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Performance of Three Resin Based Materials for Treating Uranium Contaminated Groundwater within a PRB

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Abstract

Three materials that are designed to treat uranium-contaminated water were investigated. These are a cation exchange resin, IRN77, an anion exchange resin, Varion AP, and a recently developed material called PANSIL (quartz sand coated with 2% amidoxime resin by wt.). The reaction rate, capacity, and effective pH range of the three materials are reported. The capacity and conditional distribution coefficient in neutral, uranyl contaminated synthetic groundwater containing carbonate are also reported. The suitability of each material for treating uranium-contaminated groundwaters using a permeable reactive barrier approach is then discussed.

All three materials react rapidly in the pH range 5-7, reaching equilibrium in less than 4 hours at ~23°C. The unconditioned cation exchange resin removed 8 g UO_2^{2+} per kg of resin from neutral synthetic groundwater containing 30 mg/l of UO_2^{2+}, but a lower capacity is anticipated in groundwater with either higher ionic strength or lower UO_2^{2+} concentrations. It operates by first acidifying the solution, then sorbing UO_2^{2+}, and can release UO_2^{2+} when its buffering capacity has been exhausted. The anion exchange resin is very effective at removing anionic uranyl carbonate species from solutions with a pH above 5, with good specificity. Up to 50 g/kg of uranium is removed from contaminated groundwater at neutral pH. PANSIL is

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effective at sequestering cationic and neutral uranyl species from solutions in the pH range 4.5 to 7.5, with very good specificity. The capacity of PANSIL is pH dependent, increasing from about 0.4 g/kg at pH 4.5, to about 1 g/kg at pH 6 and 1.5 g/kg around pH 7.5. In neutral groundwater containing carbonate, both the anion exchange resin and PANSIL exhibit conditional distribution coefficients exceeding 1470 ml/g, which is about an order of magnitude higher than comparable reactive barrier materials reported in the literature.

Introduction

Groundwater pollution caused by recent and/or abandoned uranium mining activities is a global ecological problem. The threat posed to the environment arises not only from the radioactive emissions from uranium series radionuclides but also from the chemical toxicity of uranium. Uranium exists in aqueous solution under oxic conditions as the linear dioxo UO_2^{2+} cation, which favours co-ordination from hard ligands in the plane orthogonal to the O=U=O axis. Thus the speciation of the uranyl ion is very pH dependent, partly due to hydrolysis, but also due to the formation of carbonate species in systems open to atmospheric CO_2 or where carbonate minerals are present. For μM uranyl concentrations, the UO_2^{2+} cation tends to predominate at pH values below about 5. In the pH range 5 to 7, other cationic species (such as UO_2OH^+, and $(UO_2)_3(OH)_5^+$) as well as neutral and anionic species (such as UO_2CO_3, and $(UO_2)_2CO_3(OH)_3^-$) are important. At pH values much above 8, only anionic species (such as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) tend to be significant [1, 2].

Permeable Reactive Barriers (PRBs) have recently become established as an economical technology for the in-situ treatment of contaminated groundwater [3, 4, 5, 6]. A PRB consists of a permeable treatment zone that is inserted underground in a natural aquifer and intercepts the pollution plume carried within the aquifer. The barrier can be a simple trench filled with reactive material or may be of the "funnel and gate" type where flow in the aquifer is channelled by

impermeable side-walls to a reactive zone or reaction vessel. For PRB treatment to succeed it is important that there is no disruption to the natural groundwater flow otherwise it may by-pass the reactive zone, so the reactive material must be more permeable than the natural soil. Also, the flow-path through the reactive material must be long enough to ensure that the period the groundwater is within the reactive zone (the residence time) is sufficient for successful treatment. A further consideration is whether immobilised contaminants can be remobilised over time by the continued flow of groundwater, especially where there is no plan to recover the reactive material after contaminant exposure.

A wide range of materials has been used to form barriers based on several different approaches to the attenuation of the pollutant concentration. These include, for example, adsorption by porous and/or high surface area materials such as activated carbon, chemical reduction by elemental metals and bioremediation. However none of these approaches is without its problems. Contaminants held by electrostatic or ionic attraction to the surface of adsorptive materials can be gradually released over time due to competition by mass-action from natural ions in the groundwater. Reductive barriers can precipitate groundwater constituents and by-products from the reducing agent, in addition to the contaminant, and are therefore prone to clogging. Furthermore, bioremediation can be problematic within a PRB as it can be difficult to maintain optimum treatment conditions within the reactive zone.

The purpose of this research was to compare the performance of three resin-based materials at treating uranium contaminated water over a range of pH, and thus to evaluate their potential for use in a PRB. The three materials are a cation exchange resin (IRN 77) which is currently used to remove radioactive cations from spent solutions and wastewater, an anion exchange resin (Varion AP) developed for uranium recovery from carbonated wastewater, and a recently developed chelating resin-based material (PANSIL) for the treatment of uranium contaminated groundwater.

In the past, ion exchange resins have not been widely considered for groundwater remediation by PRB [7]. In part this is because they are expensive in comparison with other materials (e.g. elemental iron, hydroxyapatite and zeolites). However ion-exchange resins have high capacities and fast reaction rates meaning smaller amounts of reactive material are required to treat a given volume of groundwater. Also, as these materials are likely to be deployed within the reaction vessel of funnel and gate barrier, they can be periodically recovered, regenerated and then reused. Thus, their use in PRBs may be economically viable. The new material, called PANSIL, is designed to be a robust and lower cost alternative to commercially supplied ion-exchange resins. In PANSIL the relatively expensive active component, which is a chelating agent rather than an ion exchanger, is surface-coated onto strong and relatively low cost acid-washed sand particles.

Materials

The ion-exchange resins were Amberlite® IRN 77 (manufactured Rohm and Haas Company, USA), a cation exchange resin with sulphonic acid functional groups, and Varion AP (manufactured in Hungary by Nitrokemia), an anion exchange resin with functionality based on −2,N-dimethyl pyridinium groups. The former is designed to work at pH < 5 where the uranyl cation is the major uranium specie, whereas the latter in intended for use at pH > 5 where uranyl carbonate anions predominate. The new material, PANSIL (made at the University of Leeds, UK [8]), is polyacryloamidoxime resin coated quartz sand (≈2% resin by wt.). PANSIL functionality is thought to be derived from the amidoxime groups that act as bidentate ligand systems for uranyl cations. The lone pairs of electrons on the amino nitrogen and the oxime oxygen are donated to the positive metal centre to form a five-membered ring including the metal (such rings are noted for their stability due to minimal strain). The oxime oxygen can

undergo metal-assisted deprotonation [9] further increasing the stability of the ring at intermediate pH.

Figure 1 shows electron micrographs of the three materials. The cation exchange resin consists of relatively uniform spherical particles with an average particle size of about 0.5mm. The anion exchange resin consists of relatively uniform spherical particles with an average particle size of about 1mm. PANSIL particles are sub-rounded, with some variation in size and shape, but an average particle size of about 1mm. Hazen's formula [10] indicates that the hydraulic conductivity of the cation exchange resin will be around 10^{-3}m/s, whereas those of the anion exchange resin and PANSIL will be around 10^{-2}m/s (although coarser sand could be used in the manufacture of PANSIL to increase its hydraulic conductivity). Thus these active materials, as tested, are unsuitable for use in clean coarse sand or gravel deposits (whose hydraulic conductivities are typically $> 10^{-3}$ m/s [10]), as the reactive material must usually be more permeable than the natural soil to avoid the groundwater flow by-passing the PRB.

Methods

The cation exchange resin was supplied in an H^+ form and was tested both as supplied (i.e. unconditioned), and after conditioning with NaCl to convert to a Na^+ form (8 bed volumes of 1M NaCl were passed through a column of resin at a flow rate of about 5 bed volumes per hour). Conditioning of the cation exchange resin was intended to replicate the situation where the resin's pH buffering capacity is exhausted, as may occur rapidly in groundwater (natural groundwater cations, such as Na^+ and Ca^{2+} will usually far outnumber the contaminant cations and are readily adsorbed by the cation exchange resin).

The anion exchange resin was conditioned to pH 7 with NaOH (10g of resin was added to 1 litre of distilled water and NaOH was added drop-wise until the pH was 7) before testing. The anion exchange resin is designed to sorb aqueous uranyl carbonate species, so the uranyl

solutions used with this resin were made up in 100 mg/l of bicarbonate (sodium bicarbonate) to ensure that UO_2^{2+} species were carbonated where the pH permitted. PANSIL was not conditioned before use.

The experimental programme is outlined in Table 1. The test solutions were prepared from laboratory grade reagents and distilled water. All the tests described in Table 1 were conducted at room temperature (typically 22-25°C), and no attempt was made to purge atmospheric $O_2(g)$ and $CO_2(g)$ from the solutions or to exclude them during testing. All solution samples taken for analysis were filtered to < 0.45 μm (Whatman Puradisc 25PP), had their pH measured, then they were acidified by adding a few drops of concentrated nitric acid, and stored at 4°C. Solution pH was measured using a glass pH electrode and Jenway 3150 meter. The uranium concentration in solution was measured using a spectrophotometric method based upon the complexing reagent 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (known as Bromo-PADAP) [11]. This technique has a detection limit of ~0.2 mg/l.

"Synthetic groundwater" representative of a natural groundwater contaminated with uranium (based on the groundwater at a mine tailings site in Hungary) was made up from laboratory reagents (200 mg/l $CaCO_3$, 272 mg/l $CaSO_4$, 194 mg/l $4MgCO_3.Mg(OH_2).5H_2O$, 252 mg/l $NaHCO_3$, 75 mg/l KCl), and the pH was adjusted to 7 using H_2SO_4. After pH adjustment an undissolved residue remained, so the synthetic groundwater was filtered and its composition was measured (see table 2), before the addition of either 18.6 or 55.8 mg/l $UO_2(NO_3)_2.6H_2O$ (equivalent to 10 and 30 mg/l UO_2^{2+}) which dissolved completely (samples were analysed for UO_2^{2+} concentration). After standing, the pH of the synthetic groundwater was between 6.8 and 7.8 where the dominant aqueous carbonate specie will be HCO_3^-. The synthetic groundwater contained approximately 660 mg/l of total dissolved solids (two-thirds of the value at the Hungarian mine site) and therefore represents fairly dilute groundwater.

Increasing Duration Batch tests – Increasing duration batch exposure tests were conducted on the three materials to determine the time taken for each material to reach equilibrium with a uranyl nitrate solution. The active material was added to screw top nylon bottles containing the uranyl nitrate solution, the bottles were shaken, and periodically small samples of the supernatant were taken. The liquid to solid ratio was 30:1, and the initial uranium concentration was 10 mg/l UO_2^{2+}. The solution pH was between 5.1 and 5.8 for the cation exchange resin, 7.1 and 7.3 for the anion exchange resin, and 5.5 and 6.5 for PANSIL.

Sorption Isotherms – The active material was added to nylon stoppered glass bottles containing a uranyl nitrate solution at pH 4 to 5. The L:S ratio was 200:1 for the ion-exchange resins and 30:1 for PANSIL, and the uranium concentration was between 1 mg/l and 2000 mg/l (because of their high uranium capacities, the sorption isotherm of the ion-exchange resins could not be fully defined using an L:S ratio of 30:1 without the initial solution concentrations exceeding the solubility limit of uranyl nitrate). The bottles were shaken for 24 hours (the increasing duration batch tests indicated an exposure time of 4 hrs was sufficient to reach equilibrium), and the supernatant was sampled. Control tests were conducted using acid washed sand. These tests were to determine whether sorption or precipitation had a significant effect on the test results.

Amidoxime resin (the active coating on PANSIL) is reported to be highly selective for large divalent cations [9, 12, 13]. Therefore a second isotherm determination was undertaken (at approximately the same pH as the first isotherm) to investigate the specificity of PANSIL for UO_2^{2+} in the presence of equimolar Pb^{2+}.

Column tests - Flow-through column tests (using glass columns, Tygon tubing and peristaltic pumps) were conducted to replicate the mode of contaminant exposure within a PRB. In the column tests the active materials were mixed with acid washed quartz sand to reduce the amount of active material used for a particular column length (to reduce column capacity, and

thus test duration, without reducing exposure time). In the tests on the ion exchange resins 1g of resin was mixed with 29 g acid washed sand, whereas 10 g of PANSIL was mixed with 20 g acid washed sand (reflecting the fact that the active component is already diluted 50 fold in the manufacture of PANSIL). The mixtures of sand and active materials were placed in a 25 ml glass column (length 300 mm, internal diameter ≈10 mm), which resulted in a pore volume of approximately 10 ml. The columns were then saturated by the upward flow of distilled water. Once saturation was achieved the water was displaced with the upward flow of the desired contaminant solution at a constant flow rate of 1.6 ml/hr. The selected flow rate gave a residence time for the contaminated solution within the column of about 6 hrs, which exceeded by at least 50 % the time taken for equilibrium in the preliminary batch tests. Effluent solutions were diverted through a spur at the top of the columns into covered glass collection vessels. Effluent solutions were collected once a day and their volume and pH were measured prior to acidification for UO_2^{2+} analysis. Further experimental details are given in [14]. Six column tests were conducted, two on each active material as follows;

(i) The unconditioned cation exchange resin exposed to uranyl nitrate solution containing 100 mg/l UO_2^{2+} buffered to an influent pH of 6 (using a small amount of NaOH). This test was abandoned after 12 weeks without UO_2^{2+} being detected in the effluent.

(ii) The unconditioned cation exchange resin exposed to synthetic groundwater containing 30 mg/l of UO_2^{2+} at an influent pH of ~7.5.

(iii) The conditioned anion exchange resin exposed to uranyl nitrate solution conditioned with 100 mg/l of carbonate (as sodium carbonate), containing 100 mg/l of UO_2^{2+} adjusted to an influent pH of ~6.5 with HNO_3. When the UO_2^{2+} concentration in the effluent equalled that in the influent, the column was leached with uncontaminated synthetic groundwater.

(iv) The conditioned anion exchange resin exposed to synthetic groundwater containing 30 mg/l of UO_2^{2+} at an influent pH of ~7.5.

(v) PANSIL was exposed to uranyl nitrate solution containing 30 mg/l UO_2^{2+} buffered to pH 6 until the uranium concentration in the effluent equalled that in the influent and then the column was leached with uncontaminated synthetic groundwater.

(vi) PANSIL was exposed to contaminated synthetic groundwater containing 30 mg/l UO_2^{2+} until the UO_2^{2+} concentration in the effluent equalled that in the influent and then the column was leached with uncontaminated synthetic groundwater at an influent pH of ~7.5.

In addition a control test on acid washed sand using a 30 mg/l uranyl nitrate solution at ~ pH 5 was also run.

pH controlled batch exposure tests - The effectiveness of each active material at extracting uranium from water over a range of pH was investigated by batch exposure tests. The active material was added to stoppered glass bottles containing a uranyl nitrate solution whose pH was adjusted to values between 1.5 and 11 using either HNO_3 or NaOH (covering the usual groundwater pH range of 5-9 and also that encountered in acid mine drainage). The liquid to solid ratio was 30:1, and the uranium concentration was 10 mg/l UO_2^{2+}. The bottles were shaken end-over-end for 24 hours, and the supernatant was sampled.

The leachability of uranium sequestered by PANSIL was investigated by further batch tests. Exposed PANSIL from two batch exposure tests (both with a final pH during the exposure step of ~6) was subjected to two further leaching steps. Once the initial solution had been decanted off, the PANSIL was twice shaken end-over-end in distilled water at a liquid to solid ratio of 30:1 for 24 hours. The water from both these steps was sampled.

Batch exposure tests with synthetic groundwater - Batch exposure tests were conducted on each active material using synthetic groundwater containing 10 mg/l UO_2^{2+}. The L:S ratio was 30:1, the test duration was 24 hrs, and the supernatant was then sampled.

Geochemical Modelling

Three different solutions representative of those used in this study have been numerically modelled using the PHREEQE (version phrq96) equilibrium geochemical modelling software (U.S. Geological Survey) and the CHEMVAL (version 6) database. These were a uranyl solution in the absence of equilibrium with atmospheric CO_2, a uranyl solution initially containing 100 mg/l bicarbonate, and the synthetic groundwater. All these solutions were modelled under oxic conditions and containing 10 mg/l of UO_2^{2+} (Table 3 gives the solution compositions used as input for the geochemical modelling). The speciation of these solutions is shown in Figure 2 as a percent of the total UO_2^{2+} in particular species as a function of pH.

The modelling predicts that the major uranium species in the uranyl solution are the UO_2^{2+} cation when the pH < 5, $UO_2(OH)_2$ and $(UO_2)_3(OH)_5^+$ species when the pH is between 5 and 9, and the $UO_2(OH)_3^-$ anion when the pH > 9. When the uranyl solution was modelled with 100 mg/l bicarbonate, the major uranium species is once again the UO_2^{2+} cation when the pH < 5, but it is the neutral UO_2CO_3 and $UO_2(OH)_2$ species when the pH is between 5 and 6.5, although a few percent of the UO_2^{2+} is predicted to be present as the cationic specie UO_2OH^+ until the pH exceeds 6. Above about pH 6.5, the major uranyl species are the $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ anions until the pH reaches 11, when $UO_2(OH)_3^-$ becomes important. However, a few percent of the UO_2^{2+} is predicted to be present as neutral UO_2CO_3 and $UO_2(OH)_2$ species until the pH exceeds 7 and 8, respectively.

The uranyl nitrate solutions used in this study all had ready access to atmospheric CO_2, which dissolves to form aqueous carbonate species in neutral and alkaline conditions. Geochemical modelling of uranyl solutions in equilibrium with atmospheric CO_2 reported in the literature [2, 15] indicates that the uranium speciation in such solutions is intermediate between that shown in Figures 2a and b.

The major predicted uranium species in the synthetic groundwater are the $UO_2^{2+}(aq)$ cation and neutral UO_2SO_4 when the pH < 5, neutral UO_2CO_3 species when the pH is between 5 and 6 (a few percent is present as UO_2^{2+} and UO_2OH^+ cations until pH 6). The major uranium species are $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ anions in the pH range 6 to 11, but a few percent is present as neutral UO_2CO_3 and $UO_2(OH)_2$ species while the pH is less than 8. When the pH approaches 11 anionic $UO_2(OH)_3^-$ is the major predicted uranyl specie.

Results

Increasing Duration Batch tests – The increasing duration batch exposure tests (Figure 3) indicated that an exposure time of about 2 hrs was sufficient for both the unconditioned cation exchange resin to reach equilibrium with uranyl nitrate solution at ~ pH 5.5, and for the conditioned anion exchange resin to reach equilibrium with uranyl nitrate solution at ~ pH 7.2 (in both cases the solution contained 10 mg/l UO_2^{2+}). An exposure time of less than 4 hrs was sufficient for PANSIL to reach equilibrium with uranyl nitrate solution at ~ pH 6 containing 10 mg/l UO_2^{2+}.

Sorption Isotherms – The sorption isotherm for the unconditioned cation exchange measured in uranyl nitrate at ~ pH 3.8 is shown in Figure 4a. In acidic conditions, and in the absence of competing cationic species, the cation exchange resin removes UO_2^{2+} from solution to below the analytical detection limit until the resin loading exceeds 100 g UO_2^{2+} per kg of resin. At higher resin loadings equilibrium is established between the sorbed and aqueous phase. It is estimated (for comparative purposes) that the resin loading for a solution concentration of 200 mg/l will exceed 400 g UO_2^{2+} per kg of resin.

The sorption isotherm for the conditioned anion exchange measured in uranyl nitrate conditioned with sodium carbonate in the pH range 5 to 5.1 is shown in Figure 4b. At pH 5, and with mono-valent nitrate and bicarbonate the only competing ionic species, the anion exchange

resin removes UO_2^{2+} (possibly anionic uranyl carbonate species) from solution to below the analytical detection limit until the resin loading exceeds 10 g/kg. At higher resin loadings equilibrium is established between the sorbed and aqueous phase. At a solution concentration of 200 mg/l the resin loading is about 60 g UO_2^{2+} per kg of resin.

The sorption isotherm for UO_2^{2+} on PANSIL at ~ pH 4.5 is shown in Figure 5 (a) & (b), and that for UO_2^{2+} on PANSIL in the presence of an equal molar concentration of Pb^{2+} (at about the same pH) is shown in Figure 5 (c) & (d). Below a certain limit PANSIL removes UO_2^{2+} from solution to below the analytical detection limit, and can do so in the presence of an equal molar concentration of divalent metal ions. At ~ pH 4.5 this level was between 300 and 500 mg of UO_2^{2+} per kg of PANSIL (the higher capacity was determined from a mixed UO_2^{2+}/Pb^{2+} isotherm, probably due to small differences in pH in the particular batch tests that define the capacities). Above this limit PANSIL sorbs UO_2^{2+} more weakly, establishing equilibrium between the sorbed and aqueous phase. At a solution concentration of 200 mg/l the amount sorbed at pH 4.5 is around 3 g/kg for the UO_2^{2+} solution, but about 2 g/kg in the mixed UO_2^{2+}/Pb^{2+} solution.

The sorption behaviour of UO_2^{2+} on the acid washed sand at ~ pH 4.5 is also shown in Figure 5 (a) & (b). These data indicate that uranyl interacts very weakly with the acid washed sand used to support the amidoxime resin in PANSIL. Thus it is surmised that a very small proportion of the uranyl sorption capacity of PANSIL is due any exposed sand surfaces.

Column tests - In the column test on the unconditioned cation exchange resin exposed to synthetic groundwater containing 30 mg/l UO_2^{2+}, initial breakthrough[1] of uranium occurred when the resin loading (estimated from the difference in the amounts of UO_2^{2+} that entered and exited the column) was approximately 7.5 g per kg of resin (see Figure 6). Prior to initial breakthrough the effluent pH was 2.5, but after breakthrough it was 7.5. Shortly after

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[1] In this study initial breakthrough is operationally defined as a UO_2^{2+} concentration in the column effluent persistently above the analytical detection limit.

breakthrough there was a spike in the effluent uranium concentration when it peaked at nearly twice the influent concentration. The results of this test are a sharp contrast with those of the aborted column test using uranyl nitrate at pH 6, where a resin loading of 320 g/kg was achieved without breakthrough (the effluent pH was 2.5 throughout this test).

During the column test on the anion exchange resin using uranyl nitrate conditioned to an initial pH of 6.5 – 6.9 with sodium bicarbonate, the effluent pH was typically half a unit higher than the influent. Initial breakthrough occurred when the resin loading was 80 g UO_2^{2+} per kg, and the uranium concentration in the effluent was equal to that in the influent when the resin loading was 140 g UO_2^{2+} per kg (see Figure 7a). Subsequent leaching with uncontaminated synthetic groundwater at ~ pH 7.5 resulted initially in a high UO_2^{2+} concentration in the effluent, and then a rapid decrease to a small fraction (< 2 %) of the concentration used during contamination. By the end of testing the UO_2^{2+} concentration in the effluent was below the detection limit of the measurement method.

In comparison, initial breakthrough in the column test on the anion exchange resin using synthetic groundwater at ~ pH 7.5 occurred when the resin loading was 50 g UO_2^{2+} per kg, although the effluent concentration remained low (between 0.2 and 0.6 mg/l UO_2^{2+}) until the resin loading was 90 g UO_2^{2+} per kg (see Figure 7b). The uranium concentration in the effluent was equal to that in the influent when the resin loading was 120 g UO_2^{2+} per kg. Thus the resin loading at initial breakthrough is about a third lower when there is competition from non-contaminant groundwater anions.

The PANSIL column tests showed that when exposed to uranyl nitrate buffered to pH 6, initial breakthrough occurred at a column loading of about 1.5 g UO_2^{2+} per kg of PANSIL, and influent and effluent UO_2^{2+} concentrations were equal when the average column loading was 2.8 g/kg (see Figure 8a). Subsequent leaching with uncontaminated synthetic groundwater (at ~ pH 7.5) initially liberated UO_2^{2+} from the column so that the effluent concentration spiked at nearly

three times the influent concentration, but in the long-term the PANSIL retained about 1 g UO_2^{2+} per kg. When exposed to synthetic groundwater (30 mg/l UO_2^{2+} at ~ pH 7.5), initial breakthrough occurred at an average PANSIL loading of about 1.1 g/kg, and influent and effluent UO_2^{2+} concentrations were equal when the average column loading was about 1.7 g/kg (Figure 8b). During subsequent leaching with uncontaminated synthetic groundwater the effluent UO_2^{2+} concentration showed no spike, instead it gradually declined, until in the long-term the PANSIL retained about 1.5 g UO_2^{2+} per kg.

The control column test on the acid washed sand using a 30 mg/l uranyl nitrate solution at ~ pH 5 exhibited immediate initial breakthrough, and influent and effluent UO_2^{2+} concentrations were equal when the average column loading was only 0.008 g UO_2^{2+} per kg. Thus it is assumed that the amount of uranium sorbed by the sand in column tests can be ignored.

Batch exposure tests - In the batch test on the unconditioned cation exchange resin, the resin achieved very high degrees of UO_2^{2+} removal regardless of initial solution pH, but did so by buffering the pH to below 4 where UO_2^{2+}(aq) is the dominant uranyl specie. When the cation exchange resin was pre-conditioned with NaCl, it was very effective at pH values below 6.5, but was decreasingly effective above this pH and wholly ineffective at high pH (see Figure 9a). Thus the effective range of the conditioned cation exchange resin corresponds closely with the pH range where modelling predicts that some uranium is present as cationic species in the presence of carbonate (Figure 2b); the carbonate presumably resulting from exposure of the uranyl nitrate solution to atmospheric CO_2. As would be anticipated from the predicted aqueous uranyl speciation, the conditioned cation exchange resin was wholly ineffective at removing uranium from the synthetic groundwater at ~ pH 7.5 (where uranyl species are predominantly neutral or anionic).

The variation in uranium sorption by the anion exchange resin with pH is shown in Figure 9b. It should be noted that data from all the pH controlled batch tests are presented in

terms of the final equilibrium pH. The anion exchange resin was effective in neutral and alkaline

conditions, where the modelling suggests there are significant concentrations of anionic uranyl

species (Figure 2b and c). It appears to show that the anion exchange resin was effective at pH

4.5, but this is hard to explain as the geochemical modelling indicates that there are no anionic

uranyl species below pH 5 (carbonate will out-gas as CO_2 in acidic conditions). However, it

should be noted that the sample with a final pH of 4.5 had an initial pH of 5.2 and therefore may

initially have contained a small fraction of anionic uranyl species. The anion exchange resin was

also very effective at treating UO_2^{2+} contaminated synthetic groundwater at a pH of ~7.5 (also

shown in Figure 9b).

The batch exposure tests conducted with uranyl nitrate solutions buffered to a range of

pH values show that PANSIL was effective over a pH range 4.5 to 8, with optimum performance

in the pH range 5 to 7.5 (Figure 9c). PANSIL was also very effective at treating the synthetic

groundwater (also shown in Figure 9c). The amidoxime coating on PANSIL is known to act as a

bidentate ligand for uranyl cations [9], which are the prevalent specie in acidic conditions (see

Figure 2). However in the bicarbonate buffered synthetic groundwater system at ~ pH 7.5 the

geochemical modelling indicates that the predominant uranyl species are either neutral or

anionic, with only anionic species significant above pH 8. A similar pattern is exhibited by

uranyl solutions where carbonate is present. Thus it is suggested that PANSIL is also able to act

as a ligand to neutral uranyl species. Such behaviour is not unexpected as amidoxime fibres

have been shown to preferentially adsorb uranium from seawater [17], which has a pH of ~8.

In the two-stage, distilled water (at pH 5.5), batch leaching tests on PANSIL that was

loaded with uranium at ~ pH 6, the UO_2^{2+} concentration in the leachate from the first stage was

well below the detection limit for the analytical method employed, and was undetectable in the

second stage of these tests. These tests confirmed that at the loading used in the batch tests (300

mg UO_2^{2+} per kg of PANSIL), PANSIL strongly binds UO_2^{2+}, and once bound that UO_2^{2+} remains unleached in mildly acidic uncontaminated water.

Discussion

The Cation Exchange Resin - The sorption isotherm and the aborted column test with uranyl nitrate indicate that cation exchange resin has a very high uranium sorption capacity (320 g/kg) in acid conditions where the UO_2^{2+}(aq) specie dominates. However, this capacity will be greatly reduced by competition from other cationic species (UO_2^{2+} is a very large divalent ion and is below Ca^{2+} and Mg^{2+} in the cation replaceability series for many sorbents [18]).

The column test with the synthetic groundwater (Figure 8b) suggests that the unconditioned cation exchange resin may be effective at removing uranyl species from groundwaters that are initially neutral whilst it is able to buffer the solution pH into the acid range by releasing H^+ ions. In such conditions the mechanism by which uranium is sorbed to the cation exchange resin is probably by the sorption of natural groundwater cations (e.g. Na^+, K^+, Ca^{2+}, Mg^{2+}) displacing H^+ from the resin, as evidenced by the reduction in pH to about 2.5 at the start of the column test with groundwater (see Figure 6). This pH reduction would lead to a change in the dominant uranium specie from uranyl carbonate anions towards UO_2^{2+}(aq) cations (see Figure 2c), and the subsequent sorption of the UO_2^{2+} cations to the resin.

The drawback with such a process is that the decrease in groundwater pH may be unacceptable for some PRB applications (it should be aim of any remediation technology to remove the contaminant without unnecessary changes in the groundwater chemistry). Also, the groundwater pH will revert to its original value once most of the H^+ has been exchanged off the resin, and the resin will not then interact with the uranyl carbonate species left in solution (the pH controlled batch tests showed that the Na^+ conditioned resin was ineffective in synthetic groundwater at ~ pH 7.5). Thus the resin capacity that will be achieved in a particular solution

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will depend on the relative numbers of natural groundwater cations and uranyl species present (the molar concentration of the uranyl species at uranium contaminated sites is usually very small in comparison with the non-contaminant constituents).

Shortly after breakthrough in the column test with unconditioned resin and synthetic groundwater there was a peak in the effluent uranium concentration where $C/C_o > 1$ (Figure 6). This indicates that sorbed uranium was released from the cation exchange resin even though there was no change in the influent solution, and thus that the amount of uranyl sorbed to the resin when the pH was buffered to 2.5 exceeded the equilibrium value for the contaminated synthetic groundwater at pH 7.5. This change of equilibrium was probably due to the change in the dominant uranium species in solution. It will therefore be very important to remove the cation exchange resin from a PRB before its buffering capacity is exhausted otherwise a contaminant pulse with an elevated UO_2^{2+} concentration may be released from the barrier. Further, this pulse may be followed by UO_2^{2+} being gradually released over time due to competition by mass-action from natural ions in the groundwater (if the UO_2^{2+} cation is below Ca^{2+} and Mg^{2+} in the cation replaceability series for IRN 77, then desorption could be rapid, as other large metal cations are readily replaced by other species with a stronger affinity for the resin [19]).

The Anion Exchange Resin - As expected, the anion exchange resin has a high uranium sorption capacity (80 g/kg) in neutral and alkaline conditions where neutral and anionic uranyl carbonate species (particularly $UO_2(CO_3)_2^{2-}$) dominate (Figure 7 a). However, this capacity is about a third lower in a groundwater system where there will be competition from other stable anionic species (e.g. SO_4^{2-}). Leaching of the column exposed to carbonated uranyl nitrate with uncontaminated synthetic groundwater caused a small spike in the effluent UO_2^{2+} concentration, and then a rapid decrease to below the analytical detection limit. The spike was probably caused by the groundwater anions displacing weakly sorbed anionic uranyl species from the anion

exchange resin. No leaching stage was conducted during the column test with contaminated

synthetic groundwater, but it is very unlikely that leaching the column with uncontaminated

synthetic groundwater would have caused a spike in the effluent uranyl concentration, as there

was no change in the non-contaminant constituents of the eluent.

Interestingly in the column test exposed to contaminated synthetic groundwater the

dominant divalent anion was sulphate and its concentration was 2.6 mmol/l whereas the uranyl

concentration was only 111 μmol/l, yet the uranyl capacity was only reduced by a third

compared to the carbonated uranyl nitrate system. This suggests that the anion exchange resin

has good specificity for anionic uranyl species over major groundwater anions. Nonetheless, as

the uranium is sorbed to the surface of the resin by electrostatic interaction, it could be gradually

released over time when the resin is leached by groundwater due to competition by mass action

from the groundwater anions (in particular, divalent groundwater anions such as sulphate).

PANSIL - The sorption isotherm for UO_2^{2+} on PANSIL, and that for UO_2^{2+} on PANSIL

in the presence of an equal molar concentration of Pb^{2+} (Figure 5 b & d), indicate that below a

certain capacity (termed the sequestration capacity) PANSIL removes all detectable UO_2^{2+} from

solution. The water leaching tests on exposed PANSIL (from the pH controlled batch tests)

showed that when PANSIL is loaded below that capacity, UO_2^{2+} is not readily leached. As

discussed earlier, the amidoxime coating on PANSIL can act as a bidentate ligand system with a

high degree of specificity for uranyl cations. IR spectroscopy has confirmed that PANSIL can

form strong ligand bonds with UO_2^{2+} [8]. Thus the specificity for UO_2^{2+} in the presence Pb^{2+} is

taken to indicate that uranyl sequestration by PANSIL is by this chelation mechanism. At pH

4.5 this sequestration capacity is between 300 and 500 mg of UO_2^{2+} per kg of PANSIL.

At higher loadings the sorption isotherms indicate that PANSIL sorbs UO_2^{2+} more

weakly, establishing an equilibrium between the sorbed and aqueous phase (Figure 5 a & c). In

this range, the amount of UO_2^{2+} sorption by PANSIL is reduced by competition from Pb^{2+},

which indicates a change in the sorption mechanism. This second, weaker sorption mechanism is probably electrostatic involving locations on the polymer, and/or any exposed sand surfaces exhibiting a local charge deficit.

The PANSIL column exposed to uranyl nitrate exhibited a spike and then a rapid decrease in the effluent UO_2^{2+} concentration when it was leached with uncontaminated synthetic groundwater (Figure 8 a). The spike was presumably caused by the groundwater ions displacing weakly sorbed uranyl species from the electrostatic sites. The column initially exposed to contaminated synthetic groundwater exhibited no spike when leached with uncontaminated synthetic groundwater (Figure 8 b). In fact, in this case there was a rapid decrease in the UO_2^{2+} concentration in the effluent (spikes should only occur when there is a significant change in the eluent chemistry). In this second test the amount of UO_2^{2+} that desorbed when the influent UO_2^{2+} concentration dropped to zero was small (~ 0.2 g/kg), which probably reflects that the amount of UO_2^{2+} sorption to PANSIL by the weaker non-specific mechanism will have been small when there was competition from the groundwater cations which were in molar excess.

The column capacity of PANSIL after leaching with synthetic groundwater can be considered to be an approximation to the sequestration capacity (small divalent cations in the synthetic groundwater would compete effectively with any weakly bound uranyl species for electrostatic sorption sites). Taken together, the sorption isotherm and column data indicate that the sequestration capacity of PANSIL is pH dependent, increasing from 0.3 - 0.5 g/kg at pH 4.5, to about 1 g/kg at pH 6 and possibly as high as 1.5 g/kg around pH 7.5. It is likely that this dependence of PANSIL's sequestration capacity on pH is associated with the increasing ease with which oxime oxygen can undergo metal-assisted deprotonation at higher pH.

PANSIL was very effective in the batch exposure tests with synthetic groundwater at ~ pH 7.5. The maximum sequestration capacity of PANSIL for UO_2^{2+} at this pH is about 6 mmol/kg (1.5 g/kg). The synthetic groundwater initially contained 0.8 mmol/l (31.4 mg/l) of

calcium, 1.8 mmol/l (43.0 mg/l) magnesium, and 37 µmol/l (10 mg/l) of UO_2^{2+}, which in the batch exposure tests with an L:S ratio of 30, is equivalent to 79 mmol of divalent cations per kg of PANSIL. Thus the number of divalent cations in the synthetic groundwater greatly exceeded the maximum sequestration capacity of PANSIL. Therefore, it is concluded that PANSIL preferentially sequesters UO_2^{2+} from typical neutral groundwater systems.

Comparison of the three resin based materials - The performance of the three resin-based materials in contaminated synthetic groundwater is compared with the reported performance of other PRB materials in similar solutions in table 4. At the UO_2^{2+} concentrations considered, the active materials being used for comparison remove UO_2^{2+} by surface adsorption [20, 21, 22]. Thus the comparison is made in terms of the conditional distribution coefficient, K_d (ml/g), which is the amount of a substance sorbed (µg/g) divided by its equilibrium concentration in solution (µg/ml). Generally K_d is not a unique property of a particular sorbent/solution system, and usually varies with the test conditions (particularly the particle size and contaminant concentration). Thus the test data used for comparison have been selected to ensure that the contaminant concentration, pH and L:S ratio are similar in magnitude to those used in this study.

Both the anion exchange resin and PANSIL compare very favourably with the other materials reported in table 4, particularly when it is noted that the K_d values of the anion exchange resin and PANSIL are underestimated because, for calculation purposes, the final solution concentrations were assumed to be equal to the analytical detection limit (Table 4). Indeed, the K_d values of the anion exchange resin and PANSIL are an order of magnitude higher than those reported for similarly sized bone charcoal and iron oxide pellets, and finer sized crushed phosphate rock. The conditioned cation exchange resin was ineffective in the neutral synthetic groundwater, which is anticipated for a material designed to adsorb cationic species from acidic solutions.

Reductive precipitation of UO_2^{2+} from groundwater using elemental iron is fast and very effective under reducing conditions [24, 25]. Thus elemental iron is an obvious alternative to the reactive materials listed in Table 4 (although a K_d value cannot be estimated for a reductive mechanism). For example, a barrier at Monticello in Utah, USA, reduced the UO_2^{2+} concentration in the groundwater from 739 to 0.2µg/l [25]. Moreover, an iron barrier can in theory treat a very large amount of UO_2^{2+} (although in practice barrier life depends principally on the corrosion lifetime of the iron). However, there remain some concerns about the long-term performance of elemental iron barriers because of the precipitation of corrosion minerals (iron oxyhydroxides/green rusts), microbial reduction products (FeS), and secondary minerals ($CaCO_3$, $FeCO_3$), which can decrease the iron reactivity and barrier hydraulic conductivity, and may even clog the barrier [24, 26, 27].

Finally, it should be noted that the PANSIL tested during this project was from a prototype batch, where only a proportion of acrylonitrile groups were converted to amidoxime groups, and only partial coating of the sand with the polymer was achieved (see Figure 1c). It is believed that with better optimisation of coating process, a higher degree of sand particle coating can be achieved. In addition, it is also apparent that coating with a polymer that has a higher degree of functional group conversion may be possible. Both of these factors would result in PANSIL with a significantly higher sequestration capacity.

Conclusions

In acidic solutions for which it is designed the cation exchange resin, IRN77, is very effective at removing cationic UO_2^{2+}(aq) from solution. In neutral groundwater systems where neutral and anionic uranyl species predominate, the unconditioned H^+ form of the resin can still remove a limited amount of UO_2^{2+} from solution. However it operates through sorbing the natural groundwater cations, which releases H^+ and thus reduces the solution pH. This moves the uranyl

equilibrium towards cationic UO_2^{2+}(aq), which then sorbs to the resin. Thus, in a neutral groundwater system, use of this material would produce an undesirable pH reduction. Furthermore, much of the resin cation exchange capacity will be consumed in sorbing non-contaminant species.

In solutions more alkaline than pH 5 the anion exchange resin, Varion AP, has a high capacity for anionic uranyl carbonate species. In this pH range it has good specificity for these species in the presence of aqueous sulphate and carbonate.

PANSIL is effective at sequestering cationic and neutral uranyl species when the solution pH is between 4 and 8, with optimum performance in the pH range 4.5 to 7.5. In this range PANSIL has very good specificity for uranyl species in the presence of typical groundwater ions. Once sequestered the uranium is not readily leached from PANSIL. However the uranium capacity of the pilot batch of PANSIL tested in this study is significantly lower than that of the commercially available Varion AP anion exchange resin.

Both the anion exchange resin and PANSIL were effective at removing uranyl species from neutral synthetic groundwater containing carbonate, exhibiting conditional distribution coefficients significantly higher than those reported in the literature for other similarly sized reactive barrier materials under similar experimental conditions.

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Table 1: Test programme

	Unconditioned Cation exchange resin	Conditioned Cation exchange resin	Conditioned Anion exchange resin	PANSIL	Acid washed sand
Increasing duration batch tests with uranyl nitrate	✓		✓[+]	✓	
Sorption isotherm determination with uranyl nitrate	✓		✓[+]	✓	✓
Sorption isotherm for uranyl in the presence of Pb^{2+}				✓	
pH controlled batch exposure tests with uranyl nitrate	✓	✓	✓[+]	✓[⊕]	
Batch exposure tests with synthetic groundwater		✓	✓	✓	
Flow-through column tests with uranyl nitrate	✓[*]		✓[+]	✓	✓
Flow-through column tests with synthetic groundwater	✓		✓	✓	

[+] The uranyl nitrate test solution used with the anion exchange resin was conditioned with 100 mg/l of bicarbonate (as sodium bicarbonate)

[⊕] Exposed material from tests conducted at pH 5 and 6 was subjected to distilled water leaching tests

[*] Test aborted

Table 2: Measured composition of the synthetic groundwater prior to addition of $UO_2(NO_3)_2$

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Concentration mg/l	64.9	38.4	31.4	43.0	35.5	253	182

1. Cations were measured by ICP-OES, anions were measured by HPLC-IC except for carbonate, which was measured by the flow injection method [16].
2. The error in charge balance was less than 2% of the total charge.

Table 3: Solution chemistry of relevant waters modelled using PHREEQE with the CHEMVAL6 database.

	Uranyl Solution (mg/l)	Carbonated Uranyl Solution (mg/l)	Synthetic Groundwater (mg/l)
Na^+	0	38	65
K^+	0	0	38
Ca^{2+}	0	0	31
Mg^{2+}	0	0	43
Cl^-	0	0	35
SO_4^{2-}	0	0	252
HCO_3^-	0	100	181
UO_2^{2+}	10	10	10
pH range modelled	2 - 11 [a]	2 - 11 [a]	2 - 11 [a]

[a] It was assumed that either HCl or NaOH was used to adjust the pH during modelling.

Table 4: Comparison of the performance of the resin based materials with other PRB materials (after Bryant et al., 2003). Data are presented from batch tests where the initial UO_2^{2+} concentration was between 5 and 35mg/l, the pH was between 7 and 8, and the L:S ratio was between 10:1 and 100:1.

Material	Ref	pH	Carbonate[+] (estimated) (mg/l)	K_d (ml/g)
Hydroxyapatite based materials				
Pelletized bone charcoal	[22, 23]	≈7.2	400, 580	100-370
Crushed phosphate rock	[23]	7.3	580	30-125
Iron oxide pellets	[22]	7.2	400	25
PANSIL		7.6	180	>1470[*]
Conditioned Varian AP		7.4	180	>1470[*]
Conditioned IRN 77		7.2	180	6

[*] Final solution UO_2^{2+} concentration was below the analytical detection limit. Therefore a minimum K_d value was calculated from that detection limit.

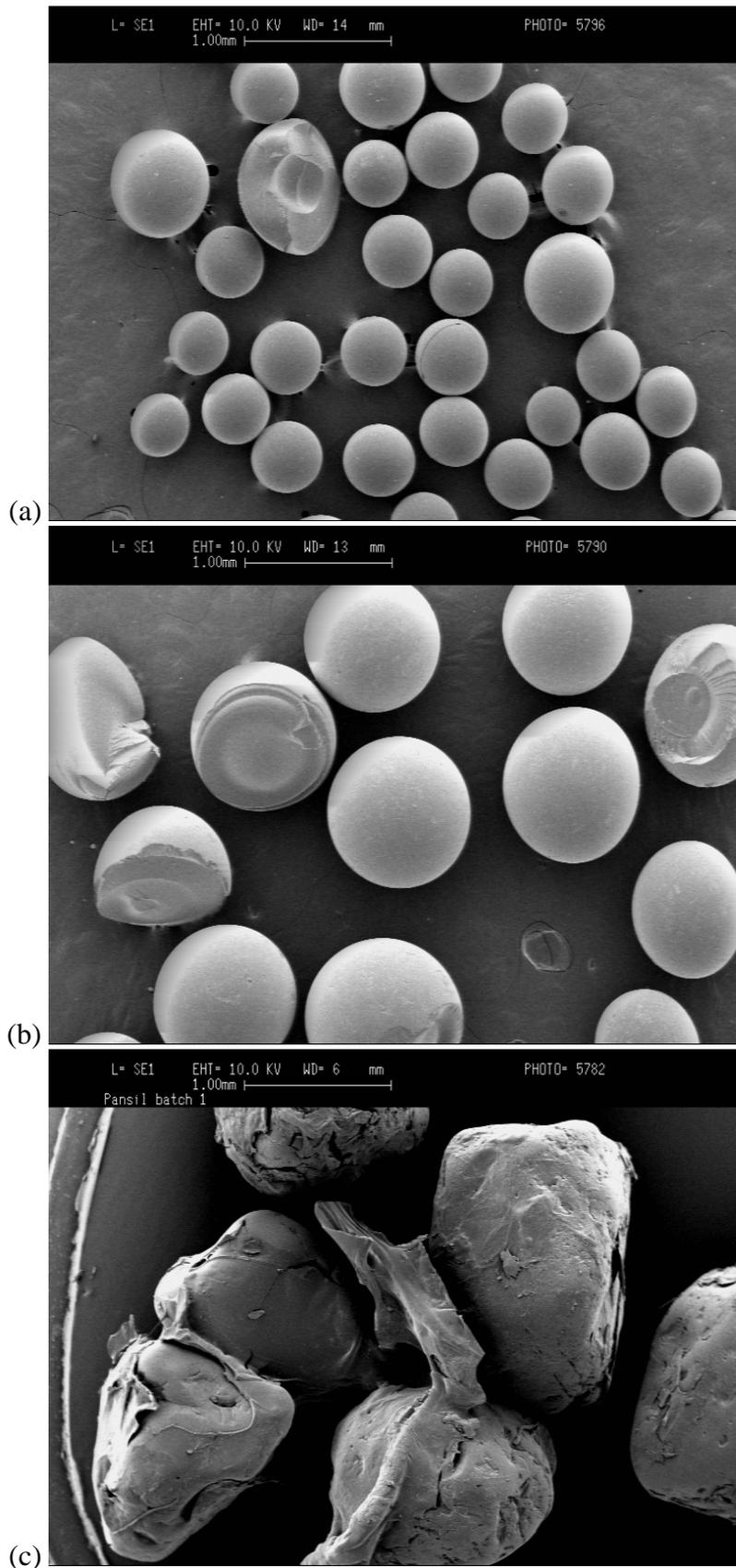[+] Between pH 7 and 8 the dominant carbonate specie will be HCO_3^-

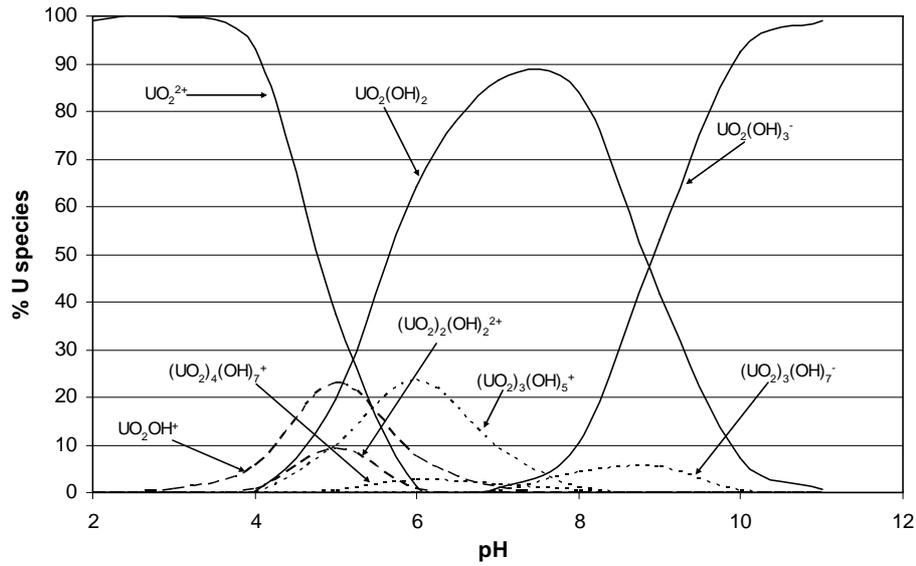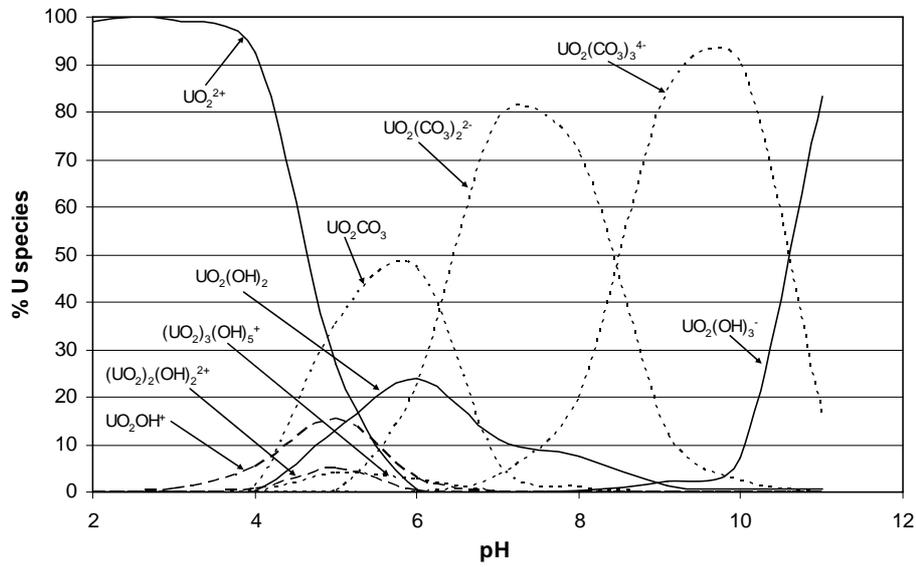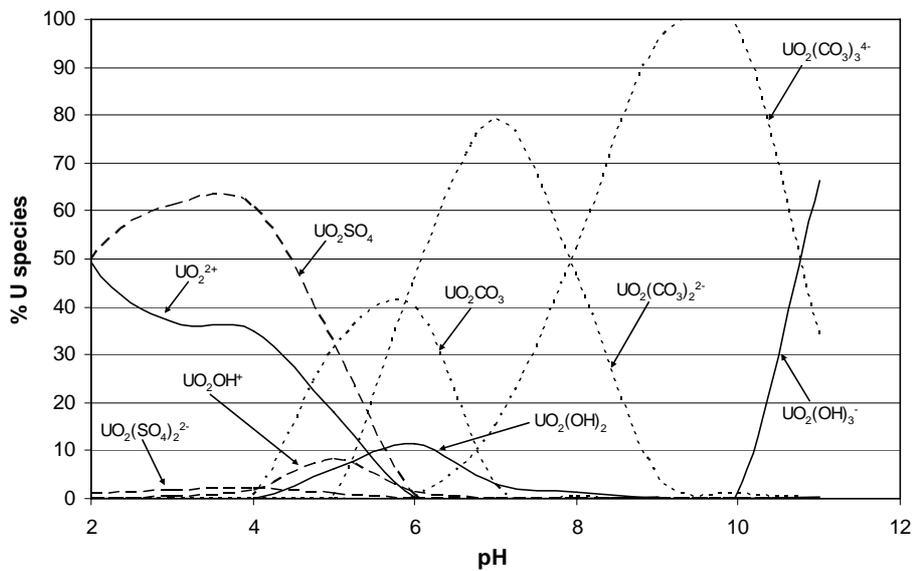**Figure 1:** Electron micrograph of (a) the conditioned cation exchange resin, (b) the conditioned anion exchange resin, and (c) PANSIL.

Figure 2: Geochemical modelling results: (a) uranyl solution, pH 2 – 11; (b) uranyl solution equilibrated with 100 mg/l of $NaHCO_3$, pH 2 - 11; (c) synthetic groundwater, pH 2 – 11.
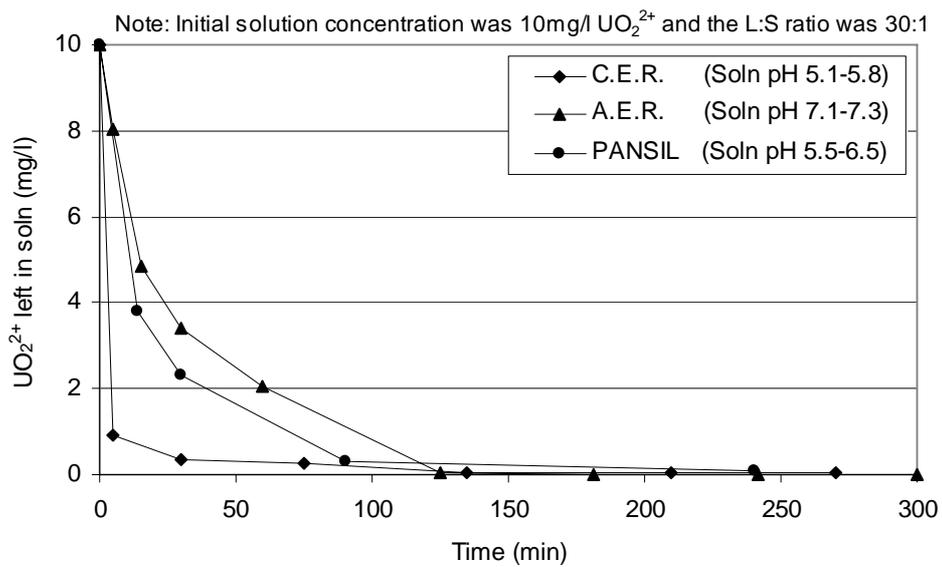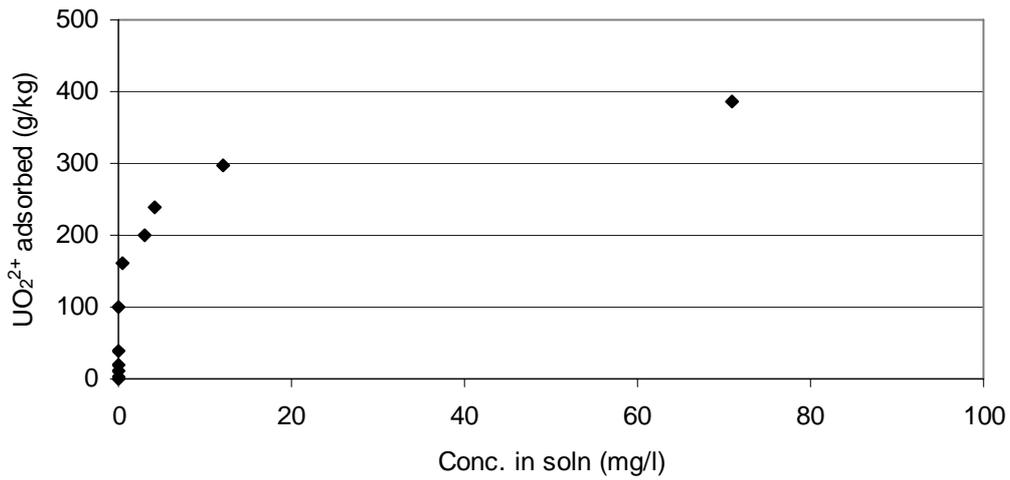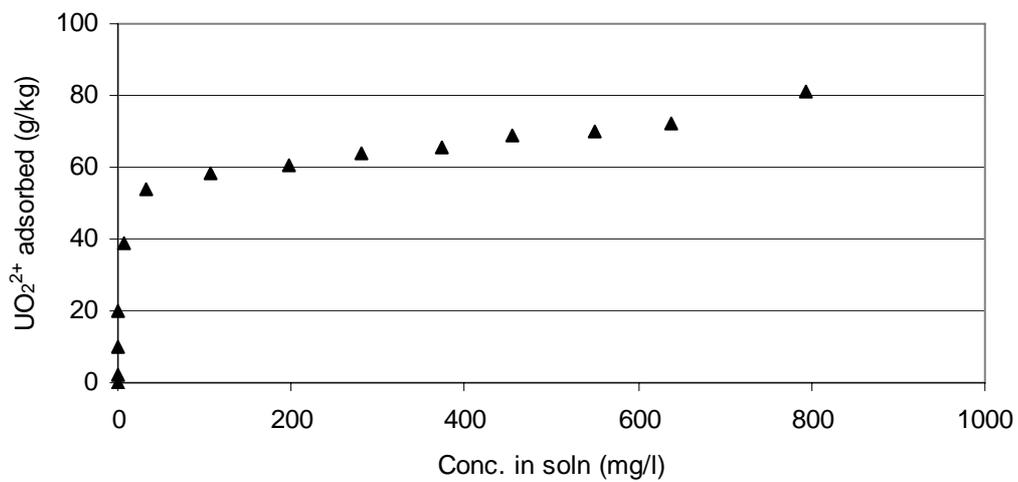
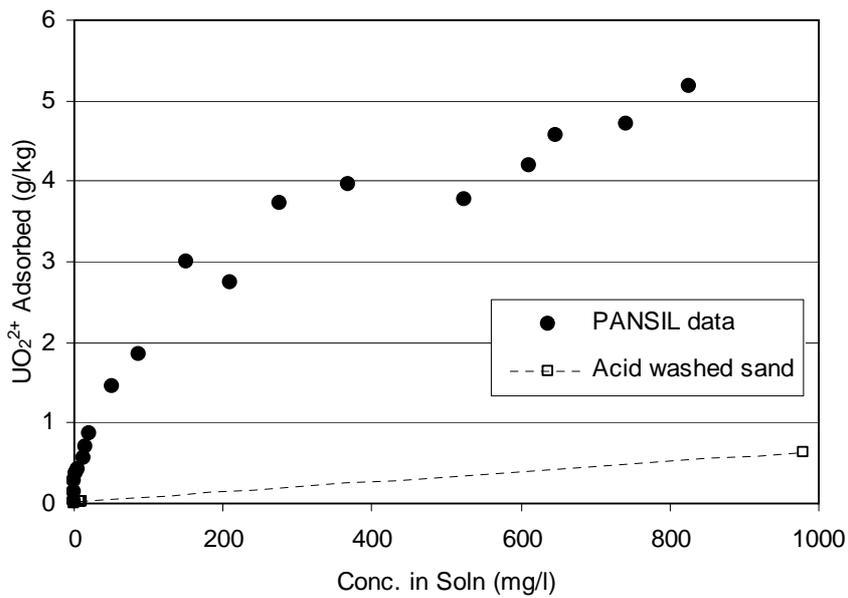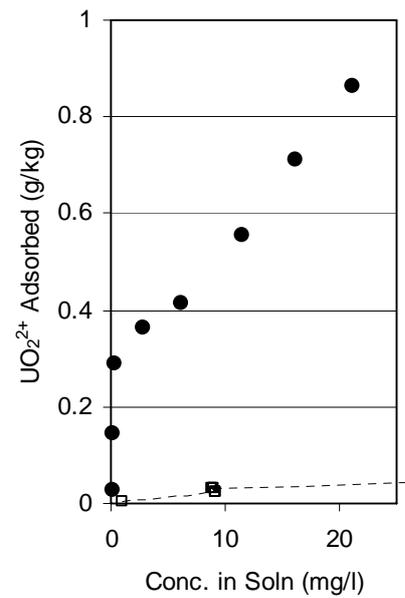**Figure 3:** Time-dependent reactions between uranyl and the three active materials.
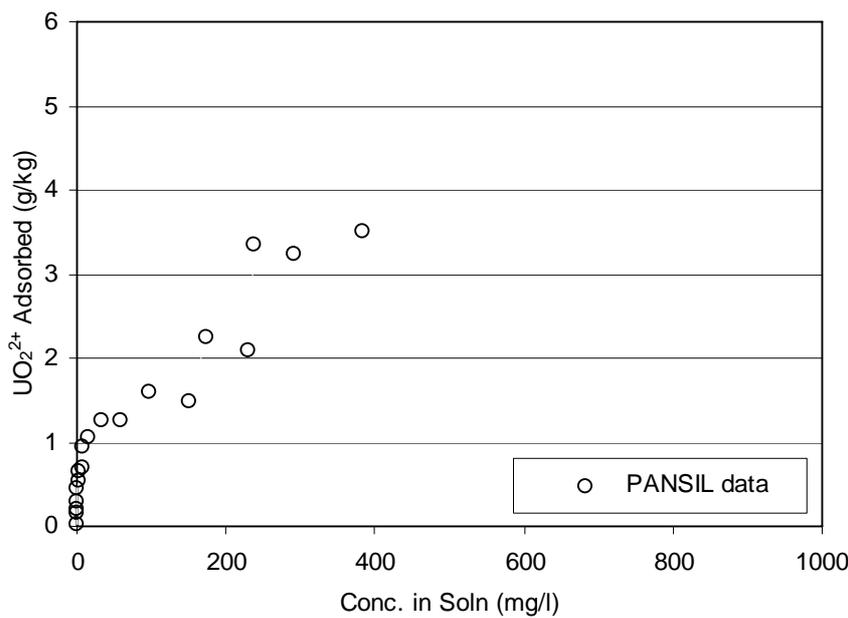
Figure 4: Sorption isotherm for (a) the unconditioned cation exchange resin in uranyl nitrate solutions at ~ pH 3.8, and (b) the conditioned anion exchange resin in uranyl nitrate solutions with sodium bicarbonate at ~ pH 5.
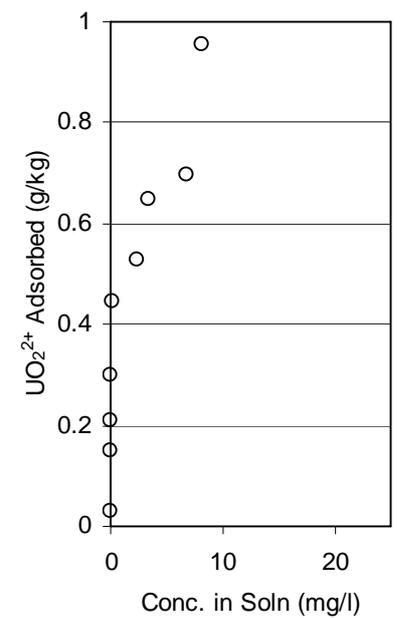
Figure 5: Sorption isotherm for UO_2^{2+} on PANSIL in (a) & (b) uranyl nitrate at pH 4.5, and (c) & (d) equal molarities of uranyl nitrate and lead nitrate at pH 4.5 (the initial sorption behaviour in both solutions is shown on expanded scales on the right). Data for the acid washed sand support is shown by the open squares in (a) & (b).

Figure 6: Column tests on the cation exchange resin using synthetic groundwater at ~ pH 7.5 containing 30 mg/l UO_2^{2+} (note: no datum point was measured for the moment at which maximum UO_2^{2+} sorption occurred).

Figure 7: Column tests on the anion exchange resin using (a) carbonated uranyl nitrate at pH 6.5 containing 100 mg/l UO_2^{2+} (after the influent and effluent UO_2^{2+} concentrations were equal, the column was leached with uncontaminated synthetic groundwater), and (b) synthetic groundwater at ~ pH 7.5 containing 30 mg/l UO_2^{2+}.

Figure 8: Column tests on PANSIL using (a) uranyl nitrate solution at pH 6 and (b) synthetic groundwater at ~ pH 7.5 (both solutions contained 30 mg/l UO_2^{2+}).

Figure 9: Variation of uranium sorption from uranyl nitrate solutions with pH for (a) the conditioned cation exchange resin, (b) the conditioned cation exchange resin, and (c) PANSIL. The mean (±1 standard deviation) of (a) 4, (b) 3, and (c) 7 tests with synthetic groundwater are also shown ($\square$). Solutions initially contained 10 mg/l of UO_2^{2+}.

Figure 1: Electron micrograph of (a) the conditioned cation exchange resin, (b) the conditioned anion exchange resin, and (c) PANSIL.

Figure 2: Geochemical modelling results: (a) uranyl solution, pH 2 – 11; (b) uranyl solution equilibrated with 100 mg/l of NaHCO₃, pH 2 - 11; (c) synthetic groundwater, pH 2 – 11.

Figure 3: Time-dependent reactions between uranyl and the three active materials.

Figure 4: Sorption isotherm for (a) the unconditioned cation exchange resin in uranyl nitrate solutions at ~ pH 3.8, and (b) the conditioned anion exchange resin in uranyl nitrate solutions with sodium bicarbonate at ~ pH 5.

Figure 5: Sorption isotherm for UO_2^{2+} on PANSIL in (a) & (b) uranyl nitrate at pH 4.5, and (c) & (d) equal molarities of uranyl nitrate and lead nitrate at pH 4.5 (the initial sorption behaviour in both solutions is shown on expanded scales on the right). Data for the acid washed sand support is shown by the open squares in (a) & (b).
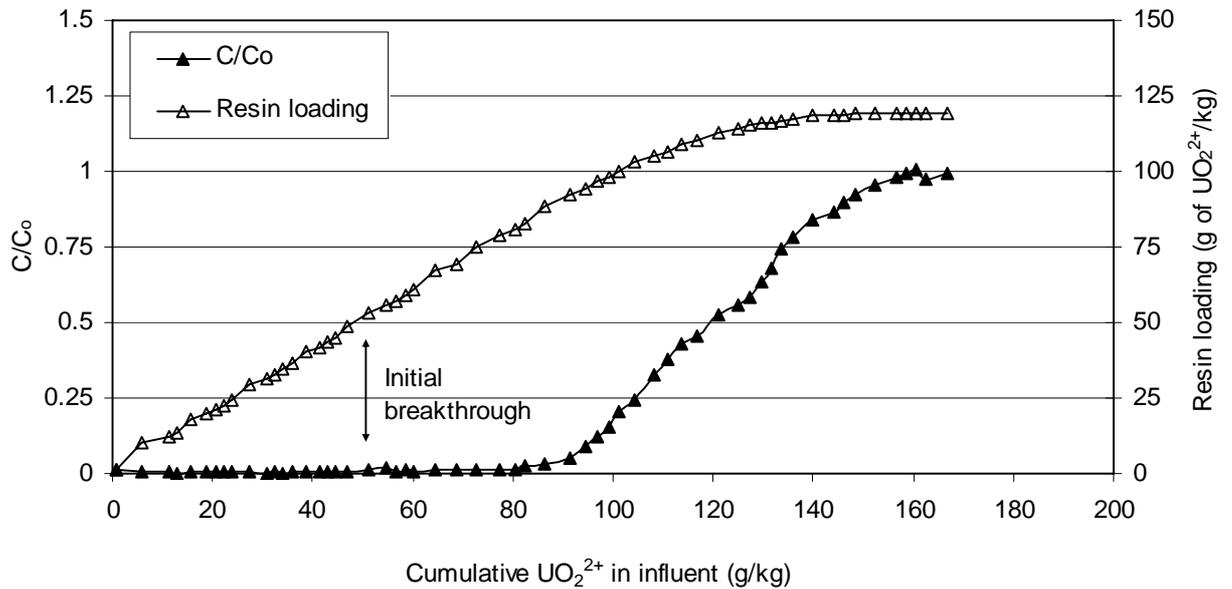
Figure 6: Column tests on the cation exchange resin using synthetic groundwater at ~ pH7.5 containing 30 mg/l UO_2^{2+} (note: no datum point was measured for the moment at which maximum UO_2^{2+} sorption occurred).
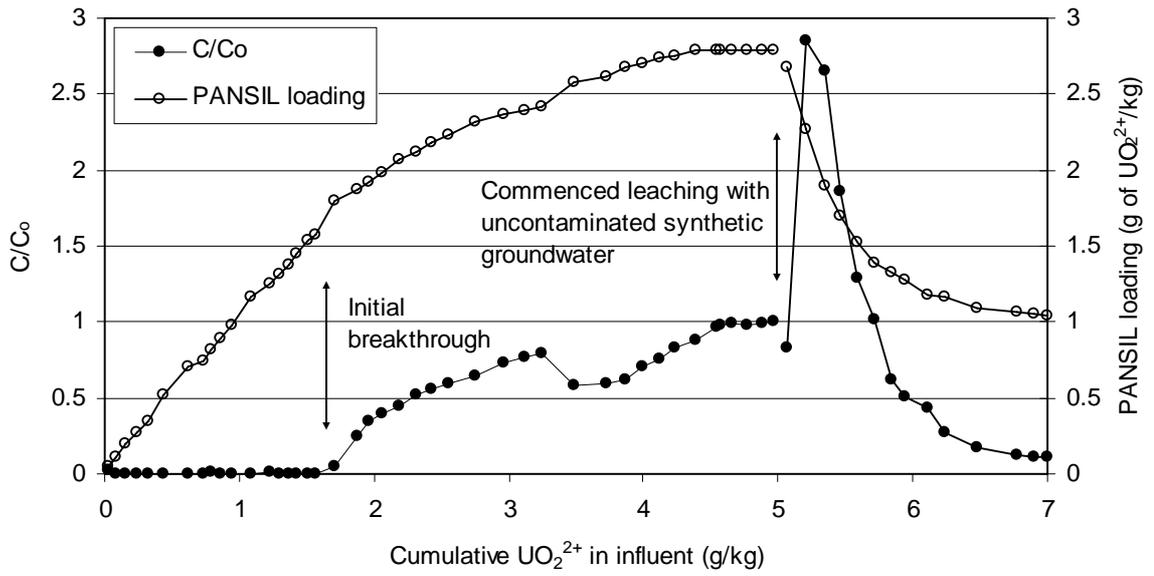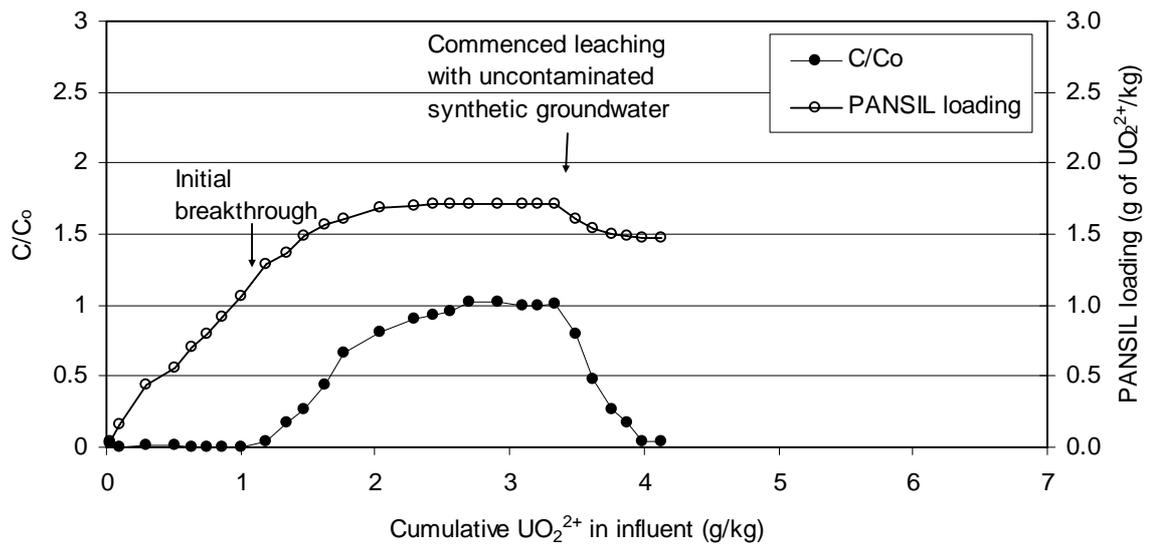
(a)

(b)

Figure 7: Column tests on the anion exchange resin using (a) carbonated uranyl nitrate at pH 6.5 containing 100 mg/l UO_2^{2+} (after the influent and effluent UO_2^{2+} concentrations were equal, the column was leached with uncontaminated synthetic groundwater), and (b) synthetic groundwater at ~ pH 7.5 containing 30 mg/l UO_2^{2+}.

(a)

(b)

Figure 8: Column tests on PANSIL using (a) uranyl nitrate solution at pH 6 and (b) synthetic groundwater at ~ pH 7.5 (both solutions contained 30 mg/l UO_2^{2+}).
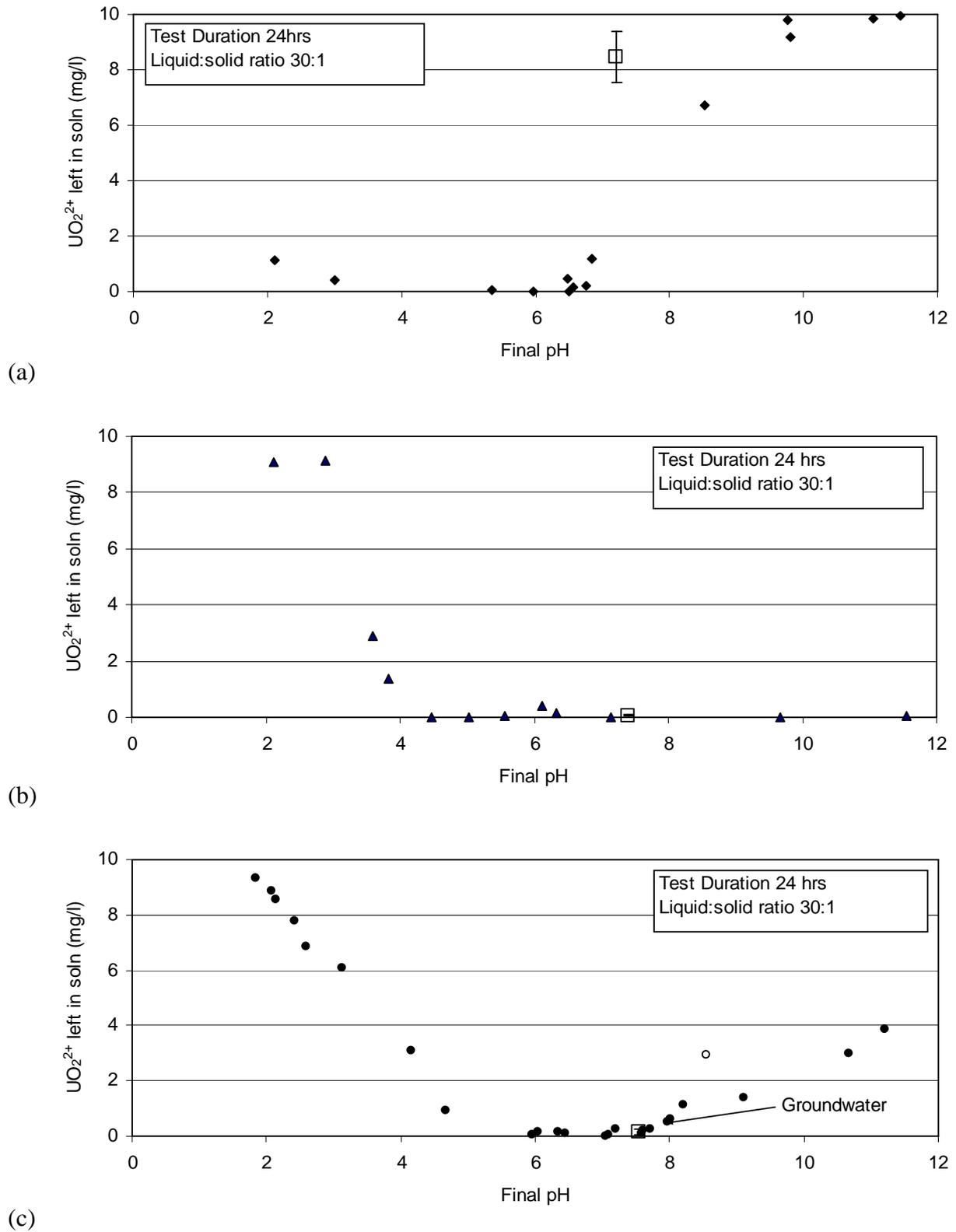
(a)

(b)

(c)

Figure 9: Variation of uranium sorption from uranyl nitrate solutions with pH for (a) the conditioned cation exchange resin, (b) the conditioned cation exchange resin, and (c) PANSIL. The mean ($\pm$1 standard deviation) of (a) 4, (b) 3, and (c) 7 tests with synthetic groundwater are also shown ($\square$). Solutions initially contained 10 mg/l of UO_2^{2+}.