# Characterizing the reactivity of metallic iron in $Fe^0$/As-rock/$H_2O$ systems by long-term column experiments

C. Noubactep

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

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

**Abstract**

The intrinsic reactivity of four metallic iron materials ($Fe^0$) was investigated in batch and column experiments. The $Fe^0$ reactivity was characterized by the extent of aqueous fixation of in-situ leached arsenic (As). Air-homogenized batch experiments were conducted for 1 month with 10.0 g/ℓ of an As-bearing rock (ore material) and 0.0 or 5.0 g/ℓ of $Fe^0$. Column experiments were performed for 2 and 3 months. Each dynamic experiment was made up of 2 glass columns in series. The first column contained 2.5 or 5.0 g of the ore material and the second column 0.0 or 5.0 g of a $Fe^0$ material. Results showed no significant reactivity difference in batch studies for all 4 materials, ZVI2 was by far the most reactive material in column experiments. This observation was attributed to the relative kinetics of production of aqueous As and Fe species under the experimental conditions and their impact on the formation of a protective film on $Fe^0$. Accordingly, no protective film could be built at the surface of the least reactive materials. The results corroborated the urgent need for unified experimental procedures to characterize $Fe^0$ materials.

**Keywords**: Column study, Intrinsic reactivity, Ore mineral, Water treatment, Zerovalent iron.

21 **Introduction**

22 Elemental metals are efficient reactive agents for the remediation of several classes of

23 environmental contaminants including arsenic, azo dyes, bacteria, halogenated organic

24 compounds, heavy metals, nitrates, nitroaromatics, radionuclides, and viruses (O´Hannesin

25 and Gillham, 1998; Bojic et al., 2004; Bartzas et al. 2006; Bojic et al., 2007; Henderson and

26 Demond, 2007; Komnitsas et al.2007; Bojic et al., 2009; Antia, 2010; Bartzas and Komnitsas,

27 2010; Bundschuh et al., 2010; Luna-Velasco et al., 2010; Noubactep, 2010a; Phillips et al.,

28 2010; Sarathy et al., 2010, Comba et al., 2011; Giles et al., 2011; ITRC, 2011; Lin et al.,

29 2011; Noubactep, 2011a; Salter-Blanc et al., 2011). Metallic iron ($Fe^0$) is currently the most

30 used material for field applications (Gillham, 2010; Comba et al., 2011; Gheju, 2011;

31 Henderson and Demond, 2011; ITRC, 2011; Salter-Blanc et al., 2011).

32 Despite the wide variety of environmental contaminants and their possible specific

33 interactions with $Fe^0$, tested materials were characterized mainly by their surface area, size

34 and interface chemistry (e.g. surface state). However, it has been traceably demonstrated that

35 none of these structural and physical characteristics is really determinant for the chemical

36 reactivity of $Fe^0$ (Reardon, 1995; Landis et al., 2001: Noubactep et al., 2005; Reardon, 2005;

37 Noubactep et al., 2009). For instance, Landis et al. (2001) reported that $Fe^0$ materials of

38 comparable particle size (comparable surface area) exhibited reactivity differences greater

39 than a three-fold for cDCE and VC degradation rates in column studies. This example

40 substantiates that a broad understanding of the chemical reactivity is urgently needed.

41 Several sources of $Fe^0$ materials have been reported in literature to be efficient for aqueous

42 contaminant removal (Landis et al., 2001; Miehr et al., 2004; Leupin and Hug, 2005;

43 Noubactep et al., 2005; Gheju and Iovi, 2006; Satapanajaru et al., 2006; Yang et al., 2006;

44 Ngai et al., 2007; Gheju et al., 2008; Gheju and Balcu, 2010; Gheju and Balcu, 2011, Wanner

45 et al. 2011). These include commercial $Fe^0$ for contaminant removal (e.g. Connelly iron,

46 Peerless iron, iron from G. Maier GmbH), commercial iron for other purposes (e.g.

47  construction steel, iron nails, steel wool), scrap iron, production by-products, $Fe^0$ prepared in-

48  situ by reduction of iron salts. Although, many tested materials have been reported highly

49  reactive and recommendable for field application, efficacy of a $Fe^0$ in terms of high removal

50  capacity for a specific contaminant in short term experiments is not a guarantee for high

51  removal capacity in field applications. Moreover, researchers working with nano-scale $Fe^0$

52  usually compare their results to that of conventional micro-scale $Fe^0$ (Noubactep et al., 2012

53  and ref. cited therein). The question is what is the reference material to which innovative

54  materials should be compared?

55  The present study is a continuation of a series of works aiming at introducing reliable tools for

56  the evaluation of the intrinsic reactivity of various $Fe^0$ materials. A method based on the

57  characterization of Fe dissolution in a 2 mM EDTA solution was first proposed (Noubactep et

58  al., 2004; 2005; 2009). The method was proven less efficient for powdered materials and for

59  materials with high proportion of fines (Noubactep, 2010b). On the other hand, $Fe^0$

60  dissolution is not necessarily coupled to contaminant removal. These limitations have led to

61  the development of a second experimental tool in which $Fe^0$ is characterized by the extent of

62  the discoloration of methylene blue (MB) in the presence of manganese dioxide ($MnO_2$) (MB-

63  test) (Noubactep, 2009). The MB-test was shown more efficient and more affordable than the

64  EDTA-test but was limited by the lack of reference $MnO_2$ materials. Both tests could enable

65  an advanced material screening. However, from the tested 18 materials seven were still

66  exhibiting very similar reactivity. Therefore, new approaches are needed.

67  A further possibility to characterize the reactivity of $Fe^0$ materials is to stress them in systems

68  where building of a protective film at their surface is likely to occur. Such a system was

69  identified recently while characterizing the solubilization of toxic species from natural rocks

70  (Noubactep et al., 2008a; 2008b). It was shown that elevated amounts of As could be leached

71  from an ore material for a long time (up to 99 days). Accordingly introducing the same

72  amount of various $Fe^0$ materials in system capable of producing As concentration as large as

73    1000 mg/ℓ could be a powerful tool to investigate the impact of As on the formation of the

74    oxide film (mixed oxides) on the process of contaminant removal by $Fe^0$. As a rule, the more

75    reactive a material, the more rapid the passivation process (protective film formation). In

76    other words, the system with the most reactive material will exhibit the least contaminant

77    removal efficiency.

78    The objective of this study is to present a new contribution to the effort for the development

79    of reliable protocols for the comparison of the intrinsic reactivity of different $Fe^0$ materials.

80    For this purpose, four selected materials from former works are tested. One of the materials

81    was essentially less reactive than the others. The 3 other materials were very closed in their

82    reactivity by both tests described above (Noubactep, 2010b). The results confirmed the

83    suitability of the used method and opened new routes for coupling the investigation of

84    contaminant release and contaminant removal under relevant conditions.

85    **Materials and methods**

86    **Solid materials**

87    **As-bearing rock**

88    The used As ore material originates from the Otto-Stollen in Breitenbrunn/Erzgebirge

89    (Saxony, Germany). The material was selected on the basis of its high arsenic content (80 %).

90    A qualitative SEM analysis shows the presence of As, Ca, F, Fe, O, S and Si (Noubactep et

91    al., 2008). The ore material is primarily a hydrothermal vein material and arsenic occurred as

92    native arsenic ($As^0$) and Loellingite ($FeS_2 - As^{-1}$) (Jones and Nesbitt, 2002) in paragenesis

93    with hydrothermal vein carbonates (for example Fe-bearing calcite or dolomite). The mineral

94    was ground and sieved. The particle size fraction $0.063 \leq d$ (mm) $\leq 0.10$ was used without

95    any pre-treatment.

96    **$Fe^0$ materials**

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

98    main characteristics of these materials are summarized elsewhere (Noubactep, 2010b). ZVI2

99    is a spherical material (d = 1.2 mm) from Würth (Germany) termed as 'Hartgußgranulat'.

100   ZVI3 are iron chips from G. Maier GmbH Rheinfelden (Germany) termed as

101   'Graugußgranulat'. ZVI4 is a direct reduced iron from ISPAT GmbH (Germany), termed

102   'Schwammeisen'. Before used ZVI4 was crushed and sieved; the size fraction 1.0-2.0 mm

103   was used. The specific surface area of the materials varies between 0.043 and 0.63 $m^2$ $g^{-1}$.

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

105   the basis of the extent of As removal by the same initial mass of $Fe^0$ (e.g. 5.0 g in columns)

106   under similar experimental conditions. The materials differ regarding their characteristics

107   such as iron content, nature and proportion of alloying elements, and shape.

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

109   by leaching with 2 mM EDTA in column study (Noubactep, 2010b). In turn, the tested nine

110   materials were selected from eighteen materials after a screening in batch experiments using

111   the EDTA-test (Noubactep et al., 2005; Noubactep et al., 2009). Both tests could not really

112   differentiate the reactivity of ZVI1, ZVI3 and ZVI4. The reactivity of these three materials

113   toward As removal from a natural rock was investigated in this study. For comparison the

114   least reactive commercial $Fe^0$ (ZVI2) was incorporated in this study.

115   **Sand**

116   The used sand was a commercial material for aviculture ("Papagaiensand" from RUT –

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

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

119   **Leaching solution**

120   The leaching solution was tap water of the city of Göttingen (Lower Saxonia, Germany). Tap

121   water was discussed as a better proxy for natural groundwater than synthetic solutions

122   (Noubactep, 2003; Noubactep et al., 2008). The rationale behind this assumption is that, in

123   many cases, natural water is just treated for iron and manganese removal. The average

124      composition (in mg/$\ell$) of the used tap water was: $Cl^-$: 7.7; $NO_3^-$: 10.0; $SO_4^{2-}$: 37.5; $HCO_3^-$:

125      88.5; $Na^+$: 7.0; $K^+$: 1.2; $Mg^{2+}$: 7.5; $Ca^{2+}$: 36.1; and an initial pH 8.3.

126      **As leaching and immobilization**

127      **Air homogenized batch experiments**

128      These experiments were conducted in special reaction vessels allowing the system to be

129      homogenized by a humid current of air supplied by a small aquarist pump. The goal was to

130      homogenize the experimental systems at atmospheric pressure ($P_{CO2}$ = 0.035 %) without

131      breaking down the materials. 10.0 g/$\ell$ of the ore material and 0.0 or 5.0 g/$\ell$ of $Fe^0$ were

132      allowed to react in sealed vessels containing 100 m$\ell$ of tap water at laboratory temperature

133      (22 $\pm$ 3 °C) for up to 30 days. At given dates, 1.5 m$\ell$ of the solution was retrieved and diluted

134      for As analysis and the same volume of tap water was added to the system.

135      **Column experiments**

136      The tap water was pumped upwards from PE bottles using a peristaltic pump (Ismatec, ICP

137      24). Tygon tubes were used to connect inlet reservoir, pump, column and outlet. Ten glass

138      columns (40 cm long, 2.6 cm inner diameter) were used in two series of experiments. The

139      columns were mostly packed with sand. The effective length, the bulk density and the

140      porosity of the packed columns were not characterized as they were not necessary for the

141      discussion of the results. The extent of As dissolution by water and the extent of its removal

142      by selected $Fe^0$ materials were the sole targets. The experiments were performed at room

143      temperature (22 $\pm$ 3 °C). A stable flow rate was maintained throughout the experiment.

144      Five parallel experiments were performed in each series. The same mass of the rock (2.5 or

145      5.0 g) was placed in a first column and 5.0 g of each tested $Fe^0$ was placed in the second

146      column (Fig. 1). In the reference system, the second column contained only sand (no $Fe^0$).

147      The experiments were stopped after 65 or 97 days when each column was leached by 19 or

148      25.0 $\ell$ of tap water (Tab. 2). The water flow rate was constant at 12.0 m$\ell$/h.

149      **Analytical methods**

150    Analysis for As was performed by inductively coupled plasma mass spectrometry (ICP-MS)

151    at the Department of Geochemistry (Centre of Geosciences, University of Göttingen). All

152    chemicals used for the experiments and analysis were of analytical grade. The pH value was

153    measured by combining glass electrodes (WTW Co., Germany). The electrodes were

154    calibrated with five standards following a multi-point calibration protocol and in agreement

155    with the new IUPAC recommendation (Meinrath and Spitzer, 2000; Buck et al., 2002).

156    **Expression of experimental results**

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

158    effluent using Eq. (1):

159         $m = P.V$                                                            (1)

160    Where P is the As concentration (in mg/$\ell$) and V the volume ($\ell$). At the end of the experiment

161    the total amount of leached As can be calculated by addition and the extend of As leaching by

162    tap water deduced. Knowing the As percentage in the natural rock (80 %), the maximal

163    leachable mass ($m_0$) of As can be calculated. The percentage (P) As leaching at each time is

164    given by Eq. (2):

165         $P = 100 * m/m_0$                                                    (2)

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

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

168         $P* = P_{rel} = 100 * P/P_{ref}$                                     (3)

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

170         $P_{fix} = 100 - P_{rel}$                                           (4)

171    **Results and discussion**

172    The particularity of As-rock/$Fe^0$ systems investigated here is that aqueous As and solid Fe

173    hydroxides and oxides for their removal are generated in-situ. It has been traceably

174    demonstrated, that $As^{III}$ and $As^V$ are removed in $Fe^0/H_2O$ systems by adsorption and co-

175    precipitation (Lackovic et al., 2000; Farrell et al., 2001; Noubactep, 2010a; Noubactep,

7

176    2011b; Noubactep, 2011c; Noubactep, 2012). As released from the used ore material was

177    recently characterized (Noubactep et al., 2008a) and the process of As dissolution will not be

178    discussed here. The basis for the characterization of $Fe^0$ materials is that the smallest As

179    concentration (relative to the reference system) is encountered in the system with the most

180    reactive material under testing conditions.

**Batch experiments**

182    Fig. 2 illustrates As dissolution in the absence (reference) or the presence of tested $Fe^0$

183    materials (ZVI1 through ZVI4) as a function of time. Both leaching kinetics and the extent of

184    As release substantially decreased with the addition of $Fe^0$. From Fig. 2 not visual reactivity

185    difference could be performed. It appears that the reactivity of all four materials is very closed

186    to each other. A look on $P_{fix}$-values (Tab. 3) shows that the relative fixation efficiency varies

187    from 30.4 to 37.3 %. A tentative order of increasing reactivity based on these values is: ZVI3

188    < ZVI1 < ZVI2 < ZVI4. Remember that the order of reactivity after the EDTA-test

189    (Noubactep et al., 2005; 2009) and the MB-test (Noubactep, 2009) were univocally: ZVI2 <

190    ZVI1 ≅ ZVI3 ≅ ZVI4. Accordingly, air-homogenized batch experiments are not appropriate

191    for the differentiation of the reactivity of ZVI1, ZVI3 and ZVI4. It is well-known that batch

192    systems can not give an image of processes occurring in nature (Wang et al. 2009). The first

193    reason in regard to the experimental conditions of this work is the possibility of super-

194    saturation of the As solution given the too long contact time (30 days) and the relative strong

195    homogenisation with air-bubbles. To account for this further characterizations were

196    performed under dynamic conditions.

**Column experiments for 65 days**

198    Fig. 3a shows the effect of tested ZVIs on As leaching from the natural ore as a function of

199    time (≤ 65 days). 5.0 g of the ore material was placed in the first column and 5.0 g of ZVI in

200    the second column (Fig. 1). From Fig. 3a a visual differentiation of ZVI2 is evident. It is also

201    evident that the reference system exhibited the highest As concentration. The cumulative sum

202  of released As (Fig. 3b) confirmed this trend. The m- and $P_{fix}$-values from Tab. 3 confirmed

203  these observations. The deduced increasing order of increasing reactivity is: ZVI3 $\cong$ ZVI4 <

204  ZVI1 < ZVI2. This classification showing that ZVI2 was the most reactive materials is

205  acceptable but the experimental conditions should be further modified to obtain a clear trend.

206  The following modifications were operated: (i) the mass of ore material was halved, (ii) the

207  first two litres of leaching solution in $Fe^0$/As-rock systems were discarded, and (iii) the

208  experimental duration was lengthened to 97 days. All other parameters (flow rate,

209  temperature) were kept constant. The rationale behind discarding the first two litres was the

210  elevated As concentration in this initial phase (Fig. 3a).

211  The next important feature from Fig 3a is that 5.0 g of the used ore material is capable of

212  producing about 17 mg/$\ell$ (reference system) As for more that two months. High As

213  concentration was intentionally tested here. By varying the mass of the ore material and the

214  particle size, As concentrations relevant for each specific size could be achieved.

215  **Column experiments for 97 days**

216  Fig. 4a shows the effect of tested ZVIs on As leaching from the natural ore as a function of

217  time ($\leq$ 97 days). A visual reactivity difference can be better performed than in Fig. 3a. The

218  visual increasing order of reactivity is: ZVI4 < ZVI3 < ZVI1 < ZVI2. The m- and $P_{fix}$-values

219  from Tab. 3 confirmed this trend with the additive information, that ZVI3 and ZVI4 are very

220  closed in their reactivity as the percent As removal ($P_{fix}$-values) was 11.9 and 11.7

221  respectively. Fig. 4b clearly confirmed the results from Tab. 3.

222  From Fig. 4a is clear that 2.5 g of the As-rock is able to produce about 16 mg/$\ell$ As for more

223  than three months. These results shows clearly that long-term experiments regarding As

224  removal can be coupled with As leaching from natural ores. By reducing the ore mass,

225  changing the particle size and using different ores, it is possible to perform long-term leaching

226  experiments in the laboratory. Such experiments could help to bridge the huge gap between

227  the laboratory and the field (Wang et al., 2009). On the other hand, parameters from such

228 systems could help to develop more reliable models to predict contaminant leaching in the

229 environment.

**Discussion**

231 The use of $Fe^0$ materials for environmental remediation is severely handicapped by the lack of

232 methods for characterization of the chemical reactivity. The current procedure of testing the

233 reactivity of $Fe^0$ for individual contaminants (Landis et al., 2001; Miehr et al., 2004; Leupin

234 and Hug, 2005; Gheju and Iovi, 2006, Wanner et al. 2011) is not very useful as no

235 comparison between two independent works is possible, even for the same contaminant.

236 Ideally, there should be a universally acceptable/accepted method to evaluate various $Fe^0$ for

237 their chemical reactivity. Accordingly, it is contemplated to propose protocols, which could

238 be used to compare the efficiency of different $Fe^0$.

239 From available works, only the characterization of $Fe^0$ by the extent of $H_2$ production

240 (Reardon, 1995; 2005) could be regarded as universally applicable method to characterise $Fe^0$

241 intrinsic reactivity. However, this protocol is not necessarily affordable and used relative high

242 $Fe^0$ masses (15.0 to 400 g). Accordingly, most simple and affordable tests should be

243 developed. The EDTA-test (Noubactep et al., 2005; 2009) and the MB-test (Noubactep, 2009)

244 are simple and affordable but they could not address the passivation of tested material.

245 In using elevated As concentrations, the present work has corroborated warnings to perform

246 contaminant removal experiments with over-saturated solutions (e.g. Kalin et al., 2005).

247 However, more than the instability of used solutions introducing biases in the extent of

248 contaminant removal by the tested process, this study has delineated the impact of elevated

249 concentrations on the passivation process. In fact, in nature, contaminants are rarely available

250 at high concentration (Henderson and Demond, 2011; Kümmerer, 2011) and contaminated

251 water enters the zone containing $Fe^0$ when an oxide scale is already formed at its surface. In

252 other words, while using elevated contaminant concentrations, an artificial system is created

253  that could not be reproduced in nature. On the other hand, elevated contaminant

254  concentrations necessarily impact the process of film formation on $Fe^0$ (Noubactep, 2010c).

255  **Concluding remarks**

256  In an attempt to access their intrinsic chemical reactivity, the performance of 3 commercial

257  $Fe^0$ (ZVI2, ZVI3 and ZVI4) and one scrap iron (ZVI1) for the removal of As has been

258  evaluated in long-term column studies. As was leached from a natural rock using the tap

259  water of the city of Göttingen as leaching solution. The results confirmed findings from

260  previous works that ZVI2 is the least reactive material (Noubactep et al., 2005; 2009;

261  Noubactep, 2010a, Noubactep 2011d). It could be further shown that ZVI1 is less reactive

262  than ZVI3 and ZVI4.

263  The test methodology consisting in leaching As with tap water can be further improved or

264  adapted to investigate several aspects of contaminant release and contaminant removal. For

265  example, by reducing the mass of the ore material, As concentration relevant to field

266  situations could be obtained and used to characterize the performance of $Fe^0$ materials for As

267  removal. On the other hand, using several leaching solutions could enable the characterization

268  of the impact of relevant ions on the process of As leaching (and/or removal). Such

269  experiments could be designed on the basis of site-specific situations. It is hoped that this new

270  experimental tool will accelerate efforts to characterize the intrinsic reactivity of $Fe^0$

271  materials.

272  **Acknowledgments**

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438

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

439       study. n.d. = not determined. Modified from Noubactep (2010b).

440

| 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 |

441

442

442 **Table 2:** Summary of the experimental conditions for As release from the As-mineral and As

443          removal by $Fe^0$ in batch and column studies for the four tested $Fe^0$ materials. '$V_T$'

444          is the total volume of tap water that has flowed into the individual columns.

445          General conditions: $pH_0 = 8.3$ and $T = 23 \pm 2$ °C.

446

|  |  | Batch | column 1 | column 2 |
|---|---|---|---|---|
| duration | (d) | 30.0 | 65.0 | 97.0 |
| As-mineral | (g) | 1.0 | 5.0 | 2.5 |
| ZVI | (g) | 0.5 | 5.0 | 5.0 |
| $V_T$ | (ℓ) | 0.1 | 19.0 | 25.0 |
| flow rate | (mℓ/h) | air bubbled | 11.9 | 11.9 |

447

448

448 **Table 3**: Extent of As release (in mg) from the natural mineral as influenced by the presence

449 of $Fe^0$ in batch and column studies. The system without $Fe^0$ is used as reference to

450 characterize the extent of As removal by individual ZVIs ($P_{fix}$ in %). As a rule, the

451 more reactive a material the bigger the m and $P_{fix}$ values. General conditions: $pH_0$
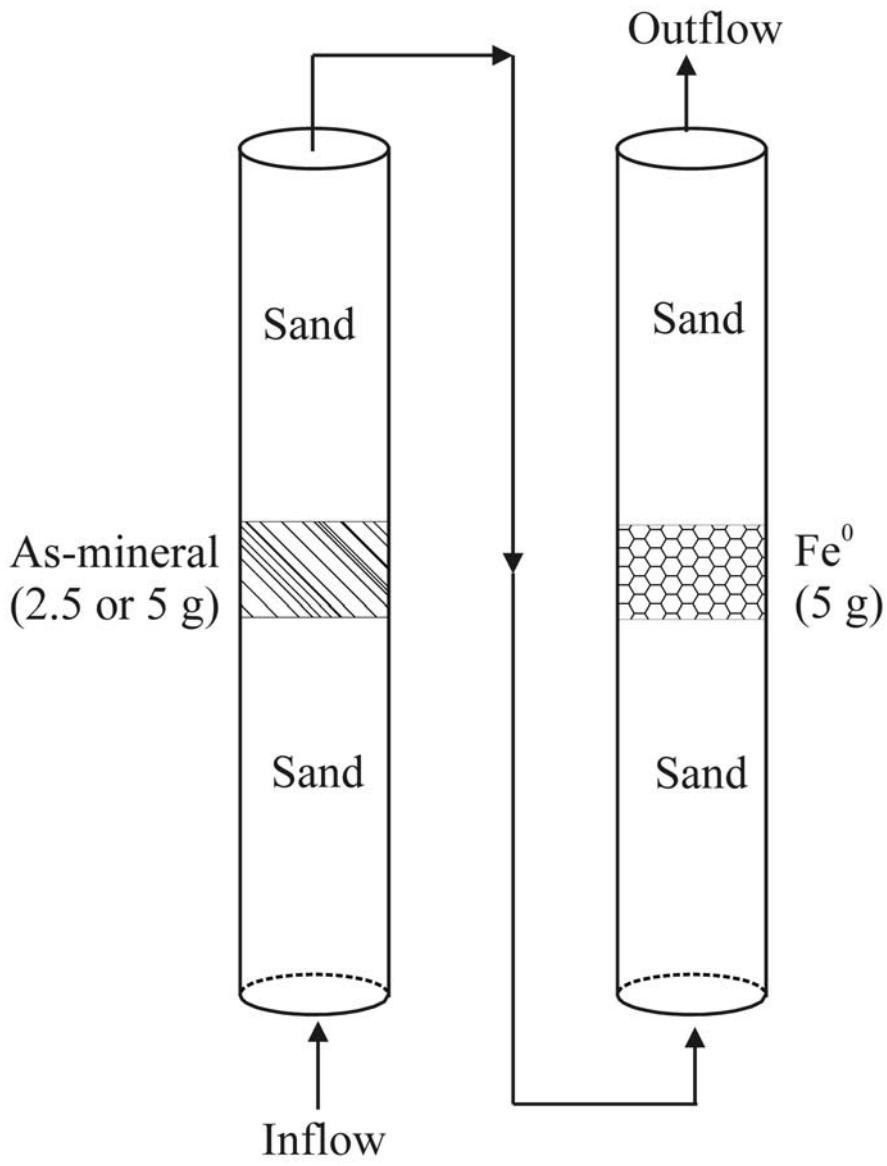
452 = 8.3 and T = 23 ± 2 °C.

453

| | Batch | | Column 1 | | Column 2 | |
|---|---|---|---|---|---|---|
| | **m** | **$P_{fix}$** | **m** | **$P_{fix}$** | **m** | **$P_{fix}$** |
| | (mg) | (%) | (mg) | (%) | (mg) | (%) |
| **reference** | 173 | 0.0 | 338 | 0.0 | 3745 | 0.0 |
| **ZVI1** | 118 | 32.2 | 307 | 9.1 | 2985 | 20.3 |
| **ZVI2** | 117 | 32.6 | 243 | 28.0 | 2782 | 25.7 |
| **ZVI3** | 121 | 30.4 | 322 | 4.6 | 3301 | 11.9 |
| **ZVI4** | 109 | 37.3 | 322 | 4.6 | 3306 | 11.7 |

454

455

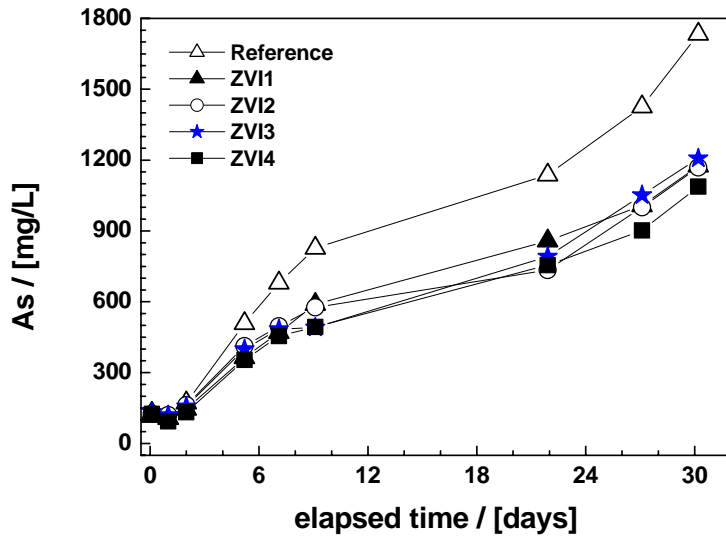455 **Figure 1**

456



457

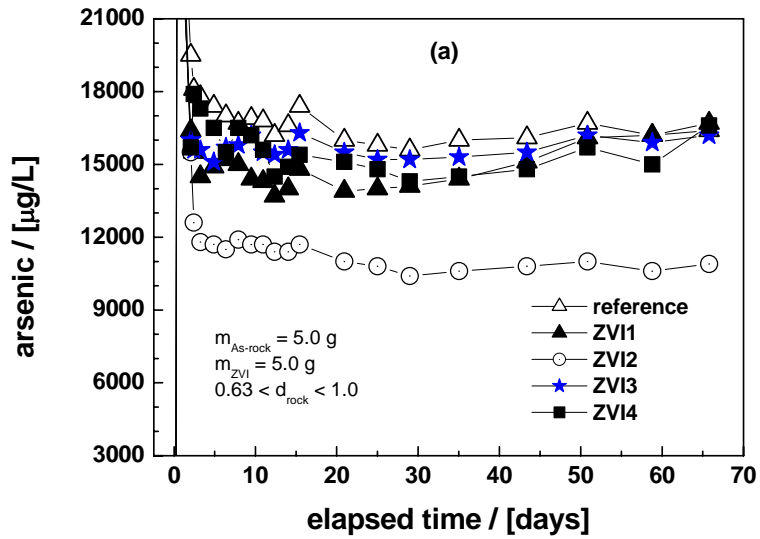458    **Figure 2**

459

460



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462    **Figure 3**

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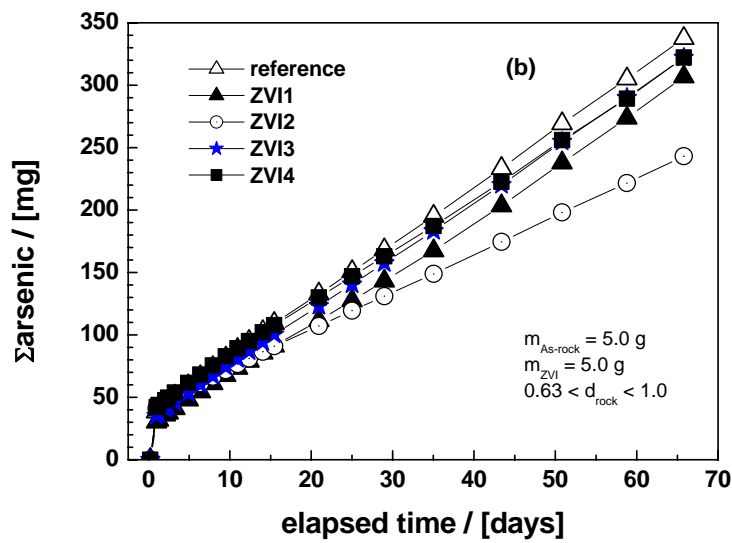


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471    **Figure 4**

472

473



(a)

474

475

476



(b)

$m_{\text{As-rock}}$ = 2.5 g
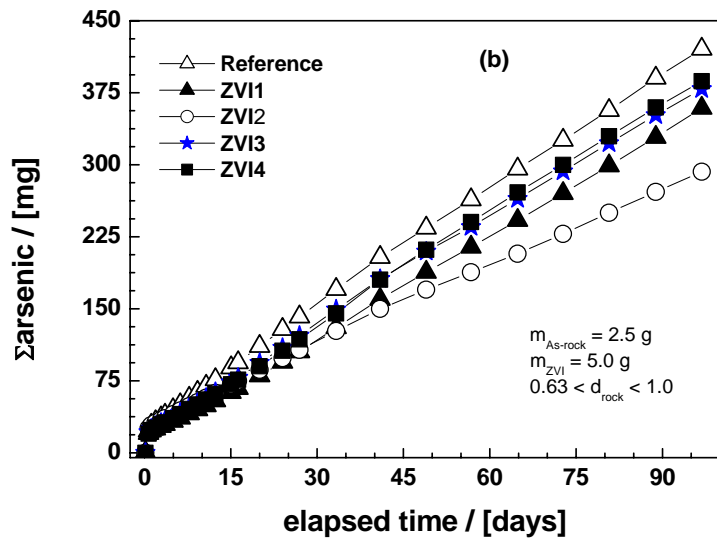$m_{\text{ZVI}}$ = 5.0 g
0.63 < $d_{\text{rock}}$ < 1.0
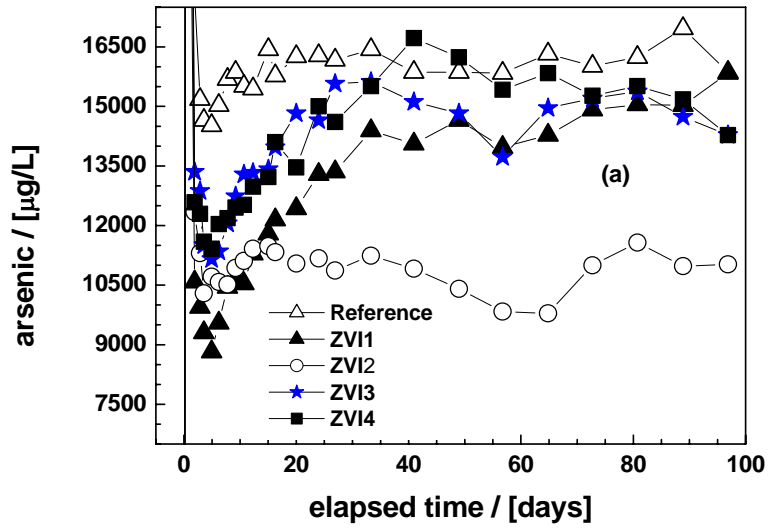
477

478

478 **Figure Captions**

479

480 **Figure 1**:

481 Schematic diagram of the experimental design for the two-columns studies. Used materials

482 were As mineral (2.5 or 5.0 g) and $Fe^0$ (5.0 g).

483

484 **Figure 2:** Arsenic release [mg/ℓ] from the base material as a function of time in air-

485 homogenized batch experiments. The lines are not fitting functions, they simply connect

486 points to facilitate visualization.

487 **Figure 3**:

488 Extent of arsenic release from the two-column-systems for 65 days by tested $Fe^0$ materials: (a)

489 variation of the extent of As release with time, and (b) cumulative As release (mg). The lines

490 are not fitting functions, they simply connect points to facilitate visualization.

491 **Figure 4**:

492 Extent of arsenic release from the two-column-systems for 97 days by tested $Fe^0$ materials: (a)

493 variation of the extent of As release with time, and (b) cumulative As release (mg). The lines

494 are not fitting functions, they simply connect points to facilitate visualization.

495