Weathering of mine wastes after historical silver mining in the Jáchymov ore district (Czech Republic) and migration of uranium

D. Pittauerová & V. Goliáš
Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Prague, Czech Republic

ABSTRACT: Weathering of 450 years old mine wastes after silver mining at Geister vein in the Jáchymov ore district (Czech Republic) and migration of uranium were studied. Specific gamma-ray activity of $^{226}\text{Ra}$, measured by field gamma-ray spectrometry, varies from 38 Bq/kg (3 ppm eU) to 3816 Bq/kg (309 ppm eU) in the observed area. The most active material forms the top layer of the dump. The gamma-ray activity of the top layer is caused mainly by $^{226}\text{Ra}$. Uranium is leached from upper layer and accumulated in fossil soils beneath. U-micas were studied using X-ray powder diffraction and EDA. The following succession of supergene alteration was found: autunite → meta-autunite → bassetite → oxidized bassetite.

1 INTRODUCTION

The landscape of the former mining district of Jáchymov has been seriously affected by long-term mining activity. After World War II, large-scale mining for uranium resulted in an accumulation of rocks in spoil tips. Some parts of the dumps show high contents of natural radionuclides (Matolín 2000).

To forecast long-term migration of uranium and other radionuclides in modern dumps, old wastes after 16th century mining for silver in the same area were studied. Uranium was of no economic importance at this time and old dumped materials therefore contain increased concentration of this metal. Results of our study are summarized in this contribution.

2 JÁCHYMOV ORE DISTRICT

2.1 Geological setting and mineralization

The Jáchymov (St. Joachimsthal) ore district is located in the western part of the Krušné hory (Erzgebirge) Mountains, 20 km N of Karlovy Vary. Ore veins occur in a metasedimentary complex, which was intruded by early Variscan diorite and gabbrodiorite stocks and late Variscian granites followed by younger dykes of variable composition and by Tertiary alkaline volcanics. Veins are characterized by Ag, Co, Ni, Bi and U mineralization and frequently show vertical zoning. Ag prevails in the uppermost zone of the veins. In the upper zone, concentration of Co, Ni, Bi and As with minor U gradually increases downwards. U (±Co and Ni and rare Ag) predominates in the middle zone of the veins. The lowest zone, which lies close to the granite basement, is mostly barren (Kolektiv 1984, Dahlkamp 1993).

2.2 Short history of mining

The discovery of the Jáchymov ore district dates back to 1516. After several years, the district became one of the most important producers of silver ores in central Europe. In 17th to 19th century, the original interest in silver was substituted by mining of cobalt, nickel and bismuth. In the early 19th century, uranium ores were collected from old dumps and later mined for paints production. After the discovery of radium, uranium ores were mined for radium. After World War II, large-scale production and export of uranium ore took place in the district. Mining was stopped in 1964. It is worth to note that radioactive waters of the district have been used for medical purposes since 1906.

3 LOCATION AND MORPHOLOGY

The explored waste-rock dump near a “no-name” shaft (we call it Geister II) is located 500 m SSW of the Rovnost I main shaft at the altitude of 935 metres above sea level. It abuts the southern slope of a large dump of the Geister Mine, which was mined repeatedly in the history.

According to historical data, the Geister II was a gin-pit opened as a by-shaft of the main Geister shaft between 1545-1550. It was active for 15 to 20 years.

The dump has approximately rectangular shape with $20 \times 25$ metres in size and about 3 to 4 metres in height. A funnel-shaped depression approx. 5 m deep, an overburdened pit bank, occurs in the SW part of the dump.

Numerous small remains after old exploration works occur near the dump, and a test pit from 1960s is located in the NW part of the studied area. NW- and SW-facing slopes of the dump were dug to collect uranium ore for uranium paints in the early 19th century.

The whole area is now re-forested with spruce; the trees are about 80 years old.

4 RADIOMETRIC METHODS

4.1 Field gamma-ray spectrometry
The area of 50 × 60 m was covered with an orthogonal net of profiles with 10-m intervals between measurement points. Gamma-ray spectrometric field measurements were performed on profiles using DISA 400 A portable spectrometer with NaI(Tl) scintillation detector. The counting time was 120 s. Two series of measurements were made: on the ground and in the height of 1 m above the ground to eliminate the influence of topography and point sources of gamma-ray activity.

4.2. Borehole gamma-ray activity measurements

Total gamma-ray activity logs were taken in shallow hammered holes (max. 160 cm deep) in two profiles across the dump with the use of KS 20 NaI(Tl) scintillation probe.

4.3. Laboratory gamma-ray spectrometry

Three test pits were dug into dumped material and samples were taken. The collected material was air-dried at room temperature, filled to Marinelli beakers and left for two weeks to restore the radioactive equilibrium between $^{226}$Ra and $^{222}$Rn. Contents of U and Ra were measured using a NaI(Tl) scintillation detector (surrounded by a passive shielding of lead and copper) equipped with the Canberra Series 10 multi-channel analyser.

5 RESULTS AND INTERPRETATION

5.1. Field gamma-ray spectrometry

The concentrations of U (Ra) and Th measured on the surface of the dump are summarized in Tab. 1. Values obtained 1 m above the ground are given in parentheses. These data are less sparse because they represent concentration of U, Ra and Th in a larger volume of material. The influence of point sources of gamma-ray activity (pieces of uranium bearing minerals) was considered.

Table 1. Concentration of U and Th measured on the surface of the dump and 1 m above its surface (in parentheses)

<table>
<thead>
<tr>
<th></th>
<th>U [ppm eU]</th>
<th>Ra [ppm eU]</th>
<th>Th [ppm eTh]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>3.1</td>
<td>(3.2)</td>
<td>3.0</td>
</tr>
<tr>
<td>Maximum</td>
<td>308.8</td>
<td>(135.5)</td>
<td>24.3</td>
</tr>
<tr>
<td>Mean</td>
<td>46.2</td>
<td>(37.1)</td>
<td>11.3</td>
</tr>
<tr>
<td>Median</td>
<td>9.5</td>
<td>(14.2)</td>
<td>10.6</td>
</tr>
<tr>
<td>I. quartile</td>
<td>5.4</td>
<td>(5.7)</td>
<td>9.5</td>
</tr>
<tr>
<td>III. quartile</td>
<td>67.0</td>
<td>(73.3)</td>
<td>12.9</td>
</tr>
</tbody>
</table>

The specific activity of $^{226}$Ra varies from 38 Bq/kg (3.1 ppm eU) to 3816 Bq/kg (308.8 ppm eU). About 55 % of the measured area shows $^{226}$Ra specific activity lower than 200 Bq/kg, 20 % ranges between 200 and 1000 Bq/kg, 15 % between 1000 and 2000 Bq/kg, 5 % between 2000 and 3000 Bq/kg and about 5 % of the area has a specific activity of $^{226}$Ra higher than 3000 Bq/kg. The contour map of the surface gamma-ray activity is given in Figure 1.

4.2. Borehole gamma-ray activity measurements

The most active material was found to be concentrated only in the top layer of the dump (to the depth of 50 cm from the surface – Fig. 2). This corresponds with the increasing amount of uranium in deeper parts of hydrothermal veins. Therefore, miners began to encounter pitchblende more often in the late stage of Ag mining.

5.2. Borehole gamma-ray activity measurements

The most active material was found to be concentrated only in the top layer of the dump (to the depth of 50 cm from the surface – Fig. 2). This corresponds with the increasing amount of uranium in deeper parts of hydrothermal veins. Therefore, miners began to encounter pitchblende more often in the late stage of Ag mining.

5.3. Laboratory gamma-ray spectrometry

The coefficients of radioactive equilibrium (Ra/U ratios) were used to describe the changes in radioactive equilibrium in vertical sections (Fig. 3).
In upper layers U is leached (concentrations up to 100 ppm) and Ra is fixed in residual phase (300-700 ppm eU). In the middle and bottom parts of the dump, U and Ra are approximately in equilibrium (120-180 ppm U). Beneath the dump, however, contents of U are high (800-1150 ppm U), and Ra shows background concentrations (about 10 ppm eU).

6 MINERALOGY

Two samples of rusty yellow tabular crystals (samples G1 and more corroded G2) were found in one piece of vein gouge from a dump layer showing high activity. Hand-picked grains were studied by X-ray diffraction on a Debye - Scherrer camera (114.6 mm, Cu/Ni radiation, 24 hours).

A mixture of uranyl phosphates was determined in these two samples:
- autunite Ca(UO$_2$)$_2$(PO$_4$)$_2$.10-12 H$_2$O,
- meta-autunite Ca(UO$_2$)$_2$(PO$_4$)$_2$.2-6 H$_2$O,
- bassette Fe$_{6}^{II}$(UO$_2$)$_2$(PO$_4$)$_2$.7 H$_2$O and
- oxidized bassette Fe$_{6}^{III}$(UO$_2$)$_2$(PO$_4$)$_2$.6(OH)$_6$H$_2$O.

X-ray powder pattern of sample G2 was more diffuse than that of G1. U-mica in sample G1 showed a weak green-yellow fluorescence under ultra-violet radiation while fluorescence of sample G was negligible. Lattice parameters of the observed minerals were calculated (Tab. 2).

<table>
<thead>
<tr>
<th>Sample G1 (less corroded)</th>
<th>Autoxunite</th>
<th>Meta-autunite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ [$\text{Å}$]</td>
<td>7.0267 (85)</td>
<td>6.9929 (79)</td>
</tr>
<tr>
<td>$c_0$ [$\text{Å}$]</td>
<td>20.883 (58)</td>
<td>8.428 (10)</td>
</tr>
<tr>
<td>$V$ [$\text{Å}^3$]</td>
<td>1031.1 (31)</td>
<td>412.16 (92)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample G2 (more corroded)</th>
<th>Bassette</th>
<th>Oxidized bassette</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ [$\text{Å}$]</td>
<td>6.9529 (98)</td>
<td>6.975 (12)</td>
</tr>
<tr>
<td>$b_0$ [$\text{Å}$]</td>
<td>17.083 (42)</td>
<td>6.975 (13)</td>
</tr>
<tr>
<td>$c_0$ [$\text{Å}$]</td>
<td>6.994 (11)</td>
<td>21.026 (53)</td>
</tr>
<tr>
<td>$V$ [$\text{Å}^3$]</td>
<td>830.6 (19)</td>
<td>1023.0 (29)</td>
</tr>
</tbody>
</table>

Electron microprobe with energy-dispersive analyser (EDA) was used to determine the semiquantitative chemical composition of the U-micas (Tab. 3), and the samples were observed using an electron microscope (Figs. 4 and 5). Both samples show a depletion in Ca (the more corroded one even a nearly total absence of Ca), which is substituted by Fe. As and Cu are present in small amounts.

| Table 3. Semiquantitative contents of elements (EDA) |
|-----------------------------|-----------------------------|
| Sample G1 | Sample G2 |
| U | U |
| $P$, Fe, Ca | $P$, Fe, As |
| Cu, As | Cu, Ca |

Meta-autunite was described at the Geister vein in Jáchymov by Ondruš et al. (1997). The study of the X-ray patterns led to suggestion that the observed mineral phases at both samples could be designated as autunite and its dehydrated form meta-autunite.
This was partly supported by results of chemical analysis, which confirmed depletion in Ca and presence of Fe. The increasing amount of bassette in the mixture of mineral phases corresponds to the increasing degree of corrosion of mineral grains and to increasing Fe contents.

X-ray powder pattern of studied oxidized Fe\textsuperscript{III} bassette is comparable to that of a synthetic prepared material (Vochten et al. 1984).

Based on the observed association of uranyl phosphates in the range of one piece of vein gangue, the following succession of alteration processes is suggested (Fig. 6).

Dehydration of autunite can be a reversible process at low temperatures (Èejka 1999). Acid solutions (pH of water leachate of dump material ranges between 3.7 and 4.5) results in the replacement of Ca by Fe and in the formation of bassette, which can be subsequently oxidized by atmospheric oxygen. Chemical oxidation is accompanied by physical disintegration of uranium phosphate grains as evidenced by high microporosity observed on electron microscope images. Vochten et al. (1984) show that the solubility of oxidized bassette is much lower than that of bassette.

Other minerals were identified: torbernite, uranophane, uraninite relics, brown wax gummite, quartz, calcite, limonite and jarosite (as a product of pyrite corrosion).

6 CONCLUSIONS

It can be concluded that U is leached and Ra is fixed in the residual phase in the upper part of the waste rock dump after historical Ag mining. In the middle and bottom parts of the dump, U and Ra are approximately in equilibrium (120-180 ppm U). Beneath the dump, however, U contents are very high and Ra shows only background concentrations. This suggests high mobility of U and low mobility of Ra in the dumped material.

Alteration succession of uranyl phosphates occurring in the active layer of the dump is: autunite meta-autunite bassette oxidized bassette.

ACKNOWLEDGMENTS

This project is funded through the Ministry of Education, Youth and Sports of the Czech Republic, Grant Project No. 113100005.

REFERENCES


