Characterizing As, Cu, Fe and U Solubilization by Natural Waters

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Abstract. The effects of carbonate concentration and the presence of in-situ generated iron oxide and hydroxide phases (iron oxyhydroxides) on arsenic (As), copper (Cu), and uranium (U) release from natural rocks were investigated under oxic conditions and in the pH range from 6 to 9. For this purpose non-disturbed batch experiments were conducted with a constant amount of each contaminant bearing rock/mineral and different types of water (deionised, mineral, spring, and tap water). For comparison parallel experiments were conducted with 0.1 M Na_2CO_3 and 0.1 M H_2SO_4. The favourable role of carbonate bearing minerals for U and Cu transport could not be confirmed by using dolomite. The presence of elemental iron and pyrite retards As, Cu and U solubilization. This study shows that using natural materials in laboratory investigations is a practical tool to investigate natural processes.

Introduction

Leaching tests are used by environmental scientists to help assess the ability of a pollutant to partition from a solid waste into surrounding aqueous phases (Meima and Comans 1998, Townsend et al. 2003). A laboratory test usually determines the leaching potential from waste materials following a pre-determined experimental protocol (AFNOR 1988, DIN 38414 S4, MSTM 2001, US EPA 1999). Typically, a leaching test involves the preparation of waste samples (e.g.,

particle size reduction) and leaching solution, the mixing of the samples with the solution, the filtration of the mixture, and the analysis of the extracts. Different batch leaching tests have been commonly used in various countries for regulatory purposes (Cappuyns and Swennen 2008, van der Sloot et al. 1997). All these tests use synthetic solutions (including dionised water) as illustrated below for three European countries. Alternative leaching methods are: (i) tank tests, (ii) column tests, (iii) field tests (Cappuyns and Swennen 2008, Townsend et al. 2003).

The German DIN 38414 S4 batch test is standardized for water, wastewater, sediment, and sludge testing. This test uses a 100-g size-reduced sample with un-buffered dionised water using a liquid-to-solid (L/S) ratio of 10:1; the test is run for 24 hours while agitating.

The French AFNOR X 31-210 batch test is standardized for granular solid mineral waste (AFNOR, 1988). The test is similar to the German batch test (DIN 38414 S4) but uses a smaller particle size (less than 4 mm).

The Dutch NEN 7349 test (NEN 1995) is a batch leaching test for granular wastes. This test is a serial batch test consisting of five successive extractions of waste material with dionised water. The test is first run at pH 4 using nitric acid at an L/S ratio of 20:1 for 23 hours, followed by four successive extractions with fresh leaching solution.

A survey of the above-enumerated batch leaching tests shows major differences in the pH value, particle size, and L/S ratio. Other important factors influencing chemical leaching from waste material may include leaching time, complexation with organic (CH_3COOH) or inorganic (CO_3^{2-}/HCO_3^-) chemicals, redox conditions, and chemical speciation of pollutants of interest. Therefore, a number of potential shortcomings of the leaching tests have been enumerated: for example (i) the arbitrary L/S ratio may not be representative of the actual field conditions; (ii) the role of kinetics is minimized as the test is performed for a standard duration; (iii) the pH of leaching fluid does not necessarily represent the pH of the leaching environment. The pH of the leachate during the test is highly dependent on the buffering capacity of the waste materials, which may lead to inaccurate determination of waste behavior in the environment (Cappuyns and Swennen 2008, Townsend et al. 2003).

In the present study, no attempt has been made to control more parameters than in previous works. The detailed field conditions at a contaminated site will certainly vary over the time. However, available contaminants are likely leached by natural waters which mostly differ in their acidity (pH value and carbonate content). Furthermore, it must be expected that the CO_2 partial pressure (and thus HCO_3^- content) below the surface may be higher than the atmospheric partial pressure (Baas-Becking et al. 1960). Therefore, in the present work the attention is focused on characterizing the leaching capacity of natural waters for four inorganics from natural materials (minerals or rocks): arsenic (As), copper (Cu), iron (Fe) and uranium (U). The experiments were performed with 10 g/L solid material in 22 mL leaching solution and under non-disturbed conditions (no agitation/stirring) for a duration of 14 days. The results indicate that the use of natural waters and natural materials may be a powerful extension of available leaching tests.

Materials and Methods

Non-disturbed batch experiments were conducted. The batches consisted in adding 22 mL of a leaching solution to 0.22 g of a contaminant-bearing rock (resulted mass loading 10 g/L). The leaching time was 14 days (336 hours). Further experiments were conducted in tap water with contaminant-bearing rock (10 g/L) and three different additives (5 g/L): (i) dolomite ($CaMg(CO_3)_2$), (ii) elemental iron (Fe^0) or (iii) pyrite (FeS_2). Thus, the extent of As, Cu and U solubilization by tap water as influenced by carbonate minerals and iron oxyhydroxides (iron oxide and hydroxide) was characterized. To mimic natural conditions dionised water (DW) and various waters were used. Table 1 summarizes the carbonate content and simulated effects. The used mineral water ($[HCO_3^-] = 1854$ mg/L or 30.4 mM) contains for instance more than 20 times more HCO_3^- than the used tape water ($[HCO_3^-] = 89$ mg/L or 1.4 mM). Two known technical leaching solutions (0.1 M Na_2CO_3 and 0.1 M H_2SO_4) were used for comparison.

The used As-bearing mineral (As-rock) originates from Otto-Stollen in Breitenbrunn/Erzgebirge (Saxony, Germany). The material was selected on the basis of its high arsenic content. A qualitative SEM analysis shows the presence of As, Ca, F, Fe, O, S and Si. The average arsenic content has been determined as 80%. The mineral is primary an hydrothermal vein material and arsenic occurred as native arsenic and Loellingite.

Two iron bearing minerals were used: (i) a Chalcopyrite ($CuFeS_2$) from Ashio (Japan) was crushed and sieved to several fractions. This mineral was not further characterized. (ii) a pyrite mineral (FeS_2) from the Harz mountains (Germany) having an elemental composition of: Fe: 40%, S: 31.4%, Si: 6.7%, Cl: 0.5%, C:0.15% and Ca <0.01% was used as a pH shifting reagent as well as an iron oxide producer in experiments aiming at characterizing the effects of iron oxides on contaminant release.

The used copper ore (Kupferschiefer) originates from Mansfeld (Germany). The material was crushed and sieved to several fractions. Typically, the Kupferschiefer from Mansfeld content up to 2 % Cu (Mäller et al. 2008, Schreck et al. 2005, Schubert et al. 2003, Schubert et al. 2008).

The used uranium bearing rock was crushed and sieved. The fraction 0.250 to 0.315 mm was used without any further pre-treatment. The rock contains around 0.6 % U and is further composed of: 74.16 % SiO_2, 0.19% TiO_2; 7.42 % 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, 0.04 % P_2O_5 and 0.18% SO_3.

The used dolomite mineral was crushed, sieved and the fraction 0.63 to 1.0 mm was used. The mineralogical composition is: SiO_2: 1.2%, TiO_2: 0.03%; Al_2O_3: 0.4%, Fe_2O_3 0.6%, MgO: 20.24%, CaO: 30.94%, Na_2O: 0.04%. Dolomite is a carbonate mineral; it is assumed that its dissolution will increase the kinetics of Cu and U which are known to form stable complex with carbonates.

The used metallic iron (Fe^0 carrier) is a scrap iron from MAZ (Metallaufbereitung Zwickau, Co.). Its elemental conditions are determined as 3.52% C, 2.12% Si, 0.93% Mn, 0.66% Cr, and 92.77% Fe. The materials were fractionated by siev-

ing. The fraction 1.0-2.0 mm was used without any further pre-treatment. The material was used as contaminant-removing agent.

Two different sources of tap water were used: (i) TW1 from the city of Göttingen (Lower Saxonia, Germany) has a composition (in 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+}: 7.5; Ca^{2+}: 36; and an initial pH 8.3. (ii) TW2 from the village of Krbeck (Lower Saxonia, Germany) has a composition (in mg/L) of Cl^-: 9.6; NO_3^-: 9.45; SO_4^{2-}: 32.9; HCO_3^-:92.5; Na^+: 8.4; K^+: 1.0; Mg^{2+}: 7.2; Ca^{2+}: 35; and an initial pH 7.8.

The used spring water (SW) from the Lausebrunnen in Krebeck (administrative district of Göttingen) was used as proxy for natural groundwater. Its composition was: Cl^-: 9.4; NO_3^-: 9.5; SO_4^{2-}: 70.9; HCO_3^-: 95.1; Na^+: 8.4; K^+: 1.0; Mg^{2+}: 5.7; Ca^{2+}: 110.1; and an initial pH 7.8.

A commercially available mineral water (MW) was used as proxy for HCO_3-rich groundwater. Its composition was: Cl^-: 129; NO_3^-: 0.0; SO_4^{2-}: 37.0; HCO_3^-: 1854; Na^+: 574; K^+: 14.5; Mg^{2+}: 60.5; Ca^{2+}: 99.0; and an initial pH 6.4.

Analysis for As, Cu and U was performed by inductively coupled plasma mass spectrometry (ICP-MS) at the Department of Geochemistry. Analysis for Fe was performed by UV-VIS spectrophotometry (using a Cary 50 from Varian). All chemicals used for experiments and analysis were of analytical grade.

The pH value was measured by combination glass electrodes (WTW Co., Germany). The electrodes were calibrated with five standards following a multi-point calibration protocol (Meinrath & Spitzer 2000) and in agreement with the new IUPAC recommendation (Buck et al. 2002).

All experiments were performed in triplicates. Error bars given in the figures represent the standard deviation from the triplicate runs.

Table 1: pH value, HCO_3-content and simulated conditions of the used waters.

Water	Code	pH	[HCO_3^-] (mg/L)	mimicked conditions
Deionized	DW	5.8	0	HCO_3-poor Water
Tap	TW1	8.3	89	Current groundwater
Spring	SW	7.6	95	Current groundwater
Mineral	MW	6.4	1854	HCO_3-rich G-water

Rationale for Choice of leaching time

A major characteristic of batch tests is the homogenization of experimental vessels to accelerate mass transport and shorten the time to reach a pseudo-equilibrium. In the present study no effort was done to accelerate mass transfer. Furthermore, the objective was not to achieve any steady state (pseudo-equilibrium) but rather to compare contaminant solubilization under different conditions. Previous studies (e.g., Noubactep et al. 2006) showed that while using essay tubes of about 20 mL capacity and tap water a leaching time of 14 days (336 hours) was sufficient to achieve reproducible leaching results in non-disturbed experiments. The suitability

of this leaching time was verified in preliminary works by investigating the effect of material particle size on the extent of contaminant release from each material (including $CuFeS_2$ – next section). The results (not shown) confirmed the well-known trend that the smaller the particle size, the larger the extend of contaminant leaching from the material into the solution. This observation validates the suitability of the used leaching time (14 days) for this study.

Results and Discussion

The solubilization extent of each contaminant after 14 days was characterised by its aqueous concentration. To characterize contaminant (As, Cu, U) solubilization from the natural materials while taking individual properties of CO_3-bearing and Fe-bearing minerals into account, Four different experiments have been performed for each contaminant bearing rock: I) rock alone, II) rock + Dolomite, III) rock + pyrite, and IV) rock + elemental iron (system I, II, III and IV). The solubilization of iron from calcopyrite ($CuFeS_2$) will be first presented.

Iron release from calcopyrite ($CuFeS_2$) in different waters

The following particle size fractions (d in mm) of chalcopyrite: d $\leq$ 0.063, 0.063 $\leq$ d $\leq$ 0.125, 0.125 $\leq$ d $\leq$ 0.200, 0.200 $\leq$ d $\leq$ 0.355, 0.355 $\leq$ d $\leq$ 0.630, and 0.63 $\leq$ d $\leq$ 1.00 were used to investigate the extent of iron release into dionised water (DW) as function of the particle size. The results depicted in figure 1 show clearly that the extend of iron release is a decreasing function of the particle size. The evolution of the final pH value (values on the experimental points – Fig.1) confirms the role of pyrite as pH shifting agent. Accordingly, the more reactive the fraction the lower the pH value and the higher the iron concentration.

Figure 2 depicts the results of iron solubilization from chalcopyrite in different leaching solutions. It can be seen that for all solutions with initial pH > 7 the extend of Fe release was low and very similar. Only dionised water (DW) and 0.1 M H_2SO_4 depicted higher Fe release. This result is consistent with the pH dependence of iron solubility (Rickard 2006). It is well-known that the dissolution of iron sulfides induces acidification (McKibben and Barnes 1986). Induced acidity accelerates further mineral dissolution. The more acidic the initial pH value, the more intensive the mineral dissolution (DW vs. 0.1 M H_2SO_4).

As, Cu and U release from natural rocks in different waters

Figure 3 depicts the results of As, Cu and U solubilization from the corresponding bearing rocks in different leaching solution. Generally, the carbonate content and the pH value of the used solution are responsible for observed differences (Appelo and Postma 2005).
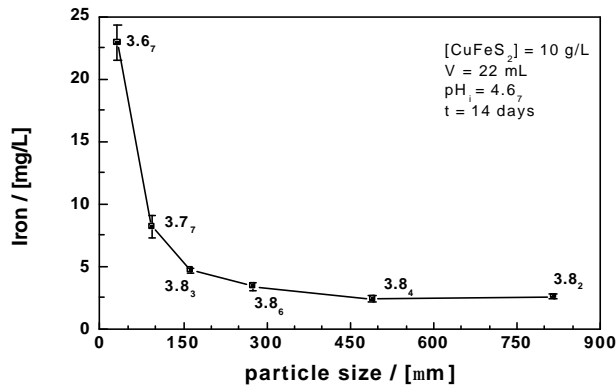
Figure 1: Dependence of the dissolved iron concentration on the particle size of CuFeS$_2$. The values on the curve are the final pH values of the tripli-cates. The represented lines is not fitting functions, its just joint the points to facilitate visualization.
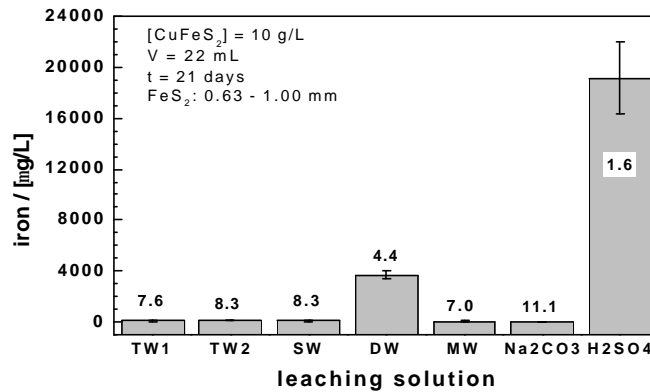

Figure 2: Total Fe concentration as a function of the leaching solution for CuFeS$_2$. The experiments were conducted in triplicates. Error bars give standard deviations.

Arsenic release is solely increased in 0.1 M H$_2$SO$_4$ (Fig 3a). This result is not sur-prising since arsenic (As^{III} or As^{V}) is available as anions. No complex formation between carbonate and As is possible. Therefore, the repeatedly reported carbon-ate enhanced solubilization of As (e.g., Anawar et al. 2004) can only occurs through an indirect mechanism, e.g. concurrence for adsorption sites.

Fig. 3 b and c show that the maximal leaching extent for Cu and U was achieved in H$_2$SO$_4$. The fact that the leaching extent was minimal in dionised wa-

ter (DW) suggests that at near neutral and basic pH values the carbonate concentrations is the major factor determining metal solubilization. In this regard, it is interesting to note that the used mineral water ([HCO_3^-] = 1854 mg/L = 30.4 mM) was more efficient at leaching both Cu and U than the 0.1 M Na_2CO_3 solutiuon ([HCO_3^-] = 100 mM). The 0.1 M Na_2CO_3 solution contents three times more carbonate than MW. Working with $NaHCO_3$ rather than Na_2CO_3 could have help to discuss these results in more details. Nevertheless, considering the pH values of both leaching solution (6.4 for MW vs. 11.2 for Na_2CO_3) it is evident, that MW is more suitable for experiments targeted at investigating natural systems. Consequently, instead of using technical solution largely and satisfactorily employed in the hydrometallurgy for instance, environmental scientists should focus their attention on available natural (or natural-near) leaching solutions.

Effects of carbonate and iron oxyhydroxides on contaminant release

Table 2 summarizes the contaminant concentrations after 14 days in the investigated systems (I through IV). Taking system I (rock alone) as reference, the results can be summarized as follows:

(i) elemental iron (Fe^0) and pyrite (FeS_2) significantly inhibit As, Cu and U release from natural materials. The major mechanism of release inhibition is co-precipitation with in-situ generated iron corrosion products (Noubactep 2007).

(ii) elemental iron (Fe^0) was more efficient in inhibiting contaminant release than pyrite (FeS_2). The higher efficiency was exhibited for U (only 12 % of the amount release in the reference system). The relative difference of the extent of contaminant release by both materials varies in the same order: U > As > Cu attesting that the same process is responsible for contaminant removal in both systems, namely the co-precipitation with in-situ generated iron oxyhydroxides.

(iii) dolomite (HCO_3^-) has no significant effect on Cu and U as the relative difference of the extent of contaminant release is very comparable to the percent standard deviation from the triplicates.

(iv) dolomite (HCO_3^-) significantly inhibits As solubilization and this is likely due to the adsorption of solubilised As onto the surface of dolomite.

Table 2. Total contaminant concentrations as influenced by the nature of the additive for 14 days. In-situ generated iron oxyhydroxides (systems with Fe^0 and FeS_2) retarded contaminant release from all used rocks. Dolomite (HCO_3^- producer) has no significant effect on Cu and U release under the experimental conditions of this work.

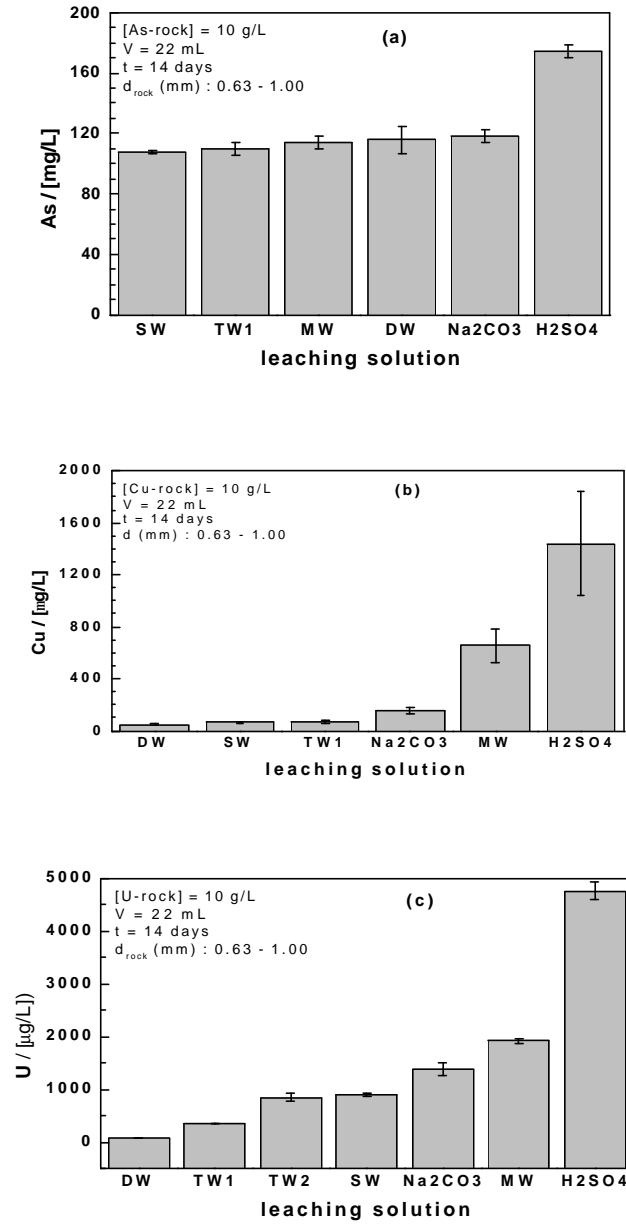| Additive	[As] (mg/L)	[Cu] (µg/L)	[U] (µg/L)
No	136 ± 2	66 ± 7	923 ± 60
Dolomit	131 ± 1	75 ± 11	963 ± 41
Pyrit (FeS$_2$)	107 ± 3	58 ± 11	743 ± 24
Iron (Fe^0)	76 ± 6	48 ± 13	114 ± 32

Figure 3: Total contaminant concentration as a function of the leaching solution for a rock particle size of 0.630–1.00 mm.

Concluding Remarks

The evaluation of potential risk to groundwater for a given contaminant is performed via two different procedures: (i) a leaching test is performed and the contaminant concentration in the leachate is compared directly to applicable water quality standards; (ii) the theoretical concentration of a contaminant in a waste (mg/kg) is compared to a risk-based leaching level. The risk-based leaching level represents the theoretical concentration of a contaminant in a waste (mg/kg) that results in a leachate concentration that exceeds the applicable groundwater standard for that contaminant (Cappuyns and Swennen 2008, Townsend et al. 2003). As discussed above a major problem of the procedure is the use of synthetic leaching solution.

The possibility of using natural / natural-near waters has been satisfactorily explored in the present study. The results presented above suggest that column tests involving a continuous flow of natural waters (as leaching solution) through site specific waste material may be a powerful tool to investigate leaching behavior under representative conditions than batch tests. Although the problems inherent to column tests may subsist (flow channeling, clogging, biological activity) this approach may allow a more realistic estimation of the evaluation of potential risk to groundwater. It can be anticipated that data gain from such experiments will be more useful for modelling purposes.

Acknowledgments

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