Radionuclides in underground water in an area contaminated with uranium mill waste

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Abstract. The uranium mine and mill at Žirovski vrh (RŽV), Slovenia stopped mining and milling in 1990. Mill tailings containing about 20 % moisture were transported to a disposal site called Boršt. The objective of this work was to study the migration of the radionuclides U-238, Ra-226, Pb-210 and Po-210 from the Boršt waste disposal site. For determination of radionuclides, gamma and alpha spectrometry, beta counting, neutron activation analysis and liquid scintillation techniques were used.

Introduction

The uranium mine and mill at Žirovski vrh (RŽV) produced its first yellow cake in late 1984 and stopped mining and milling in 1990. About 600,000 tonnes of ore were processed in this period. The facilities are located 35 km west-northwest of Ljubljana in a valley drained by the Brebovščica stream, a tributary of the river Poljanska Sora. The facilities consist of an underground mine, a mill and several deposits of mining and hydrometallurgical wastes. Fig. 1 shows a 3D view of the surroundings of the uranium mine and the waste disposal sites.

The mill tailings and mine waste pile are deposited on Carnian clastites and Noric dolomites of the Triassic strata. The Carnian clastites consist of brightly coloured siltstones, sandstones, tuffites, and more limestone developed into lens bodies. During the Alpine Orogeny the entire sequences of the region were folded, heavily sheared, cut by north-south (N-S) and northwest-south east (NW-SE) faults and overthrusted with permocarboniferous strata. Fractured porosity developed in the clastites. We have observed caverns and karst caves inside the limestone at the Boršt and Jazbec sites. Fracture porosity is also typical of Upper Triassic dolomite. Only tuffites represent a barrier to water because they are impermeable, even in fractured zones. Under the mill tailings tuffites divide the

ground water table into two parts. Water above the tuffite lens is polluted and represents a potential landslide problem. Water under the tuffite lens is unpolluted.
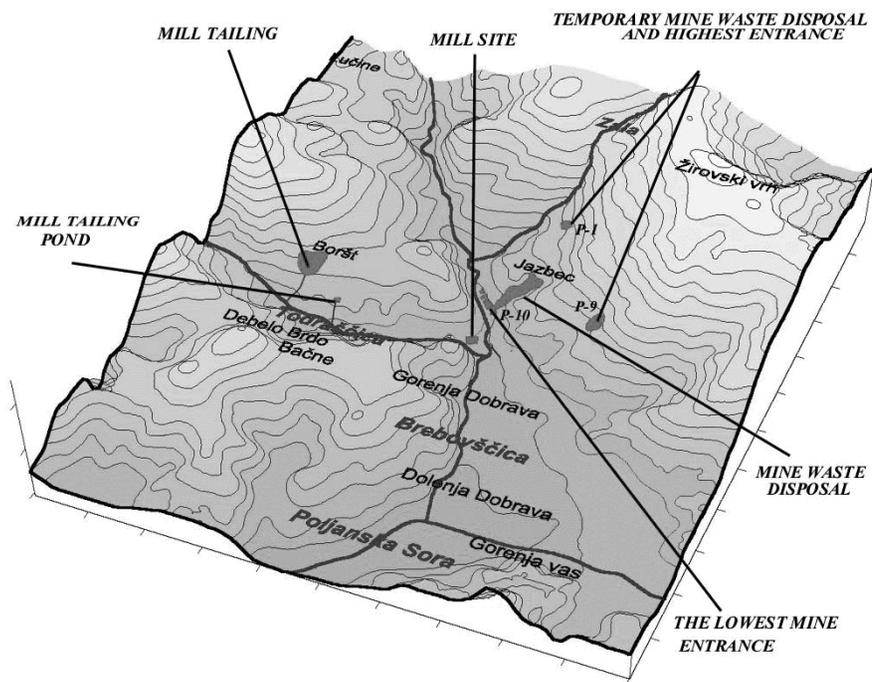

Fig. 1. 3D view of the mine region (by T. Beguš).

The RŽV mill design capacity was 160000 tonnes of ore processing per year at an average grade of about 0.1 % U_3O_8. The ore was crushed and leached with sulphuric acid. The mill tailings with about 20 % moisture were transported to the disposal site at Boršt, nearly 3 km from the processing plant. These tailings (altogether 700000 tonnes) are deposited on a sloping area. The tailings consist of sands and slimes less than 28 mesh and contain on average 8630 Bq kg^{-1} ^{226}Ra, 3930 Bq kg^{-1} ^{230}Th and 1000 Bq kg^{-1} ^{238}U. The tailings dump incorporates a system of capillary or wick drainage to capture and collect maximum amounts of moisture from the tailings deposit and discharge the water via a channel to the river. Due to heavy rains in November, 1990, a substantial part of the tailings deposit with nearly 2.5 million cubic metres of the underlying natural bedding rock began to slide. Survey results indicated an average daily movement of 1.2 mm at the beginning of the slide. Investigations by experts indicated that land movement was due to the heavy inflow of ground water. A stability study showed that lowering of the water table by about 20 m would stop the slide. Therefore a drainage tunnel was constructed under the sliding area to collect the seeping ground water. A series of drainage water wells to lower the water table are envisaged. The water from the collection ditch flows out to the local surface stream (Todraščica). A

sketch map of the area around the mill tailing site and the general direction of the underground water flow are shown in Fig. 2.
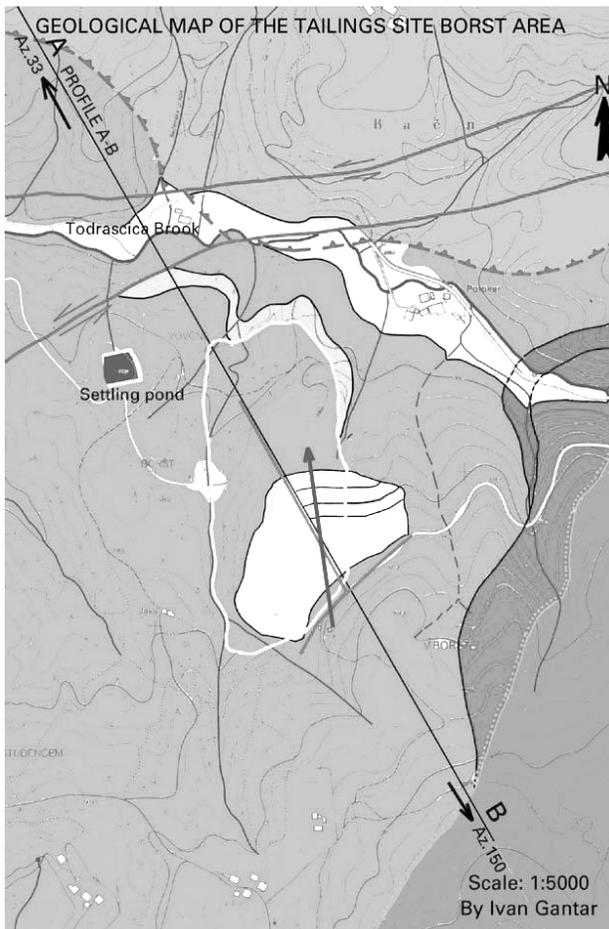
Fig. 2. Geological sketch map of the area around the mill tailings site, and general direction of the underground water flow.

The water contains dissolved uranium (1340 - 1570 mg m^3), radium (5430 - 6340 Bq m^{-3}) and high concentrations of ammonium, calcium, sulphate and chloride ions. The surface is covered temporary by thin soil layer. The effluent flows are underground water beneath the mill tailings (sampling point SDIJ), surface out-flow via the mill tailings pond Boršt and to a minor degree the underground drain-age tunnel. The flow of the underground water flow below the mill tailings (SDIJ) decreased considerably after the construction of the drainage tunnel. The concen-trations of contaminants rose five times due to lack of dilution by underground water. Fig. 3. shows a cross section of the Boršt mill tailings.
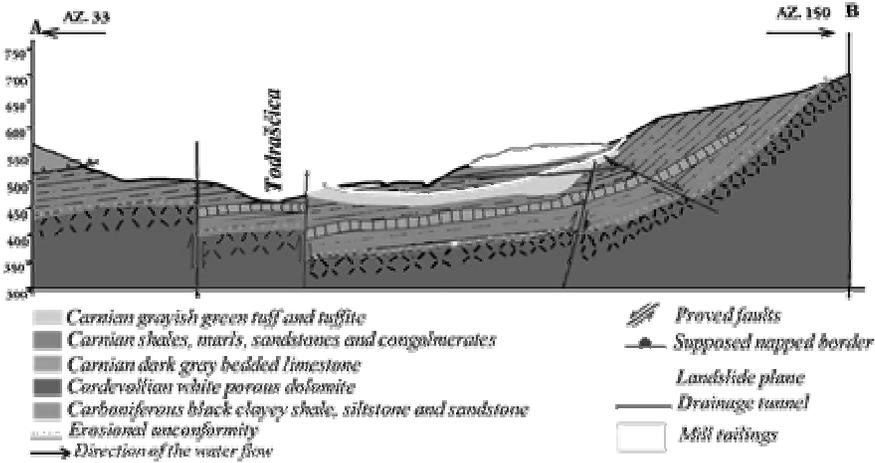
Fig. 3. Cross-section of the Boršt mill tailings.

Experimental

Determination of radionuclides in groundwater

Samples of groundwater were collected in the base rock (Fig. 4) and in the body (Fig. 5) of the Boršt mill tailings disposal site. Immediately after sampling, water were filtered through 0.45 μm filter paper and acidified with HNO_3 (1 mL HNO_3/L of water).

According to the radioactive characteristics of the radionuclides of uranium and their decay products, we determined them using radiochemical neutron activation analysis, alpha spectrometry, beta counting and liquid scintillation counting.
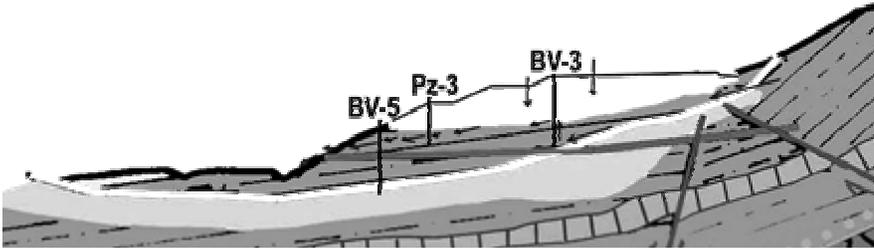
Fig. 4. Sampling points of underground water in the base rock of the Boršt mill tailings disposal site.
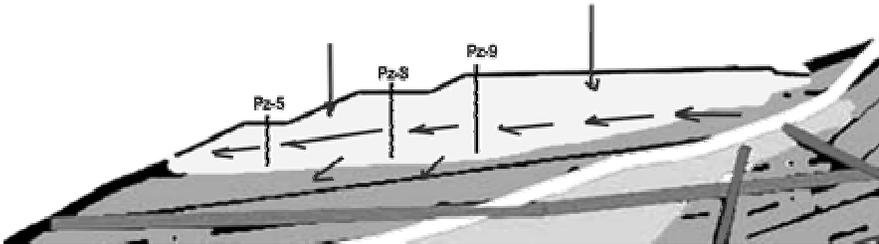

Fig. 5. Sampling points of underground water in the body of the Boršt mill tailings disposal site.

Determination of uranium by radiochemical neutron activation analysis:

Water samples were weighed and sealed into clean polyethylene ampoules. The sample weights ranged from 2.5g to 3g. The sealed ampoules were further encapsulated in polythene foil to avoid superficial contamination during irradiation and handling. Samples were irradiated in the Institute's TRIGA MK II reactor in the pneumatic tube (rabbit system) at a neutron fluence rate of 4×10^{12} ncm^{-2} s^{-1} for up to 5 min with a uranium standard (~100 ng). When ^{238}U is irradiated in a reactor the following capture reaction takes place:

$$^{238}\text{U}(n,\gamma)^{239}\text{U}(t_{1/2} = 23.5 \text{ min}) \rightarrow {}^{239}\text{Np} (t_{1/2} = 2.35 \text{ d}) \rightarrow$$
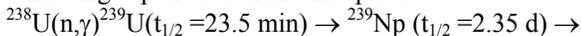
Based on earlier work (Byrne and Benedik 1988, 1995) a very sensitive method for uranium determination using selective extraction was used. The short-lived ^{239}U nuclide was extracted with 50 % TBP in toluene from 5M nitric acid follow-

ing wet-ashing in the presence of uranium carrier and conversion of uranium to the U^{6+} form with addition of perchloric acid. The organic phase was cleaned up with two washes of 5M nitric acid containing 0.2% HF. The gamma peak of ^{239}U at 74.7 keV of the sample and standard solution was measured for determination of ^{238}U content. Use of a relatively large amount of uranium carrier (50mg) allows the chemical yield to be evaluated in the gamma spectrum of the isolated uranium fraction from the 185.7 keV γ peak of ^{235}U. Gamma ray spectrometry was performed in an HP Ge well-type detector connected to a Canberra MCA by Genie-2000 Software.

Determination of ^{226}Ra by a liquid scintillation technique

The radiochemical separation procedure for determination of radium was adopted from Burnett (Burnett and Tai 1992). 1L of water was transferred to a glass beaker. After addition of ^{133}Ba tracer together with Ba-carrier, the sample was heated and stirred for approximately 30 min. The procedure was based on co-precipitation of radium with barium sulphate after addition of sulphuric acid, conversion to carbonate, nitrate and finally dissolution of nitrate in water. The chemical yield was determined after separation by measurement of the ^{133}Ba gamma peak at 355.86 keV. After the separation 10 mL of Packard ULTIMA GOLD AB scintillation solution was added. Before direct measurement, the scintillation solutions were pre-count delayed (10 min of adaptation in the dark and thermostatted in the counting chamber), and then counted immediately after separation, when only the photopeak due to ^{226}Ra (4.78 MeV) was observed.

Determination of ^{210}Pb and ^{210}Po in water

For determination of ^{210}Pb and ^{210}Po in water 25 mg Pb^{2+} carrier and ^{208}Po (~ 0.3 Bq) tracer were added to 5 L of water and then the radionuclides co-precipitated with MnO_2 (Minczewski et al 1982). The precipitate was then dissolved with a mixture of H_2O, HCl and H_2O_2, evaporated to dryness and the residue dissolved in 30-50 mL 2M HCl and loaded on a Sr resin column (Eichrom Industries Inc.). The analytical method is based on selective separation of lead and polonium by extraction chromatography with bis-4,4'(5')-t-butyl-cyclohexano-18,6-crown ether (Vajda et al 1997). The non-retained ions were washed from the column with 100 mL 2M HCl. Polonium was stripped with 6M HNO_3 while lead was removed with 6M HCl solution. A polonium source was prepared by spontaneous deposition of polonium radioisotopes onto a copper disk at 50°C and pH 1 (Benedik and Vreček 2001). Polonium radioisotopes were then measured by alpha spectrometry. Lead was precipitated as lead sulphate and the beta activity of its daughter ^{210}Bi measured at equilibrium on a beta proportional counter.

Results

The activity concentrations of dissolved long-lived radionuclides of ^{238}U, ^{226}Ra, ^{210}Pb and ^{210}Po in water in Bq m^{-3} are shown in Table 1.

Table 1. Activities of dissolved long-lived radionuclides in water in Bq m^{-3}.

Sampling point	U-238	Ra-226	Pb-210	Po-210
PZ-5	12800 ± 500	1480 ± 100	241 ± 19	184 ± 23
PZ-8	38500 ± 1200	3270 ± 130	954 ± 74	857 ± 93
PZ-9	35900 ± 1100	1620 ± 180	205 ± 16	102 ± 12
PZ-3	54 ± 6	165 ± 27	30 ± 2	17 ± 6
BV-3	13 ± 2	10 ± 18	135 ± 11	9 ± 3
BV-5	10700 ± 250	520 ± 50	431 ± 34	40 ± 6
SDIJ	9000 ± 300	500 ± 60	80 ± 8	81 ± 15

Conclusions

The aim of this study was to determine the activities of uranium, ^{226}Ra, ^{210}Pb and ^{210}Po in underground water in the base rock and in the body of the Boršt mill disposal site. The concentration of radionuclides in mill tailings were determined by direct gamma spectrometry. The mill tailings deposited on the Boršt disposal site contain on average 850 Bq kg^{-1} of uranium, 7700 Bq kg^{-1} of radium and 6500 Bq kg^{-1} of Pb-210. The results of our measurements of dissolved radionuclides show that during seepage through the pile water leached these radionuclides resulting in contamination of underground waters. The underground water in the body of the Boršt mill tailings (sampling points PZ-5, PZ-8, PZ-9) is much more contaminated than the underground water in the base rock of the disposal site (sampling points BV-3, PZ-3 and BV-5).

Acknowledgement

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