

Mine Water Quality at Abandoned Uranium Mining Sites in the Czech Republic

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Abstract The aim of study is to assess the evolving water quality of uranium mines abandoned between 1958 and 1992 in the Czech Republic. Monitoring of mine water quality was performed at all locations of previous uranium exploitation. Multivariate analyses were applied in order to identify groups of samples based on their similarity. Evaluation of hydrogeochemical evolution of waters was done using Geochemist's Workbench. The sampling proved that uranium concentrations in waters did not predominantly exceed 0.45 mg/L. In case of discharges from adits abandoned more than 40 years ago uranium concentrations were below MCL of US EPA for drinking water.

Keywords uranium, radium, mine closure, mine water, environmental impact, geochemical modelling, the first flush

Introduction

From 1945 to the mid 1990's, uranium mining was an important industrial branch in the Czech Republic, and the Czech Republic occupied a prominent global position in the production of uranium concentrate. A marked phase-out of the industry in the first half of the 1990's, especially due to a marked reduction in possibilities of sales as a result of the economic-political changes taking place at the turn of the 90's of the last century, led to the closure of many underground uranium mines. At present they are closed and flooded (Michalek *et al.* 2005). Mining operations are only performed in one underground mine in the Rozna deposit.

In the recent past, the vast majority of underground uranium mines in the Czech Republic were decommissioned by naturally flooding the mines after underground mining operations and the necessary preparations in connection with mine decommissioning were complete. Mine water levels at recently abandoned deposits are kept by pumping or gravitationally below the level of natural drainage

from deposit (decant point). This mine water level is determined for each deposit by considering the terrain morphology and man-made decant points (*e.g.* old adits) and is crucial for avoiding the uncontrollable release of contaminated mine waters that could endanger the ambient environment. The absolutely fundamental task of uranium mining in relation to the environment, both in the course of mining the deposit and subsequently during mine decommissioning and mitigating the impact of mining, is to minimize the negative effects of released radionuclides on the environment and health of the population.

In the course of development and exploitation of individual uranium deposits, the chemistry of mine water changes depending upon the extent of the drawdown area, the total surface area of exposed mine workings, the mineralogical composition of the rock environment (including residues of unmined uranium and other radioactive minerals in these mine workings), and also the depth of mining. During the flooding of underground mines as part of decommissioning, other sig-

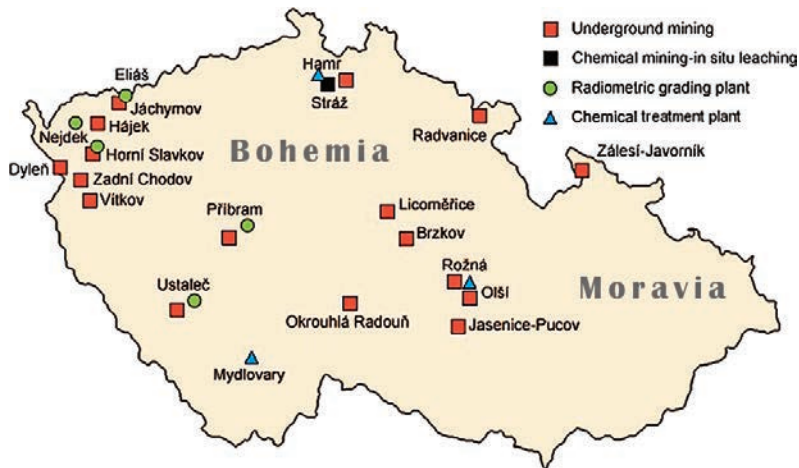


Fig. 1 Main mining and treatment sites of uranium mining in the Czech Republic.

nificant changes occur in the content of dissolved matter in the waters. This involves a several-fold increase in content of dissolved matters (uranium, radium, iron, and others) due to the previous oxidation of minerals when the deposit was being exploited. With reference to the high concentrations of dissolved matter in mine water (above the limits determined for discharge), it is necessary to treat the water drained from the flooded mines before discharging to surface water.

Uranium deposits and their exploitation in czech republic

Altogether about 110 000 t of uranium have been mined in the Czech Republic since 1945. Six main mining areas have participated in this production; a small amount has also been extracted as part of geological exploration in other regions. Uranium deposits in the Czech Republic (fig. 1) occur in the Bohemian Massif, which represents a denudation relict of the Variscan mountains and one of the greatest uranium-bearing provinces in Europe. Uranium mineralisation is represented here by endogenous and exogenous deposits: the endogenous deposits being confined predominantly to basement series and granitoid masses, and the younger, exogenous deposits confined to Permian-Carboniferous, Cretaceous and Tertiary platform formations.

The endogenous deposits are situated in the areas of Příbram, West Moravia and West

Bohemia and are formed by highly dipping ore bodies of zone, vein and metasomatic types situated in compact rocks. The prevailing thickness of ore mineralisation ranges from 1.5 to 2.0 m, and less frequently up to 10.0 m. The depth range of mining was usually from the surface to a depth of 600–700 m. The deposits of Zadní Chodov (1250 m) and above all Příbram (1550 m) were mined at great depth and the deposit of Rozna (1200 m) is still being exploited. Exogenous deposits are found in the Cretaceous sediments of North Bohemia. They are represented in places of uranium mineralisation by sandstones and siltstones. Here we find subhorizontal ore bodies of great thickness at a depth of about 250 metres. Straz pod Ralskem and Hamr are two such deposits that were exploited in the Czech Republic. The deposit of Hamr was exploited by underground mining with backfilling the worked-out stopes with a consolidated material, and the deposit of Straz pod Ralskem was exploited by the acid leaching of uranium from the ore directly in ore bodies (*in situ* leaching). With regard to the specific hydrogeological conditions and their different methods of decommissioning, this paper will not deal with the deposits of Hamr and Straz pod Ralskem.

Impact of uranium mine closure on groundwater in czech republic

Czech uranium deposits were abandoned, with the exception of Rozna deposit between 1958

and 1992. When uranium ore exploitation was finished and the mine dewatering stopped the process of spontaneous mine flooding started. Depending on excavated volumes, the depression cone area and the hydrogeological conditions of the deposit, this process took several years for each mine. In the case of deposits abandoned in the 1990's, conditions for proper mine water management were created in advance. Groundwater is pumped from the shafts, in order to preserve groundwater level below the decant level, to surface water. After treatment it is discharged to surface streams. This ensures that shallow groundwater and surface water is not threatened by uncontrolled discharges of contaminated water from flooded mines. All these deposits are systematically monitored and as soon as water quality corresponds with the limits approved by the Czech Inspectorate of Environment (CIZP) for mining site under closure the groundwater pumping can be stopped (Hajek *et al.* 2006).

Monitoring of uranium mine waters' chemical composition in the Czech Republic has been carried out systematically since the beginning of their opening and exploitation. Part of the information is currently archived in the state-owned enterprise DIAMO in Straz pod Ralskem which has been managing all abandoned uranium mines in the Czech Republic since 1990's, *i.e.* it also bears the responsibility for consequences of former uranium exploitation and processing. DIAMO, s.p. carries out systematic monitoring of abandoned mines' selected locations. Due to the tradition of uranium mining in the Czech Republic and the existence of uranium deposits abandoned from 1958 to 1992, the studies of uranium mining impacts on hydrosphere constitute valuable experience for countries with developing uranium mining. The aim of this article is to assess impacts of uranium mines closure and abandonment on groundwater in the Czech Republic including the evolution of mine water quality after the deposit is abandoned.

Studying the natural processes that take place in mine water on flooded deep mines is

very difficult due to the inaccessibility of the remote parts of the mine after flooding. More information is known about the regime of shallow circulation water chemistry, whose regular monitoring is possible. However, we still do not know exactly all of the processes in quasi-stagnant water accumulated in deeper parts of former mines. In a majority of cases it is not technically possible to monitor this water and describe the evolution of its physical-chemical properties and natural processes that affect them. Experience tells us that the quality of mine water on flooded deposits stratifies (Zeman *et al.* 2009; Nuttall and Younger 2004).

Water management of abandoned mines requires a combination of theoretic model studies and long-term monitoring of abandoned uranium mining sites that can bring empirical experience usable for validation of conceptual and numerical geochemical and transport models. The issue of water management of abandoned mines was dealt with in detail in monographs by Wolkersdorfer (2008); Younger *et al.* (2004).

In literature, we can find a number of experiences with detailed (sometimes even systematic) monitoring of individual abandoned uranium mining sites. The monitoring is very often connected to remediation activities on site. Carvalho *et al.* (2007) published an extensive regional study focused on detection of radionuclides concentrations in soils in 60 areas of former radium and uranium mining in Portugal. Nevertheless, systematic regional study focused on uranium mining impact on groundwater has not been found.

Methodology of study

The mine waters of all available sites of previous uranium exploitation with special focus on endogenous deposits were sampled in 2010. Several from these deposits are systematically monitored, but regularly analyzed chemical parameters of mine waters are highly limited (generally just TDS, U, Ra and sporadically sulphate, Fe, Mn, physical parameters).

Non-filtered water samples were analyzed in the laboratories of VSB-TU Ostrava (major ions and As, Cd, Co, Cu, Ni, Fe, Pb, Zn), Zdravotni ustav Ostrava (Ag, Al, Ba, Sb and Sr) and DIAMO, s. p., o. z. TUU Straz pod Ralskem (U and Ra). Uranium was analyzed by photometric analyses with Arsenazo III after separation of uranyl ions on silicagel (CSN 75 7614). Radium was determined by scintillation determination of ^{226}Ra after co-precipitation with BaSO_4 and PbSO_4 (PP-LAB-35-02). Ag, Al, Ba, Sb and Sr were analyzed by ICP-MS (CSN EN ISO 17294-2), other metals by AAS. In the field, conductivity, Eh, pH and temperature were measured by GREISINGER GMH 3430 (conductivity with precision $\pm 0.5\%$ of measured value), by WTW pH315i with pH electrode SenTix 21 (pH with precision of ± 0.01 pH), and by GREISINGER GmbH 3530 using the electrode GREISINGER GE 105 BNC (Eh). Alkalinity was also determined in the field using HCL titration.

The sampling method always reflected the specific conditions of each location. In some cases (mine adits, uncontrolled discharges) gravity-flow discharges were sampled (fig. 2). In the case of stagnating shafts, shallow-water samples were taken using a peristaltic pump. In the case of shafts in a dynamic state (pumped to maintain water level), pumped water was taken.

Since traditional methods (Piper diagram) failed in differentiating among water samples described by multiple parameters, multivariate methods have been applied. We applied Principal Component Analyses PCA (Jolliffe 1986) in order to transform the original set of variables to a new set of uncorrelated variables and visualize the distribution of samples based on two main components. Cluster analysis was conducted with MATLAB using Ward-Wishard clustering strategy (Manly 1994). The code generates dendrogram with similarity/dissimilarity values for samples and a computation log with information on the individual clusters (Cressie 1993).

The Geochemist's Workbench® (Bethke 2007) and PHREEQC for Windows (Parkhurst

and Appelo 1999) software were used for geochemical modelling.

Results and discussion

Apart from the uranium, radium and basic chemical and physical parameters of mine waters, Al, Ag, As, Ba, Cd, Co, Cu, Ni, Pb, Sb, Sr and Zn were also determined. With small exceptions, they correspond to the natural background and do not exceed legal limits given by Decree No. 369/2004 Sb. Concentration limits of Al, Co and Ni (Al ≈ 14.2 mg/L vs. 0.25 mg/L limit) were exceeded in the Licomerice site and in the Dylen site (below mine dump). In both cases, the enhanced metal concentrations are related to low pH (5.30 Licomerice site, 4.24 Dylen site), which increases metal mobility.

With respect to the goal of this work, our attention focused on radionuclide concentration in mine waters. The uranium mobility in mine water is controlled by a number of factors, among which pH, Eh and concentration of major ions are the most important.

Uranium concentration in most cases ranges up to 0.45 mg/L. Water discharges from adits of mines abandoned more than 40 years ago showed values below or slightly above the Maximum Contaminant Level (MCL) of US EPA (2011) for uranium in drinking water (0.03 mg/L) given by the Safe Drinking Water Act. These discharges also mostly met the provisional guideline value of U in drinking water 0.03 mg/L (WHO 2011). Limits for uranium in drinking water are, in Czech Republic, regulated by the State Office for Nuclear Safety concerning radiotoxicity and by Head Health Officer directives. Radiotoxicity reference and limit values are given by the Decree of State Office for Nuclear Safety 499/2005 Sb, appendix 10. Toxicity limits for uranium concentrations in drinking water are given by the Directive of Head Health Officer CR OVZ-32.4-19.4.2007 (0,015 mg/L since 1.1.2010).

Concentrations of U between 0.45 and 1.23 mg/L were only detected at remediation stations of Rozna and Olsi Mine. Rozna is an active dewatered mine, and on the Olsi Mine is

the mine where uranium is exploited by pumping from a deep well. Only three samples showed anomalously high uranium concentrations. These samples were taken from the pumped Příbram shafts J-19 and J-11A – No. 1 (5.61 mg/L) and No. 2 (5.44 mg/L) and the sample from a deep well at the Olsi Mine (6.43 mg/L). All these samples quite clearly represent waters of deeper circulation. Increased values of uranium content in these waters correspond well with the conclusions regarding mine water stratification.

Activity concentration of ^{226}Ra on most sampled locations range between 0.03 and 1.85 Bq/L, and elevated values (max. 17.1 Bq/L) were detected at two mining sites: Vitkov and Okrouhla Radoun. These values relate to a naturally increased background where radium is a product of uranium decay in uranium-bearing granitic rocks. In the case of radium content in mine waters, complicated and indeterminate trends depending on the time passed from the mine flooding are manifested. At a majority of deposits, increases with a low correlation coefficient appear.

In order to study natural relations among samples multiparametric analyses were conducted. The cluster analysis with use of non-standardized samples by the Ward-Wishard cluster strategy resulted in separation of 6 clusters. The analysis shows that clusters are separated on the basis of sample membership

to a geological environment: type of deposit, except for actively pumped shafts. The geological environment differentiates mine water chemistry especially in view of major ion content. The time after mine flooding did not manifest at cluster separation. That is why principal component analyses were elaborated. The components are linear combinations of data file parameters; in our case two first components accounts for 55 % variability of the 30-dimensional data file (metals were included into analyses). Interpretation of the PCA analysis brought a number of interesting conclusions, including the hypothesis regarding mine water evolution on abandoned uranium deposits.

Based on the results of PCA the evolution of mine water chemistry was described. In combination with the information on weights of parameters we can deduce which parameters most rapidly change over time after mine flooding. Those are especially TDS, and mainly the sulphate and some other major ion concentrations, as well as U concentration. Component 2 is rather significantly affected by pH-Eh conditions change and metal content in waters.

The mine water evolution seems to have obvious logical relation to the time from the site flooding and the origin of water sample in the respective depth level. Mine water chemistry systematically evolves from dewatered



Fig. 2 Mine water discharge from Barbora adit – Horni Slavkov

shafts and boreholes (samples correspond to a mixture of mine waters from various depth horizons with prevailing waters pumped from deeper levels) through shafts with a maintained water level up to the shafts with stagnated waters (sampled by peristaltic pump) and finally to gravity-flow discharges from old adits, shafts and uncontrolled discharges (abandoned more than 40 years ago).

Results of PCA are supported by natural relations observed at mines from the period of flooding through maintaining the water level under the decant level (preventing contamination of surface water) up to natural decant of waters either via adits or uncontrolled discharges. In course of mine water flooding, hydrochemical stratification (with solutes concentrations in mine water growing with depth) gradually develops due to groundwater inflows from various aquifers and depth levels.

Though the hydrochemical stratification in flooded deep mines is a generally accepted fact and has been recognised since 1970's (Cairney and Frost 1975; Younger and La Pierre 2000; Johnson and Younger 2002) it is not always appropriately respected when assessing mine water sampling. Water samples taken from shallow parts of shafts or mine water discharges are often assumed to represent mine water quality for the whole flooded mine.

Mine water samples, though they often represent gravity-flow discharges, represent groundwater circulations of various depths. If mine shafts are sampled, the sampling method also has to be taken into account.

The evaluation of mine water geochemical development was done using geochemical modelling (Geochemist Workbench and PHREEQC). Uranium mobility was assessed in relation to all hydrodynamic processes at site.

As indicated by results of physical-chemical parameters of monitored mine waters, individual types of mine water at uranium deposits can be differed just upon the standard measurements of pH, Eh and temperature. These parameters also affect total composition of water.

Upon the results of geochemical models, three time phases of deposit evolution can be identified. In the first phase in active mines or shortly after their closure, uranium in waters is relatively immobile depending on concentration of other compounds, especially sulphate, hydrogencarbonate and on Eh-pH condition. In the second phase uranium is dissolved out of the deposit. In the third phase more than 40 years after the deposit was abandoned, uranium no longer leaches from the deposit and poses no hazard to surface water courses. It is a typical description of deposit maturation. Geochemical behaviour of radium has not yet been reliably described, but its mobility in both oxidation-reduction and acid-base conditions is high. Crystallization (with Ba, Ca), precipitation (with Mn, Fe) and adsorption to Fe-Mn oxides, clay minerals and organic matter are considered to be the main geochemical barriers.

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