Simulation of the effects of geochemical reactions on groundwater quality during planned flooding of the Königstein uranium mine, Saxony, Germany

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Abstract Uranium mining in southeastern Germany resulted in significant environmental risks. Closure of the mines and subsequent rises of water levels may result in heavy-metal and radionuclide-bearing mine waters penetrating aquifers that are used for water supply. While there are certain (geo-)technical constraints on the schedule with which flooding of the mines can proceed, this process must not result in aggravating the problem of metal release. Evaluation of the likely 'natural' geochemical situation of Königstein mine after mining has ceased, and different scenarios for the release of metals indicates that rapid flooding, albeit avoiding unnecessary aeration of the waters, is likely to result in reducing conditions and consequently low U-solubilities.

Résumé L'exploitation minière d'uranium dans le sud-est de l'Allemagne est responsable de risques environnementaux significatifs. La fermeture des mines et la remontée consécutive du niveau de l'eau peuvent permettre à des eaux des mines riches en métaux lourds et en radionucléides de pénétrer dans des aquifères captés pour l'alimentation. Alors qu'il existe certaines contraintes géotechniques sur le programme de remplissage des mines, la procédure à suivre ne doit pas conduire à une aggravation du problème de la mobilisation des métaux. L'évaluation de la situation géochimique naturelle vraisemblable de la mine de Koenigstein après sa fermeture et les différents scénarios pour la mobilisation des métaux indiquent que le remplissage rapide, bien qu'il évite l'aération non nécessaire des eaux, doit vraisemblablement produire des conditions réductrices et par conséquent de faibles solubilités de l'uranium.

Resumen La minería de uranio en el sudeste de Alemania ha provocado grandes problemas ambientales. El cierre de las minas, con los consiguientes ascensos de niveles freáticos, puede producir que aguas procedentes de dichas minas, con altos contenidos de metales pesados y sustancias radioactivas, alcancen acuíferos actualmente en explotación. Aunque existen algunas restricciones geotécnicas en la manera en que se pueden producir las inundaciones, el resultado final no puede ser un empeoramiento del problema. La evaluación de la situación geoquímica que se producirá con mayor probabilidad en la mina de Königstein tras el cese de las extracciones, así como el estudio de diferentes alternativas planteadas, indican que con toda probabilidad una inundación rápida dará lugar a condiciones reductoras, y consecuentemente, a una baja solubilidad del Uranio.

Key words uranium mining · Germany · groundwater protection · hydrochemistry · hydrochemical modeling

Introduction

Shortly after the unification of the two German states in 1990, uranium mining in the Federal States of Saxony and Thuringia, which was carried out for several decades by the Soviet-German concern SDAG WISMUT, was halted. Since then, the mines have been prepared for controlled closure. The deep uranium mine Königstein, located about 25 km southeast of Dresden, capital of Saxony, and near the frontier with the Czech Republic, is of particular concern owing to the potential environmental hazards arising from flooding that would occur during closure operations. The causes of these hazards are closely associated with

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Supplemental material presenting results of water-quality analyses of mine water and groundwater from the Königstein uranium mine, Saxony, Germany, has been deposited in electronic form and can be obtained from http://link.springer.de/link/service/journals/10040.

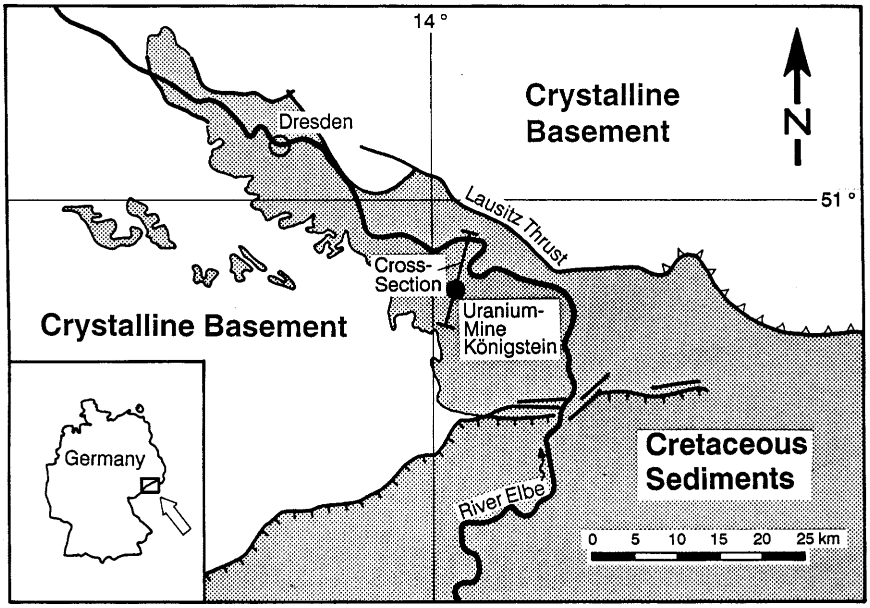

Figure 1 Location of Königstein mine in Saxony, Germany

the hydrogeological setting and the former method of uranium extraction. Locations are shown in *Figure 1*.

The present study describes a scoping assessment of the likely geochemical effects of flooding at Königstein Mine. This assessment, done in 1994 was requested by the licensing authorities and had to be based on the limited database that was available at that time, together with some semi-quantitative scenario analyses.

The Königstein waters were characterised on the basis of chemical and isotopic data and with the help of geochemical modeling techniques. The results from equilibrium simulations allow a first semi-quantitative characterisation of the solutions with a view to their reactability with the rock matrix. Further, species-predominance distributions allow conclusions regarding the likely mechanisms of migration and retention of contaminants of interest. The interpretations are put into context using the isotopic data.

Site Description and Problem Statement

A hydrogeological section of the Königstein mine is shown in *Figure 2*. The uranium mineralisation is bound to the lowermost units of a sequence of Cretaceous sediments, which belong to the infilling of a NW–SE-striking fault-controlled basin along the uppermost German part of the Elbe River, the so-called Elbtalgraben. The base of the basin as well as the bedding of the sedimentary units generally dip toward the northeastern rim of the basin, formed by the Lausitz Thrust. Alternating sedimentation of fine-grained, clayey sediments and coarser sandstones resulted in a layered hydrogeological system of four aquifers, separated by less permeable mud-rocks of variable lateral extension and thickness. The mine workings concentrate on the lowermost (fourth) aquifer and cover an area of 2 km by 5 km. Pumping in order to keep the mine dry has resulted in an extended depression cone that affects all aquifers. The resulting groundwater flow in the fourth aquifer is directed concentrically into the mine. Present water-pressure levels and water tables in the overlying third aquifer are strongly affected, too, particularly near shafts and permeable faults (*Figure 2*).

Recharge of groundwater occurs on the southwestern rim of the basin, where the units crop out. The overlying third aquifer is utilised for drinking-water supplies of nearby towns to the north. At the time of closure, pumping would cease and the mine would be flooded. The third aquifer would be put at risk once the pressure level in the fourth aquifer rises, because of the numerous poorly sealed or completely unsealed exploration bore-holes and conductive faults that transect the separating mud-rock sequence. Contaminated waters from the fourth aquifer could move up into the third aquifer. The extent to which this hydraulic situation becomes relevant, however, depends significantly on the chosen operational conditions during flooding (WISMUT 1995).

Until 1984, uranium (U) mining was carried out using conventional methods. Thereafter, the operation was switched to in-situ leaching using sulfuric acid. To this end, specific volumes of the mineralised zone were isolated hydraulically by drifts and adits, using conventional mining techniques. In order to increase the internal surface area, these so-called blocks were blasted. Sulfuric acid was applied through horizontal boreholes on top of the block, percolated through it, and was collected again in boreholes at its bottom. The U-enriched fluids were then pumped to the surface, where uranium and other heavy metals were removed by adsorption onto ion-exchange resins. Under normal

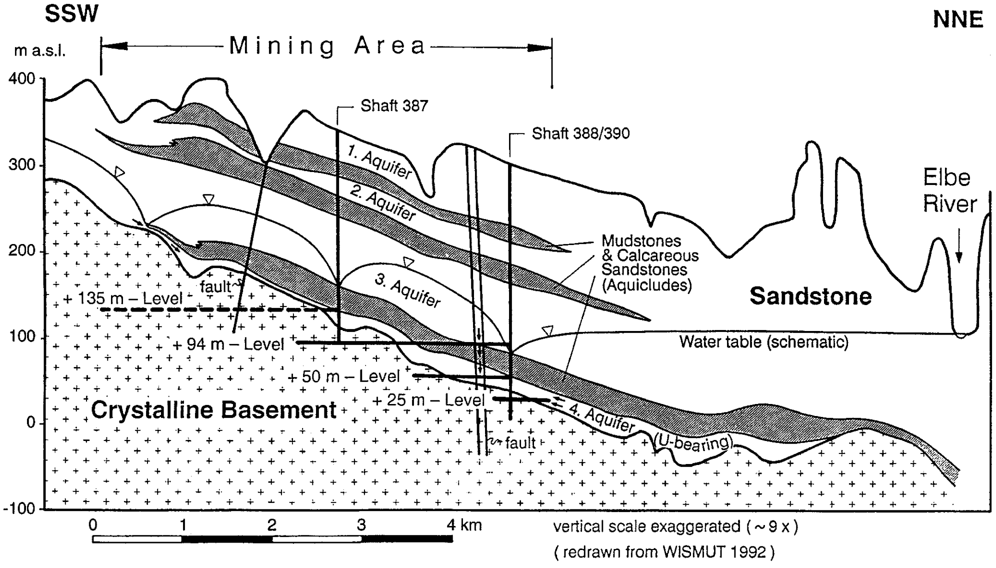

Figure 2 Hydrogeological section through Königstein mine. (After WISMUT 1992; for trace of section, see *Figure 1*)

operational conditions, the leaching fluid circulated constantly in a system of pipelines and open channels. Dilution of the process acid by admixture of groundwater within this semi-closed system and consumption by reactions required periodic topping up with fresh H_2SO_4.

At the time the decision to close down the mine was made, some new blocks had already been prepared for leaching. In these blocks, pyrite (FeS_2) oxidation due to the water-unsaturated conditions had produced sulfuric acid. The dissolution of U minerals and associated sulfides led to mobilisation of significant amounts of U (including daughter isotopes) and heavy metals, which added to the expected contaminant load. In order to study the processes of contaminant release and dispersal connected with the flooding of the mine, a 'flooding experiment' was conducted by WISMUT, but no data from this experiment were available at the time the present study was carried out. The aspects to be studied here included the effects of process acid remaining in the mine and the uptake of contaminants by the percolating groundwater. One scenario under discussion is to remove the process acid plus 'labile' uranium and heavy metals from the mine by forced 'washing,' in a process very similar to the former production process. To be more efficient, this forced washing requires a pressure level in the fourth aquifer above its pre-mining level (WISMUT 1995), which is largely responsible for the threat to the third aquifer.

The objectives of the present study are to delineate the possible and desirable hydrogeochemical scenarios on the basis of interpretations of the present and likely past hydrogeological conditions, and by utilising numerical modeling tools. Owing to the absence of the necessary kinetic data, no attempts are made to give any time-frame for the processes.

Uranium solubility is largely controlled by the prevailing redox and pH conditions, which were thought to be controlled in turn by pyrite availability and oxygen supply in the flooding waters. This study was intended to help answer various questions in the context of evaluation of closure and post-closure environmental risk scenarios for the mine, viz.:

1. Can the release of uranium and other heavy metals during the flooding be quantified, and what effect is acid leaching likely to have on the release?
2. What is the likely quantitative effect on uranium mobilisation in 'new' blocks of oxygen concentrations as great as 2 mg/L in the flooding water? and
3. What effect would the leaking of porewater from blocks already leached into 'new' blocks have?

Database

Numerous analyses are available of water samples collected in the past by WISMUT, but they are of variable degrees of completeness and quality. In order to obtain an independent set of representative samples for comprehensive analyses, about 160 potential down-mine sampling locations were surveyed for the likely origin of their waters and achievable sampling conditions. From these, 29 points were selected for sampling by a certified laboratory (Institut Fresenius – Chemisch-Biologische Laboratorien GmbH, Berlin, Germany). Sampling sought to distinguish between groundwaters proper and mine waters. The following samples are considered to be representative of:

1. Groundwaters from the overlying third aquifer (samples 3, 17, 64, 74, 117, and 121)
2. Groundwaters from the U-bearing fourth aquifer (samples 9, 56, 118, 124, 128, 134, and 149)
3. Groundwaters from the underlying crystalline basement (sample 95).

Nearly all of the 14 groundwater samples came from boreholes. The mine waters sampled were drainage from blocks at different stages of production development:

1. Mine waters from unleached, unsaturated blocks (samples 75, 76, 114, 158, and 159)
2. Mine waters from leached, but now unsaturated blocks (samples 70, 71, 72, and 73)
3. Mine waters from leached and flooded blocks (samples 81, 82, 89, 90, 91, and 103).

A total of 15 mine-water samples was collected, mainly from drainage pipes in sealing dams, but also from boreholes collecting water from unleached blocks and from piezometers (area of the flooding experiment). An overview of the sampling locations is provided in *Figure 3*.

Chemical analysis (including U_{tot}) was performed following the procedures of the German standards (DIN) using emission spectroscopy with inductively coupled plasma (ICP-OES), atomic absorption spectrometry (AAS), photometry, and volumetric or potentiometric methods. Hydroisotop GmbH, Schweitenkirchen, Germany, organised isotopic analyses and determined tritium by liquid scintillation spectrometry and deuterium and oxygen-18 by mass spectrometry. F. Buheitel, Reichertshofen, Germany, was commissioned to measure radionuclide activities by γ-spectrometry and/or delayed coincidence liquid scintillation spectrometry (Buheitel 1993). In order to have as complete a data set as possible available for later studies, the set of parameters determined (in particular with respect to the radionuclides) was more comprehensive than would be required to immediately answer the above questions. A complete list of parameters determined is shown in *Table 1*. The complete set of analytical results is given as electronic supplementary material on http://link.springer.de//link/service/journals/10040. Some problem-specific data are given in *Table 2*. Certain fluids sampled are suspected to have been in contact with steel fittings of the wells. In most cases of interest, however, relatively high flow rates during sampling probably minimised contact times, so that possible effects on Fe concentrations and redox conditions can be neglected. The quality of chemical analyses was monitored by different plausibility tests. Only in a few cases did ionic imbalances exceed 5% of the cation or anion sum, respectively, and such cases were attributed to the presence of other species not analyzed, rather than to analytical imprecision. Oxygen concentrations in samples 117 and 118 were probably affected by contamination during sampling.

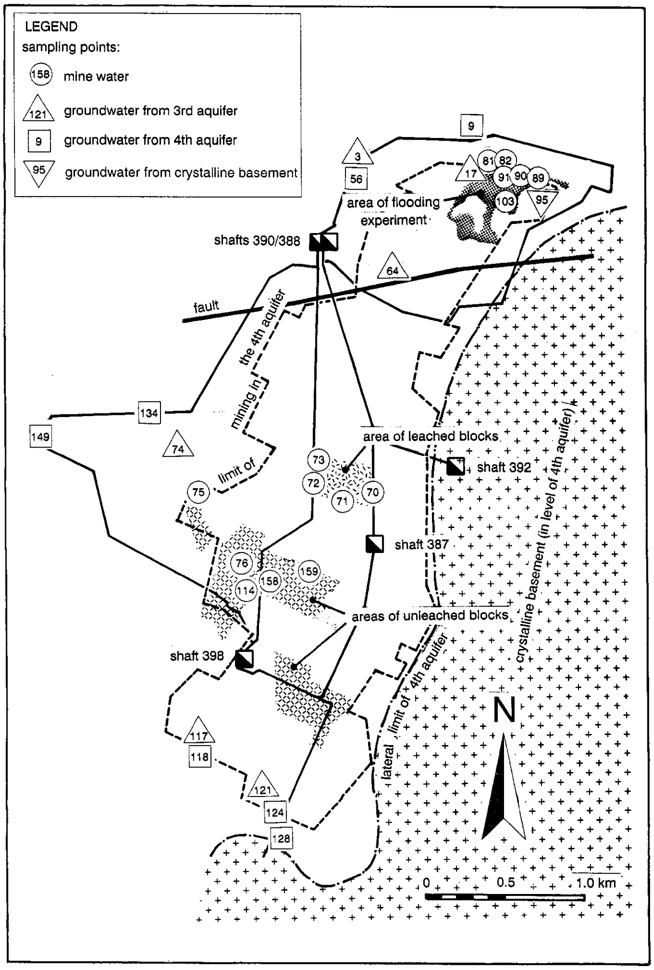

Figure 3 Locations of sampling sites in Königstein mine

Geochemical Modeling – Methodology

With the aim of semi-quantitatively deducing the likely effects of flooding on the mobility of uranium and radium, conventional speciation/solubility calculations and various scenario simulations were performed using the PHREEQE (Parkhurst et al. 1980) code. Contrary to expectations, initial calculations showed that ionic strengths generally were below 0.3 mol/L. Therefore, a model suitable to higher ionic strengths, such as EQ3/6 (Wolery 1992) with the Pitzer option, was not required. No time-dependent or space-related reaction-path simulation could be attempted considering the limited set of data available. In some samples, uranium concentrations were below the detection limit; in order to be able to assess its geochemical behaviour, a small amount of U (0.5 × detection limit = 0.01 mg/L) was added for calculation purposes.

The thermodynamic data used in this study were those from the CHEMVAL thermodynamic database version 5.0 (Chandratillake et al. 1992; Falck et al. 1996), with the addition of data for zinc, mainly taken from the National Bureau of Standards tables (Wagman et al. 1982).

Geochemical Characterisation

The samples were grouped according to their origin and with respect to their mining history:

Table 1 Chemical parameters determined in water samples from the Königstein mine

Group	Parameters
Physico-chemical parameters (measured in field)	Water temperature, electrical conductivity, pH, Eh, oxygen
Main constituents	Ca, Mg, Na, K, NH_4, Fe(+III), Fe(+II), Mn, Al, SO_4, HCO_3, Cl, NO_3, NO_2, HPO_4
Others	SiO_2, CO_2, TOC
Trace elements	Sr, Li, F, B, As
Heavy metals	Cr_{tot}, Co, Ni, Cu, Zn, Cd, Pb
Environmental isotopes	Tritium (^3H), Deuterium (^2H), ^{18}O
Radionuclides	U_{tot}, ^{226}Ra, ^{228}Ra. Additionally, in selected samples: ^{234}U, ^{238}U, ^{230}Th, ^{228}Th, ^{224}Ra, ^{223}Ra, ^{210}Pb, ^{227}Ac

(a) Relatively undisturbed solutions from the aquifers
(b) Solutions from ‘new’ blocks, presumably not affected by acid leaching
(c) Solutions from blocks already leached
(d) Solutions from the zone of experimental flooding.

It was presumed that solutions (a) should be generally representative of the geochemical background. However, in some samples anthropogenic influence was suspected. The groundwaters are weakly mineralised and of the calcium(-sodium)-bicarbonate (-sulfate)-type. The geochemical modeling indicates a slight supersaturation with respect to amorphous (chalcedony) and/or crystalline (quartz, certain clay minerals) silica phases. A pH of 6 ± 0.5 further indicates that these solutions are in near equilibrium with the sandstone matrix of the aquifer. All solutions are undersaturated with respect to calcite (log (IAP/Ksp) = –7.1 to –2.1) and sulfates. The former confirms the observation that calcite as pH-buffer is scarce in the aquifer rocks, while the latter is of interest in the context of co-precipitation of radium with phases such as gypsum.

Most of the groundwaters from the third and fourth aquifer are ‘old’ waters, containing no or only little tritium, and they have only low oxygen concentrations. In the southern part of the mine, the groundwaters are of recent meteoric origin and richer in oxygen (samples 117, 118, 121, 124, and 128). Eh values range from +210 to +520 mV. The dominating processes in the aquifers are probably the oxidation of pyrite and cation exchange. As shown in *Figure 4*, restricted oxygen availability limits pyrite-derived sulfate to a maximum concentration of about 1 mmol(eq)/L. Only at the western perimeter of the fourth aquifer are groundwaters more highly mineralised. High CO_2 concentrations and the dominance of sodium in these groundwaters is interpreted as an admixture of basement-type groundwater (cf. sample 95). Activities of uranium and thorium isotopes are low in natural groundwaters, whereas radium isotopes have the highest values of all water samples measured (sample 149: 104 Bq Ra-226/kg).

The modeling results indicate that in most solutions hexavalent uranium is the stable redox state and that they are generally undersaturated with respect to those uranium minerals reported to be present in the Königstein complex (Nekrassova 1967). Hydroxo-, silicato-, carbonato-, and fluoro-complexes dominate the species distribution in ‘undisturbed’ groundwaters represented by sample 9 of *Figure 5*.

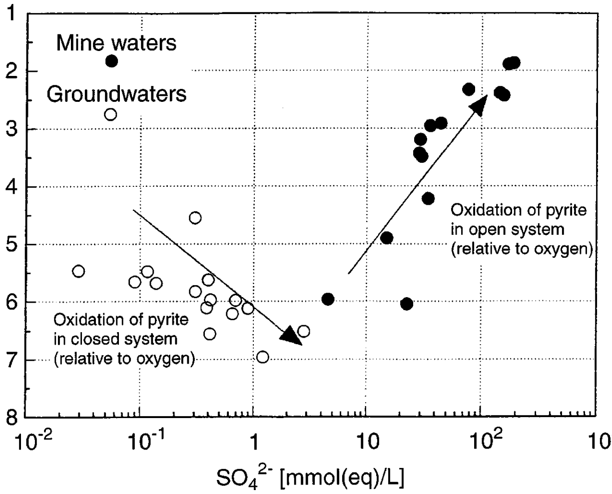

Figure 4 Relation between pH and SO_4. Plot shows relative to oxygen different evolution paths of groundwaters and mine waters due to oxidation of pyrite in closed and open systems. In groundwaters, sulfate concentration is limited by oxygen solubility; in mine waters, by solubility of gypsum

The mine waters (solutions b and c) differ from the groundwaters in a significant way, as is shown by the pH and Eh values and the amount of total dissolved solids given in *Table 2* and as visualised in the column diagram of *Figure 6*. On the basis of stable isotopes and hypotheses on their chemical evolution, the mine waters are considered to be primarily derived from groundwaters in the third and fourth aquifers. The high mineralisation is caused by the oxidation of pyrite in a system open with respect to oxygen, and/or by mixing with leachates from the U-production process. All mine waters show very low to low pH values, ranging from 1.9 to 6.1, and mostly high Eh values, ranging from +130 to +810 mV. Cation exchange on clay minerals affects pH buffering.

Solutions (b) generally have higher Eh values as a result of contact with air under unsaturated conditions, such as in samples 158 and 159. Pyrite oxidation results in high sulfate contents and low pH values. In some

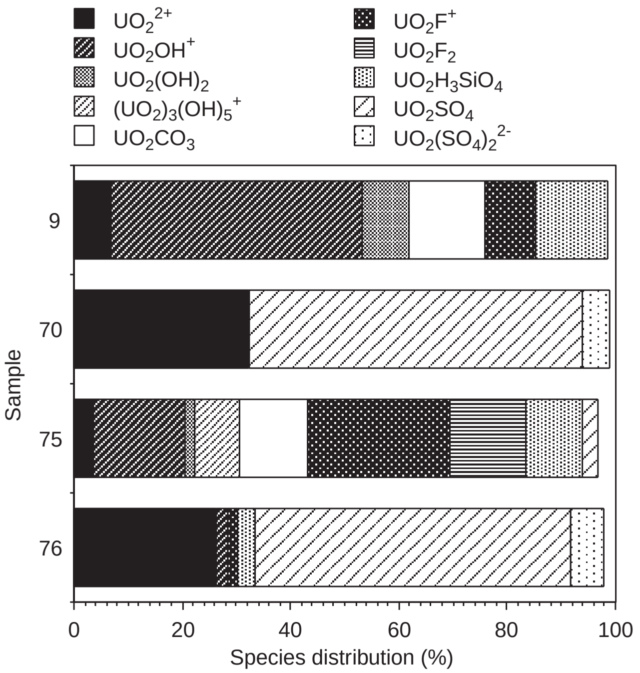

Figure 5 Percentage species distribution in: 'undisturbed' groundwater, pH = 6.09, Eh = 360 mV, $U_{tot} = 0.01$ mg/L (sample 9); leached block, pH = 3.19, Eh = 773 mV, $U_{tot} = 6.1$ mg/L (sample 70); 'new' block without pyrite oxidation, pH = 5.97, Eh = 490 mV, $U_{tot} = 1.65$ mg/L (sample 75); 'new' block affected by pyrite oxidation, pH = 4.22, Eh = 546 mV, $U_{tot} = 68$ mg/L (sample 76). The difference between the total and 100% represents minor species

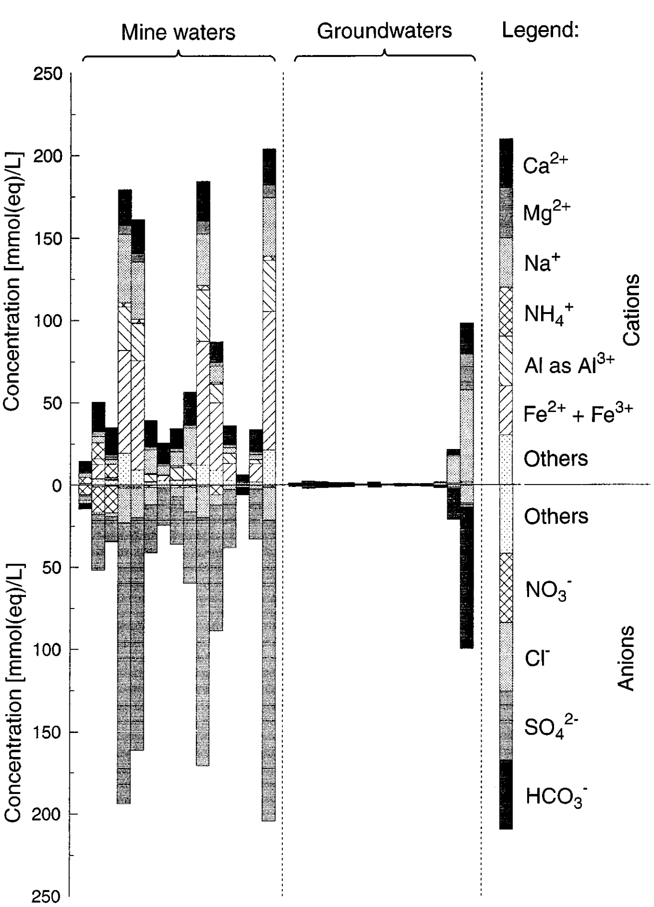

Figure 6 Geochemistry of mine waters and groundwaters from Königstein. Equivalent concentrations of dissolved constituents are shown as columns

cases, the respective blocks may have been additionally contaminated by process acid. Saturation indices around 0 in other samples indicate buffering by clay minerals. Strongly acid mine waters show massively increased concentrations of heavy metals and activities of uranium or thorium isotopes as well. Radium activities, on the other hand, are relatively low, but are not controlled by precipitation of $RaSO_4$, or by co-precipitation with minerals such as gypsum. Unfortunately, barite saturation indices could not be calculated owing to the lack of analytical data for barium. Ferri-hydroxides and -oxyhydroxides may be an important sink for radioelements, including Ra, and heavy metals, either by acting as a sorbens, or by co-precipitation. Ferri-hydroxides do not reach saturation at the relatively low pH values measured in most samples, but solutions usually show a degree of supersaturation with respect to goethite. The potential for goethite precipitation, however, does not show any correlation with measured Ra activities.

Solutions (c) are dominated by the acid-leaching process, during which sulfuric acid concentrations were technically controlled. Relatively low pH, high redox potentials, and high dissolved iron concentrations led to calculational supersaturation with respect to ferri-oxides and hydroxyl-depleted oxyhydroxides, such as goethite. The resulting precipitation, inferred from the depletion of Fe in the Fe-SO_4 plot of *Figure 7* some-

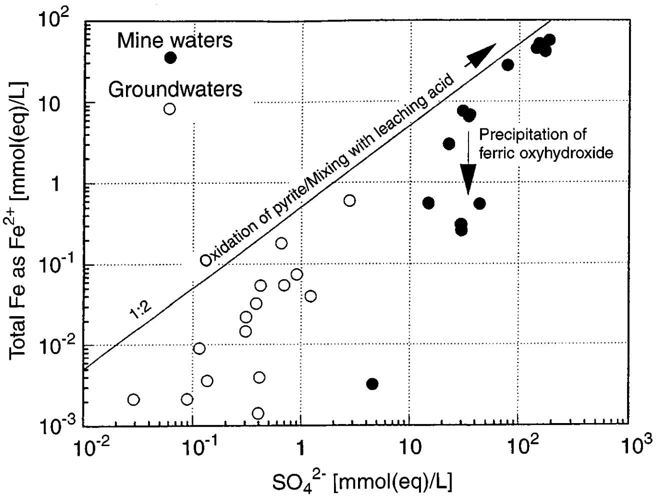

Figure 7 Relation between Fe and SO_4. Most data points are located near the line *2* SO_4 *: 1 Fe*, which shows that iron and sulfate ions have formed by the oxidation of pyrite. Depletion of Fe in several mine waters (mainly from non-leached and unsaturated blocks) is attributed to precipitation of ferric oxyhydroxides

Table 2 Chemistry of mine waters and groundwaters from Königstein mine

Sampling point no.	Water temp. (°C)	pH	Eh (mV)	Oxygen (mg/L)	TDS (mg/L)	Fe$_{tot}$ (mg/L)	SO$_4$ (mg/L)	SiO$_2$ (mg/L)	Cr$_{tot}$ (mg/L)	Zn (mg/L)	Pb (mg/L)	^{3}H (T.U.)	^{18}O (‰ VSMOW)	U$_{tot}$ mg/L	^{230}Th Bq/kg	^{226}Ra Bq/kg
Mine waters from unleached and unsaturated blocks																
75	13.1	5.97	490	0.4	1119	0.08	218	15.2	0.004	9.8	0.13	1.8 ± 1.1	−9.77	1.65	n.a.	8.53 ± 0.68
76	14.4	4.22	546	2.5	3767	179.7	1650	52	0.068	58	1.93	2.7 ± 1.0	−9.59	68	58 ± 5	1.94 ± 0.15
114	11.7	4.90	463	4.4	2658	15.1	709	21	0.11	18.9	0.45	1.4 ± 1.0	−9.47	126	n.a.	5.54 ± 0.39
158	12.0	1.88	747	1.8	12322	1171	8220	166	0.97	132	2.1	6.4 ± 1.0	−9.06	12.3	1333 ± 100	0.520 ± 0.047
159	12.1	2.40	792	8.2	10591	1240	6800	140	1.11	108	0.32	5.3 ± 0.8	−8.98	19.2	n.a.	0.106 ± 0.009
Mine waters from leached but still unsaturated blocks																
70	15.8	3.19	773	7.2	2670	7.07	1420	27	0.048	11.6	0.027	7.2 ± 1.3	−9.28	6.1	n.a.	0.310 ± 0.024
71	15.0	6.06	134	1.3	1782	82	1087	38	0.011	0.063	0.015	4.4 ± 0.9	−9.47	0.30	1.45 ± 0.13	2.97 ± 0.22
72	17.1	3.42	771	7.4	2362	8.48	1395	40	0.068	26	0.040	6.7 ± 1.2	−9.39	24	n.a.	3.16 ± 0.23
73	17.3	2.92	807	3.9	3827	15.32	2090	41	0.072	24	0.010	7.1 ± 1.2	−9.28	18.1	49 ± 6	0.0073 ± 0.0016
Mine waters from leached and flooded blocks																
81	13.6	2.43	661	0.3	11494	1410	7260	151	2.2	168	0.27	7.0 ± 0.9	−8.96	114	n.a.	0.022 ± 0.003
82	13.6	2.33	702	1.6	5928	765.1	3680	82	0.72	87	0.58	7.3 ± 1.4	−9.29	62	n.a.	2.32 ± 0.18
89	13.8	2.95	785	0.3	2487	192.1	1700	49	0.71	26	0.009	8.3 ± 1.4	−9.02	13.6	n.a.	0.407 ± 0.031
90	14.7	6.97	257	1.5	490	1.1	58	10.0	0.004	0.33	0.013	< 1.0	−9.85	0.03	n.a.	1.00 ± 0.07
91	14.4	3.50	477	1.3	2245	214.2	1460	47	0.19	11.5	0.98	8.0 ± 1.3	−9.20	2.0	0.42 ± 0.06	6.00 ± 0.45
103	14.5	1.88	651	1.2	13296	1570	8800	177	1.34	164	1.43	6.9 ± 1.0	−9.01	50	1051 ± 95	2.74 ± 0.24
Groundwaters from third aquifer																
3	12.4	5.84	342	0.2	89	0.62	14.7	7.5	< 0.002	0.022	< 0.002	< 1.5	−8.87	< 0.02	n.a.	0.170 ± 0.013
17	11.4	6.12	306	0.1	167	2.06	43	7.3	< 0.002	0.094	< 0.002	5.3 ± 1.1	−9.35	< 0.02	< 0.0010	0.329 ± 0.025
64	14.1	6.21	207	1.8	143	5.06	31	6.3	< 0.002	0.027	< 0.002	5.9 ± 1.6	−9.82	< 0.02	n.a.	0.169 ± 0.013
74	11.4	6.00	320	1.3	121	1.55	20	7.9	0.051	0.13	0.22	3.5 ± 0.9	−9.52	< 0.02	n.a.	0.100 ± 0.008
117	7.9	6.56	342	9.0	90	0.13	19.5	7.4	< 0.002	0.15	< 0.002	2.1 ± 0.7	−9.28	< 0.02	n.a.	0.147 ± 0.011
121	9.9	5.47	487	6.2	47	0.09	1.4	7.2	< 0.002	0.022	0.014	6.0 ± 1.2	−9.82	< 0.02	< 0.0022	4.65 ± 0.37
Groundwaters from fourth aquifer																
9	12.5	6.09	360	0.4	133	0.95	18.1	7.1	< 0.002	0.27	< 0.002	< 1.0	−9.64	< 0.02	0.0013 ± 0.0008	34.1 ± 2.3
56	13.3	4.56	442	0.5	42	0.42	14.5	7.2	< 0.002	0.16	< 0.002	< 1.5	−9.60	0.24	n.a.	44.0 ± 3.0
118	7.6	5.49	437	10.0	65	0.25	5.5	8.0	< 0.002	0.20	0.030	13.7 ± 1.3	−9.41	< 0.02	n.a.	0.691 ± 0.047
124	10.1	5.66	515	10.4	55	0.07	4.3	7.5	< 0.002	0.072	0.19	4.2 ± 1.1	−9.62	0.07	n.a.	4.82 ± 0.37
128	10.0	5.68	485	7.2	68	0.1	6.5	7.4	0.003	0.047	0.031	5.7 ± 1.2	−9.90	0.02	0.0011 ± 0.0007	6.34 ± 0.50
134	12.7	5.63	469	4.7	146	0.05	19	8.0	0.004	0.51	0.15	< 2.0	−9.63	0.11	n.a.	5.53 ± 0.38
149	13.2	5.99	307	1.2	1736	1.51	33	7.8	< 0.002	< 0.01	0.013	< 1.0	−10.02	< 0.02	n.a.	104 ± 7
Groundwaters from crystalline basement																
95	13.2	6.53	212	1.0	7785	16.63	133	37	< 0.002	0.018	0.025	< 1.5	−10.92	< 0.02	n.a.	3.03 ± 0.23

n.a., not analyzed

times appears to be accompanied by (co-)precipitation of dissolved chromium and lead. Whereas uranium concentrations are low in leached blocks (*Figure 5*, sample 70) and in unaffected 'new' blocks (*Figure 5*, sample 75), sulfate as a product of pyrite oxidation markedly increases the uranium solubility in 'new' blocks (*Figure 5*, sample 76).

Solutions (d) show clear signs of pyrite oxidation: low pH values and high sulfate concentrations. Eh values are lower than in solutions (c), indicating a limited oxygen availability. However, Eh values are still higher than would be expected from calculations that assume a system completely closed to the ambient air.

Geochemical Modeling Results

Conceptualisation of the Problem

The level of detail at which the conceptualisation could be performed was severely limited by the data available for this practical problem. At the time of the investigations, few data suitable to describe the source term were available. Colloidal species significantly influence uranium solubility in many environments, but for want of relevant field data this aspect had to be ignored. However, the potential for colloid formation is indicated by the potential for formation of ferri-oxyhydroxides and clay minerals.

The first modeling phase consists of a static simulation of the solutions, in order to evaluate their equilibrium state with respect to selected solid phases (see above). In a second phase, various scenarios were modeled, focusing on the effects of pyrite oxidation:

1. Equilibration of the fluids with respect to pyrite
2. Addition of oxygen (0.1–1.0–10 mg/L) while maintaining equilibrium with pyrite
3. Assumption of a sink for Fe-ions/redox buffer, i.e., additional equilibration with goethite
4. As in 2, but pH buffering by rock-matrix, represented through equilibration with gibbsite.

Potential for Pyrite Oxidation

In the absence of a detailed knowledge of pyrite distribution, all solutions were equilibrated with pyrite according to scenario (1). The equilibrations were carried out in a system closed to the ambient air. Solutions (c) did not change considerably, with the exception that a slight lowering of the Eh results in the pentavalent state becoming dominant for U. As shown in *Figure 8*, equilibration with pyrite results in significant lowering of pH and Eh of all other solutions. Both low pH and low Eh lead to uraninite and coffinite becoming supersaturated as a result of reduction of uranium to its tetravalent state.

Pyrite Oxidation in the Semi-Open System

It is numerically (and chemically) impossible to calculate an equilibrium state with both oxygen and pyrite having unlimited availability, but the actual amount of pyrite available – or accessible – is not known. The potential for pyrite dissolution and ensuing geochemical consequences were further elucidated by adding varying quantities of oxygen to selected solutions. These simulations are assumed to be representative of a scenario where oxygen is limited by its physical solubility in the circulating fluids, i.e., in a mine saturated with fluids.

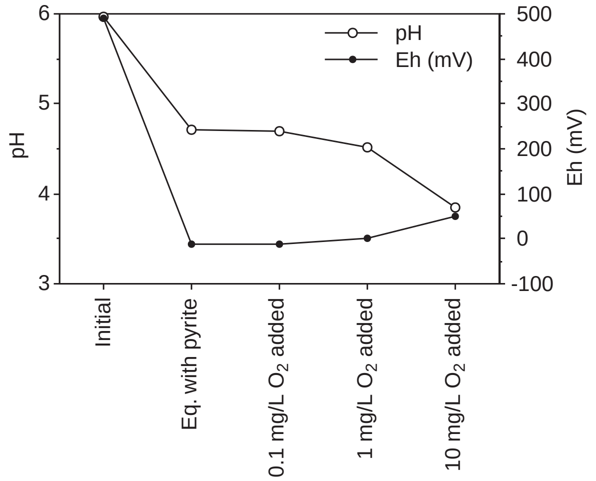

Figure 8 pH and Eh as function of oxygen added to a solution (b); equilibrium with pyrite is maintained

Assumption of a Sink for Fe Ions

Goethite is present in many parts of the rock matrix (Nekrassova 1967), and most groundwaters show a slight supersaturation with respect to it. Goethite, therefore, might act as a sink for ferric iron, promoting further dissolution of pyrite, but calculations show that, without effective buffering of the acid produced by pyrite oxidation, the solubility product of goethite cannot be reached. As shown in *Figure 9*, buffering by reactions that consume acid, such as dissolution of clay minerals (e.g., gibbsite) from the rock matrix, would raise pH to levels where goethite precipitation is possible. Uranium solubilities are reduced only slightly with increasing pH, but co-precipitation with goethite could be an important uranium sink.

Modeling of Potential Uranium Release

The data available and time constraints did not permit construction of a coupled chemical-transport model for any realistic geometry. Instead, the potential uranium release was assessed using a 'black-box' model. Two scenarios were investigated:

1. Intrusion of oxygen containing solutions into a 'new' block with an appropriate water composition, maintaining equilibrium with pyrite and uraninite

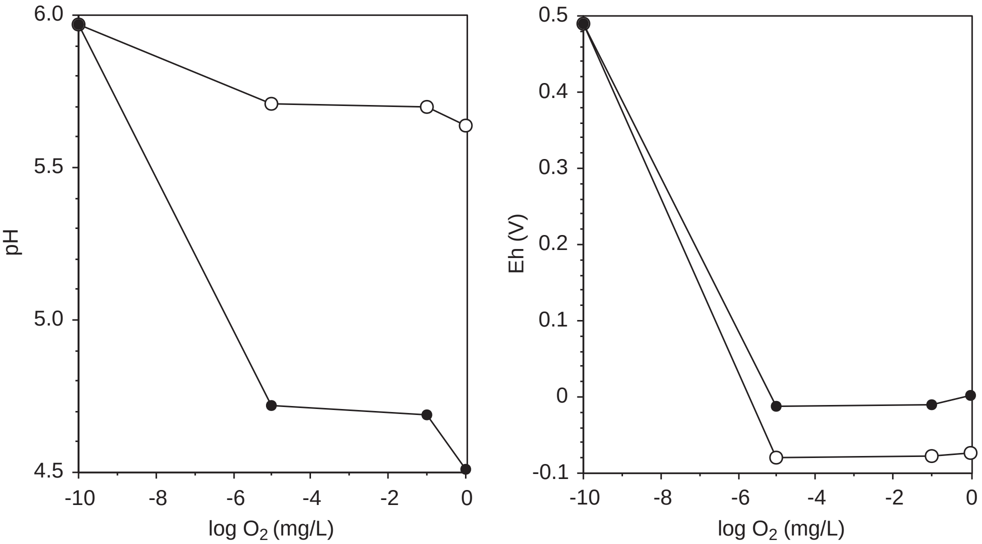

Figure 9 *Left* pH as function of adding oxygen and buffering minerals to a solution (b); *right* Eh as function of adding oxygen and buffering minerals to a solution (b). *Open circles* equilibration with pyrite and gibbsite; *dots* equilibration with pyrite only

2. Transfer of solutions from leached blocks into 'new' blocks, maintaining equilibrium with uraninite only.

Calculations for scenario 1 were performed in four steps:

I. Calculate species distribution for a given water sample (solution 1).
II. Add oxygen to solution 1 to give a concentration of 1 mg/L and recalculate species distribution (solution 2).
III. Mix solutions 1 and 2 in a 1:1 ratio and recalculate species distribution while maintaining equilibrium with pyrite and uraninite (new solution 1).
IV. Repeat III, mixing new solution 1 with solution 2, etc.

Owing to the presence of pyrite and complete consumption of oxygen, Eh and pH remain low and uranium solubility is controlled by uraninite, keeping it at a level of 10^{-7} mol/L. Modification of this scenario by performing equilibration with uraninite only, that is, pyrite dissolution and uraninite dissolution/precipitation are separated in space, yields similar results as shown in *Figure 10* (left); but in the absence of pyrite as a redox buffer, solubilities increase with increasing mixing ratios (*Figure 10*, right).

Solutions dominated by process acids transgressing from leached blocks into 'new' blocks (scenario 2) may lead to pyrite dissolution even at low oxygen concentrations. The presence of sulfate increases the solubility of iron by formation of sulfato complexes, thus promoting pyrite dissolution. This scenario was modeled by 'titrating' a solution from a leached block into a solution from a 'new' block, while monitoring pH, Eh, as shown in *Figure 11* (left) and the uraninite-limited uranium solubility (*Figure 11*, right). With increasing mixing ratios, pH declines to the level of solutions from the leached block. Eh has a sharp decline initially, and then rises again somewhat, but it always remains positive. Uranium solubilities steadily increase as pH decreases.

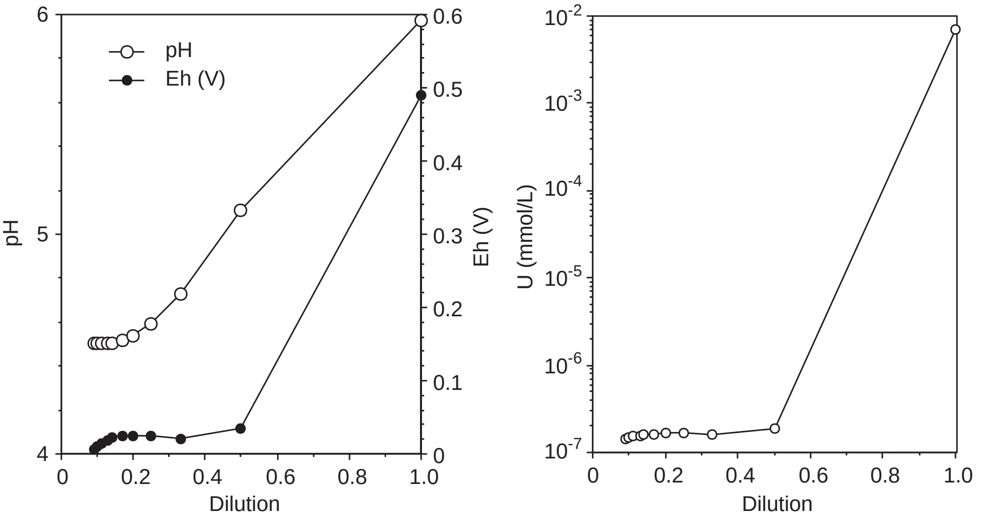

Figure 10 *Left* pH and Eh as (a) function of adding oxygen to solution (b); *right* uranium solubility as function of adding oxygen to a solution (b) and limited by uraninite only. Pyrite oxidation and equilibration with uraninite are assumed to occur spatially separated

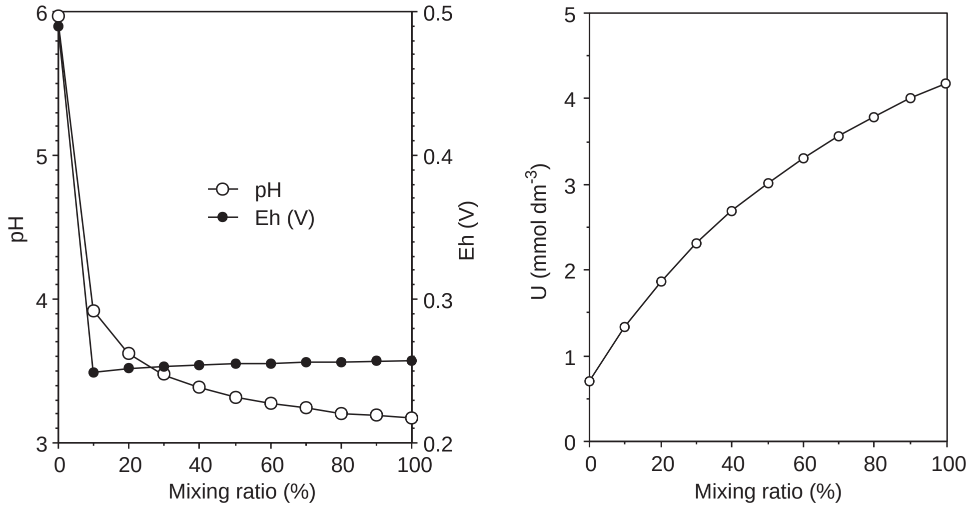

Figure 11 *Left* pH and Eh as function of adding solution (c) to a solution (b); *right* uranium solubility as function of adding solution (c) to a solution (b) and limited by uraninite

Conclusions

Based on the above considerations and geochemical modeling exercises, it is concluded that controlled, rapid flooding (if only of parts of the mine) would be desirable in order to create geochemical boundary conditions that would allow suppression of pyrite oxidation to a level determined by the availability of dissolved oxygen in the flooding water. Thus, reducing and mildly acidic conditions should be created, whereby limitation of uranium solubility by tetravalent phases would be promoted. Water-unsaturated conditions would increase oxygen availability and enhance U-solubility by formation of hexavalent aqueous species and sulfato-complexes. In the absence of (reliable) kinetic data and a sufficiently detailed hydrogeological model, it is unknown whether such conditions could be achieved in practice. Radium mobility is unlikely to be controlled by co-precipitation with alkaline-earth sulfates, but may be controlled by sorption onto ferric oxy-hydroxides, depending on prevalent pH and redox conditions.

Acknowledgments This work was carried out in 1994 under contract No. 44–4691.60 to the Sächsische Staatministerium für Umwelt und Landesentwicklung, Dresden, Germany. The results of this work may be used in the formulation of Government policy, but at this stage do not necessarily represent Government policy. The authors thank Dr. J. Luo (then also with WS Atkins International, Berlin) for his help in executing the geochemical modeling runs. The authors are also grateful to WISMUT GmbH for supporting the field work by technical and logistical assistance, and for helpful discussions.

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Sampling	description of locality	type of water	origin	material(s) of fittings	date of
point					sampling
Nr.					
75	Level 94, VF 49, drain-pipe in pressure-dam, drainage "Block 2855"	mine water	unleached and unsaturated block	steel	18/01/94
76	Level 94, F. Str. 94-8, drain-pipe in pressure-dam, drainage "SW-Flanke"	mine water	unleached and unsaturated block	steel / rubber	18/01/94
114	Level 94, F. Str. 94-9W a. Qu. 94-1, Üb. 56/27, recovery-borehole i. floor o. "Block 4435"	mine water	unleached and unsaturated block	CrNi-steel / polyethylene	18/01/94
158	Level 94, F. Str. 94-9E, 43 m a. Qu. 94-1, recovery-borehole i. floor o. "Block 4425/35"	mine water	unleached and unsaturated block	polyethylene	18/01/94
159	Level 94, F. Str. 94-9E, Üb. 46/15, open flange i. recoil-pipe, drainge of "Block 4415"	mine water	unleached and unsaturated block	CrNi-steel / polyethylene	18/01/94
70	Level 94, F. Str. 94-5W a. Qu. 94-3, drain-pipe in dam	mine water	leached, but still unsaturated block	polyvinylchloride	17/01/94
71	Level 94, Qu. 94-2N a. F.Str. 94-6, drain-pipe in dam	mine water	leached, but still unsaturated block	polyvinylchloride / steel	17/01/94
72	Level 94, F. Str. 94-5E a. Qu. 94-1, drain-pipe in dam	mine water	leached, but still unsaturated block	polyethylene	17/01/94
73	Level 94, F. Str. 94-4E a. Qu. 94-1, drain-pipe in dam	mine water	leached, but still unsaturated block	polyethylene	17/01/94
81	Level 25, VF 10, draine-pipe in pressure-dam TFDD 1.3	mine water	leached and flooded block	CrNi-steel / steel / polyethylene	14/01/94
82	Level 25, Drain.Str. 1, 50 m west of pressure-dam, valve in recoil-pipe (RL2)	mine water	leached and flooded block	CrNi-steel / polyethylene	14/01/94
89	Level 25, VF 32, 10 m a VS 85, drain-pipe in pressure-dam TFDD 1.10	mine water	leached and flooded block	CrNi-steel / steel / polyethylene	14/01/94
90	Level 25, VF 26S, 5 m a. VS 85, piezometer K 1/1	mine water	leached and flooded block	polyethylene	14/01/94
91	Level 25, VF 26S, 5 m a. VS 85, piezometer K 1/2	mine water	leached and flooded block	polyethylene	14/01/94
103	Level 25, VF 26N, 98 m a. VS 71, I. EH, piezometer K 30/2	mine water	leached and flooded block	polyethylene	14/01/94
3	Level 25, Str. 71, 422 m a. F.Str. 6, drainage-borehole 23774 (vertical to the overburden)	groundwater	3rd Aquifer	CrNi-steel / steel / rubber	13/01/94
17	Level 25, Qu. 25-2, pumping station, pipe fr. drainage-borehole parallel t. ventil.-borehole 6	groundwater	3rd Aquifer	steel	13/01/94
64	Level 94, Str. 73-1, 180 m a. R.Str. 4, anchor-borehole	groundwater	3rd Aquifer	steel / rubber	17/01/94
74	Level 94, F.Str. 94-7, drainage-borehole parallel to ventilation borehole 4	groundwater	3rd Aquifer	steel / rubber	17/01/94
117	Level 135, crossing VF 17 / VS 108E, drainage-borehole	groundwater	3rd Aquifer	polyethylene	19/01/94
121	Level 135, crossing VF 6 / VS 106, tube from drainage-borehole in VF 6 (behind dam)	groundwater	3rd Aquifer	polyethylene	19/01/94
9	Level 25, VS 93E, 0 m a. VF 0, tube from borehole B10 (parallel to VS 93E)	groundwater	4th Aquifer	polyethylene	13/01/94
56	Level 25, Str. 71, 430 m a. F.Str. 6, NW-directed drainage-borehole	groundwater	4th Aquifer	polyethylene	13/01/94
118	Level 135, crossing VF 17 / VS 108E, VF17, anchor-borehole	groundwater	4th Aquifer	steel	19/01/94
124	Level 135, VS 110 a. VF 14, drain-pipe in dam	groundwater	4th Aquifer	polyethylene / rubber	19/01/94
128	Level 135, crossing VF 18S / VS 116, VF 18S, anchor borehole	groundwater	4th Aquifer	steel	19/01/94
134	Level 25, Zug. PirnaS, 1390 m a. Zug. Pirna, borehole	groundwater	4th Aquifer	polyethylene	13/01/94
149	Level 25, Qu. Pi. 25-2, FR 24/87, borehole	groundwater	4th Aquifer	polyethylene	13/01/94
95	Level 25, Qu. 25-3, 10 m north of junction to F.Str. 5, borehole ("Mineralquelle")	groundwater	crystalline basement	steel	18/01/94

Sampling	water-	electrical	pH	Eh	oxygen	TDS	TDI	Ionic	Ca	Mg	Na	K	NH4	Fe(+III)	Fe(+II)	Mn	Al	SO4	HCO3	Cl	NO3
point	temp.	onductivity						imbalance													
Nr.	(°C)	(µS/cm)		(mV)	mg/L	mg/L	mmol(eq)/L	%	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
75	13,1	1571	5,97	490	0,4	1119	29,0	-2,3	119	13,5	60	14,9	68,7	<0,02	0,08	0,60	0,30	218	209	29	354
76	14,4	5390	4,22	546	2,5	3767	102,3	-3,2	360	35	92	34	175	130	49,7	3,2	30	1650	<5	39	957
114	11,7	5870	4,90	463	4,4	2658	69,4	0,9	327	39	65	36	145	2,1	13	3,3	9,4	709	35	84	1010
158	12,0	13100*	1,88	747	1,8	12322	373,3	-8,0	432	66	960	3,3	45,9	1160	10,6	31	235	8220	<5	745	52
159	12,1	8450*	2,40	792	8,2	10591	322,5	-0,2	415	60	808	2,0	39,5	1234	6,29	29	203	6800	<5	640	44
70	15,8	3500*	3,19	773	7,2	2670	80,4	-6,1	326	18	330	15,4	11,2	5,1	1,97	3,8	38	1420	<5	370	74
71	15,0	2300	6,06	134	1,3	1782	49,9	2,4	251	13,1	129	94	3,0	20	62	2,4	0,50	1087	21	57	0,5
72	17,1	2775*	3,42	771	7,4	2362	70,3	-5,7	245	22	196	28	18,8	6,5	1,98	7,9	68	1395	<5	195	71
73	17,3	4940	2,92	807	3,9	3827	116,4	-5,8	402	23	493	8,2	19,6	13,6	1,72	6,2	77	2090	<5	530	63
81	13,6	10000*	2,43	661	0,3	11494	355,4	7,4	482	94	720	2,6	48,5	1375	35,1	33	282	7260	<5	667	3,7
82	13,6	8060	2,33	702	1,6	5928	176,0	-2,5	251	28	231	3,5	17,0	758	7,1	11,0	101	3680	<5	221	353
89	13,8	5180	2,95	785	0,3	2487	74,1	-6,2	230	24	75	1,4	6,2	190	2,07	9,1	53	1700	<5	89	<0,5
90	14,7	569	6,97	257	1,5	490	12,5	0,2	83	9,7	24	5,2	0,41	<0,02	1,1	0,30	0,12	58	288	7,0	<0,5
91	14,4	2470	3,50	477	1,3	2245	66,5	2,0	271	23	66	17,8	5,3	198	16,2	8,4	20	1460	<5	76	0,63
103	14,5	14200*	1,88	651	1,2	13296	408,8	-0,4	440	93	820	7,8	45,3	1568	2,14	32	278	8800	<5	706	51
3	12,4	121	5,84	342	0,2	89	2,1	-2,0	16,0	1,3	2,4	1,0	0,02	<0,02	0,62	0,018	<0,005	14,7	40	4,0	<0,5
17	11,4	234	6,12	306	0,1	167	4,4	-4,8	32	2,8	4,7	1,3	0,03	<0,02	2,06	0,11	0,006	43	60	13	<0,5
64	14,1	198	6,21	207	1,8	143	3,7	-1,2	25	3,0	2,0	1,3	<0,02	0,88	4,18	0,24	0,005	31	62	6,0	<0,5
74	11,4	164	6,00	320	1,3	121	3,1	0,1	22	2,1	3,6	1,5	0,05	<0,02	1,55	0,041	0,01	20	45	9,0	7,5
117	7,9	141	6,56	342	9,0	90	2,4	7,8	18,0	1,8	4,0	1,2	0,06	<0,02	0,13	<0,005	0,007	19,5	20	12	5,8
121	9,9	76	5,47	487	6,2	47	1,1	-1,2	5,9	1,0	3,6	0,92	<0,02	<0,02	0,09	<0,005	0,005	1,4	12	9,0	5,4
9	12,5	179	6,09	360	0,4	133	3,3	3,7	22	2,7	5,7	1,4	0,03	<0,02	0,95	0,80	<0,005	18,1	70	3,0	<0,5
56	13,3	62	4,56	442	0,5	42	1,0	-1,8	4,4	0,99	2,8	0,82	0,03	<0,02	0,42	0,013	0,033	14,5	7,0	3,0	<0,5
118	7,6	95	5,49	437	10,0	65	1,6	-3,4	7,5	1,4	4,5	0,89	1,0	0,02	0,23	<0,005	<0,005	5,5	14	10	11
124	10,1	78	5,66	515	10,4	55	1,3	-8,4	6,6	1,1	3,9	1,0	<0,02	<0,02	0,07	<0,005	0,012	4,3	12	9,0	8,4
128	10,0	96	5,68	485	7,2	68	1,7	-2,6	9,9	1,8	3,4	1,1	0,02	0,03	0,07	<0,005	0,008	6,5	17	9,0	11
134	12,7	203	5,63	469	4,7	146	3,6	-1,4	10,2	2,2	23	2,5	0,06	<0,02	0,05	0,11	0,007	19	65	10	4,5
149	13,2	1883	5,99	307	1,2	1736	42,6	1,3	71	8,0	377	24	<0,02	0,37	1,140	0,86	0,061	33	1160	48	<0,5
95	13,2	7090*	6,53	212	1,0	7785	198,1	-1,7	373	268	1280	33	<0,02	12,2	4,43	0,12	<0,005	133	5250	385	0,9

Sampling	NO2	HPO4	SiO2	CO2	TOC	Sr	Li	F	B	As	Cr	Co	Ni	Cu	Zn	Cd	Pb	H-3	H-2	O-18
point											total									
Nr.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	TU	/oo VSMOV	/oo VSMOW
75	0,06	<0,05	15,2	266	0,6	0,43	0,24	2,8	0,04	0,0024	0,004	0,26	0,78	0,020	9,8	0,033	0,13	1.8±1.1	-66,3	-9,77
76	0,25	<0,05	52	<20	0,6	0,9	0,55	21	0,31	0,0034	0,068	1,21	2,2	0,20	58	0,36	1,93	2.7±1.0	-66,2	-9,59
114	0,10	<0,05	21	250	2,2	0,94	0,47	10,8	0,12	0,0084	0,11	0,49	0,88	0,24	18,9	0,13	0,45	1.4±1.0	-66,8	-9,47
158	<0,02	9,5	166	<20	6,2	0,73	0,31	18,4	1,27	1,84	0,97	1,77	3,2	3,9	132	1,40	2,1	6.4±1.0	-64,8	-9,06
159	<0,02	5,2	140	<20	5,9	0,84	0,29	18,6	1,31	1,41	1,11	1,51	2,9	3,1	108	1,05	0,32	5.3±0.8	-66,1	-8,98
70	0,06	<0,05	27	325	3,8	0,67	0,17	4,2	0,14	0,0068	0,048	0,46	0,53	0,63	11,6	0,11	0,027	7.2±1.3	-67,8	-9,28
71	<0,02	0,12	38	317	6,7	0,88	0,19	1,4	0,24	0,015	0,011	0,024	0,020	0,006	0,063	0,0020	0,015	4.4±0.9	-66,9	-9,47
72	<0,02	<0,05	40	<20	3,0	0,59	0,31	8,2	0,09	0,0016	0,068	0,90	0,99	0,60	26	0,21	0,040	6.7±1.2	-67,8	-9,39
73	<0,02	<0,05	41	<20	0,6	0,63	0,28	7,6	0,11	0,0054	0,072	0,74	0,96	0,46	24	0,21	0,010	7.1±1.2	-66,8	-9,28
81	<0,02	8,9	151	<20	17,5	1,83	0,47	18,0	1,5	1,61	2,2	4,1	9,1	3,4	168	1,42	0,27	7.0±0.9	-65,1	-8,96
82	<0,02	5,40	82	<20	5,3	0,85	0,21	8,4	0,81	2,1	0,72	2,9	6,4	1,43	87	0,51	0,58	7.3±1.4	-67,0	-9,29
89	<0,02	0,50	49	<20	0,5	0,65	0,11	5,3	0,24	0,13	0,71	1,14	2,5	1,3	26	0,18	0,009	8.3±1.4	-63,4	-9,02
90	<0,02	<0,05	10,0	72	1,0	0,15	0,11	1,9	0,05	0,094	0,004	0,13	0,078	<0,005	0,33	0,0009	0,013	<1,0	-67,1	-9,85
91	<0,02	4,1	47	<20	9,0	0,79	0,10	5,9	0,39	2,4	0,19	0,73	1,68	<0,005	11,5	0,076	0,98	8.0±1.3	-64,3	-9,20
103	<0,02	12,0	177	<20	4,5	1,53	0,46	13,5	1,63	3,7	1,34	4,4	10,9	3,9	164	1,53	1,43	6.9±1.0	-66,5	-9,01
3	<0,02	<0,05	7,5	65	0,3	0,028	<0,05	0,18	<0,03	0,0010	<0,002	<0,005	<0,002	<0,005	0,022	<0,0005	<0,002	<1,5	-65,8	-8,87
17	<0,02	<0,05	7,3	103	0,6	0,048	<0,05	0,22	<0,03	0,0014	<0,002	0,006	0,009	<0,005	0,094	<0,0005	<0,002	5.3±1.1	-67,1	-9,35
64	<0,02	<0,05	6,3	36	3,5	0,041	<0,05	0,27	<0,03	<0,001	<0,002	<0,005	<0,002	<0,005	0,027	<0,0005	<0,002	5.9±1.6	-69,2	-9,82
74	<0,02	0,12	7,9	48	0,8	0,036	<0,05	0,18	<0,03	0,0084	0,051	<0,005	0,063	0,058	0,13	0,021	0,22	3.5±0.9	-67,6	-9,52
117	<0,02	<0,05	7,4	40	0,7	0,038	<0,05	0,10	<0,03	<0,001	<0,002	<0,005	0,010	<0,005	0,15	0,0005	<0,002	2.1±0.7	-62,7	-9,28
121	<0,02	<0,05	7,2	31	0,6	0,011	<0,05	0,10	<0,03	<0,001	<0,002	<0,005	<0,002	<0,005	0,022	0,0006	0,014	6.0±1.2	-67,5	-9,82
9	<0,02	<0,05	7,1	120	0,5	0,074	0,05	0,32	0,04	0,0036	<0,002	<0,005	0,002	<0,005	0,27	<0,0005	<0,002	<1,0	-66,9	-9,64
56	<0,02	<0,05	7,2	57	0,4	0,008	<0,05	0,15	<0,03	<0,001	<0,002	0,011	0,009	<0,005	0,16	<0,0005	<0,002	<1,5	-68,5	-9,60
118	<0,02	<0,05	8,0	33	5,5	0,016	<0,05	0,13	<0,03	0,0010	<0,002	<0,005	<0,002	<0,005	0,20	<0,0005	0,030	13.7±1.3	-68,5	-9,41
124	<0,02	<0,05	7,5	<20	0,6	0,012	<0,05	0,11	<0,03	<0,001	<0,002	<0,005	0,004	0,006	0,072	0,0010	0,19	4.2±1.1	-66,7	-9,62
128	<0,02	<0,05	7,4	<20	0,5	0,017	<0,05	0,10	<0,03	<0,001	0,003	<0,005	<0,002	<0,005	0,047	0,0005	0,031	5.7±1.2	-68,1	-9,90
134	<0,02	<0,05	8,0	154	0,5	0,025	0,07	0,23	0,03	0,015	0,004	0,045	0,074	0,059	0,51	0,0027	0,15	<2,0	-68,9	-9,63
149	<0,02	<0,05	7,8	1510	0,3	0,24	0,94	2,5	0,18	0,10	<0,002	<0,005	<0,002	<0,005	<0,01	0,0006	0,013	<1,0	-68,0	-10,02
95	<0,02	<0,05	37	2000	0,4	1,0	1,62	3,9	1,11	0,28	<0,002	<0,005	<0,002	<0,005	0,018	0,0030	0,025	<1,5	-70,7	-10,92

Sampling	U	U-234	U-238	Th-230	Th-228	Ra-226	Ra-228	Ra-224	Ra-224	Ra-223	Pb-210	Ac-227	Ac-227
point	total							not corrected	corrected			not corrected	corrected
Nr.	mg/L	Bq/kg	Bq/kg	Bq/kg	Bq/k	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg
75	1,65					8.53±0.68	1.39±0.20						
76	68	1012±60	880±52	58±5	5.0±0.6	1.94±0.15	1.61±0.15	88.7±9.0	85.5±9.5	*	15±6	12.7±1.2	12.2±1.1
114	126					5.54±0.39	1.70±0.22						
158	12,3	158±11	158±11	1333±100	11.6±1.4	0.520±0.047	0.120±0.024	7.54±0.91	<1,9	*	7±3	17.9±1.7	17.1±1.5
159	19,2					0.106±0.009	0.022±0.005						
70	6,1					0.310±0.024	0.041±0.009						
71	0,30	3.71±0.34	3.25±0.30	1.45±0.13	<0,04	2.97±0.22	0.280±0.048	1.07±0.08	1,03	1.4±0.2	<2	0.055±0.007	0.055±0.007
72	24					3.16±0.23	0.41±0.08						
73	18,1	223±17	214±16	49±6	1.0±0.2	0.0073±0.0016	0.0020±0.0015	0.535±0.045	<0,1	*	3±3	2.92±0.26	2.87±0.25
81	114					0.022±0.003	0.021±0.005						
82	62					2.32±0.18	0.04±0.03						
89	13,6					0.407±0.031	0.008±0.008						
90	0,03					1.00±0.07	0.13±0.05						
91	2,0	21.8±1.7	22.9±1.8	0.42±0.06	<0,03	6.00±0.45	<0,05	0.365±0.62	0,35	*	216±75	18.2±1.7	17.6±1.6
103	50	657±49	670±50	1051±95	3.0±0.6	2.74±0.24	0.136±0.026	2.77±0.35	0.8±0.8	*	133±45	119±11	115±10
3	<0,02					0.170±0.013	0.025±0.007						
17	<0,02	0.16±0.03	0.17±0.03	<0,0010	<0,03	0.329±0.025	0.034±0.009	0.037±0.004	0,013	0.139±0.011	<1	0.0029±0.0008	0.0027±0.0008
64	<0,02					0.169±0.013	0.017±0.006						
74	<0,02					0.100±0.008	0.023±0.005						
117	<0,02					0.147±0.011	0.023±0.005						
121	<0,02	0.082±0.013	0.097±0.015	<0,0022	<0,03	4.65±0.37	0.11±0.03	0.096±0.024	0,055	0.63±0.11	<2	0.0036±0.0009	0.0034±0.0009
9	<0,02	0.27±0.06	0.14±0.03	0.0013±0.0008	<0,03	34.1±2.3	0.12±0.04	0.14±0.12	0,12	2.8±0.4	<1	0.0042±0.0012	0.0040±0.0011
56	0,24					44.0±3.0	0.23±0.08						
118	<0,02					0.691±0.047	0.36±0.04						
124	0,07					4.82±0.37	0.21±0.06						
128	0,02	0.18±0.03	0.21±0.03	0.0011±0.0007	<0,04	6.34±0.50	0.075±0.026	0.070±0.020	0,020	0.35±0.06	<2	0.0050±0.0014	0.0047±0.0013
134	0,11					5.53±0.38	1.09±0.15						
149	<0,02					104±7	1.20±0.18						
95	<0,02					3.03±0.23	3.7±0.4						