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Impact of chloride on uranium(VI) speciation in acidic sulfate ion exchange systems: Towards seawater-tolerant mineral processing circuits

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ABSTRACT

Using X-ray absorption spectroscopy, we have identified the mechanism by which chloride impacts the extraction of U(VI) by a weak base anion exchange resin from acidic sulfate solutions. The amount of chloride present affects U(VI) speciation both in the feed solutions and adsorbed by the resin, and we find three distinct U(VI) species taken up by the resin across the salinity gradient, directly corresponding to changes in levels of U(VI) extraction. These findings are integral to the effective design of mineral processing circuits incorporating seawater—a cheaper and more sustainable water source than fresh water.

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Introduction

Uranium represents the major fuel source for nuclear energy. In 2014, nuclear power generated 2410.4 TWh of electricity worldwide, 11.1% of the total global electricity production [1]. The International Atomic Energy Agency estimates this figure will rise to between 2992 and 7771 TWh by 2050 [1]. To accommodate this increased demand for processed uranium, there is continuing need to develop more efficient and cost effective strategies to separate uranium from aqueous streams, both uranium mineral processing streams, and radioactive wastewater streams. Key to effective separation and extraction strategies is a thorough understanding of the uranium speciation before, during and after separation.

The processing of uranium ores with sulfuric acid provides a number of reasons to extend our understanding of uranium speciation in acidic sulfate systems to those in which chloride is also present. There are geochemical drivers: For example, the

mobility of uranium in subsurface environments can be heavily dependent on the pH and activity of ligands present in wastewaters (i.e. tailings ponds and mine drainage sites), which are often highly acidic, with high sulfate concentrations [2,3]. Where the surrounding waters are naturally saline, such as borewaters, or seawater, the speciation of uranium may deviate from the typical uranyl sulfate complexes expected, and current thermodynamic data may not be able to predict uranium mobility [4]. There are also industrial drivers: The provision of freshwater for uranium processing circuits is not straight forward, especially in arid areas such as the interior of South Australia, where the world's largest uranium deposit is located [5,6]. There is significant potential for the uranium mining industry to reduce processing costs, and transition to more sustainable water sources, by modifying their processing circuits to accommodate saline process water such as borewater or seawater.

Salinity, however, is known to have a deleterious impact on conventional hydrometallurgical processes used for uranium separation and extraction [7,8]. Chloride concentrations of less than 0.1 M in the feed liquor streams have been shown to reduce uranium extraction by up to 20% [7,9]. Anion exchange resins are routinely used in the uranium processing industry, especially for feed liquor streams containing low uranium concentrations. Weak

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base anion exchange resins in particular, containing tertiary or secondary amine functional groups, show good selectivity for uranium over impurities, a lower susceptibility to the impact of chloride [10] and have been proposed for use in the extraction of uranium from sulfuric acid liquor streams with elevated chloride concentrations [10,11]. However, a survey of the literature indicates that the chemical mechanisms underpinning the reduced uranium extraction in the presence of chloride has not been extensively studied. In particular, it is not clear to what extent the reduced uranium uptake is due to competition with the chloride anion for surface sites on the resin, or the influence of chloride on uranium speciation. Further, the relationship between the aqueous U speciation, and the speciation of U on the resin surface, is not understood. This is crucial for determining the mechanism by which chloride impacts ion exchange circuits. Until the underpinning chemistry is understood, it will be difficult to determine how best to adapt current circuits, or design improved circuits, to tolerate saline water.

To the authors' knowledge, there are no studies concerning the speciation of U(VI) in mixed sulfate-chloride media. However, there have been a number of studies concerning the aqueous speciation of U(VI) in chloride and sulfate media separately. In acidic sulfate solutions, there is no consensus over the speciation of U(VI). Some authors have reported that the major species of U(VI) is the $\text{UO}_2(\text{SO}_4)_3^{4-}$ anion [12–14], whereas others, using spectroscopy and density function theory (DFT), have reported that the major species is the neutral ion $\text{UO}_2(\text{H}_2\text{O})_3(\text{SO}_4)$ and the anion $\text{UO}_2(\text{H}_2\text{O})(\text{SO}_4)_2^{2-}$ [15–17] and indeed, that in solution, 5-fold coordination in the UO_2^{2+} equatorial plane is much more likely than 6-fold coordination [17]. Whether the sulfate is coordinated monodentately or bidentately (and thus the number of aquo ligands in the equatorial plane) seems to depend on the ratio between sulfate and uranyl, with a high $[\text{SO}_4^{2-}]/[\text{UO}_2^{2+}]$ ratio i.e. 5–600 favouring bidentate complexation [16,18,19] and a low ratio (i.e. <3) favouring monodentate complexation [16,20,21]. In acidic chloride media, where $0 < [\text{Cl}^-] < 3 \text{ M}$, the U(VI) speciation has been shown using X-ray absorption spectroscopy (XAS) to be dominated by the $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ cation with a contribution from $\text{UO}_2(\text{H}_2\text{O})_4\text{Cl}^+$ cation [22,23].

To the authors' knowledge, there has only been one spectroscopic study concerning U(VI) uptake by an anion exchange resin, and this was from chloride media (10 M $[\text{Cl}^-]$). Using X-ray absorption spectroscopy (XAS), Allen et al. showed that the speciation of U(VI) on the surface of a strong base resin was $[\text{UO}_2\text{Cl}_4]^{2-}$, which differed from that identified in the feed solution $[\text{UO}_2(\text{H}_2\text{O})\text{Cl}_4]^{2-}$ [22].

Synchrotron-based XAS is a powerful tool that probes the average local coordination geometry of an element of interest within a sample, and as such can help identify the uranium speciation in both the feed liquor and on the resin surface. This study aims to provide a spectroscopic insight into the mechanisms by which chloride affects U(VI) speciation in sulfate-based acidic liquor streams under saline conditions, and subsequent uptake by ion exchange resins. Batch adsorption experiments will be used to quantify U(VI) extraction as a function of chloride concentration, and X-ray absorption spectroscopy will provide the identity of the U(VI) species in solution and taken up by the resin.

Experimental

Resin preparation

Batch experiments

Dowex Monosphere 77 is a macroporous tertiary amine anion exchange resin with a polystyrene divinyl benzene (PS-DVB) matrix. Its properties are described in Table 1, and its functionality

Table 1

Manufacturer specifications of weak base anion exchange resin Dowex Monosphere 77.

Parameter	Value	
Total exchange capacity	1.7	1.57 ^b
Weak base capacity	1.5	1.32 ^b
Commercial equivalent	Purolite, Lewatit	
Particle size	475–600 μm^a	
Functionality	Tertiary amine	
Form	Free base	
Moisture	40–50%	

^a Volume median diameter.

^b Experimentally determined via Harland method [24].

represented in Fig. S1. The presence of both weak base and strong base functionality was determined experimentally via the Harland method [24]. Resins were pre-treated with 20 bed volumes of 1 M H_2SO_4 in a column at 5 BV h^{-1} to convert to the sulfate form. Resins were then stored in an airtight container in 18.2 M Ω deionised water and adjusted to pH 1.6 with concentrated H_2SO_4 .

Synchrotron samples

In order to make the resin suitable for presentation to the synchrotron beam (and avoid artefacts associated with the packing of small spheres), conditioned resin (sulfate form) was dried at 40 °C in an oven for 24 h. It was then ground with a pestle and mortar into a fine powder.

Batch extractions from sulfate media

Batch experiments

AR grade reagents and 18.2 M Ω deionised water were used throughout the experiments. The simulant feed (pH 1.6) was prepared at $[\text{SO}_4^{2-}] = 0.25 \text{ M}$ (using H_2SO_4), $[\text{UO}_2^{2+}] = 0.004 \text{ M}$ (using a sulfate-based UO_2^{2+} stock solution of 100 g/L U) and at varying Cl^- concentrations (using NaCl). Small volumes of the feed solutions were retained for synchrotron analysis. All batch extractions were carried out as single contacts with the contact of 2 mL of resin with 50 mL of aqueous simulant feed, as a function of chloride concentration. The resin and aqueous feed were allowed to equilibrate for a period of 24 h at room temperature (21 °C) on an orbital shaker.

Synchrotron samples

Dry resin powder (0.1 g, approximately 0.1 mL) was contacted with 2.5 mL of feed solution in a 10 mL vial and allowed to equilibrate for a period of 24 h at room temperature (21 °C) on an orbital shaker. At 100% adsorption this equated to a resin sample containing 2.5 wt.% uranium, which is sufficient for EXAFS data acquisition. After 24 h, the sample was centrifuged at 3000 g for 10 min. The supernatant was decanted and retained for analysis, and the resin (a wet paste) was loaded directly into XAS sample holders and sealed with Kapton tape.

Distribution behaviour

The extraction percentage was determined by difference (using Eq. (1)) and the concentrations of the individual metal ions determined by either ICP-MS (U) or ICP-OES (S, Cl).

$$E_{\%} = (C_i - C_{aq})/C_i \times 100 \quad (1)$$

Where C_i is the initial metal concentration before contact and C_{aq} is the concentration of the metal ion in the aqueous phase after contact with the resin. pH measurements for solutions were determined using a silver/silver chloride reference electrode calibrated to from pH 1 to 10 using buffers. At higher acid concentrations $[\text{H}^+]$ were determined by titration and verified by

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