

EVELOPMENT OF A NOVEL APPROACH TO SOURCE MANIPULATION TO BE APPLIED AT THE FLOODED UNDERGROUND URANIUM MINE AT KÖNIGSTEIN, GERMANY

ULF JENK¹, MICHAEL PAUL¹ and RALPH SCHÖPKE²

¹WISMUT GmbH, Chemnitz, Germany; E-mail: ulf.jenk@wismut.de

²Brandenburgisch-Technische Universität Cottbus, Germany;
E-mail: schoepke@tu-cottbus.de

ABSTRACT

Within the WISMUT project, dedicated to rehabilitate the legacy of the former East German uranium industry, the flooding of five underground mines is a crucial element. Currently the mines are nearly completely flooded, and some 10 million m³ of contaminated mine water have to be annually cleaned over the long-term. In order to optimize long-term water treatment and minimize treatment costs a set of alternative approaches directly influencing the mine water body has been investigated at different scales. The paper outlines the development of a special approach for the Königstein site. After implementation of an immobilization technology in local parts of the Königstein mine (immobilization of former leaching blocks) efforts are now focused on approaches which will allow to further influence the water body of the flooded mine from ground surface. The general idea is to inject appropriate chemicals by a water stream using boreholes. Investigations performed on laboratory scale show that sodium sulfite (Na₂SO₃) raises pH and lowers redox potentials in acidic flooding waters, whereas heavy metals and uranium concentrations are lowered. To upscale these results for technical application, a pilot test has been running in a reactor of 1.3 m³ using characteristic materials (rocks, flooding water) at the Königstein site since March 2007. First results show that the pH-buffering capacity of sodium sulfite is insufficient. In a second step an optimized injection solution, containing additional sodium hydroxide, is being tested. Analysis of the observed geochemical effects and an outlook for upscaling to a technical application (pilot test) will be discussed in the paper.

1. INTRODUCTION

In the wake of World War II, the Soviet occupying power started to explore and mine uranium deposits in East Germany. Until 1990, cumulative production of some 216,000 metric tons had made Soviet-German Wismut AG the world's third largest uranium producer. More than 40 years of unrestricted mining left behind a multitude of unsecured radioactively contaminated waste sites in densely populated regions in Saxony and Thuringia.

After German reunification, the German federal government assumed the responsibility to clean up the legacies of uranium mining operations (Federal Ministry of Economics and Technology 2000), (Figure 1).

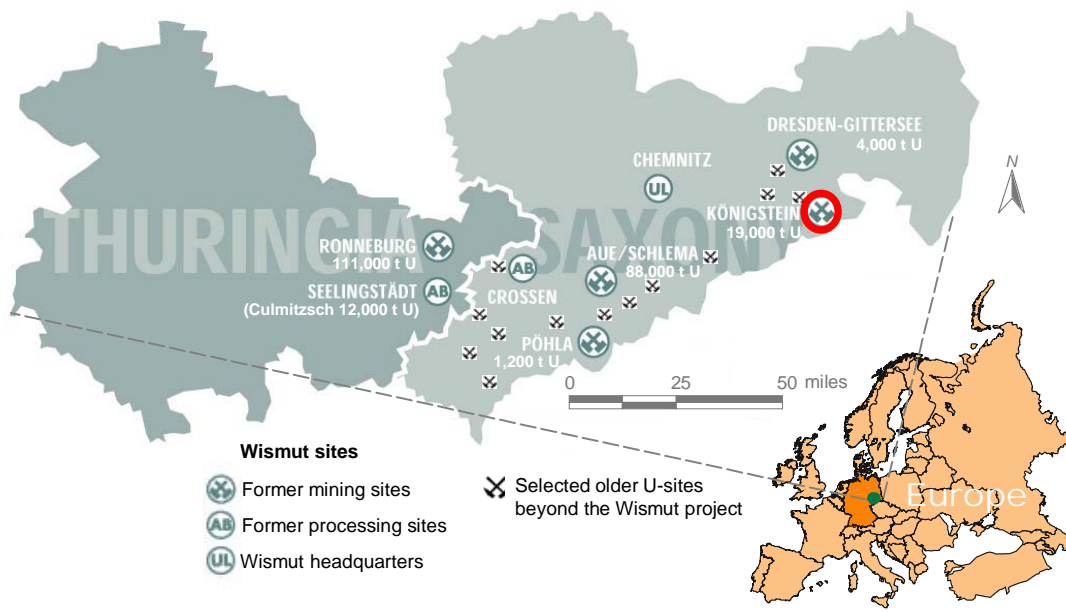


Figure 1. Wismut remediation area

Among the objects to be remediated were some 1,500 kilometers of underground workings. Initiated in 1991, decommissioning and safe closeout of the former uranium mines were among the most prominent core tasks under this large-scale environmental restoration project. The task at hand consisted of closing adits, shafts, and mining fields of several large uranium mines with a total volume in excess of 80 million m³ in a technically safe, environmentally friendly, and low-cost way (Paul et al. 2006).

By the middle of 2009 the mines are nearly completely flooded, and some 10 million m³ of contaminated mine water have to be annually cleaned over the long-term. Another long-term task will be mine environmental monitoring.

The remediation of the Königstein mine near Dresden is a very special case. The mine is situated in an ecologically sensitive and densely populated area (Figure 2). From the early sixties through 1990, approximately 19,000 t of uranium were produced.



Figure 2. Aerial view of the surface installations of the Königstein uranium mine, administrative buildings, mine shafts and water treatment plant to the left-hand side, on the right the partly covered mine dump with the Elbe River and the Königstein fortress in the rear

The uranium was extracted from the 4th sandstone aquifer, the deepest of four hydraulically isolated aquifers in a Cretaceous basin, initially using conventional mining methods, but later an underground block leaching method using sulfuric acid (2 to 3 g/l H_2SO_4) was implemented. It was especially due to the reactions of the oxidizing sulfuric acid that the geochemical nature of the deposit was substantially changed, with a high level of pollution remaining within the deposit, mainly sulfate, heavy metals and naturally occurring radionuclides.

Considering the existing pollution potential and the importance of the overlying aquifer a concept of controlled flooding was developed. Using a drift system in the deepest part of the mine (downstream) allows collection of draining flooding water and a controlled raise of water level. Collected water is treated by a conventional technology, and discharged to the Elbe River.

At present, the mine is almost half flooded, with flooding water being acidic and strongly oxidizing (Table 1); contaminant levels have significantly diminished by several years of active wash-out process.

Table 1. Hydrochemical parameters of the flooding water of the Königstein mine, May 2009

Parameter	Concentration	Parameter	Concentration
pH	2.7	Al (mg/L)	14
Eh (mV)	700	Zn (mg/L)	6
el. cond. (mS/cm)	1.7	As (mg/L)	0.015
SO ₄ (mg/L)	648	U dissolved (mg/L)	7
Fe (mg/L)	55	Ra-226, dissolved (Bq/L)	9

During further flooding, which is still object of a permitting procedure, levels are anticipated to rise in an initial phase as new mine sections with soluble contaminants will be subject to flooding.

Decline due to natural attenuation by dilution and wash-out of concentrations of hazardous substances in the water is only slow (Jenk and Schreyer 2001). With regard to pertaining discharge limits into the Elbe River and recently adopted European legislation on water protection WISMUT expects that water treatment will be needed over a long-term period.

2. IN-SITU-TREATMENT

To shorten the period for conventional water treatment and to comply with obligations of flooding permissions alternatives are investigated by WISMUT. In the focus are measures to minimize the release of contaminants into the water in-situ, i.e. to immobilize radionuclides and heavy metals locally at the site where they are currently released from their sources.

Prior to mine abandoning, leaching blocks in the mine's southern field were treated with a newly developed immobilization technology. Mobilized contaminants in the sandstone were precipitated by the injection of a solution containing Ba ions, by co-precipitation with Barite (Jenk et al 2004).

Currently last open galleries and shafts are being abandoned or backfilled. Finally, the mine will be flooded completely. Due to pumping and natural water inflow into the flooded mine (4th aquifer) convection will develop in the flooding water body from south to north. During this time period it is possible to influence the flooding water body from ground surface by injection using boreholes.

Basically, an influence of the hydrochemical conditions must have a lasting effect to restore 'close-to-pre-mining' conditions to the extent feasible. This requires that in the flooding water the redox potential must be lowered, and the pH value must be raised. As a consequence, it is expected that dissolved radionuclides and heavy metals will be fixed inside the mine and their levels reduced in the flooding water.

According to those conditions a chemical approach is being in development: injection of substances with the capacity to reduce redox potential and raise pH. The goal of the approach consists in immobilizing contaminants at their source, i.e. in the flooding water body.

Mere pH buffering of the flooding water body by addition of lime slurry would be a poor remedy as gypsum precipitation and ensuing incrustation will prevent the slurry from reaching acid waters in the sandstone leaching blocks. As a response to this boundary condition and with a view to preventing the introduction of hazardous substances, sodium sulfite was considered as a potential injection substance. It would have the additional advantage of producing only sodium and sulfate ions as reaction products and which are already present in the mine's contaminant inventory.

In a first step laboratory tests have been carried out using sodium sulfite to lower redox potential and raise pH level in flood water samples. Expected change of chemical milieu was observed and concentrations of heavy metals and uranium in flooding water dropped significantly.

3. PILOT TEST

Transfer of these findings to potential application in the flooded mine requires, as a next step, the validation of the observed effects in a scaled-up pilot test. Based on laboratory test data, a test concept was developed and a pilot plant designed.

At the end of 2006, the pilot plant housed in a container with a reactor volume of 1.3 m³ was put in place at the Königstein site. About 11 m in length, the reactor is filled with rock species that are typical of the site and with flooding water to imitate the mine at a reduced scale. In addition to inlet and outlet measuring points for feed and effluent, the tube features 4 intermediately spaced sampling points (Figure 3).

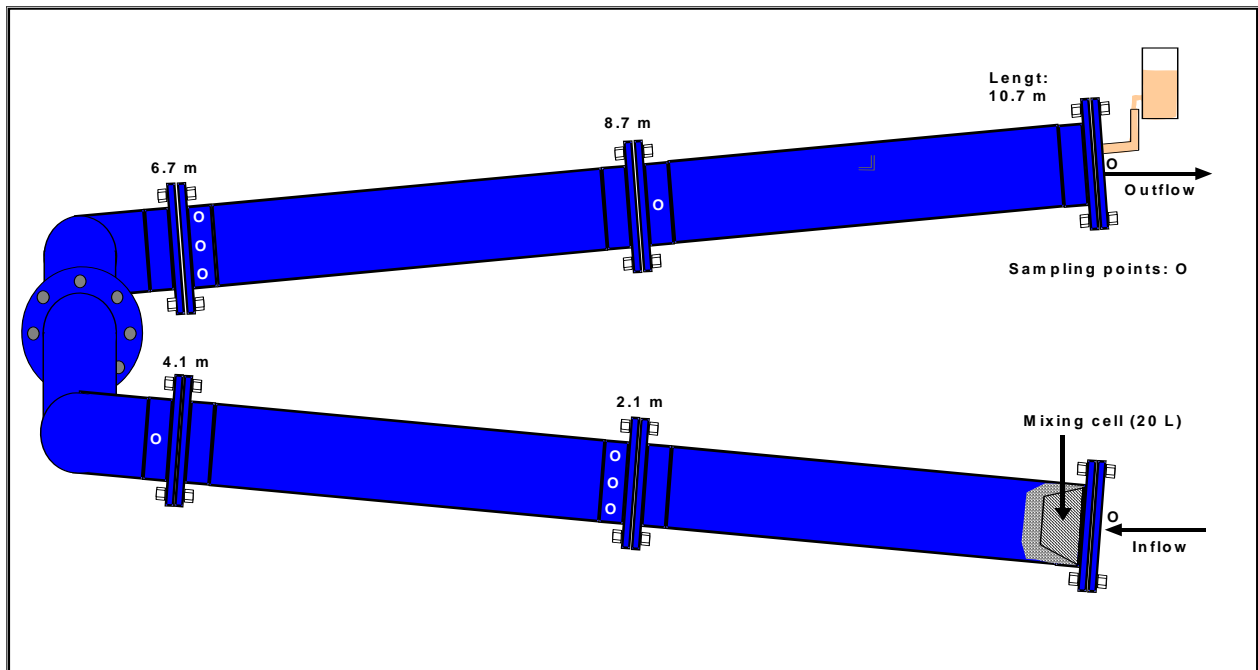


Figure 3. Experimental set-up at the Königstein mine site, schematic lateral view of reactor (blue: polyethylene reactor, yellow: overflow tank)

A horizontal flow reactor was installed inside a container to imitate at reduced scale conditions within the flooded mine such as backfilled drifts, blasted rock, joints, and areas of residual mine air.

The reactor was filled with mine-typical broken rock. Table 2 lists key parameters of the test reactor:

Table 2. Parameters of test reactor used for sulfite injection pilot test

Parameter	unit	value	parameter	unit	value
Length	m	10.7	Mass sandstone	kg	1600
Inner diameter	m	0.4	Grain size	mm	5 – 22.4
Volume	m ³	1.3	Flow rate	L/h	approx. 0.3

Sub-Test 1: Addition of Sodium Sulfite

A first pilot test on the effect of sodium sulfite was run from March 2007 to February 2008. The Brandenburg University of Technology (BTU Cottbus, Germany) contributes to the scientific analysis of the results.

The rock-filled reactor was first topped up with flooding water (pH = 2.7, Eh = 700 mV). Following 2 weeks time of exposure during which substances were dissolved from the broken rock the reactor was then continuously fed with sodium sulfite added flooding water (volume flow rate ca. 0.3 L/h). Sulfite dosing was by an upstream mixing cell and pH adjustment to pH = 6.5.

Results

The experimental set-up proved successful and provided useful results. Basically, the reactor represents a saturated horizontal filter. The heterogeneous flow behavior can be explained by the sodium retention time as the presence of three flow channels. At a filtration rate of ca. 6 cm/d the pore space was exchanged almost four times. Sampling at the outlet was spaced 2 days, at the other sampling points at intervals ranging from 2 weeks to 3 months.

Filling of the filter column with flooding water and the subsequent interaction of the broken rock with sulfite resulted in very complex reactions. These processes were attributed to precipitation and sorption processes which were traceable by modeling using the PhreeqC code.

Concentration distributions of sodium, being a largely conservative tracer, were used to determine flow patterns and behavior. The reactor may be subdivided into three theoretical flow channels with varying flow rates.

Sulfite addition resulted in the anticipated change in the reactor's hydrochemical milieu. Redox potential at the outlet was down to ca. 400 mV. In the upstream reactor section, pH-value rose to ca. 6, at the outlet to ca. 4. Hence, the desired milieu modification was basically demonstrated.

While iron was precipitated as iron(III) hydroxide, proportionate reduction of iron to iron(II) was also observed. Also, aluminum was fixed as hydroxide within the pore space. Partly uranium was fixed in the pore space, probably by co-precipitation along with Fe/Al hydroxides. Precipitation of uranium (4) minerals could not be found.

On the whole it was established that sodium sulfite was able to diminish the redox potential while pH increase was insufficient. Very high additions of sodium sulfite are required to adjust pH to > 5.

Sub-Test 2: Addition of Sodium Sulfite and Sodium Hydroxide

With a view to optimizing the injection solution, a second test phase was run from February 2008 to February 2009. In order to achieve efficient contaminant fixation, pH was to be adjusted to 6.5, and sodium sulfite was only intended to bind oxygen dissolved in the flooding water.

Both lime water and sodium hydroxide would present themselves for pH increase. The use of sodium carbonate was discarded because of the potential for uranium mobilization by the formation of uranyl carbonate complexes. Preliminary tests on the effectiveness of lime water showed precipitation of Hannebachite (calcium sulfite) part of which turned into gypsum. With regard to its high incrustation potential, the use of lime hydrate to increase pH was discarded.

Based on preliminary test results, an injection solution was developed which contains sodium hydroxide to buffer the acidic flooding water into the neutral range as well as sodium sulfite to bind dissolved oxygen.

Preliminary Results

The pilot test is targeted at developing a suitable injection solution to buffer the acidic and oxidizing flooding water body. The effect is to extend into the pore space of the leached sandstone rock. Hydrochemical data of the 2nd test phase are currently available. Opening of the reactor and analysis of the sandstone material and of solid phases formed will be performed next.

Milieu change towards the desired pre-mining conditions occurred in the reactor (pH ca. 6.0, Eh ca. 400 mV). Sludge was precipitated which predominantly consists of amorphous iron and aluminum hydroxide as well as of proportions of sulfur and silicon. Bonded to the sludge were heavy metals and natural radionuclides (co-precipitation, sorption). There was no reduction of iron(III).

Concentrations of key contaminants diminished to significantly lower levels. The combined addition of sodium sulfite and sodium hydroxide during the 2nd test phase resulted in the following reduction rates of solved pollutants:

- | | |
|---------------|--------------------|
| 1. Co, Ni, Cd | 30 – 50 % |
| 2. Zn | > 60 % |
| 3. U | > 90 % |
| 4. Ra | 50 % |
| 5. Fe, Al | almost completely. |

4. FORE CAST

A third test phase is running throughout the year 2009 during which the long term stability of contaminant fixing shall be tested. In order to allow a worst case consideration, the reactor will be fed with original flooding water. The degree to which remobilization of precipitates will occur in preferential flow channels and in the pore space of sandstone rock will be of particular interest.

A synopsis early in 2010 will evaluate the efficiency and sustainability of the approach. This will also include an economic feasibility study. In case of a positive outcome, a field test will be performed within the flooded mine to test the effectiveness of milieu change by injection from ground surface using existing boreholes. The final goal will be large scale application of in situ treatment of the entire flooding water body.

5. REFERENCES

- Federal Ministry of Economics and Technology (2000) „WISMUT - New Horizons through Remediation“, www.bmwi.de.
- Jenk, U., and Schreyer, J. (2001) „Pollutant Release Level Prognosis – A Major Input into the Flooding Concept for the Former ISL Uranium Mine at Königstein (WISMUT Germany)“. Proceedings of 8th International Conference on Environmental Management, September 30 – October 4, Bruges, Belgium.
- Jenk, U., Paul, M., Ziegenbalg, G., und Klinger, C. (2004) „Alternative methods of mine water treatment-Feasibility and technical limitations for a full-scale application at WISMUT’s Königstein mine site (Germany)“ Proceedings of the 8th International Mine Water Association Congress, Newcastle.
- Paul, M., Jenk, U., Meyer, J., Gengnagel, M. (2006). Source manipulation in water bodies of flooded underground mines – experiences from the Wismut remediation program. In: Proc. of the 7th ICARD, March 26-30, St. Louis MO, Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.