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Development of a Functionalized Polymer-Coated Silica for the Removal of Uranium from Groundwater

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A new active material for the treatment of uranium-contaminated groundwater using permeable reactive barriers has been developed. This material, called PANSIL, is an example of a tailored ligand system that selectively removes a contaminant from solution. The active medium in PANSIL is a polyacryloamidoxime resin derived from polyacrylonitrile, which is deposited from solution onto the surface of quartz sand to form a thin film coating. PANSIL is highly effective at sequestering UO_2^{2+} from solution when the pH is between about 5 and 8 and can preferentially sequester UO_2^{2+} from solutions that are typical of the groundwater from a mine tailings site, due to the stability of the polyacryloamidoxime uranyl complex formed. Uranium sequestration capacity will depend on the surface area of the sand that is resin coated, but in the batch of PANSIL tested (<2% resin by weight), it exceeds 4000 mg of UO_2 per kg of PANSIL at pH 4.5 when the dissolved UO_2^{2+} concentration is greater than 300 mg/L. PANSIL largely retains the permeability and strength of the sand employed and therefore has suitable engineering properties for permeable reactive barrier applications.

Introduction

During the past decade a new approach has been developed for the remediation of contaminated groundwater, known as a permeable reactive barrier (PRB), which is gradually superseding the more established "pump and treat" technologies (*1,2*). These barriers are located underground in a natural aquifer and intercept the pollution plume carried along by the natural contour differences in the aquifer. The barrier may be simply a trench filled with reactive material or of the "funnel and gate" type where flow in the aquifer is channeled by impermeable side walls to a reactive zone. 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 zerovalent metals, and bioremediation. However, none of these reactive materials 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 (indeed, UO_2^{2+} can be below Ca^{2+} and Mg^{2+} in the cation replaceable series for some sorbents (*3*) and is then easily replaced). Reductive barriers can precipitate groundwater constituents and byproducts from the reducing agent, in addition to the contaminant, and are therefore prone to clogging (a particular problem with zerovalent iron). Bioremediation can be problematic within a PRB as it can be very difficult to maintain optimum conditions within the reactive zone. The purpose of this research was to develop a new reactive material for the treatment of uranium-contaminated groundwater, which has a high specificity for UO_2^{2+} but does not cause the precipitation of other species or have any other unwanted impact on the groundwater.

This paper focuses on the novel use of tailored ligand systems to selectively remove heavy metals. A general strategy was adopted where the ligands were immobilized by chemical attachment to a silica surface. Uranium exists in aqueous solution as the very stable UO_2^{2+} cation, which has a linear shape, but favors coordination from nitrogen and oxygen atoms. The ligand systems which are the most selective for uranium are those with coordinating atoms arranged in a planar ring surrounding the uranyl unit orthogonal to the O=U=O axis. Calixarenes, for example, have a strong affinity for uranyl, and the 5-, 6-, and 8-ring calixarenes will remove uranium from aqueous solution with a very high degree of selectivity (*4*).

The material reported here is a polyacryloamidoxime resin derived from polyacrylonitrile (PAN). A considerable research effort has already been directed toward substances derived from PAN-based fibers used for complexing various metals, including the removal of uranium from seawater (*5–7*). PAN resin can show a degree of selectivity for heavy metals, for example, preferentially removing gold in the presence of first-row transition metals (*8*). In a study involving 30 days immersion in seawater off the coast of Japan, modified PAN-based fibers were shown to preferentially adsorb uranium, vanadium, cobalt, nickel, iron, manganese, in the presence of similar concentrations of copper and zinc, and far larger concentrations of calcium and magnesium (*7*). In another study on amidoxime resin, the resin showed great affinity for U(VI), some affinity for Pb(II) and Cu(II), but less affinity for Cd(II), Cr(III), Hg(II), and Zn(II) (*9*). The resin was most effective at removing U(VI) at pH 5 (the highest value tested) but was completely ineffective below pH 3.

However, modified PAN-based fibers were not considered to be suitable for use in PRBs due to their reduced mechanical strength after reaction (*10*) and low water permeability and the difficulties that would be associated with designing a PRB employing fibers to achieve a particular groundwater residence time. Instead, a powdered form of PAN was reacted with hydroxylamine to form the active resin (see Scheme 1), and this was deposited from solution onto the surface of quartz sand to form a thin film coating. Consequently, the overall mechanical properties of the sand were retained.

Experimental Section

Preparation of PANSIL. Sand passing a 1.204 mm sieve but retained on a 0.599 mm sieve is prepared by standing in freshly prepared aqua regia for 24 h, decanting this off, and replenishing with fresh aqua regia two more times. The sand is washed repeatedly in deionized water until the washings are clear and then washed once in acetone and air-dried. The purpose of this step is to remove all impurities and soluble

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SCHEME 1. Reaction of PAN to Polyacryloamidoxime
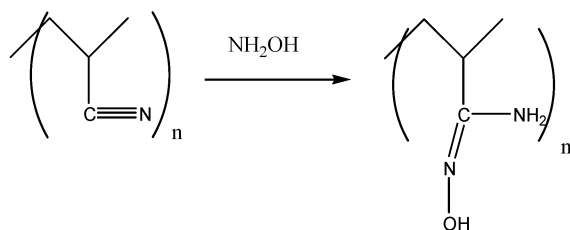
minerals and to provide clean etched sand particles to aid binding of the polymer.

Polyacrylonitrile powder (5.3 g, 0.1 mol) is suspended in a solution of hydroxylamine hydrochloride (6.9 g, 0.1 mol) in 125 mL of methanol. Sodium hydroxide (4.0 g, 0.1 mol) is added and the mixture refluxed for 4 h (the hydroxylamine, which adds across the CN triple bond as shown in Scheme 1, is produced in solution by the action of sodium hydroxide on the hydroxylamine hydrochloride salt). The mixture is allowed to cool, and then the polymer is filtered off and washed with deionized water and acetone and allowed to dry. The reaction can be monitored by infrared spectroscopy: the band due to the nitrile stretch at 2244 cm^{-1} diminishes, and the band due to the formation of an oxime at 1660 cm^{-1} grows. Not all functional groups are reacted after 4 h, but the reaction is stopped at this stage since it is believed that further modification has a detrimental effect on the coating properties of the modified polymer (a batch of modified PAN reacted for 6 h had observably poorer coating properties).

The modified PAN (polyacryloamidoxime) (2.00 g) is disaggregated by gently breaking-up the coarser particles using a mortar and pestle and dried in a desiccator before dissolving in 250 mL of dimethylsulfoxide (DMSO) at room temperature (DMSO is the only acceptable solvent that will dissolve the polymer). At the same time, 100 g of cleaned sand is dried by placing it in a round-bottomed flask and heating under vacuum to 180 °C for 2 h. The sand is allowed to cool, and the vacuum in the flask is replaced with nitrogen. When the glassware is sufficiently cool to handle, the DMSO polymer solution is poured over the sand. The flask is evacuated to degas the solution and heated to reflux under vacuum (110 °C) for 10 min (even in DMSO the polymer only readily dissolves at elevated temperatures). It is then placed on a rotary evaporator to remove the DMSO (gentle rotation ensures an even coating of the sand). When the removal of solvent is apparently finished and the mixture has a viscous fluid consistency, the sand is poured into a wide dish and allowed to stand for more than 4 days. During this time the polymer gels, and from time to time it is possible to decant off small amounts of relatively clean solvent. Occasionally the mixture should be stirred (after decanting any free solvent). Some final drying can be performed in a vacuum oven. A micrograph of modified-PAN-coated silica sand (PANSIL) is shown in Figure 1.

Surface Analysis. Three samples were specially prepared for electron microscopy. Commercially supplied silica (particle size of 2−5 mm, designed for chromatography) was used to support the modified PAN instead of sand to maintain purity and consistency. The samples were as follows:

(1) Vacuum-dried silica exposed to uranium;

(2) Polyacryloamidoxime-coated silica;

(3) Polyacryloamidoxime-coated silica exposed to uranium.

Sample 2 was primarily for visual study, whereas samples 1 and 3 were for uranium analysis.

The silica (as supplied) was heated under vacuum to 180 °C for 2 h to dry the surface. One portion of this dried silica
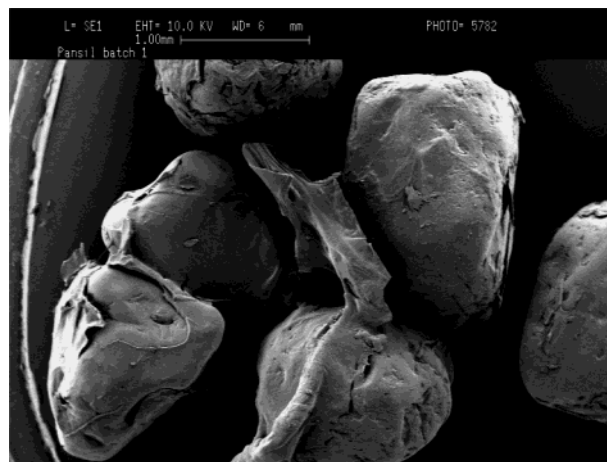

FIGURE 1. Electron micrograph of PANSIL.

(0.2 g) was suspended in a solution of uranyl nitrate in diethyl ether (0.2 mM) overnight. The solution was decanted off and the silica washed with fresh diethyl ether and allowed to dry in air to form sample 1. Polyacryloamidoxime was dissolved in DMSO, and this solution was evaporated to dryness on a second portion of the dried silica using a rotary evaporator. The resultant solid was washed with ether and dried under vacuum as sample 2. A subsample of sample 2 was suspended in the uranyl ether solution as above to form sample 3. All samples were carbon coated for microscopy.

Infrared Study. A KBr disk was made of uranyl nitrate and its IR spectrum recorded. Uranyl nitrate (217 mg, 0.55 mol) was dissolved in 10 mL of DMSO, and its IR spectrum was recorded between NaCl plates. Polyacrylamidoxime (40 mg, 0.55 mol) was dissolved in DMSO (10 mL). On mixing the polymer and uranyl solutions, the solution took on a yellow color, and on addition of water, the polymer came out of solution. The polymer was washed with water and acetone, and its IR spectrum in KBr was recorded.

Determination of the Sorption Isotherm for Uranium on PANSIL. PANSIL was added to stoppered glass bottles containing a uranyl nitrate solution whose pH was adjusted to a value between 4 and 5. The liquid:solid ratio was 30:1, and the uranium concentration was between 1 and 1000 mg/L. Control tests were conducted using acid-washed sand instead of PANSIL. The bottles were shaken end-over-end for 24 h (preliminary tests indicated an exposure time of 4 h was sufficient for the uranium concentration to reach equilibrium) at room temperature (typically 22−25 °C). The supernatant liquor was filtered at 0.45 μm (using Whatman Puradisk 25PP disposable filters), its pH was measured, and then it was acidified by adding a few drops of concentrated nitric acid and stored at 4 °C. The supernatant liquor was analyzed for uranium concentration 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.

pH-Controlled Batch Exposure Tests. The effectiveness of PANSIL at extracting uranium from water over a range of pH was investigated by batch exposure tests. PANSIL was added to stoppered glass bottles containing a uranyl nitrate solution whose pH was adjusted to values between 1.5 and 9 using either HNO$_3$ or NaOH (covering the usual groundwater pH range of 5−9 and also that encountered in acid mine drainage). The uranium concentration was either 1 or 10 mg/L, and the liquid:solid ratio was 30:1. The bottles were shaken end-over-end for 24 h at room temperature. The posttest procedure was the same as that for the sorption isotherm specimens.

TABLE 1. Measured Composition of the Synthetic Groundwater Prior to Addition of $UO_2 \cdot (NO_3)_2$[a]

	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	252.5	181.5

[a] Cations were measured by ICP−OES, and anions were measured by HPLC−IC except for carbonate, which was measured by the flow injection method (*12*). The error in charge balance was less that 2% of the total charge.
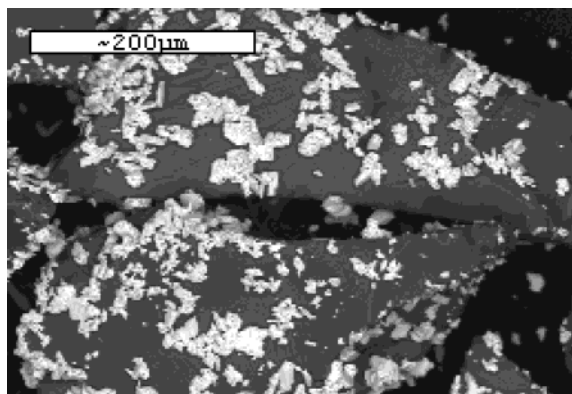

FIGURE 2. Backscattered electron micrograph of sample 3 with uranium appearing as bright areas on two silica particles.

The exposed PANSIL from four batch exposure tests (two at each uranium concentration, all with a pH during the exposure step of between 5 and 6) was subjected to two further leaching steps. Once the initial solution had been decanted off, the exposed PANSIL was twice shaken end-over-end in distilled water at a liquid:solid ratio of 30:1 for 24 h. The water from both these steps was sampled, stored, and analyzed using the procedure for the sorption isotherm specimens.

Batch Exposure Tests with Synthetic Groundwater. Further batch exposure tests on PANSIL were conducted using a solution representative of natural groundwater contaminated with uranium (the recipe is based on the groundwater at a mine tailings site in Hungary). This "synthetic groundwater" was made up from laboratory-grade reagents (200 mg/L $CaCO_3$, 272 mg/L $CaSO_4$, 194 mg/L $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$, 252 mg/L $NaHCO_3$, 75 mg/L KCl), and the pH was adjusted to 7 using H_2SO_4 (0.6 mL per L of 0.1 mol/L). After pH adjustment an undissolved residue remained, so the synthetic groundwater was filtered and its composition measured (see Table 1) before the addition of either 1.86 or 18.6 mg/L $UO_2 \cdot (NO_3)_2 \cdot 6H_2O$ (equivalent to 1 and 10 mg/L UO_2), which dissolved completely. The test duration was 24 h, and the post-test procedure was the same as that for the sorption isotherm specimens. The post-test pH was 7.6, at which pH the aqueous carbonate species is HCO_3^-.

Results and Discussion

Surface Analysis. Analysis of sample 1 using energy-dispersive X-ray (EDX) analysis detected no significant signal for uranium, indicating that uranium does not sorb to silica in amounts detectable by EDX (a spectrum is shown in Figure 1, Supporting Information). However, significant amounts of uranium were detected in EDX analysis of sample 3 (Figure 2, Supporting Information). The backscattered electron micrograph of sample 3 (Figure 2) shows that the uranium has adhered to discrete locations on the coated silica (elements with a high atomic number show up as bright

areas in backscatter images). Element mapping for silicon and uranium shows that uranium is detected only in those areas where the silicon signal is masked (Figure 3). It is, therefore, deduced that the uranium is retained in areas where the silica surface is coated with modified PAN (it should be noted that the coating on the specimens prepared for surface analysis is less continuous than that on subsequent batches of PANSIL).

Infrared Study. The literature value of the asymmetric uranyl stretching frequency, ν_{OUO}, is quoted at 925 cm^{-1} (*13*). The asymmetric stretching frequency measured for the KBr disk was 949 cm^{-1}. The asymmetric stretching frequency measured for the combined modified PAN−uranyl nitrate solution in DMSO between NaCl plates was 954 cm^{-1}. Finally, the polymer that had been exposed to uranyl nitrate exhibited a band due to the asymmetric stretch at 912 cm^{-1}. Since the ν_{OUO} frequency decreases as the uranyl−ligand bond strength increases (*14*), the shift in the asymmetric stretching frequency from 949 to 912 cm^{-1} indicates that the uranium coordinates more strongly to modified PAN than nitrate, and this effect cannot be attributed to residual DMSO left in the PAN.

Sorption Isotherm. The data showing the sequestration behavior of uranium on PANSIL is shown in Figure 4. The control tests indicated that the sorption capacity of any exposed sand is very low and that precipitation of uranium during the isotherm batch tests was not significant, and thus, even at the high concentrations used for isotherm determination, uranium is removed from solution by the modified PAN coatings. Figure 4 also shows a Langmuir isotherm that has been fitted to the data. The Langmuir model assumes nondissociative chemisorption involving a specific number of a single type of site and was developed for adsorption from the gas phase but is frequently applied to adsorption from solution. Uranium sequestration by PANSIL is thought to involve a specific number of chelating sites and is thus compatible with the Langmuir model. The sequestration capacity of the particular batch of PANSIL tested is estimated to be about 5000 mg/kg when the UO_2^{2+} concentration in solution is very high.

pH-Controlled Batch Exposure Tests. PANSIL was effective at sequestering UO_2^{2+} when the solution pH was between about 5 and 8 and reduced the uranium concentrations of both 1 and 10 mg/L solutions to values below the detection limit for the analytical technique when the pH was between 6 and 8 (see Figure 5). PANSIL was less effective below pH 5 and wholly ineffective at pH 2. In the four leaching tests on used PANSIL (from the batch exposure tests), the UO_2^{2+} concentration was substantially below the detection limit for the analytical technique after both leaching steps in all the tests. This suggests that UO_2^{2+} is strongly bound by PANSIL and will not readily be released.

Batch Exposure Tests with Synthetic Groundwater. Synthetic groundwater containing both divalent cations (Ca^{2+} and Mg^{2+}) and carbonate species (known to complex uranium at intermediate pH) had only a minor effect on the sequestration of uranium by PANSIL (Figure 6). The maximum sequestration capacity of PANSIL for UO_2^{2+} is about 19 mmol/kg (5000 mg/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 at the lower uranium concentration 4 μmol/L (1 mg/L) of UO_2, which at an L:S ratio of 30 are equivalent to 78 mmol of divalent cations per kg of PANSIL. Thus, the number of divalent cations in the synthetic groundwater exceeded the maximum sequestration capacity of PANSIL. Therefore, it is concluded that PANSIL can preferentially sequester UO_2 from typical groundwater systems.

Uranyl Sequestration by PANSIL. It is thought that polyacryloamidoxime acts as a bidentate ligand system for
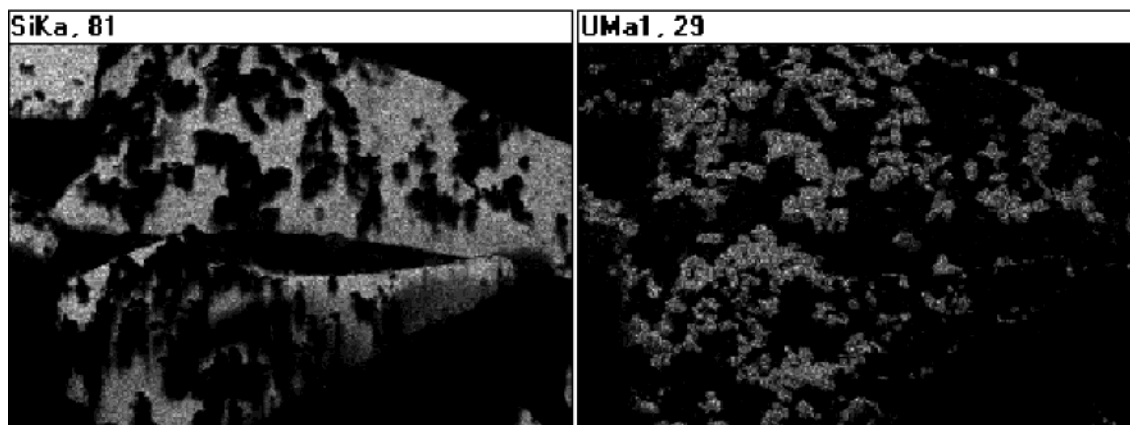
FIGURE 3. Element maps of an area of sample 3 showing (i) silicon X-ray emission (left) and (ii) uranium X-ray emission.
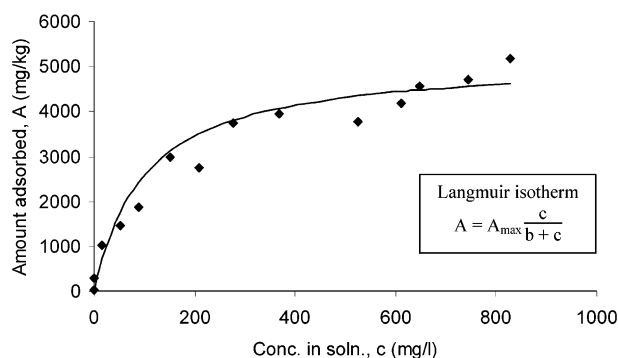

FIGURE 4. Sorption isotherm for uranium on PANSIL (pH ca. 4.5; assumed Langmuir isotherm constants are $A_{max} = 5173$ mg/kg and $b = 98.8$ mg/L)

the uranyl cation. The lone pairs of electrons on the amino nitrogen and the oxime oxygen are donated to the positive metal center to form a five-membered ring including the metal (such rings are noted for their stability due to the minimum of strain in the bonds). The oxime oxygen can undergo metal-assisted deprotonation (9), further increasing the stability of the ring at intermediate pH. Such a chelating ligand complex (where the ligand system coordinates through two or more atoms to the same metal) is considerably more stable than a similar number of monodentate ligands due mainly to the entropy increase arising from the net increase in unbound ligands.

Two factors are thought to explain the pH dependence of UO_2^{2+} sequestration by modified PAN. These are the speciation of the uranyl ion and the protonation of the lone pair electrons on nitrogens and oxygens (the active sites) in PANSIL. 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 micromolar uranyl concentrations, the UO_2^{2+} cation predominates at pH values below ca. 5. In the pH range 5–7, 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. However, at pH values much above 8, only anionic species (such as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) are significant (15, 16). At low pH, protonation of the active sites on PANSIL hinders the sequestration of cationic uranyl species. Otherwise, the active sites on PANSIL should interact effectively with cationic species but not with anionic uranyl carbonate species (indeed, strong carbonate solutions have been used to recover uranium from amidoximes (9)). PANSIL is thought to have been effective with the synthetic groundwater
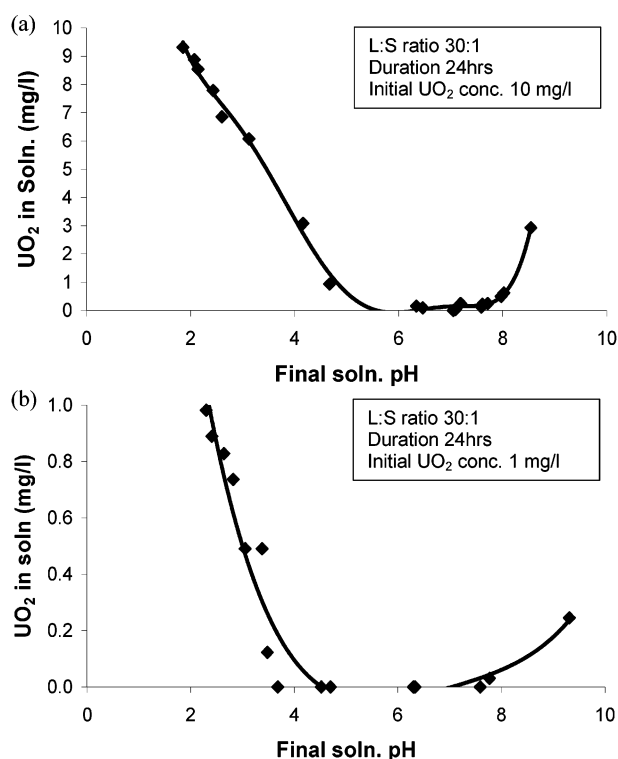

FIGURE 5. pH-controlled batch exposure tests on PANSIL: initial uranium concentration in solution (a) 10 and (b) 1 mg/L (the trendlines are polynomials that have been best-fitted to the data).

containing carbonate at a pH of 7.6 by acting through cationic species (such as UO_2OH^+) even though their equilibrium concentrations are low at this pH.

The performance of PANSIL in contaminated synthetic groundwater is compared with the reported performance of other PRB materials in similar solutions in Table 2. The comparison is made in terms of the conditional distribution coefficient, R_d (mL/g), which is the amount of a substance sorbed (μg/g) divided by its equilibrium concentration in solution (μg/mL). Generally, R_d is not a unique property of a particular sorbent/solution system and usually varies with the test conditions (particularly the contaminant concentration). Thus, the test data used for comparison have been carefully selected to ensure that the contaminant concentration, pH, and L:S ratio are in a similar range to the PANSIL tests.

PANSIL compares very favorably with the other materials reported in Table 2. The measured R_d value for PANSIL is an
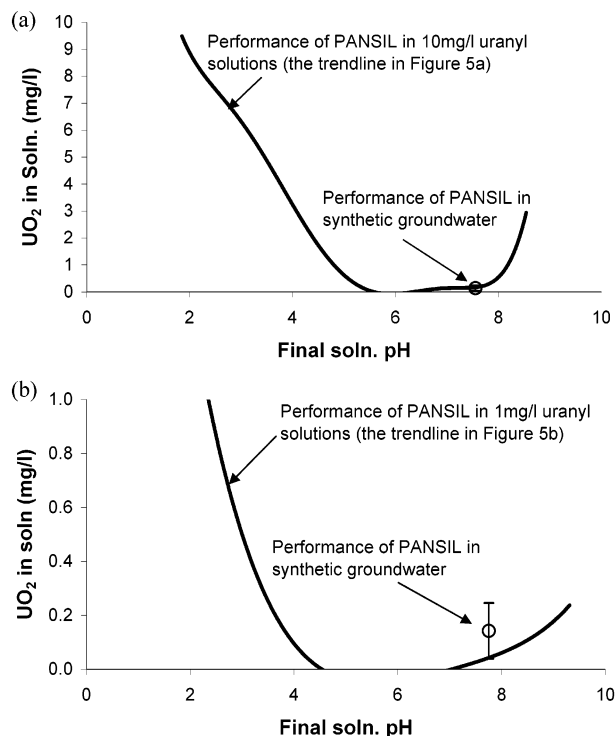
FIGURE 6. Uranium sequestration by PANSIL from synthetic groundwater: initial uranyl concentration (a) 10 and (b) 1 mg/L. In both cases the mean of seven data and ±1 standard deviation are indicated.

TABLE 2. Performance of PANSIL and Other PRB Materials

material	ref	pH	carbonate[b] (estimated) (mg/L)	R_d (mL/g)
hydroxyapatite-based materials				
hydroxyapatite powder	17	7.9	1180	75000
powdered bone charcoal	20	7.5	580	4200
pelletized bone charcoal	19,20	≈7.2	400, 580	100−370
crushed phosphate rock	20	7.3	580	30−125
powdered TiO_2 (anatase)	17	7.9	1180	50000
iron oxide pellets	19	7.2	400	25
PANSIL		7.6	182	>1470[c]

[a] Data are presented from tests where the initial UO_2 concentration was between 5 and 35 mg/L, the pH was between 7 and 8, and the L:S ratio was between 10:1 and 100:1 (full details in Table 1, Supporting Information). [b] Between pH 7 and pH the dominant carbonate species will be HCO_3^-. [c] Final solution UO_2 concentration was below the analytical detection limit. Therefore, a minimum R_d value was calculated from that detection limit.

order of magnitude higher than those reported for similarly sized bone charcoal and iron oxide pellets and finer sized crushed phosphate rock. At the UO_2 concentrations considered, the active materials being compared with PANSIL remove UO_2 by surface adsorption (17−19), and thus, their performance depends on their specific surface area. Thus, it is not surprising that fine hydroxyapatite and TiO_2 powders have very high R_d values (indeed, it would be anticipated that fine powdered modified PAN would also have a very high R_d value), but such materials are wholly unsuitable for PRB applications due to their low permeability.

It is difficult to estimate what the final production cost of PANSIL might be while the project is still at a pilot stage. However, a general indication of the likely cost can be gained by considering the cost of the raw materials and the product yield. The current global demand for PAN-based carbon fibers is presently 18 000 tons/year (21), and the cost of similar carbon fibers is around $33/kg. The hydoxylamine hydro-

chloride and sodium hydroxide reagents are inexpensive. Nearly all the original PAN is recovered after conversion as modified PAN by simple filtration, and very little modified PAN is lost in the coating step (a thin coating is left on the reaction vessel). The DMSO solvent in the coating step can be recovered from the rotary evaporator and reused, and quartz sand is cheap. As the reactions are simple to conduct and yields are high, no particular problems are anticipated in scaling-up production. The only step that will be inconvenient during large-scale production is the waiting time required for the polymer to gel, although this step does not tie-up any equipment. Given that PANSIL is about 2% modified PAN by weight, it is reasonable to anticipate that the production costs will be of a similar order to other specialized polymers considered for metal sequestration, such as ion-exchange resins.

In summary, modified PAN has three features that make it particularly attractive as an active material for PRB applications.

(1) It has good specificity for uranyl cation (and other heavy metals).

(2) It has little other impact on groundwater chemistry.

(3) By using a robust quartz sand support whose particle size can be matched to the specific application, it can be packaged in a form that will meet the permeability and durability requirements and groundwater residence times needed for an engineered barrier.

Supporting Information Available

Figures showing EDX spectra of silica and polyacryloami-doxime-coated silica after exposure to uranium; table reporting further test details for comparison of PANSIL with other PRB materials. This material is provided free of charge via the internet at http://pubs.acs.org.

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