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Application of chelating weak base resin Dowex M4195 to the recovery of uranium from mixed sulfate/chloride media

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Abstract

The use of untreated seawater or bore water in uranium mineral processing circuits may represent a cheaper and more sustainable water resource for Australia's mining operations. Using present technologies, the increased salinity from these water sources results in decreased uranium extraction and increased extraction of impurities. There is incentive to overcome these challenges, either through new technologies, or repurposing existing technologies. The ion exchange behaviour of U from sulfate media on the weakly basic chelating resin Dowex M4195 (bis-picolylamine functionality) and the effect of competing chloride and impurity metal ions (Th, Fe, Al, Cu, Ni) has been studied. Experiments to determine acid, and sulfate media behaviour, and extraction thermodynamics including the effect of increasing chloride concentration upon extraction behaviour were carried out.

Dowex M4195 was found to have pK_1 and pK_2 values at 4.13 ± 0.04 and 2.1 ± 0.1 determined at 1.0 M NaCl. Dowex M4195 shows affinity for U(VI) over Fe^{3+} and Al^{3+} in sulfuric acid media with a U(VI) pH_{50} a full pH unit below that of Fe^{3+} at 0.17 and 1.82 respectively. With increasing chloride concentrations U and Th extraction is suppressed but Fe extraction increases. At the highest chloride concentrations explored Fe is preferentially extracted over U, and Th is not extracted at all. As chloride concentration increases the extraction of U passes through a minimum (40%) before increasing to around 60% for 4.0 M chloride at pH 1.80. Al^{3+} is not extracted by M4195 under any conditions explored. Dowex M4195 does show high selectivity for Cu and Ni over everything else.

Keywords; anion exchange, uranium, Dowex M4195, ion exchange resin, mass transfer

1 Introduction

Solvent extraction (SX) remains one of the most popular techniques used in the extraction and recovery of uranium from mineral processing liquors. Despite its wide applicability, SX has drawbacks including the low ability for preconcentration, and a number of issues associated with the use of organic phases, such as the potential for solvent loss, phase disengagement in multiple contact stages, third phase formation and the generation of large volumes of liquid aqueous and organic waste streams [1].

To overcome some of these challenges, the use of strong base (SB) anion exchange resins for uranium extraction from sulfate leach liquors was implemented in the 1950s [2]. These resins have quaternary amine functionality and a wide operating pH range of 0-13. Ion exchange has advantages over traditional solvent extraction [3] in its ability to preconcentrate metal species, and eliminates issues associated with use of organic phases. Weak base (WB) anion exchange resins were introduced to hydrometallurgical processing in the mid to late 1960's [1, 3]. These resins contain tertiary or secondary amine functional

groups, and have a narrower pH range of operation, (pH 0 to pH 7-9), compared to SB resins, and are often more susceptible to silica fouling [1, 5-8]. However, weak base resins generally have better selectivity for uranium over iron, and have associated advantages regarding reduced levels of poisoning [3, 4]. This makes them potential candidates for use in Australia's uranium processing operations, where iron is a significant contaminant element. In practice, processes employing IX resins for the separation/concentration of U typically use anion exchange resins with either strong base (SBA) or weak base (WBA) functional groups. A further challenge for Australia's mining operation is the provision of fresh water for processing circuits. With the majority of mines located in arid regions, cost effective water treatment and recycling of large quantities of process liquor are integral to the economic and environmental success of these operations. The use of untreated bore water and/or seawater could significantly reduce the costs associated with U extraction in these operations, but the salinity of these types of water is known to have a detrimental effect on uranium extraction.

The effect of high chloride concentrations on the ion exchange mechanism of uranium is two-fold: 1) decreased exchange of the U-sulfato species, likely due to competition by chloride; and 2) increased exchange of iron and other impurity elements [9]. For example, chloride has been shown to decrease uranium extraction into the solvent or resin phase, where concentrations of just $2.5 \text{ g L}^{-1} \text{ Cl}$, in Olympic Dam's pregnant liquor, reduced uranium loadings at most by 20% [9].

However, with water treatment having both economic and environmental implications, it is of increasing interest to find new ways of overcoming the decreased extraction associated with using saline waters in processing circuits. Our work seeks to identify a commercially available ion exchange resin that is adaptable to use under higher chloride conditions, and as such could present a pathway for the use of seawater or bore water in uranium recovery circuits. This has the potential to reduce the substantial economic and potential

environmental burden placed on limited freshwater supplies located in places such as Australia, where a large proportion of the World's uranium is mined and processed. Rather than focussing on developing new resins to suit high chloride, acidic sulfate processing streams, our work seeks to apply current resin technologies to new processes. Our reasons are two-fold: Firstly, the mineral processing industry is a very small component of the wider industrial applications of ion exchange resins. It therefore represents a significant cost to design a new resin technology to serve this type of hydrometallurgical separation. Secondly, we suggest that current resin technologies have not been applied to their full potential due to an incomplete understanding of the chemistry involved. The innovation therefore comes from applying commercially available resins to new processes. Weak base anion exchange resins have been effectively used to separate uranium, U(VI), from sulfate-based acid processing streams [4, 10-12]. The weak base chelating resin, Dowex M4195, with *bis*-(picolyl)amine functionality, has demonstrated unique separation capabilities for first row transition metals. It has been investigated for the extraction of Cu(II) [10-13, 16- 18], Ni(II) [13-19], Co(II) [14-16, 18, 19], Cr(III)/(VI) [21, 22], Zn (II) [13, 15], Cd (II) [13, 15], Pd(II) [14, 15, 23], Au(III) [15], Pb(II) [14, 19] Fe(III) [14, 19], Mn(II) [14, 19], and Pt(IV) [15]. To the best of our knowledge, the application of Dowex M4195 to separate uranium from acid-based streams has not been carried out. However, its properties with respect to iron and other elements suggest it may still promote uranium extraction over iron with increasing chloride concentration.

The resin structure of the Dowex M4195 functional group is shown in Figure 1. From proton uptake experiments the apparent pKa for the functionality is predicted to be around $pK_1 = 3.5$ [15, 16], $pK_2 = 2.7$, $pK_3 = 1.5$ [16]. The weakly basic nature of Dowex M4195 precludes use in alkaline carbonate circuits. However, these pKa's greatly favour stripping and silica removal.

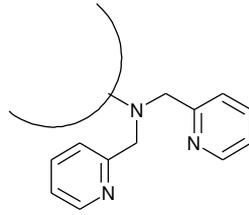


Figure 1. bis-(picolyl)amine (BPA) functionality of the Dowex M4195 resin

We present work exploring, for the first time, the extraction of uranium from sulfate media in the presence of increasing chloride using the chelating and weakly basic anion exchange resin Dowex M4195. Rather than focusing on a single element system, we have investigated the impact that the presence of metals commonly encountered in the processing of uranium have on the ability of Dowex M4195 to successfully extract uranium. We make conclusions as to the suitability of this resin for future use in high salinity uranium extraction circuits incorporating ion exchange.

2 Experimental

2.1 Reagents and stock solutions

For experimental investigations the commercially available chelating exchanger Dowex M4195 was supplied by Sigma Aldrich. The general data for this resin is given in Table 1 [24]. Prior to experimentation the resin was preconditioned by bottle rolling with $1 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$ for 24 hrs at room temperature. The resin was then washed five times with 200 bed volumes of deionized water before use, where one bed volume is described as the minimum volume of water required to wet the resin.

Table 1: Manufacturers Specifications Dowex M4195 [25]

Parameter	Value
Cu loading (pH 2, 6 g L^{-1} feed)	$35 - 42 \text{ g L}^{-1}$
Commercial equivalent	Lewatit TP-220, Purolite S960,

Particulate size	20/50 US Mesh
Functionality	Bis-Picolylamine
Form	Weak base/partial H ₂ SO ₄ salt
Moisture	40 – 60%

2.2 Determination of acid dissociation constant for Dowex M4195

The technique used to titrate the Dowex M4195 was adapted from the literature [25] using a Mettler Toledo DL15 Potentiometric Titrator fitted with a Mettler Toledo triple junction glass electrode with 3 M NaCl as the filling solution. The experimental and titration solutions contained sufficient NaCl to bring the ionic strength to 1.0 mol·L⁻¹; the temperature was maintained at 21 °C, and a slow stream of nitrogen was passed through the titration vessel in order to reduce the interference from CO₂. The resin prior to titrating was contacted with 1 mol·L⁻¹ NaOH to generate the free base form, dried at 50 °C for 24 hrs and then ground to a fine powder. The resin was then weighed out (0.05 g) and combined with 0.01 mol·L⁻¹ HCl at 1.0 mol·L⁻¹ NaCl (50 mL) and titrated with standardized 0.1 M NaOH (1.0 mol·L⁻¹ NaCl). The concentration of proton exchange groups were determined by the difference in proton concentration per mass of resin after thermodynamic equilibrium (24 hr contact time). All potentiometric titrations were performed in triplicate, in both static and dynamic modes. The potentiometric curves were fit using PSEQUAD [26] and the last pK_a fit by minimization of the standard error in the data. PSEQUAD is a comprehensive program for the evaluation of potentiometric and/or spectrophotometric equilibrium data using analytical derivatives. The calculation of the unknown free concentrations of components is based on the standard Newton-Raphson procedure by minimizing the difference between calculated and experimental data points for a given number of species affecting free protons in solution. The Gauss-Newton method is used for the refinement of these parameters [27]. This makes

the program capable of fitting polyelectrolytes and solid-liquid systems including metal ion precipitation.

2.3 Batch extractions sulfate media

All batch extractions as a function of acid concentration were carried out as single contacts with the contact of 2mL of resin with 50 mL of aqueous simulant feed. It should be noted that all contacts were performed under acidic conditions to mimic the use of seawater as the diluent for uranium leachate under expected process conditions. The resin and aqueous feed were continuously mixed for a period of 24 hrs at room temperature (21 °C) on an orbital shaker. A time of 24 hours was chosen to ensure equilibrium had been achieved. It has been shown that this period of time is sufficient ensure equilibrium is achieved in these types of systems [28]. No attempt was made to control the pH during the course of the experiment but it was measured at the conclusion of the experiment. The extraction percentage was determined by difference (using Equation 1) and the concentrations of the individual metal ions determined by either ICP-MS or ICP-OES.

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

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 from pH 1-10 using buffers. At higher acid concentrations $[H^+]$ was determined by titration and verified by chloride concentration via ion selective electrode analysis. Error was determined by triplicate measurement in aqueous feed solution concentrations prior to contact.

2.4 Determination of loading behaviour under saline conditions

All loading isotherms were carried out as single contacts with the contact of 2mL of resin with 20 mL of aqueous simulant feed. As noted above, all experiments were performed at acidic pH values. The resin and aqueous feed were continuously mixed for a period of 24 hrs at room temperature (21 °C). As mentioned previously, 24 hours was considered a suitable time scale to ensure equilibrium had been reached. As before, no attempt was made to control the pH during the course of the experiment. The data were fitted with two parameter isotherm models Langmuir and Dubinin-Radushkevich (D-R) [27]. The fitting was carried out by using linear regression and by non-linear least squares analysis using SOLVER [29].

Langmuir isotherm model (Equation 2):

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (2)$$

Dubinin-Radushkevich isotherm model (Equation 3):

$$q_e = q_D \exp(-B_D \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2) \quad (3)$$

At equilibrium in these models q_e denotes the resin metal ion concentration ($\text{mmol}\cdot\text{g}^{-1}$) and C_e is the solution phase metal ion concentration ($\text{mmol}\cdot\text{L}^{-1}$). In the Langmuir model a_L and K_L are Langmuir isotherm constants and in the Dubinin-Radushkevich model B_D is an isotherm constant and q_D is the maximum surface loading capacity, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ }^\circ\text{K}^{-1}$) and T is the absolute temperature ($^\circ\text{K}$).

It must be noted that due to the fact that the interaction of uranium anion exchangers involves a heterovalent interaction with the resin functionality, the physical assumptions underlying the theoretical derivation of most isotherm models are violated [30]. Fitting the

data to 2 parameter isotherm models whilst purely empirical in nature will allow for comparison with previous literature studies in the assessment of how well Dowex M4195 behaves in the extraction of uranium from saline sulfuric acid media. Error in the isotherm constants was calculated from the linearized form of the model using the SOLVER calculated values using the deviations of the experimental data from this best fit line.

An attempt was made to fit the isotherm data based on the mass action law for the heterovalent exchange of uranium anions in solution with salt counterions from the resin functionality. In this study stability constant values for complexation and protonation are given in MHL stoichiometric format. Notation K indicates a stepwise equilibrium reaction whereas β denotes the overall equilibrium reaction. That is, a $\log_{10} K$ value for the complexation of x metal ions, y protons and z ligands would be denoted as $\log_{10} K_{xyz}$.

3 Results

3.1 Determination of acid dissociation constants

The titration curve for ground resin at 1.0 M NaCl ionic strength is shown in Figure 2. Fitting the potentiometric titration curve using PSEQUAD [27] gives values for the proton dissociation constants which are given in Table 2.

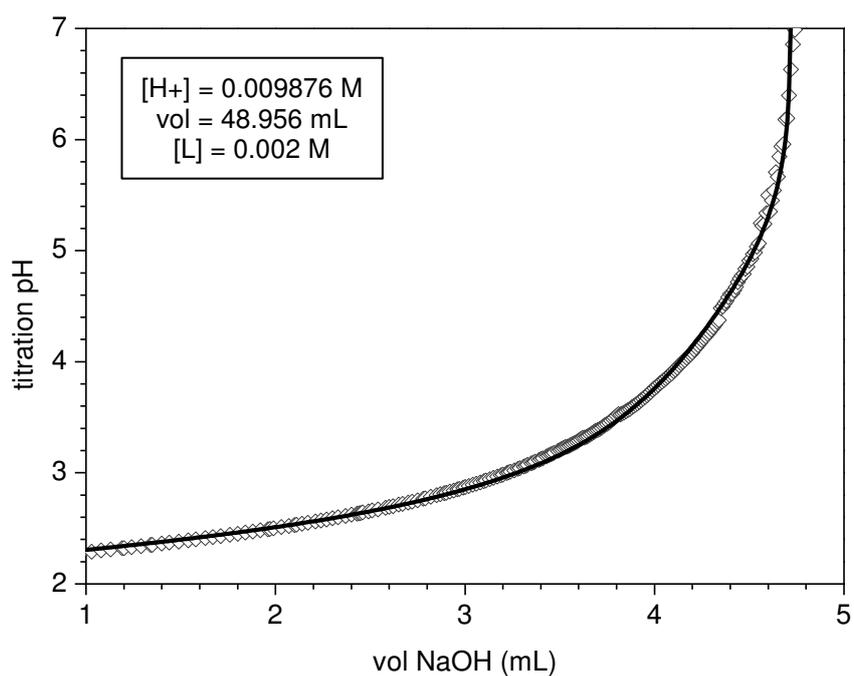


Figure 2. Potentiometric titration of Dowex M4195 at 21 °C and $I = 1.0 \text{ mol L}^{-1}$ (NaCl) data points shown as grey diamonds (\diamond). PSEQUAD program best fit is shown by black line using HL^+ , HL_2^{2+} , and HL_2^+ in the model.

Table 2. Best fit acid dissociation constants for Dowex M4195 at 21 °C and $I = 1.0 \text{ mol L}^{-1}$ (NaCl), determined using PSEQUAD

Species	MHL notation	$\log_{10} \beta$	$\log_{10} K$
HL_2^+	012	7.07 ± 0.09	
HL^+	011	4.13 ± 0.04	4.13 ± 0.04
H_2L^{2+}	021	6.2 ± 0.1	2.1 ± 0.1
H_3L^{3+}	031	UC*	-

* unable to calculate from the titration data

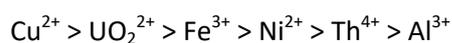
Best fit of the triplicate titration data was carried out by incorporating 3 protonated species on the surface of the resin with a total acid concentration of 0.009876 M in a volume of 48.956 mL and total BPA functionality present on the resin of 0.002 M.

Using a singly charged species HL^+ present on the resin surface and the presence of two species of HL^+ and H_2L^{2+} , the titration model resulted in poor fitting of the potentiometric titration curve in the pH 3-6 region by over predicting free proton in solution in the pH region of 4-6 and under predicting in the region of 3-4. It is not clear from the current study as to whether the anion exchange species is $\overline{H_2L(HSO_4)_2}$ or $\overline{H_2L(SO_4)}$ but it is most likely, from the conditions under which the resin was conditioned, that the pre-contact species is $\overline{H_2L(HSO_4)_2}$.

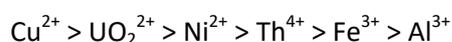
3.2 Extraction studies as a function of acid and anion concentration

3.2.1 Extraction studies as a function of acid concentration

The percentage extraction of uranium and other selected metal ions is shown in Figure 3. It is clear that there is a distinct difference in Fe^{3+} extraction behaviour as a function of pH. The trend for extraction strength as a function of low pH (around 1 mol H^+) is as follows;



Dowex M4195 does not extract Al^{3+} under any of the pH conditions tested. It must be noted from the data that Fe^{3+} is still extracted at acidic pHs over Th^{4+} and Ni^{2+} with extraction not dropping below 20% for the pH region tested. The trend for extraction at higher pH values is as follows;



The pH_{50} value for the extraction of metal ions is given in Table 3 for the metal ions tested.

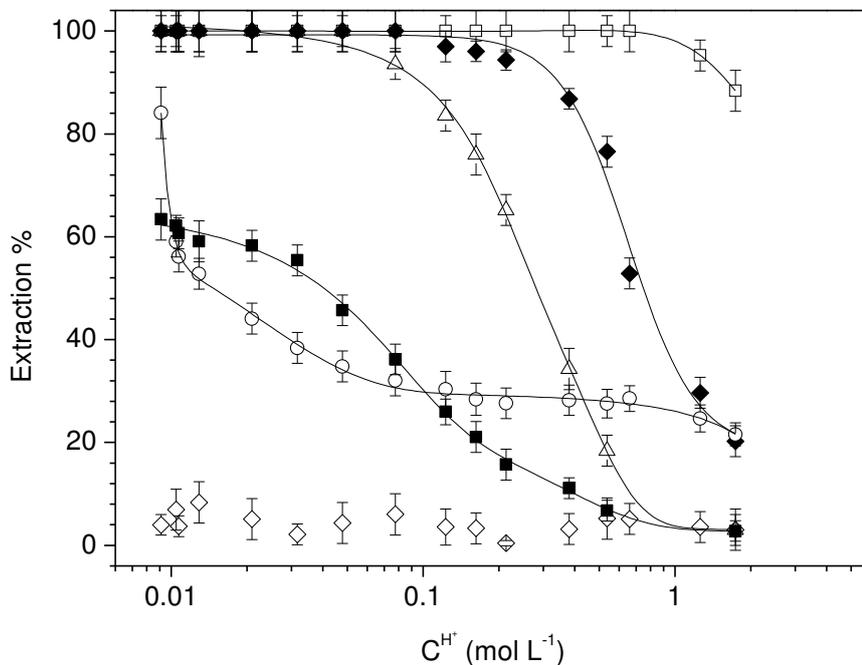


Figure 3. Extraction of selected metal ions as a function of $[H^+]$ in sulfuric acid media, 21 °C after 24 hr. contact time. \square = Cu, \triangle = Ni, \blacklozenge = U, \diamond = Al, \circ = Fe, \blacksquare = Th. Black line fit is present to guide the eye.

Table 3. pH_{50} values for the extraction of tested metal ions as a function of pH, calculated from extraction % curves.

Element	pH_{50}	Element	pH_{50}
Cu^{2+}	-0.51 ^a	Al^{3+}	NC ^b
UO_2^{2+}	0.17	Fe^{3+}	1.82
Ni^{2+}	0.54	Th^{4+}	0.97

^apredicted using non-linear regression of 4 data points, ^bNC = not calculated

3.2.2 Extraction studies as a function of sulfate concentration

The percentage extraction of uranium and other selected metal ions as a function of increasing ammonium sulfate concentration at pH 1.57 is shown in Figure 4.

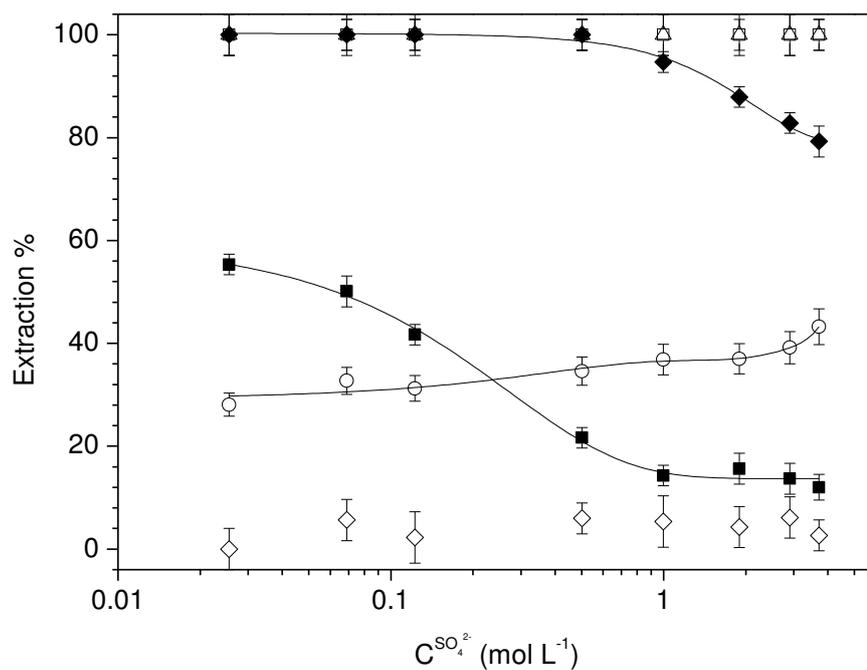
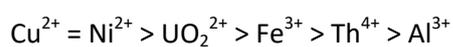
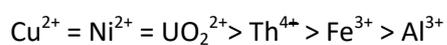


Figure 4. Extraction percentage of metal ions as a function of sulfate concentration at pH 1.47, 21 °C, and after 24 hr. contact time. □ = Cu, △ = Ni, ◆ = U, ◇ = Al, ○ = Fe, ■ = Th

The trend for extraction strength as a function of high sulfate concentration is as follows;



As sulfate concentration decreases the extraction strength changes to the following;



Dowex M4195 does not extract Al^{3+} under any of the sulfate concentrations tested. Fe^{3+} extraction increases with increasing sulfate concentration, whereas Th^{4+} and UO_2^{2+} extraction is suppressed at higher sulfate concentrations.

3.2.3 Extraction studies as a function of increasing chloride concentration

In Figure 5 the effect of increasing chloride on metal extraction by Dowex M4195 at $\text{pH } 1.80 \pm 0.05$ and $0.15 \text{ mol}\cdot\text{L}^{-1}$ sulfate is shown. The increasing concentration of chloride in the sulfate system has no effect on Ni^{2+} and Cu^{2+} extraction.

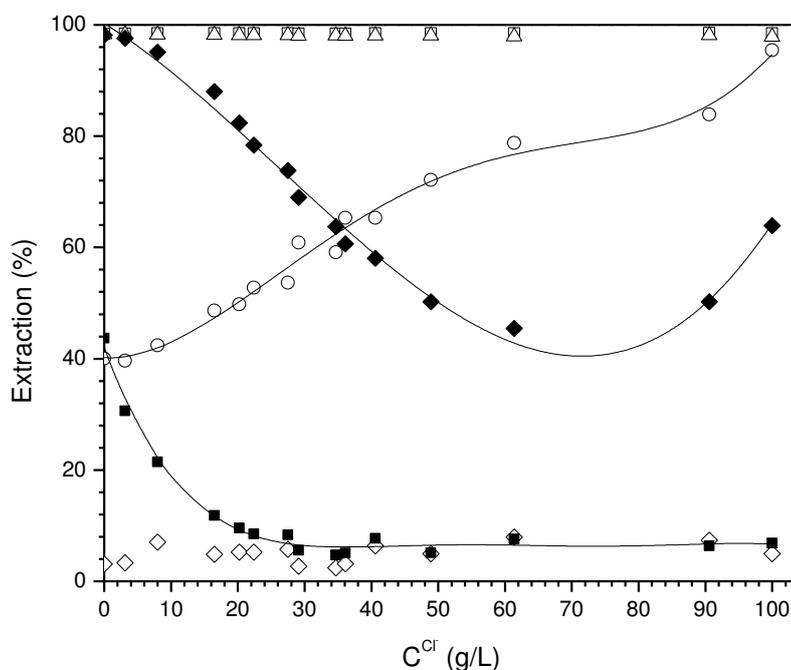


Figure 5. Extraction percentage of metal ions as a function of increasing chloride ion concentration at $\text{pH } 1.80 \pm 0.05$ in sulfuric acid, $[\text{SO}_4^{2-}] = 0.15 \text{ mol}\cdot\text{L}^{-1}$ and $21 \text{ }^\circ\text{C}$ after 24 hr.

contact time. \square = Cu, \triangle = Ni, \blacklozenge = U, \diamond = Al, \circ = Fe, \blacksquare = Th

Increasing chloride concentration suppresses the extraction of Th^{4+} and UO_2^{2+} initially. As chloride concentration increases past $2.0 \text{ mol}\cdot\text{L}^{-1}$ the extraction of UO_2^{2+} increases to reach a maximum of 64% extraction at $4.0 \text{ mol}\cdot\text{L}^{-1}$ chloride. With increasing chloride concentration in

sulfate media, the extraction of Fe^{3+} increases from 40 to 95% to the point where Fe^{3+} is more strongly extracted than UO_2^{2+} . As for the other systems, Al^{3+} is not extracted.

3.3 Isotherm behaviour under saline conditions

The result from the fitting of the isotherm data using Langmuir and Dubinin-Radushkevich models [27] are shown in Table 4. The fitting using SOLVER was carried out by minimization of the sum of square errors. Using the SOLVER correlation coefficient the Langmuir model gives the overall better correlation coefficients at low chloride concentration. The D-R isotherm gives fairly similar correlation coefficients to that of Langmuir plots and gives an insight into the thermodynamics of the exchange mechanism on the surface of the resin. For the models tested the trend in surface uptake equilibrium is predicted for increasing chloride concentration in that the initial suppression in uptake is observed until at the highest concentration of chloride where uptake is increased. The monolayer saturation capacity, q_m ($\text{mol}\cdot\text{g}^{-1}$), was calculated from the Langmuir equation using Equation (4).

$$K_L = q_m a_L \quad (4)$$

The mean free energy of sorption, E , was calculated using Equation (5).

$$E = \frac{1}{\sqrt{2B_D}} \quad (5)$$

It must be noted that the D-R isotherm over-predicts the uranium capacity of the resin whereas for the Langmuir model there is not enough higher uranium concentration data points to accurately predict the monolayer saturation capacity. With the Langmuir isotherm it is apparent that, within error, the maximum capacity does not increase until higher chloride concentrations are reached. Whereas for the D-R isotherm model the maximum

uranium capacity predicted follows the isotherm data trend regarding uptake suppression in moderate chloride concentrations to increased uptake at high chloride concentration.

Table 4. Isotherm fitting parameter calculated using various models for uranium extraction from 0.15 mol·L⁻¹ sulfate at pH 1.7 ± 0.1 as a function of chloride concentration at 21 °C and 24 hr. contact time., using non-linear least squares fitting using SOLVER.

Langmuir				
[Cl ⁻] mol·L ⁻¹	0.0	1.0	2.0	4.0
Constant	(0.0 g·L ⁻¹)	(35.45 g·L ⁻¹)	(70.90 g·L ⁻¹)	(141.80 g·L ⁻¹)
K _L	3.1 ± 0.1	0.081 ± 0.005	0.030 ± 0.001	0.047 ± 0.002
a _L (g·mg ⁻¹) (x10 ⁻³)	39.8 ± 0.4	0.8 ± 0.1	0.36 ± 0.06	0.82 ± 0.02
q _m (mg·g ⁻¹)	78 ± 4	100 ± 20	74 ± 8	57 ± 7
R ²	0.9977	0.9987	0.9967	0.9965
Dubinin-Radushkevich				
[Cl ⁻] mol·L ⁻¹	0.0	1.0	2.0	4.0
Constant	(0.0 g·L ⁻¹)	(35.45 g·L ⁻¹)	(70.90 g·L ⁻¹)	(141.80 g·L ⁻¹)
B _D (x10 ⁻⁹)	5.0 ± 0.4	8.7 ± 0.1	9.5 ± 0.1	9.6 ± 0.6
q _D (mol·g ⁻¹) (x10 ⁻⁴)	22 ± 6	9.1 ± 0.5	4.7 ± 0.2	7 ± 1
q _D (mg·g ⁻¹)	530 ± 140	216 ± 12	113 ± 5	174 ± 4
E _D (kJ·mol ⁻¹)	10.0 ± 0.4	7.57 ± 0.05	7.24 ± 0.04	7.2 ± 0.3
R ²	0.9931	0.9969	0.9982	0.9967

The divergence in the model predictions means it is difficult to ascertain whether the change in isotherm behaviour with increasing chloride in solution is dominated by a reduced number of sites for uranium uptake due to chloride competition or to a change in uranium speciation. An E_D value less than 8 kJmol⁻¹ is an indication of a physisorption uptake

mechanism [24] where above this value chemisorption dominates. In Table 4 it would seem that at low chloride concentration the uptake is a chemisorption process ($E_D = 10.0 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$) which switches to a physisorption process with the addition of chloride into the system with E_D values of 7.57 ± 0.05 , 7.24 ± 0.04 , and $7.2 \pm 0.3 \text{ kJ}\cdot\text{mol}^{-1}$ respectively.

3.4 Fitting isotherm data to an equilibrium model.

The uranium loading isotherms fitted with an equilibrium uptake model are given in Figure 6 with resultant R^2 values of 0.9979, 0.9976, 0.9967 and 0.9947 for 0, 1.0, 2.0, and 4.0 M NaCl respectively. It must be noted that in this model chelation of uranium by the M4195 bispicolylamine is not considered and an anion exchange model utilised.

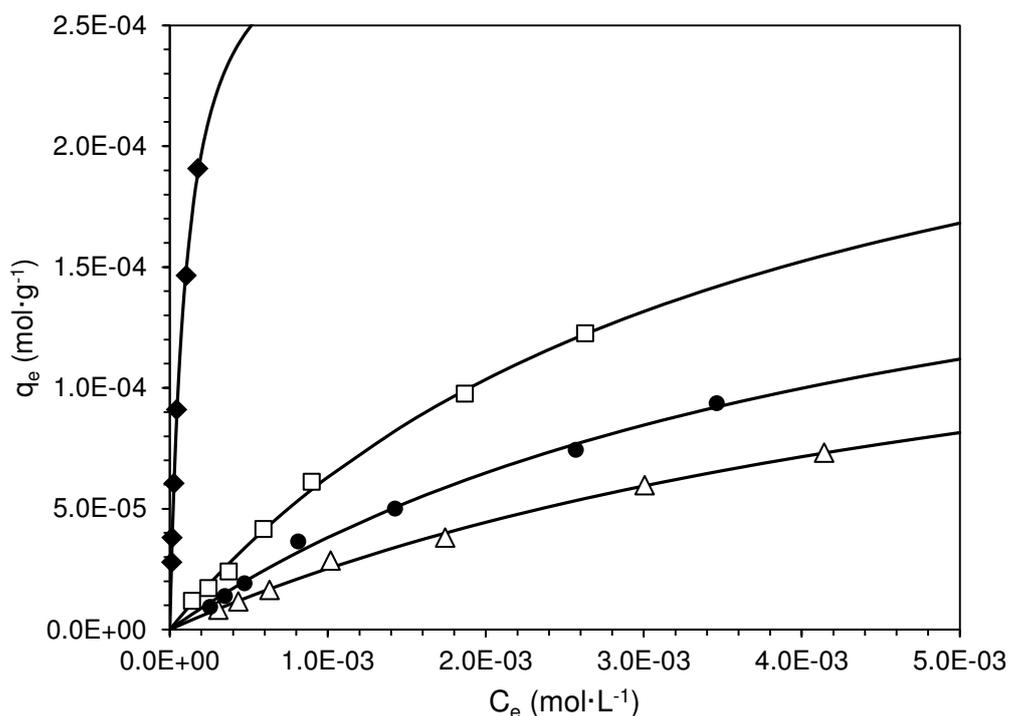
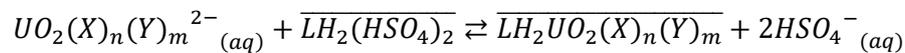


Figure 6. Uranium loading isotherms from $0.15 \text{ mol}\cdot\text{L}^{-1}$ sulfate at $\text{pH } 1.7 \pm 0.1$ as a function of chloride concentration at $21 \text{ }^\circ\text{C}$ and 24 hr. contact time. ◆ = $0.0 \text{ mol}\cdot\text{L}^{-1} \text{ Cl}^-$, $\text{pH } 1.87$, □ = $1.0 \text{ mol}\cdot\text{L}^{-1} \text{ Cl}^-$, $\text{pH } 1.83$, △ = $2.0 \text{ mol}\cdot\text{L}^{-1} \text{ Cl}^-$, $\text{pH } 1.74$, ● = $4.0 \text{ mol}\cdot\text{L}^{-1} \text{ Cl}^-$, $\text{pH } 1.61$. Model fitting is depicted by the solid black lines.

This is due to the observed suppression of U(VI) uptake with increasing chloride (implying anionic competition) and the fact that complexes of uranium with pyridylamine functionalities are unfavourable or weak in aqueous and organic solutions [31, 32]. In the model it is assumed, based on the most dominant species determined by potentiometry, at pH 1.8 that the extracting M4195 functional group is doubly protonated and associated with two bi-sulphate moieties. One Uranium complex ($UO_2L_x^{2+}$) in solution exchanges with two bi-sulphates in the following mechanism.



The isotherm was fit to the following expression;

$$y = \frac{K'_{ex} x S}{1 + K'_{ex} x} \quad (6)$$

Where;

$$K'_{ex} = \frac{K_{ex1020}(1 + \beta_{1020}[SO_4^{2-}]^2) + K_{ex1012}(1 + \beta_{1012}[SO_4^{2-}][Cl]^2) + K_{ex1004}(1 + \beta_{1004}[Cl]^4)}{[HSO_4^-]^2} \quad (7)$$

The uranium on the resin surface is given by y, x is uranium in solution and S is the total resin functionality available as $LH_2(HSO_4)_2$. The full derivation of this model is given in the supplementary information. It must be noted that this model is an approximation as there are a number of other potential species in solution that produce singular charged species, which may also compete for ion exchange sites on the resin. The stability constants used to model the uptake of uranium are given in Table 5 along with the ion exchange equilibrium

values. Log β values available for uranyl sulfate and chloride complexes were taken from the NIST database as a function of ionic strength [32]; others were fit using SOLVER by fitting Equation 7 to the isotherm data.

Table 5. Solution stability constants and ion exchange equilibrium constants used in fitting uranium uptake isotherm behaviour.

[NaCl]	log K'_{ex}	S	MHL	Species		
				$UO_2(SO_4)_2^{2-}$ 1020	$UO_2(SO_4)(Cl)_2^{2-}$ 1012	$UO_2(Cl)_4^{2-}$ 1004
0.0	3.977	3.01E-04	Log β	2.539	N/A	N/A
			Log K_{ex}	0.3434	N/A	N/A
1.0	2.447	2.88E-04	Log β	2.034	-0.3979	N/C
			Log K_{ex}	-1.416	-1.513	N/C
2.0	2.201	1.84E-04	Log β	1.556	-1.003	-3.3045
			Log K_{ex}	-2.502	-4.699	-4.5227
4.0	2.329	2.17E-04	Log β	1.556	-0.895	-2.7941
			Log K_{ex}	-2.502	-3.584	-3.2019

4 Discussion

4.1 Determination of acid dissociation constants

The speciation of Dowex M4195 at 1.0 M NaCl ionic strength as a function of pH (0.002 M BPA functionality present) is shown in Figure 8. The acid dissociation constants for Dowex M4195 presented in Table 2 give a pK_2 that is comparable with values presented previously in the literature of 2.2 and 2.7 in chloride and sulfate media respectively [15].

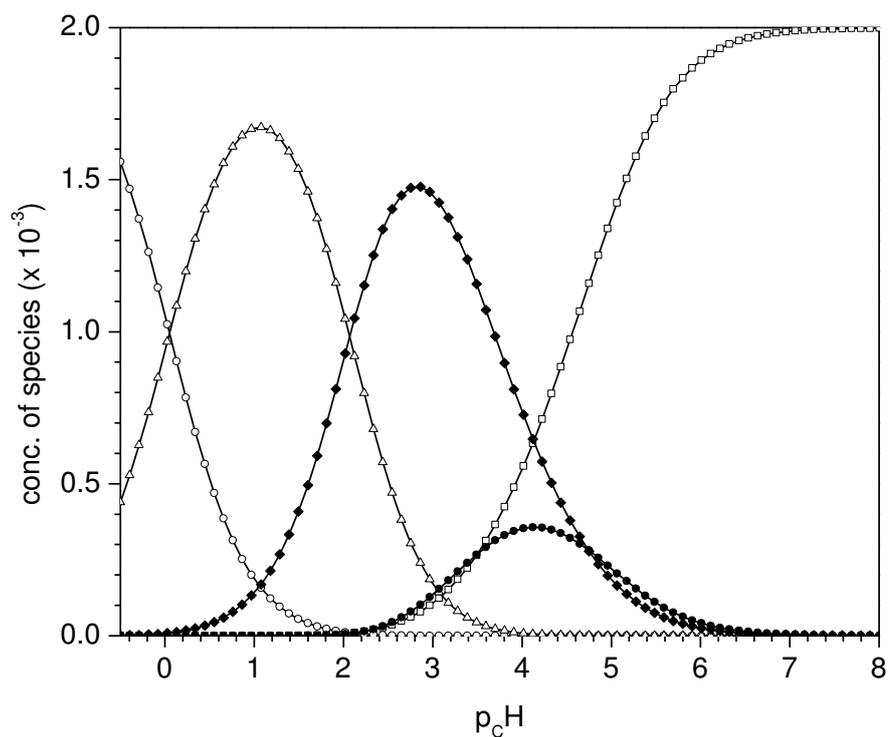


Figure 8. Speciation of M4195 as a function of pH with functionality set at 0.002 M and ionic strength 1.0 M NaCl. Speciation designated as follows; ○ = H₃L³⁺, △ = H₂L²⁺, ◇ = HL⁺, ● = HL₂⁺, □ = L_{free}, where L = BPA

It is not possible to measure the most acidic dissociation constant pK₁ using the experimental procedure outlined in section 2.2 but is predicted to be around 0.5 and 1.57 in chloride and sulfate media respectively [15]. Both of these acidic pK_a values are associated with the protonation of the pyridyl nitrogens on the BPA functional group.

The most basic acid dissociation constant for the BPA functional group (pK₁) on the M4195 resin is associated with the protonation of the aliphatic nitrogen in the structure. The measured value of 4.13 ± 0.04 using a potentiometric titration methodology is more basic than previous values cited in the literature of 3.4 and 3.5 in chloride and sulfate media, respectively, at 0.1 M ionic strength [15] and 3.5 at 1.0 M NaCl determined by equilibration studies [14]. The results presented at 1.0 M ionic strength in the literature are from

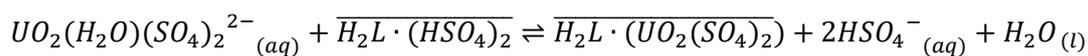
equilibration studies and are taken from pH_{50} values and as a result is a combined pH effect rather than interpolated behaviour attributed to specific BPA functionality. The existence of a HL_2 species where a proton is shared between two BPA functionalities has not been seen before for Dowex M4195 although this type of behaviour determined by titration has been seen for the aminophosphonic acid groups on Purolite S940 [25]. The sharing of protons between separate heterocyclic nitrogen groups is evidenced very well in the conformational changes of (5,6)-CHIRAGEN(0), which contains two separate (5,6)-pinene-bipyridine functionalities [33]. What can be seen from the speciation plot is that above pH 4.6 approximately 50% of the functionality or greater is present as the fully deprotonated ligand. This means that only very benign conditions are required to induce free amine functionality. This means that species that interact with the surface of the resin through a charged pairing interaction, rather than chelation, can be readily eluted from the resin.

4.2 Distribution studies as a function of acid and anion concentration

4.2.1 Effect of acid and anion concentration on U(VI) uptake

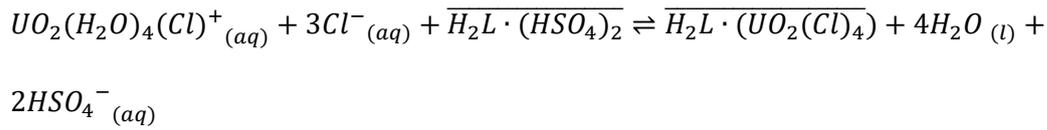
The results presented in Figure 3 show uranium uptake increases with decreasing acidity in pure sulfuric acid media with 100 % extraction occurring at $\text{pH} \geq 1$. Similar behaviour has been observed in a previous study where the extraction constant was observed to increase from pH 0.4 to a maximum at pH 1.4 [34]. The decreased extraction of uranium below pH 1 is likely due to competition of the HSO_4^- ion in an anion exchange extraction mechanism. The speciation of UO_2^{2+} in sulfuric acid media has been shown to exist as neutral UO_2SO_4 and anionic species, $\text{UO}_2(\text{SO}_4)_2^{2-}$ and $\text{UO}_2(\text{SO}_4)_3^{4-}$ under different conditions [35, 36]. There is disagreement in the literature over the dominant U(VI) speciation in acidic sulfate solutions, with a number of studies concluding the $\text{UO}_2(\text{SO}_4)_3^{4-}$ anion is dominant [36-39]. Various other spectroscopic and density function theory (DFT) studies, however, find that U(VI) speciation under these solution conditions is dominated by the neutral ion $\text{UO}_2(\text{H}_2\text{O})_3(\text{SO}_4)$

and the anion $\text{UO}_2(\text{H}_2\text{O})(\text{SO}_4)_2^{2-}$ [40-42] and indeed, that in solution 5-fold coordination in the UO_2^{2+} equatorial plane is preferred [40]. Using stability constants available in the literature [32] for the experimental conditions outlined in Figure 4, at low sulfate concentration and at pH 1.47 the predominant species in solution is the neutral $\text{UO}_2(\text{SO}_4)$. At around 0.5 mol L^{-1} of sulfate in solution the ratio of $\text{UO}_2(\text{SO}_4)$ is equal to $\text{UO}_2(\text{SO}_4)_2^{2-}$ and above this the dominant species in solution is $\text{UO}_2(\text{SO}_4)_2^{2-}$. Under experimental conditions $\text{UO}_2(\text{SO}_4)_3^{4-}$ is never present above 2% of the total U concentration. It can be surmised that under the experimental conditions, without the presence of chloride, that the dominant ion exchange mechanism in sulfuric acid/sulfate media on Dowex M4195 is as follows;



In acidic chloride media, where $0 < [\text{Cl}^-] < 3 \text{ M}$ as for this study, 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 [42, 43]. Using X-ray absorption spectroscopy, Allen et al. [42] showed that the speciation of U(VI) on the surface of a strong base resin ($\text{UO}_2\text{Cl}_4^{2-}$) differed from that present in the feed solution ($\text{UO}_2(\text{H}_2\text{O})\text{Cl}_4^{2-}$). Although their experiment was conducted under much higher chloride concentrations (10 M Cl^-) than our study (<2 M Cl^-), it is evident that there can be a change in speciation of U(VI) on uptake by the resin, and this can involve a reduction in coordination number in the UO_2^{2+} equatorial plane, likely through a de-watering process.

To our knowledge there are no studies concerning U(VI) speciation in mixed sulfate-chloride media. As such, it could be surmised that under the experimental conditions at high chloride concentrations that the dominant ion exchange mechanism in saline sulfuric acid media on Dowex M4195 follows;



We propose differing extracted uranium speciation at low and high chloride concentrations to account for the extraction behaviour detailed in Figure 5. The initial reduction in uranium extraction as chloride concentration increases, followed by an increase in uranium extraction as chloride increases further, implies that two different uranium species with different affinities for the resin as compared to the chloride ion, are extracted across the salinity range investigated here.

What is not clear from our results is whether at initially low chloride concentrations the suppression of uranium uptake is due to competition between Cl^- and $UO_2(H_2O)(SO_4)_2^{2-}$ for the ion exchange sites, or changing uranium speciation in solution to a uranium species with a lower affinity for the ion exchange site. The reduction of U(VI) extraction from 100% to 40% as solution chloride concentration increases to $\sim 70 \text{ g L}^{-1}$ and then subsequent increase in extraction to 65% as chloride concentrations approach 100 g L^{-1} would imply there is a change to the dominant U(VI) speciation in solution and hence a change in the uranium species extracted by the resin. With the aim of fully understanding the extraction of U(VI) under increasing chloride conditions we have conducted a full XAS study of U(VI) solution and resin speciation, on a WB resin, which will be the subject of a forthcoming publication along with uranium XAS speciation on a variety of chelating resins used in hydrometallurgy under sulfuric acid and acidic saline extraction conditions.

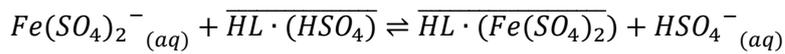
4.2.2 Effect of acid and anion concentration on impurity uptake

The pH_{50} values for the percentage extraction of copper, iron (III), nickel, thorium and uranium (IV) from sulfate media of varying acidity are presented in Table 3. The trend of copper, cadmium, nickel, zinc, loading has been previously studied from $[H^+]$ of 1×10^{-6} to

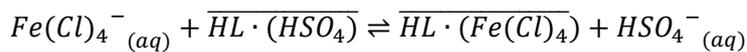
0.1 M [44, 45]. The general trend of nickel loading increasing from 0.1 M $[H^+]$ to 0.01 M $[H^+]$ agrees with the increase in percentage extraction observed in the present study, where nickel is extracted at 88 % and 100 % respectively. Copper loading was observed to increase over the range studied, 0.1 M $[H^+]$ – 1×10^{-5} M $[H^+]$ [41] in contrast to the 100 % extraction for the range 0.1 M $[H^+]$ to 0.01 M $[H^+]$ achieved in this study. This difference was attributed to the difference of the initial chloride concentration feed to the systems, which is 0.12 mmol g^{-1} in the present study opposed to 1.2 mmol g^{-1} , in the literature study, which could compete for the ion exchange sites on the resin [45]. The extraction trends as a function of sulfate concentration are presented in Figure 4. Copper and nickel show quantitative extraction across all sulfate concentrations which is evidence that the mechanism is not anion exchange, rather it is chelating, as supported by conclusions by Wolowicz and Hubicki [46].

The behaviour of iron uptake, as shown in Figure 3, shows that ferric iron is increasingly taken up with decreasing acidity on Dowex M4195. However, in a previous study, when the resin was loaded from a mixed solution where the molar concentration of metals in solution was greater than the capacity of the resin available, ferric iron uptake was suppressed to less than 20 % extraction at acidities of 0.1 and 0.01 M $[H^+]$ and decreased even further with decreasing acidity, compared to the 32 and 84 % extraction for this study respectively [45]. These results show that although ferric iron was present at almost 30 times the molar concentration of copper, the resin has a much higher affinity for copper over ferric iron. This is confirmed in Grinstead's study where at similar pH, the adsorption constant for copper is 7 times greater than that of ferric iron [34]. This is consistent with copper being extracted via a chelation mechanism, and iron by an anion exchange mechanism. Using stability constants available in the literature the most dominant species at low acidity is $Fe(SO_4)_2^-$ as well as a few hydrolysed sulfato species [32]. At high acidity the dominant species in solution is most probably $Fe(HSO_4)(SO_4)$, a charge neutral complex. However it should be noted that in the

speciation calculations in this study the $\log \beta_{121}$ was predicted to be 6.84, which is somewhat lower than the 8.10 from another recent study [47]. Ferric iron extraction increases marginally with increasing sulfate concentration. This is predominantly due to there being nearly equal concentrations of charge neutral $\text{Fe}(\text{HSO}_4)(\text{SO}_4)$ in solution with $\text{Fe}(\text{SO}_4)_2^-$ (46.7%:48.9% from speciation calculations) with approximately 4.4% being $\text{Fe}(\text{SO}_4)^+$ in solution. The increase in extraction trend could be predominantly due to activity effects. The extraction behaviour for Fe^{3+} also correlates with the amount of HL^+ present on the surface of the resin implying a Fe sulfato anion with a weak affinity for the surface is present in acidic sulfate solutions. Speciation studies indicate that this is likely to be $\text{Fe}(\text{SO}_4)_2^-$ [48];



Iron uptake by the resin increases with increasing chloride concentration, suggesting that a ferric chloride anion has a strong affinity for the surface;



Aluminium extraction was found to be low over all pHs tested and similar results are reflected in other studies [45]. Thorium uptake increases with decreasing acidity, yet does not reach 100 % extraction at any pH examined and also decreases with increasing sulfate concentration. Thorium can exist as cationic ThSO_4^{2+} , neutral $\text{Th}(\text{SO}_4)_2$ and anionic $\text{Th}(\text{SO}_4)_3^{2-}$ and $\text{Th}(\text{SO}_4)_4^{4-}$ sulfato species in solution [49]. Using stability constants from the literature [32, 41], the predominant species for thorium in solution is both the $\text{Th}(\text{SO}_4)_2$ neutral complex and $\text{Th}(\text{SO}_4)_3^{2-}$. With increasing pH and sulfate in solution the predominant thorium species becomes the tris-sulfato anion but HSO_4^- effectively out-competes the complex for surface sites on the resin.

Under increasing chloride conditions Th extraction somewhat follows the trend of U in that extraction initially decreases (in the case of Th from 40% to 10% as chloride increases from 0 – 20 g/L), again implying direct competition between a Th sulfato anionic species and Cl^- in solution. Th differs from U however in that the extraction remains low across the chloride range of this experiment, implying that Th does not form an anionic species with greater affinity for the surface than the chloride ion. Increasing the chloride concentration of feed solutions to >20 g/L may therefore be a useful way of eluting Th from U when extracted from sulfuric acid media.

4.3 Isotherm behaviour under acidic saline conditions

It is clear from comparing the sorption/retention capacities of Dowex M4195 with published values for other solid phase extractants (SPE) available in the literature that Dowex M4195 out performs the majority. For example, the retention capacity calculated from the Langmuir constant for uranium on Dowex M4195 is $78 \pm 4 \text{ mg g}^{-1}$, which is significantly higher than other SPE materials such as Amberlite XAD-4 functionalized with succinic acid ($12.33 \pm 0.02 \text{ mg g}^{-1}$), bicine ($0.90 \pm 0.01 \text{ mg g}^{-1}$), quinolone-8-ol ($2.74 \pm 0.02 \text{ mg g}^{-1}$) and o-vanilline semicarbazone ($2.89 \pm 0.02 \text{ mg g}^{-1}$) [50-53].

When comparing the sorption/retention capacities with ion exchange materials Dowex M4195 is better than EDTMP functionalised chelating resin (41.76 mg g^{-1} under optimum conditions) [54] and Amberlite IRA-910 (64.26 mg g^{-1}) [55], comparable with a polyester resin functionalised with acrylic acid (80.93 mg g^{-1}) [56] and performs less well when compared with strong base resins Amberlite IRA-910U (108 mg g^{-1}) [57].

Loading isotherm data for Dowex M4195 was converted from mols U g^{-1} resin to $\text{g U}_3\text{O}_8 \text{ mL}^{-1}$ wet settled resin and Langmuir fitting carried out. This data was used for comparison with previous literature data [50, 51] at a resin loading from an aqueous barren concentration of $150 \text{ mg L}^{-1} \text{ U}_3\text{O}_8$ as a function of chloride concentration ($\text{g}\cdot\text{L}^{-1}$) in Figure 9.

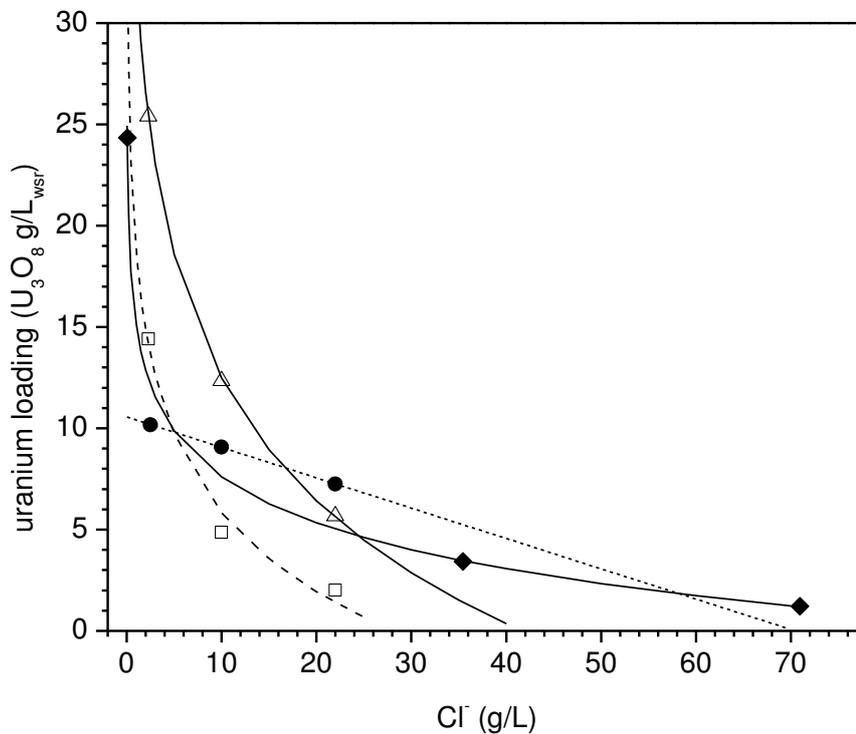


Figure 9. Predicted loading of various resins using Langmuir model parameters at a barren concentration of $150 \text{ mg}\cdot\text{L}^{-1} \text{ U}_3\text{O}_8$ lines fitted by best fit to guide the eye only. ● = polyamine WB (PA) resin; ◆ = Dowex M4195; △ = WB tertiary amine (TA) resin; □ = SB quaternary amine (QA) resin

When comparing a polyamine (PA), a tertiary amine (TA) and a quaternary amine (QA) with Dowex M4195, using a general line of best fit, at concentrations $< 5 \text{ g L}^{-1}$ and $> 2 \text{ g L}^{-1}$ the assumption can be made that;

TA > M4195 > QA > PA

At approximately 25 g L^{-1} chloride it is possible to assume that;

PA > M4195 > TA > QA

There is a limit to the validity of the data to make these assumptions but what is clear is that M4195 performs comparably with the polyamine resin at high concentrations of chloride.

The advantage to the comparison with the polyamine resin (in this case most probably Purolite S984) is that M4195 does not suffer from the same oxidative degradation problems over time [48]. This makes the Dowex M4195 resin a viable option for use at higher salinities when compared with other amine based resins. It is clear that Dowex M4195 does not outperform classic strong and weak base resins in sulfuric acid media with chloride concentrations below 20 g L^{-1} [50-52, 57-59].

To the authors' knowledge, the use of mass transfer and solution equilibrium to model uptake of uranium to M4195 is a novel approach, and thus provides insights into the uranium extraction process not seen in other studies. The overall stability constants found for the uranium sulfato species are comparable to those available in the literature [32] at 0-2 M ionic strength conditions, and thus we have confidence in the application of this novel approach to this system. At the higher chloride conditions, however, there is lower confidence in the output of the model as high order stability constants for chloride complexes have not been determined in solution, and indeed, there are only a handful of spectroscopic studies addressing uranium speciation in high ionic strength chloride media [42, 43].

The modelling is further complicated by the presence of both sulfate and chloride ions in the acidic media. To the authors' knowledge there have been no studies addressing uranium speciation in mixed sulfate-chloride media. Stability constants for low chloride ionic strength would suggest that uranium sulfato species are more likely, however, as mentioned above, there is a lack of thermodynamic data for uranium in high chloride systems, and as such it is

difficult to predict whether uranium chloro complexes will dominate in high chloride systems in which sulfate is present.

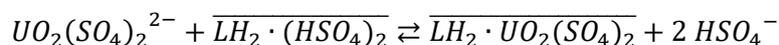
The final complicating factor is that the speciation of uranium on the resin surface may not reflect the dominant solution speciation. Work by Allen et al. [42] showed that the $(\text{UO}_2(\text{H}_2\text{O})\text{Cl}_4^{2-})$ complexes in the feed solution undergoes a reorganisation at the resin surface through a dewatering process, and $(\text{UO}_2\text{Cl}_4^{2-})$ is adsorbed by the resin. It is therefore difficult to predict the uranium species taken up by the resin, even if the solution speciation can be predicted from stability constants.

Given these complexities, it is important to remember that the resultant model fits have a large degree of uncertainty built into them. This points to the need for a targeted spectroscopic study into both the solution speciation of uranium in mixed sulfate-chloride media, and the resin speciation of the uranium extracted from the mixed media. This would allow much tighter constraints to be placed on the model, increasing the confidence, particularly for the higher chloride conditions. An X-ray absorption spectroscopy study of this kind is currently underway by this team.

5 Conclusions

Most commercial weak-base resins have a pK_a (defined as the pH value at which 50 per cent of the functional groups of the resin are protonated) in the range 6 to 8. This study shows that Dowex M4195, taking into account the most basic pK_a s in Figure 8, has a pK_a in the range of 4.0-4.5. Although this almost weak acid characteristic pK_a will not make this resin amenable to alkaline extraction processes but will make the resin more easily eluted of ions taken up through anion exchange, and less problematic in resin regeneration after silica fouling [5-8]

Under sulfate conditions with little to no chloride present the most probable mechanism for the extraction of uranium by Dowex M4195 in solution is as follows;



Where L is the bispicolylamine functionality and the straight line accent denotes extraction onto the surface of the resin. This mechanism would account for both the suppression of uranium uptake as a function of both pH and sulfate concentration under the conditions tested.

The extraction mechanism of uranium from mixed chloride-sulfate media is not straightforward and cannot be fully explained by chloride anion competition. Of particular interest is the initial reduction in uranium extraction as chloride increases, and then the subsequent increase in uranium extraction as chloride continues to increase. This may suggest a change in uranium speciation taken up by the resin, from a sulfato species that is outcompeted by chloride ion uptake, to a chloro species that outcompetes chloride ion uptake. A study into this specific behaviour is underway by this group.

It is clear that Dowex M4195 has slightly better loading behaviour in the mixed media than conventional strong base type I and weak base resins. However, it should be noted that the loadings are still low, and are likely to be below those required of the uranium processing industry for cost effective resource recovery. This study therefore suggests that for uranium processing streams incorporating seawater or bore water rather than fresh water Dowex M4195 represents a better option than currently available ion exchange technologies, but still falls short of the necessary performance criteria of >95 % extraction.

A mass transfer and equilibrium solution modelling approach was able to account for the uranium uptake from mixed sulfate-chloride media across the salinity range tested, however it should be noted that due to a lack of thermodynamic data for uranium in strongly saline

solutions, and the uncertainty surrounding uranium speciation in mixed sulfate-chloride media, there is reduced confidence in the model output as chloride concentration increases. It can be inferred from the model that to increase the extraction of uranium, when moving to higher NaCl concentrations, a strong chelating effect would be a preferred interaction and at lower concentrations a large number of polyamine sites would benefit. Both of these aspects are currently being explored.

Thorium extraction behaviour on M4195 is interesting and warrants further investigation.

Results indicate that under high chloride conditions in a mixed media solution, U(VI) can be readily separated from Th(IV) and could be beneficial in the partitioning of waste generated from mining and mineral processing.

Most evident from the data is that Dowex M4195 is more suitable for the extraction of “softer” transition metals such as Cu and Zn as it is clearly a strong chelate for these types of metal ions, and represents an efficient option for removing these contaminants from a U(VI) stream.

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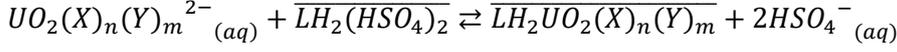
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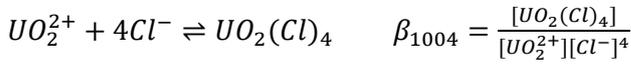
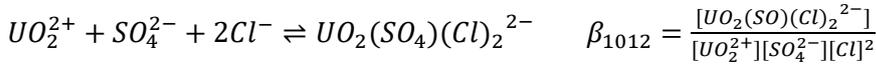
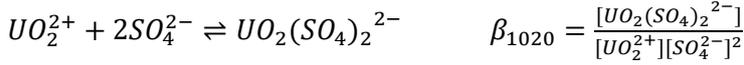
Appendix – Supplementary material

Isotherm Derivation

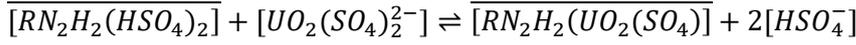
Assume amine functional group is protonated and each N is associated with a bis-sulphate moiety. One Uranium complex ($UO_2L_x^{2-}$) exchanges with 2 bis-sulphates in the following mechanism.



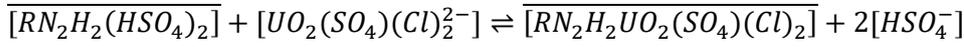
The formation of the extracted species in solution is as follows;



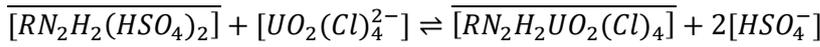
Where the extraction of these species follows the reaction equilibrium



$$K_{ex^{1020}} = \frac{\overline{[RN_2H_2(UO_2(SO_4))]}[HSO_4^-]^2}{\overline{[RN_2H_2(HSO_4)_2]}[UO_2(SO_4)_2^{2-}]}$$



$$K_{ex^{1012}} = \frac{\overline{[RN_2H_2(UO_2(SO_4)(Cl)_2)]}[HSO_4^-]^2}{\overline{[RN_2H_2(HSO_4)_2]}[UO_2(SO_4)(Cl)_2^{2-}]}$$



$$K_{ex^{1004}} = \frac{\overline{[RN_2H_2(UO_2(SO_4)(Cl)_2)]}[HSO_4^-]^2}{\overline{[RN_2H_2(HSO_4)_2]}[UO_2(Cl)_4^{2-}]}$$

If the overall extraction is the summation of these three processes then;

$$[U]_{resin} = [UO_2^{2+}]_{aq} \left(\frac{\overline{[LH_2(HSO_4)_2]}}{[HSO_4^-]^2} \right) \left(K_{ex^{1020}} \left(1 + \beta_{1020}[SO_4^{2-}]^2 \right) \right. \\ \left. + K_{ex^{1012}} \left(1 + \beta_{1012}[SO_4^{2-}][Cl^-]^2 \right) + K_{ex^{1004}} \left(1 + \beta_{1004}[Cl^-]^4 \right) \right)$$

If we consider that S = initial ligand concentration (resin functionality) then resin functionality = S-y. If we assign $[U]_{resin} = y$, $[U]_t = x$ and resin functionality = S-y then and then rest is incorporated into the extraction coefficient K'_{ex} then;

$$\frac{y}{S-y} = xK'_{ex}$$

$$y = (S - y)$$

$$y = K'_{ex}xS - K'_{ex}xy$$

$$y + K'_{ex}xy = K'_{ex}xS$$

$$y(1 + K'_{ex}x) = K'_{ex}xS$$

$$y = \frac{K'_{ex}xS}{1 + K'_{ex}x}$$

Where;

$$K'_{ex} = \frac{K_{ex}^{1020} (1 + \beta_{1020} [SO_4^{2-}]^2) + K_{ex}^{1012} (1 + \beta_{1012} [SO_4^{2-}] [Cl]^{-2}) + K_{ex}^{1004} (1 + \beta_{1004} [Cl]^{-4})}{[HSO_4^-]^2}$$