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The Effect of Contaminants on the Application of Polyamine Functionalised Ion Exchange Resins for Uranium Extraction from Sulfate Based Mining Process Waters

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Abstract

Three in-house produced polyamine functionalised ion exchange resins and Purolite S985 (a commercial ion exchange resin) have been assessed for their ability to extract UO_2^{2+} from a variety of aqueous matrices applicable to current and potential future uranium mining processes. The uptake of common contaminant species in uranium processing liquors at variable acid concentrations has been assessed, with Al^{3+} and MoO_4^{2-} showing the most extraction, with AsO_4^{3-}, Eu^{3+} and Fe^{3+} showing extractions > 10% at low $[H^+]$. Extraction of MoO_4^{2-}, AsO_4^{3-}, Eu^{3+} and Fe^{3+} was seen to decrease with increasing $[H^+]$. The impact of increasing $[Cl^-]$ on UO_2^{2+} and Fe^{3+} extraction has been determined. Fe^{3+} showed low extractions by all resins, with no dependence on $[Cl^-]$. In contrast, increasing suppression of UO_2^{2+} uptake was seen with increasing $[Cl^-]$ up to 80 g L^{-1}, with extraction remaining constant beyond this $[Cl^-]$. At high $[Cl^-]$ (> 50 g L^{-1}) Purolite S985 was seen to remove UO_2^{2+} from solution

more effectively than all synthesised polyamine resins. The presence of Fe^{3+} in solution was seen to suppress UO_2^{2+} uptake by around 10% when $[Fe]^{3+}/[UO_2]^{2+}$ increased from 0 to 2. Fe^{3+} extraction by all studied resins was promoted by the presence of UO_2^{2+} in solution. This was most prevalent with Purolite S985, with an extraction of 30% for $[Fe]^{3+}/[UO_2]^{2+}$ = 2 by Purolite S985. All resins were tested using a process water from a uranium mine and have shown an ability to selectively extract UO_2^{2+} from such solutions, with the best synthetic resin recovering 15.7% more uranium than Purolite S985.

Introduction

In recent years there has been a resurgence in interest in nuclear power. The relative stagnation in the building of new nuclear power plants throughout the 1980s and 1990s has ended, with environmental pressures such as air pollution and climate change associated with the burning of fossil fuels, the need for energy security, and population growth being major drivers behind this. However, the increased activity within the nuclear new build sector will put pressure on the supply of uranium from the mining industry.

Uranium containing minerals come in a variety of different forms, with their various constituents guiding the design of the process for uranium extraction (Table 1).[1] These minerals themselves can consist of numerous metallic species in various ionic forms. In addition, the uranium containing mineral itself is usually a minor constituent of the mined material when compared to host rock mineralogy, which often contains multiple valuable minerals that do not necessarily contain uranium. Examples include the Olympic Dam mine in South Australia which is primarily a copper mine, with uranium, gold and silver being recovered as secondary products, and the Talvivaara mine in Finland, which is a nickel-zinc-copper-cobalt mine with plans to extract uranium as a by-product.[2–4] The host rock constituents, other than uranium containing minerals, must be considered when designing the uranium extraction process, as elements contained within them can find their way into the process and cause unexpected and/or deleterious effects. The final uranium product from the process needs to be of a certain purity, so the use of extraction techniques that are

selective for the removal of uranium over a wide range of potential contaminant species is a priority.
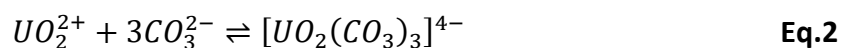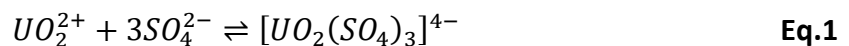
Table 1. A selection of uranium containing minerals.[1]

Mineral	Composition
Pitchblende	UO_2
Carnotite	$K_2(UO_2)_2(VO_4)_2.3H_2O$
Subagalite	$HAl(UO_2)_4(PO_4)_4.16H_2O$
Brannerite	$(U,Ca,Fe,Th,Y)(Ti,Fe)_2O_6$
Zeunerite	$Cu(UO_2)_2(AsO_4)_2.10\text{-}12H_2O$

The isolation of uranium from its ore, performed at mining facilities, is a water intensive process, with volumes of up to 216 million litres of fresh water potentially being needed at a single mine every day.[5] Uranium mines are often in arid locations, such as those in Australia, Namibia, Uzbekistan and Kazakhstan. In some instances, tensions can arise between local people and miners due to the limited amount of this precious resource available, and environmental contamination concerns.[6–8] Even in major uranium producing countries with access to plentiful fresh water supplies such as Canada and the U.S.A there are strict requirements for the purification of water prior to its release back into the environment, which can be a costly process. A move to the use of lower quality waters (particularly those of a high salinity, $[Cl]^- > 5$ g L^{-1}) is therefore being considered for uranium extraction circuits, due to competing demands on the use of fresh water.[9–19] In order to transfer to the use of such low quality waters while still maintaining the quality of the final uranium product and minimising process costs, a thorough understanding of uranium separation behaviour under such conditions during the milling process must be gained, potentially leading to the development of novel separation technologies .

After uranium ore is removed from the ground, the uranium itself is separated from the rest of the ore via a milling process. This procedure begins with the crushing of the ore to produce smaller particles with a large surface area, followed by the dissolution of uranium in which a substantial proportion of the original ore is also solubilised. The lixiviant for this process is almost always either a sulfuric acid or carbonate solution, the choice of which is

dependent upon the mineral geology. For example, orebodies containing high levels of carbonate would not be suitable for acidic leach, as acid consumptions would be considerable. If uranium is mineralised as U(VI) (UO_2^{2+}) then it is readily soluble, however, if it is present as U(IV) then an oxidant must be added to produce U(VI) to allow for dissolution. Ideally the only solubilised species from this process would be UO_2^{2+}, but that is rarely the case. Process waters produced throughout the mining flowsheet contain many other aqueous species which originate in the mined rock, including metal containing cations and anions.

After the leaching step, the remaining liquor, known as pregnant leach liquor (PLL), goes for further processing where the uranium is extracted from it, allowing the isolation of a pure uranyl containing aqueous solution. This extraction step needs to be selective for uranium over other elements present in the PLL, with the staple techniques employed being ion exchange (IX) and solvent extraction (SX), though solvent extraction is not suitable for carbonate based PLLs.[1] In addition, SX has several general drawbacks when compared with IX, including; the use of large volumes of flammable and toxic organic solvents, third phase formation, slow phase disengagement in multiple contact steps and the need for an organic soluble extractant.[9,10,20] In uranium milling circuits, IX separation processes have historically employed strong base anion (SBA) exchange resins due to their ability to extract anionic uranyl species from solution formed by the complexation of common oxoanions to the uranyl cation (Eq.1,2). These SBA resins have been seen to undergo dramatic uranyl uptake suppression in the presence of chloride, due to the competition between U-sulfate species and chloride anions for binding sites on the resin.[10,12] Additionally, the presence of Fe^{3+} in processing liquors acts to supress uranyl uptake on SBA resins.[21,22]

$$UO_2^{2+} + 3SO_4^{2-} \rightleftharpoons [UO_2(SO_4)_3]^{4-} \qquad \textbf{Eq.1}$$

$$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_3]^{4-} \qquad \textbf{Eq.2}$$

The ineffectiveness of SBA resins for uranium extraction from liquors containing high levels of chloride and iron has prompted investigations into resins with other functionalities, such as chelating ion exchange resins and weak base anion (WBA) exchange resins.[9–11,19,23] Chelating resins commonly contain functional groups such as iminodiacetic acid, aminophosphonic acid, amidoxime, and mixed sulfonic/phosphonic acid, whereas WBA resins
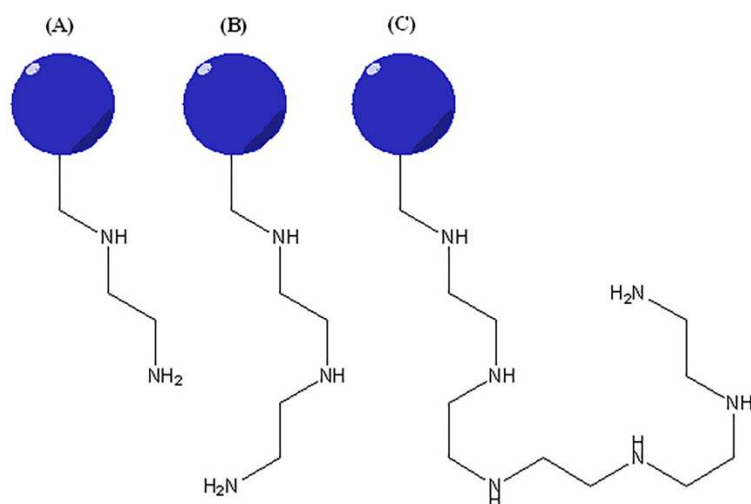
typically contain pyridyl, amine and amide functionalities.[21] Chelating resins can have high affinities for UO_2^{2+} in hypersaline conditions ($[Cl^-] > 22.6$ g L^{-1}, 0.64 M), however, they can also have very high affinities for Fe^{3+} so selectivity can be a concern.[24] At such high affinities, it may also be very difficult to elute the UO_2^{2+} from the resin in order to allow the uranium to be available for use. WBA resins were initially introduced to uranium processing circuits in the late 1960s, and have been shown to effectively extract UO_2^{2+} from aqueous sulfate conditions, though they have not seen major implementation in uranium milling processes.[9–11,19,21,25] Unlike SBA resins which can be applied both in acidic and alkaline conditions, WBA resins are unable to extract UO_2^{2+} from alkaline (carbonate) media. However, recent work in our group has shown that WBA resins are able to extract UO_2^{2+} from aqueous sulfuric acid media with comparable loading capacities to SBA resins.[19] It has also been reported that certain WBA resins are selective for UO_2^{2+} over Fe^{3+} and show a strong tolerance to dissolved chloride.[1,9–11,21,23,25–27]

This work details the use of a selection of WBA resins for uranyl extraction from sulfate based aqueous media relevant to current, and potential future, uranium extraction processes. The selected WBA resins are the commercially available Purolite S985 (Figure 1) and three previously reported polyamine functionalised ion exchange resins synthesised in house (Figure 2).[19,23,28] The uptake of common contaminant metal ions found in ore and gangue minerals has been assessed, as well as the effect of increasing concentrations of chloride and iron on uranyl extraction.

Figure 1. Functional group on Purolite S985.[29]

Figure 2. Structure of the functional groups on the synthesised resins Ps-EDA (A), Ps-DETA (B) and Ps-PEHA (C).

Experimental

Reagents and Stock Solutions

Metal salts used in uptake experiments were purchased from either Sigma Aldrich or Alfa-Aesar and used as received. Uranium used in uptake experiments was provided as solid $UO_2(NO_3)_2 \cdot 6H_2O$ by the Centre for Radiochemical Research at the University of Manchester, which was converted to a uranyl sulfate solution using a previously reported method.[28] Uranyl sulfate solutions used for EXAFS experiments were provided by the University of Sheffield. Ion exchange resin Purolite S985 was provided by Purolite. All resins were preconditioned prior to contacting with experimental solutions by contacting with 10 bed volumes of H_2SO_4 (1 M) for 24 hours followed by washing with 3 bed volumes of deionised water (18 MΩ).

Resin Synthesis

In house resins were synthesised by heating to reflux a mixture the Merrifield resin and the relevant polyamine (ethylenediamine, diethylenetriamine, pentaethylenehexamine) in 1,4-dioxane as described previously.[19] This resulted in Ps-EDA, Ps-DETA and Ps-PEHA respectively.

Contaminant Species Uptake

Sulfate salts of cationic species or sodium salts of anionic species of interest (Table 3) were dissolved in deionised water (18 MΩ) to provide a stock solution, where the concentration of each species of interest was 0.1 mM, for contaminant metal uptake studies.

Stock solution [H^+] was adjusted using aliquots of H_2SO_4 (0.01 – 2 M) solution and determined either by using a silver/silver chloride reference electrode calibrated from pH 1 – 13 using buffers (where [H^+] < 0.1 M), or were determined by titration with standardised NaOH (where [H^+] > 0.1 M). An aliquot of stock solution (50 mL) was contacted with 5 mL of wet settled resin (5 mL_{WSR}) for each resin tested and agitated on an orbital shaker at room temperature for 24 hours. Samples of the solution were taken after contacting and analysed in triplicate using inductively coupled plasma – atomic absorption spectroscopy (ICP-AES). Errors were calculated as standard errors at 95% confidence intervals from the triplicate analyses.

Table 2. Solution composition for contaminant species uptake experiments

Species	Compound	Concentration / mM	Species concentration / mg L^{-1}
K^+	K_2SO_4	0.1	3.91
Ca^{2+}	$CaSO_4$	0.1	4.01
Cu^{2+}	$CuSO_4$	0.1	6.35
Co^{2+}	$CoSO_4$	0.1	5.89
Mg^{2+}	$MgSO_4$	0.1	2.43
Mn^{2+}	$MnSO_4$	0.1	5.49
Ni^{2+}	$NiSO_4$	0.1	5.87
VO^{2+}	$VOSO_4$	0.1	5.09
Zn^{2+}	$ZnSO_4$	0.1	6.54
Al^{3+}	$Al_2(SO_4)_3$	0.1	2.70
Eu^{3+}	$Eu_2(SO_4)_3$	0.1	15.20
Fe^{3+}	$Fe_2(SO_4)_3$	0.1	5.58
MoO_4^{2-}	Na_2MoO_4	0.1	15.59
AsO_4^{2-}	$NaHAsO_4$	0.1	13.89

Effect of Cl^- on UO_2^{2+} and Fe^{3+} Loading

A series of chloride (as NaCl) containing test solutions at pH 2 (adjusted with H_2SO_4) with either uranyl sulfate (1 g L^{-1} U) or iron sulfate (1 g L^{-1} Fe^{3+}) present were prepared. Chloride concentrations were varied from 0 – 150 g L^{-1}. An aliquot of test solution (50 mL) was

contacted with each resin (2 mL) and agitated on an orbital shaker at room temperature for 24 hours. Aliquots of the solution were sampled after contacting and the UO_2^{2+} concentrations were determined by a previously reported UV/Vis spectroscopy method.[30] The method used to determine Fe^{3+} content is detailed in the next section.

Determination of Fe^{3+} by UV/Vis Spectroscopy

An aliquot of Fe^{3+} containing solution (0.1 mL) from uptake experiments   was added to ammonium thiocyanate solution (2 M, 5 mL) and diluted to 25 mL with deionised water. The resulting mixtures were then analysed for absorbance at 480 nm and compared to a calibration curve to determine the Fe concentration. Fe^{3+} solutions used to produce the calibration curve were standardised using ICP-AES.

Effect of Fe^{3+} on UO_2^{2+} Extraction

Mixed uranyl-iron sulfate solutions were made up with a constant uranium (as uranyl) concentration of 1 g L^{-1} and varying Fe^{3+} content ($[Fe^{3+}]/[UO_2^{2+}]$ ranged between 0 and 2). These solutions (50 mL) were contacted with 2 mL_{WSR} and agitated on an orbital shaker for 24 hours at room temperature. Samples of the solutions post-contact were analysed for UO_2^{2+} and Fe^{3+} concentrations by ICP-AES.

Extraction of UO_2^{2+} from Uranium Mine Process (UMP) Water

UMP (pH 4.5) was provided by ANSTO Minerals and analysed for constituents using ICP-MS (Perkin Elmer Elan 9000) (Table 3). 2 mL_{wsr} was contacted with 50 mL of UMP solution and agitated for 24 hours on an orbital shaker at room temperature. Samples of the solution were taken after contacting and analysed using ICP-MS.

Instrumentation

Concentrations of metal species in aqueous solutions were determined either by ICP-AES using a Perkin Elmer Optima 5300 dual view spectrometer, ICP-MS using a Perking Elmer Elan 9000 spectrometer or by UV/visible spectroscopy with an Avantes AvaSpec fibre optic spectrometer. The amount of each species on the solid resin was determined by difference between the aqueous phase content of each species pre- and post-contact. No evidence of

precipitation nor significant uptake/release of species of interest by the containment vessels used in these studies was observed.

*Table 3. Constituents of a process water from a uranium mine in Australia*

Species	Concentration / mg L^{-1}
K$^+$	128
Na$^+$	107
Ca^{2+}	495
Mg^{2+}	5677
Mn^{2+}	2110
UO$_2{}^{2+}$	25
Al^{3+}	291
Fe^{3+}	< 1
SO$_4{}^{2-}$	12462
PO$_4{}^{3-}$	6
SiO$_4{}^{4-}$	31

Results

Contaminant Species Uptake

Aqueous solutions containing contaminant species (Table 2) were contacted with resins in a batch system where the acid concentration was varied between 0.01 and 3 M. Extraction percentages of all tested species can be found in Supp. Info. (Tables A.1, 2, 3, 4). Figure 3 shows the extraction of $AsO_4{}^{3-}$, $MoO_4{}^{2}$, Al^{3+} and Eu^{3+} by the studied resins. These species exceeded 10% extraction using the explored resins within the range of acid concentrations investigated. The general trend in the extraction of all species was seen as a decrease with increasing [H$^+$] for all resins, with significant recovery only being seen below

$[H^+] = 0.5$ M. MoO_4^{2-} and Al^{3+} were extracted most effectively by all resins, with AsO_4^{3-} showing better extraction than Eu^{3+} on the synthetic resins. There is a clear trend in the in-house synthesised polyamine resins, where the longer the polyamine chain length, the better the extraction of MoO_4^{2-} and Al^{3+}. Purolite S985 has an extraction ability towards these species between that of Ps-DETA and Ps-PEHA. All resins showed a decrease in Al^{3+} extraction between $[H^+]$ of 1 and 3 M apart from Ps-PEHA, which remained constant.
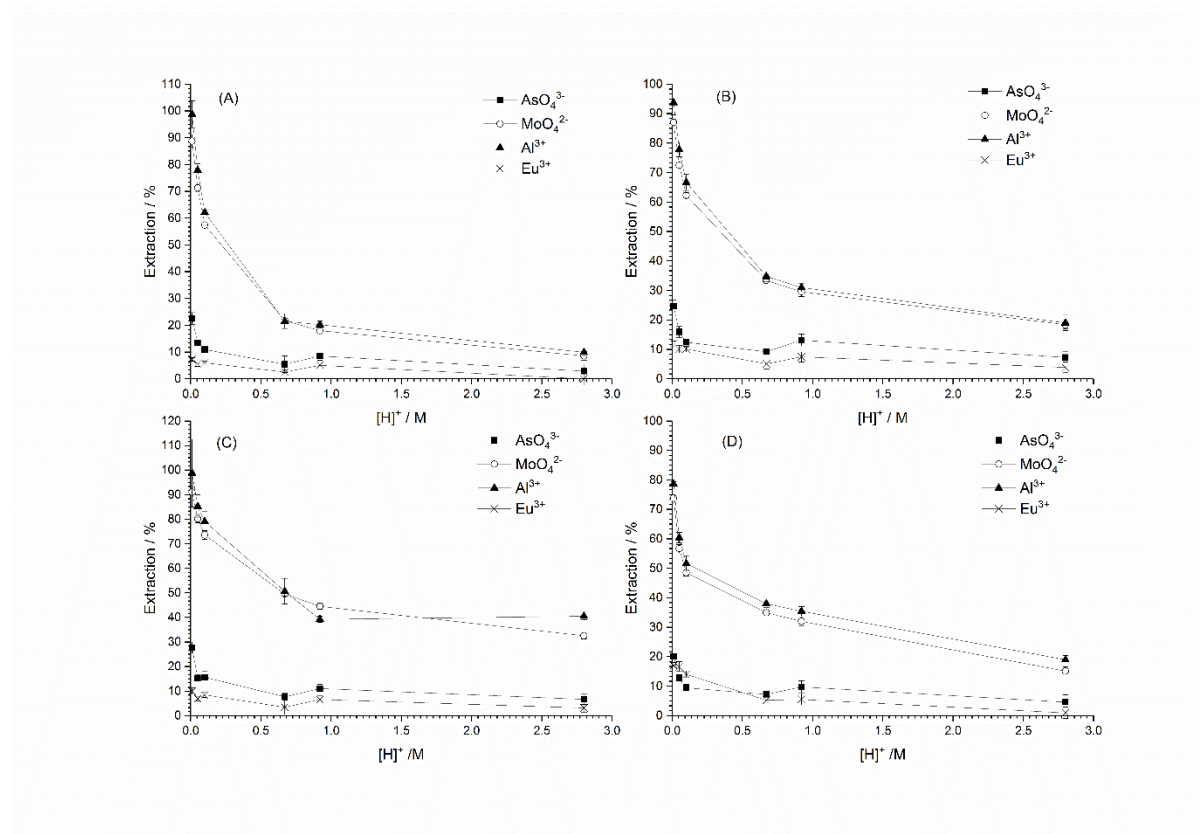
Figure 3. Extraction of $[AsO_4]^{3-}$, $[MoO_4]^{2-}$, $[Al]^{3+}$ and $[Eu]^{3+}$ from sulfuric acid media by IX resins Ps-EDA (A), Ps-DETA (B), Ps-PEHA (C) and Purolite S985 (D).

Effect of Cl⁻ on UO_2^{2+} and Fe^{3+} Loading

Single component solutions of UO_2^{2+} and Fe^{3+} were loaded by each of the studied resins separately and the collected extraction data are presented in Figures 4 and 5. The batch-wise uptake of uranium by all resins is dramatically reduced with increasing $[Cl^-]$. Above 75 g L^{-1} chloride the extraction efficiency of the resins towards uranyl appears to plateau and no further suppression of uranyl extraction observed, with Ps-EDA, Ps-DETA, Ps-PEHA and S985 showing average uranium recoveries of 14, 20, 21 and 29%, respectively. At $[Cl^-]$ above 20 g L^{-1} the commercial resin, Purolite S985, outperforms the synthesised polyamine resins, with the synthesised resins showing a trend where longer linear polyamine chains are able to

more effectively extract UO_2^{2+}, which is successfully maintained across all chloride concentrations. Below [Cl⁻] of 10 g L⁻¹, the Ps-PEHA resin outperforms Purolite S985, however, for [Cl⁻] between 10 and 20 g L⁻¹ uranium recoveries are within error for these two resins. Ps-EDA is still seen to be less effective than the other resins tested over the [Cl⁻] range studied.
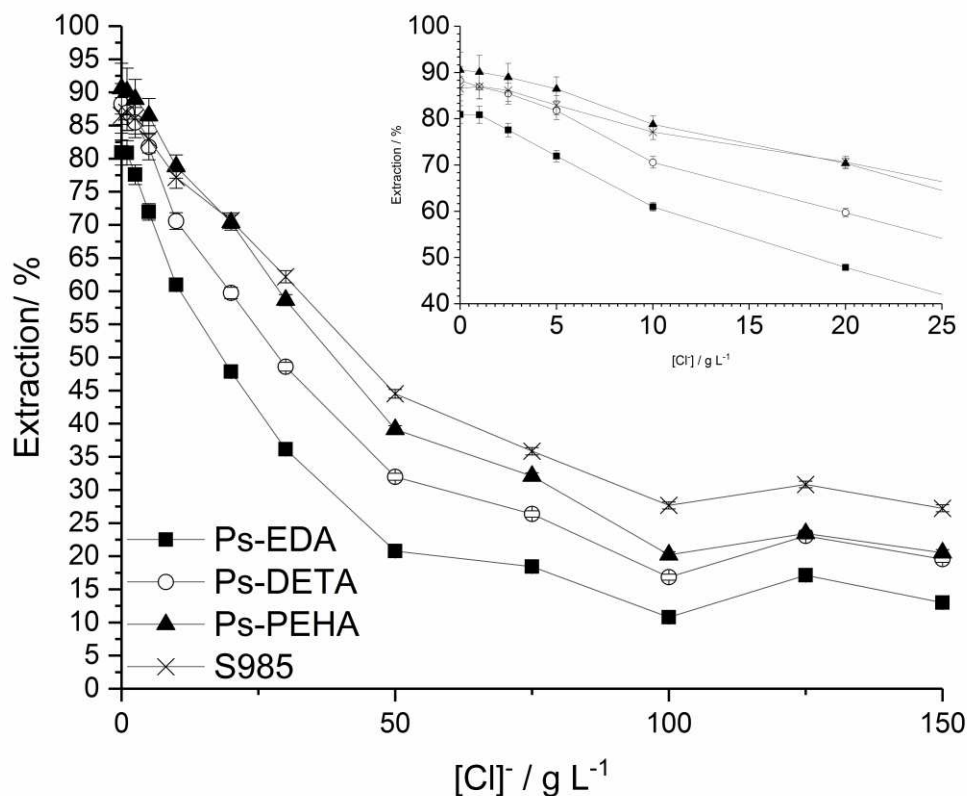
Figure 4. Extraction of UO_2^{2+} by ion exchange resins Ps-EDA, Ps-DETA, Ps-PEHA and Purolite S985 with increasing levels of Cl⁻ (as NaCl).

Fe³⁺ is not seen to be extracted effectively by any of the in-house synthesised resins, independent of [Cl⁻], with maximum extractions being below 15%. At low [Cl⁻] (< 20 g L⁻¹) Purolite S985 is seen to have a higher affinity for Fe³⁺ than any of the synthetic polyamine resins, showing a maximum iron recovery of 22% in the absence of chloride and reducing to a maximum of 8% when [Cl⁻] exceed 5 g L⁻¹. Above this concentration, no obvious trend can be identified. The formation of $FeCl_4^-$ species at high [Cl⁻] does not promote the extraction of iron by any of the tested resins, which has been observed for both ion exchange and for a solvent extraction system functioning via an ion exchange mechanism.[31]
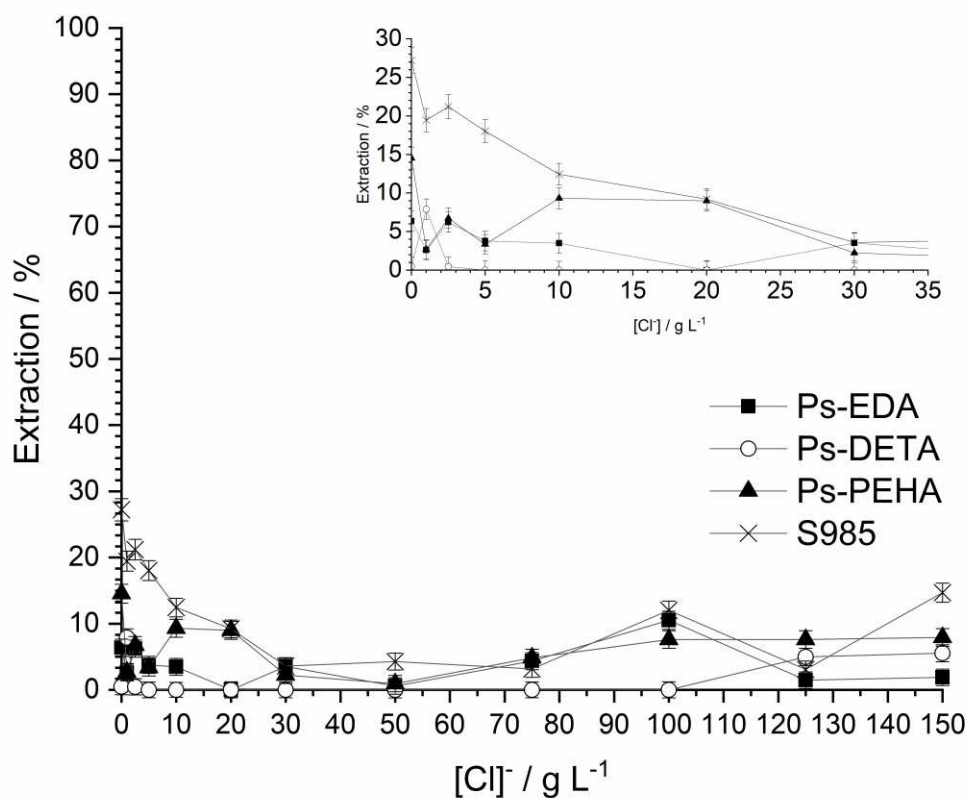
Figure 5. Extraction of Fe^{3+} by ion exchange resins Ps-EDA, Ps-DETA, Ps-PEHA and Purolite S985 with increasing levels of Cl^- (as NaCl).

Effect of Fe^{3+} on UO_2^{2+} Extraction

Mixed UO_2^{2+}/Fe^{3+} solutions at pH 2 (adjusted with H_2SO_4) were contacted with all the explored resins to assess the effect the presence of Fe^{3+} has on the uptake of UO_2^{2+}. The extent of UO_2^{2+} extraction at low [Fe^{3+}] is similar to that at low [Cl^-], however, as [Fe^{3+}]/[UO_2^{2+}] increases, uptake of UO_2^{2+} is seen to be supressed compared to the single component uranium solutions (Figure 6). Conversely, as [Fe^{3+}]/[UO_2^{2+}] increases, Fe^{3+} extraction also increases (Figure 7). This is most prominent for Purolite S985, where Fe^{3+} extraction reaches 30% for [Fe^{3+}]/[UO_2^{2+}] values around 2. Under equivalent conditions, the extraction of Fe^{3+} from single component solutions show maxima of 22% and 8% for S985 and the in-house synthesised resins, respectively. At low [Fe^{3+}] it can be seen that UO_2^{2+} is extracted selectively compared to Fe^{3+}, as Fe^{3+} extraction percentages are lower than those seen when extracting from solutions only containing Fe^{3+}. It can therefore be inferred that as [Fe^{3+}]/[UO_2^{2+}]

increases, UO_2^{2+} actually promotes Fe^{3+} extraction. There does not appear to be an obvious trend in effectiveness of Fe^{3+} extraction between the synthetic polyamine resins.

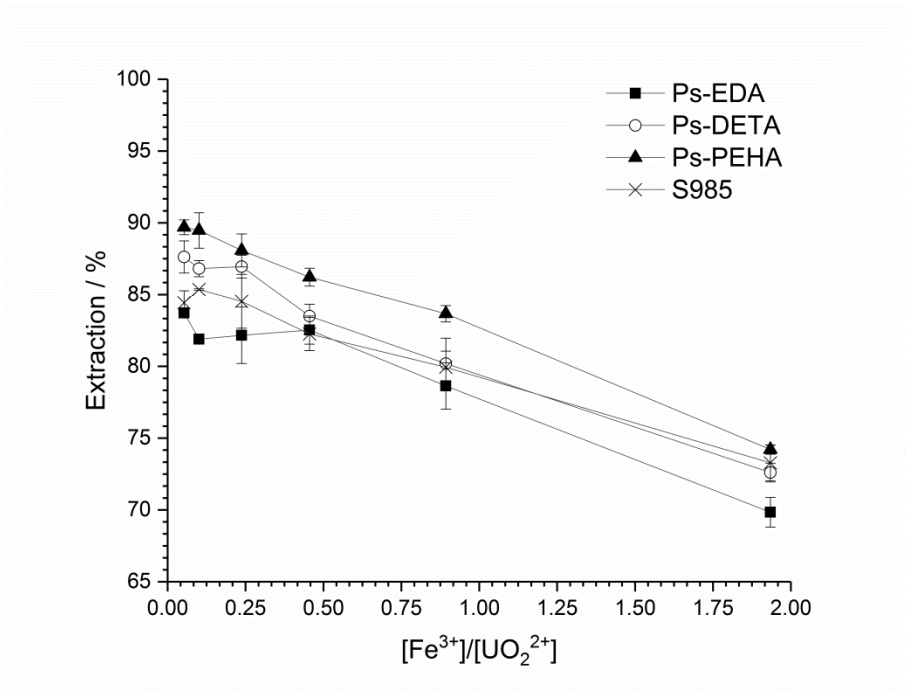*Figure 6. Uptake of UO_2^{2+} by Ps-EDA, Ps-DETA, Ps-PEHA and Purolite S985 from mixed uranium-iron solutions with increasing $[Fe^{3+}]/[UO_2^{2+}]$.*

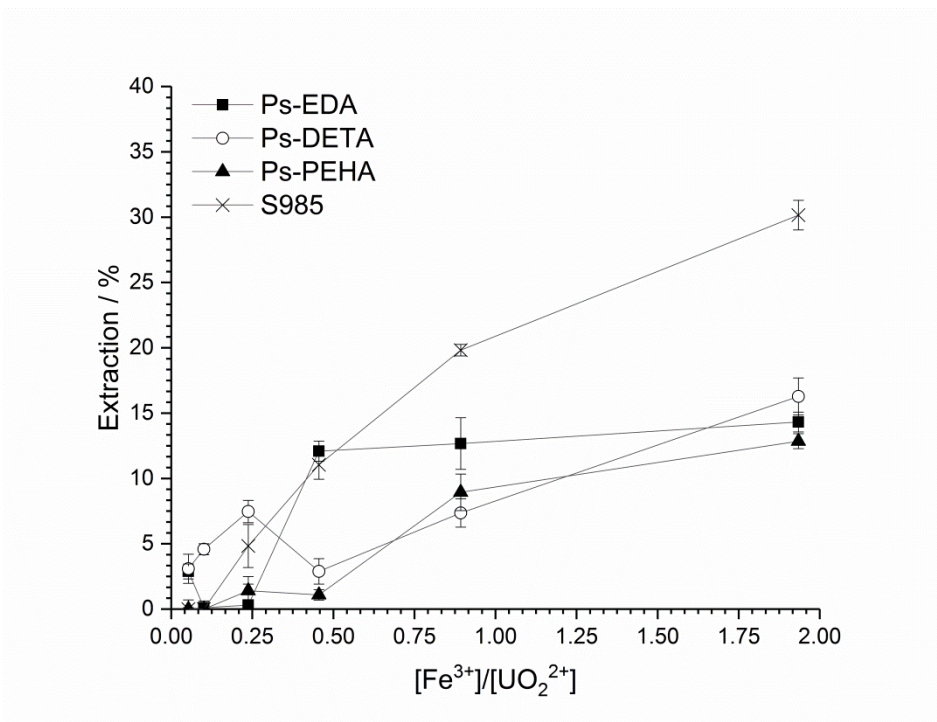*Figure 7. Uptake of Fe^{3+} by Ps-EDA, Ps-DETA, Ps-PEHA and Purolite S985 from mixed uranium-iron solutions with increasing $[Fe^{3+}]/[UO_2^{2+}]$.*
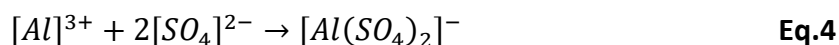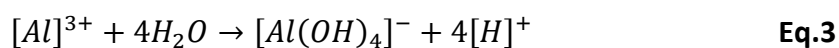
Uranyl Extraction from UMP Water

After contacting resin and UMP solution for 24 hours, a sample of solution was taken for ICP-MS analysis. UO_2^{2+} was the only species that was seen to undergo appreciable extraction, with none of the others exceeding 5% extraction on all tested resins (Supp. Info. Table A.5). Extraction data for UO_2^{2+} from the UMP solution is presented in Table 4. For the in-house produced resins, the uranyl extraction percentage is seen to increase with increasing polyamine chain length, though they appear to perform similarly, with extraction percentages differing over a range of around 4%. Purolite S985 is seen to be the least effective resin tested for uranyl extraction from the UMP solution, with an extraction 15.69% lower than the best performing resin, Ps-PEHA.

Table 4. UO_2^{2+} extraction percentages on Ps-EDA, Ps-DETA, Ps-PEHA and Purolite S985 from UMP solution

Resin	UO_2^{2+} Extraction / %
Ps-EDA	88.4
Ps-DETA	92.1
Ps-PEHA	93.4
Purolite S985	77.7

Discussion

All species used in the multi-metal extraction were cationic with the exception of MoO_4^{2-} and AsO_4^{3-}. It can be expected that extraction of the cationic species would be more suited to the use of a cation resin, and the weak base resins used for this work would not be effective. For the cationic species this almost holds true, with the exception to the rule being Al^{3+}. AsO_4^{3-} also appears anomalous, and this is discussed in the next paragraph. Al^{3+} is the most effectively extracted species on all the resins used. Though it could be possible to suggest a cation exchange mechanism where protons are exchanged with Al^{3+}, it is much more likely that an anionic Al species is forming. Al^{3+} has been observed to form anionic hydroxide and sulfate species (Eq.3, 4), so it can be theorised that it is these species which are being extracted by the resins.[32–34] However, the $log_{10}K_{eq}$ for the formation of $Al(OH_4)^-$ and $Al(SO_4)_2^-$ have been reported as -23.33 and 5.58 respectively, suggesting that the extracted species will most likely be the Al-sulfato species and not the Al-hydroxo species.[33,35]

$$[Al]^{3+} + 4H_2O \rightarrow [Al(OH)_4]^- + 4[H]^+ \qquad \textbf{Eq.3}$$

$$[Al]^{3+} + 2[SO_4]^{2-} \rightarrow [Al(SO_4)_2]^- \qquad \textbf{Eq.4}$$

All resins tested showed selectivity for the molybdate anion over the arsenate anion. As both are anionic in nature, it could be assumed that they both should have been extracted effectively. However, it has been shown that the adsorption of AsO_4^{3-} by anion exchangers can be highly pH dependent, with sorption by an imidazoline functionalized fibre showing negligible uptake below pH 2.[36] It is theorised that this is due to the relative excess of protons causing the formation of protonated aqueous species ($HAsO_4^{2-}$, $H_2AsO_4^-$, H_3AsO_4), this explanation is based purely on electrostatics, as the "less charged" species will have a lower interaction energy with the charged resin functionalities. Another possibility   is that as pH decreases, the sulfate based content (predominantly as HSO_4^- in these studied conditions below pH 2), as the acid used here was H_2SO_4. The elevated sulfate based content, either as HSO_4^- or SO_4^{2-}, will increase competition for sites on the resin and reduce the propensity for resin associated sulfate to exchange into solution via Le Chateliers Principle, thus reducing arsenate extraction. It is likely that the suppression of MoO_4^{2-} occurs for these very same reasons, but it is less susceptible to protonation. We believe that if experiments were performed at higher pH values then AsO_4^{3-} would be extracted effectively, potentially allowing for a pH based separation of arsenate from molybdate.

Suppression of uranyl uptake in the presence of chloride is a well documented phenomenon in ion exchange systems.[9–11,24] All the resins tested in this work show a tolerance to low levels of dissolved chloride, with no significant reduction in extraction efficiencies until $[Cl^-]$ exceeds 5 g L^{-1}. This behaves similarly to WBA resin Dowex M4195 at these $[Cl^-]$.[9,10] It has been previously observed that as $[Cl^-]$ increases beyond 70 g L^{-1}, uranyl begins to be extracted effectively again by WBA resins.[9–11] This has been shown to be due to the formation and sorption of $UO_2Cl_4^{2-}$ anions.[11,37] Contrary to those investigations, in this study an increase in uranyl uptake is not observed for $[Cl^-]$ above 70 g L^{-1}, uptake suppression is seen to stop at around 80 g L^{-1} chloride, with extractions of between 10% and 30% for all resins. This suppression likely arises due to the relative excess of Cl^- compared with UO_2^{2+} causing the UO_2^{2+} to be outcompeted for extraction sites on the resin. However, the consistent uranyl

extraction above $[Cl^-] = 80$ g L^{-1} infers a high affinity of the resins for uranyl, higher than that for Cl^-, as there is at least 80 times more chloride than uranyl ions present in solution.

Fe^{3+} is not seen to be extracted effectively by any of the resins tested, with a minimal dependence on $[Cl^-]$. At low $[Cl^-] < 25$ g L^{-1} it appears that Purolite S985 shows greater iron uptake than that of the synthetic polyamine resins, with a maximum extraction of 28%. This suggests that Purolite S985 may not be effective for implementation in a milling process with a PLL containing Fe^{3+} and chloride, whereas the polyamine resins may. Though uptake suppression is observed at high $[Cl^-]$, lower $[Cl]^-$ (< 5 g $^{L-1}$) may be acceptable in the presence of Fe^{3+}. As seen with UO_2^{2+}, high chloride causes a change in Fe^{3+} speciation. The $FeCl_4^-$ anion has been seen to be extracted in both IX and SX systems at high chloride concentrations.[31,38,39] However, an increase in iron uptake at high Cl^- was not observed in this work. This is consistent with what was seen for uranyl uptake at high chloride, with the resins showing a preference for the extraction of Cl^- over more complex uranyl-chloro anions.

Figure 6 shows that the presence of Fe^{3+} in solution causes the suppression of uranyl uptake from sulfate media. The extent of suppression is not large, with an increase in $[Fe^{3+}]/[UO_2^{2+}]$ from $0 - 2$ leading to a decrease in uranyl extraction of only about 15% for all resins tested. More Fe^{3+} is extracted by the resins in the presence of UO_2^{2+} than in systems devoid of it. This suggests that the uranyl is promoting the extraction of iron. It is thought that as the uranyl is absorbed to the resin as $[UO_2(SO_4)_3^{4-}]$, Fe^{3+} may be subsequently extracted by the sorbed uranyl. This phenomenon has been observed previously, where a transition metal (undefined) was co-extracted with uranium by amidoxime functionalised fibres.[40] This "sorbed bilayer" may be responsible for the suppression of uranyl uptake by blocking the access of $[UO_2]^{2+}$ to amine binding sites, and by the increased presence of anionic iron sulfate species binding to the resin. This is most visible for the Purolite S985 resin, where Fe^{3+} extraction reaches 30% at $[Fe^{3+}]/[UO_2^{2+}] = 2$.

All the tested resins showed an ability to remove UO_2^{2+} selectively from a real world UMP water with all synthetic resins outperforming Purolite S985. It is unclear why the S985 extracted 15.7% less uranyl than Ps-PEHA. They both contain 6 nitrogen atoms, which are able to become positively charged and exchange anions; however, S985 contains a branched polyamine functionality and has a hydroxyl moiety, potentially contributing to the observed differences. None of the contaminant species present in the aqueous matrix was seen to be

appreciably co-extracted by the resins. The pH of the process water was 4.5, which explains why no Al^{3+} was seen to be extracted, as it would have formed colloids.[41]

Conclusions

The three synthetic polyamine functionalised ion exchange resins and Purolite S985 have shown an enhanced tolerance to $[Cl^-]$ with regards to uranyl uptake from sulfate media. However, unlike other WBA resins, none of these resins exhibited an increase in uranyl uptake at $[Cl^-] > 80$ g L^{-1}. For the synthetic polyamine resins this is likely due to the formation of strong base active sites during the synthesis process. It is less clear why this is the case for Purolite S985, it may be the same, or it may be due to the presence of hydroxyl functional groups on the active sites.

Of a selection of species potentially present in uranium milling circuits, the only ones seen to have appreciable extractions (above 10%) were AsO_4^{3-}, MoO_4^{2-}, Al^{3+} and Eu^{3+}. MoO_4^{2-} and Al^{3+} were extracted most effectively, with extraction percentage exceeding 85 % and 90%, respectively, for all synthesised polyamine resins at pH 2. Extraction percentages were slightly lower for Purolite S985, with both showing maximums at pH 2 of between 70% and 80%. Uptake suppression of MoO_4^{2-} was seen with increasing $[H]^+$ due to the formation of less charged, protonated molybdate species and increased competition for exchange sites in the resin with increasing $[HSO_4^-]$. It is thought that there is a strong pH dependence for the extraction of $[AsO_4^{3-}]$, and these resins could be implemented in a pH based arsenate-molybdate separation process. To show this, experiments need to be performed at high pH values.

In systems containing Fe^{3+} in mixed sulfate-chloride media, uptake below 10% was observed for all synthetic resins. Purolite S985 shows Fe^{3+} uptake values of up to 28% for $[Cl^-]$ below 10 g L^{-1}, but this is supressed as $[Cl^-]$ increases. The formation of $FeCl_4^-$ is not observed to promote iron extraction at $[Cl^-]$ of up to 150 g L^{-1}. Systems containing both iron and uranium show an enhanced extraction of iron, with a slight suppression in uranium extraction. This is due to the extraction of Fe^{3+} by the sorbed uranium species. This may be problematic in uranium milling circuits which contain iron, however, the addition of Cl^- to such a system may reduce iron extraction with minimal impact on uranyl extraction. A caveat to this would be the increased cost of chloride addition, and the cost of materials able to resist enhanced corrosion from its presence.

All tested resins were shown to selectively extract UO_2^{2+} from a typical uranium mine process water, with the synthetic polyamine resins all outperforming the commercial resin, Purolite S985. The synthetic polyamine resins showed an increasing extraction trend with increasing chain length, with uranyl extractions of 88.4%, 92.1% and 93.4%, respectively, for Ps-EDA, Ps-DETA and Ps-PEHA, with that for S985 being 77.7%. Al^{3+} was not seen to be extracted from the UMP solution by any of the resins.

Acknowledgements

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