A pilot study on the effect of desferrioxamine B on uranium VI precipitation and dissolution in pH 11.5, 0.1 M NaCl solutions

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Abstract
A pilot study investigating the possible role of desferrioxamine B (DFOB) to prevent UVI precipitation in alkaline NaCl solutions was carried out. Desferrioxamine B is a hydroxamate siderophore occurring naturally in the environment. The siderophore can possibly mobilize UVI from a wide range of sources such as mine tailings, contaminated land and radioactive waste storage and disposal facilities. The results from a series of batch experiments covering a wide range of naturally occurring concentrations over relevant time scales (3 days and 2 months) show that DFOB can quantitatively prevent UVI precipitation as ≥0.2 µm precipitates when 130 µM and 420 µM of the DFOB is present in solution. The impact is minimized as its concentration decrease to below 10 µM, suggesting these ligands will have a less mobilizing effect on uranium from a geological disposal facility if present in its VI oxidation state.

Keywords Uranium · Siderophores · Desferrioxamine B · Alkaline solutions · Saline solutions · Precipitation · Dissolution

Introduction
Uranium (U) is a toxic element that threatens groundwater quality if mobilized from a solid-phase source. Uranium is present in alkaline (pH above 9) solutions in a variety of scenarios. Surface, near surface, and deep geological disposal facilities for radioactive waste often grout the waste and use cement to backfill the facility [1, 2]. Groundwater leaching of the grout waste form and cement backfill leads to alkaline (pH 9–14) and saline solutions [3]. Radioactive waste is also stored in high pH conditions free of cement and grout. For example, at Sellafield in the UK, spent fuel rods are stored in pH > 10 solutions adjusted with NaOH [4]. Tailings from U mining can contain saline solutions of pH 10 [5]. Alkaline conditions can also occur in natural systems such as at Maqarin, Jordan (pH 12.5) [6–8] and the Allas Springs, Cyprus (pH 9.25–11.71) [9].

In alkaline solutions, UVI precipitates from solution, limiting its mobility. This is a key advantage of storing nuclear waste in cementitious wasteforms and backfills. Precipitation has been observed even at the low UVI concentrations of interest in the present study (42 µM). Batch experiments conducted at pH ≥ 10 in solutions containing 28.5 µM UVI and 0.01 to 0.05 M NaClO3 showed precipitates attaching to mineral surfaces, therefore significantly reducing UVI mobility [10–12]. This process was studied in greater detail recently in a series of batch experiments with UVI and quartz, an iron-coated sandstone and a volcanic rock in solution [13]. The authors found 42 µM UVI precipitated from 0.1 M NaCl solutions and was immobilized on the iron-coated sandstone and volcanic rock between pH 10 and 12. While UVI was not immobilized chemically on quartz sand, it was physically in quartz sand columns under the same chemical conditions [14].

The above studies suggest that UVI mobility is limited under alkaline and saline conditions. However, these studies
were conducted in inorganic systems, while in the natural environment organic molecules will be prevalent. These organic molecules potentially form aqueous complexes with U\(^{VI}\), limiting precipitation. If these complexes form, then uranium mobility from contaminated land and radioactive waste storage and disposal facilities could be enhanced. One such class of organic molecules are siderophores. These are multidentate organic molecules released by plants, fungi, and bacteria in alkaline, oxygenated conditions to solubilize iron [15, 16]. Concentrations of these molecules vary with depth in the geosphere, varying from below 10 \(\mu\)M in rocks up to several mM in the rhizosphere [16–18].

Desferrioxamine B (DFOB) is a (tris)hydroxamate siderophore widely present in groundwater [19, 20]. Its structure is provided in Fig. 1 A. DFOB enhances the solubility of U\(^{IV}\) minerals between pH 3 and 8 under reducing conditions [21], and complexes with U\(^{VI}\) between pH 4 and 10 with stability constant (log \(\beta\)) between 17.12 and 22.93 [22–25]. A recent study focused on the ability of DFOB to leach U from contaminated soils in PH circumneutral solutions and complexation studies indicated the formation of mononuclear U-DFOB complexes with log \(\beta\) between 29.0 and 38.8 across a broad pH range [26]. To the best of our knowledge, there is a limited number of studies that have investigated U\(^{VI}\) interactions with DFOB above pH 10, the region where U precipitation happens. For example, a recent study grafted DFOB onto microparticles and investigated the ability of the DFOB-modified microparticles to extract U\(^{VI}\) from wastewater through batch and column experiments [27]. The pH of the batch experiments varied between pH 2 to 12 and peak absorption of U\(^{VI}\) was observed at ca. pH 9 (97% absorption), decreasing to approximately 80% at pH 12. The authors attributed this to the formation of a tertiary U\(^{VI}\)-DFOB-microparticle surface complex, with the DFOB and a carbonyl group on the surface of the microparticle material contributing to the complex. Multi-dentate organic molecules produced from cellulose degradation (\(\alpha\)-isosaccharinic) and cement degradation (D-gluconate) inhibit also the precipitation of U\(^{IV}\) at pH 13.5 [28, 29] and U\(^{VI}\) at pH 12–13 [30–32]. However, these ligands contain the carboxylate functional group rather than the hydroxamate functional group found in DFOB.

The aim of this pilot study was to study whether DFOB, a siderophore typically found in the environment, prevents the U\(^{VI}\) precipitation in alkaline NaCl solutions observed during previous studies [13, 14, 33] and to determine the possible controls of concentration and reaction time. Three types of experiments were conducted: a control experiment, a precipitation inhibition experiment, and a dissolution experiment. Stirred batch experiments were performed with 0.1 M NaCl solutions at pH 11.5 containing 42 \(\mu\)M of U\(^{VI}\) and DFOB concentrations ranging between 10 and 420 \(\mu\)M, studying thus a concentration range typically present in the environment. Stirred batch reactor experiments were conducted for up to three days to test the short-term effect of DFOB on U\(^{VI}\) particle formation. To test the long-term effects of DFOB on U\(^{VI}\) precipitate formation and ligand promoted dissolution/disaggregation, solutions were placed in a shaking tray for 56 days. Two types of long-term tests were conducted, firstly the DFOB was added at the same time as U\(^{VI}\) to see if the siderophore could prevent U\(^{VI}\) from precipitating, and secondly U\(^{VI}\) was precipitated from solution before then adding DFOB to see if the siderophore could dissolve the U\(^{VI}\). Previous studies of our group demonstrated significant precipitations of U-Na minerals from these solutions [13, 14, 33]. Samples were filtered through 0.2, 0.45 and 1 \(\mu\)m Whatman nylon filter membranes to get a constrain on the particle size. The amount of U\(^{VI}\) removed was determined in the filtrates using ICP-MS.

**Experimental**

All chemicals were analytical-grade, and all solutions were prepared with 15 MΩ.cm de-ionized water (Merck Millipore). NaOH pellets (VWR) and distilled 6 M HCl were used to prepare 1 M NaOH and HCl solutions for pH adjustment. NaCl (VWR) was used to control ionic strength. A 4.2 mM (1000 mg/L) U PerkinElmer Pure Plus standard solution was used to prepare all U\(^{VI}\) solutions and Induced Coupled Plasma Mass Spectrometry (ICP-MS) standards. Desferrioxamine mesylate salt powder (≥92.5%) from Sigma-Aldrich was used as is.

Stirred batch reactor experiments were conducted at room temperature for up to three days to test the short-term effect of DFOB on U\(^{VI}\) particle formation. All batch experiments were repeated at least twice. The experiments were conducted in 250 mL amber bottles to prevent photo-oxidation of DFOB. Solutions with a volume of 250 mL containing 0.1 M NaCl and various DFOB concentrations (4.2, 42, 130 and 420 \(\mu\)M) were prepared. An approximately 180 mL solution containing the NaCl and DFOB was initially created and adjusted to pH 11.5 so that a 5 mL representative blank could be collected. The DFOB was added in a powder

![Fig. 1 The structure of DFOB (left image, fully deprotonated as DFOB3-), and its key reactive functional group, hydroxamate (right image). Reported pKa values including the amine are 10.89, 9.61, 9.05 and 8.51 at ion strength of 1 mol dm⁻³.](image-url)
form to prepare the 130 and 420 µM DFOB solutions. A 4.2 mM DFOB stock solution was prepared and diluted to produce the 4.2 and 42 µM DFOB solutions. The 4.2 mM DFOB stock solution was freshly prepared before each experiment to minimize ligand degradation. The DFOB was added and collected as part of the representative blank. 42 µM U^{VI} was then added to the solution by diluting the 4.2 mM U^{VI} standard solution. The pH was re-adjusted to 11.5 and volume increased to 195 mL. The pH was periodically measured and adjusted throughout the experiment with 1 M NaOH and 1 M HCl to maintain the pH at 11.5. The pH was measured on collection of a sample and was adjusted if the pH changed more than ±0.05 pH units of the target value. Approximately 5 mL samples were collected and filtered through Whatman nylon membranes (0.2, 0.45, and 0.8 or 1 µm pore diameter), diluted 10 times in 2% (v/v) nitric acid and analyzed using ICP-MS. During two of the three repeats of the 420 µM DFOB experiment, samples were only filtered with a 0.2 µm nylon filter membrane.

To test the long-term effects of DFOB on U^{VI} precipitate formation and ligand promoted dissolution/disaggregation, 250 mL solutions containing 42 µM U^{VI}, 130 µM DFOB

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**Fig. 2** The effect of DFOB concentration on U^{VI} precipitation up to 3 days. Parts a), b), c), d) and e) are the results from 0, 4.2, 42, 130, and 420 µM DFOB respectively. The first, second and third experiments are shown as blue, green and orange circles respectively. The darkest shade of colour represents the smallest filter (0.2 µm) while the lightest shade represents the biggest filter (1 µm). A comparison is provided in part f) where the blue circles, green bars, orange diamonds, red triangles and grey squares represent 0, 4.2, 42, 130 and 420 µM DFOB, respectively.
and 0.1 M NaCl adjusted to pH 11.5 were placed in a shaking tray for 56 days (T=25°C, 130 rpm). Three types of experiments were conducted: a control experiment; a precipitation inhibition experiment (see three-day batch experiments method); and a dissolution experiment. At the start of the dissolution experiment, 42 µM U\textsuperscript{VI} was precipitated for 48 h, and then 130 µM DFOB was added to solution. 5 mL samples were collected and filtered through 0.2, 0.45, and 1 µm Whatman nylon filter membranes, diluted 10 times in 2% (v/v) nitric acid and analyzed using ICP-MS.

Two-month batch experiments

A series of batch experiments were conducted to determine how long the U\textsuperscript{VI} -DFOB interactions were stable following a spike addition of DFOB. The batch experiments were conducted over a 56-day (two-month) period, at the end of which a new equilibrium appeared to have been reached. During these experiments 130 µM DFOB was added to the pH 11.5, 0.1 M NaCl solution before addition of U\textsuperscript{VI}. These 250 mL samples were placed on a shaker tray at 25 °C and 130 rpm, and 5 mL samples were filtered through 0.2, 0.45 and 1 µm filter membranes typically once a week.

Dissolution experiments were conducted where 250 mL solutions containing 42 µM U\textsuperscript{VI} and 0.1 M NaCl at pH 11.5 were placed on the shaker trays for 48 h to allow U\textsuperscript{VI} to precipitate from solution. After 48 h, 130 µM DFOB was added to the solution. Control experiments were conducted in the absence of 130 µM DFOB to determine whether U\textsuperscript{VI} precipitation remained stable over the two-month timeframe. The results are presented in Fig. 3.

The two control experiments show that up to 2% of U\textsuperscript{VI} passed through the filter members over the two-month period, indicating virtually all U\textsuperscript{VI} had precipitated from solution (Fig. 3a). This shows that in the absence of DFOB, the U\textsuperscript{VI} precipitate remains stable in solution, and should be highly immobile in porous media, as observed in our previous research [14].

During the inhibition experiments, approximately 6% of U\textsuperscript{VI} was removed by all filter membranes sizes in the first week, suggesting that precipitation formation was inhibited by 94% (Fig. 3b). This means DFOB could potentially enhance the mobility of U\textsuperscript{VI} in porous media such as quartz sand. However, as time progressed, the amount of U\textsuperscript{VI} removed by the filters increased. The change in U\textsuperscript{VI} concentration in the filtrate was greatest between day 14 and 35. On day 14, between 85 and 93% of U\textsuperscript{VI} passed through the filters while by day 35, between 40 and 45% passed through the filter membranes. After day 49, equilibrium appeared to have been reached and between 28 and 34% U\textsuperscript{VI} passed through the filter membranes.

One possible mechanism responsible for increased U\textsuperscript{VI} precipitation is the degradation of DFOB [35] as has been observed for other organics such as cellulose [36]. The U\textsuperscript{VI} remaining in solution once ligand degradation had stabilized could be the result of U\textsuperscript{VI} complexes forming with the degradation products of the siderophore. Desferrioxamine B was observed to degrade to mono-hydroxamates with mass to charge (m/z) ratios of 219 and 161 in the presence of Mesorhizobium loti [37]. From our preliminary investigations it is unclear whether 100% of the DFOB degrades or whether some DFOB remains intact in solution.
The dissolution experiments indicate that 130 μM DFOB solubilized approximately 20% of the U⁶⁺ precipitates (Fig. 3c). This was stable for approximately five weeks before the particles started to reaggregate or re-precipitate. Only 12% of U⁶⁺ remained in solution after two months. This demonstrates that DFOB dissolves U⁶⁺ after it has precipitated. The reaggregation or re-precipitation may be due to the degradation of DFOB as discussed for the long-term inhibition experiments.

Note that the increased U⁶⁺ precipitation observed over the longer timescales may not be relevant in natural environments as new DFOB will likely be continually produced by plants or bacteria which may then continuously interact with U⁶⁺ preventing it from precipitating and/or enhancing dissolution of U⁶⁺ mineral phases.

**Formation of U⁶⁺ complexes with DFOB the likely mechanism preventing precipitation**

The experiments show that DFOB significantly reduces the amount of U⁶⁺ precipitation at pH 11.5. The likely mechanism responsible for these observations is the formation of U⁶⁺-DFOB complexes, as has been experimentally observed to form between pH 4 and 10 [24]. Multidentate ligands such as α-isosaccharinic and D-gluconate complex with U⁶⁺ at pH 12–13 [29–32], therefore it is possible for U⁶⁺ to complex with negatively charged multidentate organic ligands at such a high pH. A key challenge with characterizing stability constants at high pH and ionic strengths is the alkaline errors in glass electrodes, and the formation of U⁶⁺ precipitates hindering their experimental determination [31, 38]. Further studies using a combined experimental (e.g., EXAFS, UV/VIS spectrometry) and computational (e.g., Density Functional Theory) approach are warranted.

**Conclusions**

The aim of this pilot study was to test the hypothesis that DFOB in alkaline and saline solutions inhibit U⁶⁺ precipitation and to constrain possible controls of ligand concentration and reaction time. Developing a qualitative and quantitative understanding of this geochemical process is of great importance because DFOB ligands as well as other siderophores occur naturally in the environment and potentially mobilize U⁶⁺ from a wide range of sources such as mine tailings, contaminated land and radioactive waste storage and disposal facilities. The results from a series of batch experiments show that DFOB can prevent almost 100% U⁶⁺ precipitation as ≥0.2 μm precipitates for two weeks and dissolve up to 20% U⁶⁺ between two and five weeks, when 130 μM DFOB is initially present. We have previously observed that U⁶⁺ is highly mobile in porous media when U⁶⁺ is not present as ≥0.2 μm precipitates. As U⁶⁺ precipitation is prevented by addition of DFOB, and U⁶⁺ dissolution is enhanced, DFOB could have a significant impact on the mobility of U⁶⁺ in soil environments where siderophore concentrations can reach 1 mM. Further research is now required to determine the effects of different mineralogy, organic matter, and competitive cations on U⁶⁺ mobility in the presence of DFOB. The formation of a U⁶⁺-DFOB siderophore complex is a likely mechanism based on previous experimental and theoretical work, and can be explored in the future through a variety of experimental and modelling techniques including UV/Vis spectrometry, EXAFS and DFT.

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