



White Rose Consortium ePrints Repository

<http://eprints.whiterose.ac.uk/>

This is an author produced version of a paper published in **Engineering Geology**.

White Rose Repository URL for this paper:
<http://eprints.whiterose.ac.uk/archive/1327/>

Published paper

Stewart, D.I., Csöväri, M., Barton, C.S., Morris, K. and Bryant, D.E. (2006)
Performance of a Functionalised Polymer-Coated Silica at Treating Uranium Contaminated Groundwater from a Hungarian Mine Site. *Engineering Geology*, 85 (1-2). pp. 174-183.

Performance of a Functionalised Polymer-Coated Silica at Treating Uranium Contaminated Groundwater from a Hungarian Mine Site

Douglas I. Stewart⁽¹⁾, Mihály Csövéri⁽²⁾, Catherine S. Barton⁽³⁾, Katherine Morris⁽⁴⁾ and David E. Bryant⁽⁵⁾

(1) University of Leeds, School of Civil Engineering, Leeds LS2 9JT, UK

Corresponding Author; phone 0113 343-2287, fax 0113 343-2265, email d.i.stewart@leeds.ac.uk

(2) Mecsek Ore Environment Corp., Pecs, Hungary

(3) Mineral Industry Research Organisation, Leeds, LS1 2ES, UK

(4) University of Leeds, School of Earth & Environment, Leeds LS2 9JT, UK

(5) Sheffield Hallam University, Materials Research Institute, Sheffield, S1 1WB, UK

Abstract

The performance of an active material for treating uranium contaminated groundwater within a permeable reactive barrier (PRB) is reported. This material, called PANSIL, has a tailored ligand system that selectively removes the uranyl (UO_2^{2+}) cation from solution. The active uranyl ligand 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 effective at sequestering cationic and neutral uranyl species when the solution pH is above 4, due to the stability of the polyacryloamidoxime-uranyl complex formed. However the rate of sequestration decreases rapidly when the pH exceeds about 8 where neutral uranyl species are present only at very low concentrations. It can preferentially sequester UO_2^{2+} in the presence of typical divalent groundwater cations. In mildly alkaline conditions the sequestration performance in groundwater is sensitive to the concentration of uranyl complexing ligands, such as bicarbonate. Such behaviour has important consequences for PRB design as it will determine the barrier thickness required to treat a particular groundwater flow rate.

Introduction

Groundwater pollution caused by uranium mining activities is a widespread ecological problem in both Europe and North America. Some of these workings are now abandoned which exacerbates the pollution problems. The threat posed to the environment arises not only from the radioactive emissions from decaying uranium atoms but also from the toxicity of uranium species. Uranium exists in aqueous solution as the very stable UO_2^{2+} cation, which has a linear shape, but favours co-ordination from ligands in the plane orthogonal to the O=U=O axis. Thus the speciation of the uranyl ion is 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. This results in the groundwater chemistry of uranium being quite complex and the treatment of contaminated groundwater can be difficult.

Permeable Reactive Barriers (PRBs) have recently become established as an economical technology for the in-situ treatment of groundwater for many contaminants (see for example Gavaskar, 1999; Puls et al., 1999; Blowes et al., 2000; Boyd and Hirsch, 2002). A PRB consists of a permeable treatment zone that is formed underground in a natural aquifer and intercepts the pollution plume carried along by the natural head differences in the aquifer. The reactive component may immobilize the contaminant by one of a number of different attenuation mechanisms (for example, adsorption, chemical reduction, bioremediation, etc.) and a wide range of materials have been used to form barriers.

The purpose of this research was to investigate the performance of a recently developed active material called PANSIL for the treatment of uranium contaminated groundwater within a PRB. Fibres of the material used as the active component of PANSIL have been shown to preferentially adsorb a range of heavy metals in the presence of alkali, alkali-earth and first row transition metals (Lin et al., 1993b; Rivas et al., 2000; Suzuki et al.,

2000). However such fibres are not suitable for use in PRBs due to their reduced mechanical strength after reaction (Lin et al., 1993a) and low permeability, as well as difficulties in designing a PRB with fibres to achieve a particular groundwater residence time. In PANSIL the relatively expensive active component is surface coated onto strong and relatively low cost acid washed sand particles. Thus PANSIL largely retains the properties of the sand and therefore has suitable engineering properties for permeable reactive barrier applications.

PANSIL has been extensively investigated in the laboratory (Bryant et al., 2003; Stewart et al., 2003; Barton et al., 2004), and this paper focuses on its performance with uranium contaminated groundwater extracted from near a mine tailings disposal site in Hungary.

Materials

PANSIL is polyacrylamidoxime resin coated quartz sand ($\approx 2\%$ resin by wt., Bryant et al., 2003) whose functionality is thought to be derived from the amidoxime groups that act as bidentate ligands 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. The oxime oxygen can undergo metal-assisted deprotonation (Rivas et al., 2000) further increasing the stability of the ring at intermediate pH. Figure 1 shows an electron micrograph of PANSIL, which consists of sub-rounded particles, with an average particle size of about 1mm.

The typical stable elemental chemical composition of groundwater extracted from near a mine tailings disposal site in Hungary is given in table 1. The pH of this groundwater is about 7. The uranium concentration at the site varies from several hundred μg of UO_2^{2+} / l to just over 1 mg of UO_2^{2+} / l. The groundwater from a single well at this site was used as the influent in the large column test. The concentrations of important ions in the influent water

were measured periodically during the experimental programme and average values are shown in table 2 (Na^+ , K^+ and Cl^- concentrations were not measured in the column influent). The uranium concentration in the column influent was 1.4 mg of UO_2^{2+} / l.

“Synthetic groundwater” representative of a natural groundwater contaminated with uranium was also used in the laboratory programme. It was made up from laboratory grade reagents (200 mg/l CaCO_3 , 272 mg/l CaSO_4 , 194 mg/l $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, 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 was measured (see table 3), before the addition of either 18.6 or 55.8 mg/l $\text{UO}_2 \cdot (\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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, at which pH the aqueous carbonate species is HCO_3^- .

Methods

The efficiency of PANSIL at sequestering uranium from solution was investigated by: (i) a column test with groundwater from the Hungarian mine site; (ii) two small column tests with (a) uranyl nitrate solution buffered to pH 6, and (b) contaminated synthetic groundwater; (iii) a series of pH controlled batch exposure tests with uranyl nitrate solution over the pH range 1.5 to 11; and (iv) batch exposure tests with contaminated synthetic groundwater. Prior to the main test programme, a series of increasing duration batch exposure tests were conducted on PANSIL with a uranyl nitrate solution at a liquid to solid (L:S) ratio of 30:1 (see Stewart et al., 2003, for details). These tests indicated that an exposure time of less than 4 hrs was sufficient for PANSIL to reach equilibrium with a uranyl nitrate solution containing 10 mg of UO_2^{2+} / l at ~pH 6.

Column Test with Site Groundwater – A large column test (length 840 mm, cross-sectional area 100 mm²) was conducted using PANSIL to treat the groundwater from the Hungarian mine site. The flow-direction in the column was from bottom to top, and the test was run at room temperature (20 - 25°C). The test duration was 256 days, and the total volume of water passed through the column was 4290 ml at a flow-rate of ~ 17 ml/day. The porosity of the PANSIL in the column was 40.7%, so the flow-volume was equivalent to 126 pore volumes, with a residence time of 2 days. Thus, the superficial seepage velocity was about 0.4 m/day, which is at least an order of magnitude higher than the groundwater flow velocity at the Hungarian mine tailings site.

The volume of effluent was monitored daily, and collected for analysis approximately once a week. The total uranyl concentration in both the original groundwater and the column effluent was determined by a fluorimetric method, where the fluorescent intensity of a fused pellet containing the uranyl from the solution sample is compared with that of a blank pellet. A URANUS fluorimeter manufactured by ALGADE (France) was used. Measurements were made on pellets containing the residue after evaporation of 0.1 ml of solution which was mixed with 10% sodium fluoride and 90% sodium carbonate and fused at 910°C. The detection limit was about 10 µg/l and usually three replicate measurements were made.

Small Column Tests - In the small column tests 10g of PANSIL was mixed with 20g of acid washed quartz sand as a diluant in order to reduce the amount of active material used for a particular column length. Dilution of the PANSIL was necessary in order to shorten the time taken for uranyl breakthrough without altering the residence time of the water within the column. In this study breakthrough is defined as the point beyond which there is a detectable and thereafter increasing UO₂²⁺ concentration in the column effluent. The PANSIL/sand mixture was placed in a 25 ml glass column, which resulted in a pore volume of ~ 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. This flow rate gave a residence time for the contaminated solution within the column of about 6 hrs. Effluent solutions were diverted through a spur at the top of the columns into covered collection vessels. Effluent solutions were collected once a day, and their volume and pH were measured prior to acidification for UO_2^{2+} analysis. Two column tests were conducted as follows;

- (i) 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; then the column was leached with uncontaminated synthetic groundwater.
- (ii) 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; then the column was leached with uncontaminated synthetic groundwater.

In addition a control test on acid washed sand only, using a 30 mg/l uranyl nitrate solution at ~ pH 5, was also run. In this test, initial breakthrough occurred immediately, and influent and effluent UO_2^{2+} concentration were equal when the average column loading was only 0.008 g/kg. Thus it was assumed that uranyl sorbed by the sand in the column tests can be ignored.

pH Controlled Batch Exposure Tests - The effectiveness of PANSIL at removing uranyl from water over a range of pH values was investigated using 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 11 using either HNO_3 or NaOH . The liquid to solid ratio was 30 : 1, and the uranium concentration was 10 mg of UO_2^{2+} / l. The bottles were shaken end-over-end for 24 hours, and the supernatant liquor was sampled.

The leachability of uranyl sequestered by PANSIL was also investigated. Exposed PANSIL from two batch exposure tests (with a final pH during the exposure step of between 5 and 6) was subjected to two further leaching steps using distilled water as the leaching

solution. In each leaching step the PANSIL was 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 then analysed for uranium.

Four longer duration batch exposure tests were conducted over the pH range of 8 to 11. In these tests, small aliquots of the test solution were taken for UO_2^{2+} analysis after 24, 48 and 96 hrs. After 96 hrs the contaminant solution was decanted off, and the exposed PANSIL was subjected to three further leaching steps. In these leaching steps PANSIL was shaken end-over-end in distilled water at a liquid to solid ratio of 30:1 for 24 hours. The leaching solution from each step was analysed.

Batch exposure tests with synthetic groundwater – Further batch exposure tests were conducted to investigate the effectiveness of PANSIL at treating the synthetic groundwater. The L:S ratio was 30 : 1, the uranium concentration was 10 mg of UO_2^{2+} / l and the test duration was 24 hrs.

The small column tests and all batch tests were conducted at room temperature and atmospheric $\text{CO}_2(\text{g})$ was not excluded. Solution samples ($< 0.45 \mu\text{m}$) were analysed for pH and then acidified with nitric acid, and stored at 4°C prior to analysis. The uranyl concentration was measured using a spectrophotometric method based upon the complexing reagent 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (known as Bromo-PADAP) which has a detection limit of $\sim 0.2 \text{ mg/l}$ (Johnson and Florence, 1971).

Results

Column Test with Site Groundwater – Throughout the large column test using the Hungarian groundwater the influent uranyl concentration was approximately 1.4 mg of UO_2^{2+} / l. For the first 192 days of testing the effluent uranyl concentration was typically less than 0.05 mg of UO_2^{2+} / l, and no individual measurement was greater than 0.13 mg of UO_2^{2+} / l

(Figure 2a). At some point between 193 and 198 days breakthrough occurred, and the UO_2^{2+} concentration in the effluent reached about a third of the concentration in the influent by the end of testing. The column loading at breakthrough was about 35 mg of UO_2^{2+} per kg of PANSIL. The pH of the column effluent was ~ 8.1 throughout the test (Figure 2b). Both the bicarbonate concentration and the calcium concentration were lower in the column effluent than in the site groundwater possibly due to oversaturation of CaCO_3 as the column effluent was more alkaline (pH ~ 8.1) than the site groundwater (pH ~ 7) (Figure 2c & d).

Laboratory Column tests – The smaller laboratory column tests on PANSIL 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 3a). Subsequent leaching with uncontaminated synthetic groundwater (at \sim 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 \sim 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 3b). During subsequent leaching tests 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.

Batch exposure tests - The 24 hr 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 4). PANSIL was also very effective at treating the synthetic groundwater (also shown in Figure 4).

In the two-stage, distilled water, 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 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 of UO_2^{2+} per kg of PANSIL), PANSIL strongly binds UO_2^{2+} , and once bound that UO_2^{2+} is retained in mildly acidic uncontaminated water.

The results of the additional longer duration batch exposure tests are reported in Figure 5. When the $\text{pH} > 8$ the time taken for PANSIL to reach equilibrium is greater than 48 hrs (and may exceed 96 hrs), which is far longer than at pH 6 where equilibrium was reached in less than 4 hrs. Also, at $\text{pH} > 7$ the amount of UO_2^{2+} sorbed after 96 hours decreased with increasing pH.

The leachate from the first distilled water leaching step on the PANSIL exposed for 96 hrs contained 1 mg of UO_2^{2+} / l when the pH was 8 during exposure, with the leachate concentration increasing slightly with pH to 1.3 mg of UO_2^{2+} / l at pH 11. The leachate from the second leaching step contained 0.6 mg of UO_2^{2+} / l when the pH was 8, increasing with pH to 1 mg of UO_2^{2+} / l at pH 11. The UO_2^{2+} concentration in leachate from the third leaching step was below the detection limit for all the experiments. Thus, for exposure at pH 8, 82% of the UO_2^{2+} in the original solution was still attached to the PANSIL, reducing to 48% for exposure at pH 11.

Discussion

To understand the variation in performance of PANSIL with pH and solution composition, numerical modelling has been undertaken using PHREEQE (Version phrq96) equilibrium geochemical modelling software (U.S. Geological Survey) and the CHEMVAL (Version 6) database. Three solutions were modelled: (i) uranyl nitrate conditioned with 100

mg/l carbonate (as sodium carbonate) to replicate the effect of atmospheric CO₂; (ii) the synthetic groundwater; and (iii) the groundwater from the Hungarian mine site. All these solutions were modelled under oxic conditions, the first two with a uranyl concentration of 10 mg/l of UO₂²⁺, and the Hungarian groundwater with a uranyl concentration of 0.8 mg/l of UO₂²⁺. The calculated speciation of these solutions is shown in Figure 6 as a percent of the total UO₂²⁺ in particular species as a function of pH. In general the uranyl speciation in the three solutions follows similar trends, with the UO₂²⁺ cation important below pH 5, neutral UO₂CO₃ and UO₂(OH)₂ species important 5 < pH < 7, and anionic uranyl carbonate species dominant above pH 7. However significant differences are that the neutral UO₂SO₄ specie is also predicted to be important between pH 2 and 5 for both groundwaters, and that the neutral UO₂(OH)₂ specie persists at a percentage level to above pH 9 in the carbonated uranyl nitrate system, whereas it is below 1% by pH 8 in the synthetic groundwater and pH 7 in Hungarian site groundwater.

As stated earlier, PANSIL functionality is derived from the amidoxime groups that act as bidentate ligands for UO₂²⁺, where the amino nitrogen and the oxime oxygen donate lone pair electrons to the positive metal centre to form a five-membered ring. Thus two factors are thought to explain the pH dependence of UO₂²⁺ sequestration by PANSIL in the batch exposure tests. At low pH, protonation of the lone pair electrons on the nitrogen and oxygen sites effectively blocks the active sites on PANSIL. Otherwise it is the speciation of the uranyl ion that controls the effectiveness of the interaction.

In the 24 hour batch tests using uranyl nitrate solutions that were in equilibrium with atmospheric CO₂, PANSIL was effective up to a pH of between 7.5 and 8. At such pH values the geochemical modelling indicates that the dominant uranyl species are either neutral or anionic. Likewise PANSIL was effective with the bicarbonate buffered synthetic groundwater system at ~ pH 7.5 where, again, the dominant uranyl species are either neutral

or anionic. Thus, as the amino and oxime ligands on PANSIL are unlikely to interact effectively with anionic uranyl carbonate species, it is suggested that PANSIL is sequestering the neutral uranyl species.

In the extended duration batch tests using uranyl nitrate solutions, PANSIL was still reasonably effective in the alkaline range, but reaction times were far longer than at pH 6. There seem to be two possible mechanisms by which PANSIL could operate in this range. Either PANSIL can sorb anionic species (probably electrostatically to locally slightly positive sites on the PANSIL), or the amino and oxime ligands sequester neutral species (albeit present at very low concentrations at high pH) and thus, as equilibrium between the various uranyl species in solution could be continually re-established, PANSIL may slowly sequester significant amounts of uranium. The performance of PANSIL in alkaline conditions is compatible with a combination of both of these mechanisms operating. The extended time periods required to reach equilibrium (> 96hrs) are compatible with sequestration of a minor species. In addition, the retention of significant amounts of uranium after three leaching steps suggests that much of the uranium is strongly sequestered, presumably by bidentate amidoxime ligands. However, the fact that 20% of the UO_2^{2+} sorbed at pH 8 was subsequently leached (increasing to 40% of the sorbed UO_2^{2+} at pH 11) indicates that there is some weakly sorbed uranyl present on the PANSIL at these pH values, which may represent weak physisorption of anionic uranyl carbonate species.

In laboratory column tests PANSIL was very successful at treating both uranyl nitrate exposed to atmospheric CO_2 at pH ~ 6 and the synthetic groundwater at pH ~ 7.5, with a capacity in the range 1 - 1.5 g of UO_2^{2+} per kg of PANSIL. However the capacity for uranyl sorption of PANSIL measured in column tests with the groundwater from a Hungarian mine site was significantly lower, at ~ 35 mg UO_2^{2+} per kg of PANSIL. Given the relatively small differences between the synthetic groundwater and the Hungarian groundwater (the former

contained 30 mg of UO_2^{2+} / l and 180 mg/l of carbonate at ~ pH 7.5, the latter contained 1.4 mg of UO_2^{2+} / l, ~ 600 mg/l of carbonate at pH 8.1), the large difference in column capacities is initially very surprising. However both these solutions are mildly alkaline, so geochemical modelling suggests that PANSIL must operate by sequestering neutral species. The geochemical modelling predicts that the lower uranyl and higher carbonate concentrations of the Hungarian groundwater resulted in a significantly lower $\text{UO}_2(\text{OH})_2$ concentration in mildly alkaline conditions than in the synthetic groundwater. It is therefore suggested that this resulted in a slower rate of reaction in the Hungarian groundwater. Thus a residence time of 6 hrs was more than sufficient to remove most of the uranium from the synthetic groundwater (where ~ 1.5% of the uranyl is calculated to be $\text{UO}_2(\text{OH})_2$), but a residence time of 2 days was only just sufficient to successfully treat the Hungarian groundwater (where less than 0.05% of the uranyl is calculated to be $\text{UO}_2(\text{OH})_2$). Breakthrough probably occurred in the Hungarian groundwater column because the sequestration capacity of the PANSIL near the inlet end of the column became exhausted leading to a reduction in the effective residence time of the column.

The extended residence time required to treat the Hungarian groundwater does not necessarily mean that PANSIL cannot be used to treat that solution because a PRB can, within reason, be designed to achieve the required residence time. The groundwater flow velocity at the Hungarian mine site is more than an order of magnitude lower than used in the column test, but as PANSIL is likely to be used within a “funnel and gate” type barrier (where the groundwater is channelled through a reactive zone), the flow velocity used in the column test is of the right magnitude. However, the residence time within the barrier can be extended by increasing the barrier thickness; to a degree this can be achieved without increasing the amount of active material by adding an inert diluant, such as clean sand, to increase the volume of the reactive zone.

Conclusion

PANSIL is effective at sequestering cationic and neutral uranyl species when the solution pH is above 4, due to the stability of the polyacryloamidoxime-uranyl complex formed. However the rate of sequestration decreases rapidly when the pH exceeds about 8 where neutral uranyl species are present only at very low concentrations. Under such conditions PANSIL is thought to sequester those neutral species, and can slowly accumulate significant amounts of uranyl as equilibrium is continually re-established between the various uranyl species in solution. Thus optimum performance is obtained in the pH range 4.5 to 7.5. Once sequestered under these pH conditions, the uranium is not readily leached from PANSIL.

PANSIL can preferentially sequester uranyl from solutions that are typical of the groundwater from a mine tailings site. However it has been shown that its performance is sensitive to the exact groundwater water chemistry. Small changes in the pH and the concentration of uranyl complexing ligands such as bicarbonate can dramatically affect the sequestration rate, which is an important design parameter for a PRB as it controls the barrier thickness required to treat a particular groundwater flow rate.

This work has demonstrated the important role of geochemical modelling in developing an understanding of the behaviour of PRB materials in groundwater of different composition, and in particular the importance of bicarbonate complexation of UO_2^{2+} on the performance of PANSIL. It is recommended that geochemical modelling of the groundwater be a standard part of PRB design.

Acknowledgement

This work is part of the PEREBAR project (Long-term performance of permeable reactive barriers used for the remediation of contaminated groundwater) funded by the 5th Framework Programme of the European Union (EVK1-CT-1999-00186). For information about the project see {www.perebar.bam.de}. The authors would like to acknowledge the help of Dr Nick Bryan, Radiochemistry Research Centre, Dept of Chemistry, Manchester University, with the PHREEQE modelling.

References

- C.S. Barton, D.I. Stewart, K. Morris and D.E. Bryant (2004). Performance of Three Resin Based Materials for Treating Uranium Contaminated Groundwater within a PRB. *Journal of Hazardous Materials B116*, 191-204.
- D.W. Blowes, C.J. Ptacek, S.G. Benner, C.W.T. McRae, T.A. Bennett, R.W. Puls. (2000). Treatment of inorganic contaminants using permeable reactive barriers. *J. Contam. Hydrology*, 45 123-137.
- G. Boyd, R.M. Hirsch (2002). Foreword, Handbook of Groundwater Remediation Using Permeable Reactive Barriers, Academic Press pp. xvii.
- D.E. Bryant, D.I. Stewart, T.P. Kee, C.S. Barton (2003). Development of a functionalised polymer-coated silica for the removal of uranium from groundwater. *Environmental Science and Technology*, **37** 4011-4016.
- A.R. Gavaskar (1999). Design and construction techniques for permeable reactive barriers. *J. Haz. Mat.*, **68** 41-71
- D.A. Johnson, T.M. Florence (1971). Spectroscopic determination of uranium(VI) with 2-(5-Bromo-2-Pyridylazo)-5-Diethylaminophenol. *Analytica Chimica Acta*, **53** 73-79.

- R.W. Puls, D.W. Blowes, R.W. Gillham (1999). Long-term performance monitoring for a permeable reactive barrier at the U.S. Coast Guard support center, Elizabeth City, North Carolina. *J. Haz. Mat.*, **68** 109-124.
- B.L. Rivas, H.A. Maturana, S. Villegas (2000). Adsorption behaviour of metal ions by amidoxime chelating resin. *J.Appl.Polym.Sci.*, **77**, 1994-1999.
- D.I. Stewart, C.S. Barton, T.P. Kee, D. Bryant (2003). Metal-sequestering ligand based media for treating contaminated groundwater using porous sequestration barriers. Deliverables 16 and 17 report, PEREBAR Project, European Union (EVK1-CT-1999-00186).
- T. Suzuki, K. Saito, T. Sugo, H. Ogura, K. Oguma (2000). Fractional elution and determination of uranium and vanadium adsorbed on amidoxime fiber from seawater. *Anal. Sci.*, **16**, 429-432.
- W.P. Lin, Y. Lu and H.M. Zeng (1993a). Studies of the preparation, structure and properties of an acrylic chelating fiber containing amidoxime groups. *J.Appl.Polym.Sci.*, **47** (1), 45-52.
- W.P. Lin, Y. Lu and H.M. Zeng (1993b). Extraction of Gold from Au(III) ion containing solution by a reactive fiber. *J.Appl.Polym.Sci.*, **49** (9), 1635-1638.

Figure Captions

Figure 1: Electron micrograph of PANSIL.

Figure 2: Column tests on PANSIL using the groundwater from a Hungarian mine site containing ~ 1.4 mg/l UO_2^{2+} .

Figure 3: Column tests on PANSIL using (a) uranyl nitrate solution at pH 6 and (b) synthetic groundwater at \sim pH 7.5 (both solutions initially contained 30 mg/l UO_2^{2+}).

Figure 4: Variation of uranium sorption with pH by PANSIL in uranyl nitrate solutions containing 10 mg/l of UO_2^{2+} . The mean (± 1 standard deviation) of 7 tests with synthetic groundwater (\square) is also shown.

Figure 5: Effect of test duration on UO_2^{2+} by PANSIL at high pH

Figure 6: Geochemical modelling results; (a) uranyl nitrate containing 100 mg/l of carbonate, (b) the synthetic groundwater, and (c) the groundwater from the Hungarian mine site.

Table 1: Typical groundwater composition at the Hungarian mine site (the uranyl concentration tends to vary spatially and temporally but is about 1 mg/l).

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
Concentration mg/l	70	17	168	53	45	337	484

Note: The error in charge balance is less than 0.5% of the total charge.

Table 2: Average measured composition of the Hungarian site groundwater used as the column influent (Na⁺, K⁺ and Cl⁻ concentrations were not measured during the column experiment).

	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	HCO ₃ ⁻	UO ₂ ²⁺
Concentration mg/l	163	67	385	595	1.4

Table 3: Measured composition of the synthetic groundwater prior to addition of UO₂.(NO₃)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

Note: The error in charge balance is less than 2% of the total charge.

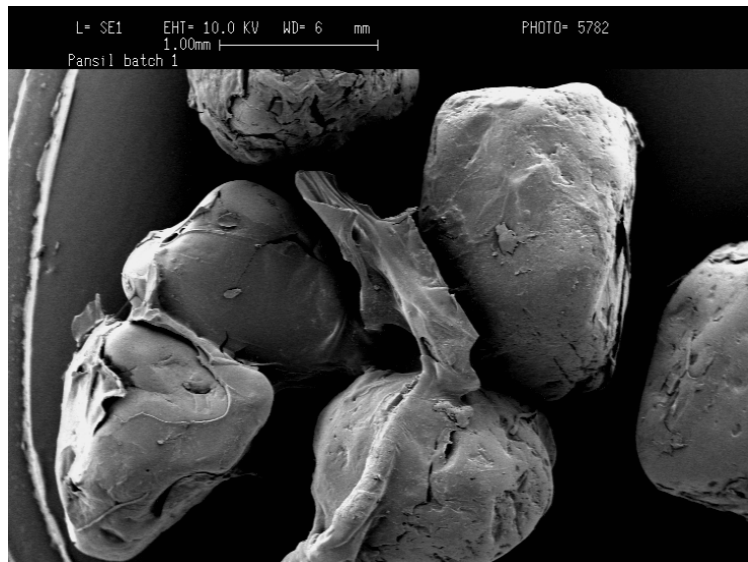


Figure 1: Electron micrograph of PANSIL.

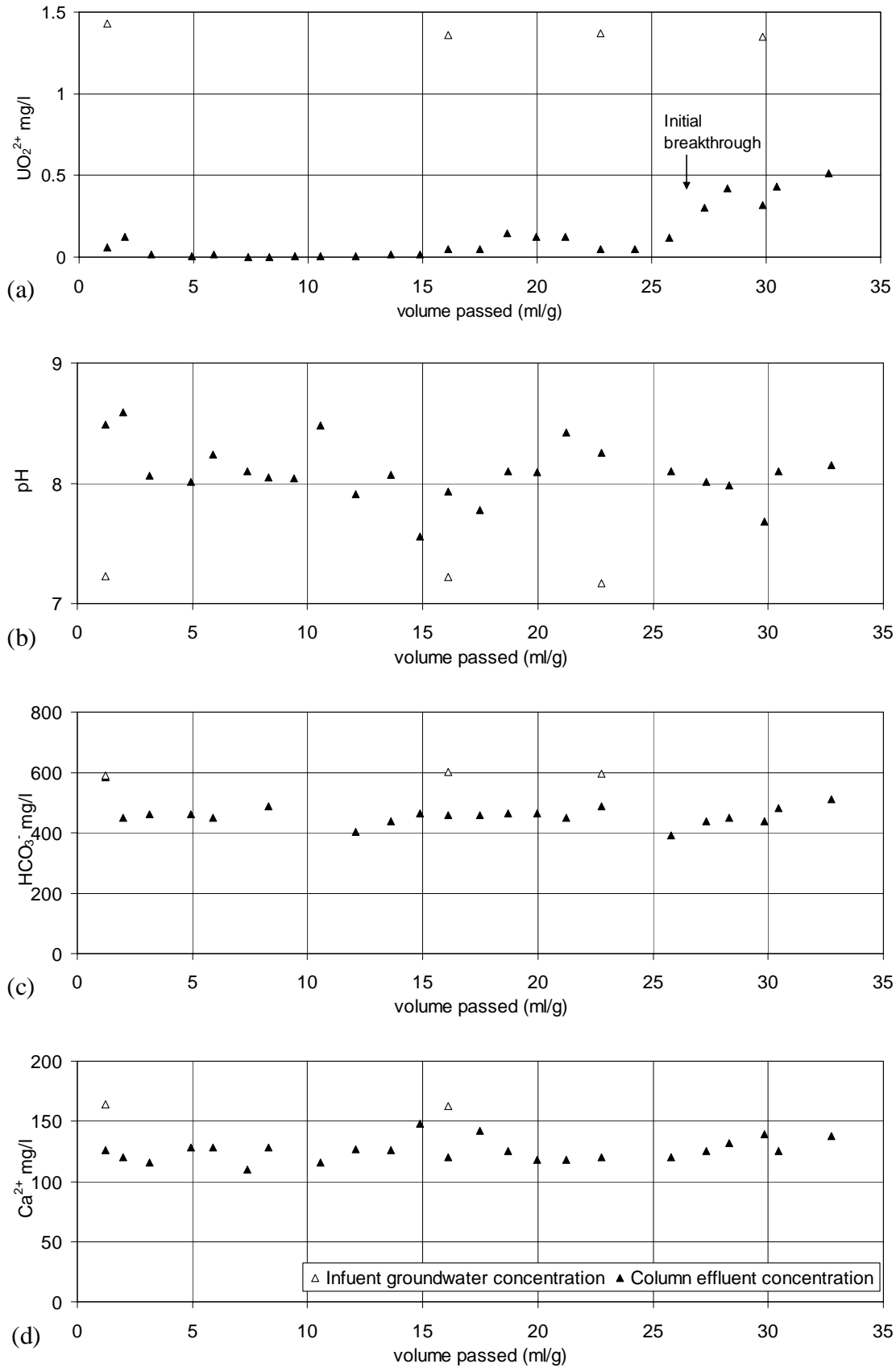
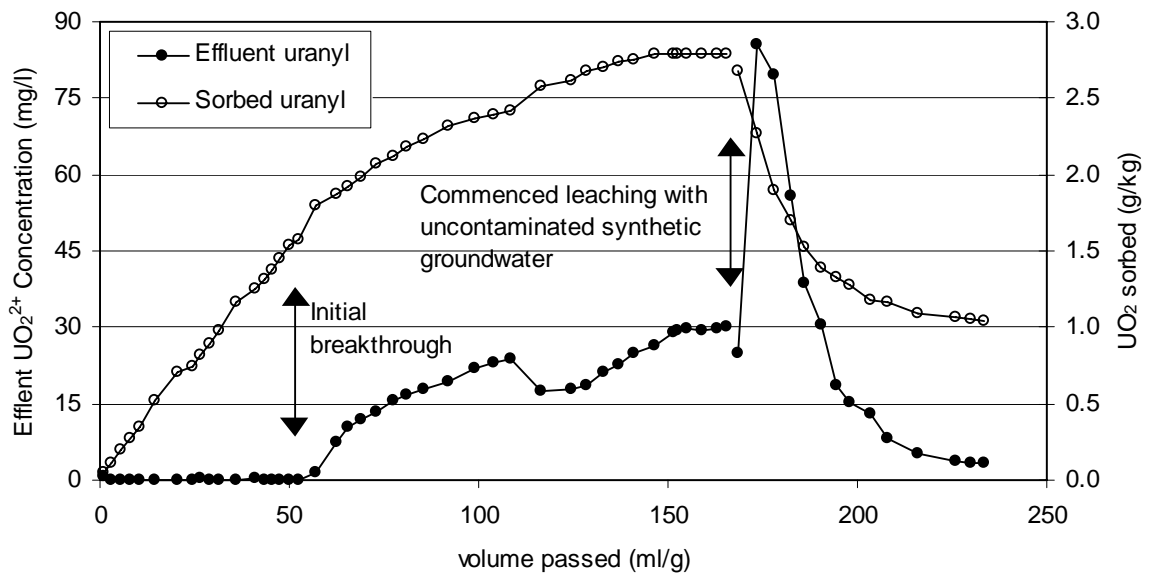
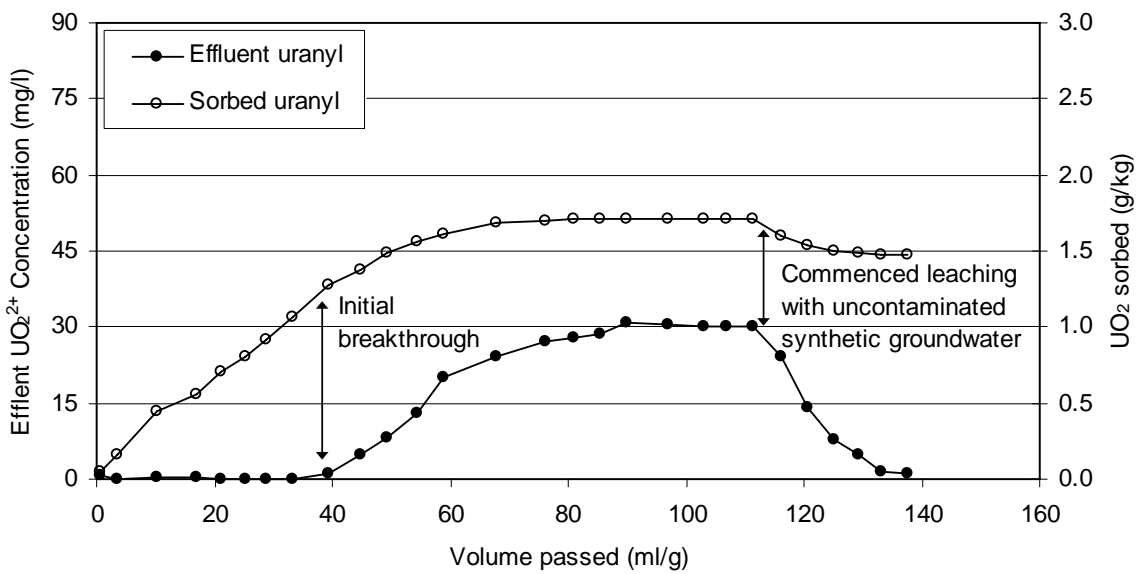


Figure 2: Column tests on PANSIL using the groundwater from a Hungarian mine site containing ~ 1.4 mg/l UO_2^{2+} .



(a)



(b)

Figure 3: Column tests on PANSIL using (a) uranyl nitrate solution at pH6 and (b) synthetic groundwater at ~ pH 7.5 (both solutions initially contained 30 mg/l UO_2^{2+}).

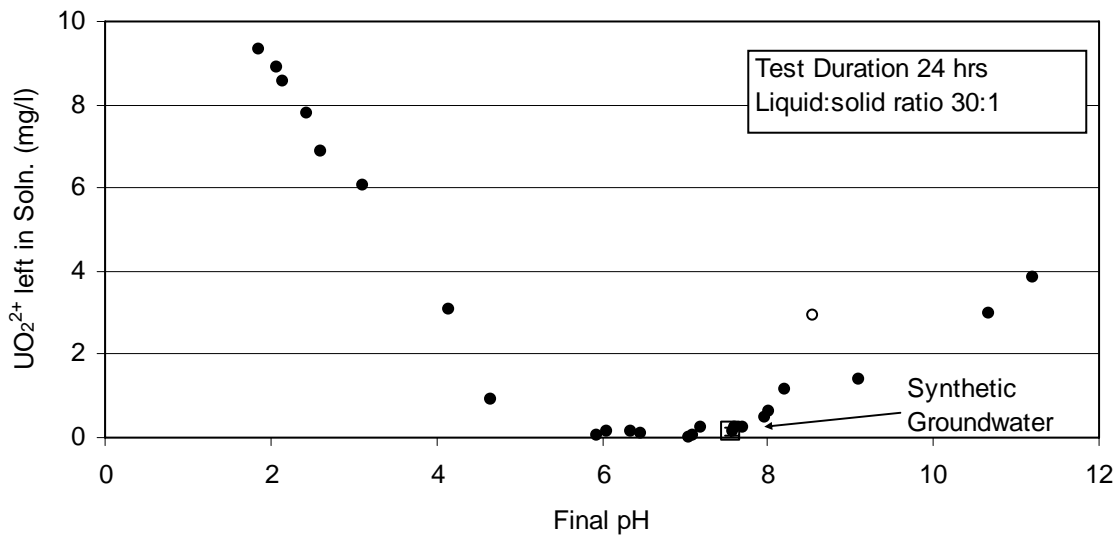


Figure 4: Variation of uranium sorption with pH by PANSIL in uranyl nitrate solutions containing 10 mg/l of UO_2^{2+} . The mean (± 1 standard deviation) of 7 tests with synthetic groundwater (\square) is also shown.

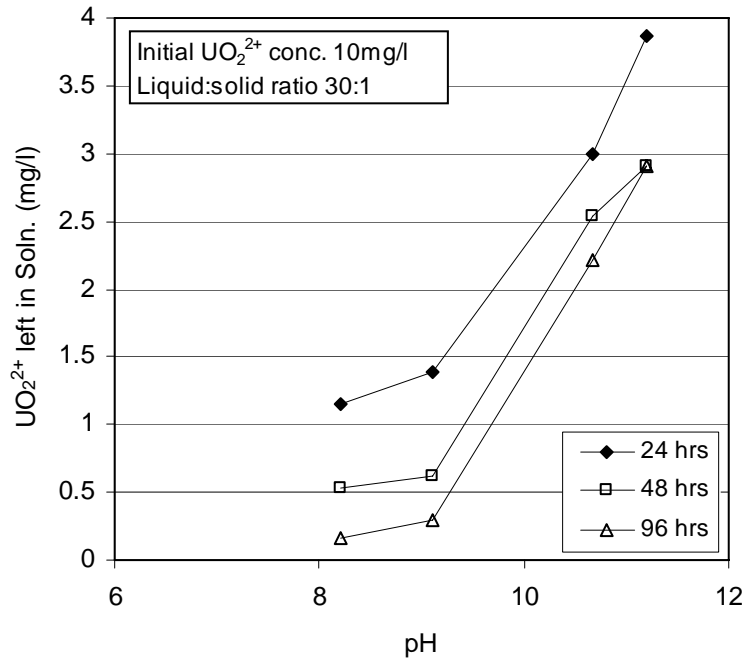
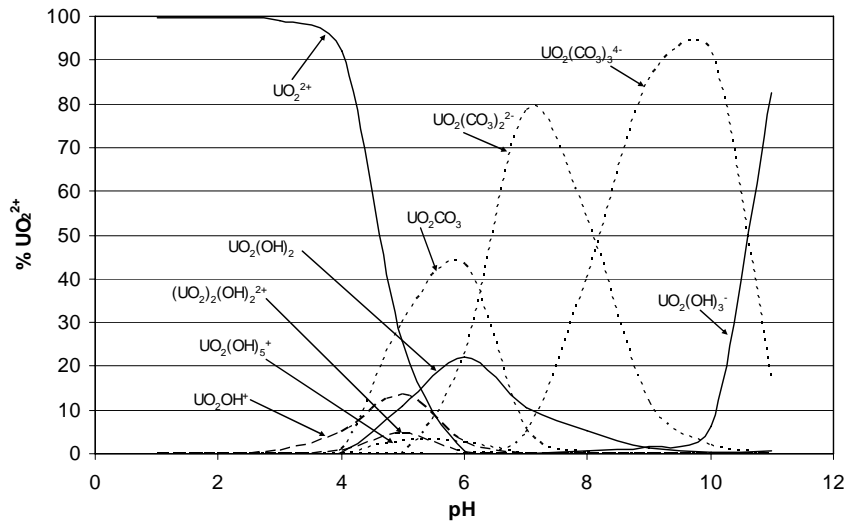
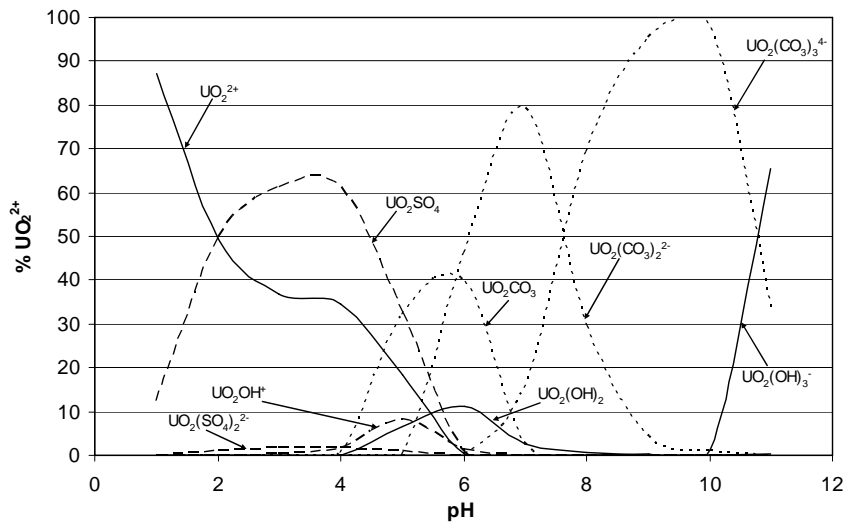


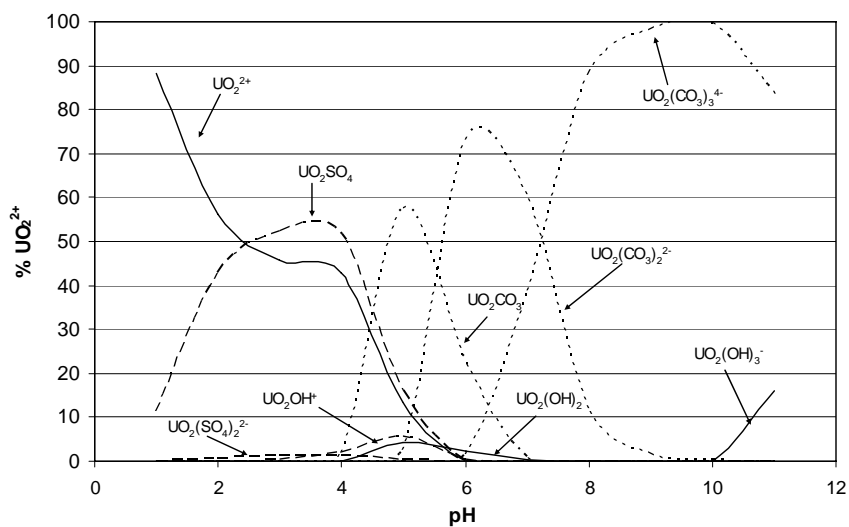
Figure 5: Effect of test duration on UO_2^{2+} by PANSIL at high pH



(a)



(b)



(c)

Figure 6: Geochemical modelling results; (a) uranyl nitrate containing 100 mg/l of carbonate, (b) the synthetic groundwater, and (c) the groundwater from the Hungarian mine site.