Determination of long-lived radionuclides in underground water

P. Tavčar[1], I. Gantar[2], U. Repinc[1], R.Jakopič[1], L. Benedik[1]
[1]Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
[2]Žirovski vrh Uranium mine, Todraž 1, 4224 Gorenja vas, Slovenia

ABSTRACT

The objective was to study the migration of the long-lived radionuclides ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb *and* ^{210}Po *from the Jazbec waste pile of the uranium mine into underlying karstic drainage channels. By analysis of different radionuclides in water samples we were able to determine which karstic channels drain the waters from the Jazbec waste pile. The results of the analysis show that a connection between karstic cracks under the Jazbec waste pile and the larger karstic channel in the Brebovščica valley exists. The pollution of the larger karstic channel is small due to dilution and/or strong adsorption of radionuclides on cave clays*.

INTRODUCTION

Uranium ore was found in the Žirovski massif in 1960. Ore production started at the beginning of the eighties (Novak 1977). A deep, narrow valley called Jazbec was chosen for deposition of mine waste, where 1,600,000 tons of mine waste, poor ore and red mud were deposited. Red mud was a by-product of uranium oxide production. The average uranium concentration in the mine waste is 75 g U_3O_8/t.

The geological structure of the rocks underlying the mine waste pile is rather complicated, consisting of carboniferous schists and Triassic carbonate rocks, cut by a subvertical fault that caused the karst channels in the bedrock of the Jazbec creek valley and in the main valley of the Brebovščica river to fill with water. Polluted water seepage from the Jazbec mine waste pile into the rock base and thereafter into the karstic channels leads to underground water pollution. We do not know the details of the karstic channels in which the water from the mine waste pile flows, and we needed to investigate which karstic channels are subject to polluted water inflows from the Jazbec mine waste pile, to what degree the water is polluted and possible interconnections among the karstic channels.

Figure 1. Location of the Jazbec mine waste pile and its piezometers.

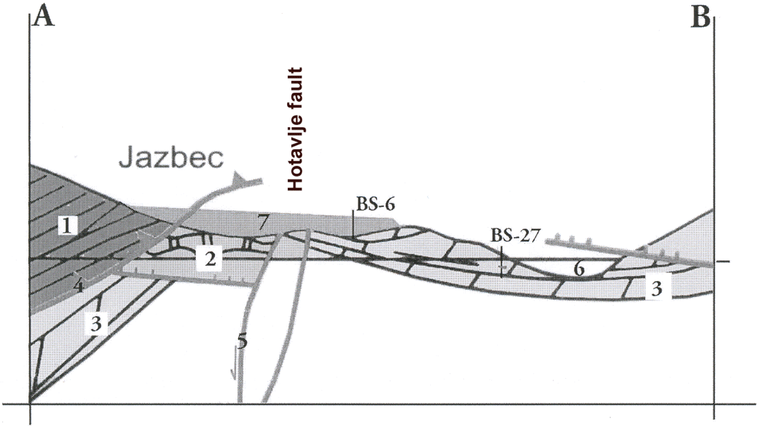
GEOLOGICAL AND HYDROGEOLOGICAL CHARACTERISTIC OF THE ROCKS

The rock base of the Jazbec mine waste pile consists of Upper Triassic Carnian limestone and Norian dolomite. Due to a prominent sub-vertical fault that runs beneath the centre of the waste pile, the carbonate rocks became intensely karstified, as is evident in the configuration of smaller caves and karstic channels, and created the opportunity for karstic water flow. The channel of the Brebovščica stream is temporary filled with water during high rainfall, while the channels in the dolomite under the bed of the Brebovščica valley are permanently filled with water that flows along the course of the valley toward the spring called Mrzlek (Gantar 1996). By siting the piezometers BS 27, BS-29 and VPO-1 in the Brebovščica valley we proved the existence of smaller karstic water channels, but interconnections among individual karstic water channels could not be verified (Beguš 1999).

Alluvial deposits at the bottom of the valley consist of clayey gravel and clays. For this reason we cannot observe mixing of the stream water and underground water in the area influenced by the mine.

UNDERGROUND WATER IN THE MINE WASTE PILE AREA AND IN THE BREBOVŠČICA VALLEY

Underground water in the Jazbec mine waste pile was investigated and its level and pollution has been continually measured with emphasis on radionuclides. The underground water level is approximately 5 m above the rock base of the mine waste pile. The underground water level hardly changes due to the good water permeability of the mine waste material and the base rock (Beguš et al 1997). Some of the underground water in the mine waste pile flows out through drainage pipelines that were built-in during the construction of the foundation of the mine waste pile and lead into the Brebovščica stream, and some leaks into the underlying rock base and the karstic water body.

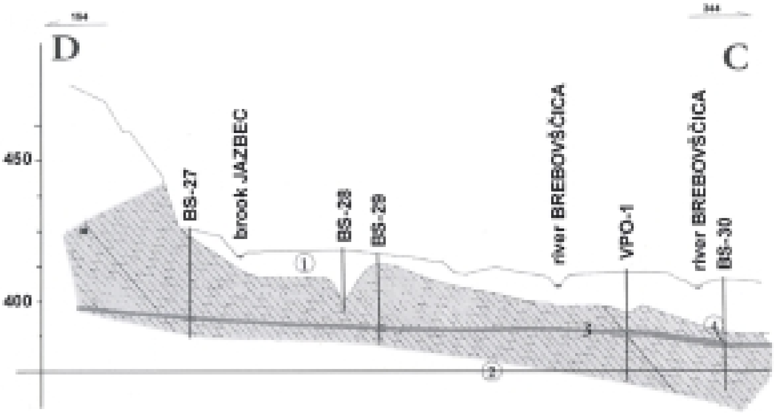


1 Carboniferous schists; 2 Upper Triassic (Carnian) limestone; 3 Upper Triassic (Norian) dolomite; 4 Thrust plane; 5 Fault; 6 Alluvial sediments; 7 Jazbec Mine waste pile

Figure 2. Geological cross-section A-B of the Jazbec mine waste pile (Mlakar and Placer 1999).

The average uranium concentration in the underground water within the Jazbec mine waste amounts to between 2.9 mg/L and 4.6 mg/L, depending on the rainfall during sampling. The underground water level was measured with six piezometers in the past. Only one of these six piezometers (BS-6) is now accessible due to waste pile reshaping. Water samples were taken from BS 6 for the investigation. In this way we obtained the water samples needed to acquire data on the pollution source.

We proved the existance of larger karstic channels by the four deep piezometers BS-27, BS-29, BS-30 and VPO-1 that were built-in to the Brebovščica river valley. In addition, we measured underground water pollution in the karstic water body of the Mrzlek spring.



1 Alluvial sediments; 2 Triassic (Norian) dolomite; 3 Underground water; 4 Proven Karstic channels;

Figure 3. Profile D-C along the Brebovščica river valley.

There is no interconnection between surface water streams and underground water in the dolomite, because alluvial sediments of very poor permeability fill the bottom of the valley, as was demonstrated by tests with shallow piezometers in the alluvial sediments of the Brebovščica stream. To avoid possible impact of the surface water on underground water, we performed sampling during the dry season, when underground water can be found only in the karstic channels around 25 m under the valley bottom.

EXPERIMENTAL

SAMPLING

Samples of groundwater were collected at six different sites: one was taken under the Jazbec waste pile, four samples were collected from the main karstic channel and one from the Mrzlek spring. The positions of the sampling wells and the spring are shown in Fig.1,2 and 3. Water was filtered through a 0.45 µm filter and acidified with HNO_3 (1 mL HNO_3 L^{-1} of water). According to the radioactive characteristics of the radionuclides of uranium and their decay products, each radionuclide was determined using different techniques: alpha spectrometry, beta counting and radiochemical neutron activation analysis, as follows.

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 flux rate of $4x10^{12}$ 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:

$^{238}U(n,\gamma)^{239}U(t_{1/2} = 23.5\text{ min}) \rightarrow {}^{239}Np\ (t_{1/2} = 2.35\text{ d}) \rightarrow$

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 following 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 same gamma spectrum of the isolated uranium fraction from the ^{235}U peak at 186 keV. Gamma ray spectrometry was performed in an HP Ge well-type detector connected to a Canberra MCA by Genie-2000 Software.

DETERMINATION OF ^{230}TH BY ALPHA SPECTROMETRY

To 4L of water sample spiked with a known amount (~80 mBq) of ^{229}Th tracer, $FeCl_3$ and ammonia solution were added to allow coprecipitation at pH 9. The iron hydroxide precipitate was separated by centrifugation and finally wet-ashed three times with 1 mL HNO_3. The residue was dissolved in 20 mL 7M HCl. The solution was transferred to the top of an anion-exchange column of Dowex 1x8, 100-200 mesh conditioned with 7 M HCl and allowed to flow through at about 1 mL min^{-1}. Thorium radioisotopes pass through the column while uranium and other interfering radioisotopes are retained on the column. The thorium fraction was cleaned three times. Each time thorium was loaded on the column in 7M HCl and eluted with 60 mL of 7 M HCl. The thorium fraction was evaporated to dryness and the residue dissolved in 1 M HCl. A thin layer source for alpha spectrometric measurement was prepared by microprecipitation (HASL-300 1997) and the activities of ^{229}Th and ^{230}Th were measured on an alpha spectrometer.

DETERMINATION OF ^{226}RA BY ALPHA SPECTROMETRY

To a 500 mL water sample spiked with ^{133}Ba tracer, 2 mL H_2SO_4 and 0.5 g K_2SO_4 were added and shaken until dissolved. With stirring, 30 mg Pb^{2+} was added in portions to allow good coprecipitation of radium and barium. After settling, the suspension was centrifuged and washed with distilled water. The $PbSO_4$ precipitate containing radium and barium was dissolved in 3 mL 0.1M EDTA, prepared in 0.5M NaOH. 250 μg of 0.3 mg/mL Ba^{2+} solution was added together with 4 mL of saturated Na_2SO_4 solution. With stirring, 1:1 acetic acid solution was added until pH 4-5 is reached, thus precipitating $BaSO_4$, while Pb^{2+} ions remain in solution. Immediately after, 0.2 mL of a 0.125 mg/mL $BaSO_4$ suspension was added, acting as a seeding precipitate to obtain small particles. The suspension was allowed to settle for 30 min, then shaken in an ultrasonic bath for

10 s and poured into a filter funnel previously washed with 1 mL of ethanol (80%). The last traces were washed out of the beaker with water, finally the filter with $BaSO_4$ deposit was washed with ethanol and allowed to dry under a heating lamp. The filters were glued to 25mm diameter backing discs, measured on a gamma spectrometer for ^{133}Ba yield determination and on an alpha spectrometer for determination of ^{226}Ra (Lozano et al 1997).

DETERMINATION OF ^{210}PB AND ^{210}PO BY BETA COUNTING AND ALPHA SPECTROMETRY

For determination of ^{210}Pb and ^{210}Po in water 25 mg Pb^{2+} carrier and ^{208}Po (~ 0.1 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 to 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, Vreček and Benedik 2002). 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 AND DISCUSSION

The activity concentrations of dissolved long-lived radionuclides of ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po in water samples in Bq m^{-3} are shown in Table 1.

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

Sampling point	^{238}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po
BS-6	37000 ± 3000	69 ± 9	148 ± 7	31 ± 3	17 ± 4
BS-27	4000 ± 300	5 ± 1	10 ± 1	2.7 ± 0.7	0.7 ± 0.4
BS-29	3800 ± 300	0.3 ± 0.1	8 ± 1	3.0 ± 0.8	2.5 ± 0.6
VPO-1	20 ± 2	< 0.2	4.7 ± 0.5	<1	< 0.6
BS-30	46 ± 3	0.22 ± 0.06	3.6 ± 0.5	<1	0.9 ± 0.3
Mrzlek	234 ± 10	< 0.2	4.8 ± 0.4	2.5 ± 0.7	1.4 ± 0.4

Analyses of water from the piezometers show that an interconnection exists between underground water of the Jazbec mine waste pile and underground water in the karstic dolomite base, and that the karstic channels are interconnected. Pollutant concentrations evenly decrease from BS-6 downstream toward the Mrzlek spring. There are evidently unpolluted water inflows, which dilute polluted water from BS-6. However, the details of such unpolluted karstic channels are still unknown. We expect to discover them with a piezometer network that will be installed after the mine waste pile remediation.

If we examine pollutant concentrations in the piezometers, we can see that the concentrations of ^{238}U , ^{226}Ra, ^{210}Pb and ^{210}Po in the Mrzlek spring are higher than in the piezometers VPO-1 and BS-30. This shows that polluted water flows into the Mrzlek spring from other karstic channels that were not detected with the piezometers. Considering the very low concentrations of pollutants, we can make the inference that the polluted water inflow into larger karstic channel is either small, or that the dilution is very large, or that the absorption of pollutants on cave clays is high.

CONCLUSIONS

Analyses of polluted underground water in the karstic water body in the Triassic dolomite of the Brebovščica valley show a direct interconnection between karstic crevasses and caverns under the Jazbec mine waste pile and larger karstic channels in the Brebovščica valley. The channels, demonstrated by bore-holes, are interconnected and their outflow is probably the Mrzlek spring. The karstic water body in the rock base of the Brebovščica valley is evidently very ramified.

We can infer from the fact that the concentrations of pollutants in the underground water decrease downstream of the mine waste pile that there is a large dilution due to karstic water inflows. The possibility also exists that part of the pollutants are absorbed on cave clays that are present in the karstic channels and that pollution with radionuclides of the underground water will rise with demobilisation of the absorbed pollutants.

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