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# Batch adsorption study of uranium on various ion exchange resins as an alternative method to solvent extraction

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**Abstract.** The project is aimed at recovering uranium from scrap material containing useful amounts of Low Enriched Uranium. The common method of recovering uranium is by using acidic or alkaline medium for dissolution, followed by solvent extraction using tributyl phosphate in kerosene. However the normal challenge with solvent extraction is the generation of enormous liquid waste which is slightly radioactive. Therefore in this project we studied the adsorption of uranium on various ion exchange resins in order to use it as an alternative method to solvent extraction. Uranium solution from the scrap materials was used, and different ion exchange resins such as Amberjet 1600 H, PPC100H, Purolite S940 and S950 chelation resin, and Purolite A500 were tested under various conditions for the adsorption of uranium. The strong acid cation resins show no selectivity between the uranium and aluminium species, both species were fully adsorbed irrespective of the pH. The strong base anion resins had good uranium adsorption attaining 100%, they also show a pH effect for the aluminium adsorption. The use of ion exchange resins, especially with anion resins showed promising results and potential for use as an alternative to solvent extraction.

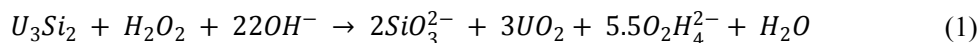
## 1. Introduction and background

The South African Fundamental Atomic Research Installation reactor (SAFARI-1) currently uses Low Enriched Uranium (LEU) silicide fuel. Therefore during the fabrication process of fuel for nuclear research reactors, scrap material is generated. This scrap material contains un-irradiated uranium and silicon as major elements, the other elements present are traces of Mg, Fe and Mn which originate from the aluminium alloy used as cladding material. The uranium and silicon are used as starting material to produce uranium silicide ( $U_3Si_2$ ), which is crushed and mixed with aluminium powder to produce a solid piece, the so-called fuel plate meat [1].

Since the introduction of LEU silicide fuel for research reactors, investigations regarding dissolution and recovery have been ongoing in order to recover the valuable uranium. For dissolution, the common methods entail acidic [2] or alkaline dissolution [3]. The common acidic routes use nitric acid, especially for the dissolution of LEU silicide fuel plates, especially those with aluminium cladding in high concentrations (3 to 6 M) [4]. However, even with higher concentrations, long dissolution times were still encountered by Touron and Cheroux (2001), whereby the cladding was removed after 3 hours using 3 to 6 M nitric acid and complete dissolution was only obtained in 6 to 8 hours [5]. However, to improve the dissolution rates, catalysts such as HF,  $H_2O_2$ , KIO [6] and  $Hg^{+2}$  have been recommended [7]. The challenge during  $HNO_3$  dissolution is the precipitation of silicon due to its low solubility in concentrated nitric acid [3]. While in an alkaline medium, the dissolution of the uranium silicide fuel plate scrap material is normally conducted using a two-step process. The first step remove almost the entire aluminum from both the cladding and the fuel meat with either NaOH or a combination of NaOH- $NaNO_3$ , followed by dissolution of the remaining  $U_3Si_2$  particles in NaOH plus  $H_2O_2$  at about 70 °C [8]. Alternatively, the remaining  $U_3Si_2$  particles could be dissolved in a



solution of NaClO (12% w/v) [9] or HF plus H<sub>2</sub>O<sub>2</sub> [10]. Similar to the acidic medium, the comminuted particles of U<sub>3</sub>Si<sub>2</sub>, after the cladding has been removed, are shown to dissolve faster in the peroxide solution, according to the chemical reaction as described in equation 1. The challenge with alkaline dissolution is the decomposition of the peroxide [11].



Normally, after dissolution of the scrap material or fuel plate, the uranium is recovered by liquid-liquid extraction using TBP in kerosene because of its high selectivity for the uranyl nitrate species (UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>) from aqueous solutions [12]. However, the challenge with solvent extraction is the generation of an enormous amount of liquid waste, which is slightly radioactive.

The aim of this work was to study uranium adsorption on various ion exchange resins, in order to use ion exchange (IE) as a possible alternative method to solvent extraction (SE). IE is regarded as an inherently cheaper method than solvent extraction [13], with the benefit of resin transformation for reuse in another cycle. IE is also used in combination with solvent extraction (Eluex process), for example it was used in high uranium concentrations of up to 900 ppm [14]. IE was used to extract uranium from leach liquor, the resin eluted with sulfuric acid then uranium was extracted using the SE process. Ion exchange resins are widely used in various areas from water softeners [15] to waste water treatment, such as the recovery of uranium from ground water [16]. There are many ion exchange resins reported in literature that are suitable for uranium adsorption from various waste streams, such as activated charcoal used to separate uranium from other alkaline metals, alkaline earth metals and lanthanide metals [17], Amberjet IRA-400 to adsorb uranium in acid leach [18], and Amberjet 1200 H (AHR) was used to study the uptake behavior of uranium from a nitric acid medium [19]. Other types of ion exchange resins used in irradiated fuel for the recovery of <sup>99</sup>Mo are TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> [20].

Ion exchange technology was previously used in earlier unpublished internal Necsa projects for the recovery of uranium from waste streams generated from purification processes via the PUREX method. Some of the resins used were Amberlite IRC-747, Diphonix, Purolite S940, and Amberjet 4400 Cl<sup>-</sup>. These resins were used in this study as the previous studies indicated them as the best for this application.

## 2. Experimental

### 2.1. Materials and method

The fuel plate scrap material was supplied by the Nuclear Energy Corporation of South Africa (Necsa). The leaching was conducted using two separate methods. The first method used 3 M nitric acid with HF as a catalyst at 70 °C, and the second method used NaOH-NaNO<sub>3</sub> (dissolution 1) and NaOH-H<sub>2</sub>O<sub>2</sub> (dissolution 2) at 65 to 70 °C. Screening tests of the resins were conducted using synthetic solutions of uranium, aluminium, silicon, and magnesium to test adsorption of the uranyl nitrate species UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> as well as adsorption of the other species (i.e. aluminium, silicon and magnesium). The reagents were of analytical grade supplied by LABCON South Africa. After leaching, samples were taken to measure the concentrations of the elements (U, Al, Si, Mg) using ICP-OES (Model: ARCOS FHS12) and UV/Vis spectrophotometry. The UV/Vis spectrophotometer (Biochrom Libra S60) was only used for the measurement of the uranium concentration in the range of 20 to 200 mg/L using the Na<sub>2</sub>CO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> method. Different pH targets were attained by dilution of the pregnant leach to the desired volume and the adsorption experiments were conducted using an incubator shaker (Model: ISKO 80) at room temperature at a speed of 200 rpm. All adsorption tests were conducted using 1 g of resin with 50 mL solution for each experiment for a period of 24 h. The list of ion exchange resins used is given in Table 1.

**Table 1.** List of ion exchange resins used for adsorption of uranium species.

Resin name	Type	Form	Functional group	Capacity
Amberjet 1600 H	Strong acid cation	H <sup>+</sup>	Sulfonic acid	2.4 eq/L
PPC100H	Strong acid cation	Na <sup>+</sup>	Sulfonic acid	2.0 eq/L
Purolite S950	Chelating	Na <sup>+</sup>	Aminophosphonic	24 g/L
Puromet MTS9500	Chelating	Na <sup>+</sup>	Aminophosphonic	26 g/L
Purolite S940	Chelating	Na <sup>+</sup>	Aminophosphonic	20 g/L
Puromet MTA5012	Strong base anion	Cl <sup>-</sup>	Type I Quaternary Ammonium	1.15 eq/L
MTA8000PPSO4	Strong base anion	SO <sub>4</sub> <sup>2-</sup>	Quaternary Ammonium	1.6 eq/L
Purolite A500	Strong base anion	Cl <sup>-</sup>	Type I Quaternary Ammonium	1.15 q/L

### 2.2 Modelling of speciation

Uranium usually exists as different species in acidic and alkaline medium, depending on various factors such as the pH. Software (Hydra/Medusa software), similar to that used by Khawassek (2018) [19] to predict uranium species under nitric acid conditions, was used to calculate the species of uranium and aluminium under HNO<sub>3</sub>, and under NaOH plus H<sub>2</sub>O<sub>2</sub>, conditions. The calculated uranium species in HNO<sub>3</sub> corresponded to the work done by Khawassek (2018). At a pH below 4, the uranium species were found to be UO<sub>2</sub>NO<sub>3</sub><sup>+</sup> and UO<sub>2</sub><sup>2+</sup> suggesting good uranium adsorption at low pH with cation resins. However, at the same pH range of 0 to 4, the aluminium and magnesium species co-exist as cation species, namely AlOH<sup>2+</sup> and Mg<sup>2+</sup>. The predicted uranium and aluminium anion species under NaOH-H<sub>2</sub>O<sub>2</sub> conditions are UO<sub>2</sub>(OH)<sub>3</sub><sup>-</sup> and UO<sub>2</sub>(OH)<sub>4</sub><sup>2-</sup> found from pH 10 and above, while the aluminium species Al(OH)<sub>4</sub><sup>-</sup> appears from pH 8. This suggests a good adsorption for both uranium and aluminium using an anion resin. The complex Na<sub>2</sub>UO<sub>2</sub>(O<sub>2</sub>H)<sub>4</sub>, was however not predicted by the software. The adsorption percentages were calculated from the differences between the initial and final concentrations according to equation (2). Where C<sub>0</sub> and C<sub>e</sub> are the initial and final concentrations of the solution.

$$\% \text{ ads} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

## 3. Results and discussion

### 3.1 Acidic medium adsorption

The strong acid cation (SAC) resins and chelating resins were tested for uranium adsorption from the acidic solution. The batch tests were conducted for a period of 24 hours, using 1 g sample of resin with 50 mL. The solution had concentrations of 90.65 mg/L uranium, 135.15 mg/L aluminium, 53.12 mg/L silicon, and 9.56 mg/L magnesium with a pH of 1.26. The results showed more than 90% adsorptions for both uranium and aluminium, but more aluminium was adsorbed as compared to uranium. The magnesium adsorption was always 100% for all the resins (Table 2). Silicon was eliminated since the small traces existing were not adsorbed for all the resins tested and the majority precipitated after dissolution and the precipitate was separated by centrifugation. The adsorption of both uranium and aluminium was expected from the calculations, as the UO<sub>2</sub>NO<sub>3</sub><sup>+</sup> and Al<sup>3+</sup> species were dominant from pH 1 to 4, however the results showed no distinct selectivity between the adsorption of the uranium and aluminium species, even though the initial aluminium concentration was higher than that of uranium. The similarity of the results, especially for the 1600 H and PPC100H resins, could be due to the similarity of the functional groups and the large capacity of 2.4 and 2.0 eq/L, respectively, while the similarity between the S950 and MTS9500 could be due to the same Na<sup>+</sup> form and aminophosphonic functional group.

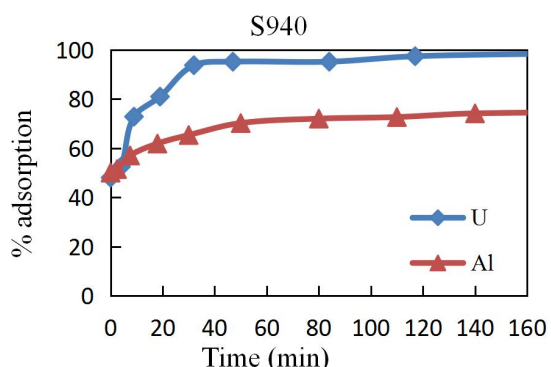
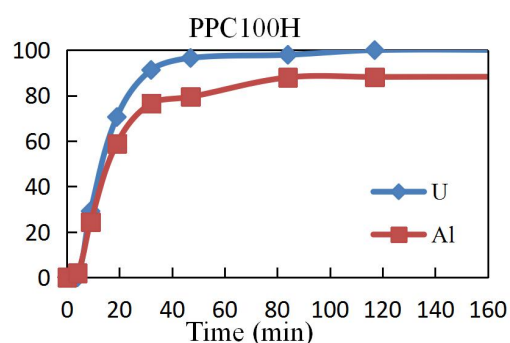
**Table 2.** Adsorption percentages from acidic leach with concentrations of 18 mg/L U and 27 mg/L at pH 1.26.

Resin	U adsorption (%)	Al adsorption (%)	Mg adsorption (%)
1600 H	91.6	95.9	99.4
S940	89.8	91.3	100
MTS9500	92.5	97.4	100
PPC100H	91.1	95.7	99.7

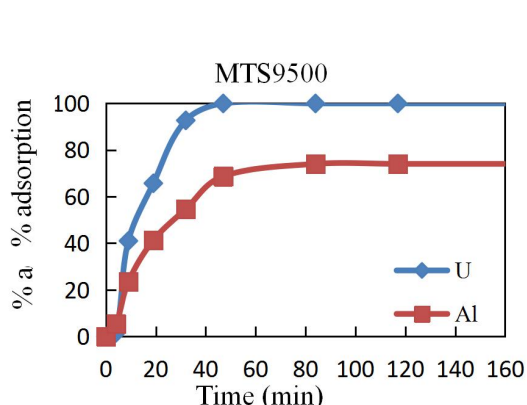
Increasing the pH to 2 showed minor changes, with slight increases on the uranium adsorption and slight decreases on the aluminium adsorption, while magnesium adsorption remained almost similar and is not included in Tables 3. However, there was a noticeable slight increase at pH 3 with all resins reaching 100% adsorption for both uranium and aluminium species (Table 3). This indicated the effect of pH and initial concentrations for both uranium and aluminium. At low pH with higher concentration, the adsorption was about 90% and increases as the concentrations decreased when diluted to pH 2 and 3.

**Table 3.** Adsorption percentages from acidic leach of pH 2 and 3.

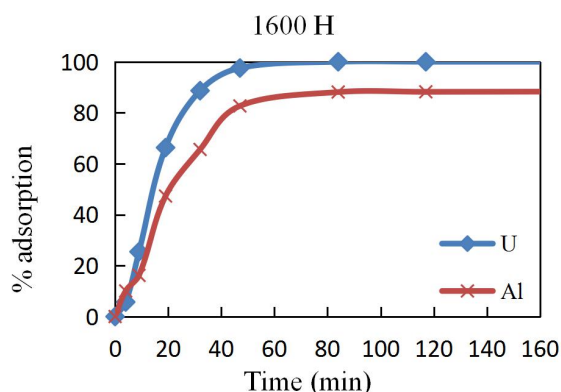
Resin	pH 2 adsorption		pH 3 adsorption	
	U (%)	Al (%)	U (%)	Al (%)
1600H	96	92	100	99
S940	95	98	99	99
MTS9500	100	88	100	99
PPC100H	100	96	100	99

**Figure 1.** Effect of contact time on U and Al adsorption on S940**Figure 2.** Effect of contact time on U and Al adsorption on PPC100H

The influence of contact time with the strong acid cation and chelating resins was determined at pH 1.26 and the study time ranged from 0 to 160 min. The solution contained uranium and aluminium concentrations of 40.46 and 59.25 mg/L, respectively. All resins showed practically similar uranium adsorption, attaining around 70% within the first 20 min. The quickest adsorption (72%) was with S940 (Figure 1), followed by PPC100H (Figure 2) and MTS9500 (Figure 3), while the 1600 H resin was the slowest, attaining 60% uranium adsorption within the same time (Figure 4). A similar uptake was also observed for aluminium adsorption, the adsorption uptake within 20 min varied from 36 to 58%. PPC100H showed the quickest uptake (58%), followed by 1600 H (47%) and MTS9500 (41%). The S940 showed the slowest uptake for aluminium as compared to the other resins.



**Figure 3.** Effect of contact time on U and Al adsorption on MTS9500



**Figure 4.** Effect of contact time on U and Al adsorption on 1600 H

3.2 Alkaline medium adsorption

The concentrations after the alkaline dissolution were 1152 mg/L U, 254 mg/L Al, 226 mg/L Si, and 10 mg/L Mg with a pH of 12.8 and about 80% of the aluminium was removed by the first dissolution. At pH 10, all resins show similar results, with 100% adsorption for the uranium species, predicted as  $UO_2(OH)_3^-$  (Table 4). The aluminium adsorption was also similar with all resins attaining around 93%, and the same for silicon with all resins attaining around 85%. The two resins A500 and MTA5012 were expected to produce similar results due to the similarity in their functional groups and the Cl-form.

**Table 4.** Adsorption from alkaline leach (pH 10) with 20 mg/L U, 10 mg/L Al and 30 mg/L Si.

Resin	U adsorption (%)	Al adsorption (%)	Si adsorption (%)
A500	100	93.4	85.9
MTA5012	100	93.4	85.7
MTA8000PPSO4	100	92.8	82.8

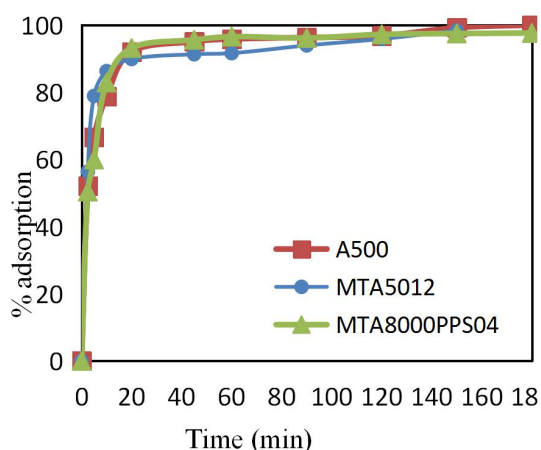
Increasing the pH to 11 and 12 had no significant change on the uranium adsorption for all three resins however; it caused a decrease in the aluminium adsorption. At pH 11 the aluminium adsorption dropped to about 66% for A500, 82% for MTA5012, and 86% for MTA8000PPSO4 (Table 5). A further decrease was observed at pH 12.6 to an average of 32% for all resins (Table 5). The low adsorption of the aluminium species was unexpected, since the  $Al(OH)_4^-$  species was predicted to be stable from about pH 10 to 14. The observation made was that the aluminium adsorption decreases at higher concentrations of both the uranium and aluminium. Thus, at pH 10 with low concentration of both U and Al, a complete uptake of both species was observed, the resins able to adsorb all amounts available. But at high concentrations pH 11 and 12, the aluminium adsorption dropped, suggesting that the adsorption might follow the order of adsorbing uranium species first, and only then aluminium filling the vacant sites.

**Table 5.** Adsorption from alkaline leach (pH 11) with 129 mg/L U, 75 mg/L Al and 58 mg/L Si.

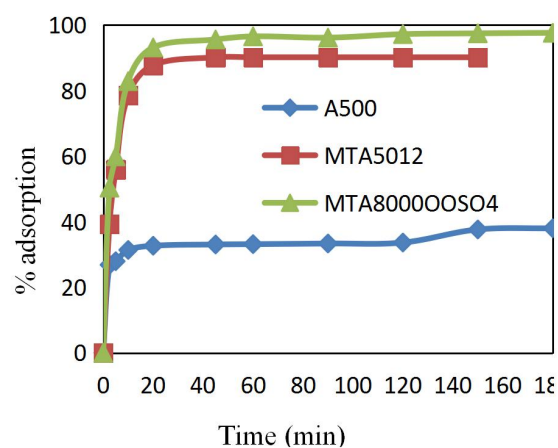
Resin	Adsorption at pH 11			Adsorption at pH 12		
	U (%)	Al (%)	Si (%)	U (%)	Al (%)	Si (%)
A500	100	66.3	75.9	98.7	33.9	39.4

MTA5012	100	82.2	78.0	98.0	32.1	40.7
MTA8000PPSO4	100	86.2	71.3	99.4	30.6	27.1

The influence of contact time in alkaline dissolution was determined at pH 12.6 over a time period of 180 min. The different resins showed similar uptake for the uranium species, adsorbing about 90% within 30 min (Figure 5). The aluminium uptake was similar for MTA5012 and MTA8000PPSO4, both attaining almost 100% over 180 min (Figure 6), while the A500 only adsorbed less than 40%.



**Figure 5.** Effect of contact time upon U and Al adsorption with MTA8000PPSO4



**Figure 6.** Effect of contact time upon U and Al adsorption with A500

#### 4. Conclusions

The obtained results showed that the strong acid cation resins had no distinct selectivity for uranium cations, making it difficult to separate the uranium from the aluminium. The adsorption was also not sensitive to either the pH or the initial concentration of the solution. Full adsorption was obtained for both uranium and aluminium, most likely due to the high capacity of the strong acid cation. The adsorption efficiency would be determined in future work using column experiments.

However, the strong base resins, especially MTA8000PPSO4 and A500 showed good uranium adsorption with less aluminium adsorption at high pH, above 12. This indicated that it could be used with high uranium concentrations and aluminium will not be adsorbed due to a low loading capacity of about 1.6 eq/L. However, another alternative to remove all the aluminium could be further rinsing of remaining residues after the first dissolution step with the NaOH-NaNO<sub>3</sub>. The uranium after adsorption could be eluted using a solution of NaOH, NaCl or sulphuric acid, depending on the resin form. The uranium can then be recovered from the pregnant eluates by precipitation.

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