

210   **3.3   Uranium removal in two-column experiments**

211   Table 3 and Figure 3 summarize the results of U leaching (reference system) and removal by

212   four Fe^0 materials in the two-column experiment mode. It is clear from Fig. 3 a and b, that a

213   differentiation of ZVI1 and ZVI3 is not possible. ZVI4 is clearly the most reactive material.

214   This observation is confirmed by P_{fix} values from Tab. 3 (83.4 % U removal). Accordingly the

215   order of increasing reactivity for the Fe^0 materials is: ZVI2 < ZVI1 $\cong$ ZVI3 < ZVI4. It should

216   be noted that in this experimental procedure, the U concentration was still higher than 20 µg/L

217   (WHO MCL value) after 70 days. On the contrary, in Fe^0 systems the U concentrations were

218   lower than 15 µg/L after 55 days (see Fig. 4). This observation corroborates the suitability of

219   long term column experiment with natural rocks and minerals for more reliable data. In such

220   experiments, the natural material could be initially washed with the used water to eliminate

221   fines at the surface and avoid the artificial peak at the beginning of the experiment.

222   Alternatively, the first pore volumes (e.g. 10 or 20) can be discarded and the Fe^0

223   characterization starts when the initial peak is over.

224   As a rule of thumb it can be considered that any natural rock or mineral from which relevant

225   contaminants could be leached for a long time (e.g. 2 months) at concentrations larger to the

226   MCL value is suitable for this type of experiment. To optimise the experimental conditions,

227   the material particle size and the used amount should be carefully tested. Testing a large

228   number of materials under such conditions could enable the establishment of a data base

229 which could be used to bridge the huge gap between short term laboratory experiments and

230 long-term processes on the field.

3.3   Discussion

232 Since the discovery of Fe^0 materials as water treatment medium [32] several groups of Fe-

233 based materials have been tested for their suitability for field application [17,33-42].

234 However, apart from Reardon [33,39] and Noubactep et al. [17,18] all Fe^0 characterization

235 attempts were based on the extent of the removal of selected contaminants by the materials.

236 Given that large variability of experimental conditions [18,22,35], available results are not

237 really comparable. Furthermore, there is still no single standard test (or proposition therefore)

238 for the characterization of the intrinsic reactivity of used materials. This situation is not

239 acceptable, efforts should be directed at developing such tests. The objective being to generate

240 the chain of knowledge on which the promising technology of using Fe^0 for water treatment

241 will be further developed.

242 The next point will be to characterize materials and group them for individual purposes. For

243 example, Fe^0 for drinking water, Fe^0 for wastewater, Fe^0 for carbonate-rich groundwater, or

244 Fe^0 for MnO_2-containing soils. The objective should not be to select the most reactive

245 material but the material that is appropriate for a given objective (site-specific). For example a

246 material suitable for carbonate-rich groundwater could be too reactive for a MnO_2-containing

247 soil because the reactivity is sustained by MnO_2 [43-45]. Similarly, plating a Fe^0 could be

248 superfluous or even disadvantageous at certain sites. In other words, plating Fe^0 to generate

249 bimetallic systems or even composites should be justified by field requirements. For this

250 purpose a better material characterization is needed.

251 After the development of a two simple tests for the characterization of intrinsic Fe^0 reactivity

252 using a diluted EDTA solution [17-19], the present study has used a natural near system to

253 further differentiate the reactivity of Fe^0. It is shown that the proper characterization of the

254 reactivity of Fe^0 materials is necessarily time consuming. In fact the 30 day-experiment was

255   not really conclusive. A clear conclusion could only be given after the 84 day-experiments. It

256   should be recalled that the 62 day-column-experiment with EDTA [19] was not sufficient to

257   differentiate the reactivity of Fe^0 tested here. It appears that an attitude change is necessary to

258   overcome the current impasse characterized by the intensive production of non comparable

259   data.

260   It has already been reiterated that all current data for the characterization of Fe^0 materials

261   (surface area, elemental composition, surface charge, surface roughness, surface state…) are

262   not sufficient to evaluate/predict the intrinsic reactivity of Fe^0 materials [18]. Only a

263   purposeful characterization of available materials will enable the manufacture of new efficient

264   materials. On this path, efforts should be directed at obtaining particularly corrosive materials

265   which are necessarily composite containing for instance over-proportional proportions of

266   corrosive alloying element like S or Mn. It is likely, that such material with electrochemical

267   cells in the whole body will be more reactive in the long term than bimetallic or multi-

268   metallic coatings. The fundamental suitability of Fe^0 composites for water treatment and their

269   superiority over conventional Fe^0 materials has been demonstrated by Hussam et al. [9,46].

270   These authors replaced conventional iron shavings/fillings by a porous composite iron

271   material and could transform a highly efficient but not sustainable system (3-Kolshi filter)

272   into a highly functional and sustainable system (SONO filter) [46].

273   **4   Concluding remarks**

274   The future of Fe^0 as water treatment material, and thus the fate for the Fe^0 remediation

275   technology as a whole, depends on the ability of researchers to traceably define/characterize

276   used materials. Since used materials considerably affect the success of the systems, there is a

277   dire need to optimize material characterization. This basic operation has the advantage of

278   minimizing system failures at the origin.

279   This work has presented a possible way for the characterization of Fe^0 intrinsic reactivity in

280   long-term column studies using natural near conditions. A beneficial side-effect of the

281 presented concept is the investigation of the process of contaminant release from natural rocks

282 and minerals and the investigation of contaminant in multi-contaminant systems at

283 concentrations close to those encountered in nature. Using such systems will ease the bridging

284 on the huge gap between short term laboratory experiments and field observations [47].

285 Finally, a full commitment of Fe^0 remediation operators with independent researchers is

286 needed to enable applied research to develop relevant scientific models and management

287 schemes based on sound laboratory results from long-term experiments.

Cited references

298 [1] V.L. Snoeyink, D. Jenkins, Water Chemistry, John Wiley & Sons (1980) 480 pp.

299 [2] T. Wigmans, Industrial aspects of production and use of activated carbons, Carbon 27

300 (1989) 13–22.

301 [3] R.D. Vidic, M.T. Suidan, U.K. Traegner, G.F. Nakhla, Adsorption isotherms: illusive

302 capacity and role of oxygen, War. Res. 24 (1990) 1187–1195.

303 [4] S.J.T. Pollard, G.D. Fowler, C.J. Sollars, R. Perry, Low-cost adsorbents for waste and

304 wastewater treatment: A review, Sci. Total Environ. 116 (1992) 31–52.

305   [5] M. Streat, J.W. Patrick, M.J. Camporro-Perez, Sorption of phenol and p-chlorophenol

306   from water using conventional and noval activated carbons, Water Res. 29 (1995) 467–

307   472.

308   [6] M.K. Doula, Simultaneous removal of Cu, Mn and Zn from drinking water with the use of

309   clinoptilolite and its Fe-modified form, Water Res. 43 (2009) 3659–3672.

310   [7] I. Ali, The quest for active carbon adsorbent substitutes: inexpensive adsorbents for toxic

311   metal ions removal from wastewater. Sep. Purif. Rev. 39 (2010) 95–171.

312   [8] A.H. Khan, S.B. Rasul, A.K.M. Munir, M. Habibuddowla, M. Alauddin, S.S. Newaz, A.

313   Hussam, Appraisal of a simple arsenic removal method for groundwater of Bangladesh,

314   J. Environ. Sci. Health A35 (2000) 1021–1041.

315   [9] A. Hussam, A.K.M. Munir, A simple and effective arsenic filter based on composite iron

316   matrix: Development and deployment studies for groundwater of Bangladesh, J.

317   Environ. Sci. Health A 42 (2007) 1869–1878.

318   [10] T.K.K. Ngai, R.R. Shrestha, B. Dangol, M. Maharjan, S.E. Murcott, Design for

319   sustainable development – Household drinking water filter for arsenic and pathogen

320   treatment in Nepal, J. Environ. Sci. Health A42 (2007) 1879–1888.

321   [11] C. Noubactep, A. Schöner, P. Woafo, Metallic iron filters for universal access to safe

322   drinking water. Clean Soil Air Water 37 (2009) 930–937.

323   [12] D.D.J. Antia, Sustainable zero-valent metal (ZVM) water treatment associated with

324   diffusion, infiltration, abstraction and recirculation. Sustainability 2 (2010) 2988–3073.

325   [13] A.M. Gottinger, Chemical-free arsenic removal from potable water with a ZVI-amended

326   biofilter, Master thesis, University of Regina (Saskatchewan, Canada) (2010) 90 pp.

327   [14] M.I. Litter, M.E. Morgada, J. Bundschuh, Possible treatments for arsenic removal in

328   Latin American waters for human consumption, Environ. Pollut. 158 (2010) 1105–1118.

329   [15] C. Noubactep, Metallic iron for safe drinking water worldwide. Chem. Eng. J. 165

330   (2010) 740–749.

331 [16] C. Noubactep, A. Schöner, Metallic iron: dawn of a new era of drinking water treatment

332   research? Fresen. Environ. Bull. 19 (2010) 1661–1668.

333 [17] C. Noubactep, G. Meinrath, P. Dietrich, M. Sauter, B. Merkel, Testing the suitability of

334   zerovalent iron materials for reactive walls, Environ. Chem. 2 (2005) 71–76.

335 [18] C. Noubactep, T. Licha, T.B. Scott, M. Fall, M. Sauter, Exploring the influence of

336   operational parameters on the reactivity of elemental iron materials. J. Hazard. Mater.

337   172 (2009) 943–951.

338 [19] C. Noubactep, Characterizing the reactivity of metallic iron in $Fe^0/EDTA/H_2O$ systems

339   with column experiments, Chem. Eng. J. 162 (2010) 656–661.

340 [20] C. Noubactep, Characterizing the reactivity of metallic iron upon methylene blue

341   discoloration in $Fe^0/MnO_2/H_2O$ systems. J. Hazard. Mater. 168 (2009) 1613–1616.

342 [21] C. Noubactep, The fundamental mechanism of aqueous contaminant removal by metallic

343   iron. Water SA 36 (2010) 663–670.

344 [22] C. Noubactep, S. Caré, Designing laboratory metallic iron columns for better result

345   comparability. J. Hazard. Mater. (2011) doi: 10.1016/j.jhazmat.2011.03.016.

346 [23] D. Langmuir, Uranium solution-mineral equilibria at low temperatures with application

347   to sedimentary ore deposits, Geochim. Cosmochim. Acta 42 (1978) 547–569.

348 [24] M. Kalin, W.N. Wheeler, G. Meinrath, The removal of uranium from mining waste water

349   using algal/microbial biomass. J. Environ. Radioact. 78 (2005) 151–177.

350 [25] G. Meinrath, P. Spitzer, Uncertainties in determination of pH, Mikrochem. Acta 135

351   (2000) 155–168.

352 [26] R.P. Buck, S. Rondinini, A.K. Covington, F.G.K. Baucke, C.M.A. Brett, M.F. Camoes,

353   M.J.T. Milton, T. Mussini, R. Naumann, K.W. Pratt, P. Spitzer, G.S. Wilson,

354   Measurement of pH. Definition, standards, and procedures (IUPAC Recommendations

355   2002), Pure Appl. Chem. 74 (2002) 2169–2200.

[27]   WHO, Uranium in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality. Geneva, World Health Organization (WHO/SDE/WSH/03.04/118) (2003).

[28] T.B. Scott, I.C. Popescu, R.A. Crane, C. Noubactep, Nano-scale metallic iron for the treatment of solutions containing multiple inorganic contaminants. J. Hazard. Mater. 186 (2011), 280–287.

[29] R. Gauglitz, M. Holterdorf, W. Franke, G. Marx, Immobilization of heavy metals by hydroxylapatite, Radiochim. Acta 58–59 (1992) 253–257.

[30] F.G. Simon, V. Biermann, C. Segebade, M. Hedrich, Behaviour of uranium in hydroxyapatite-bearing permeable reactive barriers: investigation using ^{237}U as a radioindicator. Sci. Tot. Environ. 326 (2004) 249–256.

[31] F.G. Simon, V. Biermann, B. Peplinski, Uranium removal from groundwater using hydroxyapatite. Appl. Geochem. 23 (2008) 2137–2145.

[32] G.W. Reynolds, J.T. Hoff, R.W. Gillham, Sampling bias caused by materials used to monitor halocarbons in groundwater, Environ. Sci. Technol. 24 (1990) 135–142.

[33] E.J. Reardon, Anaerobic corrosion of granular iron: Measurement and interpretation of hydrogen evolution rates, Environ. Sci. Technol. 29 (1995) 2936–2945.

[34] R.L. Landis, R.W. Gillham, E.J. Reardon, R. Fagan, R.M. Focht, J.L. Vogan, An examination of zero-valent iron sources used in permeable reactive barriers, 3rd International Containment Technology Conference (10-13 June 2001), Florida State University, Tallahassee. Orlando, FL. (2001) 5 pages.

[35] R. Miehr, G.P. Tratnyek, Z.J. Bandstra, M.M. Scherer, J.M. Alowitz, J.E. Bylaska, Diversity of contaminant reduction reactions by zerovalent iron: Role of the reductate, Environ. Sci. Technol. 38 (2004) 139–147.

[36] A.H. El-Shazly, A.A. Mubarak, A.H. Konsowa, Hexavalent chromium reduction using a fixed bed of scrap bearing iron spheres. Desalination 185 (2005) 307–316.

382 [37] O.X. Leupin, S.J. Hug, Oxidation and removal of arsenic (III) from aerated groundwater

383   by filtration through sand and zero-valent iron, Wat. Res. 39 (2005) 1729–740.

384 [38] O.X. Leupin, S.J. Hug, A.B.M. Badruzzaman, Arsenic removal from Bangladesh tube

385   well water with filter columns containing zerovalent iron filings and sand, Environ. Sci.

386   Technol. 39 (2005) 8032–8037.

387 [39] E.J. Reardon, Zerovalent irons: Styles of corrosion and inorganic control on hydrogen

388   pressure buildup, Environ. Sci. Tchnol. 39 (2005) 7311–7317.

389 [40] M. Gheju, A. Iovi, Kinetics of hexavalent chromium reduction by scrap iron, J. Hazard.

390   Mater. 135 (2006) 66–73.

391 [41] M. Gheju, A. Iovi, I. Balcu, Hexavalent chromium reduction with scrap iron in

392   continuous-flow system: Part 1: Effect of feed solution pH, J. Hazard. Mater. 153 (2008)

393   655–662.

394 [42] M. Gheju, I. Balcu, Hexavalent chromium reduction with scrap iron in continuous-flow

395   system. Part 2: Effect of scrap iron shape and size, J. Hazard. Mater. 182 (2010) 484–

396   493.

397 [43] D. Burghardt, A. Kassahun, Development of a reactive zone technology for simultaneous

398   in situ immobilisation of radium and uranium, Environ. Geol. 49 (2005) 314–320.

399 [44] A. Ghauch, H. Abou Assi, A. Tuqan, Investigating the mechanism of clofibric acid

400   removal in Fe^0/H_2O systems. J. Hazard. Mater. 176 (2010) 48–55.

401 [45] A. Ghauch, H. Abou Assi, S. Bdeir, Aqueous removal of diclofenac by plated elemental

402   iron: Bimetallic systems, J. Hazard. Mater. 182 (2010) 64–74.

403 [46] A. Hussam, Contending with a development disaster: SONO filters remove arsenic from

404   well water in Bangladesh, Innovations 4 (2009) 89–102.

405 [47] T.-H. Wang, M.-H. Li, S.-P. Teng, Bridging the gap between batch and column

406   experiments: A case study of Cs adsorption on granite, J. Hazard. Mater. 161 (2009)

407   409–415.

408

409

409   **Table 1**. Elemental composition and specific surface area (SSA) of iron materials used in this

410   study. n.d. = not determined. Modified from ref. [19]. The materials are range in increasing

411   order of the carbon content to ease comparison with previous work.

412

ZVI	Element (%)							SSA
	C	Si	Mn	Cr	Mo	Ni	Fe	(m^2/g)
ZVI4	1.96	0.12	0.09	0.003	n.d.	<0.001	86.3	0.63
ZVI2	3.39	0.41	1.10	0.34	n.d.	0.088	91.5	0.043
ZVI1	3.52	2.12	0.93	0.66	n.d.	n.d.	99.8	0.29
ZVI3	3.13	2.17	0.36	0.077	n.d.	0.056	96.7	0.50

413

414

414 **Table 2:** Extent of uranium fixation by apatite, dolomite, and Fe^0 materials in one-column

415 experiments. It can be seen that the column containing 20 cm of glass beads (Glass beads 3)

416 could significantly removed U. The extent of U removal by Fe^0 varies from 10.0 to 16.0 %. 3

417 g of U-mineral was used and each column was flooded by a volume V_T of spring water. m_f is

418 the leached mass of U, P is the percent leaching relative to the total amount of U in the

419 mineral and P* is the relative percent of U leaching. The sand column is the reference system.

420

System	Material	V_T	m_f	P	P*
	(g)	(L)	(mg)	(%)	(%)
Ref.	0.0	17.32	10.43	29.0	100.0
Glass beads 1	5 cm	17.46	11.32	31.4	108.6
Glass beads 2	10 cm	17.48	10.56	29.3	101.3
Glass beads 3	20 cm	18.25	9.82	27.3	94.2
Apatite	6.0	17.67	9.77	27.1	93.7
Dolomite	6.0	17.16	9.63	26.7	92.3
ZVI1	1.2	16.96	9.05	25.1	86.8
ZVI2	1.2	17.40	9.39	26.1	90.0
ZVI4	1.2	17.96	8.77	24.4	84.1
ZVI3	1.2	18.10	9.01	25.0	86.4

421

422

422 **Table 3:** Extent of uranium fixation by Fe^0 materials in two-column experiments. The extent

423 of U removal by Fe^0 varies from 37.3 to 83.4 %. 5 g of U-mineral was used and each column

424 was flooded by a volume V_T of natural water. m_f is the leached mass of U, P is the percent

425 leaching relative to the total amount of U in the mineral and P* is the relative percent of U

426 leaching. The sand column is the reference system. 4.0 g of Fe^0 was used in each system.

427

System	V_T	m_f	P_U	P*	P_{fix}
	(L)	(mg)	(%)	(%)	(%)
Ref.	23.9	18.40	30.7	100.0	0.0
ZVI1	23.9	7.13	11.9	38.8	61.2
ZVI2	24.3	11.53	19.2	62.7	37.3
ZVI3	23.9	7.08	11.8	38.5	61.5
ZVI4	24.1	3.06	5.1	16.6	83.4

428

429

429 **Figure 1**:

430 **Figure 1°** (left)

431
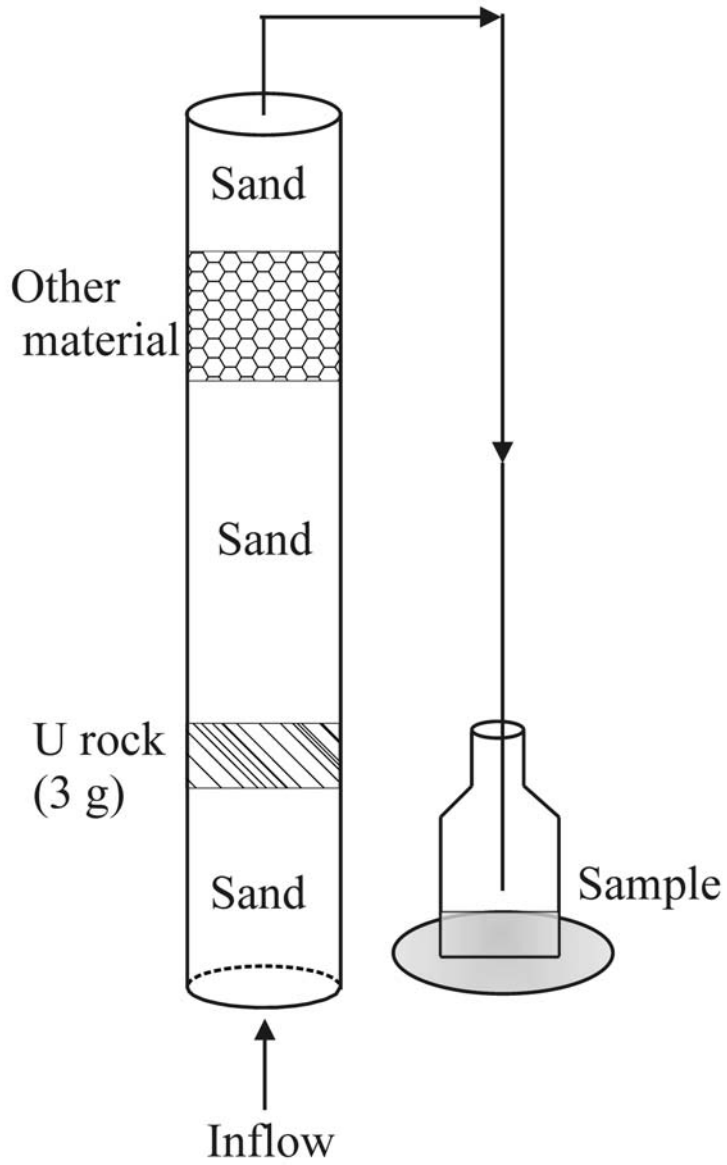
432

433

433   **Figure 1b** (right)

434

Outflow

Sand   Sand

U rock   Fe⁰
(5 g)   (4 g)
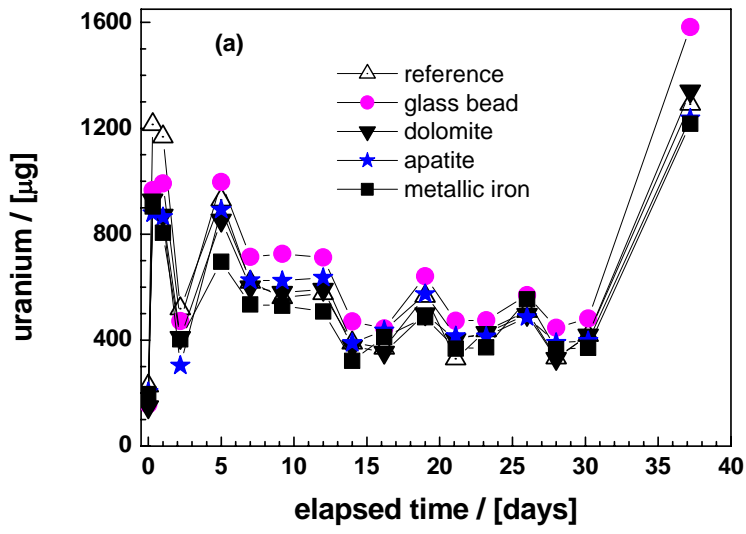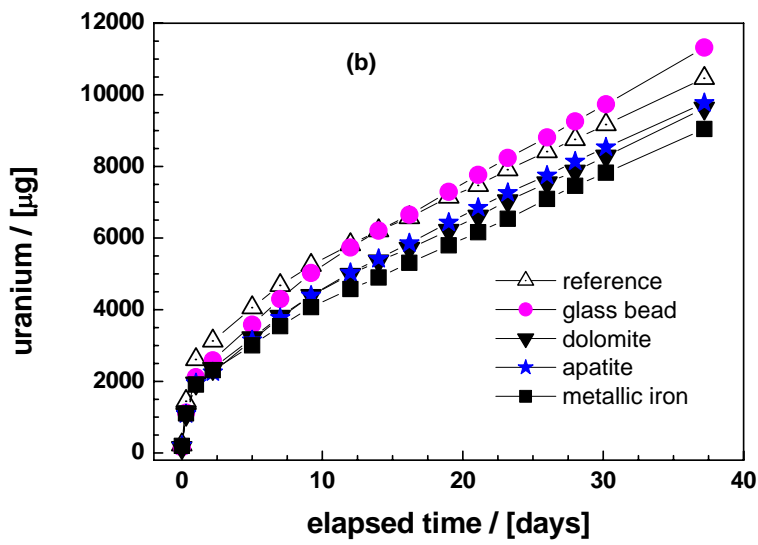
Sand   Sand

Inflow
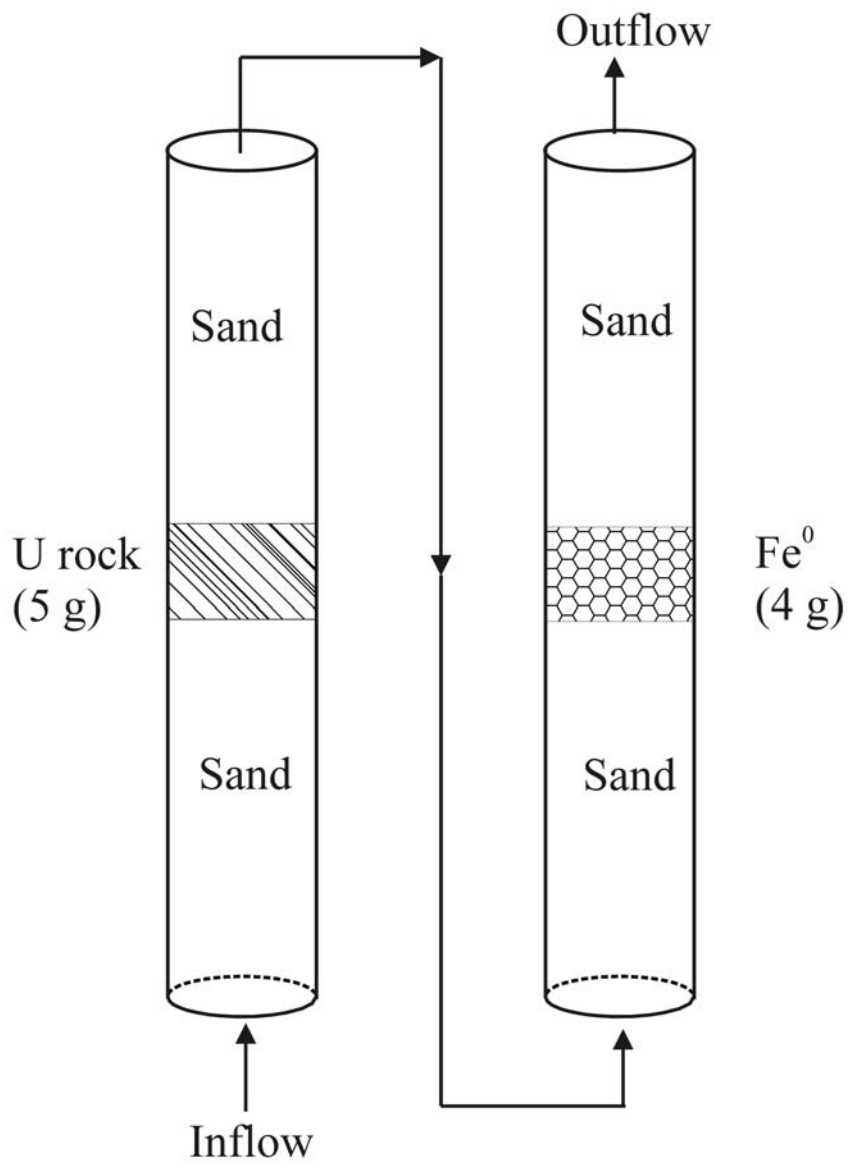
435

436

437
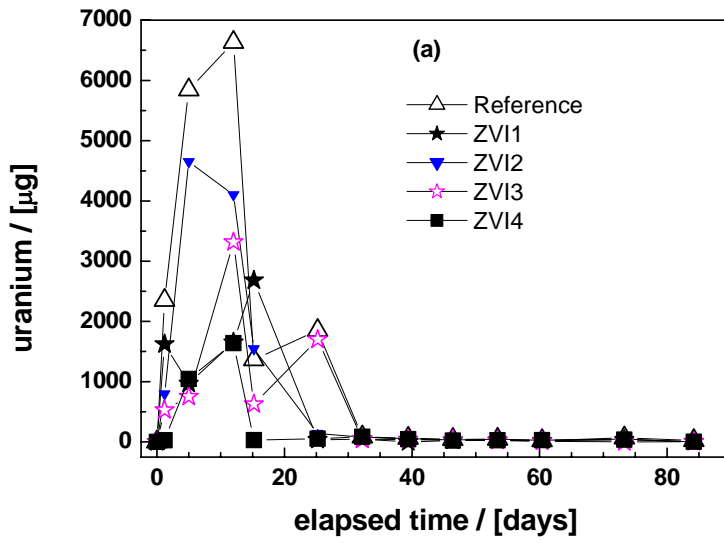
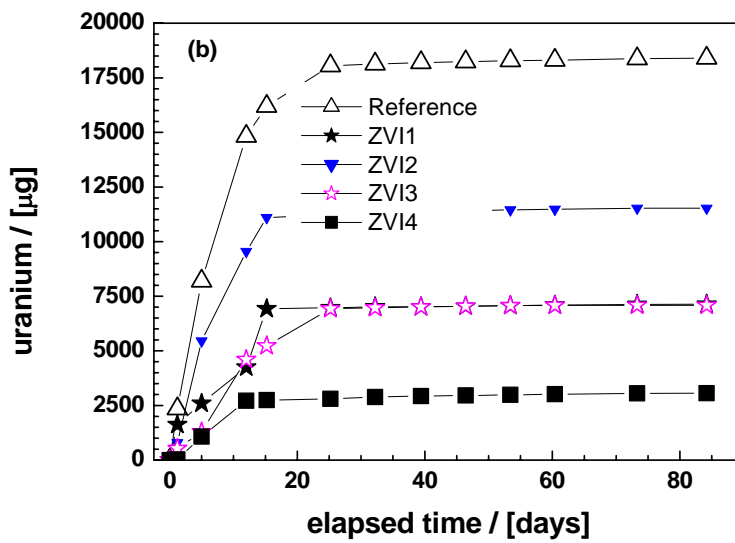437 **Figure 2**
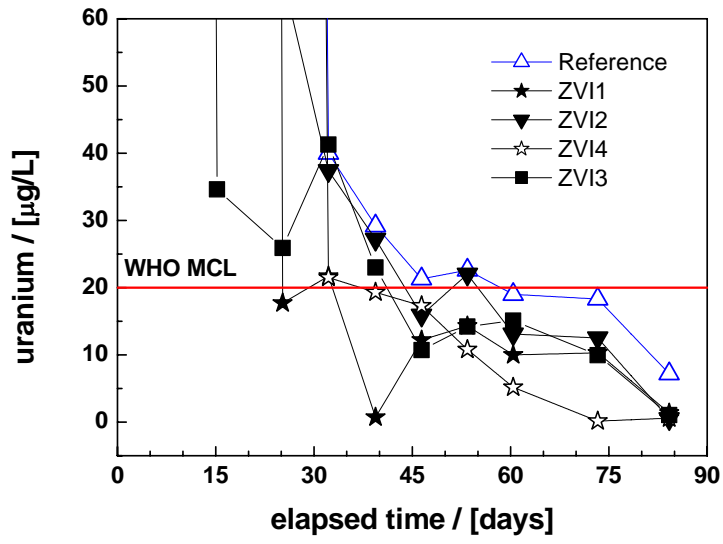

438

439

440

441

442

442   **Figure 3:**

443

444

445

446

24

446 **Figure 4**

447

448

449

Figure Captions

450 **Figure 1**:

451 Schematic diagram of the experimental design: one-column (left) and two-column

452 experiments (right). For the one-column experiments used materials were Fe^0 (1.2 g),

453 dolomite (6.0 g), apatite (6.0 g) and glass beads (5.0, 10.0 and 20.0 cm).

454 **Figure 2**:

455 Representative trend of uranium release from the one-column systems for 37 days by tested

456 materials: (a) variation of the extent of U release with time, and (b) cumulative uranium

457 release (µg). The lines are not fitting functions, they simply connect points to facilitate

458 visualization.

459 **Figure 3**:

460 Extent of uranium release from the two-column-systems for 84 days by tested Fe^0 materials:

461 (a) variation of the extent of U release with time, and (b) cumulative uranium release (µg).

462 The lines are not fitting functions, they simply connect points to facilitate visualization.

463 **Figure 4**:

464 Comparison of the evolution of the residual U concentration in the five systems of the two-

465 column experiment with the WHO MCL (20 µg/L). It is shown that up to day 75 the U

466 concentration of the effluent from the reference system was too high. Up to this date, lower U

467 concentration in other system is attributed to the reactivity of Fe^0 materials. The lines are not

468 fitting functions, they simply connect points to facilitate visualization.