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In-Situ Mitigation of Effluents from Acid Waste Rock Dumps Using Reactive Surface Barriers – a Feasibility Study

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Abstract. The long-term mitigation of pore waters of acid waste rock dumps formed during uranium mining in the former G.D.R. requires new remediation approaches. A study was performed to evaluate the feasibility of reactive surface barriers (RSB) as part of an alternative covering system. One topic of the investigation was to evaluate suitable reactive materials for the mitigation of radionuclides and heavy metals in an acid milieu. PHREEQC geochemical modeling included equilibrium and mixing calculations to evaluate the chemical interactions between dump waters and reactive materials. The engineering feasibility of RSB was evaluated calculating a mass balance considering different dump water hydraulics, layer thickness and pore water concentrations. The main findings are that a RSB of zero-valence iron (Fe^0) causes a long-term mitigation of uranium and zinc. Alkaline hydroxides ($Ca(OH)_2$, $Ba(OH)_2$) cause the mitigation of radium-226. The feasibility of PO_4-compounds as a RSB for uranium mitigation was not definitively determined. Laboratory tests are on the potential use of these reactive materials as RSB are planned.

Key words: dump remediation, geochemical barrier, mine water treatment, reactive materials, radionuclide fixation, surface barrier, zero valent iron

Introduction

The former uranium mining activities in the eastern part of Germany resulted in large complexes of mines, tailings and waste rock dumps, which contain high amounts of radionuclides and heavy metals (Friedrich et al. 2000; Bieler et al. 1999). Some of the effluent waters of the rock dumps are characterized by pH values as low as 3 due to residues of acid from ore processing and pyrite oxidation. The treatment of these waters is necessary in order to minimize the environmental impacts of uranium mining. Due to the high costs of classical pump-and-treat technologies, geochemical barriers have been used increasingly in the last decade as an alternative strategy for remediation of water (U.S. Dept of Energy 1996). Geochemical barriers are zones of high geochemical reactivity, where contaminants are immobilized in-situ by redox processes, co-precipitation, adsorption or biological processes. Usually they are classified as naturally formed or man-made (artificial) geochemical barriers. The development of reactive barrier systems for removal of radionuclides and heavy metals from percolating waters requires an improved understanding of the elementary processes that control the interactions between dissolved contaminants and barrier material.

A special type of geochemical barrier is the reactive surface barrier (RSB), where a layer of the reactive material is located under the mineral soil of an alternative covering system. The reactive surface barrier will only be activated if there is a hydraulic breakdown of the mineral soil cover. When the covering system has lost its functionality, precipitation will percolate through the mineral soil cover and chemical reactions with the barrier will be initiated. After leaching, the dissolved reactive substances will be transported into the dump material and react there with the contaminated pore waters.

At the Schüsselgrund mine dump site near Königstein, Germany, the concept of RSB was proposed as part of the remediation strategy. The aim of this study was to evaluate the feasibility of several reactive materials with suitable chemical properties for efficient mitigation of uranium and radium-226 in an acid milieu. The results of this study are applicable to many other uranium dumps with similar geochemical characteristics. The main data on hydrogeology, hydrology and geochemistry of the Schüsselgrund site are given in Schneider et al. 1999 and Schneider et al. 2001. The main contaminants of the pore waters are uranium (20-30 mg/l) and radium-226 (about 1 Bq/l). In addition, contaminants such as zinc (50-150 mg/l), nickel (2-4 mg/l), and sulphate (2-4 g/l) are present in the pore water. A schematic cross section of the proposed reactive surface barrier at the Schüsselgrund mine dump is given in Figure 1. At present, only the slopes of the dump are covered with mineral soil.
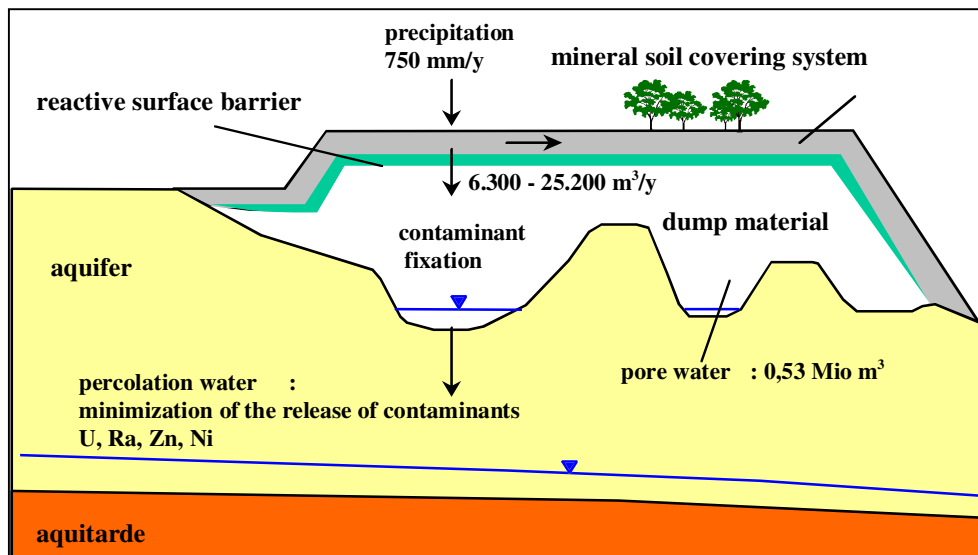
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Figure 1. Schematic cross section of a reactive surface barrier. All data were taken from the mine dump of the Schüsselgrund site (Schneider et al. 1999, Schneider et al. 2001). The high infiltration rate assumes the hydraulic breakdown of the soil cover.

In this paper, we present the results on the theoretical framework on the application of RSB, including the following topics:

- selection of suitable reactive materials for the mitigation of uranium and radium on the basis of published data and case studies

- characterization of the chemical in-situ conditions of soil and pore waters

- prediction and sensitivity analysis of the changes in chemical milieu due to interaction of reactive materials with infiltrating waters by geochemical modeling

- geochemical modeling of the mixing processes between dump pore waters and dissolved RSB materials

- evaluation of the long-term mitigation time scales and a mass balance of necessary amounts of RSB

These investigations are part of a comprehensive feasibility study evaluating the geochemical effectiveness of RSB and the technical conditions for realization. The results are being used to guide laboratory and field experiments for the use of RSB in acid milieu.

Methods and materials

Selection of suitable reactive materials

Beside its chemical properties, the main criterion for a suitable RSB material is long-term functionality, ideally for at least 250-1000 years. Suitable reactive materials for the mitigation of radionuclides in an acid milieu were selected on the basis of an international literature review (Hydroisotop-Piewak GmbH, 1999). Three types of reactive material: zero valent iron (Fe^0), alkaline hydroxides ($Ca(OH)_2$, $Ba(OH)_2$), and PO_4-compounds (apatite: Na_2HPO_4 and hydroxyl apatite: $Ca_5(PO_4)_3O$) were selected for further investigation. The mitigation of radionuclides using these reactive materials is due to different processes (Arey et al. 1999, Gauglitz et al. 1993, Gu et.al. 1998, Hedin et.al. 1994, Stefanova et.al. 1993, Waybrandt et al. 1995, Xu et al. 1992, 1994, Zoumis 1998).

The change in geochemical milieu by Fe^0 and alkaline hydroxides causes a reduction of uranium(VI) to the barely soluble uranium(IV) (Gu et al. 1998, Morrison et al. 2001). When Fe^0 is oxidized, iron hydroxides are formed, which can remove additional uranium by sorption (Gu et al. 1998, Morrison et al. 2001). In the case of reactive PO_4-compounds, insoluble uranium-phosphate-complexes will be formed. The main process for the mitigation of radium is co-precipitation with sulphates. In this study, $Ba(OH)_2$ was used as a chemical equivalent for radium

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Geochemical modeling

Geochemical modeling for the prognosis of the geochemical behaviour of the barrier materials was performed using PHREEQC, version 1.6 (Parkhurst 1995). For this study, the WATEQ4F thermodynamic database was used complete with data for Fe^0 from Pearson (1994) and Pearson and Waber (1999). Data for the solubility of $Ba(OH)_2$ and Na_2HPO_4 were taken from Rauscher et al. (1972). The calculations were used as a prognostic tool to ensure that the reactive properties of the proposed barrier materials will immobilize the contaminants under the prevailing geochemical conditions at the investigated dumpsite. Since the modeling was confined to equilibrium processes, the time scales were unknown and the accuracy of thermodynamic data for radionuclides was limited, the investigations did not aim at detailed mass balances of chemical development. Instead, the objective was qualitative predictions on the direction of changes in the geochemical condition and saturation indices (SI). The geochemical modeling included speciation calculations, redox reactions and mixing calculations, while sorption of radionuclides was not included in the study at this step due to the prognostic character of the calculations and the lack of reliable sorption data available for this study.

Model for the hydraulic conditions in the mine dump

The current percolation rate through the Schüsselgrund mine dump ranges from about 50 to $100 \cdot 10^3$ m^3/year, as shown by water balance calculations (Schneider et al. 1999). The remediation concept for the dump comprises an alternative covering system with 0.5 m of low-permeability mineral soil below 1.5 m of vegetation-compatible soil. As results of hydrological modeling show, a short-term infiltration rate of 5 % (about 6300 m^3) of the annual precipitation (750 mm) can be reached using this covering system. Taking into account root development and alteration of the soil cover, about 20 % (about 25.200 m^3) of the annual precipitation will eventually percolate into the dump. A pore water content of 530.000 m^3 can be estimated from soil mechanical measurements (Figure 1).

The time scale for complete reaction of the RSB solution with contaminants dissolved in the pore water of the Schüsselgrund mine dump depends on the kinetics of the involved reactions and on the velocity of the hydraulic mixing of infiltrating water with the dump water. Information on the hydraulic mixing properties can be estimated from a distribution of residence times, which have been derived from environmental isotopes (Schneider et al. 1999). The most reasonable mixing model is characterized by inhomogeneous percolation and subsequent mixing of waters with different residence times in the dump. The different components consist of stagnant pore waters (assumption: more than 50 years), old percolation water (about 9 years, according to ^3H and ^{85}Kr), and young percolation water (less than 2 years, according to ^2H and $\delta^{18}O$). This is in accordance with a residence time in the dump water of about 7 years, which was calculated from the ratio of pore water volume (530.000 m^3) and the current percolation rate ($50-100 \cdot 10^3$) m^3/year.

Results

Hydrochemical composition of the dump waters and the mineral soil percolation water

Hydrochemical data for the pore waters of the Schüsselgrund mine dump was obtained from two observation wells located in the dump material (Table 1). Due to missing barium analyses, model input concentrations for barium have been estimated to be close to the detection limit ($1 \cdot 10^{-4}$ mg/L) based on the fact that sulfate reaches values up to 4450 mg/L.

Table 1. Hydrochemical data used for geochemical modeling of the two pore water wells in the Schüsselgrund mine dump. The Ra-226-value is only for documentation and not part of the geochemical model.

	date	pH	E_H (V)	T (°C)	O_2 (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	Mn (mg/L)
well 1	9.3.99	3.3	0.75	9.6	4.5	253	6.3	537	78.5	42.8	15.6
well 2	6.6.95	2.9	0.62	12.4	7.6	521	14.4	503	80.0	473	27

	date	Cl (mg/L)	SO_4 (mg/L)	NH_4 (mg/L)	NO_3 (mg/L)	P (mg/L)	H_2SiO_3 (mg/L)	Ni (mg/L)	Zn (mg/L)	U (mg/L)	^{226}Ra (Bq/L)
well 1	9.3.99	318	2120	8.7	2.8	0.06	23.9	1.1	34.9	9.3	0.097
well 2	6.6.95	678	4450	15.7	12.3	0.14	107	3.6	160	30	3.9

Speciation calculations shows that in both dump water wells, most of the solid phases are undersaturated, except for stable iron phases (goethite and hematite) and quartz. As expected, dissolved calcium and sulphate are close to equilibrium due to gypsum formation. The strong undersaturation of the pore water with respect to uranium phases most probably is due to the hydraulic properties of the dump. Most of the infiltrating waters enter the dump on preferential flow paths with low residence times. These flow paths have been exhausted of uranium minerals due to leaching for the last three decades. Elevated uranium levels in the exploited water of the dump wells result from an admixture of pore waters from less flushed parts of the dump that have a high uranium content.

The hydrochemical composition of the pore water after the mineral soil cover is emplaced will be a mixture of the current dump water and the percolation water of the mineral soil. The hydrochemical composition of the mineral soil percolation water was estimated from a nearby shallow well with groundwater that is only slightly mineralized, characterized by a pH of 4.3 and a redox potential of 595 mV. Although the carbonate content of the planned covering system will be low (about 2 weight%), dissolution of calcite will increase the pH of the infiltrating precipitation. Due to inhomogeneous distribution of carbonates within the soil cover and possible flowpaths that become calcite free after some time, the carbonate contents and resulting pH values of the percolating water may vary spatially and temporally.

Percolation water after reaction with the surface barrier materials

When the infiltrating water has passed through the mineral soil cover, reactions with the reactive material will start. The geochemical composition of the resulting water strongly depends on the amount of substance that is dissolved from the barrier. In order to integrate these kinetic effects, stepwise PHREEQC modeling was performed by equilibrating the percolating water with different amounts (0.1 to 20 mmol/L) of reactive material. The results of of pH, E_H and the concentration of the reactive substance for reaction with 5 mmol/l and 10 mmol/l RSB material, respectively are presented in Table 2.

Table 2. Results of equilibrium calculations for the barrier percolation water using an amount of 5 mmol/L and 10 mmol/L reactive material.

Reactive material	reactive ion	Starting solution			Equilibrium in case of using 5mmol reactive material			Equilibrium in case of using 10mmol reactive material		
		pH	E_H (mV)	C (mol/L)	pH	E_H (mV)	C (mol/L)	pH	E_H (mV)	C (mol/L)
Fe^0	$Fe(II)^{2+}$	6.9	+750	$< 1 \cdot 10^{-8}$	10.7	−450	$1.7 \cdot 10^{-5}$	11.9	−600	$6.3 \cdot 10^{-4}$
$Ca(OH)_2$	Ca^{2+}	6.9	+750	$1.3 \cdot 10^{-3}$	12.3	+390	$3.1 \cdot 10^{-3}$	13.2	+330	$1.4 \cdot 10^{-2}$
$Ba(OH)_2$	Ba^{2+}	6.9	+750	$2.5 \cdot 10^{-7}$	12.4	+390	$1.9 \cdot 10^{-3}$	13.9	+280	$9.1 \cdot 10^{-2}$
Hydroxyl apatite	$H_2PO_4^-$	6.9	+750	$1.8 \cdot 10^{-7}$	7.0	+750	$2.1 \cdot 10^{-5}$	7.0	+750	$2.1 \cdot 10^{-5}$
Na_2HPO_4	HPO_4^{2-}	6.9	+750	$1.1 \cdot 10^{-7}$	7.4	+720	$2.7 \cdot 10^{-3}$	7.6	+700	$5.5 \cdot 10^{-3}$

The initial pH of the percolation water before contact with the RSB was assumed to be nearly neutral. Sensitivity tests where the reactive material reacts with percolation water of different pH, ranging from 4.3 to 7.8 (due to different carbonate content) show only minor influence of the initial pH on the geochemical milieu (pH and redox) of the resulting solution. Therefore the geochemical modeling of Tab. 2 was performed using a reasonable pH value of 6.9 (corresponding to a carbonate concentration of 1.7 mmol/L).

The modeling results in Table 2 show that a small amount of Fe^0 and alkaline hydroxides causes significant changes of the geochemical milieu in the percolation water. The calculated pH for the reactive materials $Ca(OH)_2$ and $Ba(OH)_2$ indicate the highest neutralization potential. Depending on the applied amount of reactive $Ba(OH)_2$, about 0.1 to 100 mmol/L Ba^{2+} will be available to mitigate radium. Due to the high sulfate concentrations in the dump water, the Ba^{2+} most likely will precipitate as $BaSO_4$, providing the potential for co-precipitation of the radium activity of the dump water of about 1 bis 4 Bq/L (about 10^{-10} mmol/L). The PO_4-compounds have no influence on redox conditions, but will increase the concentrations of HPO_4^{2-} and $H_2PO_4^-$ in the percolation water up to $5 \cdot 10^{-3}$ mol/L. These ions make possible the formation of uranium complexes that are low in solubility.

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Mixing of reactive surface barrier materials and dump waters

The fate of the contaminants during mixing between the dump water and the RSB percolation solution has been investigated using PHREEQC mixing calculations. In order to check the sensitivity of the resulting pH and E_H values on the mineralization of the dump water, equal amounts of reactive solutions, corresponding to 5 mmol/L and 20 mmol/L (almost saturated conditions), were mixed with different dump water compositions (well 1 and 2, see Table 1). As shown in Figure 2, higher concentration of dissolved reactive material will cause lower E_H values and an alkaline milieu for Fe^0 and alkaline hydroxides. Only a small sensitivity has been found for solutions containing PO_4-compounds. A higher reactivity of the barrier materials was calculated for the dump water of well 1 in most of the sensitivity calculations, see Figure 2.
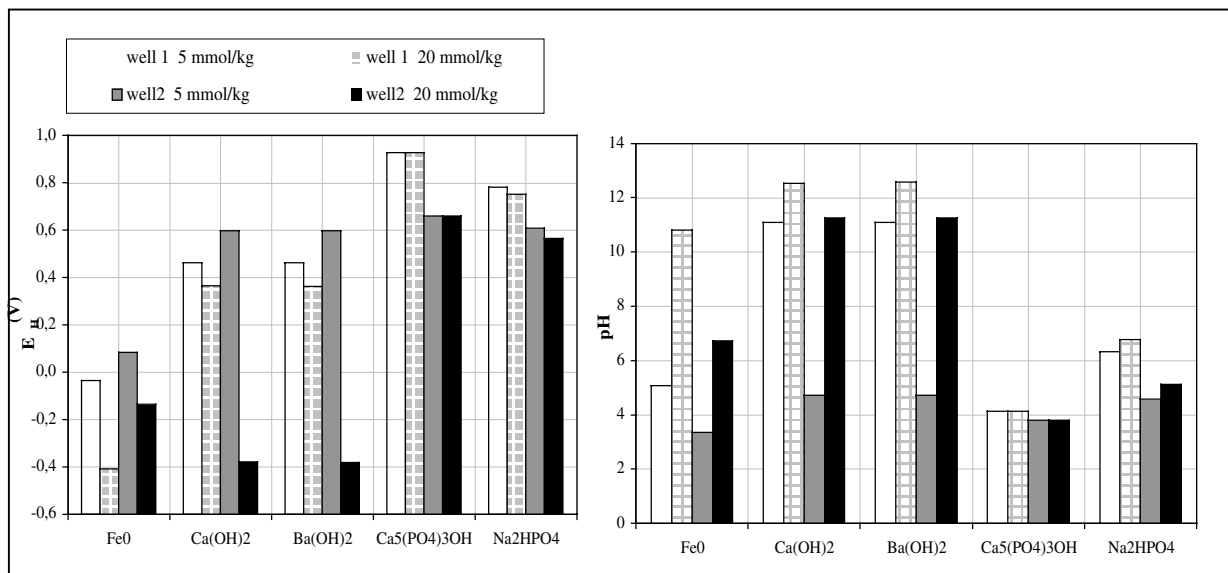

Figure 2. Calculated pH and E_H resulting from mixing of different reactive solutions (5 and 20 mmol/L reactive material) with dump water from wells 1 and 2. Mixing ratio in all cases was 1:1.

All further mixing calculations focused on the saturation indices (SI) of the relevant contaminants in the dump water. For model input, hydrochemical data of dump well 2 and a reactive solution corresponding to 5 mmol/L RSB material were chosen, which represents a worst case scenario (low reaction potential and high contaminant contents). Due to the uncertainties of the mixing ratio of dump water to barrier percolation water, the calculations were performed gradually, in 10% steps. The results for the reactive materials Fe^0 and $Ca(OH)_2$ are presented in Figure 3 where the saturation indices (SI) of the dominating solid phases of uranium, zinc and nickel are shown as a function of mixing ratio.

Precipitation of uranium is restricted to the use of Fe^0 as a reactive material. In this case, uraninite and coffinite are the dominant uranium phases. A mitigation of uranium by Fe^0 can even be expected, if the mixing ratio of barrier percolation water to dump water is as low as 0.1. According to the saturation indices of zinc and nickel, a mitigation of these contaminants can be accomplished by the barrier materials Fe^0 and $Ca(OH)_2$. The highest effectiveness for the precipitation of ZnS (sphalerite) will be reached using Fe^0. A super saturation of zinc phases was calculated for a proportion of barrier percolation water to dump water of 0.3. In the case of nickel, positive SI only resulted when there was less than 30 % dump water in the mixing solution.

Reactive material $Ca(OH)_2$ will reveal super saturation of uranium phases only when the proportion of barrier solution to dump water is in the range of 0.6 to 0.8. All other mixing steps result in undersaturation of uranium. On the basis of geochemical modeling, the question of whether mitigation of uranium by reactive $Ca(OH)_2$ will be feasible or not remains ambiguous.
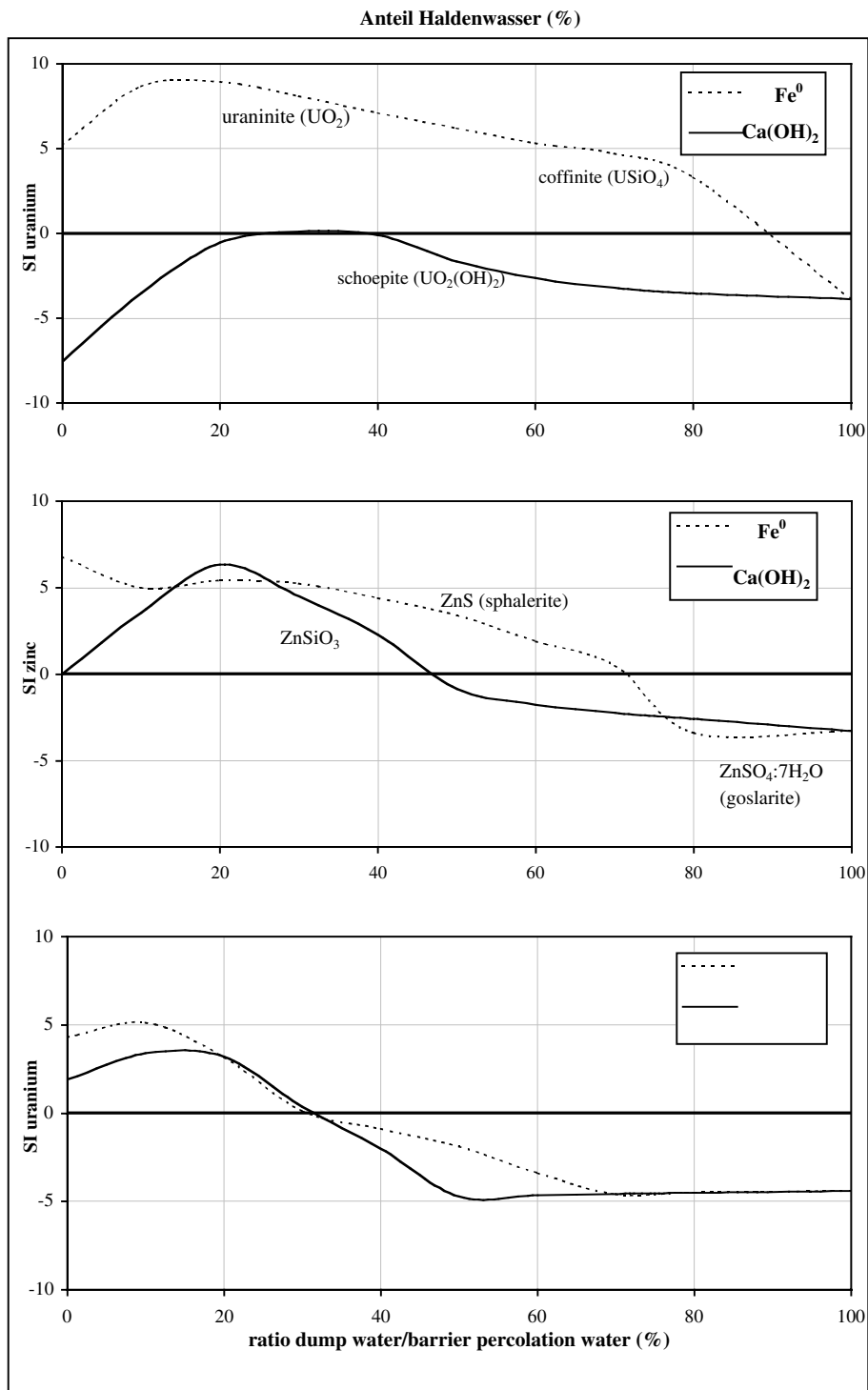
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Figure 3. Saturation indices (SI) of the dominant solid phases of uranium, zinc, and nickel in the mixing system of dump water (k-94017) and barrier percolation water with reactive materials Fe^0 and $Ca(OH)_2$.

The results of the mixing calculations for the reactive materials $Ba(OH)_2$, hydroxyl apatite and Na_2HPO_4 are presented in Figure 4. The graphs show the calculated saturation indices of the dominant solid phases of uranium and barium. No positive saturation index for uranium was found in the mixing solution with reactive PO_4^- compounds. This may be due to preferential formation of soluble metal complexes (for instance, $FeH_2PO_4^{2+}$) leaving only a few ligands for uranium phases in solution. The significantly positive saturation index of barite for all mixing calculations with reactive $Ba(OH)_2$ indicates a strong potential for precipitation of barium sulphate. In such a case, co-precipitation of radium according to the molar mass ratio of barium and radium in the dump water is highly probable.
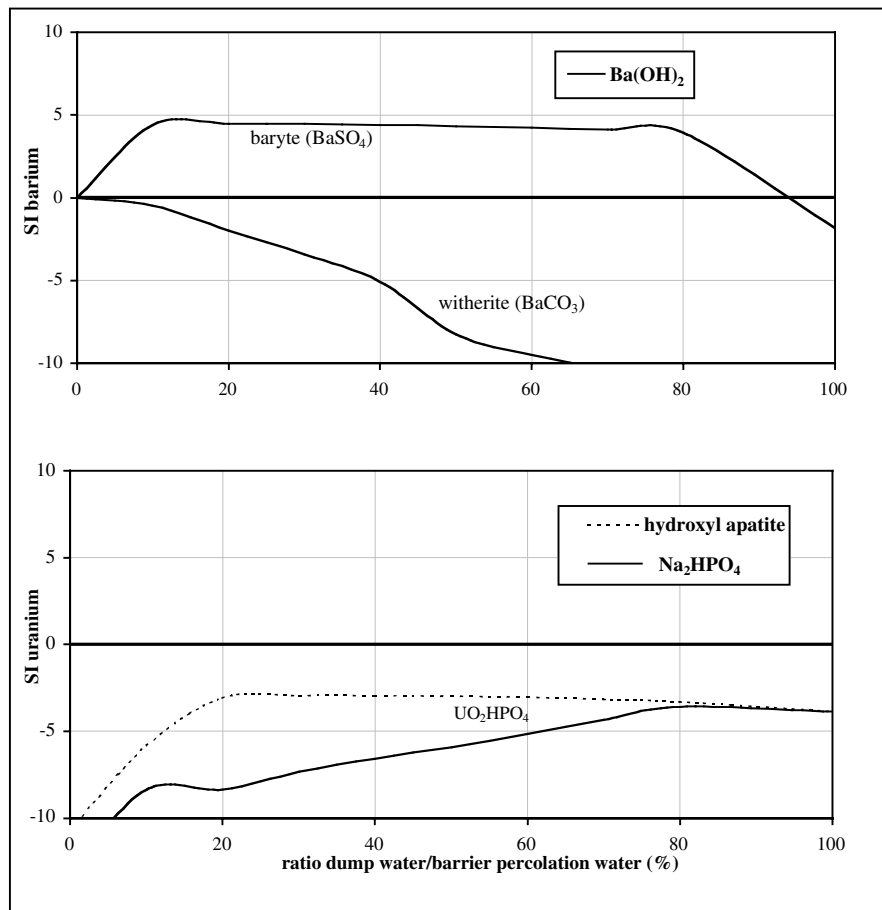
Figure 4. Saturation indices (SI) of the dominating solid phases of uranium and barium in the mixing system dump water (k-94017) and barrier percolation water with reactive materials PO_4-compounds and $Ba(OH)_2$.

Mass Balance of Reactive Surface Barrier Materials

Besides the evaluation of geochemical interactions between the barrier percolation water and the dump water, the feasibility of RSB's from an engineering point of view has been the second objective of the study. This includes the mitigation time scale and the mass balance of the barrier material. Due to technical reasons, the maximum thickness of the reactive barrier is limited to 0.3 m. A chemical balance was calculated to evaluate the available amounts of reactive ions and the time of exhaustion of the reactive barrier. A reactive material has to be excluded as geochemical barrier if leaching of the barrier may cause a structural break down of the barrier layer with subsequent subsidence of the mineral soil cover. On the other hand, the geochemical barrier must provide enough reactive ions for the mitigation of the contaminant potential of the dump. The data given in Table 3 were provided by comparison of the annual dissolved mass of the reactive ions and the total mass of the barrier.

Table 3. Calculation of the mass balance for the reactive materials to mitigate the contaminants dissolved in the pore water of the Schüsselgrund mine dump.

Reactive material	$Ca(OH)_2$		Fe^0		hydroxyl apatite	
mineral soil cover percolation rate	5 %	20 %	5 %	20 %	5 %	20 %
mass of reactive barrier [10^6 kg]	112		151		155	
moles of reactive barrier [10^6 mol]	1517		2707		309	
dissolved reactive material [10^3 kg/a]	10.7	42.9	17.6	70.4	316	1266
reactive solution [10^3 mol/a]	145	580	315	1260	2039	8155
lifetime of reactive barrier [years]	10500	2600	8600	2150	490	120

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Mitigation timescale of the Schüsselgrund dump site

The geochemical mitigation timescale will be controlled by the time needed for complete mixing of the barrier solution with the dump water. The mixing process can be approximated by two model approaches. The first involves a piston flow-like penetration of the barrier solution into the dump, mixing at the interface to the dump water; the second assumes fast infiltration of the barrier solution on preferential flow paths, mixing by exchange of reactive ions with pore water in the low permeable pore matrix. The simple piston flow model may be valid in the case of homogeneous dump compositions. However, for the Schüsselgrund mine dump with a well-known heterogeneous composition, the latter scenario is much more reasonable for estimation of the mitigation time scale. Using the estimated infiltration rates and the known dump water volume on the one hand (piston flow), and the compartment model of dump water with different residence times derived from investigations of environmental isotopes on the other hand (preferential flow), the time scale of complete mixing corresponding to the mitigation time scale can be calculated. Results for both model approaches are given in Table 4. The most realistic time scale, about 68 years, for the Schüsselgrund mine dump is provided by model 2.

Table 3. Calculation of the mitigation time scales for the Schüsselgrund mine dump using reactive surface barriers.

Scenario	time scale for 5 % percolation rate	time scale for 20 % percolation rate
model 1: piston-flow, mixing at infiltration front	84	21
model 2: preferential flow paths, mixing by exchange with pore water	68	34

Neither model takes into account contributions of contaminants from stagnant pore solutions (solid rocks, filter cakes) due to the very low mass flux from these reservoirs, which is mainly controlled by diffusion. However, due to elevated uranium contents and ongoing release of acid from these reservoirs, the inflow of dissolved reactive material to the dump water has to be maintained over a much longer time scale to prevent contaminants from remobilization. In contrast to the time scale of hydraulic mixing (Table 2), the time scale that is needed to balance out the contaminant potential of the dump water (e.g., the neutralisation of H^+ in the dump water by OH^- from $Ca(OH)_2$) is usually much faster (0.6 to 2.3 years in the case of $Ca(OH)_2$).

Conclusions

The feasibility of using several RSB-suitable reactive materials for the mitigation of radionuclides and heavy metals was evaluated. In the case of nickel, mitigation by Fe^0 and $Ca(OH)_2$ only occurred when the dump water constituted less than 30 % of the mixing solution. Fe^0 may be the most suitable reactive material to mitigate uranium and zinc in an acid milieu. The changes in geochemical milieu by oxidation of Fe^0 cause a reduction of uranium(VI) to uranium(IV). The precipitation of uraninite and coffinite causes a fixation of mobile uranium. In addition to redox changes, uranium-sorptive iron hydroxides will be formed after transformation of Fe^0 to Fe^{2+}. According to its chemical properties (dissolution rate), a lifetime of 2150-8500 years has been calculated for the reactive barrier.

Alkaline hydroxides have been identified to be the only suitable reactive material for the mitigation of radium-226. The super saturation of barite in all mixing calculations using reactive $Ba(OH)_2$ as a reactive material indicates a significant precipitation potential of barium sulphate. This will cause co-precipitation of radium-226 sulphates. Due to the general undersaturation of uranium in all other mixing calculations, the suitability of $Ca(OH)_2$ as a reactive material for the mitigation of uranium cannot be definitively determined from geochemical modeling. In contrast to Fe^0 and alkaline hydroxides, PO_4-compounds have no redox-effective properties. The reactivity of these materials is characterized by the formation of insoluble uranium-phosphate-complexes. The dissolution rate of PO_4-compounds was calculated to be the highest of all of the materials investigated. This causes a shorter lifetime of barriers made of PO_4-compounds. Since no positive saturation index for uranium has been observed in the model calculations, a preferential complexation of other metals has to be assumed.

The theoretical study strongly suggests that the use of RSB can provide a sustainable mitigation concept for radionuclides and heavy metals in an acid milieu. Taking into consideration the prognostic character of the theoretical modeling, one has to realise that the results can only be ensured by lab and field measurements. Based on the results of this feasibility study, laboratory experiments have been initiated. According to the different reactivities of the investigated barrier materials, a mixture of different reactive materials has to be considered as a combined mitigation concept. Our experiments will investigate if mixed reactive materials remain reactive for the mitigation of radionuclides and heavy metals when barrier material interactions are taken into account.

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