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Influence of hydrothermal wood degradation products on the uranium adsorption onto metamorphic rocks and sediments

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The influence of highly functionalized saccharic and phenolic polymers that are formed in the process of hydrothermal wood degradation on the uranium(VI) adsorption onto metamorphic rocks and sediments from the Saxon uranium mining sites Schlema-Alberoda and Königstein was investigated in a laboratory study. Uranium(VI) adsorption from a simulated mine water takes place on the majority of rocks and sediments such as granite, gneiss, basalt, sandstone and clay marl. Exceptions are phyllite and clay stone that do not bind any uranium from the mine water. Polymeric wood degradation products such as fragments of celluloses and lignin increase the uranium(VI) adsorption whereas the presence of saccharic and phenolic monomers (vanillic acid and gluconic acid) leads to a lower adsorption.

Introduction

A central task in the restoration of the decommissioned uranium mining areas in Saxony and Thuringia (Germany) is the flooding of the large and deep underground mines.[1,2] In this process the interaction of water with the mine wood leads to the degradation of the wood and to the dissolution of decomposition products in the mine water. These organic substances play an important role in water chemistry, especially their ability to complex radionuclides and heavy metals[3,4] since they change the radionuclide species and with this their migration behavior. The aim of this study is to characterize the influence of the wood degradation products on the uranium(VI) adsorption onto mining site specific rocks and sediments. For this purpose distribution ratios (R_S) were determined without and in the presence of the degradation products by means of batch experiments. R_S values, in addition, were determined in the presence of vanillic acid and gluconic acid as typical monomeric lignin and cellulose destruction products.

The large vain-type uranium deposit around the granite massif of Aue (western region of Erzgebirge Mountains) was mined over 40 years with the total output of 80.8 kt uranium. The Schlema-Alberoda mine there is one of the biggest worldwide (total volume of 40 million m^3) and reaches down to 1.8 km.[5] The shafts and galleries are heavily reinforced with wooden pit props. About 3–4 million m^3 spruce and pine trunks containing about 0.6–1 million tons cellulose and 0.3–0.5 million tons lignin were introduced in this big underground mine. The mine has been under flooding since 1991 and half of the mine was watered in 1997. The uranium content in the mine water increased continuously from 2 to 6 ppm. The 20 million m^3 mine water contained at this time nearly 100 tons dissolved uranium. Environmental risk arises from the mine water contamination and the migration of uranium, radium (80 GBq) and arsenic (50 t).

About 18.0 kt of uranium was mined from the Königstein deposit in the Saxon sandstone region from 1967 to 1990. The mining technique was oxidative uranium extraction from 55 million tons sandstone with 2–5 ppm UO_2 by underground in-situ leaching with sulfuric acid. Now nearly 2 million m^3 of highly acidic leaching solution remained unextractable in the mine containing about 40 tons of uranium and 15000 tons of sulfate. In the process of flooding this solution will be diluted by groundwater.[6]

Wood stability under water depends on the kind, the pretreatment and the degree of damage during its operation time in the mine. In the case of spruce and pine wood stability is reported to be 50–100 years. Preservation by alkali fluorides and dichromates increases the stability and attack by fungi and bacteria accelerates the degradation.[7] Taking a wood-to-water ratio of 30 kg/m^3 and an annual decomposition of 0.3 kg/m^3 the introduction of organic substances into the mine water amounts to yearly 0.3 kg/m^3 causing a DOC level of 10 to 20 ppm.

Wood decomposition in water under aerobic conditions occurs as a microbiell-mediated hydrolytic and oxidative-radical depolymerisation of the cellulose fibres, the polyoses and the lignin that forms fragments of lower molecular weight among them carbohydrates, saccharic acids, vanillin and phenolcarboxylic acids as degradation intermediates.[8–11] Wood degradation can be simulated in the laboratory by hydrothermal treatment i.e. by boiling wood ships with water.[12,13]

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Table 1. Composition and origin of the rocks and sediments

Rock/sediment	Mineral constituents	Occurence
Phyllite	muscovite, chlorite, quartz, (recrystallized ordovicic and pre-cambric rocks)	Schlema site, Erzgebirge/Saxony
Granite	potash feldspar, plagioclase, quartz, biotite, muscovite, (caledonian magma intrusion)	Demitz-Thumitz site, Lusatia granite massif/Saxony
Gneiss	feldspar, quartz, biotite, muscovite, (magmatic origin)	mediaeval slagheap, Freiberg site/Saxony
Basalt	anorthite-rich augite, hornblende, chlorite, (magmatic origin)	Northern Bohemia, Czech Republic
Diabase	saussurite, quartz, hornblende, chlorite, (varistic volcanite)	
Calcite	pure mineral	Nueva Leon/Mexico
Sandstone	quartz, kaolin, limonite (ta), goethite (ta)	Königstein mining site/Saxony
Clay stone	kaolinite, orthoclase, muscovite, quartz, marcasite, chalcopyrite, leucoxene (ta)	Königstein mining site/Saxony
Clay marl	chalky-clayey aleurolithe, calcite, kaolinite, quartz	Königstein mining site/Saxony

(ta): trace amounts.

Table 2. Specific surface and density of the crushed rocks and minerals

	Phyllite	Diabase	Calcite	Gneiss	Granite	Basalt
Surface[1]	33	19	2	5	6	46
Density[2]	124	142	149	133	131	160

[1] Specific surface, m^2/g.
[2] Density of the crushed rock [g/cm^3], particle size: 63–630 μm.

Table 3. Sediment characterization: quartz content, specific surface, porosity, acid neutralization capacity and cation exchange capacity

Rock/sediment	Quartz, vol %	Surface, m^2/g	Porosity, vol %	ANC,[1] meq/kg	CAC,[2] meq/kg
Sandstone[3]	78–88	<1	18–24	10–28	0.5–6
Claystone	10–20	10–12	18–20	104–170	20
Lime marl	70–72	10–13	6–7	2 200–3 800	60–90
Lime marl (calcite-deficient)	44–65	7–9	20–24	300–650	18–2

[1] Acid neutralization capacity.
[2] Cation exchange capacity.
[3] Cenomanian and turonian sandstone.

Experimental

Characteristic of the geological materials and the mine waters

Rocks and sediments that are typical for the Erzgebirges mining area and the Königstein mine in the Saxon sandstone region were included in this study (Table 1).

The mining-site phyllite is a fine slate-like metamorphic rock that was formed by recrystallizing ordovicic and precambric rocks in deeper crust's layers 400–500 million years ago. The main mineral constituents are muscovite, chlorite and quartz. The granite came from the Lusatia granite massif (Demitz-Thumitz quarry) the biggest granitic area of Middle Europe that was formed as result of a magma intrusion during the caledonian tectogenese 400 million years ago. It is composed of potash feldspar, plagioclase, quartz, biotite and muscovite. Gneiss, a metamorphic rock of magmatic origin with bright-streaky feldspar and quartz and dark bands of biotite and muscovite came from a mediaeval slagheap at Freiberg (Saxony). The basalt is a magmatic rock from northern Bohemia that consists of anorthite-rich augite, hornblende and chlorite. Diabase as a green varistic volcanite is rich in saussurite (a metamorphic plagioclase) with some quartz, hornblende and chlorite. Calcite as colorless and transparent fission rhombohedrons was the pure mineral found at Nueva Leon (Mexico).

The rocks and minerals were crushed by a jawcrusher and sieved by a set of sieves with different mesh sizes. The grain fraction of 63–630 μm was used in the experiments. The specific surface and density of the geomaterials pretreated in that way are listed in Table 2.

The sediments included in this study came from different strata of the Königstein mine body and the northern downstream near field. They were deposited in the limestone time about 80 million years ago in the following sequence: cenomanian sandstone – clay stone – clay marl – turonian sandstone. They are characterized by a relatively high surface and porosity (Table 3).

In the sandstones quartz dominates within 90–96%. The grains are bond together by some clay (5–8% kaolin) and by superficial quartz remineralization. Mineralizations of limonite and goethite are found in the pores and along the fissures and gaps of the younger turonian sandstone. The clay stone is mainly composed of kaolinite with some orthoclase and muscovite. Quartz is less than 20%. Marcasite, chalcopyrite and leucoxene are the opaque constituents (≤5%). Finely dispersed organic carbon is the result of former plant decomposition. The clay marl represents a calcareous clay (chalky-clayey aleurolithe) with about 12% calcite in addition to kaolinite and quartz. Part of the clay marl in the mine and and its near field is changed to a calcite-deficient sediment by local influence of sulfuric acid from the marcasite oxidation.

The water of the Schlema mine is rich in sulfate (~2 g/l) and carbonate (~1 g/l) coming from the pyrite oxidation and the dissolution of calcite and dolomite (Table 3). Uranium and organic substances are present to 4–5 mg/l and 10–15 mg/l, respectively. The mine water at Königstein is acidic (pH 2.5) and contains sulfate up to 3 g/l. The final uranium content is assumed to be higher than at the Schlema site (now 25 mg/l). The inflowing groundwater has a low mineral content (Table 3).

Hydrothermal mine wood degradation products and pine-wood lignin

Solutions of wood degradation products were prepared at the Institute of Plant and Wood Chemistry Tharandt of the Technische Hochschule Dresden by boiling chips of original mine wood in water under reflux or by treating in an autoclave at 9 MPa and 70 °C under nitrogen.[14] In this treatment 7 to 14 wt% of the wood was dissolved resulting in a weakly acidic hydrothermal extract with pH 3–4. The solutions contained 200 to 1400 mg/l DOC consisting of phenolic and saccharic compounds in about equal parts. The dissolved organic matter has a wide molecular weight distribution. The phenolic compounds are in the upper range (10–170 kD) and most of the saccharides are below 3 kD. The lignin degradation products (5–6 wt%) consist of phenolic polymers with strongly shortened side chains at the structure units. Monomeric compounds, mainly vanillin and its oxidation products, such as vanillic acid (4-hydroxy-3-methoxybenzoic acid) and protocatechuic acid (3,4-dihydroxybenzoic acid) are present in low content. Higher molecular saccharides represent the main part of the polysaccharide decomposition products (4–5 wt%). Cellobiose was found in the range of 0.02 to 0.46 wt%. Monosaccharides amount to 0.5 wt%, among them arabinose (35–60% of the monomers), glucose (20–33%), xylose/mannose (12–27%) and galactose (3–8%). Saccharic acids such as 4-O-methyl-glucuronic acid, gluconic and glucuronic acid as well as galacturonic acid are present up to 0.1 wt%.[15] The leached compounds are highly functionalized: 7.8 mmol/g strongly acidic groups with $pK_{Diss.} = 4.4$ and 6.3 mmol/g weakly acidic groups with $pK_{Diss.} = 8.5$.[16]

Lignin samples were also prepared at the Institut of Plant and Wood Chemistry Tharandt by extraction of spruce wood with methanol in alkaline solution and precipitation of the lignin by carbon dioxide.[17] This lignin is characterized by a high purity and only a small matrix damage. Some ether cleavages during the wet extraction led to an increase of phenolic OH content to about 3 meq/g. The lignin was dissolved in water by adding an equivalent of sodium hydroxide.

Analytical grade vanillic acid (4-hydroxy-3-methoxybenzoic acid, Fluka) and D-gluconic acid (Merck) were used without further purification.

Adsorption experiments

The adsorption experiments were carried out in a 12-ml polypropylene tube by equilibrating 1 g geomaterial with 5 ml aqueous phase containing the U(VI) and the wood extract. To avoid any influence of dissolved organic matter in the original waters the aqeous-phase solutions were prepared according to the corresponding analysis (Table 4). In case of metamorphic rocks from the Erzgebirgs the composition of mine water from the Schlema-Alberoda site was used and in the experiments with the Königstein sediments a solution representing the ground water of that site. First the samples were pre-equilibrated for two weeks. Then aliquots of uranyl sulfate stock solutions and of the wood extract were added to set uranium concentrations in the range of $3.2 \cdot 10^{-7}$ to $3.2 \cdot 10^{-5}$ mol/l (0.076–7.62 mg/l) and contents of organic matter to 16 and 166 mg/l. Each sample was spiked with 40 Bq ^{234}U (10 µl ^{234}U solution of 4 kBq/ml, Amersham/Buchler). After that the pH was adjusted to pH 7±0.2 with small amounts of 10^{-2}M NaOH. The samples were gently shaken for 4 to 6 weeks at constant temperature (25 °C). In that time stady-state was reached. Then the final pH was measured and the phases were carefully separated by centrifugation at 3000 rpm for 5 minutes. The supernatant in addition was filtered through a 0.45-µm membrane. The distribution ratios (R_S, ml/g) were determined by liquid scintillation counting. For that reason 4 ml gelling scintillator (ReadyGel™) was added to 3 ml of the liquid phase.

Table 4. Composition of the mine water at the Schlema-Alberoda site and the ground water in the Königstein area

Element	Mine water (pH 6.8), mg/l	Ground water (pH 4.5), mg/l
Na (AAS)	528	4.5
K	38.6	0.16
Ca	309	4.97
As	3.33	0.01
Mg (ICP/MS)	299	0.80
Al	<0.1	0.05
Si	10.9	4.20
Fe	7.88	2.36
Zn	0.07	0.37
Ba	0.05	0.08
Th	<0.001	0.003
U	5.73	0.46
Sulfate (IC)	1880	26.7
Chloride	100	3.9
Carbonate	1160	26.8
Nitrate	<0.5	<1
DOC	9.2	1.6

The ^{234}U impulse rates were measured in comparison to a spike aliquot and a blank in a liquid szintillation counter (Beckmann). Distribution ratios were calculated according to:

$$R_S = \frac{N_{tot} - N_{liq}}{N_{liq}} \times \frac{v_{liq}}{m_{sol}} \text{ ml / g}$$

R_S values that can be determined under this conditions range from 0.7 to $6 \cdot 10^3$ ml/g. The lower limit results as the the lowest well-defined measured value from the mean blank (4.58 cpm, $n = 33$) and its standard deviation (0.54 cpm) from $N_{min} = N_{blank} + 6\sigma_{blank}$. Taking the same relationship the upper limit comes from the impulsrate of the total activity which was counted until the error was below 2%. R_s values result as the mean of 8–12 equilibrations under the same conditions. The error is given as confidence interval according to the Student *t*-distibution with a probability of 95%.

Results

Uranium adsorption onto Ore Mountains rocks and minerals

Uranium adsorption from the DOC-free mine water takes mainly place on diabase and calcite with R_S values of 4.8 and 4.5 ml/g, respectively, i.e., about 50% of the uranium is bound on these solids at the given phase ratio (Table 5). Adsorption under the influence of wood degradation products (WDP) and, especially, in the presence of spruce-wood lignin (LIG) is increasesd to R_S between 9.2 and 108 ml/g, corresponding to an adsorption of 66.7 to 95.6%. Gluconic acid (GLA), a monomeric cellulose breakdown compound, decreases the adsorption to about 30% (R_S: 2.41/2.01 ml/g) and vanillic acid (VNA), an intermediate of the lignin destruction, reduces the adsorption only little (by 5%). A small influence of organic matter content is seen in case of uranium adsorption on diabase and calcite in the presence of VNA and GLA.

Granite, basalt and gneiss adsorb 17 to 24% uranium (R_S: 1.05/1.61 ml/g) from the DOC-free mine water. In the presence of wood leachate, adsorption increases for basalt and granite up to 39% (3.14 ml/g) and 46% (4.30 ml/g), respectively. Evident adsorption takes place in the presence of LIG: 68.8 to 78.7% of the uranium are adsorbed on these rocks (R_S: 11.0–18.5 ml/g). GLA diminish the adsorption to a level less than 12% ($R_S \leq$ 0.7 ml/g), whereas VNA is of no influence.

Uranium adsorption on phyllite is the least. The distribution ratios are all below the detection limit of 0.7 ml/g, i.e. less than 12% uranium is bound from all solutions. Arnold et al.[18] reported that in the pH range 6 to 7.5 about 96% of uranium is adsorbed onto phyllite from a solution of 0.1M $NaClO_4$ under aerobic conditions. In our case the liquid phase contains all the constituents of the mine water. We think that especially the high concentration of divalent metal ions, Ca^{2+} and Mg^{2+} up to 500 mg/l, and the high content of carbonate, up to 1.2 g/l, prevent the uranium adsorption by competition for the adsorption sites and uranium(VI) complexation in the liquid phase.

Uranium adsorption onto Königstein sediments

Uranium is preferentially bound to sandstone: more than 90% are adsorbed (Table 6); especially the limonite-rich turonian sandstone adsorbs uranium with a high distribution ratio: R_S amounts to 142 ml/g (96.6%). The adsorption is considerably reduced under the influence of the organic substances: (1) wood leachate and lignin reduce adsorption on the cenomanian and the limonite-rich sandstone by 23% and 3% (R_S: 10.3/73.5 ml/g), respectively, (2) vanillic acid by 11% and 27% (R_S: 19.2/11.6 ml/g). In case of gluconic acid uranium adsorption on cenomanian sandstone decreases by 90% (R_S: 3.3 ml/g). A distinct dependency on the organic matter content is observed, e.g., gluconic acid lowers the adsorption cosiderably: R_s decreases from 142 ml/g without GLA over 76.8 ml/g at 16 mg/l GLA to 26.4 ml/g at 166 mg/l GLA. But in the case of wood-degradation products a decrease is only observed at 166 mg/l: R_S goes down from 142 to 70 ml/g.

The level of adsorption on clay marl is much lower: 37–68% (R_S: 5.2–10.7 ml/g). Wood leachate and lignin enhances the adsorption by 17% and 9%, respectively, and the adsorption from vanillic and gluconic acid solution is reduced by 14% (R_S from 5.5 to 2.9 ml/g).

Table 5. Uranium(VI) adsorption onto rocks and minerals from Schlema-Alberoda site; influence of wood degradation products on the distribution ratio

	Phyllite	Diabase	Calcite	Gneiss	Granite	Basalt
pH	8.19 ± 0.05	8.10 ± 0.06	8.08 ± 0.11	8.14 ± 0.08	8.32 ± 0.10	8.23 ± 0.12
R_S (w.ORG)	<0.7	4.75 ± 1.24	4.47 ± 0.79	1.08 ± 0.29	1.02 ± 0.55	1.61 ± 0.18
R_S (WDP)	<0.7	9.20 ± 1.61	14.6 ± 3.5	1.33 ± 0.6	4.30 ± 2.72	3.14 ± 1.11
R_S (LIG)	<0.7	50.3 ± 10.3	108 ± 40.8	11.0 ± 3.9	15.5 ± 4.7	18.5 ± 8.0
R_S (VNA-16)[1]	<0.7	5.17 ± 1.03	3.94 ± 0.53	1.26 ± 0.20	1.33 ± 0.14	1.59 ± 0.21
R_S (VNA-166)[2]	<0.7	3.75 ± 0.29	3.84 ± 0.62	1.22 ± 0.07	<0.7	1.42 ± 0.11
R_S (GLA-16)[1]	<0.7	3.32 ± 0.47	3.83 ± 0.44	1.12 ± 0.34	<0.7	1.27 ± 0.12
R_S (GLA-166)[2]	<0.7	2.41 ± 0.19	2.01 ± 0.48	<0.7	<0.7	<0.7

[1,2] Content of organic matter: 16/166 mg/l.
w.ORG: Without organic substances.
WDP: Hydrothermal wood leachate.
LIG: Spruce-wood lignin.
VNA: Vanillic acid.
GLA: Gluconic acid.

Table 6. Uranium(VI) adsorption onto sediments from the Königstein site; influence of wood degradation products on the distribution ratio

	Sandstone, cenomanian	Sandstone, turonian	Clay marl	Claystone	Clay marl, calcite-deficient
pH	7.58 ± 0.20	7.05 ± 0.14	7.56 ± 0.10	3.42 ± 0.16	3.72 ± 0.14
R_S (w.ORG)	47.1 ± 20.5	142 ± 25.3	5.18 ± 1.71	<0.7	1.39 ± 0.39
R_S (WDP-16)[1]	50.2 ± 12	150 ± 42.4	8.38 ± 1.2	2.57 ± 0.6	1.10 ± 0.4
R_S (WDP-166)[2]	12.7 ± 4.4	69.8 ± 14.0	10.8 ± 4.8	2.87 ± 1.1	1.52 ± 0.8
R_S (LIG)	10.3 ± 1.9	85.3 ± 14.1	7.5 ± 2.4	<0.7	3.42 ± 1.0
R_S (VNA-16)[1]	17.0 ± 5.8	76.9 ± 13.6	4.25 ± 0.72	<0.7	1.36 ± 0.29
R_S (VNA-166)[2]	19.2 ± 6.8	11.6 ± 1.2	2.99 ± 0.38	<0.7	2.77 ± 0.72
R_S (GLA-16)[1]	19.1 ± 4.1	76.8 ± 14.3	4.08 ± 0.48	<0.7	1.77 ± 0.15
R_S (GLA-166)[2]	3.32 ± 1.0	26.4 ± 4.7	2.81 ± 0.21	<0.7	2.51 ± 0.30

[1,2] Content of organic matter: 16/166 mg/l.
w.ORG: Without organic substances.
WDP: Hydrothermal wood leachate.
LIG: Spruce-wood lignin.
VNA: Vanillic acid.
GLA: gluconic acid.

The studied claystone binds uranium only in the presence of wood leachate; about one third of the uranium is adsorbed in the range 16 to 166 mg/l WDP (R_S: 2.6–2.9 ml/g). The reason may be that this sediment acidifies the aqueous phase (from pH 7.3 to 3.4) and some of the higher molecular organic matter precipitates with part of the uranium on the surface of the sediment particles. The same phenomenon of pH decrease was observed in the experiments with the calcite-deficient clay marl. Uranium adsorption onto that sediment ranges from 18% to 40% (R_S: 1.1–3.4 ml/g) without any evidence for the organic matter to affect the adsorption.

Conclusions

The study demonstrates quite clearly that uranium(VI) adsorption onto the predominating rocks and minerals of the Erzgebirge mining sites and onto the essential sediments of the Königstein uranium deposit from the typical mine and ground waters is strongly influenced by products of the natural wood degradation process.

The adsorption behavior of the rocks and minerals is characterized (1) by a strong increase of adsorption in the presence of the wood degradation products in the typical sulfate- and carbonate-rich mine water of that region and (2) by a small decrease of the adsorption under the influence of vanillic acid and gluconic acid as monomers of the natural cellulose and lignin breakdown. The phyllitic rock represents an exception because uranium adsorption under all conditions is relatively low. The behavior of the sedimentary sandstones is characterized (1) by a much higher adsorption in comparison to the rocks and minerals and (2) by a strong decrease of that adsorption with the content of organic matter. The adsorption onto the clay sediments is not so pronounced and an influence of the organic matter is only seen in case of clay marl.

The reason for that tendencies may be that (1) the colloidal polymers strengthen the adsorption by coagulating and precipitating on the rocks and sediments and (2) the monomers decrease the adsorption on the geomaterials because of its ability to form stable uranium(VI) complexes in the aqueous phase.[19]

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