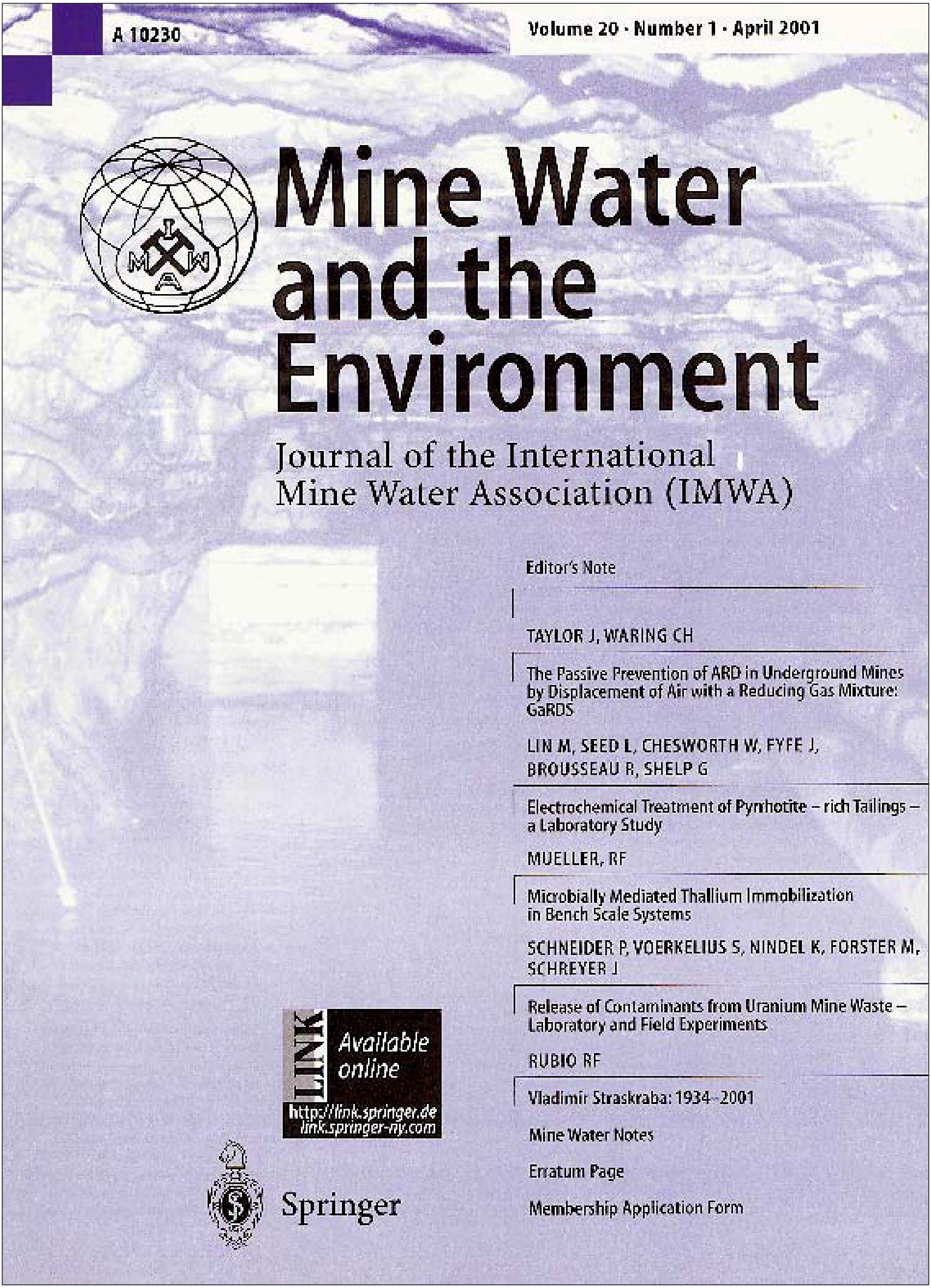
A 10230

Volume 20 · Number 1 · April 2001

Mine Water and the Environment

Journal of the International Mine Water Association (IMWA)

Springer



Mine Water and the Environment (2001) 20: 30–38 © IMWA Springer-Verlag 2001 ***Technical Article***

Release of Contaminants from Uranium Mine Waste – Laboratory and Field Experiments

P. Schneider[1], S. Voerkelius[1], K. Nindel[2], M. Forster[1], J. Schreyer[2];

[1] Hydroisotop-Piewak GmbH, Oberfrohnaer Strasse 84, D-09117 Chemnitz, Germany
e-mail: Hydroisotop-Piewak@t-online.de
[2] Wismut GmbH, Jagdschänkenstrasse 29, D - 09117 Chemnitz, Germany; e-mail: k.nindel@wismut.de

Abstract. The Königstein Uranium Mine was closed in 1990, ending uranium production in the former GDR. As a result of the mining operation, a dump of about $4x10^6$ m^3 was left at Schüsselgrund valley near Königstein. As part of the reclamation of the mine and the dump, abandoned equipment, radioactive soil, and building wastes will have to be disposed of. The aim of this investigation was to define the characteristics of the abandoned materials and mine wastes in order to identify a suitable remediation approach for these materials. It was important to evaluate their long-term behaviour in order to determine if it would be safe to dispose of the abandoned materials in the Schüsselgrund mine dump before closing and covering it. After in-situ remediation of the dump, groundwater will become the most important pathway for the migration of radioactive and toxic contaminants into the environment. If the disposal of the abandoned materials significantly increases the risk of contaminant potential or release, safer disposal strategies will have to be found. The investigation focused on the potential geochemical interactions, the mineralogical characteristics, and the time scales of fixation/release of contaminants from the wastes. To evaluate chemical interactions of contaminants and dump material, a total of 19 columns and 5 field tests were installed. Experiences from three years of experiments are reported.

Introduction

The Königstein Uranium Mine in Saxony, East Germany was closed in 1990, ending uranium production in the former GDR. Following the closure of the Königstein mine site, various mine wastes and abandoned materials have to be disposed of because of their radiological contamination. These substances include iron and aluminium scrap material (partly contaminated with mineral oil), rubble, asbestos cement, impregnated wood, plastics, paper and water treatment residues. The amounts of material vary from a few cubic meters of paper to thousands of cubic meters of water treatment residues.

Since there is no radioactive waste disposal site in Saxony, alternative disposal options had to be identified. The most obvious approach was to use the existing Schüsselgrund mine dump and to add all of the abandoned materials to the mine waste before reclamation. The release of radionuclides, metals, and other contaminants from these materials would be determined by the hydrogeochemical milieu in the dump, the chemical interactions between the different materials, and the possible effects of ligands and sorptive substances that could be associated with the dump material (Hydroisotop-Piewak GmbH 1996). In order to assess the potential impact that this could have, the long-term behaviour of the dump material and abandoned materials (separate and together) were investigated.

Wastes in the Schüsselgrund mine dump are of varied composition and are heterogeneously distributed. We find mine residues of host rock (sandstone), iron, and building rubble from the abandoned mine as well as water treatment residues (sludge and filter cake). The bulk of the sandstone material is of block size proportions (> 6.3 cm). Due to the deposition of radioactive mine waste, an inventory of about 540 t of uranium is currently deposited at the Schüsselgrund site (Table 1).

Table 1. Radioactive inventory of Schüsselgrund mine dump (Hydroisotop-Piewak GmbH 1998)

Material	Uranium [g/kg]	Thorium-230 [mg/kg]	Radium-226 [mg/kg]	Lead-210 [mg/kg]
dump material	56.8	1.9	0.05	$5.7*10^{-4}$
filter cake	96.4	45.2	0.16	$1.9*10^{-3}$
water treatment sludge	70.9	4.7	0.06	$6.6*10^{-4}$

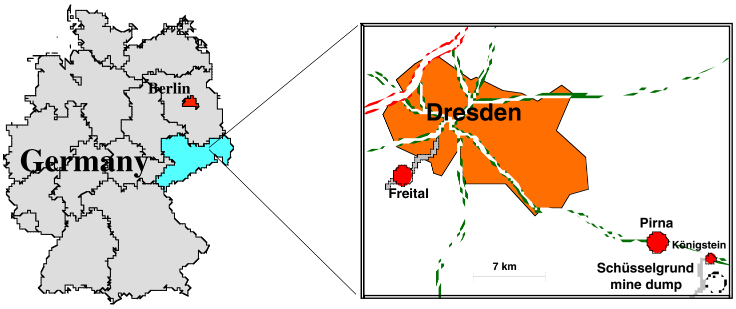


Figure 1. Location of the study site.

Due to partial acid in-situ leaching of uranium with sulphuric acid, dump waters are characterised by low pH (about pH 3). To consider acid and neutral hydrochemical milieus, two types of column experiments were performed with leached and unleached dump material. To provide a reference to the site, five field tests were installed adjacent to the dump plateau. These contained dump material and different kinds of mine waste: scrap, organic matter, plastic, and paper. Drainage speed and residence times in the field were supposed to be similar to those in the dump (Schneider et al. 1999a).

Site Characterization

The Schüsselgrund mine dump is situated near Königstein in the southeast of Saxony, Germany next to the Sächsische Schweiz National Park (Figure 1). It was filled from 1967 to 1990. The dump has a thickness ranging from 10 to 30 m and a slope ratio of 1: 2.5. The site receives an average annual precipitation of 750 mm with maxima in March, April, and August.

In most parts of the dump, an impermeable basement is missing. As a consequence, percolating dump waters can directly enter the first groundwater level. Beneath the dump, we have found that the water in both the first and second aquifer is significantly contaminated near a narrow strip of faulted rock. The main contaminants of concern are uranium and radium but zinc, nickel, and sulphate are present as well. There is no apparent release of arsenic, as is known to occur at other uranium mining sites in Saxony. The amount of infiltrating dump waters ranges from about 50 to $100\cdot10^3$ m^3/year, based on calculations of the dump water balance (Hydroisotop-Piewak GmbH 1997).

Investigations for the Deposition of Abandoned Material

Experimental Concept

To evaluate chemical reactions of contaminants with dump material, a total of 19 large (3.9 L) columns were installed in the laboratory and 5 test sites were established adjacent to the dump plateau. The selection of the column fillings were based on the supposition that similar reacting materials could be deposited together in the dump material to save disposal space. Due to the nature of the materials, the potential effects on geotechnical stability also had to be considered. The laboratory and field experiments started in 1995. After 18 months of operation, the release of radionuclides and heavy metals from the columns and test fields had stabilised.

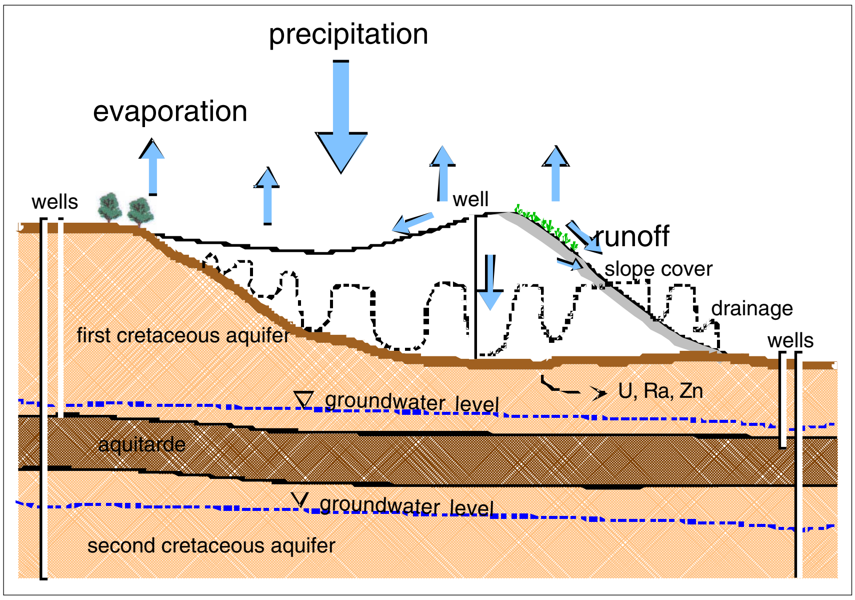


Figure 2. Schematic cross section of the Schüsselgrund site.

The columns were filled using 90% dump material and 10% abandoned material. Due to the complex chemical reactions of a mixed disposal, the following different column experiments were prepared:

- alkaline substances: asbestos, filter cake (column W7),
- organic matter: wood, roots, paper, grass (columns W4, W5, W6, W14),
- material with small reacting ability: plastics, porcelain, glass and gum (columns W2, W12, W13, W17),
- iron/aluminium scrap material (column W8),
- two combined materials (columns W3, W16, W17, W18, W19),
- all substances (columns W9, W20),
- comparison columns with dump material (columns W1, W15, W11).

The columns were percolated using pH 3 and 7 solutions to simulate saturated conditions. The percolation rate of 2.7 L per week for the column experiments corresponded to a ten year time scale for the dump. One column and one test field were filled only with dump material for comparison with the Schüsselgrund mine dump. The columns were 190 mm in diameter, 500 mm long and 3.9 L in volume and made of acrylic glass. Before filling the columns, the material was dried, homogenised and reduced in size (main grain size 0.1 to 20 mm, maximal grain size 50 mm).

For the field experiments, the dump material was not reduced in size, but was used as found at the dump. Due to exposure to natural precipitation, drainage speed and residence times in the field experiments were approximately the same as in the dump (about 750mm/a). There were four field plots, each 5 x 5m in area, 1m deep (see figure 3) and provided with a drainage system that can be sampled. The bottom of the test plots was filled with dump material. At a depth of 60cm, a 20cm layer of abandoned material was arranged. The test fields were filled with dump material as follows:

- M1: comparison field test with dump material only,
- M2: dump material and grass/wood/roots,
- M3: dump material and plastics,
- M4: dump material and paper.

In addition, a lysimeter was established containing mineral oil contaminated scrap material. The field tests functioned under unsaturated and oxidising conditions. The effluent waters from the test fields have a lower pH than the column waters because of inhomogeneous material deposition and atmospheric contact.

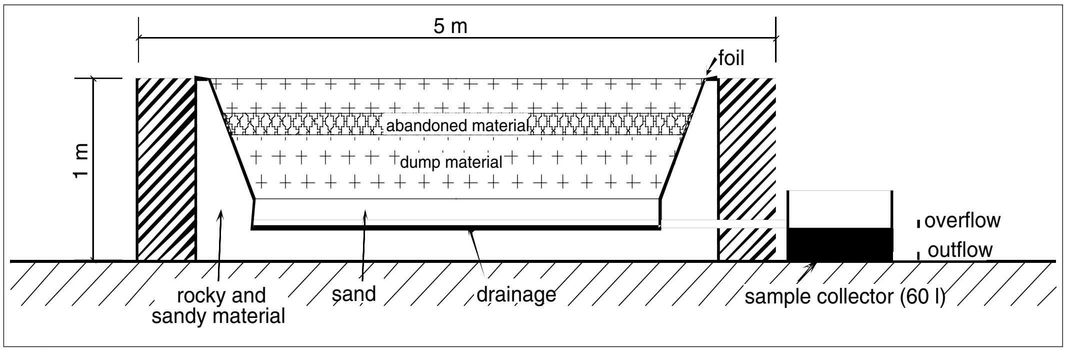


Figure 3. Cross section of the test fields.

The effluent waters were analysed for pH, electric conductivity, redox potential, major ions, metals, and radionuclides, initially weekly and later monthly. In addition, the column filling materials were characterised mineralogically and studied using liquid chromatography for dissolved organic carbon. The arsenic contents of the abandoned paper and the adsorptive characteristics of the plastics and scrap were also investigated. Geochemical modelling was also conducted. The field tests are still in operation.

Characterization of Material

The mineralogical composition of the dump material and underlying sandstone was investigated to establish their buffering capacity. Dump material is of varied composition. We have found mining material (sandstone), abandoned material from the buildings (scrap iron and building rubble), and water treatment residues (sludge and filter cake). Only the water treatment residues showed a significant buffering capacity. The sandstone is nearly free of carbonates (<1 weight %) and therefore has neither buffering nor sorption capacity for metals and radionuclides (Hydroisotop-Piewak GmbH 1996).

Due to their layered lattice structure, muscovite and kaolinite have low potential for sorption to higher valent metal compounds. High sorption capacity would be found for montmorillonite and smectite, but none of these minerals was found in the samples. That means that there is no significant adsorption potential for heavy metals and radionuclides in the deposited sandstone.

To evaluate the possibility of organic contaminant transport by humic acids, liquid chromatography was used to determine dissolved organic carbon (LC-DOC) and spectral adsorption coefficients. Materials of column W4 (organic matter) and the reference column were extracted with H_2O and NaOH. In both water extracts, DOC contents of about 1 mg/L were found. The DOC contents of the alkaline extracts showed a different composition (W4 47.5 mg/L, W1 23 mg/L). The DOC components were identified as humus, humic acids, fulvic acids, low molecular acids and hydrophobic organic matter. Beside these component building blocks, amphophilic substances and polysaacharides were detected. Due to the very slow decomposition rate of wood material, only small amounts of humic acids were found in the effluents after two years of investigation.

During these investigations, no significant release of metals occurred in the effluents of the columns containing the plastic and scrap material was found. This may be ascribed to sorption of contaminants on the surfaces of these materials. To evaluate this, HCl and EDTA eluate samples of the material surfaces were analysed for iron, manganese, copper, nickel, chromium, zinc, lead, arsenic, and cadmium.

Results and Discussion

The effluent contaminant concentrations from the columns were very high for about three months and then decreased and reached natural values. The pH values of effluent waters from the columns were either acidic or neutral (see Figure 4). Acid effluents were formed in columns with alkaline (W7) and combined materials (W19) as well as in the reference column. Organic matter in the columns caused neutral effluents (W6, W14; W20–all contaminants). After 1.5 years of observation, all column effluents of abandoned materials showed a lower conductivity than the reference column with dump material. This may be ascribed to contaminant sorption on the surfaces of the abandoned material.

Like the columns, the contaminant concentrations in the field test effluent water were initially very high but then decreased. However, all of the field test effluent waters became acidic because of residual leaching acid and pyrite weathering. The conductivity of leached dump material was significantly higher than of unleached material. Some of this data is shown in Figure 5.

Arsenic concentrations as high as 1.3 mg/L were found in acidic effluent waters associated with the abandoned paper. Concern about the potential of arsenic release caused by paper has resulted in discussions of alternative disposal options. Special investigations were performed to find the origin of the arsenic. Due to the high solubility of arsenic with glucose, as discussed by Irgolic (1994), samples of the paper material were extracted and analyzed for glucose and other organics, but this has not clarified the cause of the arsenic release.

The eluates from the plastic surfaces were determined to contain zinc (75%) and iron (23%). Beside these metals, lead (1,4 %) and arsenic (0,15 %) were also present. Arsenic sorption on the surfaces of scrap material was presumably due to due to the formation of iron hydroxides.

When investigating the extent of leaching from dump material, one has to consider that the mobility of radionuclides and heavy metals depends not only on the sorptive capacity of the rock, but also on the physico-chemical processes occurring inside the dump (e.g., weathering of the material removed during the mining process). During the infiltration, the conductivity of the columns varied depending on the pH. The effluent waters from the test fields showed conductivities between 1 and 8 mS/cm. The values from the laboratory columns were significantly lower (0.1–1.0 mS/cm). Metal concentrations (U, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) in the effluent waters in the columns were low (0.01–10 mg/l). For most elements, these values occurred during the first year of investigation. The dissolved organic carbon content of the column and field tests containing organic matter increased due to the decomposition processes.

A mass balance of the metal release of the columns was calculated for copper, nickel, chromium, zinc, lead, arsenic, cadmium and uranium (Table 3). The highest release of copper, chromium and lead was found in the effluent waters of columns with organic matter (W4, W14, W18). The release of zinc is determined by the sorption on surfaces of plastics or scrap in the columns. The highest zinc release was determined in the reference columns (W15, W11).

Table 2. Qualitative results of mineralogical characterisation of the column fill (x-ray-investigation), where *x = low quantity, xxxx = high quantity, and* b.d.l.= below detection limit.

Material	**quartz**	**kaolinite**	**muscovite**	**gypsum**
comparison column before test	xxxx	xx	xx	x
comparison column after test	xxxx	xx	xx	b.d.l.
iron and aluminium scrap, plastics	xxxx	xx	xx	b.d.l.
wood	xxxx	xx	xx	b.d.l.
paper	xxxx	xx	xx	b.d.l.
all contaminants	xxxx	xx	xx	b.d.l.
asbestos, porcelain, glass	xxxx	xx	xx	b.d.l.

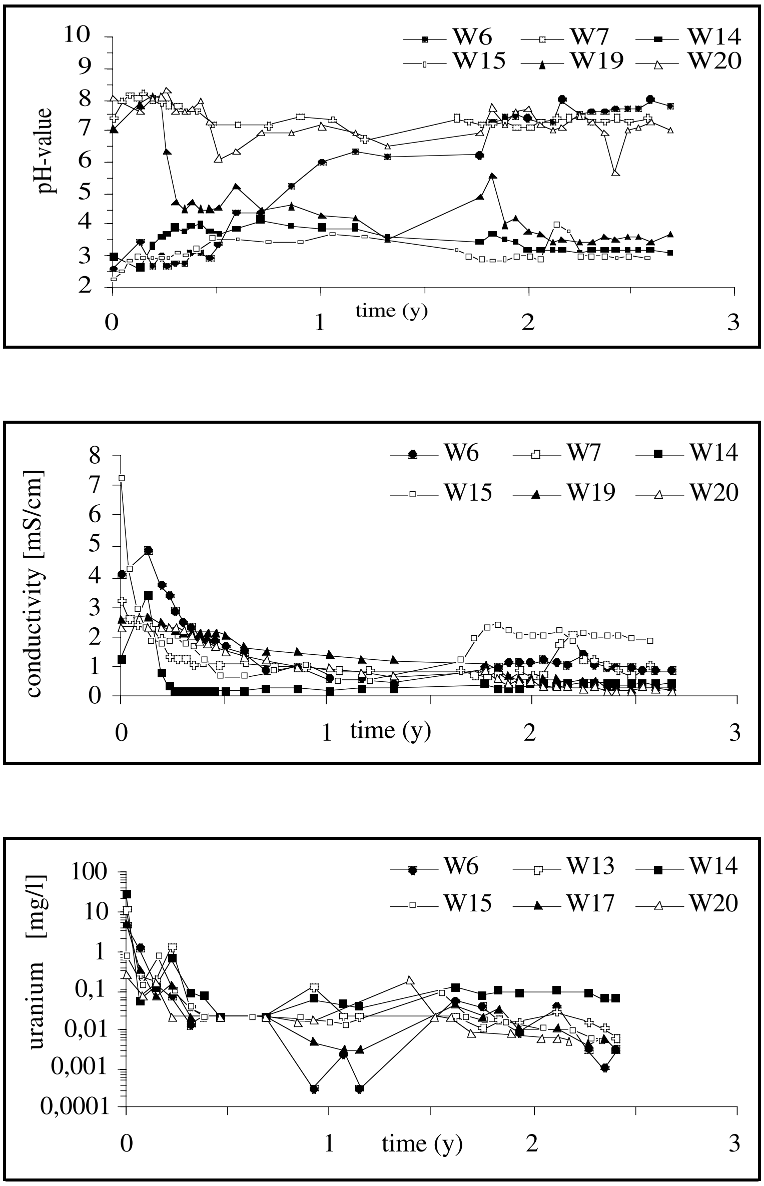


Figure 4. The pH value, electric conductivity and concentration of uranium in effluent water from selected columns containing abandoned material and dump material.

Based on the time dependence of the contaminant concentrations and the geochemical milieu in the columns, different groups of effluent waters could be distinguished. Only the experiments with paper exhibited an increase in arsenic. In all experiments with abandoned materials of the test fields and columns, the concentration of uranium and zinc decreased by a factor of 5–10 within the investigation period. For cadmium, copper, iron, and thorium, the concentrations decreased by a factor of 20 or more, and this decrease occurred within one year. Different behaviour was investigated for radium-226. The variability of the activity was high, but the activity was increasing slowly. Scrap column showed a decrease of radionuclides and metals. The chemical results of column and field experiments are shown in table 4. Columns filled with filter cake showed very low concentrations of metals and radionuclides because of the calcium and magnesium. Water treatment residues could be used as buffer material for acidic dump waters. Formation of secondary minerals (mainly gypsum) was determined by x-ray-investigation and geochemical modelling.

The conductivity of the effluents of the test fields was similar except M 4 (paper). Over the whole duration of the experiments the conductivity of the effluents of field M 4 was about 1 mS/cm higher than the in other test fields. In contrast to the columns higher zinc concentrations were analyzed at the lysimeter (scrap). No mineral oil was found after a six-month period. An increase of chromium concentrations was observed in the test field M2 during the decomposition process of wood, due to the impregnation of the wood for mining uses (figure 5).

Conclusions

The impact of the Schüsselgrund Mine Dump on the aquatic environment was evaluated based on the evolution of the contaminants dissolved in the dump water and the amount of water released from the dump per year. For the waste material,

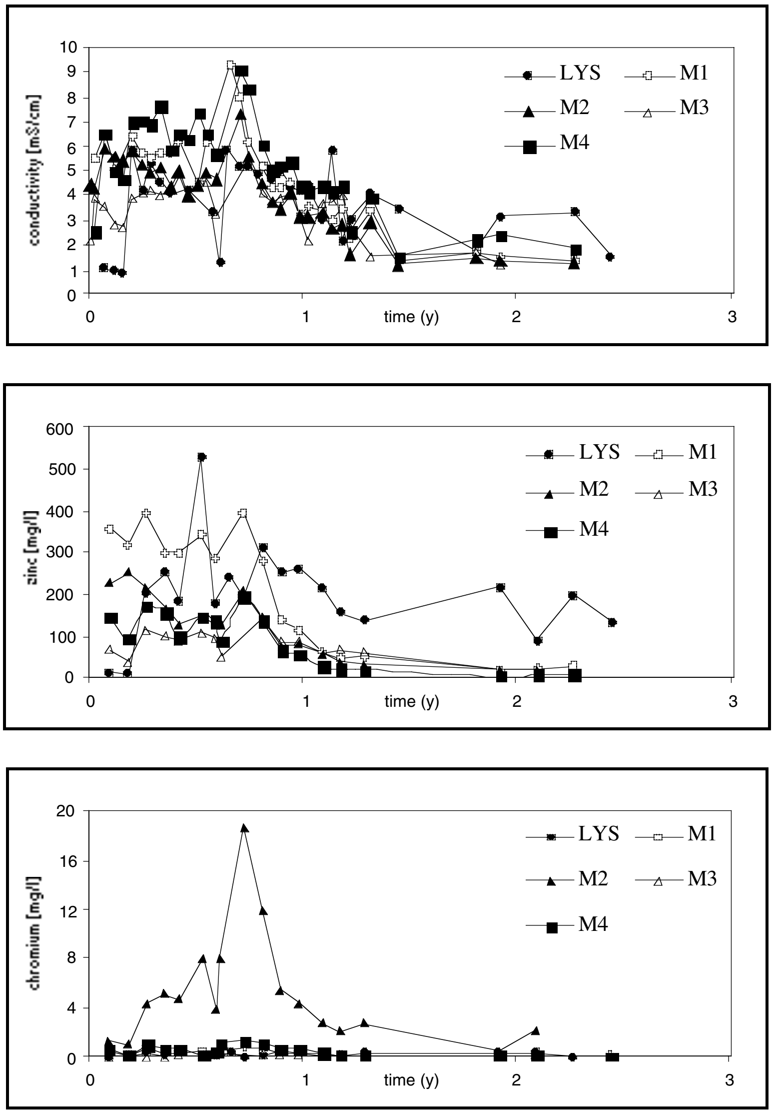


Figure 5. Concentrations of selected elements in the test fields: M1 (dump material), M2 (organic matter), M3 (plastics), M4 (paper), lysimeter (scrap with mineral oil).

Table 3. Total quantity (in mg) of heavy metals released in the columns for an investigation period of 1.5 years (n.a.= not analyzed).

column	Cu	Ni	Cr	Zn	Pb	As	Cd	U
W 1	19	20,9	5,9	871,4	21,4	8,1	4,7	n.a.
W 2	1	3,2	5,5	28,2	1,5	28,3	0,1	n.a.
W 3	3,8	17,8	1,3	689,9	2,9	2,1	2,1	n.a.
W 4	759,9	27,4	595,6	551,4	12,1	11	4,2	n.a.
W 5	7,3	19,1	2,9	755	6,4	56,6	4	164,4
W 6	2,9	20,9	2	547,4	3,3	17,2	3,4	60,8
W 7	1,7	4,8	0,8	55,2	4,3	0,7	0,2	19,6
W 8	1,4	13,2	1	208,1	1,6	0,5	8	n.a.
W 9	3	1,7	0,7	27,5	n.a.	3,2	0,2	n.a.
W 11	36	15,6	3,8	571,7	138,3	0,6	4,5	n.a.
W 12	1,1	0,8	0,8	25,1	1,5	16,8	0,2	n.a.
W 13	20,7	17,8	1,9	841,3	32,4	0,5	12,6	147,9
W 14	727,2	24,5	239	678,2	119,4	1,5	5,5	312,7
W 15	15,7	18,8	5,6	1086,3	n.a.	7,6	3,8	n.a.
W 16	0,9	1,3	1,5	25,7	1,1	24,7	0,2	n.a.
W 17	4,7	16,4	1,3	664,7	2,1	0,7	4,9	60,7
W 18	900,9	24,9	347,4	671,3	17,2	4,6	4,5	200,5
W 19	1,5	28,6	0,8	237,5	7,1	0,6	0,4	n.a.
W 20	2	2,9	0,8	81,2	2,7	1	0,2	n.a.

Table 4. Summary of test results for the abandoned materials.

material	results
dump material (leached, unleached)	dump material has no buffering capacity to acidification, concentrations of heavy metals and radionuclides are continuously washed out
scrap metal (iron and aluminium)	formation of iron hydroxides causes fixation of radionuclides and most metals despite acid reaction milieu
Scrap metal contaminated with mineral oil	formation of iron hydroxides causes fixation of radionuclides and most metals despite acid reaction milieu, decomposition of mineral oil
rubble, asbestos cement, glass, porcelain	carbonate content causes alkaline pH and low heavy metal and radionuclide contents, asbestos causes arsenic mobilisation
impregnated wood (mining waste)	decrease of pH, increase of chromate, no mobilisation of radionuclides, decomposition process of wood is slower than of grass
grass (from surface remediation)	formation of acids causes decrease of pH, constant dissolved organic carbon, increase of nitrogen, low salt concentrations
plastics (remediation material)	in acid and neutral milieu decrease of pH, low concentrations of all elements, no reactions plastics - radionuclides
paper (remediation material)	in acid and neutral milieu decrease of pH, heavy metals and radionuclides are mobile, very high arsenic concentrations
water treatment residues (filter cake)	in acid and neutral milieu carbonate content causes alkaline pH and very low arsenic, heavy metal and radionuclide contents

the long-term behaviour of mine waste reactions with dump material must be considered. For the abandoned wastes, different waste materials require different disposal solutions. The disposal of water treatment residues (filter cake), asbestos cement, rubble, glass and porcelain in the Schüsselgrund mine dump causes no additional contaminant release. Due to the release of copper, chromium and lead, organic material should not be disposed of in contact with dump material. These materials should be shredded and composted. During the decomposition process, grass material lost 50% of its volume. This is a significant finding in terms of geotechnical stability. It is recommended that these materials be disposed of in a box in the dump material and covered with clay. Plastics pose no geochemical problem. Due to the sorption of zinc on the surface of plastics, co-disposal will actually minimise contaminant transport. However, there may be associated geotechnical problems. That is why the cavities of the plastics should be filled with water treatment sludge. Scrap material fixes metals and radionuclides and can be deposited with the dump material, assuming that geotechnical aspects are considered. It is not possible to deposit the abandoned paper in with the dump material, due to the potential for arsenic release.

Acknowledgements

This paper is dedicated to Dr. M. Forster, the powerful partner of the Hydroisotop-Piewak GmbH, who died suddenly in July, 1999. We are grateful to D. Klotz of GSF Neuherberg for the preparation and realisation of the column experiments. We also thank W. Knabe, S. Kurz and Dr. H. Schramm of the Sanierungsbetrieb Königstein for construction of the test fields. Thanks to Dr. C. Kretschmar for helpful discussions and critical remarks.

References

Hydroisotop-Piewak GmbH (1996) Langzeituntersuchung zur Einlagerung organischer Materialien sowie doppelt kontaminierter Materialien in die Halde Schüsselgrund, unveröffentlichte Studie an die WISMUT GmbH, 31.12.1996.

Hydroisotop-Piewak GmbH 1997 Ergebnisbericht zur Berechnung des Wasserhaushaltes der Halde Schüsselgrund - Hydrologisches Jahr 1996/97, unveröffentlichter Bericht an die WISMUT GmbH, 19.12.1997.

Hydroisotop-Piewak GmbH (1998) Präzisierung der hydrogeologischen, hydraulischen und hydrochemischen Verhältnisse in der Schüsselgrundhalde und deren Umfeld, unveröffentlichte Studie an die WISMUT GmbH, 03.04.1998.

Irgolic K (1994) Arsen: Bindungsformen in Böden, Löslichkeitsbestimmende Faktoren, Erfassung aktuell gelöster und mobilisierbarer Anteile. Institut für analytische Chemie, Karl Franzens – Universität Graz Österreich

Schneider P, Nindel K, Schreyer J, Forster M, Piewak M (1999a) Complex hydrochemical and isotopic investigation to specify the environmental impacts of a uranium ore disposal site - practical approach, investigation methods and results, In Int Symp Mining and the Enviroment II, Sudbury, pp 737 - 743.

Schneider P, Osenbrück K, Nindel K, Voerkelius S, Forster M, Schreyer J (1999b) Current and future impact of a uranium mine waste disposal site on groundwater. In Int Symp of the International Atomic Energy Agency on Isotope Techniques in Water Resources Development and Management, Vienna, 1999. IAEA-SM-361-20. Published on CD-rom S4_Schneider.pdf.