Investigation of arsenic emissions from flooded ore mines of the Westerzgebirge region, Saxony, Germany

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Abstract The Westerzgebirge ore mining region in the southern part of Saxony (Germany) is, from a geochemical perspective, characterised by high arsenic concentrations. Therefore, many mining and milling legacies are significant arsenic emitters, which lead to high arsenic concentrations in the regional surface water receiving stream Zwickauer Mulde. The paper analyses arsenic release from flooded uranium mines and includes a short discuss of the results of mineralogical-geochemical investigations of encountered arsenic bearing minerals.

Key Words Mine flooding, arsenic mobilisation, arsenic minerals

Introduction

For decades, the monitoring of flooded ore mines located in the Westerzgebirge has revealed high arsenic concentrations in mine water discharges in the order of 0.1 – 1 mg/L. At the same time, the Zwickauer Mulde being the central receiving stream in the Westerzgebirge region, also exhibits comparatively high arsenic concentrations of about 0.01 mg/L plus elevated arsenic concentrations in suspended sediments whereby the river is out of compliance with current stream water quality targets. The assessment and prognosis of mine-related arsenic emissions is one of a variety of tasks under the ongoing mine rehabilitation activities.

The Erzgebirge mountain chain extends along the south-western periphery of Eastern Germany on both sides of the border with the Czech Republic. Regional geology is characterised by crystalline and metamorphous rock formations. On a European scale, the Erzgebirge represents an outstanding metallogenetic province, its ore mineralisations are predominantly of hydrothermal and pneumatolytic origin and occur as vein or strata-bound mineralisations. Types of chemical bonding include oxidic, sulphidic, arsenidic or mixed types of bond, with some of the ore metals occurring in their elemental forms. Accompanying minerals (gangue) are for the most part oxides and carbonates. The ore deposits have been mined ever since the Middle Ages (historic mining).

After World War II, uranium ores were mined on a large scale. In the proximity of the historic Schneeberg ore mining site, the Schlema-Alberoda mining district emerged as the dominant production site with a total extraction volume of ca. 80,000 t of uranium. The mining activities impacted a densely populated area and required the rehabilitation of surface and underground uranium mining legacies following German reunification and the abandonment of the uranium mine in 1990 for economic reasons. Reclamation measures are being conducted by the national Wismut GmbH and include the controlled flooding of the Schlema-Alberoda mine.

Characterisation of mining-related sources of arsenic

In the surroundings of the Schlema-Alberoda uranium mine, geogenic, historic-anthropogenic and contemporary-anthropogenic sources of arsenic are interfering with each other. The adjacent historic Schneeberg ore mine has been in operation with interruptions from the 15th to the 20th. Underground workings developed during that period totalled a cavity volume of some 1.5 million m^3. Prospecting for uranium in the Schneeberg ore mine after WWII had revealed only small reserves. As a consequence, the mine was definitely abandoned as early as the 1950s and flooding of the mine was initiated in 1958. Now, this mine is an orphan site. As a result of continued hydraulic drainage provided by the historic Markus Semmler adit to the Zwickauer Mulde, a major part of the mine workings are air-filled. Annual flow from the flooded part of the mine is in the order of 3 to 6 million m^3. In spite of flows through the mine going on for decades now, this otherwise low polluted mixed water still exhibits elevated arsenic levels of about 0.3 mg/L (Meyer et al. 2008).

Bordering the Schneeberg site to the northeast, the Schlema-Alberoda uranium mine of Wismut GmbH was mined from 1947 through 1990. Reaching a maximum depth of 1.800 m below ground surface, the underground workings comprise a cavity volume of currently ca. 37 million m^3. The mine layout comprises vertically 62 levels with a total tunnelling length of 4.200 km, as well as 80 pit and blind shafts and a great number of other vertical raises. These drives served to explore, develop and mine several thousand ore blocks using ‚cut and fill' mining techniques. Approximately 10 million m^3 of backfill were left behind in the worked-out areas (predominantly self-fill).

In addition to a number of small-scale sludge ponds, the intense mining activities produced above ground mine dump complexes with a footing of some 3 km^2 and a bulk volume of ca. 45 million m^3. Annual seepage draining from the mine dumps to the Zwickauer Mulde is in the order of ca. 0.7 million m^3 with arsenic levels varying between 0.05 mg/L and individual peaks of up to 0.4 mg/L (s. Fig. 1). With the deposit largely depleted, the uranium mine was decommissioned by 1990 and then closed-out on a scheduled basis. Multistage mine flooding initiated in 1991 is now in its final phase.

The rising flood water is contaminated and undergoes chemico-physical treatment (removal of U, Ra-226, As, Fe, Mn) at the Schlema-Alberoda WTP before discharge to the Zwickauer Mulde. Annual flood water volumes range from 6 to 8 million m^3. During the flooding period, arsenic levels in the flood water decreased from an initial level of 7 mg/L to currently 1 mg/L. Current indications would increasingly suggest a stagnation of concentration levels. Depending on stream flow conditions in Zwickauer Mulde the treatment goal for arsenic varies from 0.1 to 0.3 mg/L. Residual arsenic levels in treated flood water are for the most part in the order of ca. 0.1 mg/L (s. Fig. 1).

Taking additional data from other flooded mines in the Westerzgebirge region into account it becomes quite obvious now that - in comparison to other contaminants either exhibiting continuously decreasing levels or being already washed out – arsenic, in contrast, will continue to be emitted in significantly elevated levels and pollute the receiving streams. Against this background mineralogical-geochemical investigations were performed with a view to identifying the release mechanisms.

Mineralogical-geochemical studies on arsenic release

Encountered arsenic minerals

While the Schlema-Alberoda deposit was prospected priority was on uranium and on radium. As arsenic was largely disregarded this precludes any attempt to quantify arsenic reserves in retro-

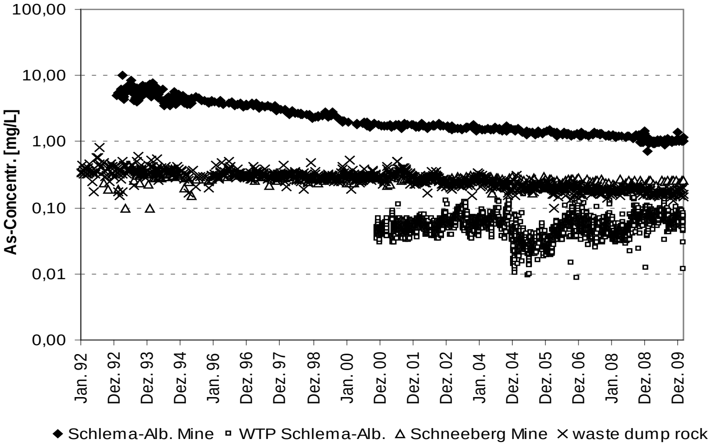

Figure 1 *Concentration vs. time plots for arsenic in different water streams of the Schlema region based on monitoring data for 1992—2010: a) Mine water Schlema-Alberoda, b) treated mine water of the Schlema-Alberoda mine (WTR), c) mine water Schneeberg, d) typical seepage of waste rock dumps of the Schlema site*

Table 1 *Typical ore mineralisations of arsenic-bearing minerals in Westerzgebirge region*

Formation	Bi-Co-Ni-U-Ag	Ag-S	Pb-Zn-Cu-Ag
As-Minerals	Elemental Arsenic [As]; Loellingite [$FeAs_2$]; Co-Ni-Fe mixed arsenides [$(NiCo)As_3$]	Elemental Arsenic [As]	Arsenopyrite [FeAsS]
Mines/ mine section	Throughout Schlema-Alberoda and Schneeberg mines	Near surface in both mines; Schlema-Alberoda also at great depth	Only locally in both mines

spect. Elevated arsenic levels in ores encountered in deeper mine sections during later mining phases required the application of specific occupational safety measures. Mineralogical classification of arsenic-bearing ore minerals in qualitative terms with due respect to the Schneeberg ore mine is shown in the subsequent table.

Investigation material and methods

In specialist literature, very few published studies consider the mobilisation behaviour of deposit-specific arsenic-bearing minerals, except for arsenopyrite and elemental arsenic (Gmelin 1952). Therefore exemplary studies in terms of empirical-analytical knowledge gain were carried out. For this purpose and based on the classification as outlined in Table 1, typical ore samples were selected from mine dumps under rehabilitation. For decades, these minerals had been exposed to natural weathering processes under pH-neutral or oxidising, respectively, environmental conditions.

Mineralogical tests were conducted on the selected basic specimens in terms of a more detailed characterisation of primary and secondary minerals. In addition to geochemical and x-ray phase analyses, comprehensive microscopic studies as well as microprobe investigations and solubility tests were performed on polished specimens (Klemm et al. 2007). The samples considered had been exposed in situ both to oxygenic mine dump seepage as well as to low-oxygen mine water. At regular intervals the samples were removed from the solubility tanks and microscopically examined for hydro-chemical material removal. On the basis of recorded abrasion, mass losses due to water solubility were assessed in quantitative terms. More details of this investigation will be published in a special paper next year.

Results

Mineralogical investigations revealed that the major portion of selected arsenic-bearing ore samples exhibited significant weathering phenomena. Formation of arsenic-bearing oxidation products (oxides, arsenates) was not only determined by the chemism of primary ores but also by their internal structure or texture, respectively. Internally jointed ore samples, for instance, as well as arsenides made up of dendritical crystal structures exhibited abundant oxidation formations. Samples of elemental arsenic in particular featured weathering portions [As_2O_3] of up to 35 %. Solubility tests on polished samples provided first cut data on solubility rates. Selected results of estimated material losses are provided in Table 2.

Test results permit a qualitative classification of basic specimens into stability classes of water solubility. Elemental arsenic turned out to be utmost instable and therewith water-soluble, fol-

Table 2 *Averaged estimates of As mass losses derived from solubility tests*

As Mineral	Mass loss [$kg/m^2 * a$]	
	Mine dump seepage	Mine water
Elemental Arsenic [As; Sb depleted]	3.6	3.0
Elemental Arsenic [(As; Sb rich]	2.8	3.0
Niccolite [NiAs]	1.4	1.3
Rammelsbergite [$NiAs_2$]	0.2	0.2

lowed by low-sulphur mixed arsenides with differing Co-Ni-Fe conditions. Next in line were pure Co and Ni arsenides. Loellingite and arsenopyrite showed highest stability (low water solubility). In addition to the type of mineral, solubility is also determined by its microstructure and the type of accompanying minerals (gangue). Particularly high and dynamic arsenic mobilisations from elemental arsenic arise from its high degree of oxidation for the benefit of arsenolithe (As_2O_3) which is relatively well soluble in water. Weathering crusts of arsenates (Fe, Co, Ni), on the other hand, seem to have a solubility-decreasing effect. Significant dependence of solubility from the water redox potential was not established.

Conclusions

The investigations carried out provided basic evidence of the presence of a significant potential of soluble arsenic. Mining activities apparently gave rise to comprehensive weathering of primary arsenic-bearing minerals. In accordance with the established stability classes it might be assumed that instable arsenic-bearing ores provoke particularly intense mobilisation of arsenic during initial mine flooding stages but will then deplete over the mid-term. In contrast, more stable arsenic minerals can contribute to comparatively moderate but long-term arsenic emissions as reflected by current flood monitoring data. According to investigation results such residual arsenic emissions are not dependent on the redox condition of the flood water. The presence of hydroxidic/amorphous iron compounds within the flooded mines is the only known limiting factor as they may provoke effective arsenic adsorption. Given the absence of pertinent exploration data on arsenic-bearing ores in particular, a defendable prognosis of arsenic emissions from the Schlema-Alberoda and Schneeberg mines will continue to present a major problem.

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