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The Effect Of Ph, Ionic Strength, Selected Ligands And Metals Cations On Uranium(VI) And Arsenic(V) Competitive Sorption Onto Elemental Iron

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Abstract
This study investigates the effect of pH, Ionic Strength, Selected Ligands and Metals Cations on the partitioning of uranium between the aqueous phase and elemental iron, along with its corrosion products, in the presence and absence of arsenic. To this end, a series of batch isotherm and kinetic experiments were conducted, allowing up to 24 hours of equilibration under dark conditions using aluminum foil. Most experimental rectors contained a 10 mM KCl background electrolyte, spiked with either 50 µM uranium alone or 50 µM of each uranium and arsenic. Speciation calculations using PHREEQC indicate that within a pH range of 3–5, the species UO_2^{2+} and $H_2AsO_4^-$ dominate, whereas $UO_2(OH)_2$ and $HAsO_4^{2-}$ are more prevalent between pH 6 and 9. Uranium sorption onto elemental iron and its corrosion products showed a strong dependence on pH, with arsenic enhancing uranium removal efficiency across the entire experimental pH spectrum studied (3–9). While ionic strength also affected uranium behavior, its influence was less significant compared to pH. Despite the presence of metal cations from background electrolytes such as 10 mM KCl, NaCl, $BaCl_2$, $CaCl_2$, and $MgCl_2$, no substantial competitive effects were observed, given an average experimental error margin of approximately 10%. At pH 4.5, uranium and arsenic speciation remained dominated by UO_2^{2+} and $H_2AsO4_4^-$. Additionally, uranium removal remained largely consistent across different ligands (KCl, KNO_3, K_2CO_3, K_2HPO_4, and K_2SO_4), although minor variations in uranium speciation were noted, particularly in the presence of carbonato species.

***Keywords**: uranium ; arsenic; sorption; Elemental iron iron; electrolyte*

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I. Introduction

Groundwater pollution with arsenic (As) and uranium (U) is a pressing environmental health issue. Arsenic contamination in groundwater is predominantly of geogenic origin such as volcanic activity with elevated levels of arsenic and other trace elements like uranium. In certain regions, groundwater can be enriched with arsenic due to interactions with geothermal fluids (Sappa et al., 2014). Additionally, water-rock interactions in aquifers rich in arsenic-bearing minerals, such as arsenopyrite and pyrite, can mobilize arsenic into groundwater, especially under reducing conditions that favor its solubility (Herath et al., 2016). Surface sediments having high solid-phase arsenic concentrations can contribute to groundwater contamination, whether through natural processes or because of anthropogenic activities (Polizzotto et al., 2005; Keshavarzi et al., 2011). In Bangladesh, significant arsenic levels in tube well water have been linked to the reduction of iron oxides, which releases arsenic into groundwater (Flanagan et al., 2012). Furthermore, anthropogenic influences, such as agricultural practices using arsenic-rich fertilizers and improper disposal of industrial waste, can exacerbate the contamination problem (Sandhi et al., 2022). The use of arsenic-rich pesticides and fertilizers, especially in agricultural settings, can lead to the accumulation of arsenic in soil and water systems through runoff and leaching (Sandhi et al., 2022; Lapworth et al., 2017). Moreover, mining operations can release arsenic from the earth, further exacerbating groundwater contamination issues (Baloch et al., 2020). Both uranium and arsenic can be released into groundwater from similar sedimentary environments where reduced conditions prevail, thereby increasing their concentrations simultaneously (Keshavarzi et al., 2011; Baloch et al., 2020). Worth mentioning that the natural solubility of uranium varies with geochemical conditions, such as pH and redox potential (Lopez et al.,2020). For example, studies have noted that uranium concentrations were significantly influenced by geochemical processes at various hydrogeological settings, such as the crystalline basement aquifers where uranium is naturally enriched (Coyte et al., 2018). Activities such as uranium mining, milling, and improper disposal of radioactive waste are significant contributors to elevated uranium levels in groundwater. Following mining operations, residual uranium can leach out and contaminate surrounding groundwater, especially if the waste is not managed properly (Naik et al., 2024; Christensen et al., 2004). Moreover, past industrial practices at sites like the Hanford Site in Washington have resulted in legacy contamination, where previously stored uranium waste continues to affect groundwater quality well beyond remediation efforts (McKinley et al., 2007; Wellman et al., 2011).

Given the environmental and health implications of uranium and arsenic contamination, understanding the competitive sorption results of these metals onto elemental iron is critical for effective remediation strategies. Studies have shown that zero-valent iron can effectively reduce U(VI) to U(IV), which is less soluble and less toxic, providing a dual benefit of sorption and chemical reduction (Florez et al., 2017; Catalano et al., 2006). The simultaneous presence of arsenic and uranium in groundwater necessitates an understanding of their competitive sorption dynamics. Research highlights that the sorption efficiency of one contaminant can be significantly impacted by the presence of the other, primarily due to competition for limited binding sites on iron surfaces (Prat et al., 2009; Florez et al., 2017). This highlights the need for studies that inform the relative affinities of these metals for iron to optimize remediation approaches. Effective remediation strategies often incorporate materials that facilitate the sorption and precipitation of contaminants. By utilizing zero-valent iron in permeable reactive barriers (PRBs), the transport and concentration of uranium and arsenic can be controlled. Furthermore, understanding the sorption characteristics can help in designing these PRBs to maximize efficacy and longevity (Tesoriero et al., 2019; Srivastava et al., 2021). Besides, high concentrations of arsenic and uranium in drinking water pose significant health risks, including toxicity and carcinogenic effects. Therefore, effective remediation through competitive sorption mechanisms can protect public health by delivering cleaner water supplies and reducing contamination in affected aquifers (Akter & Ali, 2011; Wellman et al., 2011).

Overall, the sorption dynamics of uranium (VI) and arsenic (V) onto elemental iron are complex processes influenced by several key factors, including pH, ionic strength, the presence of selected ligands, and competitive effects from metal cations.

The Effects of pH

The sorption of both uranium and arsenic is heavily influenced by pH, affecting the species present in the aqueous solution and the surface charge of the sorbent. Beazley et al. found that uranium precipitation rates are highly dependent on pH, with significant precipitation occurring at pH levels of 5.5 and 7.0, while minimal precipitation was observed at pH 4.5, which was attributed to the low solubility of uranium under acidic conditions (Beazley et al., 2007). Similarly, Dębiec-Andrzejewska et al. reported that arsenic's sorption efficiency with iron-based sorbents is optimal in the pH range of 3.5 to 9.5, with decreased efficiency in very acidic conditions due to enhanced solubility of iron oxyhydroxides (Dębiec-Andrzejewska et al., 2018). The maximal sorption of arsenic typically occurs at pH values of around 4, with significant suppression observed outside this range due to the increasing negative charge of iron oxides that diminishes the attraction of As species (Ling & Zhang, 2017). Further studies have also highlighted contrasting behaviors of arsenic species under varying pH levels. Jovanović et al. indicated that As(III) sorption is significantly higher than As(V) at a neutral pH of 7, suggesting that the molecular form of arsenic may facilitate stronger interactions with iron-coated materials compared to ionic species (Jovanović et al., 2011). Additionally, Mamindy-Pajany et al. demonstrated that arsenic sorption onto iron oxides like hematite and goethite was enhanced in acidic conditions, with retention decreasing at alkaline pH levels due to reduced availability of binding sites (Mamindy-Pajany et al., 2008). Overall, the dependence of sorption capacity on pH emphasizes the necessity for precise pH control in remediation strategies involving iron-based materials.

The Ionic Strength and its effects

Ionic strength also plays a pivotal role in the competitive sorption dynamics of U and As. Increased ionic strength can modify the activity coefficients of the ions present, affecting their effective concentration in the solution and consequently their respective interactions with surface sites on iron. In systems where competing ligands are present, such as phosphate, both As and U might experience altered sorption due to reduced electrostatic interactions at higher ionic strengths, which can lead to increased solubility of oxyanions like arsenate (Seaman et al., 2001; Perez, 2025). Furthermore, high ionic strength environments tend to stabilize solute species, which may reduce sorption efficiency due to competition with other ions, such as phosphates, present in the solution (Seaman et al., 2001; Su & Puls, 2001). Conversely, studies have noted that at low concentrations, ionic strength may enhance the effective sorption of U as it reduces the solubility of dissolution products and maintains favorable interaction conditions with iron surfaces (Bachmaf & Merkel, 2010). Singh et al. have shown that increasing ionic strength can enhance U(VI) adsorption onto ferrihydrite, which is related to changes in the structure of surface complexes formed at higher electrolyte concentrations (Singh et al., 2012). Violante and Pigna discussed how different ionic environments can influence competitive sorption behaviors among oxyanions (Violante & Pigna, 2002).

The effects of ligands

The presence of ligands significantly influences the sorption of both U and As. For instance, humic acid (HA) enhances the mobility of arsenic in the aqueous phase as it competes for sorption sites alongside arsenate (Seaman et al., 2001; Mikutta & Kretzschmar, 2011). The complexation of U and As with ligands shifts their speciation, which influences their adsorption behavior onto iron surfaces. Several studies indicate that organic ligands can facilitate or inhibit metal ion sorption depending on the competition for binding sites on the sorbent (Bachmaf & Merkel, 2010). Moreover, ligands such as carbonates can form complexes with uranium, shifting its speciation towards forms that exhibit lower adsorption capabilities, like uranyl carbonato complexes in alkaline conditions (Schmeide et al., 2000). In some experiments, the presence of phosphate was observed to severely inhibit arsenate sorption, with a noted decrease in sorption efficiency inversely related to phosphate concentration (Dixit & Hering, 2003).

The effects of metal cations

Competitive sorption behavior also arises from the presence of metal cations in solution. When U and As co-occur with other metal species, like Fe(II), their adsorption can be disproportionately affected due to limited surface sites on iron, leading to notable inhibition of one metal ion by another (Catalano et al., 2011). For example, Fe(II) demonstrated a significant competitive inhibition effect on arsenate sorption at neutral pH conditions, suggesting that when both metals are present, preferential adsorption may occur based on factors like kinetics and surface site accessibility (Catalano et al., 2011). Furthermore, the tendencies of both arsenate and arsenite to form surface complexes can lead to distinctly different adsorption efficiencies and mechanisms when competing for shared binding sites on iron oxides (Appelo et al., 2002). Semião et al. also found that the presence of cationic metal species can modify the charge and structural characteristics of iron surfaces, affecting the binding affinity for both U and As. For example, at low concentrations of iron, arsenate can inhibit Fe(II) sorption due to competitive adsorption (Semião et al., 2010). Conversely, iron minerals often enhance the sorption of both metals when present at optimal conditions, highlighting a complex interplay between the different metal ions in solution (Catalano et al., 2011).

Overall, the sorption of uranium and arsenic onto elemental iron entails intricate interactions modulated by pH, ionic strength, ligand presence, and competition with metal cations. Each variable can critically alter the speciation and efficiency of sorption, necessitating a comprehensive understanding to optimize remediation strategies for waters contaminated with these hazardous elements. The evidence from various studies underscores the complexity of these interactions and highlights the necessity for tailored approaches in environmental management practices. This paper is aimed at investigating the mechanisms governing competitive sorption of uranium and arsenic onto elemental iron and its corrosion products focusing on the effects of water pH, ionic strength, selected ligands, and metal cations in controlled laboratory settings.

II. Materials And Methods

Elemental Iron

The elemental iron used throughout the experimental process is the scrap metallic iron known as S69 supplied by the German company Metallaufbereitung Zwickau. The collected scrap metallic iron was crushed and sieved using the German DIN 66165-1 standard resulting in various grain sizes. The scrap metallic iron used in this study underwent no further treatment after crushing. The chemical composition analysis of the sieved zero-valent iron used throughout revealed 92.8 % Fe, 3.5 % C, 2.1 % Si, 0.9 % Mn and 0.7 % Cr. The fractions 0.25-0.5 mm (25 %) and 0.5-0.8 mm (75 %) with a surface area of 0.29 m2/g (BET method, N2 at 77 K).

Reagents and Solutions

All the reagents of analytical grade used in this research included uranyl nitrate 6- hydrate U02(N03)2.6H20 from Chemapol (Germany) and sodium arsenate Na2HAs04.7H20 from Baker (Germany). These chemical compounds were dissolved in doubled distilled water with electrical conductivity of 0.056 µs/cm used as solvent to prepare uanium and arsenic solutions used throughout the laboratory experiments. The analytical determination of uranium was carried out using arsenazo III (1,8- dihydroxynaphthalene- 3 ,6-disulphonic acid- 2, 7 -bis[(azozj-pheny larsonic acid)] from Riedel-de- Haen (Germany) used as 0.15 % (m:v) aqueous solution, 200 mg of high purity Zn granules from Fluka (Germany), HCI 37 % from Baker (Germany), ascorbic acid from Chemapol (Germany) and oxalic acid from Chemapol (Germany).

Sorption Experiments in Batch Reactors

The reaction vessels used in all batch sorption experiments, but the ionic strength were the 250 mL capped glass erlenmeyer in a 1:50 (w:w) solid to solution ratio mixing 4g of the sieved fractions 0.25-0.5 mm (25 %) and 0.5-0.8 mm (75 %) scrap metallic iron mixed with 200 mL of relevant simulated groundwater as background electrolyte solution. The specific case of the ionic strength effect related experiments, sorption tests were undertaken using a solid to solution ratio of 1:10 (w:w) in 20mL centrifuge tubes reactors. To minimize photochemical reactions, the batch reactor vessels were covered with aluminum foil. A six hour hydration time was applied to the mixture scrap metallic iron as sorbent and the relevant analogue groundwater as background electrolyte solution prior to adding uranium or arsenic, and both uranium and arsenic at the desired concentrations. 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.

Determination of Uranium Concentrations, Data Treatment and plots

The concentrations of uranium at the equilibration time were determined by photometry using the arsenazo **III** method, described in detail elsewhere including in papers by Savvin (1961) and Meinrath et al. (1999). pH was measured with combined glass electrodes (WTW GmbH, Germany). Sorption experimental results are reported in micro molar (µM) as:

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

where:

Co is the initial concentration, C the equilibration concentration and *gfw* the gram formula weight (mass) of the sorbed chemical.

Speciation Computations

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

X-ray Diffraction

The X-ray Diffraction of the sparingly soluble uranyl arsenate precipitate was determined at the Laboratory of the Institute of Mineralogy at the Technische Universität Bergakademie Freiberg, Germany. The analysis for the determination of the sparingly soluble precipitate was carried using the X-ray diffraction with a 3000TT diffractometer operating at Cu Kα radiation with a diffracted beam graphite monochoromator, and a proportional counter and automatic divergence slit. The data collected in the 2Θrange 5-80^0, step 0.025^0, and counting time 3 seconds per step.

III. Results

Uranium and Arsenic speciation

The speciation computations of the groundwater simulated KCI as experimental background electrolyte solution spiked with either 50 µ*M* U(VI) or both U(VI) and As(V) used to evaluate the significance of the pH edge (3 to 9) and ionic strength (pH 4.5) on uranium sorption onto zero valent iron is shown in figure 1. The species of uranium UO_2^{+2} and of arsenic H_2As0_4- are the main types for the pH range 3 to 5, whereas $U0_2(OH)_2$ and $HAsO_4^{-2}$ dominate in the pH range 6 to 9.

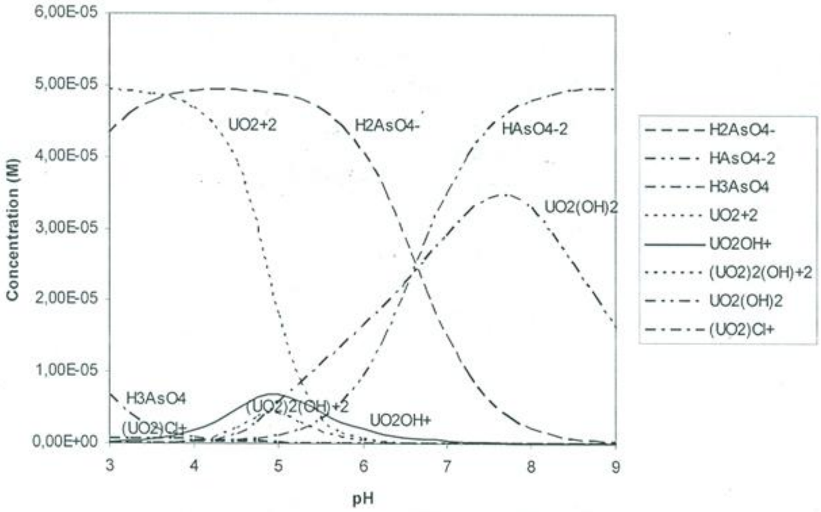

Figure 1: Speciation calculation of the experimental bi-component system for 50 µM uranium-arsenic in 0.01 M KCl background electrlyte (LLNL thermodynamic database)

The initial aqueous speciation of the 0.01M KCl experimental background electrolyte solution spiked with 50 µM U(VI) or 50 µM of both U(VI) and As(V) used to assess the effect of pH in the range of 3 to 9 and of ionic strength at pH 4.5 on uranium sorption on scrap metallic iron was also calculated using the PHREEQC hydrogeochemical code (Parkhurst and Appelo, 1999) and its embedded and revised WATEQ4F thermodynamic database for arsenic species (Nordstrom and Archer, 2003). This database extensive arsenic and uranium data and related predictions match well with this study major laboratory observations (Mbudi and Merkel, 2005).

Furthermore, to account for probable uranyl-arsenate species, the simulations input files were supplemented with thermodynamic data of aqueous uranyl-arsenate complexes formation constants as shown in the reactions (i), (ii), and (iii) given by Rutsch et al. (1997) whereas thermodynamic data for the solid phase KUO_2AsO_4 (reaction iv) and for the neutral aqueous species $UO_2(OH)_2$ (reaction v) were taken respectively from Wagman et al. (1982) and Grenthe et al. (1992).

$$UO_2^{2+} + HAsO_4^{2-} \Leftrightarrow UO_2(HAsO_4) \qquad \log K = 18.76 \qquad \textbf{(i)}$$

$$UO_2^{2+} + H_2AsO_4^{-} \Leftrightarrow UO_2H_2AsO_4^{+} \qquad \log K = 21.96 \qquad \textbf{(ii)}$$

$$UO_2^{2+} + 2H_2AsO_4^{-} \Leftrightarrow UO_2(H_2AsO_4)_2 \qquad \log K = 41.53 \qquad \textbf{(iii)}$$

$$KUO_2AsO_4 + 2H^{+} \Leftrightarrow H_2AsO_4^{-} + K^{+} + UO_2^{2+} \qquad \log K = -4.17 \qquad \textbf{(iv)}$$

$$2H_2O + UO_2^{2+} \Leftrightarrow UO_2(OH)_2 + 2H^{+} \qquad \log K = -10.31 \qquad \textbf{(v)}$$

Figure 2 portrays the resulting pH dependent distribution of major aqueous uranium and arsenic species whereas figure 3 illustrates the incorporation of Rutsch et al. (1997) formation constants to account for possible uranyl-arsenate species.

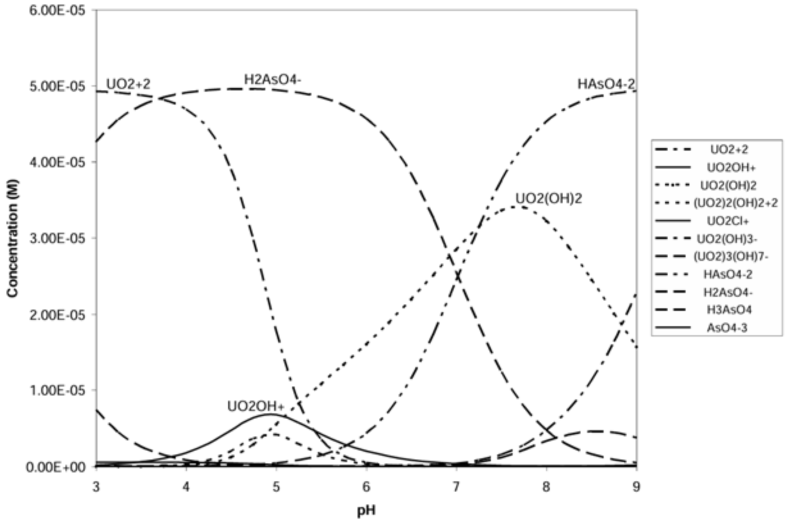

Figure 2: Aqueous speciation calculation of the experimental bi-component system 50 µM uranium-arsenic in a 0.01 M KCl Background electrolyte solution (WATEQ4F thermodynamic database)

UO_2^{+2}, $H_2AsO_4^-$ and UO_2HAsO_4 are dominant species for the pH range 3 to 5 whereas $H_2AsO_4^-$ alone prevails up to pH 7 until its concentration equals that of $UO_2(OH)_2$ around 2.75E-05 M. In the pH range 6 to 9, $UO_2(OH)_2$ and $HAsO_4^{-2}$ dominate. Moreover, figure 3 clearly indicates the presence of the uranyl-arsenate species UO_2HAsO_4 in the pH range 3 up to 7 with a climax at pH 5.

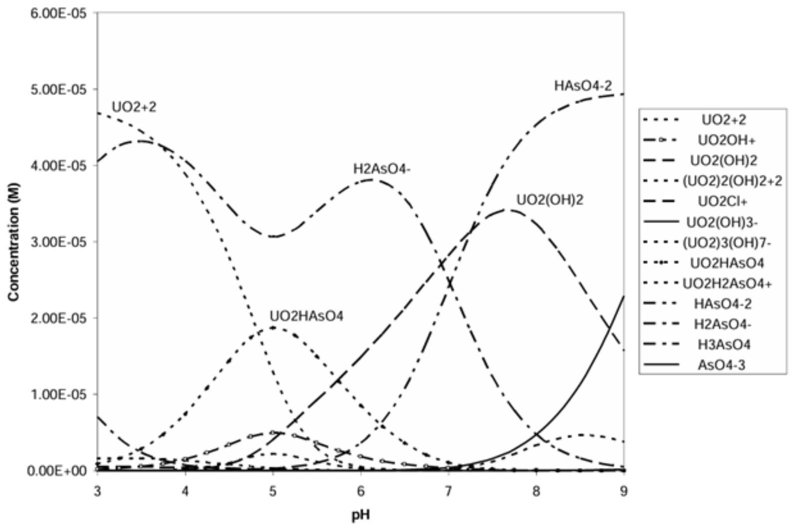

Figure 3: Simulated aqueous speciation of the experimental bi-component system of 50 μM Uranium-Arsenic in =.0.01 M KCl Background electrolyte solution considering Rutsch et al. (1997) complexes formation constants.

Sorption experimental results assessing the effects of pH, ionic strength, ligands and meal cations are presented in figures 4 to 7 herein and reported in micro molar (μM) of fixed uranium calculated as aforementioned.

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 4). 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 for the pH range 3-5. This trend is less apparent for the pH-range 7-9 as inferred from the figure 4 insert. For all the pH-ranges, the highest removal rate is observed after 10 hours of equilibration. Only the bi-component uranium-arsenic system at pH 5 presents the highest fixation rate after 2 hours of equilibration.

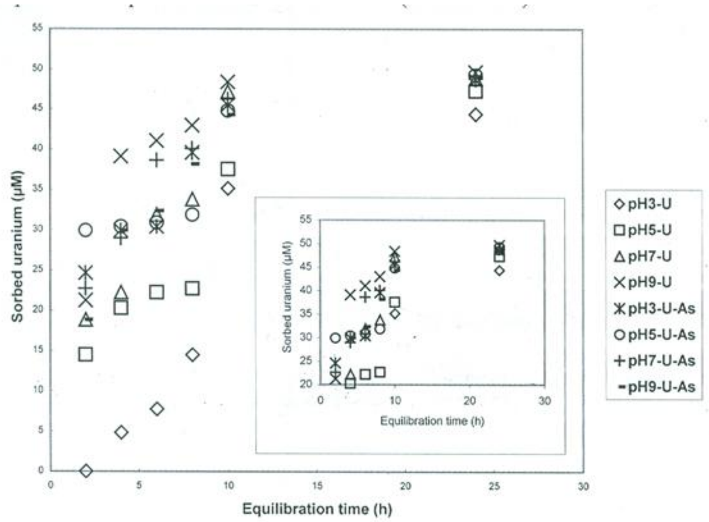

Figure 4: Effect of pH on uranium (initial aqueous concentration: 50μM) sorption kinetics onto scrap metallic iron either in the absence or in the presence of arsenic (50μM) in 0.01M KCl

Effect of Ionic Strength

By changing ionic strength, it appears that the removal of uranium alone or with arsenic on scrap metallic iron and its corrosion products at the initial experimental pH of 4.5 is less apparent than the above pH dependency. A log-log scatter plot (figure 5), however, shows roughly S-shaped isotherms ranging from the respective systems of 0.010 mM KCl U-As, 1.0 mM KCl U-As, 10 mM KCl U and 10mM KCl U-As with respect to the aqueous uranium concentration (abscissa axis).

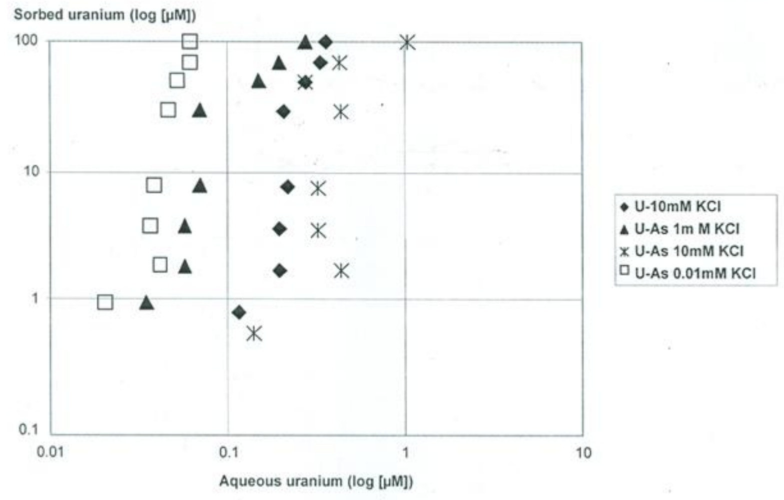

Figure 5: Effect of varying ionic strength for different background electrolyte KCl concentrations solutions spiked with U alone or U in the presence of As as log-log isotherm scatter plot of uranium removal on the surface of scrap metallic iron and corrosion products (experimental conditions: 50 µM U(VI) alone or both U(VI) and As(V))

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 behavior 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 $H_2As0_4^-$ and $HASO_4^{2-}$ as main arsenic species at the experimental pH 4.5 for all background electrolytes. For uranium, UO_2^{2+} and $U0_20H^+$ are the main species for all the studied systems excepted for PO_4^{3-}, CO_3^{2-} or SO_4^{2-}, where (UO_2HP0_4, $UO_2(H_2P0_4)_2$), (UO_2C0_3, $UO2(CO_3)_2^{2-}$) or (UO_2SO_4, UO_2^{2+}), respectively, may be present too.

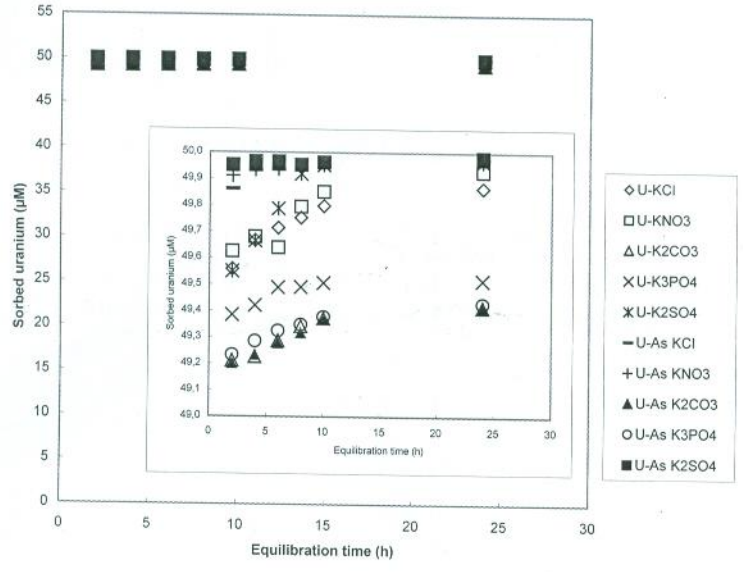

Figure 6: Effect of 0.01 M ligand on uranium (initial aqueous concentration: 50 µM) sorption kinetics onto scrap metallic iron either in the absence or in the presence of arsenic (50 µM) at initial pH 4.5

The Effect of Metal Cations

The selected alkali and earth-alkali mono- and divalent metal cations, such as K+, Na+, Ba^{2}+, Ca^{2}+, and Mg2+, prepared from their respective Cl salts and spiked with either 50 uM 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.

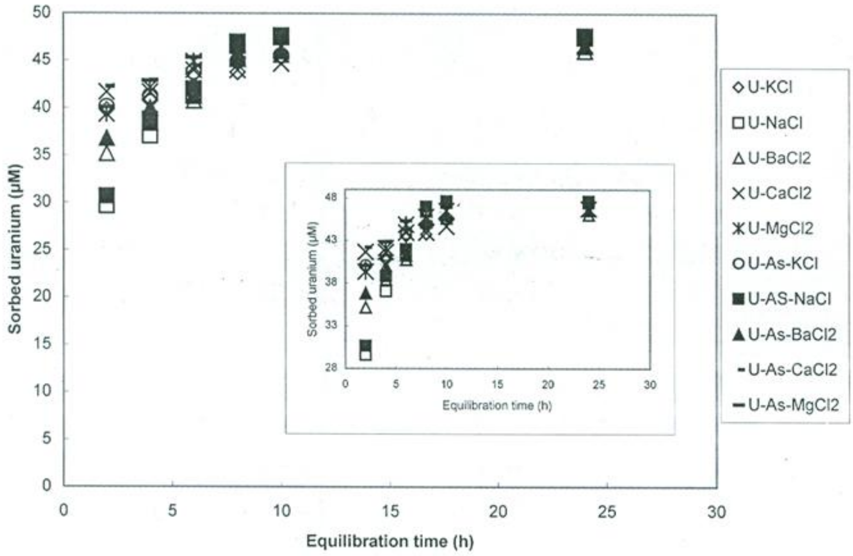

Figure 7: Effect of 0.01 M background electrolyte cation on uranium (initial aqueous concentration: 50 µM) sorption kinetics onto scrap metallic iron either in the absence or in the presence of arsenic (50 µM) at initial pH 4.5

pH dependent saturation index calculations of the sparingly soluble potassium uranyl arsenate

PHREEQC simulations predicted the likelihood of uranium removal through the potassium uranyl arsenate from chloride, nitrate and sulphate ligands rather than from the phosphate and carbonate. For the latter, the comparative saturation index of the sparingly soluble potassium uranyl arsenate compound in phosphate was much towards the precipitation of the compound than in carbonate. Overall, the presence of arsenic has enhanced uranium fixation for all sort of species including in solutions where much more mobile uranyl carbonato species prevailed.

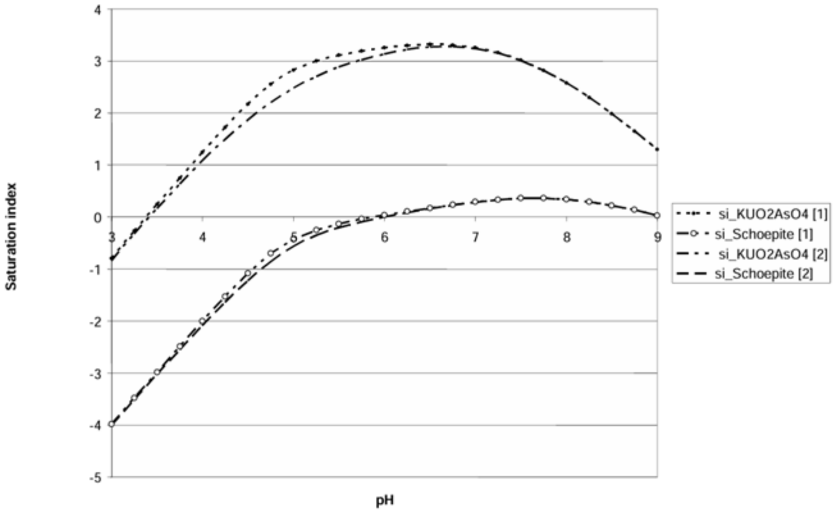

Figure 8: pH dependent simulated distribution of the saturation index of the compound KUO_2AsO_4 and Schoepite without uranyl arsenate complexes formation constants given by Rutsch et al (1997) [1] compared to their incorporation in the calculations [2].

Evidence of uranium removal through precipitation of potassium uranyl arsenate compound

Figure 8 shows simulated pH dependent saturation indexes of an unnamed compound KUO_2AsO_4 compared to Schoepite whereas figure 9 gives XRD characterization of this potassium uranyl arsenate as the sparingly soluble mineral which may be the primary control of uranium behavior in the systems with 0.01M KCl as background electrolyte solution as predicted by the hydrogeochemical modeling code PHREEQC.

The yellowish precipitate or mineral coating observed in KCl based systems was characterized as $KAsUO_6[3H_2O]$. It is suggested that the compound is closely related to or may be most likely abernathyite. However, the unknown compound has higher potassium and lower hydronium content at the cation position than the natural abernathyite as originally identified from Temple Mountain, Emery County, Utah, USA.

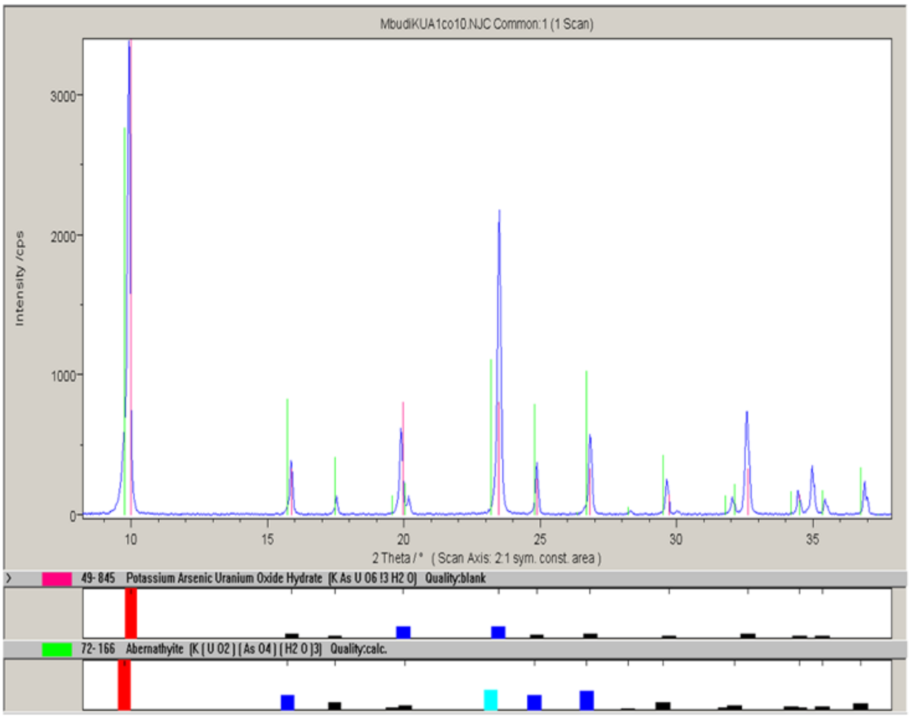

Figure 9: XRD comparative patterns of the potassium uranyl arsenate oxy-hydrate $KAsUO_6$ $[3H_2O]$ compound from the reactors and the mineral Abernathyite $[K[UO_2][AsO_4][H_2O]_3]$

IV. Discussion

The zero valent iron scrap metallic iron used in this study was hydrated for 6 hours 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 KCI 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 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 time, sustainable total anoxic conditions leading to the reduction of uranium and arsenic are unlikely to occur as argued by Noubactep et aI. (2006) and revealed by EXAFS (Manning et aI., 2002; Mbudi et aI., 2007). Overall, in the context of the sorption behavior of uranium(VI) and arsenic(V) onto zero-valent iron, the hydration of metallic iron plays a pivotal role in determining the availability of reactive sites for metal ion interaction. This study corroborates findings from Duster et al. (Duster et al., 2017), who highlighted the significance of surface interactions at varying ionic strengths, and Anagnostopoulos et al. (Anagnostopoulos et al., 2017), indicating that hydration influences the stabilization of aquo complexes necessary for effective metal ion adsorption. Given that the surface chemistry of iron alters with pH and ionic strength, and that substantial quantities of iron oxides form as colloidal particles, the concentration of reactive hydroxyl groups at the iron surface dictates the competitive sorption environment among uranium, arsenic, and existing ligands (Anagnostopoulos et al., 2017).

Besides, the pH dependency of uranium sorption kinetics either alone or in the presence of arsenic (figure 4) suggests competition for sorption sites between uranium and H^+ up to 10 hours of equilibration time. Beyond 10 hours 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. Furthermore, The notable effect of pH on uranium sorption kinetics is underscored by results showing a profound interaction with aqueous species under varied pH conditions. This aligns with the conclusions drawn by Li et al. Li et al. (2022) and Yang et al. (Yang et al., 2018), both of whom established that pH affects metal speciation and thus the efficacy of ion exchange and surface complexation mechanisms. Particularly, it was observed that in alkaline conditions, uranium forms predominantly uranyl hydroxo complexes facilitating stable sorption (Fan et al., 2017). Moreover, the presence of arsenic fosters cooperative sorption through the formation of uranyl arsenates, as observed in conditions where the pH favors their precipitation (Mehio et al., 2016). The assertion that coexistence leads to enhanced uranium removal can also be illustrated by Ladshaw et al. (Ladshaw et al., 2015), who postulated that complexation enhances metal stability against competition from other ions.

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 KCI. 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 aI., 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+, Mg2+, and Ba^2+. These "hard" cations coordination chemistry classification rarely undergo complexation and competition with uranium (Turner et a\., 1981; Stumm and Morgan, 1996). Moreover, Ionic strength significantly influences the competitive dynamics between uranium and background electrolytes. Studies indicate that inner-sphere complexes, which provide a more stable interaction, prevail under conditions of higher ionic strength (Nikitenko et al., 2005). The findings from Anagnostopoulos et al. (Anagnostopoulos et al., 2017) reinforce the notion that surface complexation prominently dictates the binding dynamics, with inner-sphere complexation prevailing over outer-sphere interactions influenced by ionic strength. The experimental data suggests that despite potential precipitation events, adsorption remained the dominant mechanism in low ionic strength conditions, as net charge interactions and complex formation governed adsorption efficiency (Duster et al., 2017).

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. The lower uranium adsorption rates observed in carbonate and phosphate dominated media highlight the competitive nature of these stable complexes formed in solution that inhibit effective uranium binding (Fan et al., 2017). These findings resonate with previous studies, such as those by Missana et al. (Missana et al., 2023), which documented how strong ligand binding can prevent effective sorption of metals by competing for adsorption sites. Thus, while precipitation/co-precipitation reactions complicate the landscape of metal sorption, notably in complex matrix systems, the clear predominance of adsorption mechanisms can often lead to enhanced removal efficiencies of uranium in the presence of competing ions, contingent upon the specifics of ion chemistry and environmental conditions.

V. Conclusion

In conclusion, this study underscores that uranium sorption onto scrap metallic iron is highly sensitive to pH and governed by the chemistry of the aqueous phase, particularly the speciation of uranium and arsenic. The availability and nature of sorption sites are influenced by competing ions and inorganic ligands, with ionic strength modulating the competitive interactions between these species. The findings highlight the dominant role of pH in controlling uranium sorption efficiency, while the minimal impact of alkali and alkaline earth metal cations—as well as common inorganic ligands—suggests limited competitive interference under the tested conditions.

The research also reveals a complex interplay between adsorption and precipitation mechanisms, with evidence supporting a significant role for precipitation and co-precipitation processes, especially in the presence of arsenic under mildly acidic to near-neutral pH conditions. Although inner-sphere adsorption may contribute to uranium retention, the enhanced removal observed in arsenic-containing systems points to the importance of co-precipitation pathways. These insights offer valuable guidance for optimizing uranium remediation strategies in contaminated environments.

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