

Uranium Remediation by Ion Exchange and Sorption Methods: A Critical Review

Various types of solid phase sorbents are studied and evaluated

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The solid phase materials or sorbents applied to the removal of uranium from industrial waste streams and surface waters are reviewed. The speciation of the element in the environment is discussed. A series of examples on uranium remediation from the recent literature using the different kinds of solid phase sorbents are reviewed in detail and evaluated. The criteria for making the best choice of ion exchanger are discussed with suggestions for further evaluation of the described technologies.

1. Introduction

1.1 General Background on the Element

As the world's consumption of energy increases there has been an increased interest in nuclear energy. Uranium is one of the most common elements used in nuclear reactors as well as in weapons and other

military uses. It is the heaviest and most abundant naturally occurring radioactive element, making up 2.4 mg kg⁻¹ of the earth's crust. It can be easily dissolved, transported and precipitated within ground and surface waters by slight changes in the environment. With half-lives of millions to billions of years, uranium atoms slowly break down to a host of radioactive byproducts: thorium-230, radium-226, radon-222 and the radon daughters: lead-210 and polonium-210 (1, 2). For uranium to be used as an energy source, the ore must be enriched to obtain higher concentrations of a particular isotope, ²³⁵U. ²³⁵U is fissionable and releases a large amount of energy in the form of heat but also produces large amounts of radioactive waste. Currently, the spent uranium can only be stored, reprocessed or disposed of underground (3).

U(IV) is stable in reducing environments, is slightly soluble and is the least mobile form of uranium. Uraninite (UO_{2+x}) is the most common reduced mineral species and is the main ore mineral in many uranium deposits (2). U(VI) is stable in oxidising environments and its compounds are the most soluble and therefore the most mobile (4, 5). It can also form complexes with hydroxides, carbonates, sulfates and phosphates (5). Therefore, in the presence of oxygen U(IV) is oxidised to U(VI) which allows the uranium to dissolve in water as the uranyl cation (UO₂²⁺). The dissolution of uraninite is shown in Equation (i).



1.2 Uranium Speciation

Recovery of uranium from surface and ground water waste streams depends strongly on the type of uranium species in solution. Determining the distribution of these species is a complex analytical problem and various extraction techniques are required to determine speciation (6–8). These species can be in the form of colloids or dissolved ions. Extraction is therefore not an ideal method for determining uranium speciation because the process can change the original species present (8). In aqueous environments uranium speciation can be determined by computational modelling and analytically. However, analytical methods remain to be improved. Therefore much of the speciation of uranium is determined by thermodynamic speciation modelling that uses the equilibrium constants or the Gibbs free-equation to arrive at species distribution (8). We present here three Eh-pH diagrams that illustrate the variability of speciation under different environmental conditions.

The speciation diagram for uranium where the total [U] = 1 M is shown in Figure 1 (9). In a reducing environment the major species in solution is neutral UO_2 , over a wide range of pH, making ion exchange useless under these conditions as a method of uranium recovery. This occurs in humic soils. Under oxidising conditions, as in surface waters, the uranyl cation, UO_2^{2+} , is predominant only at very low pH and would be an important species in acid mine drainage, accompanied by hydroxide-bridged cationic uranium cluster species. At higher pH hydrolysis of uranyl leads to the formation of neutral

oxo-hydroxo-species such as $\text{UO}_2(\text{OH})_2$ (Figure 1). Thus in the absence of other coordinating ions ion exchange would be limited for uranium remediation.

At low total [U] the speciation changes drastically. The UO_2^{2+} along with crystalline U_4O_9 are the major species in an oxidising environment up to about pH = 5.5 (Figure 2) (10, 11). Above this pH neutral and anionic hydroxyl complexes are the major species and in reducing environments UO_2 is again the major species. Thus at low [U] the uranyl cation becomes more dominant making cation exchange more useful in the absence of other ligands such as sulfate and carbonate.

In air, with carbon dioxide concentrations of 0.3% the picture changes again. UO_2^{2+} is still the dominant species up to about pH = 5, but above pH = 7 anionic carbonate complexes become important, making anion exchange a viable option (Figure 3) (12). The exceptional stability of these carbonate complexes makes their formation favourable over a wide range of concentrations such as those referred to in Figures 1 and 2. Modelling of these uranium solutions suggests that under reducing conditions UO_2 exists in its hydrated form, shown as $\text{U}(\text{OH})_4$ in Figure 3.

To summarise, because the UO_2^{2+} is a strong Lewis acid it can complex with many different compounds via oxygen atoms especially in natural waters. At dilute concentrations ($<10^{-6}$ M) $\text{UO}_2(\text{OH})^+$ is the dominant hydrolysed species and above this concentration a mixture of $\text{UO}_2(\text{OH})_2$, $\text{UO}_3(\text{OH})_4^{2-}$ and $\text{UO}_2(\text{OH})_5^{3-}$ forms are also observed. In seawater, uranium exists in

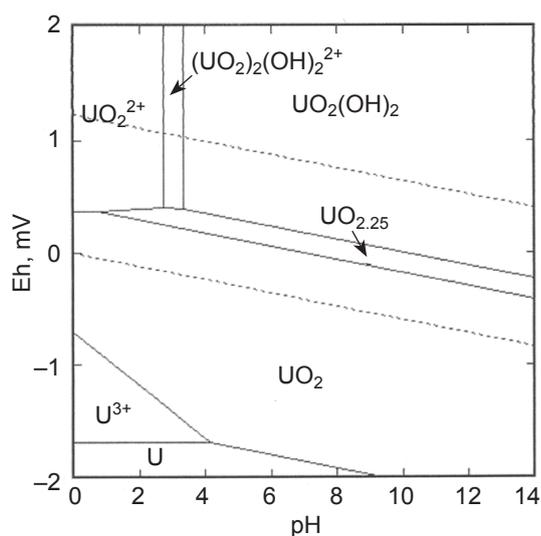


Fig. 1. Uranium Eh/pH diagram for high uranium concentration (total [U] = 1M) (dashed lines represent the zone of stability for water) (9)

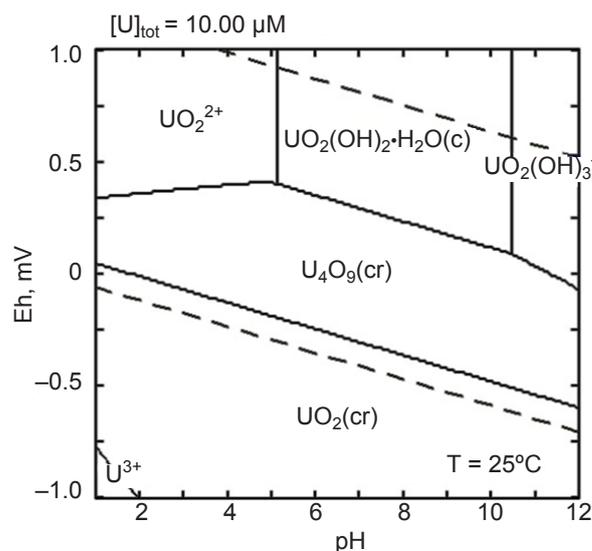


Fig. 2. Uranium Eh/pH diagram for low uranium concentration (total [U] = 10 μM) (dashed lines represent the zone of stability for water) (10, 11)

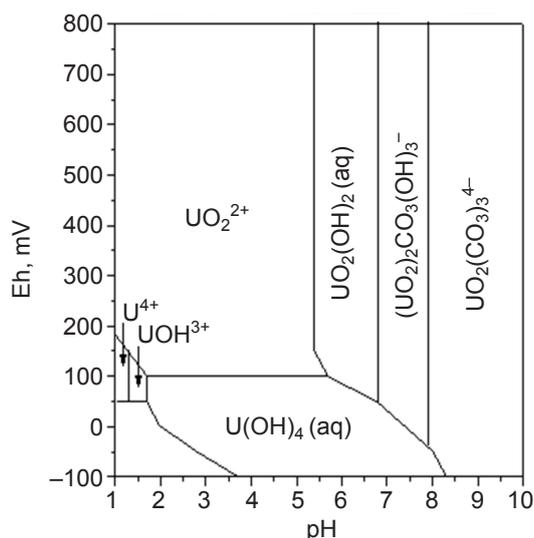


Fig. 3. Uranium speciation in air in the presence of 0.3% carbon dioxide (12)

the form of carbonate complexes, such as $UO_2(CO_3)_3^{4-}$, $UO_2(CO_3)_3^{2-}$ and $UO_2(CO_3)$ (12).

In consideration of the discussion above it is imperative that a detailed study of the environment must be taken into account when considering a U remediation project. This type of sensitivity is not peculiar to U, but is also important for other metals in their higher oxidation states such as manganese, vanadium, molybdenum and tungsten. It should be noted here that that acid mine drainage in general is often characterised by high sulfate which complexes with uranium. These are discussed in Section 2.1. Although 1 M total [U] is never found in waste streams, comparison of Figure 1 with Figures 2 and 3 provides a view towards the sensitivity of uranium to changes in concentration.

2. Examples of Uranium Recovery with Polymer Based Adsorbents

Ion exchange resins based on organic polymers, specifically polystyrene, are by far the most widely used solid phase sorbents for remediation and recovery of toxic and valuable metals. The functional groups used for uranium are varied and include amidoxime on polystyrene and on acrylic based copolymers and fibres (13–15). Most recently, magnetic core-shell particles coated with functionalised polymers have been employed for uranium recovery (16, 17). The three case studies discussed here use commercially available polystyrene resins and focus on the three

types of uranium streams encountered in the industries associated with uranium mining and processing: (i) ore processing; (ii) recovery of uranium from industrial waste; (iii) recovery of uranium from acid mine drainage.

2.1 Recovery of Uranium From Acid Leaches of Ores as Sulfate Complexes

The overall process used for uranium ore enrichment and recovery is given in Scheme 1 and the chemical composition of the ore is given in Table I (18). The ore was leached with $50 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$ and the final pH adjusted to 1.5 with ammonia. At this pH a clear solution was obtained that contained $1.163 \text{ g l}^{-1} \text{ U}$, $1 \text{ g l}^{-1} \text{ Fe}$, 25 ppm V and $0.52 \text{ g l}^{-1} \text{ P}$. 150 mL of ammonia was required to neutralise 4 l of leach solution. The conditions for treating the 4 l of leach by ion exchange are given in Table II.

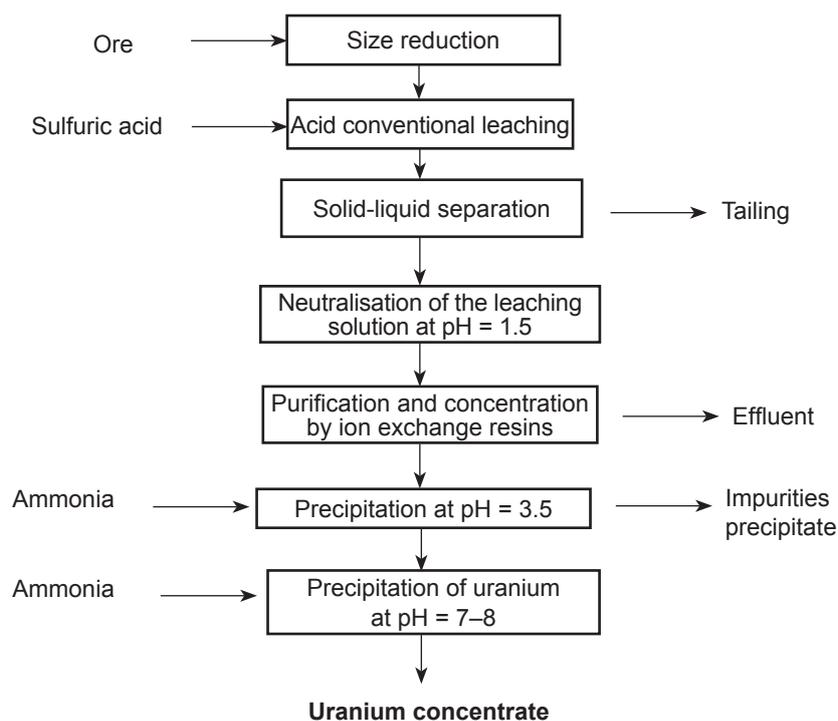
The Type I strong base anion resin, Amberlite® IRA-400, that has a trimethyl ammonium ion on cross-linked polystyrene in the chloride form was used for the ion exchange step. The ion exchange process used to extract uranium from the leaching solution is based on the high binding constants of the anionic sulfate complexes of uranium relative to the anion on the anion exchange resin (chloride) primarily due to their higher negative charge. The uranium is fixed

Table I. Composition of the Uranium Ore (18)

Chemical composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	U	PO ₄
Content, %	65	15	10	0.01	0.2	0.1

Table II. Conditions for Fixation of the Ore Leach on the Ion Exchange Column (18)

Condition, units	Value
Internal diameter of resin column, cm	0.5
Height of resin bed in column, cm	43
Resin volume, ml	20
Flow rate, ml min ⁻¹	2.23
Retention time, min	3.6
Bed volume, ml	20



Scheme I. Stepwise process for concentration and recovery of uranium from an ore (18)

primarily as a 3:1 complex and to a lesser extent as a 2:1 complex (Equations (ii)–(iv)) (19):



The uranium fixation reaction is shown in Equation (v):



where R = resin; X = HSO_4^- ; Cl^- ; NO_3^- .

The major species in solution is the uranyl trisulfate tetra-anion. In principle, this anion will take up four strong base sites and so loading effective concentrations of the feed will be limited. The high charge on this anion also leads to poor stripping. Thus, although the capacity of the resin was high at 67.2 g U l⁻¹ resin, the concentration factor was negative. The final strip solution had 1.0 g U l⁻¹ and was 1.63 g U l⁻¹ solution before ion exchange. Stripping the column required over 200 ml of dilute nitric acid. Anionic ferric sulfate complexes competed with the U sulfate complexes. The percent recovery from the feed was only 75%. The overall process is fairly efficient but the poor capacity of the resin and the large amount of the expensive nitric acid needed for stripping could make

this process noncompetitive with the alternative, solvent extraction (20).

2.2 Recovery of Uranium from Carbonate Solutions of Industrial Waste Streams

Uranium carbonate industrial waste streams from a Brazilian nuclear production plant were treated by an ion exchange process using a Type II strong base anion exchange resin, IRA-910A with a dimethyl 2-hydroxy ethyl functional group (21). The stream needed to be boiled for 6 h to lower the total carbonate concentration before it could be treated. In order for ion exchange to be effective total carbonate concentration has to be <5 g l⁻¹. Table III describes the chemical composition of the waste stream before and after carbonate removal.

The breakthrough and stripping profiles under various loading rates and with different stripping solutions are shown in Figure 4. Flow rate did not have a big effect on breakthrough but stripping with various carbonate solutions did.

The best strip was with 3 M carbonate, which gave a U concentration of 2.7 g l⁻¹, a respectable concentration factor of about 43. Interestingly, the uranium-depleted effluent could be used for the strip and gave a concentration of 2.3 g l⁻¹ after dilution from 2.3 M to 1.3 M carbonate concentration. The final effluent contained <4 mg l⁻¹ uranium which met the plant specifications but is well

above the Brazilian government’s recommended release level of 0.02 mg l⁻¹ (see Table IV). However, it should be pointed out that without further dilution or a polishing step this level of uranium is still highly dangerous from a toxicity point of view, especially if the effluent is discharged into surface waters. The authors did not specify this.

An older report on the removal of uranium carbonate from industrial waste is discussed here as it contains important information on the effect of competing ions and used a more dilute uranium carbonate feed (22). The authors used a strong base anion exchange resin and although they did not specify the exact nature of the resin it is assumed here that it was a Type II resin

Table III. Chemical Composition of the Waste Stream Before and After Carbonate Removal (21)

Analyses	Units	Original industrial effluent	Industrial effluent after carbonate removal
U	mg l ⁻¹	43	63
CO ₃ ²⁻	g l ⁻¹	170.9	4.0
F ⁻	g l ⁻¹	0.35	0.5
NH ₃	g l ⁻¹	78.4	9.0
Fe	mg l ⁻¹	2	3
Na	mg l ⁻¹	<0.1	<0.1
pH	–	10.1	9.7

Table IV. Chemical and Radiochemical Analysis of the Acid Mine Water (23)

Determination	Acid mine water ^a	Permissible level
U	12.0	0.02
Th	0.8	b
²²⁶ Ra	3.5 Bq l ⁻¹	b
Mn	173.0	1.0
Ca	158.0	b
Mg	8.9	b
Al	170.4	b
Zn	41.0	5.0
Fe	180	15.0
SO ₄ ²⁻	1400	b
F ⁻	110	10.0
SiO ₂	57.0	b
pH	2.7	6.0–9.0

^aUnless indicated, units are expressed in mg l⁻¹ (except pH)

^bPermissible level not defined by Brazilian legislation CONAMA 357/2005

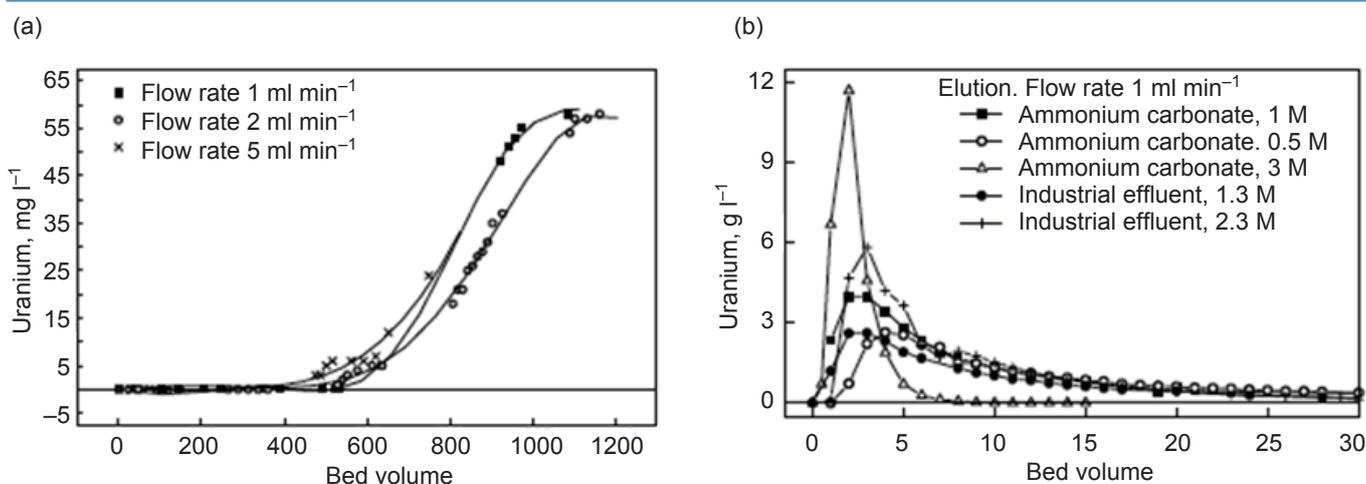


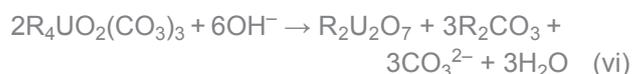
Fig. 4. (a) Breakthrough and (b) elution profiles for uranium recovery from industrial waste (21)

based on the fact that the more recent studies used this type of resin. Two feed solutions were tested. Solution A contained 0.010 M carbonate and comparable amounts bicarbonate, chloride and sulfate as their sodium salts while Solution B contained only 35×10^{-4} M carbonate and both solutions contained 7×10^{-4} M uranium added as $\text{UO}_2(\text{NO}_3)_2$ (Table V).

When tested individually all the ions in Solution A as well as $\text{UO}_2(\text{CO}_3)_3^{4-}$ showed adsorption isotherms that obeyed the Langmuir and Freundlich models starting with the chloride form of the resin. Correlation coefficients were very good, with the Freundlich model showing a better correlation for $\text{UO}_2(\text{CO}_3)_3^{4-}$, 0.99 versus 0.87 for the Langmuir model. These equilibrium studies allowed the establishment of a selectivity order for the competing ions: $\text{UO}_2(\text{CO}_3)_3^{4-} \gg \text{NO}_3^- \gg \text{SO}_4^{2-} \sim \text{CO}_3^{2-} > \text{HCO}_3^- > \text{Cl}^-$ with selectivity coefficients of 537, 98, 7.5, 7.4 and 5.2. The pH at which this order

of selectivity was established was not provided for the equilibrium isotherm studies but maximum loading of $\text{UO}_2(\text{CO}_3)_3^{4-}$ occurs at pH = 6.5–7.0. Table VI shows the pH dependence of uranium loading for Solutions A and B. It can be seen that the presence of competing ions had only a slight effect on uranium loading, peaking at 6.5–7.0 in agreement with the reported selectivity values (Table VI). Subsequent spectroscopic studies suggested that at the optimal loading a portion of the uranium is converted to $\text{U}_2\text{O}_7^{2-}$. The lower charge on this species accounts for the increased loading of uranium at pH = 6.5–7.0.

Although uranium loading showed a clear maximum at pH = 6.5–7.0 stripping with neutral salts such as NaCl or NaNO_3 only recovered ~60% of the uranium loaded at this pH. Stripping with additional ethanol or HCl did not recover any significant amounts of uranium. Stripping with $\text{Na}(\text{NO}_3)$ was very efficient for columns loaded at pH = 9, but loading was much lower at this pH (Table VI). The authors did not consider using a carbonate leach at high pH as suggested by the observed selectivity coefficients and by the equations governing the conversion of $\text{UO}_2(\text{CO}_3)_3^{4-}$ to the apparently nonexchangeable $\text{U}_2\text{O}_7^{2-}$ in the resin phase (Equation (vi)):



where R = resin site.

Overall taking the two studies together, it would appear that loading at pH = 6.5–7.0 and stripping with

Table V. Composition of the Feed Solutions and Column Configuration (22)

Run	Solution components, mol l ⁻¹				pH
	Na ₂ CO ₃	NaHCO ₃	NaCl	Na ₂ SO ₄	
A	0.010	0.025	0.015	0.010	3.0–9.0
B	35.70×10^{-4}	–	–	–	5.0–9.1

Concentration of uranium: 7.14×10^{-4} mol l⁻¹ $\text{UO}_2(\text{NO}_3)_2$.
Column configuration: ID = 0.8 cm, length = 10 cm. Resin weight = 0.5 g

Table VI. pH Dependence of Uranium Loading for Solutions A and B (22)

	Uranium loading capacity from composition of A at different pH values								
	pH								
	3.0	4.0	5.0	6.0	6.5	7.0	8.0	9.0	
mg U g ⁻¹ dry resin	199	223	271	370	352	235	183	171	
Relative loading capacity	1.16	1.30	1.58	2.16	2.06	1.37	1.07	1	
	Uranium loading capacity from composition of B at different pH values								
	pH								
	5.0	6.0	6.5	7.0	7.5	8.0	9.1		
mg U g ⁻¹ dry resin	49	300	398	423	392	188	179		
Relative loading capacity	0.27	1.68	2.22	2.36	2.19	1.05	1		

carbonate at pH >9.0 would be the best approach, even in the presence of significant amounts of competing ions.

2.3 Removal of Uranium from Acid Mine Drainage using Strong Base Ion Exchange Resins

This study compared the effectiveness of Type I (Dowex™ Marathon™ A) with Type II (Amberlite® IRA-410u) strong base resins (Figure 5) for the removal of uranium from high sulfate acid mine drainage (23). Table IV shows the chemical and radiochemical profile of the waste stream. The uranium is present as sulfate complexes and considering the large excess of sulfate and the low pH the major species in solution is likely $UO_2(SO_4)_3^{4-}$ (Equations (ii)–(iv)). The other ions in solution are present as cations except for sulfate, silicate and fluoride which have lower negative charges but could compete with the $UO_2(SO_4)_3^{4-}$. Column experiments were performed on 5.0 ml volumes of each resin at pH values of 2.7 and 3.9 in a 1.2 cm ID column at a flow rate of 24 BV h⁻¹ (Figure 6). The Type II resin IRA-410u performed significantly better than Dowex™ A (Table VII). Both resins performed at only about 40–60% of their theoretical value (1 equiv. g⁻¹ for IRA-410u and 1.3 equiv. g⁻¹ for Dowex™) probably because of the interference of other anions. However, the authors were unclear about whether these theoretical values took into account the higher negative charges on the sulfate complexes. Performance was slightly better for both resins at the higher pH. Sulfate and fluoride levels were monitored and revealed that indeed sulfate does compete but fluoride does not (Figures 7(a) and 7(b)).

The authors report an economic analysis of the uranium recovery based on the adsorption data. However, this is meaningless in the absence of elution

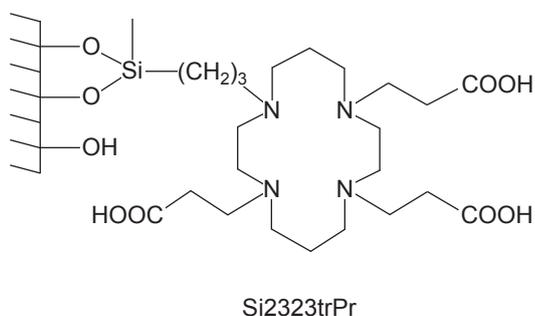


Fig. 5. Structure of the silica bound cyclam ligand (41)

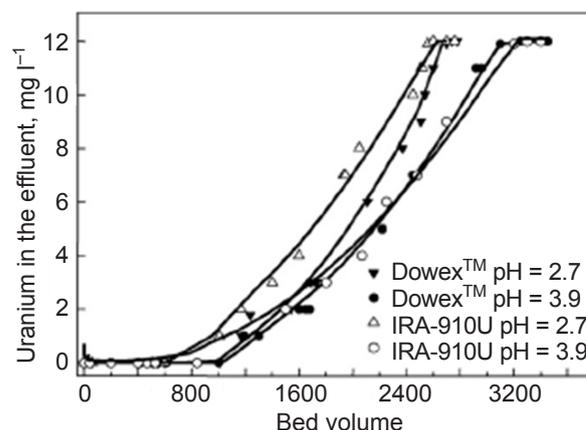


Fig. 6. Adsorption profile for uranium on the two strong base resins. Flow rate = 2.0 ml min⁻¹, bed volume = 5.0 ml, 24 BV h⁻¹ (23)

Table VII. Maximum Loading Capacities and Distribution Coefficients for Uranium (23)

Resin	K _D , ml g ⁻¹		Q _{max} , mg U g ⁻¹ resin	
	pH 2.7	PH 3.9	pH 2.7	pH 3.9
IRA-910U	6667	6887	100	108
Dowex™ A	5889	6435	72	79

data, especially in light of the poor stripping reported for the sulfate complexes above (21). The value of this study is the demonstration that Type II resins work better than Type I strong base resins and that unbound sulfate competes with the uranium sulfate complexes. No cycle testing is provided. In the absence of this data the scale up analysis reported in the paper is of little value.

3. Uranium Removal Materials Based on Silica and Other Inorganic Matrices: Overview

In the past 20 years there has been considerable development in the area of silica gel based chelator materials for metal ion removal and recovery. This is due, in part, to the development of new methods for synthesising silica gels but also because silica gel offers some advantages over the widely used and highly developed polymer based materials (Section 2). Silica gel does not shrink or swell with changes in pH or temperature and has a hydrophilic surface that affords faster mass transfer kinetics (24).

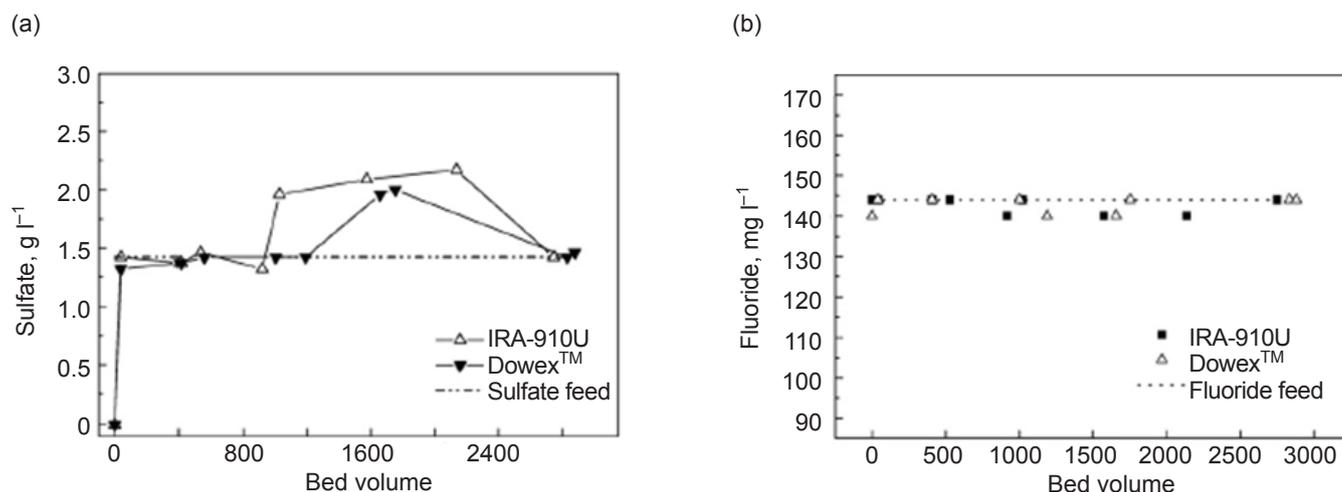


Fig. 7. (a) Sulfate comes through at the feed concentration up to 900 BV and then increases indicating sulfate adsorption in competition with U; (b) fluoride comes through at the feed level all the way through indicating no adsorption (23)

On the other hand, strong alkali degrades silica while polystyrene is quite stable at high pH. In general, polystyrene shows more resistance to mechanical shock but has a higher cross section for neutron capture limiting its use for actinide separations and recoveries. Each matrix has its advantages and disadvantages and these will be summarised later in this review.

Silica gels used as solid phase sorbents are of two general types, amorphous silica gels and mesoporous silica gels. Amorphous silica gels are made by the fusion of sodium carbonate and silicates at high temperature (~1100°C) to produce sodium silicate (water glass), which is dissolved in water and then reprecipitated with acid under carefully controlled conditions. The porosity, particle shape and size are very sensitive to the precipitation conditions and subsequent curing. The conditions for precipitation used in industry are

proprietary. The silica gels available commercially for use as solid-phase sorbents can be made in a wide range of particle sizes (25–500 µm) and all have high porosities and surface areas. Table VIII illustrates the physical properties of the midrange particle sizes available from different suppliers (24). Amorphous silica gels can also be made as nanoparticles (25). As expected, these have much lower porosities but higher total surface areas. Amorphous silica gels can also be made by the sol-gel route using siloxanes (Si(OR)₄) and functionalised siloxanes (SiR(OR)₃) that provide direct functionalisation of the surface (26). This approach offers more control over pore-size distribution, a parameter that can affect the uniformity of mass transfer kinetics in ion exchange applications. The sol-gel method can afford much narrower pore size distributions (26). Most recently, it has been shown

Table VIII. Physical Properties of Commercially Available Amorphous Silica Gels (24)

Supplier	Diameter, mm	Pore diameter, Å	Pore volume, ml g ⁻¹	Porosity, %	Surface area, m ² g ⁻¹
Crosfield	90–105	267	2.82	84.7	422
Qingdao Haiyang	150–250	194	2.39	85.0	493
Qingdao Meigao	180–250	378	2.86	85.3	303
Nanjing	180–250	164	2.30	85.8	561
Nanjing Tianyi	80–250	150	2.28	85.6	526

that rice hull ash can be converted to amorphous silica gel by simply extracting the material with 1 M sodium hydroxide and then precipitating with acid. The resulting gel can be converted into useful solid phase sorbents but lack the mechanical strength of the commercially available amorphous gels (27).

Mesoporous silica gels differ from amorphous silica gels in that they are ordered phases made by the sol-gel method using a templating agent, usually a detergent such as cetyl ammonium bromide (28) or more recently block copolymers containing hydrophilic and hydrophobic segments (29). The block copolymers provide the option of removing the template by solvent extraction while the ionic detergent requires calcination at 400–500°C. Both methods provide highly ordered phases of nanoparticles with pore diameters in the 2–10 nm range with very high surface areas (>700 m² g⁻¹) and good mechanical strength. Commercially available mesoporous silica gels are marketed by many suppliers as MCM-41 and SBA-15, which differ slightly in their physical properties. Because these mesoporous silica gels are made by the sol-gel method they offer the opportunity of direct surface functionalisation using Si(OR)₄ and SiR(OR)₃ (26, 29).

For the purposes of uranium recovery and remediation the cheaper more porous amorphous silica gels are probably a better choice than the mesoporous gels, while for catalysis the higher surface area and more mechanically strong mesoporous materials, and the related zeolites, are a better choice. In comparing the silica matrix with the polymer based materials described in Section 2, the latter have seen a much wider use, but as described at the beginning of this section silica gel offers some distinct advantages.

3.1 Commercially Available Silica Based Ion Exchange Materials

Steward Advanced Materials, USA, offers Self Assembled Monolayers of Mesoporous Silica (SAMMS[®]) functionalised with 3-propane thiol for gold, silver and mercury recovery. The ordered silica pores are very small but form a high surface area-ordered material. The silica matrix is made using a detergent template followed by calcination. These materials were developed at Pacific Northwest Labs by the group of Glen Fryxell and have been used in a variety of metal capturing applications, including uranium that will be discussed in Section 3.3.2. The materials show high capacity but are difficult to strip and are expensive to produce. This material has not seen widespread use in

the base metals industry. There are many studies on their use for actinide metal recovery, but none on the commercial scale.

IBC Advanced Technologies, USA, makes both polystyrene and silica based materials modified with macrocyclic ligands that are highly selective for a given metal. The ligands work on so-called molecular recognition technology (MRT) and are based on size selectivity rather than covalent binding constants. They are quite expensive but according to their website this technology has seen a wide range of applications in the mining industry. The company has presented the results of these projects at numerous conferences but access to the actual data is limited and their product web pages come up blank.

SiliCycle Inc, located in Quebec, Canada, markets a selection of metal scavenging agents based on silica gel modified with propyl groups bearing a purportedly selective metal scavenging agent. Ligand loadings vary from 0.3 to 1.2 mmol g⁻¹, slightly lower than related polymer based materials. They have lower bulk densities than polystyrene sorbents similar to silica polyamine composites (SPC) (*vide infra*). Pore size is quoted at 6 nm, in the same range as that reported for both amorphous and mesoporous silica gels with particle sizes in the range of 40–60 μm. The website does not provide metal capacities or longevity data for the materials. The website offers quantities of up to 500 g but states that bulk quantities are available. These amino propyl resins (SiliaBond[®] Amine) do not stand up well to repeated use and the EDTA modified propyl silanes (SiliaMetS[®] Triaminetetraacetic Acid (TAAcOH)) actually lose capacity with increasing pH (30). Finally, all of these products list very general metal selectivity according to the website without any quantitative data on preferences within mixtures. Metals are listed as scavengers or preferred scavengers. No uranium selective adsorbents are listed on the website. The main application of these materials is most likely the removal of excess metals after a bench scale chemical reaction.

Johnson Matthey Plc is currently developing a series of silica polyamine composites (SPC) that use a chloropropyl/methyl silane mixture to modify an amorphous silica gel surface that is subsequently treated with polymeric amines, and then further modified with metal selective ligands (31, 32). The polyamine surface is much more robust than the aminopropyl modified surface in that the multipoint anchoring provides a more stable composite surface and elevating the metal

capturing ligand away from the surface eliminates ligand interactions with the surface. This group of sorbents has been extensively compared with polystyrene analogues and offer distinct advantages. Separations are sharper as a result of better column utilisation factors, no shrink-swell during pH changes and lower bulk densities (33). Functionality is available over a range of metal selective ligands, including analogues of the strong base resins (34, 35) and amino phosphonic acid groups that have been applied to uranium remediation (*vide infra*) (36). These materials have been employed on a large scale by the mining industry for remediation and recovery of transition metals.

3.2 Silica Based Hybrid Materials for Uranium Recovery

The literature is full of sorbents based on mesoporous and amorphous silica gels. Their surfaces allow a wider degree of functionalisation relative to organic polymers because the silanisation step offers an almost infinite choice of functional groups that can be further modified (37–39). Here, we have chosen representative examples of inorganic and hybrid materials that have been specifically designed for uranium recovery from waste streams.

3.2.1 Uranium Recovery with Chelator Ligands Bound to Amorphous Silica

Murexide is a commonly used organic indicator that changes colour on complexation with metals. Recently, this commercially available ligand has been bound to silica gel and has shown a high affinity for uranyl ion and for thorium (Scheme II) (40). These investigators used acid-activated amorphous silica (6 nm pore diameter, 63–212 μm). The resulting murexide composite showed very good capacities for uranyl ion over a wide pH range with a maximum batch capacity of 1.13 mmol g^{-1} at pH = 5.5. Flow capacities of $\sim 0.5 \text{ mmol g}^{-1}$ were realised at relatively rapid flow rates of 10 ml min^{-1} . The

material could be regenerated efficiently with 0.1 M HCl but no cycle testing is reported and the actual loading of the murexide ligand is not reported. This could have been easily done by nitrogen analysis before and after reaction of murexide with the amino propyl modified silica. The most appealing aspect of this new ligand is its high degree of selectivity for uranyl ion. It shows exceptionally high selectivity values for uranium *versus* other anions and cations (selectivities of 70–1000) with only Zr^{4+} and Th^{4+} and the anions VO_3^{3-} , PO_4^{3-} and $\text{C}_2\text{O}_4^{2-}$ causing significant interference (Table IX).

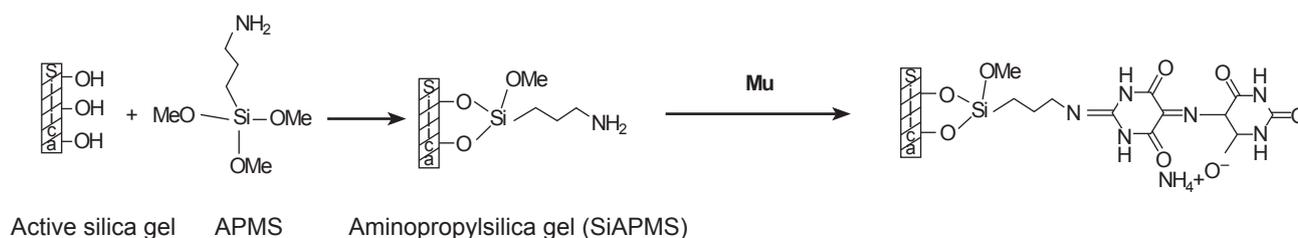
Another class of ligand that has shown excellent properties for uranyl ion recovery are the carboxylate modified cyclams bound to silica (Figure 5) (41). The silica gel used was Kieselgel 60 (bead size 0.2–0.5 mm, 35–70 Mesh, specific area 550 $\text{m}^2 \text{g}^{-1}$).

These composites were made by either adding the cyclam to a 3-chloropropyl group on silica followed by reaction of the remaining three N atoms with an acrylic acid or by preassembly of the trimethoxysilyl-tris-acrylate ligand to the chloropropyl surface.

Table IX. Tolerance for Competing Ions for the Murexide Modified Silica Gel (40)

Foreign ion	Tolerance limit ^a
K^+ , Cl^- , Na^+ , NO_3^- , CH_3CO_2^-	>1000
I^- , SO_4^{2-} , Cd^{2+} , Tl^+ , Mg^{2+} , Ca^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+}	1000
La^{3+} , Ce^{3+} , Al^{3+} , MoO_4^{2-} , Cs^+	100
Fe^{3+} , Co^{2+} , Zn^{2+} , Cr^{3+}	70
VO_3^- , PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$	7
Th^{4+} , Zr^{4+}	2

^aThe concentration ratio of the foreign ions to the U(VI) ions



Scheme II. Protection and binding to silica of the HOPO ligand (40)

Different cyclams were grafted to silica gel and the best performance was obtained with the cyclam shown in **Figure 5**. As expected from the Eh-pH diagrams (**Figures 1 to 3**) in the introduction the highest uranium capacity was obtained at pH = 4–5 (dynamic $K_d = 158 \text{ ml g}^{-1}$ at pH = 4). This study reports regeneration studies with very little loss in capacity over nine load regeneration cycles, with typical loadings of $0.25 \text{ mmol UO}_2^{2+} \text{ g}^{-1}$ gel. However, the stripping kinetics were poor; even though complete recovery was realised in the nine cycles, large volumes of 2 M nitric acid were required.

A schematic diagram for a continuous extraction of uranium in the presence of other actinides is shown in **Figure 8** and used two 12 l columns one loaded with unmodified silica gel for use as a pre-filter and the second loaded with the cyclam modified silica. This system was used to capture a mixture of U, Am and Pu at concentrations typical for radioactive waste. All three metals were removed to below detection limit.

Interestingly, the distribution coefficient almost doubles on going from 298 K to 353 K. This may be characteristic of all amorphous based silica gels as it has been observed with related silica polyamine composites (42). Overall, this study is the most complete evaluation of a solid phase uranium adsorbent and lacks only selectivity studies relative to other ions that are associated with uranium waste streams.

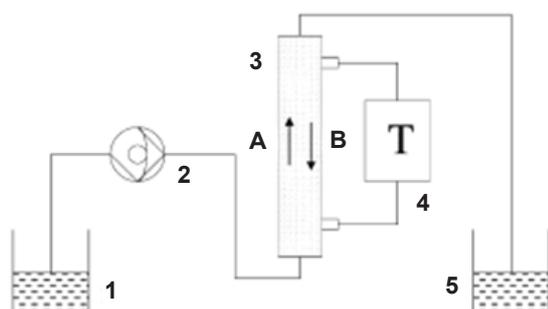


Fig. 8. Schematic drawing for continuous extraction experiments: 1 contaminated solution (A) or concentrated solution (B); 2 peristaltic pump; 3 column filled with silica gel-bound macrocycles; 4 thermostated jacket; 5 decontaminated solution (A) or 2 N nitric acid solution (B) (41)

A silica polyamine composite modified with an amino phosphonic acid functional group has been used to selectively recover uranium from a mock solution that profiles the acid mine drainage found in the gold mine tailing around Johannesburg, South Africa (43). The previously reported polyamine composite, BPAP, is schematically represented in **Figure 9** (36). Amorphous silica with a 180–250 μm particle size distribution, a 38 nm average pore diameter and a $303 \text{ m}^2 \text{ g}^{-1}$ surface area was used for this study.

The mock solution was run through a 5 ml column with a flow rate of 1.0 ml min^{-1} at pH = 2.5. The mock solution contained 175 mg l^{-1} Fe, 55 mg l^{-1} Zn, 18 mg l^{-1} Ni, 81 mg l^{-1} Co, 78 mg l^{-1} Mn, 123 mg l^{-1} U, 41 mg l^{-1} Cu, 195 mg l^{-1} Ca and 82 mg l^{-1} Mg. After 15 bed volumes (75 ml) were passed through the solution, all the metals except Fe and U reached their feed concentrations. Stripping with 2 M H_2SO_4 was not effective but stripping with 2 M Na_2CO_3 removed all of the uranium along with some of the Fe and Ca. The strip solution contained only minor amounts of the divalent transition metals and the Fe and Ca could be precipitated as their hydroxides and carbonates by subsequent pH adjustment. Thus, the divalent transition metals mainly passed through the column but Fe^{3+} and Ca^{2+} co-loaded with UO_2^{2+} . On stripping with carbonate all of the uranium is removed as soluble $\text{UO}_2(\text{CO}_3)_n^{m-}$ ($n = 2, 3; m = 2, 4$) complexes. The wt% uranium is increased from 17% in the feed to 45% in the strip (**Figure 10**).

For this process to be useful the remaining Fe^{3+} and Ca^{2+} must be removed to fully regenerate the column. This could be done with EDTA as has been previously shown (44). The valuable aspect of this report is that the BPAP can be used to effectively separate uranyl cation from divalent transition metal ions.

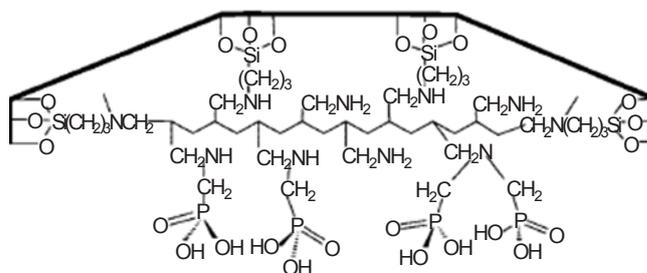


Fig. 9. Schematic representation of the amino-phosphonic acid modified silica polyamine composite, BPAP (36)

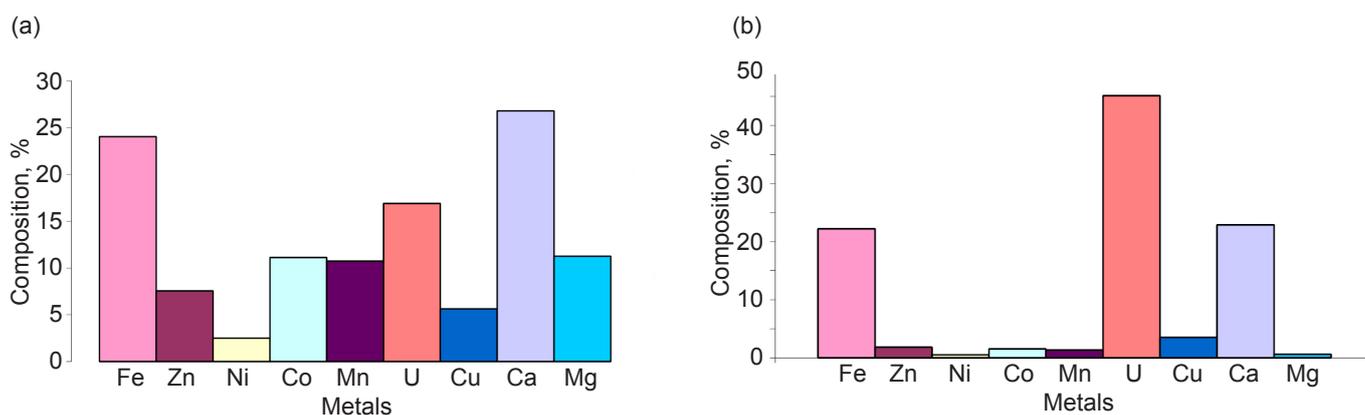


Fig. 10. (a) Composition of acid mine drainage mock solution; and (b) composition after loading and carbonate stripping on BPAP column (43)

3.3.2 Uranium Recovery with Chelator Ligands Bound to Mesoporous Silica

A recent study surveyed the effectiveness of variously functionalised MCM-41 mesoporous silica gels (75–250 μm particle size, 480 $\text{m}^2 \text{g}^{-1}$, 7 nm pore diameter) and compared them with polystyrene chelator resins having the same functionality and with various forms of MnO_2 (45). Three functional groups were tested: sulfonic acid (SCX), iminodiacetic acid (IDAA, referred to as EDTA in the Tables) and 3,4-hydroxypyridinone (HOPO–) (Figure 11). Ligand loadings were 0.67, 0.29 and 1.3 mmol g^{-1} respectively, using $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{R}$ (R = functional group) procedures.

These modified SAMMS[®] were compared with two polystyrene resins: a strong base anion exchange resin (SAX) and Chelex[®] 100 (EDTA, actually IDAA),

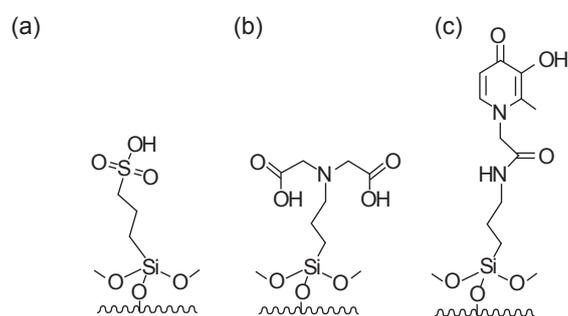


Fig. 11. Surface functionalities synthesised on nanoporous silica and tested for this study. The functional groups are: (a) sulfonic acid (SCX); (b) iminodiacetic acid (IDAA); (c) 3,4-hydroxypyridinone (HOPO) (45)

two different mesh sizes of MnO_2 (70–200 μm and $<5 \mu\text{m}$) and MnO_2 adsorbed onto a polystyrene sulfonic acid resin.

The materials were used as sorbents for the radioactive isotopes of actinide and lanthanide elements present in trace amounts in seawater (3 pbb for U) and the Columbia River (~70 pbb for U). Experiments were conducted in batches (for example, lanthanides together with other isotopes: ^{234}Th , ^{237}Np , ^{233}Pa and ^{233}U) and determined using either gamma emission or liquid scintillation. Standard solutions were used and compared with the data from Columbia River water and Galveston Bay water in order to evaluate the contribution of organics and other ions to the observed distribution coefficients. Samples were counted until the counting error of the fitted peak area was less than 10%, which typically required counting times on the order of 102 to 103 min. The activity of each analyte was used to determine a mass-weighted distribution coefficient (K_D , l kg^{-1}), Equation (vii):

$$K_D = \frac{A_S}{A_W} \frac{V}{m} \quad (\text{vii})$$

where A_S is the total activity of the isotope retained in the sorbent, A_W is the total activity remaining in solution, V is the volume of the batch experiment (50 ml), and m is the mass of sorbent in kg.

Distribution coefficients are reported for all six of the isotopes in the standard solutions for each adsorbent in both the river water and seawater. There are relatively small differences between ions but the big differences are between the adsorbents and type of water. We discuss only the data for uranium here (Table X).

Table X. Uranium Distribution Coefficients^a (45)

Sorbent	Columbia River water	Galveston Bay seawater
Blank silica	4.0 ± 0.02	3.4 ± 0.02
SCX-SAMMS [®]	4.0 ± 0.02	2.9 ± 0.03
SAX resin	5.3 ± 0.2	3.7 ± 0.02
Chelex [®] 100 resin	5.2 ± 0.1	3.1 ± 0.02
EDTA-SAMMS [®]	4.1 ± 0.1	2.9 ± 0.02
HOPO-SAMMS [®]	5.2 ± 0.04	4.8 ± 0.05
MnO ₂ in resin	6.1 ± 0.4	2.0 ± 0.1
MnO ₂ 60–200 mesh	<1	<1
MnO ₂ < 5 μm	5.1 ± 0.1	3.0 ± 0.02

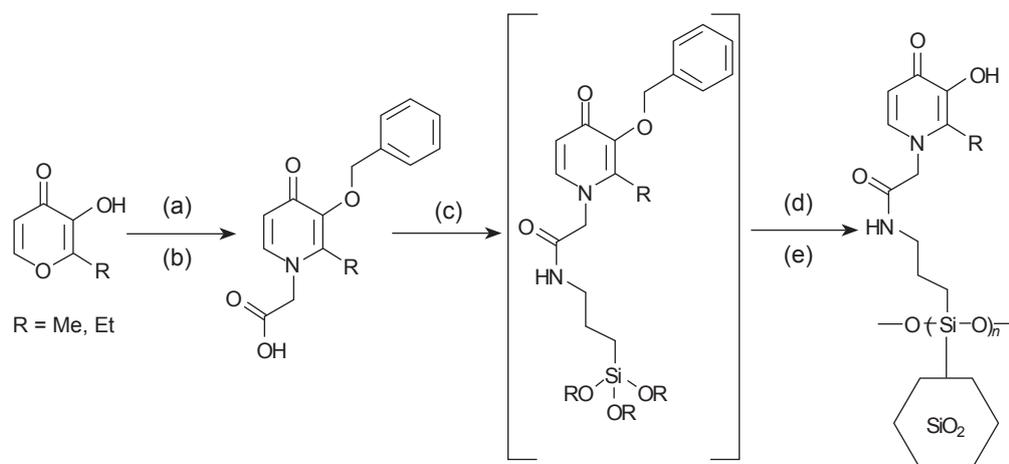
^alog K_D, ml g⁻¹

The biggest difference in log K_D is between the two water sources, where the values are much lower for the bay water than for the river water by about two orders of magnitude on average. This suggests there are more interfering ions in the seawater and is a very valuable contribution. Between the different sorbents, the polystyrene sulfonic acid with MnO₂ (SCX-MnO₂) was by far the best for the river water and the worst for the seawater, pointing to the affinity of this adsorbent for a

wide variety of cations. The IDAA (EDTA) chelator worked better on the polystyrene than on the SAMMS[®] and the SCX SAMMS[®] is no better than blank silica. HOPO SAMMS[®] showed the best all around performance for both river water and seawater. Most interesting is that the anion exchange resin performed relatively well for both samples but the authors ignored this in their conclusion, as well as a detailed discussion of solution pH. Given the complex nature of uranium speciation this was a significant fault with this otherwise elegant and informative study. More work needs to be done to evaluate saturation capacities and the stability of the sorbents.

A recent report from the group that pioneered the development of SAMMS[®] compares the performance of the mesoporous phase MCM-41 with amorphous silica gel for loading of the HOPO ligand or a benzyl protected HOPO ligand and subsequent uranium capture (**Scheme III**) (46).

It was thought that protection of the phenolic OH would improve the efficiency of the coupling step between HOPO and the aminopropyl silane. Two different types of silica were used for these experiments, a surfactant templated mesoporous silica MCM-41, and an amorphous, chromatographic silica (Davisil[®] 634 and 635, Aldrich). The batch of MCM-41 has a specific surface area of 800 m² g⁻¹, an average pore size of 3.5 nm (very uniform pore size distribution), and a pore volume of 1.29 cm³ g⁻¹. The smaller pores of MCM-41 are more easily crowded during monolayer deposition, but the very high surface area of this support suggests that it might be possible to get a higher functional loading in the SAMMS[®] made using this support.



Scheme III. Synthetic steps for binding the HOPO ligand to silica gels (46)

Also, the highly uniform pore size distribution makes it possible to monitor dimensional changes in pore size with each reaction. The amorphous Davisil[®] silica gels used had specific surface areas of 480 m² g⁻¹, and an average pore size of ~6.0 nm (broad pore size distribution, up to ~20.0 nm), and a pore volume of 1.67 cm³ g⁻¹. The difference between Davisil[®] 634 and 635 is their granulation – Davisil[®] 634 has 75–150 μm particles (100 to 200 mesh), while Davisil[®] 635 has 150–250 μm particles (60–100 mesh). The larger pores of the Davisil[®] silica make this support more amenable to making monolayers with large bulky ligands, like the benzyl-protected HOPO ligands.

The authors experimented with the impact of different methods of cleaving the protecting group and found that this had little effect on mass weighted K_D using the usual formula (47). The type of medium (blood, plasma, river water) had a major effect on the efficiency of U(VI) with the highest being the more homogeneous river water (Table XI).

The most important result of this study is that the amorphous silica gel performed better in every medium and regardless of the method of deprotection. Even without using the protecting group the amorphous silica-HOPO performed better than the protected MCM-41-HOPO. This makes an important point with regard to silica adsorbents and remediation. Porosity, not uniformity is the key property for a good solid phase sorbent. Less porous ordered phases are better suited to structural investigations and catalysis where they give better resolution of the environment and better stereoselectivity.

A different approach, using functionalised polymers adsorbed onto ordered silica phases has been reported (48). An ordered nanoporous silica (MSU-H) with a hexagonal array structure that has a specific surface area of ~700 m² g⁻¹ and nanopores of ~4 nm in average diameter was used in the study. Three common polymers: poly(ethyleneimine), carboxymethyl, poly(ethyleneimine) and polyacrylic acid were used in the study. The silica gel was activated by treatment with hydrochloric acid and then the polymers were mixed with the gel for a set period of time. After washing and drying the polymer-silica composite was exposed to solutions of uranyl ion of various concentrations. Very poor distribution coefficients are reported (~10²) for all three polymers and most importantly, 15% of the uranium leached off the material after one day. No stripping data is reported and it is likely that the polymer would have desorbed with any reagent that was capable

Table XI. The Effect of Cleavage Method of the Benzyl Protecting Group, the Type of Silica Used and the Adsorption Medium on the Distribution Coefficient for U(VI) with HOPO Modified Surfaces (46)

Silica	Cleavage method	Matrix	K_D
MCM-41	Old ^a	Buffer	>100,000
MCM-41	Old	Blood	7000
D-634	None (Bz ether)	River water	5800
D-634	Old	River water	10,000,000
D-634	Old ^c	River water	100,000,000
D-634	New ^d	River water	100,000,000
D-634	New	Blood	55,000
MCM-41	New	Plasma	32,000
MCM-41	New	Blood	6100
D-635	Unprotected	River water	>10,000,000
D-635	Unprotected	Plasma	10,000
MCM-41	Unprotected	Plasma	12,000
MCM-41	Unprotected	Blood	8900

^a18 h at 25°C, ^bReference (58), ^c4 days at 25°C,

^dNew = 50–60°C for 18 h

for recovery of the uranium. This report is presented here as an example of what does not work for designing a solid phase sorbent for uranium.

3.4 Layered Sulfide Materials for Uranium Capture

An entirely different type of sorbent based on layered sulfides is reported here for comparison with the more developed polymer and silica based sorbents discussed so far. Very recently, the layered sulfide material, K₂MnSn₂S₆ (KMS-1) has been shown to be an effective ligand for Rb⁺, Cs⁺ and UO₂²⁺ (49, 50). The metal ions exchange for potassium that sits between layers of MnS₆ (0.32 occupancy) or SnS₆ (0.68 occupancy). The exchange is driven by the greater affinity of the larger cations for the soft sulfur atoms on the surface of each

layer. In the case of UO_2^{2+} the rod-like shaped ion lies horizontally between the layers in order to directly interact with the S atom (Figure 12).

The material can reduce uranium levels from a variety of sources over a wide range of pH to very low levels, even in the presence of other cations (Table XII). In most cases 98–99% of the uranium is removed and an average of 84% where other cations are present at very high levels.

Thus, KMS-1 is very effective for removal of trace levels of U from real-world water samples. KMS-1 is:

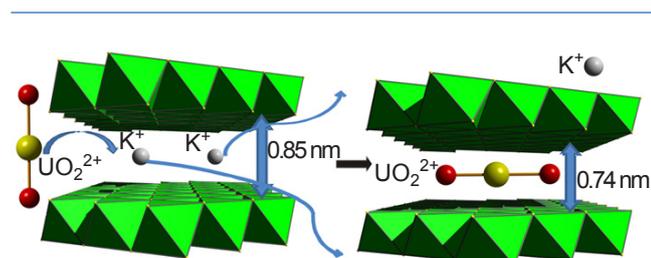


Fig. 12. Proposed mechanism for displacement of K^+ by UO_2^{2+} (49, 50)

(a) inexpensive and easy to make (51), (b) very stable in the atmosphere and water, (c) highly selective for UO_2^{2+} with very fast sorption kinetics, (d) easily regenerated with 2 M $\text{Na}_2(\text{CO})_3$, an affordable and environmentally friendly method, and (e) reusable for at least six cycles. The material lost about 40% of its capacity after the first regeneration cycle but then remained constant for remaining five. It represents one of the most promising solid phase adsorbents for efficient and cost-effective treatment of wastes and groundwater containing highly toxic U levels. For removal of low levels of uranium it stands out relative to the other adsorbents discussed in this review, but it would not be suitable to an industrial or mining environment where much higher levels of uranium must be processed and where a 40% loss in capacity after one cycle is not acceptable.

4. Concluding Remarks

This review focused on the application of the two main types of solid phase adsorbents used for uranium

Table XII. Removal of UO_2^{2+} by KMS-1 from Various Water Sources (49)

Sample	pH	Adsorption, ml g^{-1}	U concentration, ppb		Removal, %
			Initial	Final ^a	
Distilled water, 0.34 M NaCl	3	1000	2500	12–22	99.1–99.5
Distilled water, 0.15 M NaNO_3	6.5	1000	3250	103–128	96.1–96.8
Potable water ^b	7	100	36	0.5–0.7	98.1–98.6
Lake Michigan water ^c	7.3	100	34.2	0.9–1.1	96.8–97.4
Contaminated seawater, Gulf of Mexico	8.2	16–50	1308	1.2–6.5	99.5–99.9
Contaminated seawater ^d , Pacific Ocean	8.2	20–50	1278	1.1–2.0	99.8–99.9
Contaminated seawater, Gulf of Mexico	8.2	100	39	5.3–8.5	78.3–86.5
Original seawater ^e , Gulf of Mexico	8.2	100	3.8	0.6–0.9	76.3–84.2

^aRange of concentrations obtained from three different experiments

^bPotable water as found in Evanston, IL, contains 10.7 ppm of Na^+ , 32.9 ppm Ca^{2+} , 8.5 ppm Mg^{2+} , 7 ppm K^+ , and other ions of insignificant concentrations

^cWater samples from Lake Michigan, Evanston, IL, contain 20 ppm Na^+ , 24 ppm Ca^{2+} , 8.8 ppm Mg^{2+} , 2.7 ppm K^+ and other ions of insignificant concentrations

^dThe cations with the highest concentrations in these seawater samples were Na^+ (8557 ppm), Mg^{2+} (820 ppm), K^+ (500 ppm) and Ca^{2+} (262 ppm)

^eThe cations with the highest concentrations in these seawater samples were Na^+ (9486 ppm), Mg^{2+} (897 ppm), K^+ (556 ppm) and Ca^{2+} (274 ppm)

recovery in various forms, polymer-based (organic) and silica-based (inorganic) materials. The first challenge an end user must face is which of these matrices to choose, as there is considerable overlap in functionality. **Table XIII** summarises the differences between the organic and inorganic exchangers (52).

As can be seen from **Table XIII** organic ion exchangers usually have higher capacities and better mechanical stability. The Achilles heel of the polymer-based materials is their sensitivity to radiation and heat. However, with the appropriate choice of a polymer-based resin this can be minimised.

A separate set of problems associated with anion exchange resins is fouling with intrinsic organic contaminants. This is usually dealt with by treating with brine at elevated temperatures. Due to the poor thermal stability of strong base anion exchange resins this usually results in a loss of capacity for the regenerated resin. Strong acid cation exchange resins have a problem with fouling due to calcium sulfate precipitation on regeneration with sulfuric acid. This is alleviated by back washing with warm lime followed by acid regeneration.

The Achilles heel of the inorganic exchangers is high pH, silica in particular degrades rapidly at pH>13. Organic-inorganic hybrid materials slow this process down but do not eliminate it (53).

In choosing the right ion exchange resin for a given application the properties of the waste are of primary concern. Total suspended solids should be less than 4 mg l⁻¹ or prefiltering is necessary for both organic and inorganic exchangers. The waste should have a low dissolved ionic solids content of less than 1–2 g l⁻¹. In the specific case of radionuclides, they need to be in the anionic form to be suitable for ion exchange with strong base anion exchangers. This can usually be done with pH adjustment but this will raise the total ion content and may affect removal efficiency (52).

For uranium removal from industrial waste or groundwater containing high levels of sulfate or carbonate the commercially available strong base anion exchange resins are currently the best option as discussed in Section 2. However, strong base silica polyamine composites with a higher tolerance for solutions with high ion concentration (upper limit for

Table XIII. A Comparison of the General Properties of Organic and Inorganic Ion Exchangers (52)

Property	Organic exchangers	Inorganic exchangers	Comments
Thermal stability	Fair to poor	Good	Inorganics are especially good for long term stability
Chemical stability	Good	Fair to good	Specific organics and inorganics are available for any given pH range
Radiation stability	Fair to poor	Good	Organics are very poor in combination with high temperatures and oxygen
Exchange capacity	High	Low to high	The exchange capacity will be a function of the nature of the ion being removed, its chemical environment and the experimental conditions
Selectivity	Available	Available	For some applications, such as caesium removal, inorganics can be much better than organics, owing to their greater selectivity. Ion selective media are available in both organic and inorganic forms
Regeneration	Good	Uncertain	Most inorganics are sorption based, which limits regeneration
Mechanical strength	Good	Variable	Inorganics may be brittle or soft or may break down outside a limited pH range
Cost	Medium to high	Low to high	The more common inorganics are less costly than organics
Availability	Good	Good	Both types are available from a number of commercial sources
Immobilisation	Good	Good	Inorganics can be converted to equivalent mineral structures, organics can be immobilised in a variety of matrices or can be incinerated
Handling	Good	Fair	Organics are generally tough spheres, inorganics may be brittle; angular particles are more friable
Ease of use	Good	Good	If available in a granulated form both types are easy to use in batch or column applications

polystyrene is 4 meq ml⁻¹) are under development and may prove competitive for these applications (35).

As stated clearly in Section 3.3.2 mesoporous materials are not a good choice for remediation projects. These materials and the related zeolites have found a wide range of applications in catalysis, medicine and many other fields. Their smaller pore sizes make them more difficult to regenerate, they do not tolerate bulky ligands well and the lower porosities generally lead to slower exchange kinetics (47). In addition they are more expensive to make.

For the inorganic exchangers discussed here to make an impact on uranium remediation, investigators need to focus more on testing regeneration and evaluation of usable lifetime. In fact, for the particular examples presented in Section 2 on polystyrene resins this is also an issue. In the nuclear industry regeneration and resin lifetime are central issues (52). Large-scale remediation of uranium waste streams is just beginning to receive attention and the processes and procedures developed in the nuclear industry should serve as model for this emerging field (52).

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