Long-term performance of reactive materials in PRBs for uranium remediation

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Abstract. Elemental iron (Fe^0) and hydroxyapatite (HAP) were evaluated as reactive materials in PRBs for uranium remediation. Laboratory experiments were carried out and a pilot-scale reactive barrier with Fe^0 was installed in Pécs (Southern Hungary). Results of 2.5 years of operation are reported. The PRB has a considerable influence on groundwater composition: uranium concentrations decrease from 900 µg/l to <10 µg/l, TDS drop from 1,000 mg/l to 500 mg/l.

Introduction

Long-term performance of permeable reactive barriers (PRBs) was investigated by a consortium of eight partners within the FP 5 project PEREBAR funded by the European Union (Roehl et al. 2005). The main part of the research was focused on the remediation of groundwater contaminated with uranium. Laboratory and field experiments were carried out with a variety of reactive materials suitable for groundwater remediation.

Furthermore a case study was performed for the former Hungarian uranium ore mining and processing site near the city of Pécs in Southern Hungary, where mining started in 1958 followed by milling in 1962. About 46 million tons of rock were mined and the ore processing resulted in the accumulation of 27.5 Mt of tailings and approximately 19.3 Mt of waste rocks on the site, containing 2.3 Kt of uranium in total (Csövári 1998). As part of ongoing remediation activities a pilot-scale PRB was installed to investigate the long-term performance of PRBs for groundwater protection against uranium pollution.

This paper presents results of laboratory tests with elemental iron (Fe^0) and hydroxyapatite (HAP) as reactive materials as well as performance data of the pilot-scale PRB in Pécs.

Laboratory tests

Two long-term column studies were performed using artificial groundwater (AGW) for test periods of up to 30 months. The tested materials were shredded cast iron (granulated grey cast iron, 0.3 - 1.3 mm) supplied by Gotthard Mayer, Rheinfelden, Germany, and food quality grade hydroxyapatite ($Ca_5(PO_4)_3OH$, 99 % < 0.4 mm) supplied by Chemische Fabrik Budenheim CFB, Germany.

Experimental

In both experiments the reactive material was mixed with filter sand (0.25 - 1.0 mm) and placed into columns of 50 cm height and 5.9 cm inner diameter with a layer of filter sand at either end to achieve uniform flow conditions within the reactive material. Table 1 lists the specifications of the individual columns.

The columns were operated in up-flow mode using a peristaltic pump set to a flow rate of 1.6 ml/min. Average flow rates ranged between 1.0 and 1.4 ml/min due to wear of pump tubes. The composition of the AGW was based on groundwater chemistry data at the site of the experimental PRB in Pécs (Table 2).

The groundwater is characterized by high uranium, bicarbonate, and sulfate concentrations. At room temperature AGW A was supersaturated with respect to calcite and precipitates caused blockages of the recharge tubing. Therefore the AGW composition was modified in experiment B.

In the second experiment the columns contained less reactive material and the uranium concentration of the AGW was increased by a factor of 20. Furthermore,

Table 1. Specification of the columns used in long-term experiment A and B.

Column	Reactive material (RM)	Mass ratio RM/sand	Mass of RM g	Height of reactive zone cm	Reactive pore volume l
A2	HAP	0.20	306	40	0.45
A3	HAP	0.10	158	40	0.45
A4	Fe^0	0.70	1795	40	0.47
A5	Fe^0	0.50	1160	40	0.47
A6	Fe^0	0.30	587	40	0.42
B1	HAP	0.10	90	20	0.23
B2	HAP	0.10	90	20	0.23
B3	Fe^0	0.05 / 0.15	174	10 / 20	0.35
B4	Fe^0	0.05 / 0.15	173	10 / 20	0.34

Table 2. AGW composition in comparison to the groundwater at the field site in Pécs.

	pH	EC[a] µS/cm	U(VI) mg/l	TDS[b] mg/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	SO_4 mg/l	TIC[c] mg/l	Cl mg/L
AGW A	7.0	910	0.49		80	41	60	14	300	250	50
AGW B	7.5	1082	9.6		17	61	95	21	382	114	43
Pe-4[d]	7.22	1671	1.14	1197	166	63	105	20	381	591	
Hb01/1[e]	7.10	1496	0.72	1030	168	53	86	20	361	474	

[a] Electrical conductivity

[b] Total dissolved solids

[c] Total inorganic carbon calculated as HCO_3^-

[d] Monitoring well located approximately 15 m upstream of the PRB in Pécs, average values for the monitoring period 13.03.-11.11.2002

[e] Monitoring well located approximately 15 m downstream of the PRB in Pécs, average values for the monitoring period 2000-2002 prior to the installation of the PRB

the Fe^0-columns B3 and B4 were set up similar to the pilot-scale PRB in Pécs, with a zone of low iron concentration (5 %) at the entrance followed by a larger zone of higher iron content (15 %), in order to improve the long-term hydraulic conductivity of the Fe^0-columns.

Results

In both column experiments Fe^0 and HAP exhibited an uranium retention of more than 99 %. Effluent uranium concentrations were below the limit of detection (13 to 87 µg/l and 2 to 11 µg/l in experiment A and B respectively) of the spectrophotometric method employed for routine uranium analysis. Measurements with ICP-MS yielded maximum effluent uranium concentrations of 1.3 µg/l corresponding to an uranium retention of at least 99.7 % for all columns.

In experiment A no breakthrough was observed during 19 to 30 months of column operation, which corresponds to the treatment of 0.35 l to more than 8.7 l of AGW A per g of reactive material. In experiment B, however, a breakthrough occurred in both HAP-columns with effluent uranium concentrations exceeding the proposed limit of 20 µg/l in drinking water (Merkel and Sperling 1998) after the treatment of 3.2 l of AGW B per g HAP (Fig. 1, data for column B1 not shown).

When 5.4 l/g had passed through the columns B1 and B2, more than 75 % of the influent uranium concentration was measured in the effluents. Column B1 was dismantled for analysis after treating a total of 6.0 l/g and sorbing 48.7 mg U/g HAP. The operation of column B2 was continued substituting AGW B with uranium-free AGW. Effluent uranium concentrations of B2 remained in the range of several mg/l, i.e. between 15 % and 60 % of the uranium concentration of AGW B.

The Fe^0-columns in experiment A suffered from loss of permeability. After one year of operation the columns with 70 % and 50 % Fe^0 became basically impermeable, with coefficients of hydraulic conductivity k as low as $1.5x10^{-8}$ and $1.8x10^{-8}$ m/s, and had to be dismantled. In contrast the HAP-columns maintained a good hydraulic conductivity for 30 months (k-values decreased by about two orders of magnitude to $3x10^{-6}$ m/s). In experiment B neither Fe^0- nor HAP- columns showed problems with respect to hydraulic conductivity. Column B3 was dismantled after treating 4.0 l/g Fe^0 though no breakthrough had occurred but a total of 38 mg U/g Fe^0 (3.8 %) had been sorbed.

After the experiments the column material was analyzed and the uranium distribution within the columns was determined. The results are displayed in Fig. 2 with uranium accumulation calculated as ppm, i.e. mg U / kg reactive material in each sample.

In all Fe^0-columns highest uranium concentrations were found within the first 10 cm of the reactive zone with a maximum load of 250,000 ppm U on Fe^0 (25 %) in column B3, 7.5 cm above the filter layer of sand (Zone I). Hardly any uranium

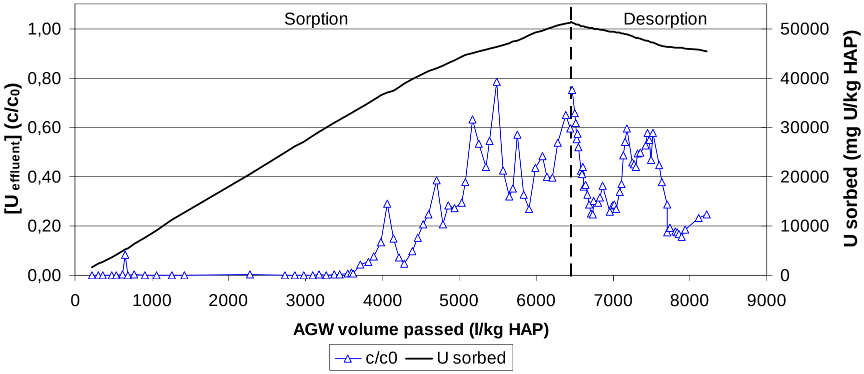

Fig. 1. Breakthrough curve and subsequent desorption of uranium from column B2. At the vertical dashed line AGW B was substituted by AGW without uranium. c/c_0 is the ratio of effluent uranium concentration to influent uranium concentration during the sorption phase. The solid line indicates the cumulative sorption of uranium onto the column.

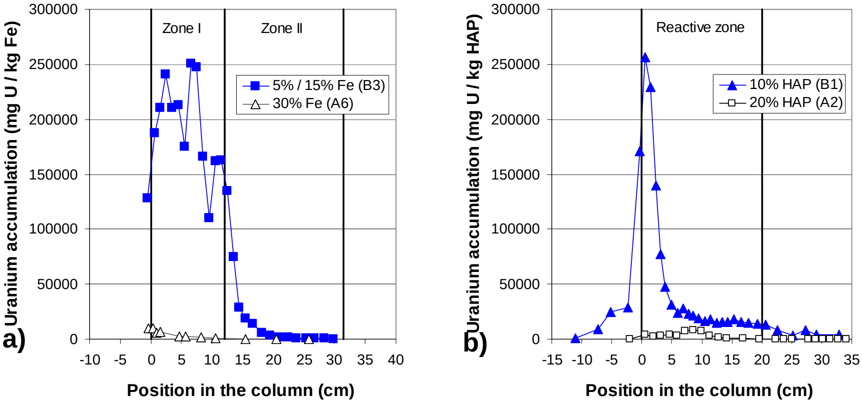

Fig. 2. Uranium distribution within Fe^0-columns (a) and within HAP-columns (b).

was found above 20 cm height. In the HAP-columns, however, the uranium distribution was different. In experiment A the load reached its maximum with 8,000 ppm U on HAP at a height of 9 to 10 cm while about 3,000 ppm were found at the beginning of the reactive zone. In experiment B the maximum load was 250,000 ppm U on HAP at the entrance of the reactive zone. Uranium concentrations leveled off at 15,000 ppm above a height of 5 cm (Fig. 2).

Field tests: experimental permeable reactive barrier

An extensive site selection procedure including geophysical screening methods, core drilling, and hydrogeological characterization of several sites was performed. Based on these investigations the Zsid-valley, which links the waste rock piles with a shallow aquifer that serves as a source for drinking water, was found suitable for the construction of a pilot-scale PRB (Csővári et al. 2005a).

The geology of the valley is characterized by sediments. The upper 1-2 m layer consists of clay and clayey sand ($k \sim 2x10^{-7}$ m/s), under which mainly sand and patches of clayey sand are present (3-4 m, $k \sim 1x10^{-5}$ m/s). At a depth of 6-7 m a thick sandstone formation can be found (>10 m, $k \sim 1x10^{-13}$ m/s) on top of which a thinner cracked zone is situated ($k \sim 1\text{-}2x10^{-6}$ m/s). The groundwater composition in the valley exhibited elevated uranium as well as high bicarbonate and sulfate concentrations (Table 2).

Design and construction of the PRB

In August 2002 a continuous PRB with a length of 6.8 m, a depth of 3.9 m, and a width of 2.5 m was installed into the aquifer using open trench excavation, 38 tons of shredded cast iron as reactive material, and approximately 60 m^3 of sand. The reactive zone consists of two sections: the first section is 0.5 m wide and contains 0.39 t/m^3 Fe^0 with a particle size of 1-4 mm while the second section is 1.0 m wide and contains 1.28 t/m^3 Fe^0 with a particle size of 0.2-1.2 mm.

To achieve good flow conditions the Fe^0 was mixed with sand and on both sides of the reactive zone a 0.5 m wide drain was built of sand. The bottom, sides, and top of the PRB are separated from the host soil with HDPE for directing the inflow. Fig. 3 shows the PRB during and after construction. A monitoring system consisting of 28 monitoring wells in and around the PRB was also installed (Fig. 4). The PRB does not need any maintenance.

Performance of the PRB

The PRB has been in operation for two and a half years. Up to now there have been no problems and the PRB performs well. Monitoring data for 2005 are presented in Table 3. Uranium was measured using a fluorimetric method with a detection limit of some µg/l.

In the first reactive zone a slight increase in pH was observed and most of the uranium (>96 %) and part of the total dissolved solids (7 % TDS), especially calcium and bicarbonate, were removed from the inflowing groundwater. At the same time elevated iron concentrations of more than 5 mg/l were observed.

In the second reactive zone pH values increased further while uranium was re-

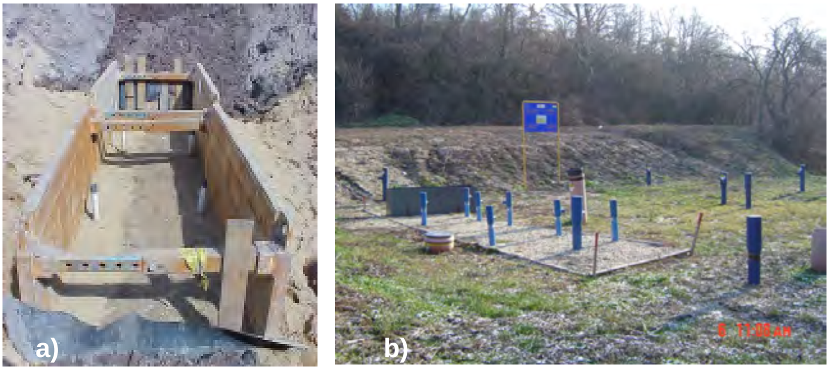

Fig. 3. Pilot-scale PRB and monitoring wells in Pécs during (a) and after (b) construction.

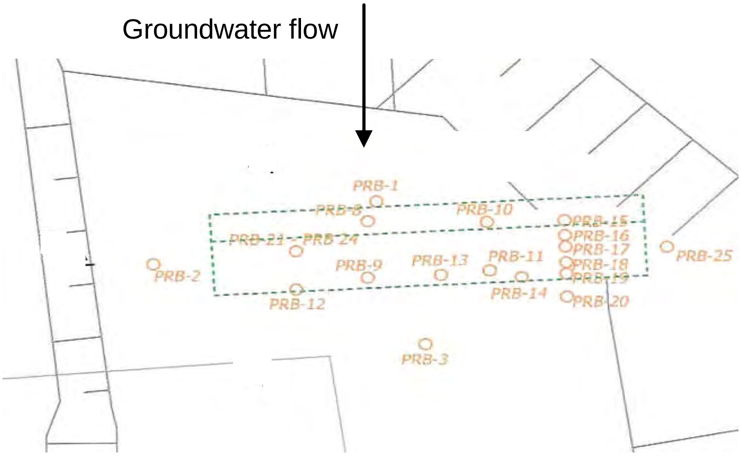

Fig. 4. Location of the monitoring system within and around the PRB. The monitoring wells Pe-4, located approximately 15 m upstream, and Hb01/1, located approximately 15 m downstream of the PRB, are not displayed.

moved to effluent concentration levels of 10 µg/l. In comparison to the inflowing water TDS, sulfate, and bicarbonate concentrations decreased by 50 % and calcium concentration was reduced by 93 %. Iron concentration dropped to 30 µg/l.

Effect of PRB on water chemistry of the test site

The PRB was built as a continuous wall intersecting only part of the valley's groundwater flow. Nevertheless the PRB has a remarkable effect on the water chemistry of the valley. This effect can be evaluated by the data of well Hb01/1 downstream of the PRB, which monitors the water passing the valley. Table 4 presents data for a five year period prior to and after the construction of the PRB in August 2002.

It can be seen that water chemistry in monitoring well Hb01/1 changed significantly: uranium concentration dropped from 718 µg/l to below 50 µg/l. TDS also decreased together with calcium, magnesium, and bicarbonate. At the same time water quality upstream of the PRB only changed to a minor extent (data not given). Therefore the observed changes in the water quality of monitoring well Hb01/1 can be attributed to the performance of the pilot-scale PRB.

The overall effect of the PRB on uranium concentration in the valley is illustrated by the isolines in Fig. 5 based on monitoring data not given in the tables above. The figure shows that uranium is removed with high efficiency. Because of the limited dimensions of the PRB lateral flow of contaminated water is bypassing

Table 3. Monitoring data of the PRB as of March 22nd 2005 after 31 months of operation.

Well	Location	pH	EC µS/cm	U(VI) µg/l	TDS mg/l	Ca mg/l	SO_4 mg/l	HCO_3 mg/l	Fe mg/l
PRB-1	Inflow	6.9	1400	940	1010	150	320	525	0.002
PRB-10	Zone I	7.3	1330	37	937	125	300	275	5.5
PRB-11	Zone II	8.7	865	10	550	10	185	299	0.03
PRB-14	Outflow	8.7	780	2	540	14	170	268	0.03
PRB-3[a]	Downstream	8.5	420	56	240	5	95	116	0.017
PRB-25	Side (left)	8.7	1380	290	1020	180	280	641	5.03
PRB-2	Side (right)	7.4	930	190	640	37	190	317	0.099

[a] Water is probably diluted by lateral water flow

Table 4. Effect of the pilot-scale PRB on water chemistry of the Zsid valley, measured at well Hb01/1 approximately 15 m downstream of the PRB.

Monitoring date/period	pH	EC µS/cm	U(VI) µg/l	TDS mg/l	Ca mg/l	Mg mg/l	SO_4 mg/l	HCO_3 mg/l	Fe mg/l
2000-2002	7.1	1496	718	1030	168	53	361	474	<0.01
08/2002-03/2003	7.7	923	70	540	54	33	170	299	<0.01
06.07.2004	7.8	780	40	465	28	26	150	305	0.18
22.03.2005	7.7	740	42	500	28	30	186	226	0.064

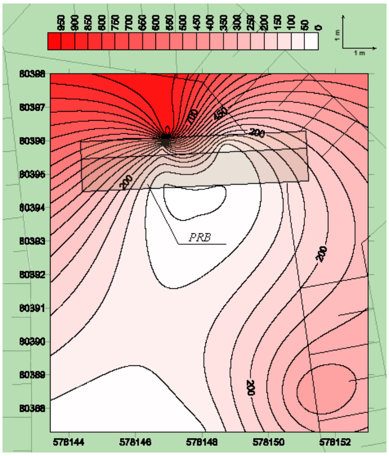

Fig. 5. Isolines of uranium concentrations in and around the pilot-scale PRB.

the barrier and results in gradually increasing uranium concentrations further downstream. If the PRB were a full-scale barrier it would cross the whole valley and stop the migration of uranium with the groundwater flow entirely.

Discussion

The results of the column experiments demonstrate that Fe^0 is well suited for uranium remediation. Uranium loads of up to 25 % can be achieved provided that hydraulic conductivity is maintained. Loss of permeability in Fe^0-columns can be attributed to the formation of secondary minerals. Reduction of dissolved oxygen to ferric oxyhydroxides causes clogging in the lower part of Fe^0-columns (Mackenzie et al. 1999). Under anaerobic conditions $Fe(OH)_2$, $FeCO_3$, and $CaCO_3$ precipitates can be found as mineral solubility decreases with increasing pH due to iron corrosion, especially in the presence of elevated carbonate concentrations.

As most of the uranium was found in the lower part of the Fe^0-columns where most of the precipitation processes occur, both reductive precipitation (Reaction 1) and adsorption onto corrosion products (Reaction 2 (Bargar et al. 2000)) are feasible (Cantrell et al. 1995).

$$Fe^0 + UO_2(CO_3)_2^{2-} + 2\,H^+ \rightleftarrows Fe^{2+} + 2\,HCO_3^- + UO_2(s) \qquad (1)$$

$$\equiv Fe(OH)_2 + UO_2^{2+} + CO_3^{2-} \rightleftarrows \equiv FeO_2\text{-}UO_2CO_3^{2-} + 2\,H^+ \qquad (2)$$

Possible reaction mechanisms of HAP with uranium include the dissolution of HAP (Reaction 3) with subsequent precipitation of uranium phosphate minerals like autunite (Reaction 4 (Arey et al. 1999)) as well as surface complexation (Reaction 5 and 6 (Fuller et al. 2002)).

$$Ca_5(PO_4)_3OH + H^+ \rightleftarrows 5\,Ca^{2+} + 3\,PO_4^{3-} + H_2O \tag{3}$$

$$2\,UO_2^{2+} + Ca^{2+} + 2\,PO_4^{3-} \rightleftarrows Ca(UO_2)_2(PO_4)_2 \tag{4}$$

$$\equiv OH + UO_2^{2+} \rightleftarrows \equiv O\text{-}UO_2^{+} + H^+ \tag{5}$$

$$\equiv O_3P\text{-}OH^+ + UO_2^{2+} \rightleftarrows \equiv O_3P\text{-}O\text{-}\ UO_2^{2+} + H^+ \tag{6}$$

As these processes do not involve redox reactions, no change of pH and therefore no significant precipitation and clogging of pore space occurs. The observed uranium distribution within the HAP-columns as well as kinetic experiments indicate two different retention mechanisms: fast but reversible sorption of up to 15,000 ppm of uranium onto surface sites and a slow, possibly irreversible, process that accounts for uranium loads up to 25 % if residence time is sufficient. However, no solid uranium phase such as meta-autunite could be identified via x-ray diffraction analysis of HAP column material. Therefore further efforts are necessary to clarify the reaction mechanism especially with respect to uranium desorption that was observed in Experiment B.

The monitoring data of the field experiment show that the PRB performs well. Considering the high sorption capacity of Fe^0 for uranium that was demonstrated in the column experiments, loss of permeability due to clogging with precipitates has to be regarded as the limiting factor for PRB performance. The decrease in TDS indicates that precipitation takes place. In zone I Fe^0 corrodes readily causing an increase in pH and dissolved iron, as well as a decrease in redox potential and uranium, the latter via reductive precipitation or co-precipitation with $Fe(OH)_2$.

With increasing pH minerals such as calcite and siderite precipitate as their solubility is reduced. This effect is more pronounced in zone II due to its higher Fe^0 content. It is supposed that sulfate reduction and subsequent formation of FeS also take place in zone II. Based on TDS monitoring data for the past 2.5 years approximately 0.5 kg/m^3 of solids precipitate from the passing water within the PRB. The accumulation of these compounds may lead to decreasing permeability within the PRB body. So far no adverse effects have been observed but the hydraulic performance of the PRB will be investigated in future work.

Decreasing pH-values within the barrier might be an indicator for decreasing efficiency of the PRB. In 2002 pH in zone II was 9.43 (Csövári et al. 2005b) compared to 9.5 and 8.7 in 2004 and 2005 respectively. For column experiments such a decrease in pH was explained by the development of preferential flow paths due to clogging (Kamolpornwijit et al. 2003; Simon and Biermann 2005). However, in PRBs a change in flow pattern or a reduced iron corrosion rate due to coating of Fe^0 surfaces seem more likely, especially as iron concentrations in zone I decreased from 17 mg/l in 2002 to 5.5 mg/l in 2005. Nevertheless the PRB is still very effective for removing of uranium from ground water.

Conclusions

The purpose of the column experiments was to perform accelerated testing of the processes within PRBs so that ageing effects become visible earlier than in natural systems. Therefore higher flow rates and higher uranium concentrations were used. In experiment B 4000 l/kg Fe^0 were treated with the Fe^0-columns compared to about 50 l/kg Fe^0 that passed the PRB so far. Uranium sorption was simulated and the importance of water composition (TDS, Ca, TIC) and Fe^0 content for the overall performance became apparent. However, barrier life-time calculations based on column tests can only give a rough estimate as complex groundwater conditions and geological processes cannot easily be simulated in the laboratory.

The pilot-scale PRB in Pécs demonstrates the high efficiency of Fe^0 for uranium remediation. A small decrease in the reactivity of the PRB is observed, which manifests itself in the decreasing pH of the water in the second zone of the barrier.

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