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Bog ground aquifer system as a natural analogue for future redox conditions in flooded underground mines

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To characterize the future redox milieu caused by natural degradation of wood in flooded mines, the aquifer of a highland bog ground was studied as a natural analogue site. Going from the surface to a depth of one meter in the bog water, the redox potential measured with a platinum electrode changes from 593 mV to –95 mV. From the depth-water analyses and analyses of bog gas extracted from the ground, an Eh value of –119±5 mV could be calculated. Methane and hydrogen sulfide were found in the gas, characterizing the strongly reducing condition in the bog ground. From that, the conclusion for the future mine situation can be drawn that uranium(VI) and arsenic(V) will be reduced and precipitated as $U(OH)_4$ and As_2S_3. In that way, decontamination of the mine water takes place as a consequence of a natural attenuation process.

Introduction

A main task in the restoration of the uranium mining areas in Saxony and Thuringia (Germany) is the flooding of the large underground mines.[1–3] This procedure is a decisive measure because the removal of the mine water requires an expensive water treatment to meet environmental standards. Other reasons are that open and aerated mines release considerable amounts of radon and its daughter products and that the dewatering and ventilation consume much energy.[4,5] Large amounts of wood that was used to reinforce the shafts and galleries go down under water in this mine flooding process. Oxygen consuming processes such as the pyrite oxidation and the microbially mediated oxidation of organic matter create and maintain anaerobic conditions in the deeper water layers.[6,7] First, the reduction of oxygen takes place followed by the reduction of nitrate, manganese(IV) and iron(III). If the redox potential is low enough fermentation reactions and the reduction of sulfate and carbon dioxide occur.[8,9]

Environmental problems arise from the toxic and radioactive substances in the mine water, especially from uranium and arsenic which are transported with the flowing water in the underground. For example, about 240 tons of uranium and 120 tons of arsenic are dissolved in $3.6\cdot10^7$ m^3 flood water of the Schlema/Alberoda mine (western part of Erzgebirge).[10] This mine was equipped with $3\cdot10^6$–$4\cdot10^6$ m^3 wood (about $1.2\cdot10^6$ tons). This corresponds to $0.6\cdot10^6$–$1.0\cdot10^6$ tons of cellulose and $0.3\cdot10^6$–$0.5\cdot10^6$ tons of lignin. It is estimated that the wood decomposition takes place in about 100 years[11] and that the fragments of that degradation process contribute annually to the dissolved organic carbon (DOC) with 300 mg/l, maintaining an equilibrium content of 10–20 mg/l DOC in the mine water.[12]

The scientific question now is: which substances in the mine water can be reduced under the influence of the wood degradation, especially, is the reducing milieu strong enough to immobilize uranium as uranium(IV) hydroxide and arsenic as arsenic(III) sulfide?

It is impossible to answer this question by a direct measurement of the oxidation-reduction (redox) potential in the depth of the mine water or by analyzing water samples because there is no access to the deeper water layers. Another reason is the fact that the organic substances in the mine water are now dominated by organic residues of the former mining process such as oil, lubricant and detergent. The contribution of wood degradation products to the DOC at the current time is low and for the reducing conditions, it cannot be correlated to the wood decomposition in the mine water. For this reason it is necessary to look for a natural system that represents the future situation in the flooded mine in a way that the reducing milieu is unambiguously caused by the process of natural wood decomposition.

Such an approach is well known from performance assessment studies for radioactive waste repositories. A lot of knowledge in that field, e.g., for radionuclide retention, migration and distribution, came from the investigation of “natural analogues”, at former uranium mining sites[13] or at the locations of the Oklo natural fission reactors.[14]

We think a natural analogous site with respect to the future redox situation in the water of flooded underground mines caused by wood degradation is the highland bog “Kranichsee” near the town Johanngeorgenstadt at the ridge of the Erzgebirge.[15]

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This place is characterized by (1) permanent growing and sinking of crippled pines and bushes, (2) microbial decomposition of wood and plant material in the bog water, (3) similar amounts of DOC as expected in the flooded mine, and (4) reducing conditions in deeper water layers. That is why in our opinion this system could be regarded as a natural analogue for the future redox conditions in the water of heavily wood reinforced and now flooded uranium mines. We assume that the present redox conditions in the bog ground aquifer approximate to the future situation in the water of the flooded mine. Therefore, we have investigated the bog ground in this direction in detail.

Experimental

The redox situation in the highland bog was characterized by field measurements and by analyzing water samples and gas collected from the ground at one meter depth. In the case of the in-situ measurements, the redox potential (Eh), oxygen content, pH and temperature were determined with respect to the depth of the bog water. For this reason, a plastic pipe made of PVC about 1.20 m long and 60 mm inner diameter with some lateral slots at the lower end was successively driven into the bog ground. At a given depth, the water was repeatedly pumped out from inside of the well-like pipe to remove the surface water. Then, the sensors were placed at the bottom of the well and the above mentioned parameters of the inflowing water were measured at a particular depth. This procedure was repeated 8 to 10 times. The results in Table 1 represent the mean values with their average deviations. We used field measuring instruments of Fa. Wisenschaftlich Technische Werkstätten, Weilheim (Germany) with sensors CellOx® 352 for O_2 and SenTix ORP® Pt and glass electrode for Eh and pH determinations.

At the same time, water samples were taken from the well bottom at one meter depth by pumping in nitrogen filled bottles under exclusion of air. The light brown water was then filtered through cellulose acetate (0.45 μm) under inert gas.

The bog water was analyzed for cations, anions and DOC using atom absorption spectroscopy (AAS 4100, Perkin Elmer), inductively coupled plasma mass spectrometry (ICP-MS Elan 5000, Perkin Elmer), anion chromatography (Dionex®) with conductivity detection and DOC analysis by measuring CO_2 with an infrared detector after burning in an oxygen stream (according to the German standard: DIN EN 1484, 1997). Carbonate was determined as CO_2 after expelling with phosphoric acid according to the same method and hydrogen sulfide was analyzed by spectrophotometry with N,N-dimethyl-1,4-phenylenediamine (German standard: DIN 38 405, 1992). Results are given in Table 2.

The bog gas was extracted from the moor ground by covering about one square meter of the water surface with a thin plastic foil and stirring the deeper water layers with a long rod. The ascending gas was collected as big bubbles under the foil at the water surface. The gas was transferred in special water-filled vessels by a small and long plastic tube. Three bog gas samples were analyzed by gas chromatography (Perkin Elmer) using a molecular sieve column and thermal conductivity detection. The mean fractions in volume per cent are listed in Table 3.

Table 1. Results of field measurements

Depth, cm	Temperature, °C	Oxygen concentration, mg/l	pH	Eh, mV/SHE
0	8.3 ± 0.1	8.91 ± 0.30	3.7 ± 0.1	593.0 ± 15.0
30	8.2 ± 0.1	1.82 ± 0.40	4.3 ± 0.1	138.4 ± 8.0
60	6.8 ± 0.2	0.36 ± 0.10	5.0 ± 0.2	112.0 ± 10.0
100	4.2 ± 0.1	≤0.1 (d.l.)	5.3 ± 0.1	–95.0 ± 10.0

d.l.: Detection limit.

Table 2. Chemical composition of bog water

Component	Na	Mg	Al	Si	K	Ca	Mn	Fe	Zn	Ba
mg/l	0.696	0.117	0.070	0.830	0.460	0.390	0.009	0.190	0.011	0.012

Component	Pb	U	Cl^-	SO_4^{2-}	S^{2-}	CO_3^{2-}	DOC
mg/l	0.003	0.0015	1.60	0.25	0.177	39.6	44.3

Table 3. Composition of the bog ground gas

Component	CH_4	CO_2	H_2S	H_2	N_2	O_2
ν, vol. %	52.2 ± 1.7	3.28 ± 0.74	$1.27 \cdot 10^{-3}$	<0.1	44.5 ± 1.8	<0.1

The bog water was characterized by a large amount of DOC (up to 55 mg/l) and a low amount of dissolved minerals (less than 25 mg/l). Methane and nitrogen were the main components of the bog gas, followed by a small amount of carbon dioxide and a trace of hydrogen sulfide.

Results and discussion

Results of the bog ground field measurements

The change of the oxidation-reduction conditions with the depth of bog ground water can be characterized as follows:

(1) The oxygen content at the bog surface was 9–11 mg/l. That corresponds to oxygen saturation at the given temperature (8 °C). The mean value of measured redox potentials was 593±15 mV (Table 1).

(2) Going to deeper water layers we found an evident decrease in the oxygen content and of the redox potential. Oxygen disappeared completely and Eh dropped down to –95±10 mV (Table 1). The measurements at the deepest point were accompanied by an intense smell of hydrogen sulfide. This means that strongly reducing conditions are predominant at one meter depth in the bog ground.

Redox potentials calculated from the analytical data

The calculation of Eh values from the analytical results was carried out by applying the law of mass action on the corresponding redox reaction.

In general we have to set:

$$\mathrm{Ox} + m\,\mathrm{H}^+ + n\,\mathrm{e}^- \leftrightarrow \mathrm{Red} + p\,\mathrm{H_2O} \qquad (1)$$

and

$$K_a = \frac{a_{\mathrm{Re}d} \cdot a_{\mathrm{H_2O}}{}^{p}}{a_{Ox} \cdot a_{\mathrm{H}^+}{}^{m} \cdot a_{\mathrm{e}^-}{}^{n}} \qquad (2)$$

If we introduce $p\varepsilon=-\log[\mathrm{e}^-]$, the law of mass action can be written:

$$\log K_a=\log([\mathrm{Red}]\cdot f_{Red})-\log([\mathrm{Ox}]\cdot f_{Ox})+m\cdot\mathrm{pH}+n\cdot p\varepsilon \quad (3)$$

From Eq. (3) the redox potential is calculated according to:

$$Eh=\frac{2.303RT}{F}\cdot p\varepsilon$$

with

$$\frac{2.303RT}{F}=0.05499\ \mathrm{V}$$

for 277 K (4 °C).

At first the redox potential for the surface water was calculated from the measured oxygen content ($3.13\cdot10^{-4}$ mol/l, pH 3.7). An Eh value of 0.931 V results from:

$$\log K=\log[\mathrm{O}_{2(aq)}]-4\,\mathrm{pH}-4\,p\varepsilon=-86.0$$

The following redox reactions with CH_2O representing the organic matter (DOC) could be evaluated by using the analytical results and the corresponding equilibrium constants that are listed in Table 4:

$$\mathrm{CO}_{2(gas)}+8\,\mathrm{H}^++8\,\mathrm{e}^-\leftrightarrow\mathrm{CH}_{4(gas)}+2\,\mathrm{H_2O} \qquad \text{(System 1)}$$

$$\mathrm{CH_2O}_{(aq)}+2\,\mathrm{H_2O}\leftrightarrow\mathrm{H_2CO}_{3(aq)}+4\,\mathrm{H}^++4\,\mathrm{e}^- \qquad \text{(System 2)}$$

$$\mathrm{CH_2O}_{(aq)}+4\,\mathrm{H}^++4\,\mathrm{e}^-\leftrightarrow\mathrm{CH}_{4(aq)}+\mathrm{H_2O} \qquad \text{(System 3)}$$

$$\mathrm{SO_4}^{2-}+10\,\mathrm{H}^++8\,\mathrm{e}^-\leftrightarrow\mathrm{H_2S}_{(gas)}+4\,\mathrm{H_2O} \qquad \text{(System 4)}$$

$$\mathrm{SO_4}^{2-}+10\,\mathrm{H}^++8\,\mathrm{e}^-\leftrightarrow\mathrm{H_2S}_{(aq)}+4\,\mathrm{H_2O} \qquad \text{(System 5)}$$

The equilibrium constants for Systems (1), (4) and (5) were calculated from the molar free energies of the reactants[18,19] and recalculated for 4 °C. The constants for the systems involving organic matter ($CH_2O_{(aq)}$) were calculated using the free standard enthalpy of –221.6±1.1 kJ/mol.[20,21]

Table 4. Redox system, species concentration, equilibrium constant and calculated Eh value

System	Equilibrium	c_{Ox},[1] mol/l	c_{Red},[1] mol/l	$\log K_a$ 298 K/277 K	$p\varepsilon$[2]	Eh,[2] mV
1	$CO_{2(gas)} \Leftrightarrow CH_{4(gas)}$	0.0361	0.574	22.912/26.276	–2.166	–119.1
2	$CO_{2(aq)} \Leftrightarrow CH_2O^3$	0.0328	$1.48\cdot10^{-3}$	–/12.341	–2.165	–119.1
3	$CH_{4(aq)} \Leftrightarrow CH_2O_{(aq)}$	$1.48\cdot10^{-3}$	$1.22\cdot10^{-3}$	8.764/12.448	–2.167	–119.2
4	$SO_4^{2-} \Leftrightarrow H_2S_{(gas)}$	$2.60\cdot10^{-6}$	$1.40\cdot10^{-5}$	41.653/45.039	–1.219	–67.0
5	$SO_4^{2-} \Leftrightarrow H_2S_{(aq)}$	$2.60\cdot10^{-6}$	$5.19\cdot10^{-6}$	40.656/44.295	–1.133	–62.3

[1] Results of analytical determinations.

[2] $p\varepsilon$ and Eh were calculated using Eq. (3).

[3] CH_2O stands for natural organic matter (DOC) of the mean composition $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$.[16,17]

The activity coefficient for 1 : 2-electrolyte was calculated by means of the Davis equation with the ionic strength of $8.22 \cdot 10^{-4}$ mol/l. We found 0.865 for 4 °C.

Considering the conversion of organic carbon to methane and carbon dioxide (System 2 and System 3), the redox potentials of the bog ground water at a depth of one meter were calculated to be –119.1 mV and –119.2 mV (4 °C, pH 5.3), respectively (Table 4). Nearly the same value (–119.1 mV) results from the rate of methane to carbon dioxide in the bog gas (System 1). From that, the conclusion can be drawn that there is equilibrium between organic matter, methane and carbon dioxide. The results show that strongly reducing conditions are dominant in that bog water layer.

Deviating from this, the conversion of sulfate to sulfide results in –64.7±2.3 mV (System 4 and System 5), which is about 54 mV above the mean value of the carbon system. The reason may be that equilibrium in this case is not approached. Stumm and Morgan[8] pointed out that different redox processes in natural waters couple very slowly with each other giving different redox levels for the same compartment. That means this reaction does not determine the redox potential of the bog water. This reaction proceeds as a subordinated process under the dominating influence of the conversion of organic matter.

Lindberg and Runnells[22] evaluated more than 600 water analyses and found that redox potentials measured under aerobic conditions are always too low (up to 230 mV). Our "in-field" measured surface water potential of 593 mV in comparison to the calculated 931 mV is also considerably too low. This water is rich in oxygen and represents a strongly oxidizing medium. Under anoxic conditions the differences go in the other direction. Detected Eh values are up to 250 mV too high.[22] Eh for the deep water was calculated to be –119 mV (from the DOC-methane and DOC-carbon dioxide ratio). We found that the reducing environment at depth in the bog ground is stronger than the corresponding values of the field measurements at the same point (–95 mV). These discrepancies are caused by insufficiently adjusted equilibria of the involved species in the water as well as at the electrode interface.

In general, the transition from the oxidizing to the reducing zone is caused by the oxygen consuming microbial degradation of the plant material. The reducing medium created is so strong that sulfate is reduced to sulfide and organic material is transferred to methane. A similar phenomenon with an even stronger gradient is observed in flooded soil, especially in rice fields.[23] There, the oxygen is consumed within a few centimeters as a result of root respiration and the oxidation of cellulotic substances on one hand and insufficient oxygen delivery from the surface on the other hand. Oxygen in that way decreases from 11 mg/l to zero over a very short distance and redox conditions change to such a degree that methane is produced and released into the atmosphere.

Predicted mine water redox condition

Under the assumption that the reducing conditions in the flooded uranium mines develop to the same intensity as in the bog ground, some important water constituents will successively be reduced, often with the consequence that their mobilities change drastically.

Some important redox reactions taking place in the mine water were calculated using the current flood water composition (Table 5) and the data of Sigg and Stumm[18] and Brookins[19] for the Eh-pH functions. The concentration of the involved species as a function of potential is illustrated in Fig. 1.

The first decrease of redox potential is caused by the consumption of dissolved oxygen. The further decrease comes from the reduction of manganese oxides, such as pyrolusite, manganite and hausmannite. That takes place in the range of 547 to 529 mV resulting in an increase of the Mn^{2+} concentration from $3.6 \cdot 10^{-5}$ to $1.5 \cdot 10^{-4}$ mol/l (from 2 to 8 mg/l Mn^{2+}), i.e., solid oxides are dissolved to manganese(II) according to:

$$\mathrm{MnO}_{2(solid)} + 4\,\mathrm{H}^{+} + 2\,\mathrm{e}^{-} \leftrightarrow \mathrm{Mn}^{2+} + 2\,\mathrm{H_2O}$$

$$\log\,[\mathrm{Mn}^{2+}] + \log f_{2+} + 4\,\mathrm{pH} + 2\,p\varepsilon = 41.59$$

Stronger reducing conditions lead to the reduction of uranium(VI) and iron(III). A decrease of Eh to a level of 240 mV in acidic solution (pH≤4.8) causes the reduction of uranium(VI) to insoluble uraninite. In neutral solution, if carbonate is present with a concentration of $2.0 \cdot 10^{-2}$ mol/l, the redox potential has to fall down to 70 mV to precipitate uranium. If the uranium content decreases by three orders of magnitude (from 6.0 to 0.006 mg/l) redox potential changes from 67 to –22 mV. That uranium immobilization obeys the equations:

$$\mathrm{UO_2(CO_3)_2}^{2-} + 2\,\mathrm{H}^{+} + 2\,\mathrm{e}^{-} \leftrightarrow \mathrm{UO}_{2(solid)} + 2\,\mathrm{HCO_3}^{-}$$

$$2\log\,([\mathrm{HCO_3}^{-}]\cdot f_{-}) - \log\,([\mathrm{UO_2(CO_3)_2}^{2-}]\cdot f_{2-}) + {}$$

$$+\,2\,\mathrm{pH} + 2\,p\varepsilon = 17.69$$

Table 5. Main components of the mine flood water (pH 7.0–7.5)

Component	Na	Ca	Mg	Fe	Mn	U	As	SO_4^{2-}	CO_3^{2-}	DOC
mg/l	448	308	305	7.6	4.0	6.1	3.1	1950	1155	10.0*

* Concentration of carboxylic groups: 0.04 mol/l (caused 10 mg/l DOC).

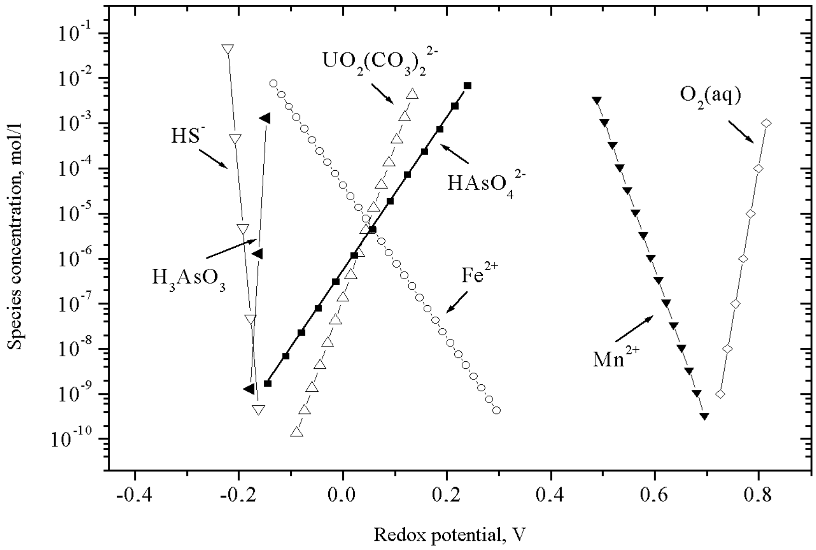

Fig. 1. Reduction of oxygen, Mn(IV), Fe(III), U(VI) As(V) and sulphate under mine water condition

If the redox potential falls below zero, iron oxides such as goethite, haematite and magnetite are dissolved. Eh values between 5.6 and –30 mV relate to concentrations of Fe^{2+} in the range of $3.6\cdot10^{-5}$ to $1.4\cdot10^{-4}$ mol/l (2–8 mg/l Fe^{2+}). Since flood waters of the mines in the Erzgebirge are rich in carbonate (0.02 mol/l), iron(II) can precipitate as siderite. These reductions are described by;

$$Fe(OH)_{3(solid)} + 3\,H^+ + e^- \leftrightarrow Fe^{2+} + 3\,H_2O$$
$$\log([Fe^{2+}]\cdot f_{2+}) + 3\,pH + p\varepsilon = 16.20$$

In competition to the iron(III) reduction, 99.9% of arsenic(V) is reduced to arsenic(III) in the Eh range of +107 to –70 mV according to:

$$HAsO_4^{2-} + 4\,H^+ + 2\,e^- \leftrightarrow H_3AsO_3 + H_2O$$
$$\log[H_3AsO_3] - \log([HAsO_4^{2-}]\cdot f_{2-}) + 4\,pH + 2\,p\varepsilon = 28.54$$

In the case of $[HAsO_4^{2-}]_0 = 4.14\cdot10^{-5}$ mol/l and $[H_3AsO_3]_0 = 4.14\cdot10^{-8}$ mol/l, the decrease in arsenic(V) concentration as a function of redox potential results from:

$$\log[HAsO_4^{2-}] = p\varepsilon + 2\,pH + \log f_{2-} - 20.153$$

With the beginning of the HS^- formation, arsenic(III) is then pecipitated as As_2S_3 (auripigment). In the case that $4.0\cdot10^{-5}$M H_3AsO_3 (3 mg/l) is present, this reaction starts at a HS^- concentration of $4.9\cdot10^{-11}$ mol/l, corresponding to a redox potential of –156 mV. Arsenic(III) is quantitatively precipitated by a HS^- concentration of $4.9\cdot10^{-9}$ mol/l, which is reached at a potential of –170 mV, i.e., the immobilization of arsenic as auripigment takes place in an Eh intervall of 14 mV. The decrease in H_3AsO_3 by precipitation as As_2S_3 follows:

$$2\,H_3AsO_3 + 3\,HS^- + 3\,H^+ \leftrightarrow As_2S_3 + 6\,H_2O$$
$$-2\log[H_3AsO_3] - 3\log([HS^-]\cdot f_-) + 3\,pH = 61.06$$

With a further small Eh decrease, the sulfate reduction increases. If the redox potential lowers from –182 mV to –197 mV the sulfide-to-sulfate ratio increases from 10^{-5} to 10^{-3}, i.e., the concentration of sulfide increases from $2.0\cdot10^{-7}$ to $2.0\cdot10^{-5}$ mol/l. That is calculated from:

$$SO_4^{2-} + 9\,H^+ + 8\,e^- \leftrightarrow HS^- + 4\,H_2O$$
$$\log([HS^-]\cdot f_-) - \log([SO_4^{2-}]\cdot f_{2-}) + 9\,pH + 8\,p\varepsilon = 33.70$$

Starting with a sulfate concentration of $2.0\cdot10^{-2}$ mol/l, the formation of sulfide leads also to the precipitation of FeS_2. For that, a potential of –154 mV is required. That means the reversal of the pyrite oxidation takes place parallel to auripigment formation as:

$$FeOOH_{(solid)} + 2\,SO_4^{2-} + 19\,H^+ + 15\,e^- \leftrightarrow$$
$$\leftrightarrow FeS_{2(solid)} + 10\,H_2O$$
$$-2\log([SO_4^{2-}]\cdot f_{2-}) + 19\,pH + 15\,p\varepsilon = 98.34$$

Sulfate reduction proceeds in the range of –160 to –240 mV. The reduction of the $7.2\cdot10^4$ tons of mine-water sulfate requires $5.8\cdot10^9$ equiv electrons. The microbial transformation of $0.8\cdot10^6$ tons of wood cellulose can actually provide $2.7\cdot10^{11}$ equiv electrons, but it is unknown which part will be available for the sulfate reduction. That is why a forecast regarding the generation of methane cannot be made. We assume the sulfate reduction would be a long-term process.

Sulfate in that respect is a first natural barrier that cannot be easily overcome in the mine water. Thus, it is unlikely that Eh in the near future will decrease below –250 mV.

Reduction of dissolved organic matter at a level of 10 mg/l requires a redox potential of –294 mV. That can be calculated from:

$$CH_2O_{(aq)} + 4\,H^+ + 4\,e^- \leftrightarrow CH_{4(aq)} + H_2O$$

$$\log\,[CH_{4(aq)}] - \log\,[CH_2O] + 4\,pH + 4\,p\varepsilon = 8.764$$

First arguments for this reduction scenario come from the mine near the village Pöhla (Erzgebirge), which was flooded in the early nineties (till 1995).[24] The uranium content in the outflowing water of this mine dropped down by more than one order of magnitude (from 3.3 to less than 0.05 mg/l) over a period of 5 years. It is surprising that the activity of ^{226}Ra increased from $0.8 \cdot 10^{-3}$ to $6.0 \cdot 10^{-3}$ Bq/m^3. If this release of ^{226}Ra could be attributed to the reduction of $(^{226}Ra,Ba)SO_4$ the reducing milieu in the deep water layer would be strong enough to precipitate arsenic as arsenic(III) sulfide. The level of arsenic in the outflowing water had been constant in the first 4 years after flooding. Since 1999 the arsenic content has been decreasing from 5.0 to 3.0 mg/l. This could mean that after reduction of uranium(VI), the redox potential sank below –150 mV with the consequence that arsenic(III) sulfide began to precipitate.

DOC-bound uranium fraction

In addition to the possible reductive immobilization, uranium can be bound to the organic matter to form colloidal organometallic compounds. It is well known that uranium forms stable complexes with humic acid. POMPE et al.[25,26] investigated the complexation of uranium by humic acids of different origin, amongst them the humic acid from the same highland bog that we studied in this work. The stability constant for the uranium humate complex, UO_2HA, was found to be $1.45 \cdot 10^6$ ($\log \beta = 6.16 \pm 0.76$) and for the formation of the partially hydrolyzed complex $UO_2(OH)HA$ from UO_2OH^- a value of $6.76 \cdot 10^5$ was derived. The dissociation constant of the humic acid given as $pK^{(a)}$ is -4.58 ± 0.03.

A uranium speciation for the flood water of the Schlema/Alberoda mine was carried out by means of the computer program RAMESES[27] using the mean composition of the flood water (Table 5) and the stability constants of the predominant hydroxo complexes and carbonato complexes listed in Table 6 and the stabilities of the above mentioned humate complexes.

Since uranium was mined from phyllitic rock rich in calcite and dolomite, the flood water contains a high concentration of carbonate (up to 0.02 mol/l). The concentration of uranium is $2.6 \cdot 10^{-4}$ mol/l (3.5–6.5 mg/l), DOC lies between 8 and 12 mg/l, corresponding to a mean concentration of functional groups (that are able to bind metal ions) of $4.0 \cdot 10^{-5}$ mol/l. The pH is in between 7.0 and 7.5 and the ionic strength was calculated to be $8.2 \cdot 10^{-4}$ mol/l.

It is seen in the speciation diagram (Fig. 2) that above pH 4.5 most of the uranium(VI) is present as carbonato complexes. Uranium(VI) bound to humic acid occurs between pH 3.5 and 6.0, but only to a small degree. At pH 7 the concentration of uranium(VI) humate species is about $1.4 \cdot 10^{-9}$ mol/l (P1 in Fig. 2) and up to pH 7.5, the concentration decreases to $1.8 \cdot 10^{-10}$ mol/l (P2 in Fig. 2) (Table 7). That means only $5.6 \cdot 10^{-4}$% of uranium is bound to humic substance and can, therefore, be transported in a colloid-borne way.

Another argument against the assumption that DOC can favour uranium migration is that the anoxic conditions are generated by the decomposition of the organic material, i.e., the electrons for the uranium(VI) reduction come from the DOC. Thus, the complexation can be regarded as a pre-step for the reduction which then can be accomplished by an intra-molecular mechanism.

Arsenic(V) and arsenic(III) occur in the mine flood water as anionic species such as $H_2AsO_4^-$, $HAsO_4^{2-}$ and $HAsO_3^{2-}$. An interaction of these species with humic acid is unknown.

Table 6. Stability of mine water relevant uranium(VI) hydroxo and carbonato complexes[28]

Hydroxo complexes		Carbonato complexes	
Species	$\log {}^*\beta^0_{n,m}$ [1]	Species	$\log K^0$ [2]
UO_2OH^+	-5.2 ± 0.3	UO_2CO_3	9.68 ± 0.04
$UO_2(OH)_2$	-10.3	$UO_2(CO_3)_2^{2-}$	16.9 ± 0.12
$(UO_2)_2OH^{3+}$	-2.7 ± 1.0	$UO_2(CO_3)_3^{4-}$	21.6 ± 0.05
$(UO_2)_2(OH)_2^{2+}$	-5.62 ± 0.04	$(UO_2)_2CO_3(OH)_3^-$	-19.0 ± 0.5
$(UO_2)_3(OH)_4^{2+}$	-11.9 ± 0.3	$(UO_2)_3CO_3(OH)_3^+$	-17.5 ± 0.5
$(UO_2)_3(OH)_5^+$	-15.6 ± 0.12	–	–
$(UO_2)_4(OH)_7^+$	-22 ± 1	–	–

[1] ${}^*\beta^0_{n,m}$: Overall formation constant: $m\,UO_2^{2+} + n\,H_2O(l) = (UO_2)_m(OH)_n^{2m-n} + n\,H^+$.

[2] K^0: Equilibrium constant: $m\,UO_2^{2+} + n\,CO_3^{2-} + q\,H_2O(l) = (UO_2)_m(CO_3)_n(OH)_q^{2m-2n-q} + q\,H^+$.

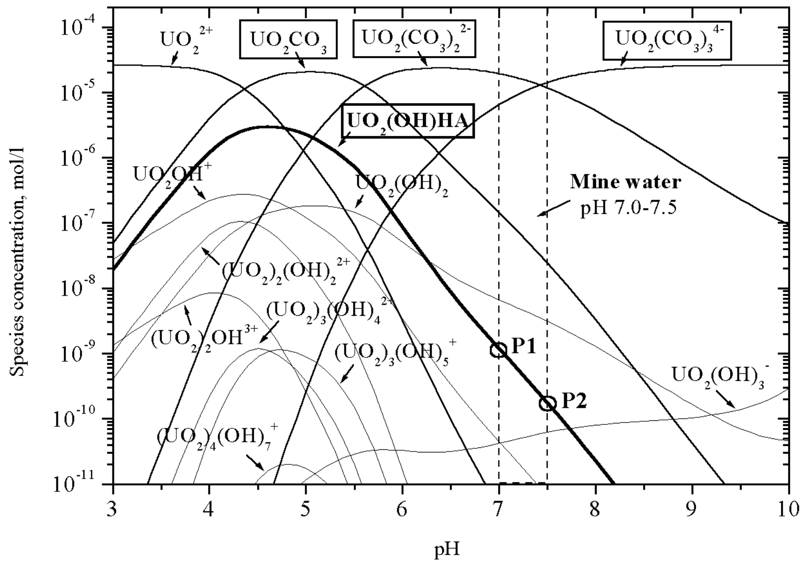

Fig. 2. Speciation of uranium(VI) under mine water condition. Formation of the uranium(VI)-humate complex $UO_2(OH)HA$ (P1 – complex concentration at pH 7, P2 – concentration at pH 7.5)

Table 7. Concentration of uranium(VI)–humate complex as a function of pH

pH	5.5	6.0	6.5	7.0	7.5
$[UO_2(OH)HA]$, mol/l	$6.5 \cdot 10^{-7}$	$9.0 \cdot 10^{-8}$	$8.8 \cdot 10^{-9}$	$1.4 \cdot 10^{-9}$	$1.8 \cdot 10^{-10}$

Conclusions

From the redox situation in the bog ground aquifer we deduced that a highly reducing environment will be developed in the deep water of flooded wood-reinforced underground mines. This process is driven by permanent microbial wood degradation. Mine water contaminants such as uranium(VI) and arsenic(V) will be reduced in a long-term process. Uranium precipitates as water-rich uraniumdioxide. The uranium content in the water of the Pöhla mine, flooded eight years ago, is decreasing slowly. The question is whether the reducing environment in the mine water develops to the same intensity as in the bog ground. If the reducing milieu is so strong that sulfate reduction starts then arsenic(III) will be precipitated as arsenic(III) sulfide. A first sign is that the radium content in the water of the Pöhla mine has increased. This phemonenon can only be understood if solid barium-radium sulfate is dissolved by sulfate reduction.

This reductive immobilization of uranium and arsenic in water of flooded mines would be highly desirable because that would store them as insoluble solids at the mine ground and exclude them from transportation with the flowing water.

In that way, a natural cleaning process is driven by the permanent microbial wood degradation. The risk of contamination of adjoining ground water tables decreases in such a degree as the reductive immobilization proceeds.

The present redox situation in the bog ground water is assumed in general to be comparable with the future conditions in water of flooded underground mines. Under this aspect, the bog ground can be considered as a natural analogue for such mines. The influence of the degradation of structural wood reinforcements in flooded mines on the mine water chemistry should be considered in the environmental risk assessment for such sites and in modeling the long-term behavior of flooded underground mines.

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