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The Effect of Background Electrolyte Chemistry on Uranium Fixation on Scrap Metallic Iron in the Presence of Arsenic

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ABSTRACT

This study reports on the influence of selected background electrolyte parameters (pH, ionic strength, ligand and cation concentration) on the partition of uranium between the aqueous phase and elemental iron and its corrosion products in the presence or absence of arsenic. To this end, batch isotherm and kinetic experiments up to 24 h of equilibration time were performed in the dark using scrap metallic iron as sorbent. In most experiments, the background electrolyte was mainly 10 mM KCl spiked with either 50 µM uranium alone or uranium and arsenic both at the same 50 µM concentration. The subsequent uranium and arsenic speciation calculations points to UO_2^{2+} and $H_2AsO_4^-$ as major species for the pH-range 3 to 5 whereas in the pH-range 6 to 9 $UO_2(OH)_2$ and $HASO_4^{2-}$ prevail. The sorption of uranium on elemental iron and corrosion products is pH dependent. The presence of arsenic seems to enhance the removal of uranium for the entire pH-range 3-9. The ionic strength also influence uranium behaviour but its effect is much less apparent than the pH. In terms of uranium removal efficiency, within an average of more or less 10 % experimental error there is no evidence of competition from metal cations dissociated from respectively 10 mM KCl, NaCl, $BaCl_2$, $CaCl_2$ and $MgCl_2$ background electrolytes. Uranium and arsenic speciation remained dominated by UO_2^{2+} and $H_2AsO_4^-$ for the background electrolyte pH 4.5. A similar uranium removal rate was observed when comparing different ligand effect as respectively 10 mM KCl, KNO_3, K_2CO_3, K_3PO_4 and K_2SO_4 despite a slight change in uranium speciation in particular when uranium carbonato species dominated.

Key words: uranium, arsenic, sorption, scrap metallic iron, electrolyte

1. INTRODUCTION

Uranium and arsenic mainly from mining and milling of uranium rich ore bodies are contaminants of concern due to their long term stability in the environment and their chemical toxicity. To date, the reactivity of metallic iron and corrosion products in removing uranium and arsenic in groundwater is still not well understood. Uranium removal by elemental iron is taught to be reductive precipitation or co-precipitation, adsorption or the combination of both (Fiedor et al., 1998; Noubactep et al., 2006). There is also no consensus on arsenic removal by zero valent iron, Fe(0), described either as co-precipitation of the reduced As(III) from As(V) or as adsorption of both As(V) and As(III) on iron corrosion products or other pre-existent oxyhydroxides (McRae et al., 1999; Mallans et al., 2002).

While most authors agree on the efficient removal of both uranium and arsenic by Fe(0) and corrosion products, some have reported discrepant behaviour of uranium *vs.* arsenic in contact with metallic iron and iron oxyhydroxides (Mallants et al., 2002). The reasons for the latter are manifold and include the complex yet not well understood (geo)chemistry of uranium and arsenic, surface properties of the metallic iron and its corrosion products and the water chemistry.

This paper assesses the mechanisms controlling uranium sorption onto elemental iron and its corrosion products in the presence of arsenic. It emphasizes on the effects of water pH, ionic strength, inorganic ligands, and metal cations. It is ultimately aimed at uncovering whether arsenic enhances or inhibits uranium sorption in the systems under consideration.

2. EXPERIMENTAL

2.1 Reagents and Solutions

Uranium and arsenic solutions were prepared from analytical grade uranyl nitrate 6-hydrate $UO_2(NO_3)_2.6H_2O$ (Chemapol, Germany) and sodium arsenate $Na_2HAsO_4.7H_2O$ (Baker, Germany) dissolved in doubled distilled water of 0.056 µs/cm used as solvent throughout. The analytical determination of uranium required the use of 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), HCl 37 % (Baker, Germany), ascorbic acid (Chemapol, Germany) and oxalic acid (Chemapol, Germany).

2.2 Scrap Metallic Iron

The raw scrap metallic iron known as S69 (Metallaufbereitung Zwickau, Germany) of elemental composition as 92.8 % Fe, 3.5 % C, 2.1 % Si, 0.9 % Mn and 0.7 % Cr was crushed and sieved. The fractions 0.25-0.5 mm (25 %) and 0.5-0.8 mm (75 %) throughout has a surface area of 0.29 m^2/g (BET method, N_2 at 77 K). The scrap metallic iron used in this study underwent no further treatment after crushing.

2.3 Batch Sorption Experiments

All but ionic strength batch sorption experiments were carried out in 250 mL capped glass erlenmeyer in a 1:50 (w:w) solid to solution ratio mixing 4 g of scrap metallic iron with 200 mL of relevant background electrolyte solution. For studying ionic strength effect, sorption experiments were carried out with a solid to solution ratio of 1:10 (w:w) in 20 mL centrifuge tubes. The reaction vessels were covered with aluminium foil to minimize photochemical reactions. A hydration time of 6 h was applied to the sorbent using appropriate background electrolyte prior to adding uranium or arsenic at the desired concentration. The reaction vessels were only wrist shaken up and down up to 10 times at the beginning and left to equilibrate for up to 24 h without further shaking.

2.4 Analytical Procedure and Data Plots

Uranium was analysed by photometry using arsenazo III method described in detail elsewhere (Savvin, 1961; Meinrath et al., 1999). pH was measured with combined glass electrodes (WTW GmbH, Germany).

Sorption experimental results are reported in micro molar (µM) as:

$$\frac{C_0 - C}{gfw}$$

where C_0 is the initial concentration, C the equilibration concentration and gfw the mass of the sorbed chemical.

2.5 Speciation calculations

Speciation calculations were performed with PHREEQC (Parkhurst and Appelo, 1999) and the embedded Lawrence Livermore National Laboratory (LLNL) thermodynamic database.

This database extensive arsenic and uranium data and related predictions match well with this project major laboratory observations (Mbudi and Merkel, 2005).

3. RESULTS

The speciation calculation of the KCl experimental background electrolyte spiked with either 50 µM U(VI) or both U(VI) and As(V) used to assess the effect of pH (3 to 9) and ionic strength (pH 4.5) on uranium sorption onto scrap metallic iron is shown in figure 1. UO_2^{2+} and $H_2AsO_4^-$ are the main species for the pH range 3 to 5, whereas $UO_2(OH)_2$ and $HAsO_4^{2-}$ dominate in the pH range 6 to 9.

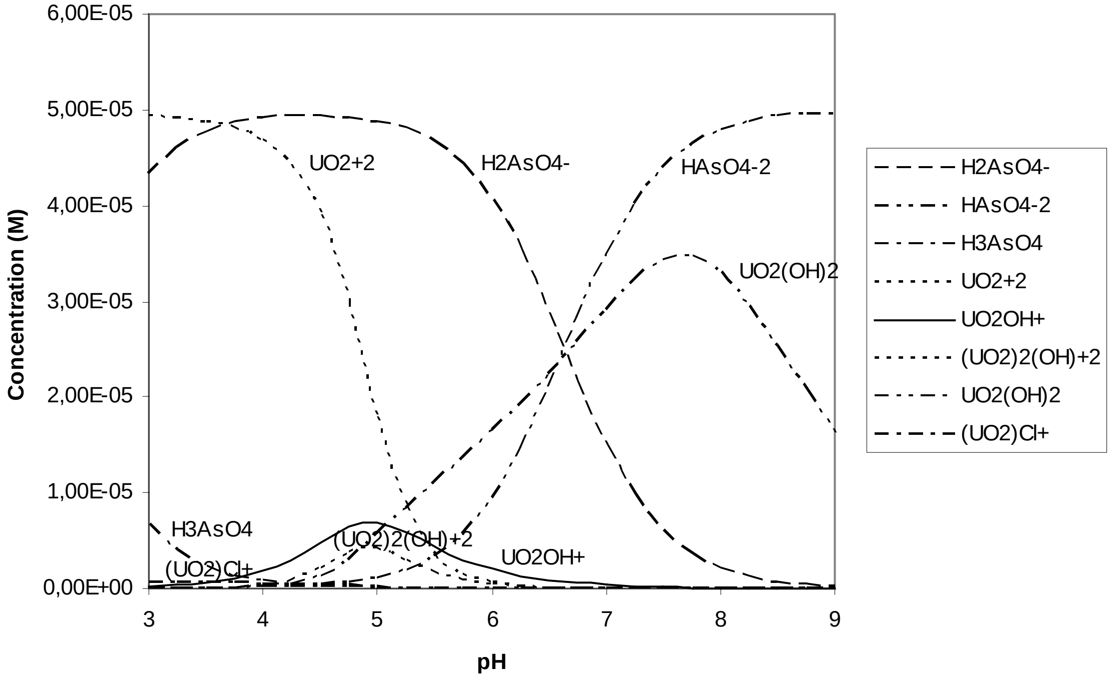

Figure 1: Speciation calculation of the experimental bi-component system for 50 µM uranium-arsenic in 0.01 M KCl background electrolyte

3.1 Effect of pH

The sorption kinetics of uranium onto scrap metallic iron either alone (mono-component) or in the presence of arsenic (bi-component) depends on pH (figure 2). The uranium sorption rate is clearly much slower in the system at pH 3 with background electrolyte spiked with uranium alone than in the presence of arsenic. The overall highest rate of uranium removal is exhibited at pH 9 by the system with uranium alone. The presence of arsenic seems to enhance the sorption of uranium in particular for the pH range 3-5. This trend is less apparent for the pH-range 7-9 as inferred from the figure 2 insert. For all the pH-ranges, the highest removal rate is observed after 10 h of equilibration time. Only the bi-component system uranium-arsenic at pH 5 presents the highest fixation rate after 2 h of equilibration time.

3.2 Effect of Ionic Strength

By changing ionic strength, it appears than the removal of uranium alone or with arsenic on scrap metallic iron at the initial experimental pH of 4.5 is less apparent than the above pH dependency. A log-log scatter plot (figure 3), however, shows roughly S-shaped isotherms ranging from 0.010 mM KCl U-As, 1.0 mM KCl U-As, 10 mM KCl U and 10 mM KCl with respect to the aqueous uranium concentration (abscissa axis).

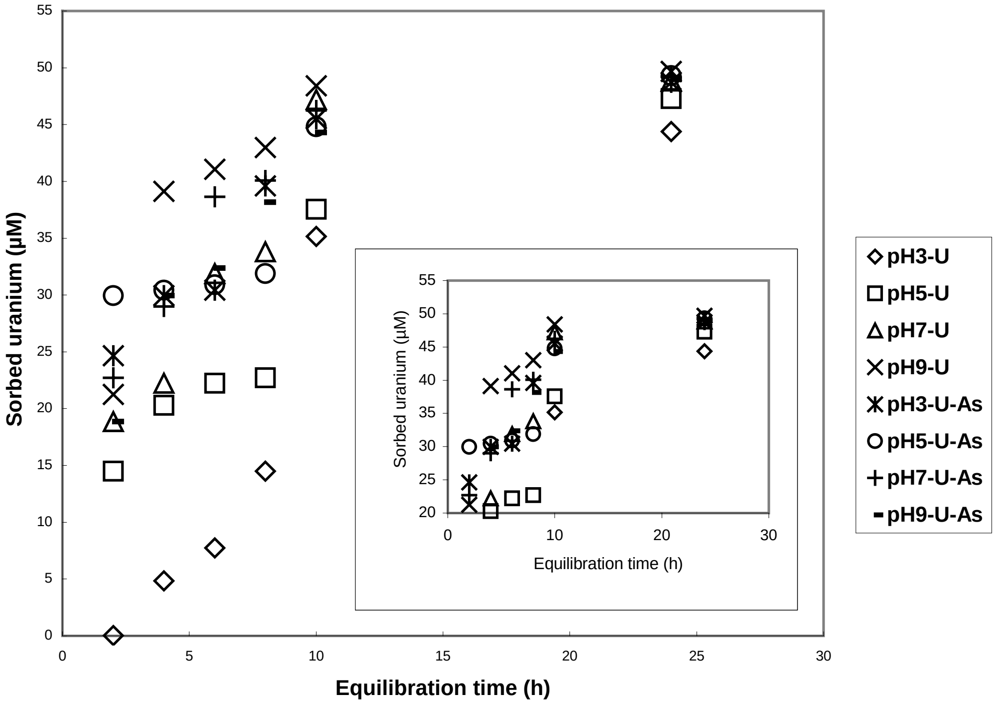

Figure 2: Effect of pH on uranium (initial aqueous concentration: 50 µM) sorption kinetics onto scrap metallic iron either in the absence or in the presence of arsenic (50 µM) in 0.01 M KCl

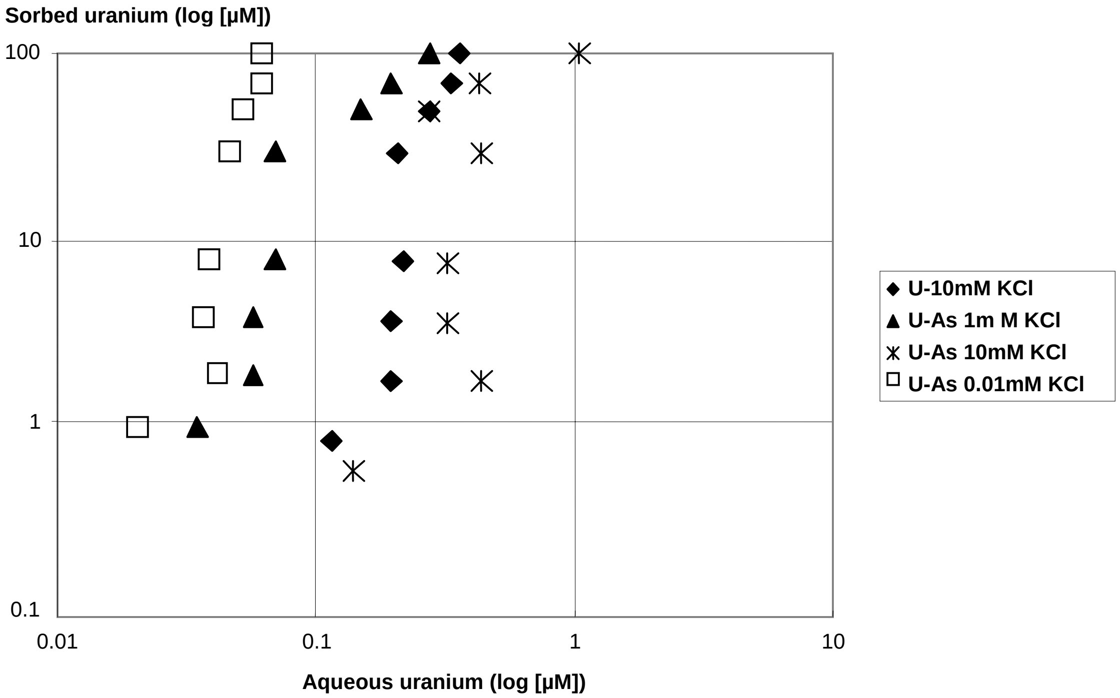

Figure 3: Effect of ionic strength on uranium removal as log-log isotherm scatter plot in the presence of scrap metallic iron alone or in the presence of 50 µM arsenic (experimental conditions: for different KCl concentrations, 50 µM U(VI) or both U(VI) and As(V))

3.3 Effect of Ligands

Within an average of more or less 10 % experimental error, the scatter plot of uranium sorption (figure 4) in the presence of 10 mM inorganic ligands such as Cl^-, NO_3^-, CO_3^{2-}, PO_4^{3-} and SO_4^{2-} prepared from their respective potassium salts shows a quasi-linear maximal rate throughout. The initial pH of 4.5 seems optimal for uranium sorption in both mono-component and bi-component systems. However, the insert showing uranium behaviour within the 10 % of maximal removal shows that the carbonate and phosphate media have the lowest rate. The addition of As(V) seems in both carbonate and phosphate solutions to decrease the rate of uranium removal.

Speciation calculations with PHREEQC pointed out $H_2AsO_4^-$ and $HASO_4^{2-}$ as main arsenic species at the experimental pH 4.5 for all background electrolytes. For uranium, UO_2^{2+} and UO_2OH^+ are the main species for all the studied systems excepted for PO_4^{3-}, CO_3^{2-} or SO_4^{2-}, where (UO_2HPO_4, $UO_2(H_2PO_4)_2$), (UO_2CO_3, $UO_2(CO_3)_2^{2-}$) or (UO_2SO_4, UO_2^{2+}), respectively, may be present too.

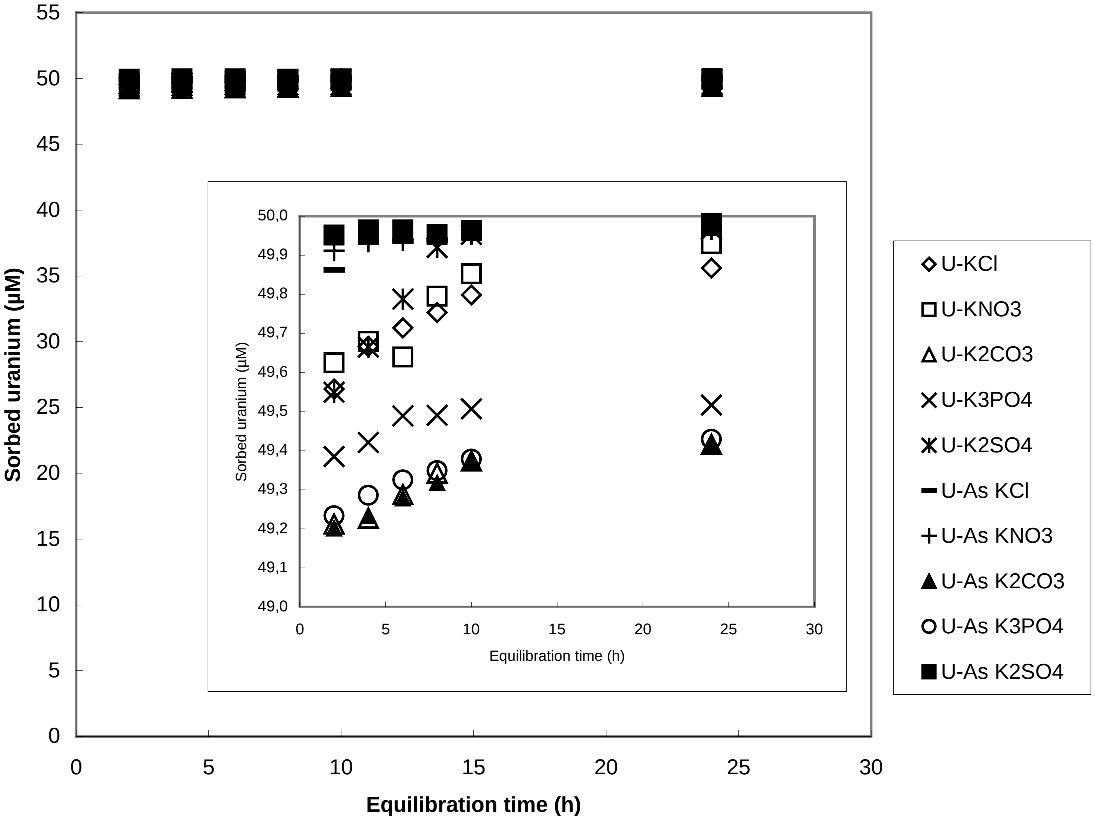

Figure 4: Effect of 0.01 M ligand on uranium (initial aqueous concentration: 50 µM) sorption kinetics onto scrap metallic iron either in the absence or in the presence of arsenic (50 µM) at initial pH 4.5

3.4 Effect Metal Cations

The selected alkali and earth-alkali mono- and divalent metal cations, such as K^+, Na^+, Ba^{2+}, Ca^{2+}, and Mg^{2+}, prepared from their respective Cl^- salts and spiked with either 50 µM uranium or uranium and arsenic seem to play a different role in the overall behaviour of uranium removal kinetics, but the presence of arsenic did not affect it, within a 10 % experimental error.

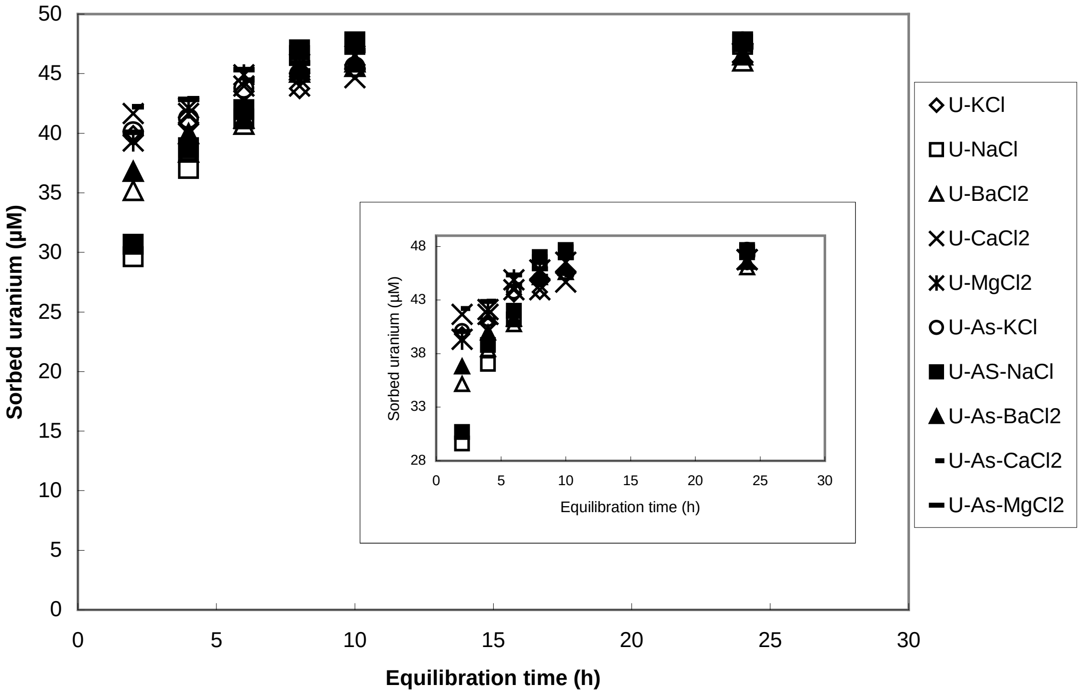

Figure 5: Effect of 0.01 M background electrolyte cation on uranium (initial aqueous concentration: 50 µM) sorption kinetics onto scrap metallic iron either in the absence or in the presence of arsenic (50 µM) at initial pH 4.5

4. DISCUSSION

The scrap metallic iron used in this study was hydrated for 6 h using a relevant background electrolyte prior to the addition of the uranium or uranium and arsenic. This important hydration step determines, depending on the starting pH, the amount of colloidal particles of sparingly soluble iron oxides as corrosion products. For a background electrolyte such as 0.01 M KCl used in the effects of the pH and ionic strength experiments, PHREEQC calculations predict major aqueous iron species being Fe^{2+}, and Fe(II) and Fe(III) chlorides, and hydroxyl species. In such the systems, the reactivity of hydroxyl functional groups formed at iron (hydr)oxide surfaces with uranium from the aqueous phase depends on the later speciation, the competition with H^+, the existing ligands and the competing metal cations. It must also be stressed that the relatively high concentration of 50 µM uranium and arsenic used in the experiments mainly for analytical reasons make most of the systems prone to precipitation/co-precipitation processes in addition to adsorption. In such relatively short hydration and equilibration times, sustainable total anoxic conditions leading to the reduction of uranium and arsenic are unlikely to occur as argued by Noubactep et al. (2006) and revealed by EXAFS (Manning et al., 2002; Mbudi et al., 2007).

The pH dependency of uranium sorption kinetics either alone or in the presence of arsenic (figure 2) suggests competition for sorption sites between uranium and H^+ up to 10 h of equilibration time. Beyond 10 h where most systems in figure 2 reach their maximal uranium removal lays the domain of mostly co-precipitation of uranium with iron hydroxyl species or formation of uranyl arsenates. The presence of arsenic seems to enhance uranium sorption through cooperative sorption of newly formed uranyl arsenates rather than competitive. However, for the system with uranium alone at pH 9, uranium co-precipitation seems to be achieved through reaction involving dominant species

$UO_2(OH)_2$ and the negatively charged aqueous iron hydroxyl species such as $Fe(OH)_4^-$. Overall, deprotonation/protonation reactions at the iron surfaces coupled with precipitation/co-precipitation seems to control uranium removal from the aqueous phase.

The dependency of uranium sorption with respect to ionic strength suggests no competition between uranium and the mono-valent metal K^+ of the background electrolyte KCl. It may also means that despite the relatively higher uranium and arsenic input concentration prone to precipitation/co-precipitation, adsorption of uranium through formation of inner-sphere surface complexes of the type $(\equiv FeO_2)(UO_2)$ could play an important role (Waite et al., 1994).

The interpretation of uranium sorption dependency on ionic strength as signature of no competition of the electrolyte cation is consistent with kinetic sorption experiments with all the selected alkali and earth-alkali metal cations as well as for the inorganic ligands which also show no competition with uranium. Within a 10 % margin of experimental error, there is no evidence of competition neither with mono-valent cations K^+, Na^+ nor with divalent ones Ca^{2+}, Mg^{2+}, and Ba^{2+}. These "hard" cations coordination chemistry classification rarely undergo complexation and competition with uranium (Turner et al., 1981; Stumm and Morgan, 1996).

The apparent low rate of uranium removal in carbonate and phosphate media could be assumed to be due to the relatively strong and stable uranyl-carbonato and uranyl-phosphato complexes which consequently are prone to keeping uranium moderately to highly mobile with respect to hydroxyl species.

5. CONCLUSION

Uranium sorption onto scrap metallic iron alone or in the presence of arsenic depends strongly on the aqueous phase chemistry and chiefly its speciation. The pH of the aqueous phase has a predominant role in uranium sorption rate. The uranium removal dependency on ionic strength seems to be validated by the lack of competition from both alkali and earth-alkali metal cations as well as inorganic ligands. While inner-sphere adsorption may play a role, precipitation/co-precipitation of uranium seems to plays an important role enhanced by the presence of arsenic mainly from middle acidic to near neutral conditions.

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