Uranium removal using elemental iron and hydroxyapatite in permeable reactive barriers

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ABSTRACT

Permeable reactive barriers (PRBs) offer an alternative as opposed to more cost-intensive active water treatment methods, e.g. pump-and-treat. Long-term performance of PRBs has been examined by a consortium of 8 partners in the European project PEREBAR. Research has been focussed on uranium removal from groundwater contaminated by mining activities. Good removal results have been achieved by reducing U(VI) to U(IV) using elemental iron. Possible reaction paths are reductive precipitation and adsorption on to corrosion products of Fe^0.

Uranium concentration can be reduced without changing the oxidation state by producing low-solubility uranium phosphates, e.g. precipitating uranyl ions with hydroxyapatite (HAP) and so forming autunite $Ca(UO_2)_2(PO_4)_2$ *or chernikovite* $H_2(UO_2)_2(PO_4)_2$. *Other possible reaction mechanisms for uranium removal with HAP are ion exchange processes and surface sorption with HAP (on two possible surface groups).*

Understanding uranium behaviour in contact with the reactive materials is a prerequisite for design and lifetime prediction of permeable reactive barriers containing elemental iron or HAP. As a radioindicator ^{237}U *was applied in this study for tracking uranium movement through a test column without disturbing the system by taking samples or dismantling the apparatus. The experiments enabled to determine the maximum uranium concentration of the reactive materials (approx. 3000 mg/kg). The columns were dismantled after the experiment, and the reactive materials and by-products were analysed. The results are presented and their influence on the long-term performance of PRBs is discussed. A pilot reactive barrier was installed within the project in Pécs (Southern Hungary) and first results from operation are reported.*

INTRODUCTION

Uranium contamination in groundwater resulting from uranium mining and processing occurs world-wide at numerous locations. In view of its toxicity rather than radioactivity, a limiting concentration of 0.02 to 0.002 mg/l is being currently considered.

Approximately one third of the global uranium production was mined in Europe. Table 1 displays the production of uranium of the world's largest producers (OECD 2001). The data for the Russian Federation and several other states are based on IAEA secretariat estimation.

Table 1. Global producers of uranium (Uranium production total to 2000 in tons)

Country	**Uranium production**	**Country**	**Uranium production**
USA	353,796	Niger	81,853
Canada	340,523	France	73,664
Germany (former GDR)	213,380	Namibia	72,127
South-Africa	153,337	Gabon	27,872
Russian Federation*	114,223	Hungary	21,030
Czech Republic	107,080	Romania*	17,729
Uzbekistan	95,758	Bulgaria	16,720
Australia	91,157	Ukraine (since 1992)	10,000
Kazakhstan	88,372	China (since 1990)	7,435

** IAEA secretariat estimation*

Uranium occurs mainly in the oxidation states +4 and +6. The hexavalent uranium, i.e. the uranyl ion UO_2^{2+} is more mobile than U(IV) compounds. Good removal results have been obtained by the reduction of U(VI) to U(IV) by elemental iron:

$$Fe + UO_2^{2+}(aq) \rightarrow Fe^{2+} + UO_2(s)$$ **Reaction 1**

The reduction of UO_2^{2+} occurs spontaneously as illustrated in Figure 1. The solubility of uraninite UO_2 is in the range of 10^{-8} mol/l in a pH range between 4 and 14. Below 4 uranium becomes soluble. The behaviour of uraninite has been intensively studied because of its application as nuclear fuel and because it is a main constituent of uranium pitchblende (Bickel 1996). The measurement on the dissolution of spent fuel in deionized water under non-oxidising conditions provided results in the range of 10^{-9} to 10^{-5} mol/l. Solubility is enhanced under oxidising conditions where UO_2 can be transformed into the uranyl ion and if complexation reactions can occur. It is therefore important that Eh is below the U(IV)/U(IV) curve in the U(IV) stability field. With CO_2 present the boundary line is shifted towards lower Eh at high pH. This behaviour is displayed in Figure 1.

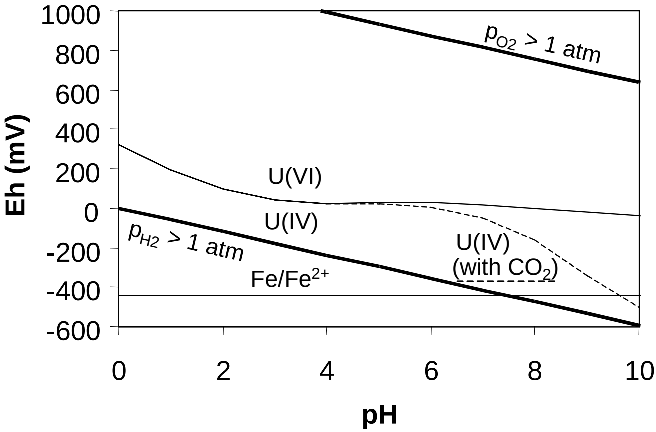

Figure 1. pH-Eh Diagram showing the boundary line between U(IV) and U(VI) without and in the presence of 0.01 bar CO_2.

At elevated pH values in the presence of CO_2 (at 0.01 bar which is typical for groundwater conditions) it is more difficult to transform uranium to the oxidation state +4. An excellent review on the complex uranium solution equilibria is given by Grenthe (Grenthe 1992).

Lowering the uranium concentration without changing the oxidation state is possible by the formation of low soluble uranium phosphates, e.g. precipitation of uranyl ions using phosphate forming $(UO_2)_3(PO_4)_2$ (log K_{sp} = - 49.09 (Brown 1981)) or using hydroxyapatite (HAP) or bone char (HAP with a small amount of carbon) forming autunite $Ca(UO_2)_2(PO_4)_2$ (log K_{sp} = - 47.28, (Brown 1981)) or chernikovite $H_2(UO_2)_2(PO_4)_2$ (log K_{sp} = - 45.48, (Grenthe 1992)). The mechanism of the interaction of uranium with HAP is not yet completely understood. Jeanjean et al. proposed a dissolution-precipitation mechanism (Jeanjean 1995). If autunite or chernikovite is the precipitation product the reaction may occur via the sequence displayed below.

$Ca_5(PO_4)_3OH \Longleftrightarrow 5\ Ca^{2+} + 3\ PO_4^{3-} + OH^-$ **reaction 2**
$H^+ + OH^- \Longleftrightarrow H_2O$ **reaction 3**
$2\ UO_2^{2+} + Ca^{2+} + 2\ PO_4^{3-} \Longleftrightarrow Ca(UO_2)_2(PO_4)_2$ **reaction 4**
$2\ UO_2^{2+} + 2\ H^+ + 2\ PO_4^{3-} \Longleftrightarrow H_2(UO_2)_2(PO_4)_2$ **reaction 5**

Ion exchange processes (see reaction 6) or surface sorption using HAP (two possible surface groups, reaction 7 and reaction 8) are described by the following equations (Wu 1991, Leyva 2001).

$\equiv Ca^{2+} + UO_2^{2+} \Longleftrightarrow \equiv UO_2^{2+} + Ca^{2+}$ **reaction 6**
$\equiv OH + UO_2^{2+} \Longleftrightarrow \equiv O\text{-}UO_2^{+} + H^+$ **reaction 7**
$\equiv O_3P\text{-}OH^+ + UO_2^{2+} \Longleftrightarrow \equiv O_3P\text{-}O\text{-}UO_2^{2+} + H^+$ **reaction 8**

In the work of Fuller et al. (Fuller 2002) autunite and chernikovite have been identified as solid phases after adding uranyl ions to a saturated solution of hydroxyapatite. Evidence for adsorption of U(VI) to hydroxyapatite surfaces as an inner-sphere complex was found for certain concentration ratios.

Arey et al. postulated the formation of secondary phosphate phases but could not identify any controlling phase such as autunite (Arey 1999).

The present paper summarises the results of column experiments performed using elemental iron and hydroxyapatite for uranium removal from groundwater. By using ^{237}U as a radio indicator it was possible to follow the movement of the contamination front through the test column without sampling or dismantling.

EXPERIMENTAL

A test column made of black polyethylene with a wall thickness of 12 mm, an inner diameter of 100 mm and a height of 540 mm was filled with a mixture of sand and reactive material (elemental iron or HAP). Elemental iron was provided by Gotthard Maier, Rheinfelden, Germany (granulated grey cast iron, 0.3 to 1.3 mm), HAP by CFB Chemische Fabrik Budenheim, Germany (food grade quality, fine white powder, 99 % < 0.42 mm). Sand was normal filter sand (0.8 – 2 mm). A uranium solution containing ^{237}U was run through the column at a flow rate of approximately 0.28 l/h. Porosity of the reactive mixture was around 30 %. Two experiments with different sand / elemental iron mass ratios were carried out using elemental iron as a reactive material. The experimental parameters are listed in Table 2.

Table 2. Experimental details

	Iron (1)	Iron (2)	HAP
Concentration of Uranium	3.1 mg/l	2.8 mg/l	3.1 mg/l
Flow rate	0.286 l/h	0.276 l/h	0.286 l/h
Feed of uranium onto the column	0.89 mg/h	0.773 mg/h	0.89 mg/h
Length of reactive zone in test column	0.15 m	0.5 m	0.2 m
Mass of reactive material (sand and iron/HAP)	1.92 kg	6.5 kg	2.9 kg
Mass ratio sand/reactive material (iron or HAP)	90:10	80:20	90:10

^{237}U was produced by exposing ^{238}U to high energy (>5 MeV) photon radiation from an electron accelerator:

$^{238}U + h\nu \rightarrow {}^{237}U + n$ **reaction 9**

The half-life of ^{237}U is 6.75 days. This isotope emits both γ– and X-rays with the following photon emission energies: 59.5 keV (γ), 97 keV (X), 101 keV (X), 114 keV (X), 118 keV (X) and 208 keV (γ), making it easily detectable, e.g. using a scintillation counter.

The isotope was produced through a photoneutron reaction induced to natural uranium. U_3O_8 (86.99 % NatU = 86.36 % ^{238}U, correspondingly) was irradiated with 30 MeV bremsstrahlung from the electron linear accelerator of BAM. The total exposure period was 100 min. Thereafter, the oxide was dissolved in concentrated nitric acid. After dilution with distilled water an aliquot of 150 ml was dissolved homogeneously in 100 l of demineralised water resulting in a total uranium concentration for the batch experiment of around 3 mg per l.

The solution containing a ^{237}U tracer was run through the test column filled with the respective reactive material and sand. Absorption of photon radiation by the polyethylene pipe of the column was found negligible. A γ–detector was scanned vertically along the column recording the number of counts. The experimental set-up is displayed in Figure 2. A correction for radioactive decay of the nuclide was performed. The test procedure is described in detail elsewhere (Simon 2003).

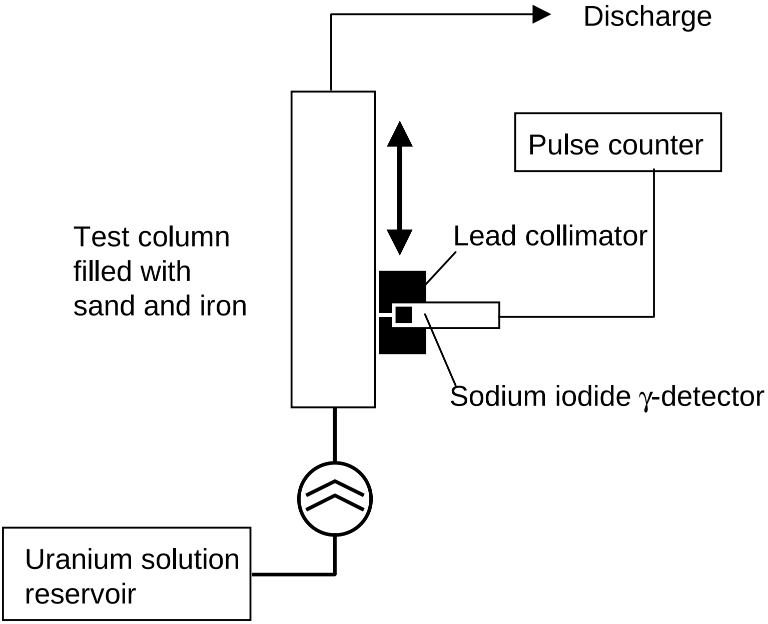

Figure 2. Schematic representation of the experimental set-up

RESULTS

The activity of ^{237}U was measured as a function of column length after different time intervals. The experiments were finished after 18 days, i.e. after nearly 3 half-lives of the isotope (experiment 2 with elemental iron continued for 36 days). The uncorrected activity at that time diminished to 14.5 % of the initial value (2.5 % in experiment 2 with elemental iron). Figure 3 displays curves recorded at different intervals of time.

The individual curves start with a positive slope, reach a maximum and then decline to almost zero at the end of the column. The number of counts correlates to the concentration of the ^{237}U isotope in the column. This value is also proportional to the total uranium concentration after correction for the radioactive decay because a definite ^{237}U/^{238}U ratio was set by the irradiation in the linear electron accelerator (see reaction 9). The areas below the curves in Figure 3 are proportional to the total load of uranium on the column, if the concentration of the solution and the flow parameters are kept constant. Therefore the plot of the areas below the individual curves in Figure 3 versus time should result in straight lines. Figure 4 displays that this is true. The mass of uranium retained in the columns can be calculated from the product of uranium concentration, time and flow rate.

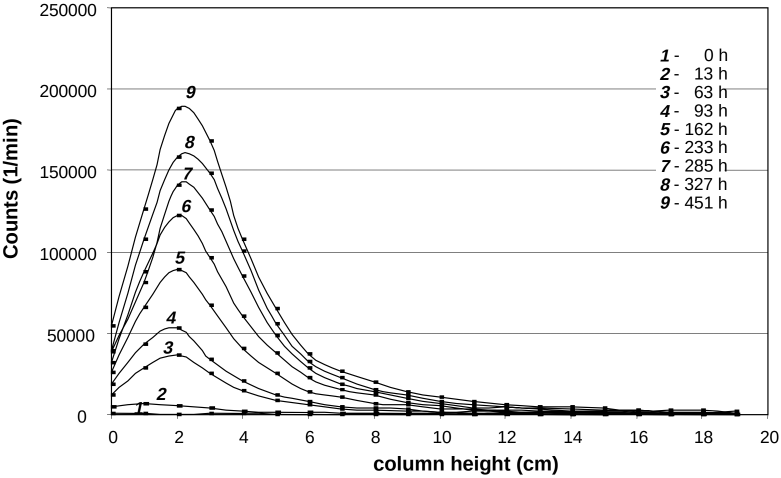

Figure 3. Activities measured in the columns after different time intervals of the experiments with HAP as reactive material.

Figure 3 clearly shows that uranium moves forward through the column. To quantify the velocity of movement of the contamination front the position was arbitrarily set to that point where less than 5000 counts have been recorded (20000 counts in experiment 2 with elemental iron due to higher initial radioindicator concentration). Plotting this position against time of the different measurements should result in straight lines if the reactive material (elemental iron or HAP) is distributed homogeneously within the column. This is displayed in Figure 5.

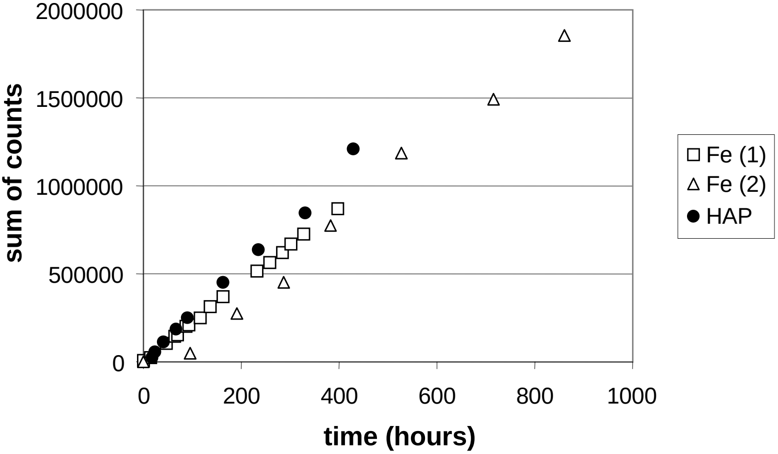

Figure 4. Integral number of counts as a function of time for all experiments. The product of flow rate, concentration and time yields the mass of uranium loaded onto the column.

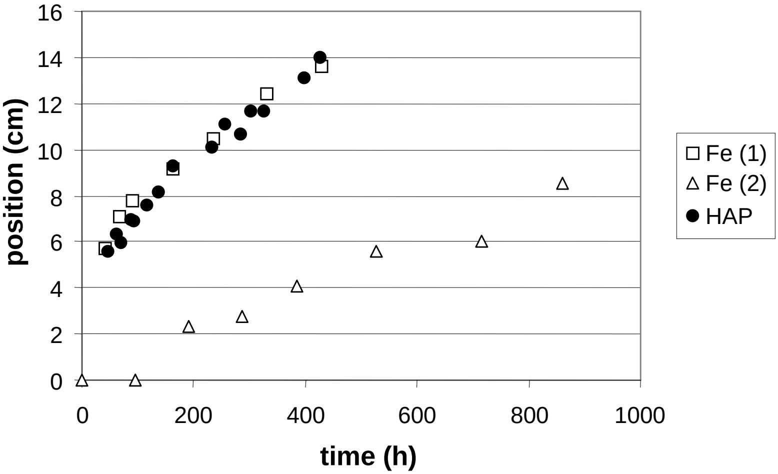

Figure 5. Movement of the contaminant front through the columns as measured by ^{237}U radioindicator.

The sand/HAP mixture and iron/sand mixture in experiment 1 was placed on a pure sand layer at a height of approx. 5 cm of the measured column section which can be seen from the positive axis intercept (see Table 2). The slope of the curves is the migration velocity of the contamination front and the values of the results are displayed in Table 3.

Table 3. Results of the experiments

	Iron (1)	Iron (2)	HAP
Velocity of the contamination front (cm/h)	$19.6\text{x}10^{-3}$	$9.6\text{x}10^{-3}$	$21.2\text{x}10^{-3}$
Calculated breakthrough after	766 h	5189 h	944 h
Stoichiometric factor (mol/mol, see text)	1:1200	1:1390	1:487
Calculated maximum concentration of uranium on reactive material (mg/kg)	3550	3019	2916
Retardation R (see text)	620	1100	573

Having the velocity of the contaminant front the break-through of the contamination through the layer of reactive material in the column and the stoichiometric factor of the reaction of uranium with elemental iron or HAP can be calculated.

It has been shown that the rate of the removal of groundwater pollutant is a function of the surface of the reactive material (Johnson 1996). No attempt has been made in the present work to quantify the influence on the reactivity by the surface, i.e. the grain size of the reactive material. This effect has been discussed in detail for elemental iron elsewhere (Johnson 1996). The stoichiometric factor of uranium removal using HAP according to reaction 4 to reaction 8 was estimated to be 1 : (487 +/- 19). The stoichiometric factors found in the experiments with elemental iron are by more than a factor of 2 higher and are in good agreement. Iron particles used had a grain size around 1 mm. Reductive precipitation occurred at the surface only so that most of the iron did not get into contact with the pollutant. HAP particles are much smaller which leads to a stoichiometric factor much lower than that of the coarser iron.

The experimental data enable the extrapolation of the maximum uranium concentration on the reactive material iron or HAP. These values are also listed in Table 3. From these data the distribution coefficient K_d can be calculated by division with the concentration of the uranium containing solution. From the distribution coefficient K_d the retardation factor R can be calculated (Simon 2000)
as
$R = 1 + (\rho/\Theta)\ K_d$
with ρ representing the bulk density and Θ the porosity.

For average conditions ρ/Θ is 6 kg/l (Appelo 1993). Retardation calculated by dividing velocity of uranium solution by velocity of the contaminant front resulted in similar values.

DISCUSSION

Both elemental iron and HAP are able to retain uranium from groundwater. In the case of elemental iron the reductive precipitation of uranium is accompanied with an increase in pH (see **Reaction 10** - **Reaction 12**).

$Fe \rightarrow Fe^{2+} + 2\ e$ **Reaction 10**
$2\ H_2O + 2e \rightarrow H_2 + 2\ OH^-$ **Reaction 11**
$O_2 + 2\ H_2O + 4\ e \rightarrow 4\ OH^-$ **Reaction 12**

Long-term column experiments with iron as a reactive material showed that the pH increased initially by 2 pH units from pH 7 in the feed water to pH 9 in the column effluent. But after about 2 to 3 months the effluent pH decreased and stabilised around pH 8 after 7 to 8 months of operation (see Figure 6). This change in pH could indicate a change in the uranium retention mechanism from reductive precipitation (**Reaction 1**) to a sorptive removal on iron oxyhydrate surfaces. In contrast to this the pH of the effluent from columns with HAP as reactive material remained nearly unchanged.

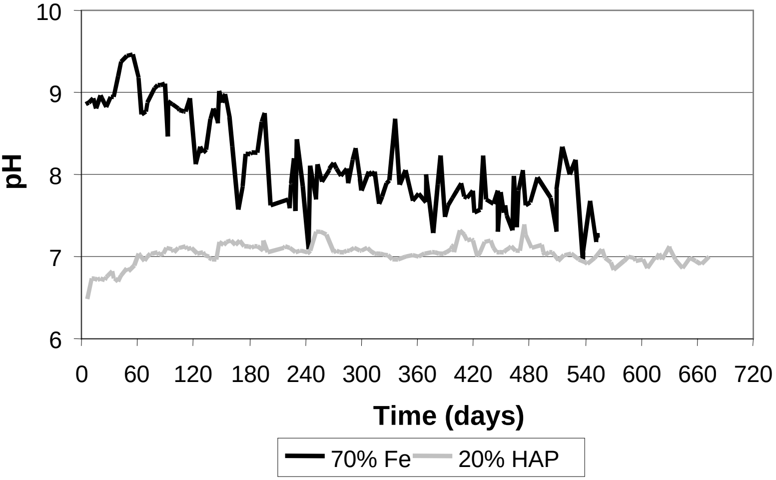

Figure 6. pH of the effluent from long-time column experiments.

Long-term experiments were carried out without radioindicator but with artificial groundwater containing calcium and magnesium (see Table 4). As the solubility of calcite and dolomite decreases with increasing pH, calcium precipitation occurs within iron columns. Alkaline earth elements are almost completely removed from the artificial groundwater with more than 800 mg of carbonates formed for every litre that passes through each column. This accumulation of solid material could lead to a loss of permeability and finally to a failure of the system. These precipitates were found after dismantling test columns and test boxes after operation with uranium containing artificial groundwater as displayed in Figure 7.

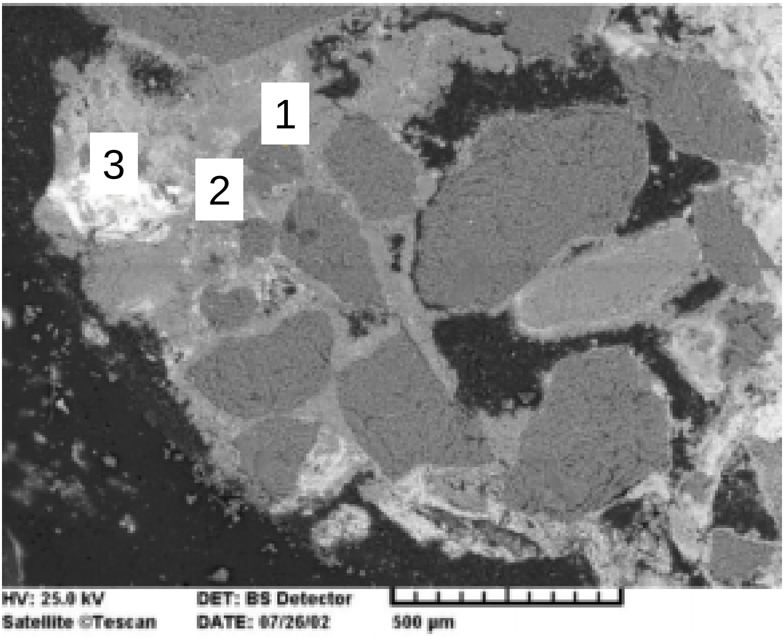

Figure 7. Image from secondary electron microscopy (SEM) from sand:iron mixture. 1 is a sand particle, 2 is mainly precipitated $CaCO_3$, 3 is an iron particle. The surface is covered with $Fe(OH)_2$ and $FeCO_3$ precipitation. Result from Dr. A. Debreczeni and I. Gombkötö, University Miskolc, Hungary.

Table 4. Composition of artificial groundwater used for long-term column experiments

	Concentration	
U	492	µg/l
Na	275	mg/l
K	5	mg/l
Ca	180	mg/l
Mg	108	mg/l
Cl	119	mg/l
SO_4	870	mg/l
HCO_3	741	mg/l
pH	6.8	

Flow conditions chosen in the column experiments represent an acceleration compared to natural conditions. The velocity in our column was around 5 pore volumes per day, i.e. 2.5 m/d, which is approximately five times faster than natural groundwater velocities. A permeable reactive barrier designed with a proportional design as in our experiments would persist for more than three years with the same pollutant concentration at natural velocities. The period of proper functioning could even be longer. Morrison found that the removal efficiency increased again after a breakthrough in his column experiment after 3000 pore volumes when the flow velocity was decreased by a factor of 10 (Morrison et al. 2001).

These results with HAP are in agreement with the results of a technical demonstration at Fry Canyon in Utah using HAP which is promising (Naftz 1999). In contrast to the reaction of lead with HAP where hydroxypyromorphite $Pb_{10}(PO_4)_6(OH)_2$ as sparingly soluble mineral is formed after dissolution of HAP (Ma 1993, Chen 1997) uranium removal might occur via sorption on HAP surfaces. In the non-mined Coles Hill uranium deposit phosphate mineral precipitation has been verified (Jerden 2003). However, it was stated that the formation of autunite group minerals require a longer time interval. Such a transformation was described by Sowder et al. for schoepite ($(UO_2)(OH)_2$) (Sowder 1996).

Whether sorption of uranium occurs via a sequence as displayed in reaction 7 or reaction 8 strongly depends on the speciation of uranium as a function of pH. The uranyl ion UO_2^{2+} is stable at low pH values only. If phosphate and carbonate are present, speciation is dominated by carbonato complexes ($UO_2CO_3(aq)$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) at a pH of 8 and above. Between pH 4 and 7 soluble phosphato complexes ($UO_2H_2PO_4^{+}$, $UO_2HPO_4(aq)$, $UO_2PO_4^{-}$, etc.) are formed (Giammar 2001). Therefore ternary complexes adding anions such as carbonate or phosphate are also conceivable. Structures have been suggested for such ternary complexes for uranium on hematite surfaces (Bargar 2002) and for uranium on HAP (Bargar 2002).

Stability of sorption complexes or mineral phases is essential to obtain the desired behaviour of a PRB system using HAP for uranium removal. Evidence exists that under normal conditions uranium remains immobile (Giammar 2001). Proper functioning of a PRB system depends on the adequate design. With the data found in this study it is possible to calculate the amount of reactive material necessary for contaminant removal. However, lessons learned from the demonstration at Fry Canyon show that site characterisation and groundwater flow patterns are the most important parameters. If groundwater does not completely pass the reactive medium, removal efficiency is poor.

The cost of HAP as a reactive material is comparable to that of granular iron and is around 350 US$ per ton (EnviroMetal Technologies Inc. , Conca 2000). Lower prices for HAP are feasible if waste materials, e.g. fishbone or phosphatic clay (Singh 2001) containing HAP are used.

FIELD EXPERIMENT

Uranium mining and processing activity in Hungary was developed in the southern part of the country, in the Mecsek mountains, near the city of Pécs. The mined out rock amounted to 46 million tons from which different wastes resulted. Mining activity was terminated at the end of 1997. Rehabilitation of the former industrial sites is in progress. Among different remediation tasks one of the most important issues is the restoration of the quality of groundwater contaminated by seepage from tailings, waste rock piles and heap leaching residues. It was possible A pilot-scale permeable reactive barrier was built at the site near Pécs during the course of the PEREBAR project (http://www.perebar.bam.de). The PRB test facility has been in operation since August 2002.

The PRB consists of two different zones, zone I with a lower content of coarse elemental iron (12 % by volume or 0.39 t/m^3, grain size 1 – 3 mm) and zone II with a higher content of fine elemental iron (41 % by volume or 1.28 t/m^3, grain size 0.2-3 mm).

On both sides (upstream and downstream) sand layers were inserted to distribute water inflow and outflow. The PRB is sealed with clay and geosynthetic clay liners at the bottom and with a geomembrane (high density polyethylene) at both sides and on the top. The design is displayed in Figure 8. The total mass of elemental iron as a reactive material was 38 t, from which 5 t was coarser material.

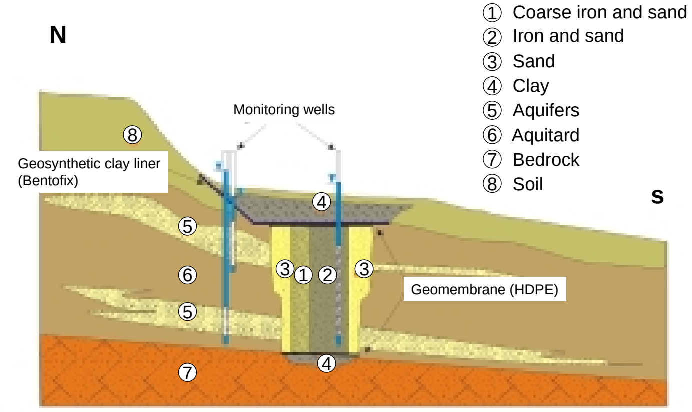

Figure 8. Sketch of the design of the PRB near Pécs.

Good removal results for uranium (99 %) were obtained in the first 7 months of operation. Table 5 lists average values for different parameters for the operation period. It can be seen that the pH increases in the PRB by almost 2 pH units and that alkaline earth elements are almost completely precipitated. The impact of these precipitates on the long-term performance of the installation will be investigated in further research.

Table 5. Change of water chemistry in the PRB (average values for the period from August 2002 to March 2003). All data in mg/l except for pH.

Component	**Inflow**	**W1***	**E1***	**W2***	**E2***	**Outflow**
Ca	167	141	136	19	21	30
Mg	62	65	63	50	45	30
Fe	0	3.9	17	1.1	1.9	0.2
Na	105	110	107	105	94	105
Cl	44	44	45	47	45	45
SO_4	397	357	340	212	218	118
HCO_3	610	575	602	258	243	248
U	0.98	0.21	0.007	0.004	0.044	0.009
pH	7.15	7.62	7.64	9.43	9.27	9.10

** measuring point with PRB*

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