Uranium Fate in Saturated Porous Media under Arsenic, Iron and Bacteria Influence: The Role of Potassium

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Abstract. Uranium (U) and arsenic (As) of leachates from mine tailing dumps are a notorious cause of environmental concerns. Iron (Fe) oxides and metal reducing bacteria are well known immobilizers of U and/or As in unsaturated and saturated porous media. This paper describes investigations on geochemical controls of U fate under the influence of As, Fe and bacteria. Batch experiments were performed in glass test tubes using natural iron minerals and scrap metallic iron in setups designed to ascertain the kinetics and the influence of arsenic and iron. The effect of the background electrolytes NaCl or KCl and related ionic strengths were also considered. The experiments suggest prevalent role of the scrap iron's corrosion products but also of those of potassium (K) and calcite. Similarly, four glass columns (40 cm height, 2.4 cm diameter) were packed in weight/weight proportion of 90% sand and 10% scrap Fe (0.2-0.8 mm). Two columns without metallic Fe were filled with 50% sand and 50% glass beads and 100% sand respectively. Five columns including a control were leached at 0.12-0.39 ml/min with a 0.01M KCl or NaCl background electrolyte spiked with 0.05mM of U (11.9mg/l) and As (3.7mg/l). Two columns were leached with Schneckenstein (Saxony, Germany) Uranium tailings leachate upgraded to 0.05 mM U and As and a parallel continuous feed of a solution of 1mM glucose. Effluents samples collected regularly for a total of 77 pore water volume (5 litres) show fixation of more than 95% of both U and As in all columns were scrap Fe was present. The control column, however, has shown an unexpected fixation of both U and As between 90-95% suggesting precipitation/co-precipitation of both U and As through sparingly soluble minerals such as Abernathyite $KUO_2AsO_4 . 4H_2O$ as predicted by PHREEQC (LLNL database). Thus, K may be an efficient and cost effective amendment for immobilizing both U and As in contaminated porous media through precipitation/co-precipitation mechanisms if As and U are present at high concentrations. However, the reduction of both arsenic and uranium is limited by the solubility product of Abernathyite maintaining uranium and arsenic concentrations in the range of tens of µg/L. Potassium as an essential intracellular nutrient might also play a double role of enhancing bacteria mediated biotransformation and immobilization of uranium and arsenic.

Introduction

Uranium is mainly used for nuclear power plants as alternative source for energy production. This trend is primarily subsequent to the steady increase in world population, higher oil and gas demand and hence rapid depletion of fossil fuel reserves and the advances in nuclear power plant operations triggered by the Russian Chernobyl accident and the subsequent radioactive fall out. Thus, current ongoing and increasing uranium mining fused with past poor management of uranium mine tailings will remain a major source of uranium and associated metals and metalloids in natural waters. Among numerous metals and metalloids associated with uranium in most geological contexts, arsenic is the most widely known due to the massive poisoning in Bangladesh and India's west Bengal as a result of exposure to arsenic contaminated water. Both uranium and arsenic dissolved in natural fresh waters are of much human health concern due to their notorious chemical toxicity. Therefore, a wealth of studies and knowledge designed to better understand the aquatic chemistry, fate and transport of uranium and arsenic in groundwater systems gathered over the last decades have been published.

Furthermore, studies related to uranium and arsenic competitive fate and transport in saturated porous media are scarce. One of the rare papers within this line is the one Merkel (2003) using PHREEQC geochemical code to simulate uranium mine water dilution taking into account the influence of redox sensitive arsenic, iron and organic matter kinetics on uranium fate. It is worth mentioning, however, that most studies related to uranium and arsenic are linked to their removal efficiency by specific reactive materials primarily zero valent iron (Uhrie et al., 1996; Schneider et al., 2001a, 2001b, Mallans et al. 2002, Morrison et al. 2002, Mbudi and Merkel, 2005). Yet, few studies have reported divergent fate of uranium and arsenic in natural environmental settings where iron and bacteria play a prominent role (Seidel et al. 2002; Wolkersdorfer 1995; Kalin et al. 2002). Iron and bacteria occur widely in subsurface and control many geochemical processes. Therefore, this study conceived within this framework is a part of ongoing laboratory experiments aimed at contributing to a better understanding of the mechanisms controlling uranium fate in saturated porous media under arsenic, iron and bacteria influence. This laboratory approach is mainly motivated by current limitations of geochemical models related to thermodynamic database uncertainties (Nistche et al. 2000), and lack and/ or reliability of those data particularly for most arsenic species (Zhu and Merkel, 2001; Merkel, 2004).

Experimental setup

The chemicals and reagents used in this study were all of analytical grade and include uranyl nitrate 6-hydrate $UO_2(NO_3)_2.6H_20$ (Chemapol, Germany), Sodium Arsenate $Na_2HAsO_4.7H_20$, HCl 37% (Baker, Germany). Arsenazo III (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo2)-phenylarsonic acid)] (Riedel-de-Häen, Germany) used as 0.15% (m/v) aqueous solution, 200 mg of high purity Zn granules (Fluka, Germany), ascorbic acid and oxalic acid both of Chemapol used as 1g each in 100 ml water. All solutions that needed water as solvent were prepared using deionised ultra-pure water throughout. All batch and most column experiments were carried out with input or influent of solution of background electrolyte of either KCl or NaCl in order to avoid potentially competing ions. The selected salts release in water monovalent ions K^+, Na^+, Cl^- generally considered to be conservative, inert and nonsorbing (Dzombak,1990). Also, in all batch and column experiments, mixtures of solid sorbents were made on weight/weight basis.

Batch test tubes

All batch experiments were conducted in 1/10 solid (2g) to solution (20mL) ratio using 25 ml capped glass test tubes in duplicate. The first set of experiments were performed with mixed natural iron minerals of a grain size of 25% (0.25mm-0.5mm) and 75% (0.5mm-0.8mm) with a spike of 0.05 mM of uranium or uranium and arsenic in 0.01M KCl or 0.01 NaCl. XRD characterized the compound referred to as goethite-quartz as 97.89±0.29% goethite and 2.11±0.29% quartz. The second sorbent simply referred to as pyrite-calcite-ankerite was in fact a mixture of calcite (10%) of the grain size (0.2-0.5mm) and a more complex natural mixture XRD characterized as pyrite (74.76±1.23), calcite (10.95±0.72%), ankeriteFe0.54 (5.66±0.81%), sphalerite Fe (4.52±0.33%), chloritellb-2(2.14±0.93%), galena (1.49±0.06%) and quartz (0.48±0.33%).The equilibration time spanned from 168 up to 500 hours. Similarly, raw scrap metallic iron (1-10cm long) obtained from Metallaufbereitung Zwickau (MAZ) known as S69 and containing 92.8%Fe, 3.5%C, 2.1%Si, 0.9%Mn and 0.7%Mn (Noubactep et al. 2003) was crushed and used in the range size 25% (0.25mm-0.5mm) and 75%

(0.5mm-0.8mm) for related sets of experiments without further treatment. A similar set of batch experiments equilibrated scrap metallic iron alone or as a compound of 90% scrap iron (25% 0.25-0.5mm, 75% 0.5-0.8mm) and 10% calcite (1.25-0.25 mm). The background electrolyte of 0.01M was either NaCl or KCl spiked with uranium in the molar range of 0.001 to 0.1 mM or constant uranium (0.05mM) and varying arsenic concentrations so as arsenic/uranium molar ratio range from 0.02 to 2. Also, in order to establish the probable influence of K, further experiments with uranium and/or arsenic concentrations varying from 0.001mM to 0.1mM in a KCl background electrolyte of 0.01mM and 10mM respective ionic strengths were left with scrap metallic iron for one week long to obtain equilibrium conditions.

Column systems

A total of six glass columns of 2.4 cm diameter, 40cm height, glass wool filter within the top cap and about 0.5 cm layer of granule silica beads at bottom and covered with aluminium foil were used. The quartz sand termed F32 (Quarzwerke Frenchen, Germany) with an average grain size of 0,24mm and a specific theoretical surface area of $102 cm^2/g$ was used throughout in all columns. XRD investigations found 98.6±0.26% quartz and 1.4±0.26% calcite. The quartz sand contained 99.7% SiO_2, 0.2% Al_2O_3, and 0.03% Fe_20_3. This sand used in all six columns was washed with diluted (1:10) 65% nitric acid and kept in for 24 hours, rinsed with deionised water and air-dried in the laboratory. One control column was packed with 50% glass beads (0.2-0.8mm) and 50% quartz sand. Four columns were filled with 10% scrap iron of grain size ranges of 25% (0.25mm-0.5mm) and 75% (0.5mm-0.8mm) and 90% quartz sand whilst the last column was filled with washed sand only.

All six columns were first filled half with deionised water and then respectively filled with sand/mixture resulting in an average porosity of 0.3 and an average pore water volume of 65 mL. The influent solutions were pumped from bottom to top at an average rate of 0.16 mL/min using a high precision tubing pump with planetary drive ISMATEC IPC 24 canals (Ismatec SA, Switzerland). The columns were conditioned by pumping in several pore volumes first of deionised water and of either 0.01M KCl or NaCl. The possible bacteria influence was investigated in two columns. One of the column contained sand only and the other sand and scrap iron. For these columns, however, conditioning and flushing was achieved by pumping of several pore volumes of deionised water first and then by 0.01M glucose. These two columns were thereafter supplied from the top with a 25 mL of a diluted 1:1000 supernatant aliquot in a 0.01M glucose background. This aliquot was derived from 25 g soil of Schneckenstein Uranium tailings (Saxony, Germany) taken from the bottom part of a 5m deep tailing material mixed with 250 ml 0.01 M glucose as $C_6H_{12}O_6.H_2O$ using a 500ml Erlenmeyer placed in a horizontal shaker for 1 hour. A tracer test was performed using Cl. The influent solutions used throughout for all columns were spiked with 0.05mM uranium (11,9mg/L) and arsenic (3.7 mg/L) in 0.01M Nacl or 0.01M KCl background electrolyte, or in the leachate collected at the Schneckenstein Uranium tailings location coded PNP9. This leachate contained originally in mg/L 1.4F$^-$, 7.5Cl$^-$, 3.6 NO$_3^-$,210 SO$_4^-$, 47 Na$^+$, 2.4 K$^+$, 45 Ca^{2+}, 13.4 Mg^{2+}, 0.05Fe, 0.035Mn, 0.09Cu, 0.006 As, and 0.691U. The upgraded leachate to 1/1 (Uranium/Arsenic) molar ratio with 0.05mM uranium and 0,05mM arsenic (3.7 mg/l) was pumped in two specified columns in parallel with a 1 mM glucose solution by mixing through a Y connector before entering the column at the average same pumping rate of 0.16 ml/min.

Analytical techniques

Master parameters pH and Eh were measured with combined glass electrodes (WTW GmbH, Germany).All samples collected from batch and columns experiments were filtered with a 0.2µ filter (Schlecher & Schuell, Germany and Sartorius, Germany) and medium pore size filter of the brand FILTRAK (Germany), preserved with 1/1 nitric acid and later cooled at 4 Celsius grad. Uranium was analysed by photometry using arsenazo III method. It involves the sequential addition of two times 2ml concentrated HCl and high purity 200 mg Zn granule to 3mL of water sample aimed at reducing U (VI) to U (IV). At the completion of the resulting reaction, 250 µl of oxalic-ascorbic acid solution, and 250µl of arsenazo III are added to mask major interference and complex uranium. A HACH UV-VIS spectrophotometer with a 1 cm cuvette was used for the absorbance determination at a wavelength adjusted to 665nm. Total arsenic was measured with an Atomic Absorption Spectrometer Zeiss AAS 4 EA. A five points procedure was used to calibrate both spectrometers.

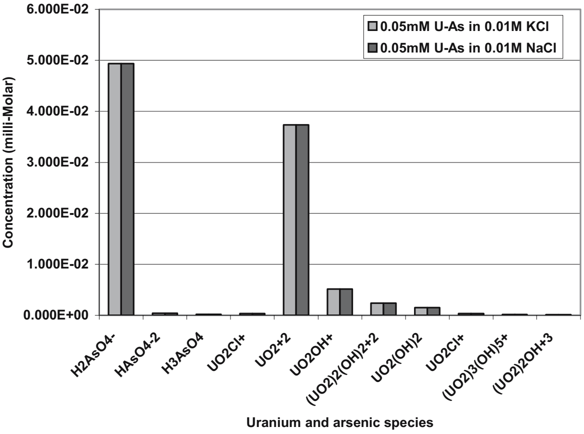

Fig. 1. PHREEQC simulation output of major uranium and arsenic species content of the synthetic groundwaters used in most experiments (pH = 4.5, Lawrence Livermore National Laboratory thermodynamic database).

Results and discussion

Comparability of batch and column experiments is not straightforward. Thus, both batch and column experiments are presented separately and the discussion emphasises on the role of potassium on uranium fixation.

In the following graphs uranium or arsenic fixation is expressed normalized with respect to the solution initial concentration C0 and the concentration C at the end of the experiment equilibration time.

Assuming that the Lawrence Livermore National Laboratory thermodynamic database provided and used in Phreeqc (Parkhurst and Appelo, 1999) is reliable in particular for arsenic, Fig. 1 suggests that most reactions at mineral water interface are controlled by $H_2AsO_4^-$ and UO_2^{+2} for both 0.01 M KCL and 0.01 NaCl background electrolytes of synthetic groundwaters. Owing to the slightly equal amount of both major species in either 0.01M KCl and 0.01M NaCl, it is expected that pH dependent protonation/deprotonation reactions and intrinsic behaviour of Na or K make the difference. Potassium is known somewhat to react faster in water than sodium. Thus, in 0.01 M KCl for example, PHREEQC predicts uranium and arsenic fixation through the co-precipitation of the sparingly soluble $KUO_2AsO_{4(s)}$ is likely:

$$KUO_2AsO_4 + 2.0000\ H^+ = + 1.0000\ H_2AsO_4^- + 1.0000\ K^+ + 1.0000\ UO_2^{++}$$

$$\log\_k \quad -4.1741$$

The closest related mineral to the PHREEQC compound KUO_2AsO_4 is the hydrated form known as Abernathyite ($KUO_2AsO_4.\,4H_2O$).

The static batch systems

The role of potassium on the rate of uranium fixation on natural iron minerals under arsenic influence

Due to iron minerals high surface areas, they control the fate and transport of most metals including uranium and arsenic. Fig. 2 portrays the rate of uranium respectively arsenic fixation on natural iron minerals.

In a mono-component solution of 0.05mM uranium respectively arsenic in 0.01M KCl background electrolyte, both elements behave very differently with respect to the sorbents. This is an illustration of the typical discrepant behaviour of uranium and arsenic reported in the literature.

Almost all arsenic is immobilized by pyrite-calcite-ankerite and the reaction rate seems time independent whereas only more or less 78% of uranium is immobilized in similar conditions and the reaction seems in rather slower and still in metastable state at the end of the 500 hours maximum equilibration. On contrary, uranium is better immobilized by goethite-quartz than arsenic. While the first is in equilibrium after about 200 hours, the latter is not in equilibrium after 500 hours.

By and large, this discrepant behaviour of uranium and arsenic with respect to the studied adsorbents is probably related to both elements intrinsic properties with regard to surface complexation sites and charges. Although common iron oxide in aquifer systems, goethite is reported as a lesser absorbent of arsenic on a per gram basis compared to ferrihydrite for example (Stollenwerk, 2003). This relatively poor adsorption of arsenic on goethite is commonly explained by this mineral better crystallinity. In this particular case there might be lower concentrations of surface-complexation sites that can neutralize the major arsenic species H2AsO4- . In contrast, the uranyl hydrolysis complexes adsorption by goethite seems very effective. Gabriel et al. (1998) suggest that uranium sorption in similar case occurs through the creation of inner surface complexes probably in identity coordination with surfaces iron centres. On the contrary, the higher adsorption of arsenic on pyrite-calcite-anchorite (90%) and calcite (10%) is probably due mainly to the well known calcite higher arsenic adsorbing capacity.

Figs. 3 and 4 show uranium and arsenic fixation rate in similar experimental setting as in Fig. 2 above but in bi-component 0.05mM uranium-arsenic spike in either 0.01M NaCl or 0.01M KCl and shorter equilibration time up to 168 hours.

As noted by Stollenwerk (2003), carbonate minerals are probably the main control of arsenic aqueous concentrations. In fact calcite surface displays positive or negative charge respective above or below its zero-point-of charge that is reported by Foxall et al (1979) to occur at pCa=4.4. This property might explain why calcite can preferably adsorb metal anion species such as $H_2AsO_4^-$ to metal cation species such as uranyl UO_2^{2+}. This reason might explain why uranium shows much lesser adsorption on pyrite-calcite-ankerite (90%) and calcite (10%) that can also be explained by the formation of carbonato uranyl complexes known as very mobile.

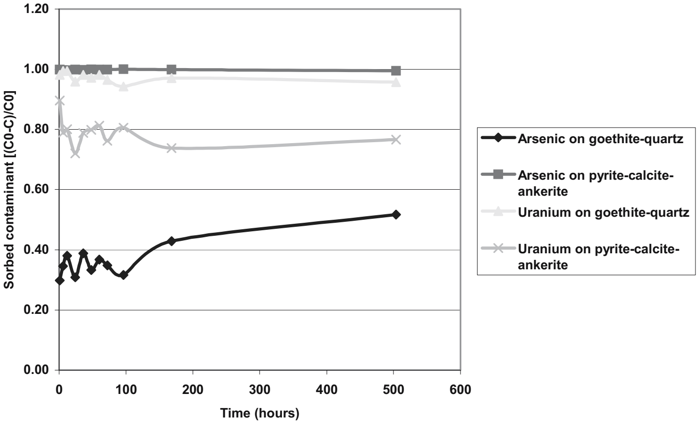

Fig. 2. The rate of uranium and arsenic fixation on natural iron minerals. Initial mono-component uranium or arsenic solution concentration C0 amounts 0.05mM in 0.01M KCl at pH 4.5.

Fig. 3 pinpoints two main phases of uranium sorption on goethite-quartz under arsenic influence: a probable fast adsorption phase that goes on up to around 40 hours followed by a plateau that can most likely be precipitation related. Both curves suggest that pyrite-calcite-ankerite remove much more uranium for the first 16 hours than goethite-quartz does. Thus, the addition of arsenic which is better fixed on carbonate surfaces as illustrated in Fig. 2 enhances co-precipitation of uranium with adsorbing arsenate complexes. After 20 hours there is a slight de-

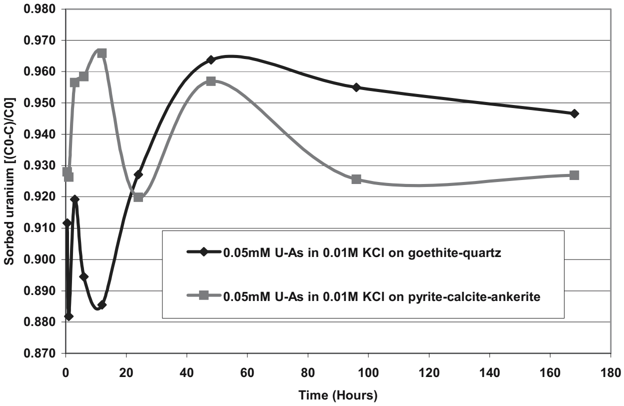

Fig. 3. Uranium removal by natural goethite-quartz and pyrite-calcite-ankerite (90%) and calcite (10%) from a solution of 0.01M KCl spiked with 0.05mM U-As at overall starting pH of 4.5.

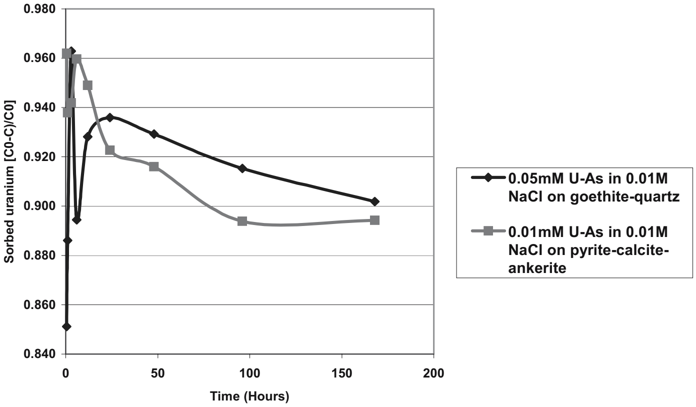

Fig. 4. Uranium removal rate by natural goethite-quartz and pyrite-calcite-ankerite (90%) and calcite (10%) from a solution of 0.01M NaCl spiked with 0.05mM U under the influence of 0.05mM As at overall starting pH of 4.5.

crease on the amount of uranium removed from solution that can be related to calcite dissolution and subsequent increase in uranium carbonato complexes which are much more mobile. Taken as a whole, Fig. 3 not only indicates that the addition of arsenic promotes uranium removal by both minerals but also in comparison with Fig. 4, the removal is much more efficient in KCl background electrolyte solution than in NaCl background buffer. The reason for better uranium removal from KCl solution might be the faster reactivity of K with water compared to Na. In fact both background electrolytes have in common the same content in major uranium and arsenic species and have the tendency to raise the pH through formation of NaOH and KOH when reacting with water.

The sorption curves in Fig. 4 show a similar trend of uranium sorption in both goethite-quartz and pyrite-calcite-ankerite. It seems, however, that it Fig. 4 the systems have not yet reached equilibrium even at the end of a week long equilibration time. Again as shown in Fig. 1 above, both systems U-As-NaCl and U-As-KCl starting solutions have similar major uranium and arsenic aqueous species. Therefore, differences in uranium fixation rate might only be explained at reactions at the interface water minerals. The Systems control is much more related to sorbent minerals intrinsic properties and partly to the reaction rate of Na versus K related species with water. Hence the likelihood of uranium co-precipitation within sparingly soluble solids such as KUO_2AsO_4 or its hydrated form abernathyite is probable.

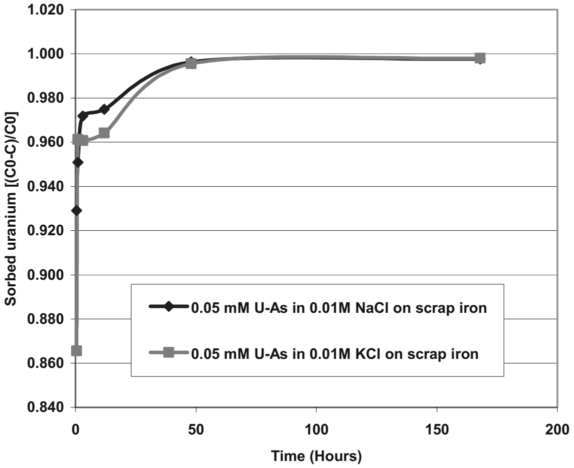

Fig. 5. Uranium removal rate by scrap iron from a 0.01 M NaCl respectively 0.01 M KCl contaminated with 0.05 mM U-As at starting pH of 4.5.

The role of potassium on the rate of uranium fixation on iron corrosion products under arsenic influence

As expected and suggested by Figs. 5 and 6, freshly formed iron corrosion products remove uranium faster and more efficiently than well crystallized and aged iron minerals in similar experimental conditions.

The removal of uranium in either background electrolyte 0.01 M NaCl or 0.01 M KCl of the same ionic strength show similar rate curves pattern as expected. The similarity is particularly expressed by a kinetically controlled fast reaction rate at the beginning of the first 12 hours. This is probably due to the fact that both solutions contains uranyl UO^{2+} as major species which seems at least at the beginning of the curve being reduced and precipitated by newly formed $Fe2^{+}$ species. The last portion of the curve after more or less 50 hours reactive time show a plateau suggesting the domain of chemical equilibrium and of the prevalence of precipitation/co-precipitation of newly formed iron oxides with either uranium or arsenic. It is also the domain of non iron related minerals such as the solid KUO_2AsO_4 or its hydrated form abernathyite KUO_2AsO_4. $4H_2O$ is likely to precipitate considering the prevalence of both major species $H_2AsO_4^-$ and UO_2^{+2} in solutions. Both solutions also show in between both curves first and third portions, a transitional or second portion where surface sites seem to show much preference of uranium from the 0.01M NaCl solution than the 0.01 KCl solution. The reason for this preference is unclear except the fact that the portion is probably the domain where both reductive precipitation, adsorption and probably also precipitation/co-precipitation co-exist and control the system.

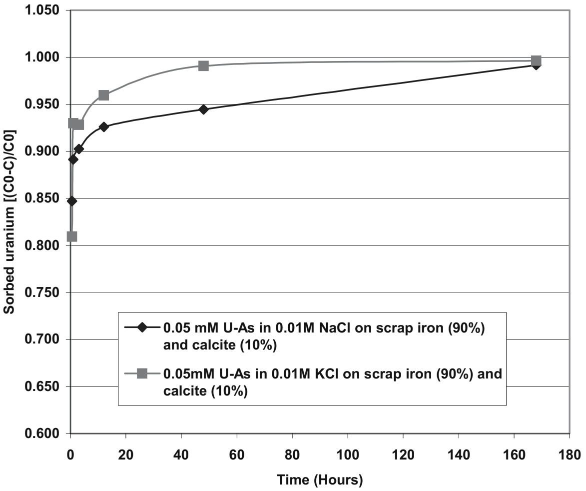

Fig. 6. Rate of 0.05 mM uranium removal under 0.05m M arsenic influence as bi-component initial solution of respectively 0.01M KCl and 0.01M NaCl background electrolytes at pH 4.5 to equilibrate with scrap iron (90%) and calcite (10%).

Furthermore, carbonates are known to be not only ubiquitous but also a major control of most hydrogeochemical reactions as does iron. As for the previous experiments that resulted in results discussed above, it was also important to consider the addition of calcite and how it can affect uranium removal as presented in Fig. 5.

In fact, the addition of 10% calcite to the system presented in Fig. 5 suggests a slightly slow uranium removal rate and efficiency particularly for the 0.01M NaCl solution. Fig. 6 also reveals that the system 0.01M NaCl is less favourable to uranium fixation than its counterpart system 0.01 M KCl. Up to a week after the reactions started; it seems still not have reached chemical equilibrium. On the contrary also, Fig. 6 seems to add in evidence already inferred from Figs. 3 and 4 on the fact that the addition of calcite in the system 0.01M KCl where uranium and arsenic at higher concentration such as 0.05mM U-As promotes uranium removal rather than decreases it. The latter is particularly the case in mono-component uranium system where calcite dissolution rather enhances the formation of carbonated uranium species lesser prone to fixation by iron oxide surfaces. The reason might simply be found on the hypothesis that uranium is not thermodynamically a good electron acceptor in a system where Ca-UO_2-CO_3 complexes are prevalent. In fact, the mere presence of Ca has been shown to even inhibit the U(VI) reduction by well known uranium scavenger micro-organisms such as the facultative Shewanella putrefaciens (strain CN32) and the obligate (Desulfovibrio desulfuricans and Geobacter sulfureducens) anaerobic bacteria (Brooks et al 2003).

The enhancement of uranium fixation under the influence of 0.05mM As in 0.01M KCl experimental conditions where Ca-UO_2-CO_3 complexes might be induced by calcite dissolution is not fully elucidated. Ca-CO_3 system might better promote the reductive precipitation of arsenic and of uranium through sparingly soluble minerals such as abernathyite. In order to ensure whether this apparent greater K promoted uranium better removal also hold at different arsenic concentrations, a new set of experiments resulted in Figs. 7 and 8.

The role of potassium and the influence of arsenic concentration on uranium fixation on iron corrosion products

Fig. 7 clearly shows that calcite addition inhibit the overall uranium fixation from both 0.01 M NaCl and 0.01M KCl with a steady decreasing trend with increasing uranium input concentrations starting around 0.002mM.

Besides the much greater mobility of carbonato uranium species that might be released by calcite dissolution, there is also the calcium itself as competing metal for the same surface sites that might otherwise adsorb uranium.

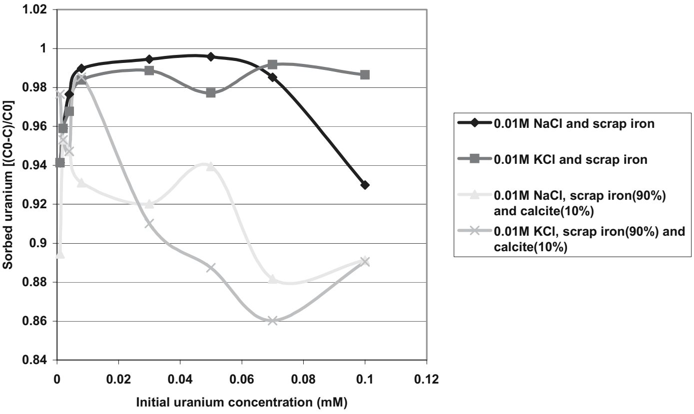

Fig. 7. Comparative removal of uranium concentrations varying from 0.001mM (0.238 mg/L) to 0.1mM (23.81 mg/L) in 0.01M NaCl and 0.01M KCl background electrolytes in contact with respectively scrap iron alone or mixed with 10% calcite (staring solution pH of 4.5).

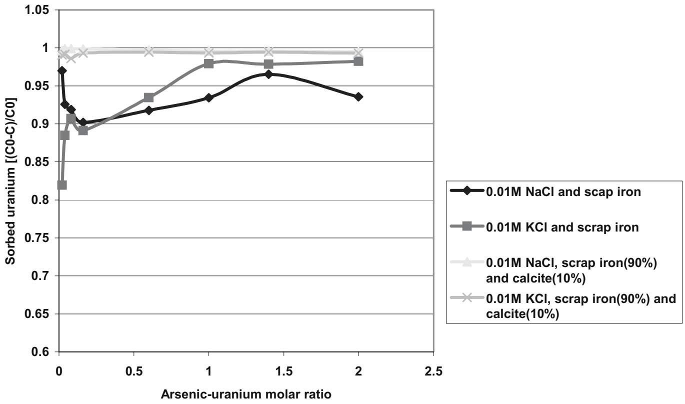

Fig. 8. Removal of uranium from solutions of 0.01M NaCl and 0.01M KCl background electrolytes whereby arsenic to uranium molar concentrations ratio varies from 0 to 2. The arsenic concentrations increased within the range of 0.001mM (0.075 mg/L) to 0.1mM (7.5 mg/L) with uranium concentration kept constant at 0.05mM (11.9 mg/L). The solid phase comprised respectively scrap iron alone or mixed with 10% calcite and the solution staring pH equals 4.5.

The results of the addition of arsenic in molar concentrations ratio to uranium varying from 0 to 2 for arsenic concentrations increased within the range of 0.001mM (0.075 mg/L) to 0.1mM (7.5 mg/L) with uranium concentration kept constant at 0.05mM (11.9 mg/L) is portrayed in Fig. 8. Also, the one week equilibration time under experimental conditions that resulted in Fig. 8 seems to promote uranium removal more efficiently (more than 98%) in the systems that contained calcite under both 0.01 M NaCl and 0.01 KCl buffers. Precipitation or co-precipitation of uranium with arsenic and related carbonated species is probably the main removal mechanism.

On the contrary, the systems with scrap iron alone as solid phase, in particular in the experimental setup where potassium was present as 0.01 M KCl, uranium removal is at its maximum starting at arsenic to uranium molar ratio of one. At arsenic to uranium molar ratio close to or less than 0.08, the system with 0.01M NaCl uranium removal is better. However, this system also shows fixation efficiency with decreasing trend for arsenic to uranium ratio ranging between around 0.001 to 0.008.

Taken as a whole, Fig. 8 suggests that in the systems without calcite under 0.01 M NaCl or 0.01 M KCl, uranium fixation is dependent to arsenic to uranium molar ratio. The probable role of K in enhancing uranium removal is much more prominent in the system without calcite and starting at arsenic to uranium molar ratio of unity.

Overall, from Figs. 1 to 8, experimental results indicate a clear potassium role in promoting uranium fixation in systems where arsenic is present. In order to better ascertain the role of potassium in uranium fate under arsenic influence, the effect of varying the KCl background electrolyte ionic strength has to be investigated in more detail.

The effect of the KCl background electrolyte ionic strength on uranium fixation by scrap iron and iron corrosion products under arsenic influence

Fig. 9 shows that the influence of KCl background electrolyte ionic strength varying from 0.01mM to 0.01 M is more noticeable from uranium concentrations ranging from 0.001mM (0.238 mg/L) to 0.03 mM (7.1 mg/L). This first portion of both three curves seems to be dominated by the prevalence of fixation mechanism other than precipitation/ co-precipitation that is likely the case for the portion beyond 0.03mM uranium.

As could be expected based on Fig. 1 through 9 above, at equal 0.01 M KCl ionic strength, the system with 0.05mM arsenic better removes uranium due to the co-existence of both reductive adsorption and precipitation/co-precipitation reaction mechanisms. In contrast, a similar system with 0.05mM uranium and arsenic but with only 0.01 mM KCl shows the lowest uranium removal efficiency.

By and large, batch experiments described above reveals that potassium can play a controlling role in uranium fate under the influence of varying concentrations of arsenic and varying iron sources as natural minerals and scrap.

Experiments designed to verify some of the batch findings in a dynamic system are still needed.

The dynamic column systems

The comparison of batch systems above and the column results illustrated in Fig. 10 is not clear-cut. This is due to the additive effects of the advective, dispersive and diffusive physical mass transport and related chemical transfer processes of uranium under arsenic, iron and micro-organisms influence in 0.01 M NaCl, 0.01KCl, and complex and upgraded Schneckenstein Uranium Tailings leachate PNP9. Thus, comparability reason, column results are presented in the same format of uranium removal efficiency as per batch results rather than the usual breakthrough curves. In all four columns where scrap iron is present, the fixation of uranium is almost total with however a slightly lower position of the 0.01M NaCl related curve with respect to others and to the 0.01 M KCl in particular. Whether potassium has a particular role in the fixation of uranium in columns where scrap iron is present is difficult to establish in a dynamic system considering the similarity of major uranium and arsenic species in both background electrolyte solutions NaCl and KCl. However, in column containing 50% quartz sand and 50 glass beads, the more than 90% average removal of uranium for the total of 77 pore volume (5Litres) elution can not be explained by its retention in glass beads or filters alone. The only plausible explanation is the precipitation of uranium and arse-

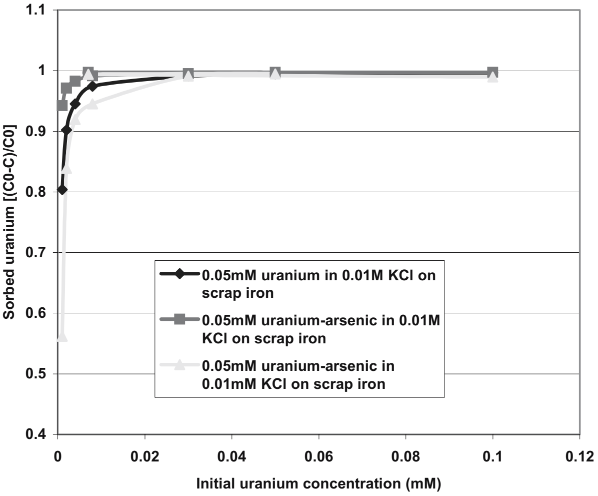

Fig. 9. Uranium fixation under changing ionic strength from 0.01mM KCl to 0.01M KCl spiked with 0.05 mM uranium alone or with 0.05mM arsenic for a one week equilibration time. The solid phase in the reactor vessel was scrap iron alone and the input solution pH was 4.5.

nic through abernathyite as predicted by PREEQC simulation pending on the accuracy of its LLNL data base for this particular solid species.

It is also worth mentioning the similar and unexpected removal effectiveness in another quartz sand column with a liquid biomass seed of natural bacterial consortia from Schneckenstein Uranium Tailings obtained in a procedure described above. The reason for this high removal of uranium might be found in the fact that the column was leached with influent water from the tailings upgraded to 0.05mM uranium-arsenic with a continuous parallel feed of 1mM glucose as the biomass carbon source. This result suggests the likelihood of natural attenuation potential of the uranium tailings. Recent and ongoing studies by Solenska-Pobel (2002) using both direct molecular approaches through Polymerase Chain Reaction (PCR) and the traditional bacteria culture approach in uranium waste piles across the German states of Saxony and Thuringia have come to the conclusion that in all uranium wastes investigated, predominant bacteria groups are mainly those known to biotransform metals. In addition, dilution with the continuous use of 1mM glucose at the average same pumping rate of 0.16 mL/minute is equally important to mention.

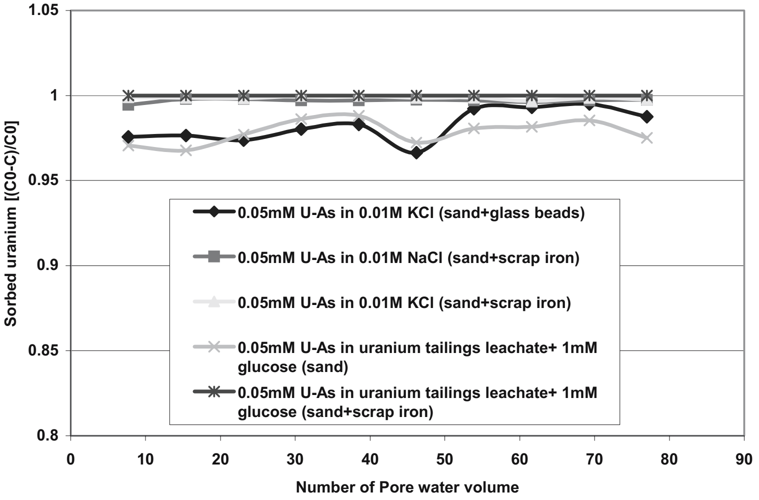

Fig. 10. Removal effectiveness of 0.05mM uranium under 0.05mM arsenic, iron and micro-organisms influence in 0.01M NaCl, 0.01M KCl at pH 4.5 and Scheneckenstein Uranium Tailings PNP9 upgraded to 0.05mM uranium-arsenic concentration at near neutral pH.

Conclusions and environmental implications

This study has shown that even at a laboratory controlled and simplified conditions using mostly synthetic water reduced at minimal composition of either 0.01M NaCl or 0.01M KCl, the fate and transport of uranium under arsenic, iron and bacteria is as complex as the intrinsic hydrogeochemistry of each element involved. Yet, the following conclusions can be drawn from this study experimental conditions and setup.

With respect to iron, uranium fate is different according to the nature of iron sources considered. In general, scrap metallic iron and related freshly formed iron corrosion products better immobilize uranium than natural and old aged iron minerals. In both cases, the presence of calcite which is probably the main control of the much reported discrepant behaviour of uranium and arsenic in aqueous environment also greatly inhibits uranium fixation effectiveness.

The presence of uranium and arsenic particularly at higher concentrations of tens of µg/L can promote uranium and eventually also arsenic precipitation/co-precipitation through sparingly soluble mineral such as abernathyite. Thus, potassium plays an important role in enhancing such uranium and arsenic fixation in systems with or without the presence of calcite. Furthermore, potassium as an essential intracellular nutrient can also play a double role of enhancing bacteria mediated biotransformation and immobilization of uranium and arsenic.

Overall the most important environmental implications is that the addition of potassium can be a valuable alternative option in mitigating both uranium and arsenic contaminants from impacted water bodies where both elements are in higher concentrations. Such aquatic systems with higher uranium and arsenic concentrations are mainly spent mine water or acid mine drainage. In this latter case also, potassium can still play an important remediation role in combination with calcite which is also a pH buffer in order to promote precipitation/co-precipitation of both uranium and arsenic.

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