Arsenic Release From a Natural Rock under near-natural Oxidizing Conditions

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Abstract

The solubilization of arsenic (As) from an ore material (native Arsenic [As, trig.] with Lollingite [$FeAs_2$, rh.]) was characterized in leaching tests lasting for $\leq$ 99 days. The experiments were performed with materials of different particle sizes ($\leq$ 2 mm), in different waters and under test conditions relevant to As mobilization at near surface contaminated sites. The impact of dolomite [$CaMg(CO_3)_2$], metallic iron (Fe^0), and pyrite (FeS_2) on As release was accessed. Two different types of batch experiments were conducted with a constant amount of the base material and different types of water (deionised, mineral, spring, and tap water). For comparison parallel experiments were conducted with 0.1M EDTA, 0.1M Na_2CO_3 and 0.1M H_2SO_4. The results indicated no significant effect of carbonate addition on As solubilization. Fe^0 and FeS_2 addition essentially slowed the initial As solubilization. H_2SO_4 was the sole leaching agent significantly influencing As solubilization from the base material. The general trend assuming that "the smaller the particle size the quicker the As release" was not strictly verified because in samples of smaller particle sizes (d < 0.063) As was partly oxidized to more stable species.

Key Words: Carbonate, Native arsenic, Solubilization

Introduction

The presence of arsenic (As) in many minerals, mining wastes, industrial wastewater and waterways is a serious pollution problem [1-4]. The treatment of such contaminated materials by conventional techniques is often expensive. A recent development to remediate such a contamination is the implementation of permeable reactive barriers [5-10]. Most of the current full-scale reactive barriers use metallic iron (Fe^0-based alloys widely termed as zerovalent iron) as treatment medium. An iron reactive barrier can be placed immediately down gradient of the contaminant source (e.g. mining wastes) to prevent a plume from developing. Arsenic is leached from mining wastes by infiltrating surface water or flowing groundwater to the reactive barrier. Therefore, to properly design a treatment wall, it is essential to characterize the leaching behaviour of natural waters for contaminant source materials (natural ores, mining wastes). The bicarbonate (HCO_3^-) content of subsurface waters has been controversially discussed in the literature as possible important parameter controlling their As mobilization capacity as discussed below.

In the last decades substantial efforts were made to elucidate the origin of As in contaminated groundwaters [1, 11-22]. The univocal result of these efforts is that As mostly originates from natural background sources. However, the individual processes leading to As release and their relative importance are yet to be fully elucidated [16, 23-28]. There are three main theories concerning As release into the environment [29-32]: (i) competitive exchange of bicarbonate, phosphate or silicate, (ii) oxidation of arsenic-bearing minerals, and (iii) reductive dissolution of iron and manganese hydroxides. The distribution of arsenic in the environment depends on the partitioning between the aqueous and solid phase. The main processes controlling the distribution are: (i) complex formation, (ii) adsorption/desorption, precipitation/dissolution, (iii) biotic and abiotic oxidation/reduction [18, 22, 29, 33].

The most common arsenic species in natural water, sediment, and groundwater are: (i) neutral arsenite ($As(OH)_3^0$), and the negatively charged arsenate ($H_2AsO_4^-$ and $HAsO_4^{2-}$). Native As

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54   (As^0) and lower valent As-minerals (As^{-III} and As^{-I}) are stable only under strongly reducing

55   conditions. Arsenite (As^{III}) is more toxic to humans and has higher mobility in the

56   environment than arsenate (As^V) [27, 34]. The increased attention on the health effects due to

57   consumption of As contaminated water has prompted a very strict maximum contaminant

58   level (MCL = 10 µg/L). The mobility of As species and their adsorption by metal oxides and

59   hydroxides have been reported to be strongly influenced by carbonate ions. This effect is

60   usually attributed to competitive adsorption of carbonate and anionic As^V species on available

61   solid surfaces (e.g. ref. 35). However, Kim et al. [16] postulated the formation of As^{III}-

62   carbonate complexes, which increases the mobility of arsenic in anoxic aquifers [23, 36].

63   Neuberger and Helz [25] confirmed the formation of As^{III}-carbonate complexes by measuring

64   the solubility of As_2O_3 in concentrated carbonate solutions (up to 720 mM as HCO_3^-).

65   However, their data suggested that As^{III}-carbonate complexes will be negligible at HCO_3^-

66   concentrations found in most natural waters (1.3 to 5.5 mM). On the other hand Kim et al.

67   [19] showed an acceleration of the oxidation of As^{III}-carbonate relative to non-complexed

68   As^{III} [$As(OH)_3^0$]. These findings are conflicting with the hypothesis of Kim et al. [16] because

69   stable As^{III}-complexes should impair As^{III} oxidation. Therefore, the possibly important role of

70   As^{III}-HCO_3^- complexes in natural waters remains to be properly addressed. An approach to

71   this end is to characterize the solubility of As from a natural mineral containing As^{-III}, As^{-I},

72   As^0 or As^{III} through waters with HCO_3^- contents pertinent to natural situations.

73   The objective of the present work is to contribute to the elucidation of the role of As^{III}-HCO_3^-

74   complexes in the process of As transport in the environment. For this purpose, the process of

75   As release from a natural As-mineral by natural-near waters of various HCO_3^- contents under

76   oxic conditions was characterised. The used As-ore contained mostly native arsenic (As^0) and

77   Lollingite (As^{-I} - $FeAs_2$). Because As is stable in the aqueous phase as As^{III} and As^V and the

78   experiments are performed under oxic conditions, it is expected that the stability of As^{III}-

79   HCO_3^- complexes will influence the extend of As solubilization (total dissolved As – next

3

80   section). The advantage of the used As-mineral (proxy for tailings materials) upon sediments

81   used by for example by Anawar et al. [23] is its relative simple composition. The used waters

82   content 0.0 to 30 mM HCO_3^-.

Background of the experimental methodology

84   In arsenic tailings and mining wastes the As dissolution process typically involves oxidation

85   and destabilization of As minerals such as native arsenic (As^0) possibly resulting in high

86   concentrations of species stable under aqueous conditions (As^{III} and As^V). The transport of

87   As^{III}-species in natural waters (neutral pH range) has been reported to be influenced by the

88   carbonate concentration (HCO_3^-, P_{CO2}) which forms complexes with As^{III} [19, 23, 36]. As^{III}

89   complexation with HCO_3^- should influence the further oxidation to As^V [19]. In particular, in

90   the presence of limited amounts of HCO_3^-, As^{III} oxidation to As^V should be impaired if the

91   complexes are more stable than $As(OH)_3^0$. However, Kim et al. [19] reported on the

92   acceleration of the oxidation of carbonate-As^{III} complexes in comparison to free As^{III}

93   [$As(OH)_3^0$]. Because As^V species do no form complexes with HCO_3^-, the net effect of HCO_3^-

94   ions should be the decrease of As release from used As^0-mineral, as excess As^V from oxidized

95   carbonate-As^{III} should precipitate as As^V oxides. Alternatively excess As^V might remain in a

96   meta-stable solution yielding higher As concentrations. Therefore, the effects of HCO_3^- on

97   As^0 release by natural-near waters may be summarized in a simple hypothesis: under oxic

98   conditions and near-neutral pH value, the extent of As release from native arsenic is

99   influenced (decreases or increases) by increasing HCO_3^- concentrations (Assumption 1).

100 The used methodology for the investigation of As release from_native arsenic by waters

101 consists in testing the validity of Assumptions 1 by following the extent of As release (total

102 As concentration) in the presence of various amounts of HCO_3^-. To support the discussion, the

103 effects of the mineral particle size and that of selected additives (dolomite, metallic iron and

104 pyrite) on the extent of As release in tap water will be investigated. Therefore, the secondary

105 aim of this study is the characterization of the influence of a carbonate-bearing mineral

106 (dolomite) and the effect of in situ generated iron species on the As release from an ore

107 material under near-natural conditions.

108 **Materials and Methods**

109 **Solid materials**

110 The used As ore material originates from Otto-Stollen in Breitenbrunn/Erzgebirge (Saxony,

111 Germany). The material was selected on the basis of its high arsenic content (80%). A

112 qualitative SEM analysis shows the presence of As, Ca, F, Fe, O, S and Si (Fig. SI1 –

113 Supporting Information). The ore material is primary an hydrothermal vein material and

114 arsenic occurred as native arsenic (As^0) and Loellingite (FeS_2 - As^{-I}) [37] in Paragenesis with

115 hydrothermal vein carbonates (for example Fe-bearing Calcite or Dolomite). The mineral was

116 ground to the following particle size fractions: $0.063 \leq d$ (mm) ≤ 0.125 (d_1), $0.200 \leq d$ (mm) $\leq$

117 0.355 (d_2), $0.355 \leq d$ (mm) ≤ 0.630 (d_3), $0.63 \leq d$ (mm) ≤ 1.00 (d_4), and $1.0 \leq d$ (mm) ≤ 2.0

118 (d_5).

119 The used metallic iron (Fe^0-based alloy) is a scrap iron from MAZ (Metallaufbereitung

120 Zwickau, Co.). Its elemental (weight %) conditions are determined as 3.52% C, 2.12% Si,

121 0.93% Mn, 0.66% Cr, and 92.77% Fe. The materials were fractionated by sieving. The

122 fraction 1.0-2.0 mm was used without any further pre-treatment. The material was used as As-

123 removing agent.

124 Pyrite mineral was crushed and sieved and the fraction 0.315 to 0.63 mm was used. The

125 elemental composition (weight %) is: Fe: 40%, S: 31.4%, Si: 6.7%, Cl: 0.5%, C:0.15% and

126 Ca <0.01%. The material served as a pH shifting reagent as well as an iron oxide producer

127 (As-removing agent).

128 Dolomite mineral was crushed, sieved and the fraction 0.63 to 1.0 mm was used. The

129 mineralogical composition (weight %) is: SiO_2: 1.2%, TiO_2: 0.03%; Al_2O_3: 0.4%, Fe_2O_3

130 0.6%, MgO: 20.24%, CaO: 30.94%, Na_2O: 0.04%. Dolomite is a carbonate mineral; it is

131   assumed that its dissolution will increase the kinetics of As release [23]. Arsenic adsorption

132   and co-precipitation with carbonate mineral has also been reported [38, 39].

133   **Leaching solutions**

134   To mimic natural conditions various waters were used. Dionised water (DW) was used as a

135   HCO_3^- free solution (reference system). Table 1 summarizes the carbonate content and

136   simulated effects. The used mineral water ($[HCO_3^-]$ = 1854 mg/L or 30.4 mM) contains for

137   instance more than 20 times more HCO_3^- than the used tape water ($[HCO_3^-]$ = 89 mg/L or 1.4

138   mM). Three technical leaching solutions (0.1 M) partly used for sequential extraction were

139   selected and used for comparison: ethylenediaminetetraacetic acid (EDTA), sodium carbonate

140   (Na_2CO_3), and sulphuric acid (H_2SO_4).

141   The used tap water (TW) of the city of Göttingen (Lower Saxonia, Germany) has a

142   composition (mg/L) of Cl^-: 7.7; NO_3^-: 10.0; SO_4^{2-}: 37.5; HCO_3^-:88.5; Na^+: 7.0; K^+: 1.2; Mg^{2+}:

143   7.5; Ca^{2+}: 36; and an initial pH 8.3.

144   The used spring water (SW) from the Lausebrunnen in Krebeck (administrative district of

145   Göttingen) was used as proxy for natural groundwater. Its composition was (mg/L): Cl^-: 9.4;

146   NO_3^-: 9.5; SO_4^{2-}: 70.9; HCO_3^-: 88.5; Na^+: 8.4; K^+: 1.0; Mg^{2+}: 5.7; Ca^{2+}: 110.1; and an initial

147   pH 7.8.

148   A commercially available mineral water (MW) was used as proxy for HCO_3-rich

149   groundwater. Its composition was (mg/L): Cl^-: 129; NO_3^-: 0.0; SO_4^{2-}: 37.0; HCO_3^-: 1854;

150   Na^+: 574; K^+: 14.5; Mg^{2+}: 60.5; Ca^{2+}: 99.0; and an initial pH 6.4.

151   *Arsenic release experiments*

152   Two different types of batch experiments were conducted:

153   *Not homogenized batch experiments*: 0.22 g of the As-bearing ore and 0.0 or 0.11 g of the

154   additive (dolomite, metallic iron or pyrite) were allowed to react in sealed sample tubes

155   containing 22.0 mL of the leaching solution at laboratory temperature (about 22 °C) for 14

156   days. The tubes had a graduated capacity of 20.0 mL but were filled to a total volume (22.0

157 mL) to reduce the head space. The solid:solution ratios were 10 g/L for the As-mineral and 5

158 g/L for the additives. After equilibration, 1.0 ml of the supernatant solution was retrieved at

159 the top of each tube for As analysis. To compare the leaching capacity of the tested waters

160 some experiments were conducted with 0.1 M EDTA, H_2SO_4, and Na_2CO_3.

161 *Air homogenized batch experiments*: These experiments were conducted in special reaction

162 vessels allowing the system to be homogenized by a humid current of air supplied by a small

163 aquarist pump. The goal was to homogenize the experimental systems at atmospheric pressure

164 (P_{CO2} = 0.035 %) without breaking down the materials. 10 g/L of the As-bearing ore of

165 various particle sizes and 0 or 5 g/L of dolomite, metallic iron, pyrite were allowed to react in

166 sealed vessels containing 100 mL of tap water at laboratory temperature (about 22 °C) for up

167 to 99 days. At given dates 1.5 ml of the solution was retrieved and diluted for As analysis and

168 the same volume of tap water was added to the system.

169 The pH value was recorded at selected dates. The redox potential was not recorded based on

170 the mineral composition and previous works showing their insignificant variation under the

171 experimental conditions [40, 41].

172 **Analytical method**

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

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

175 chemicals used for experiments and analysis were of analytical grade.

176 The pH value was measured by combination glass electrodes (WTW Co., Germany). The

177 electrodes were calibrated with five standards following a multi-point calibration protocol and

178 in agreement with the new IUPAC recommendation [42].

179 Not homogenized batch experiments were performed in triplicate. Error bars given in the

180 figures represent the standard deviation from the triplicate runs.

181

182   **Results and Discussion**

183   *Effect of leaching solution (HCO_3^- content)*

184   The processes that enable As to be dissolved and leached from the ore body are known and

185   used in the hydrometallurgy [43, 44]. To access the reactivity of materials for As retention or

186   removal in the laboratory, many operational leaching solutions have been defined for various

187   sequential extraction schemes [45-48]. All these solutions are more aggressive than natural

188   waters. To check the ability of natural waters to leach As from the studied ore material,

189   parallel experiments were conducted with different waters (Table 1) and the results were

190   compared with that of 0.1M EDTA, 0.1M Na_2CO_3 and 0.1M H_2SO_4. Table 2 and Fig. 1

191   summarise the results. It can be seen from Tab. 2 that the pH value variation was less than 2

192   pH units for all waters. Therefore, despite considerable variations in the HCO_3^- content (0.0 to

193   30 mM), the experiments were conducted in the pH range (4.0 to 9.5 - Tab. 2) relevant for

194   natural systems. It can be seen that As release was fairly constant to 112 mg/L (1.5 mM) as

195   the HCO_3^- contents varies from 0.0 to 30 mM. Therefore, assumption 1 (influenced As release

196   with increasing HCO_3^-) is not verified. Moreover, the leaching behaviour of 0.1 M Na_2CO_3

197   (pH > 9.5; 100 mM carbonate) was not significantly different from that of the system without

198   carbonate (deionised water - Fig. 1a). Assuming that As was fully oxidized to As^V, these

199   results may suggest that the surface area provided by 0.22 g of As-mineral (d_3) could have

200   been insufficient to significantly influence As solubilization through desorption from the

201   mineral matrix. Therefore, varying the HCO_3^-/CO_3^{2-} content has no impact on As release. To

202   check the validity of this hypothesis another experiment with a higher As-mineral mass

203   loading (20 g/L) of a more reactive particle fraction ($d_1 < d_3$) was performed; the results are

204   discussed below. In the experiment with 10 g/L base material, the release efficiency with

205   particle size d_1 was 1.7 times larger than that of d_3. In doubling the mineral mass loading (20

206   g/L) a clearer effect of HCO_3^-/CO_3^{2-} on As release is expected. Figure 1a shows that only 0.1

207   M H_2SO_4 could significantly enhance As release. Two processes are likely responsible for this

208 observation: (i) increased As solubility with decreasing pH, and (ii) the acidic dissolution of

209 the matrix of the ore material [4].

210 The results of the experiment with 20 g/L of the As-mineral (d_1) are presented in Fig. 1b.

211 Depending on the leaching solution the extend of As release was 3.0 to 7.3 times lower that

212 for As-mineral (d_3). The largest decrease of As release was exhibited by the system with

213 H_2SO_4. and the lowest in the system with Na_2CO_3. The major reason for decrease As release

214 with decreasing particle size is (i) either the agglomeration of particles or (ii) the fact that

215 As^0/As^{-I} in the ore material was already oxidized to more stable species (As^{III}, As^V) as

216 discussed below (next section). Fig. 1b also shows that that the leaching behaviour of waters

217 are very closed (0.4 mM) and higher than the leaching capacity of H_2SO_4 (0.3 mM). This

218 result is not surprising because the initial mineral dissolution of the mineral at pH 1 yield

219 elevated concentration of element from the matrix of the ore material (including Ca, Fe und

220 Si) which subsequently precipitated as the pH increased to the final value of 5.7. During this

221 process As is adsorbed, precipitated or co-precipitated [49, 50]. Therefore, the major

222 mechanism responsible for increased As release in experiments with the coarser ore material

223 ($d_3 > d_1$) is the higher As solubility at lower pH values. The value of the pH at the end of the

224 experiments (1.4 for d_3 and 5.7 for d_1) gives an idea of the extend of the dissolution of the

225 mineral and its matrix (extend of As co-precipitation). Fig. 1b also shows relatively elevated

226 As released in 0.1 M Na_2CO_3 in comparison to natural-near waters. This behaviour can be

227 attributed to the displacement of adsorbed As from the matrix of ore material. This conclusion

228 is supported by the fact that the extend of As released in 0.1 M Na_2CO_3 was very similar to

229 that in 0.1 M EDTA. EDTA is an unspecific leaching agent which leaches or desorbs metals

230 and metalloids from contaminated materials [51].

231 In conclusion, the effects of H^+ (as H_2SO_4), EDTA and Na_2CO_3 on the process of As^{-I}, As^0

232 solubilization could be clearly evidenced but no effect of HCO_3^- (0.0 to 30 mM) could be

233 observed, confirming the results of Neuberger and Helz [25] that As^{III}-carbonate complexes

234 will be negligible in natural waters.

Effect of the ore particle size

236 Particle size is an important aspect of mineral dissolution [40, 52]. It can be assumed that a

237 range of particle sizes will have varying dissolution rates. The current assumption is the

238 smaller the particle size the quicker the dissolution. The <2 mm fractions of the studied As-

239 mineral can be considered as the most "reactive fraction" and five different sub-fractions have

240 been used for this batch experiments. Figure 2 and 3 summarize the results.

241 The results from Fig. 2a confirm the general assumption that "the smaller the particle size, the

242 faster the dissolution rate" [40, 53]. These results were obtained in not homogenised batch

243 experiments and can be regarded as the initial dissolution rate. Noubactep et al. [41] showed

244 that under these experimental conditions a steady state (pseudo-equilibrium) is obtained for U

245 release only after several months (> 500 days).

246 Figure 2b from air-homogenised batch experiments confirms that this trend is strictly true

247 only for the first few days of the experiment. During this time readily soluble As from all

248 particle sizes is released into the solution. Afterwards, powder agglomeration evidently

249 influence As release behaviour for small particle sizes ($d_i \leq d_2$) as no effort was undertaken to

250 disperse agglomerates. Even when such efforts are made (e.g. sonication) the elimination of

251 powder agglomeration is never completely achieved [54-57]. Agglomeration effects are

252 possibly responsible for the lower extent of As release by the particle sizes d_1, d_2 and d_3

253 comparatively to d_4 and d_5 (Fig. 2b). Based on the relative abundance of the fraction d_3 it was

254 used all other experiments. Another argument for decreased As dissolution with decreasing

255 particle size in air-homogenised experiments is the fact that the more reactive fractions might

256 have readily oxidized from As^{-I}/As^0 which precipitate on the surface of the material and

257 inhibit As^{-I}/As^0 solubilization. Therefore, in air-homogenised experiments with $d_i \leq d_3$, the

258 solubility of As oxides (or that of a mixture of native As and As oxides) was characterized.

259   Because As oxides are more stable under oxic conditions that native As, the lesser extend of

260   As release is not surprising. The behaviour of As release under oxic conditions (air-

261   homogenised experiments) supports the assumption that in non-disturbed experiments As^{-I}/As^0 is oxidized to As^{III} and As^V.

262

263   Figure 3 depicts the evolution of the pH as the function of the time in air-homogenised batch

264   experiments. It can be seen that, as a rule, the pH value uniformly decreases with increasing

265   reaction time. The initial value is close to 8.3 and the value at the end of the experiment is

266   close to 6.0. The evolution of the system with pyrite is an exception and will be discussed

267   later.

268   *Effect of additives*

269   Another way to qualitatively characterize the effect of reactive material on As release

270   consisted in mixing the rock and an additive in the so-called "air-homogenized batch

271   experiments". Figure 4 summarizes the results of the variation of the As concentration.

272   Figure 4 (a and b) clearly shows that As release was significantly influence by the presence of

273   metallic iron (Fe^0), dolomite and pyrite (FeS$_2$). All additives lower the extent of As release. In

274   particular the presence of dolomite (HCO$_3^-$-bearing mineral) does no increase As release.

275   Noubactep et al. [41] reported a substantial increased of U release from a natural rock while

276   using the same dolomite mineral and the same experimental conditions. The retardation of As

277   release by dolomite is due to (i) As adsorption onto used mineral and dolomite, (ii) As co-

278   precipitation with dolomite mineral [38, 39]. As discussed above As^{III}-carbonate complexes

279   which would have competed with adsorption and co-precipitation to enhance mineral

280   dissolution (as reported for uranium) should be regarded as negligible. Therefore, decreased

281   As^0 solubilization in the presence of dolomite can be regarded as a confirmation of the results

282   of Neuberger and Helz [25] that As^{III}-carbonate complexes are negligible in natural waters.

283   The primary mechanism responsible for the retardation of As release in the presence of Fe^0

284   and FeS$_2$ is adsorption onto and co-precipitation with Fe^{II}/Fe^{III} oxyhydroxides from Fe^{II}

285 oxidation [49, 58, 59]. Fe^{III} results from FeS_2 and Fe^0 oxidation. As removal by Fe^0 carriers

286 has been widely discussed in the recent literature [6-10, 61] and will not be repeated here. The

287 mechanism of the retardation of As release through FeS_2 will be discussed in some details.

288 Figure 3 shows a pH decrease in the initial phase of the experiment with pyrite. This is due to

289 pyrite oxidation that normally increases the As solubility as discussed above for H_2SO_4.

290 Under the experimental conditions (neutral pH, oxic), however, dissolved Fe^{II} ions from

291 pyrite lead upon oxidation by dissolved oxygen to $Fe(OH)_{3(am)}$ precipitates that are excellent

292 sorbents for As [35]. This fact explains the low As concentration in the initial phase of the

293 experiment (Fig. 4b). After this initial phase (4–5 days), the As concentration progressively

294 increased. From Fig. 3 it can be seen that once the acidification capacity of the pyrite is

295 consumed [61] and the pH of the system progressively increased. After about 3 weeks, the As

296 concentration start to increase continuously, suggesting that the adsorptive capacity of in situ

297 produced $Fe(OH)_{3(am)}$ and that of pyrite by-mineral are consumed while the As-mineral

298 continues to release As into the solution (Fig SI2 – Supporting Information).

299

300 **Conclusions**

301 This study reiterates that the presence and abundance of bicarbonates ions (HCO_3^-) does not

302 have any significant influence on the leaching behaviour of natural waters ($6.0 \leq pH \leq 9.5$) for

303 arsenic. Therefore, conflicting results reported for As leaching from sediments [23] may be a

304 misinterpretation of processes occurring in the sediment and yielding increased As release

305 with increasing HCO_3^-/CO_3^{2-} concentration. Identifying/discussing these processes was not

306 the aim of this study. Rather, it is shown how the improper consideration of the chemistry of a

307 system may yield troublesome result interpretation which could be propagated in the

308 literature. Therefore, caution may be paid while referencing published results. In particular,

309 the experimental designs and their appropriateness to consistently solve the posed problem

310 should be checked for individual works. In this regard, it should be noticed that Anawar et al.

311 [23] used 100 mM solutions of $BaCO_3$, Na_2CO_3, $MnCO_3$, and $NaHCO_3$ (and one gram of

312 sediment) to achieved their results. The carbonates concentration were thereby 3 to 60 times

313 higher as those used in the present work and up to 18 times larger as the concentration of

314 natural waters (≤ 5.5 mM).

315 Since the leaching behaviour of near-natural waters for As is very similar it can be

316 emphasized that the site-specificity for As leaching and transport will mostly depend on the

317 presence of natural organic chelating agents (humic substances) in the aquifer. Furthermore,

318 the composition of the matrix of the As-bearing phase or mineral has to be considered. For

319 example if the matrix contents abundant level of pyrite, its dissolution will yield iron oxides

320 which inhibit/retard As transport within the source area. The most possible precise knowledge

321 of the composition of the matrix and the accurate estimation of the As amount within it will

322 help to properly design a reactive wall for successful remediation.

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478

478 **Table 1:** pH value, HCO_3-content and simulated conditions of the used waters (n.d.: not

479 determined).

480

Water	Code	pH	[HCO_3^-] (mg/L)	Simulated conditions	Example
Deionized	DW	5.8	n.d.	HCO_3-poor Water	Rain water
Tap	TW	8.3	89	Current groundwater	Infiltrating R-water
Spring	SW	7.6	112	Current groundwater	Groundwater
Mineral	MW	6.4	1854	HCO_3-rich G-water	HCO_3-rich GW

481

482

483 **Table 2:** Variations of the pH value in the three systems of not homogenized batch

484 experiments using a rock material particle size d_5 (0.355 ≤ d (mm) ≤ 0.630).

485 System 2 and 3 were performed with spring water (pH_i ~7.8). pH_i = initial pH

486 value and pH_f = pH value at the end of the experiment. $\Delta pH = pH_f - pH_i$.

487

System 1				System 2		System 3	
Solution	pH_i	pH_f	ΔpH	d_i (mm)	ΔpH	Additive	ΔpH
TW	8.3_3	7.1_6	-1.1_7	d_1	-0.4_3	**pyrite**	-0.4_8
SW	7.8_4	7.6_0	-0.2_4	d_2	-0.4_2	**Fe^0 carrier**	-0.2_6
DW	5.7_7	7.7_1	1.9_4	d_3	-0.3_7	**dolomite**	-0.1_9
MW	6.3_9	7.1_2	0.7_3	d_4	-0.2_9	**reference**	-0.3_5

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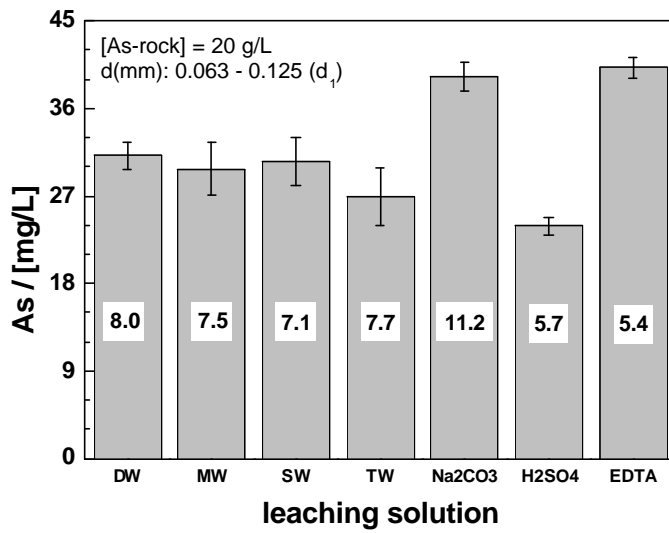
489   **Figure 1**
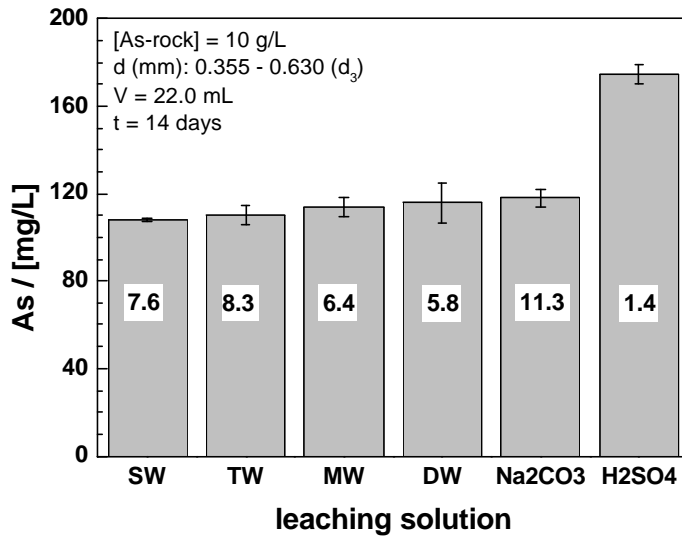
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495   **Figure 2**

496

The chart shows As / [mg/L] versus particle size (d4, d3, d2, d1) as a bar graph with the following parameters:

[As-rock] = 10 g/L
V = 22.0 mL
t = 14 days
$pH_i = 7.8_4$
$d_1 < d_2 < d_3 < d_4$

Bar values (pH labels inside bars): d4: 7.5_5; d3: 7.4_7; d2: 7.4_2; d1: 7.4_1

497

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499

As / [mg/L] versus elapsed time / [days] for d_1, d_2, d_3, d_4, d_5.

[As-rock] = 10 g/L
[FeS$_2$] = 5 g/L
V = 100 mL

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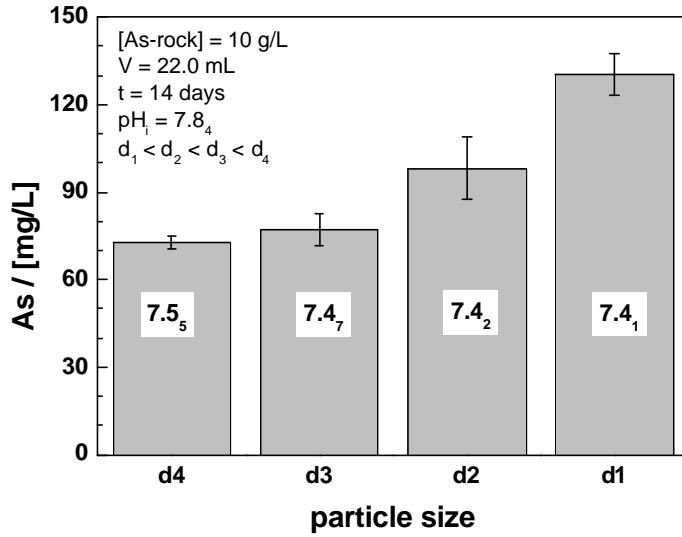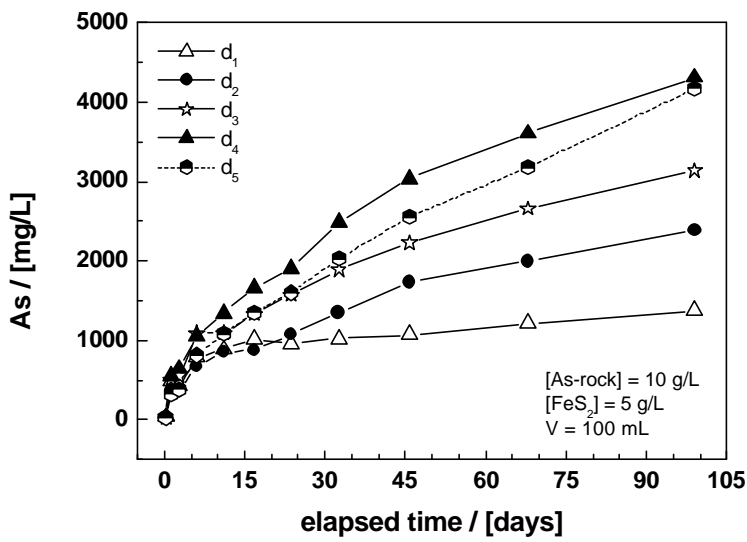
Figure 3

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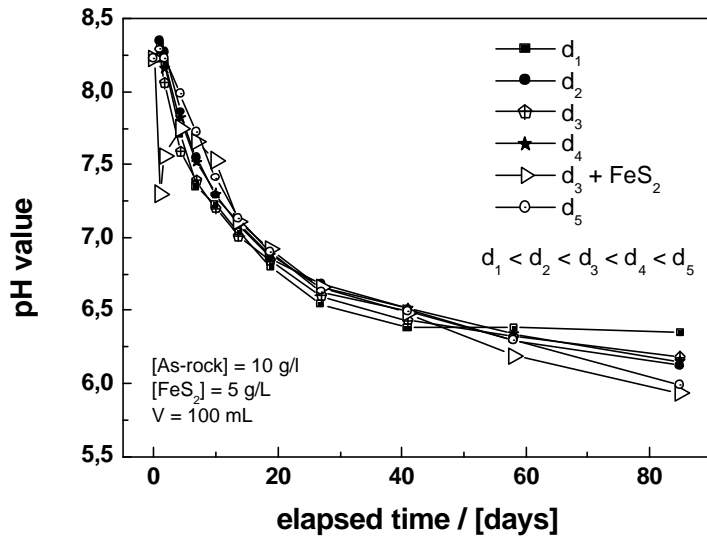
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508 **Figure 4**

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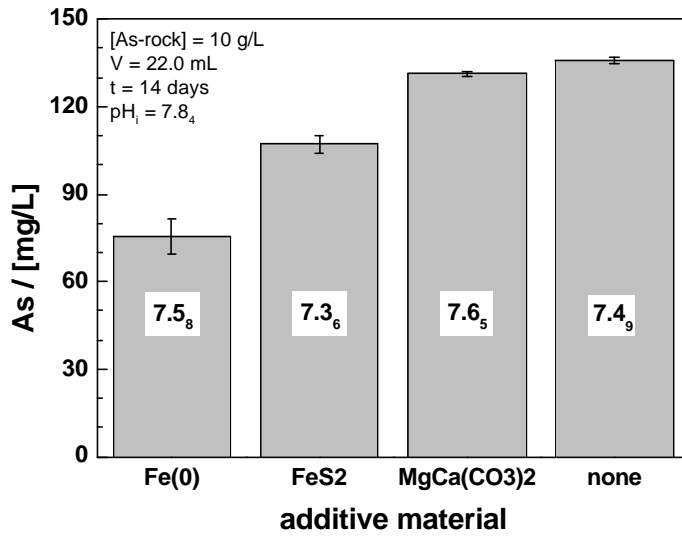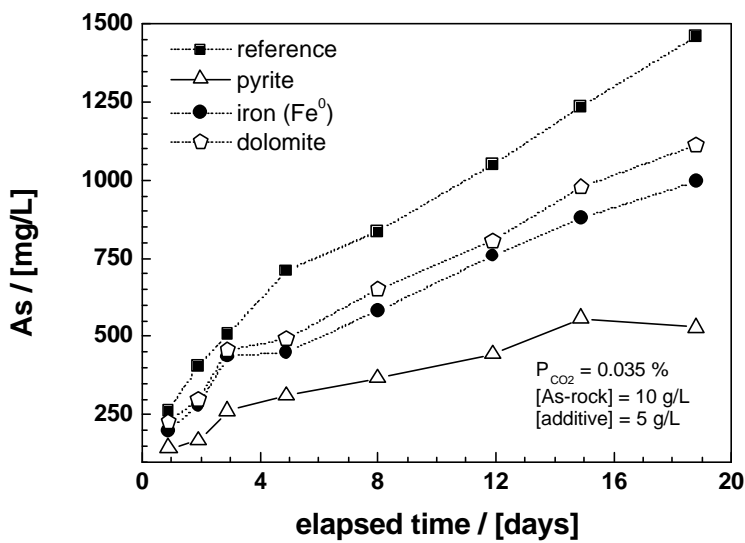
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Figure Captions

Figure 1:

Arsenic release (mg/L) from the As-mineral by different leaching solutions for 14 days in not homogenised batch experiments: (a) 10 g/L of As-mineral d_3 and (b) 20 g/L of As-mineral d_1. Error bars provide standard deviations of triplicate experiments. The values in the bars represent the final pH value of individual leaching solutions.

Figure 2:

Arsenic release (mg/L) from the base material as function of the rock particle sizes ($d_i \leq 2$ mm): (a) in not homogenised batch experiments for 14 days, and (b) in air-homogenised batch experiments. The values on the bars indicated the final pH (initial pH 7.8). Error bars provide standard deviations (triplicate experiments). The values in the bars represent the pH value at the end of the experiment (day 14). The lines are not fitting functions, they simply connect points to facilitate visualization.

Figure 3:

Time dependence variation of the pH value in air-homogenised batch experiments addressing the effect of the rock particle sizes (initial pH 8.3). The lines are not fitting functions, they simply connect points to facilitate visualization. The data for the system with pyrite (FeS_2) are included.
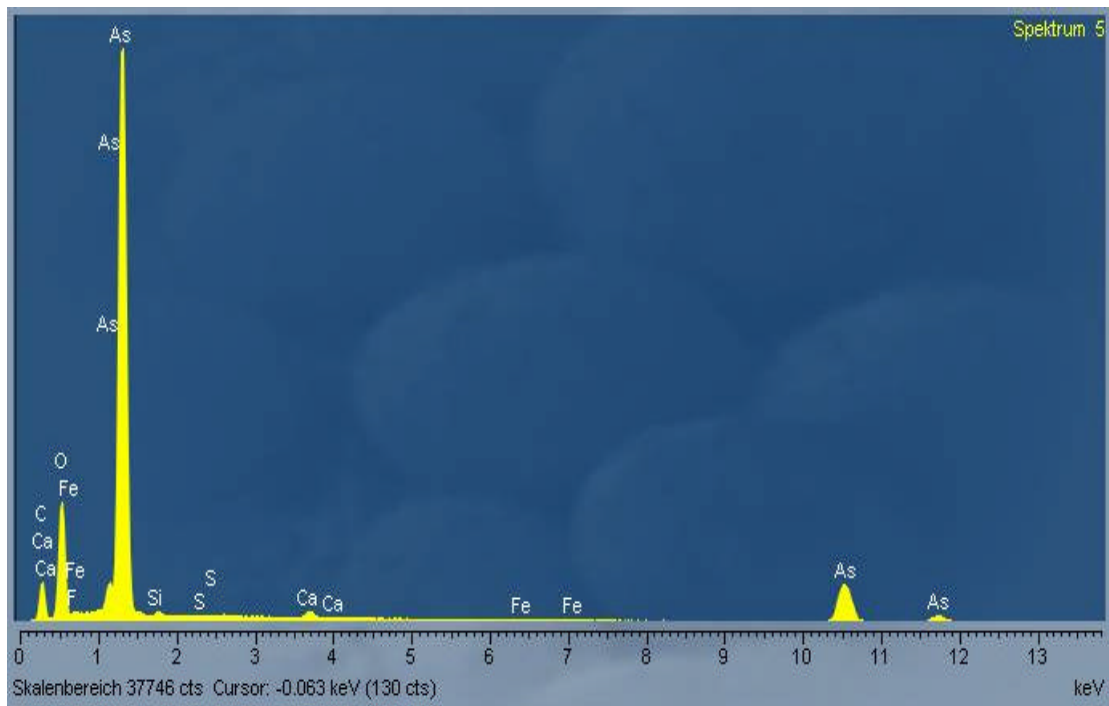
Figure 4:

Arsenic release (mg/L) as a function of additive material: (a) for 14 days in spring water (not homogenised batch experiments), and (b) for ≤ 19 days in tap water (air-homogenised batch experiments). The values in the bars represent the pH value at the end of the experiment (day 14). The not homogenised batch experiments were conducted in triplicate. Error bars give standard deviations. The lines are not fitting functions, they simply connect points to facilitate visualization.

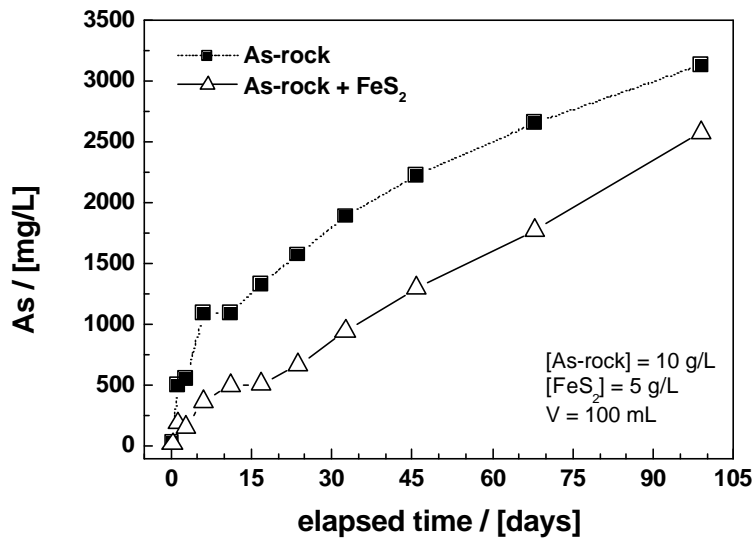538 **Supporting Information**

539 **Figure SI1**

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542 **Figure SI1:** Typical SEM spectrum of the surface of the used As-material. The mineral is
543 primary an hydrothermal vein material and arsenic occurred as native arsenic.

544

544   **Figure SI2**

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546

547   **Figure SI2**: Impact of pyrite (FeS_2) on the evolution of As concentration as function of time

548   in an air homogenized batch experiments for 99 days. P_{CO2} is the atmospheric

549   partial pressure of CO_2 (open system). The particle size of used materials was:

550    $0.315 \leq d$ (mm) ≤ 0.63. The represented lines are not fitting functions, they just

551   joint the points to facilitate visualization.

552