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TECHNICAL ARTICLE

In Situ Mine Water Treatment: Field Experiment at the Flooded Königstein Uranium Mine (Germany)

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Abstract Within the WISMUT environmental remediation programme, the rehabilitation of the former uranium mine at Königstein is a very special case due to its use of underground leaching and its location near the Elbe River. The mine water is acidic, oxidizing, and polluted with uranium and other contaminants, and must be pumped to the surface and treated. In-situ water treatment approaches have been investigated to optimise further flooding and shorten the period of conventional water treatment. In 2010/2011, a field-scale experiment was carried out: about 120 t of alkalinity were successfully injected into the partially flooded mine. Tracer signals and geochemical reactions achieved general expectations. Based on the results, a site-specific technology concept was developed to flood the mine to its natural decant level.

Keywords Alkalinity · Field experiment · In situ mine water treatment · Injection

Introduction

With a cumulative production of about 220,000 tonnes (t) of uranium, the former East German uranium mining company SDAG WISMUT was one of the world's largest uranium producers. When more than 40 years of uranium mining in Saxony and Thuringia came to an end in 1990, the operations left behind a great number of radioactively contaminated waste sites, many of them located within densely populated areas. In the wake of German reunification, the Federal Republic of Germany assumed responsibility for the cleanup of these legacies in 1991. The German Federal government earmarked approximately 6.6 billion € to implement Europe's largest environmental restoration project. The former Soviet-German mining company was transformed into a government-owned enterprise, Wismut GmbH, to rehabilitate the former mining and processing sites and ecologically restore the affected regions. Physical operations, such as the closure of mines and the rehabilitation of waste rock piles and plant areas, were to a large extent completed by the end of 2012. Water management at the sites, with particular focus on the treatment of contaminated waters, is the most challenging long-term task that remains.

The Königstein mine site is located within the Pirna Cretaceous basin south of Dresden, Saxony, near a protected landscape area bordering the Sächsische Schweiz National Park (Fig. 1). The Königstein uranium deposit is associated with the lowest of four sandstone aquifers, which are hydraulically connected to the Elbe River. The deposit extends across about 25 km^2, of which some 6 km^2 were developed for mining, with the overlying third aquifer being partly and the fourth aquifer being completely dewatered within the range of the mine. Underground oxidation of sulphides exposed by the dewatering has generated high levels of acidity.

In 1984, conventional mining at the site shifted to an underground in situ leach technology using dilute sulphuric acid as a response to decreasing uranium grades in the mineralized sedimentary rock. Especially due to the reactions of the oxidizing sulphuric acid (2–3 g/L H_2SO_4), the geochemical nature of the deposit was substantially

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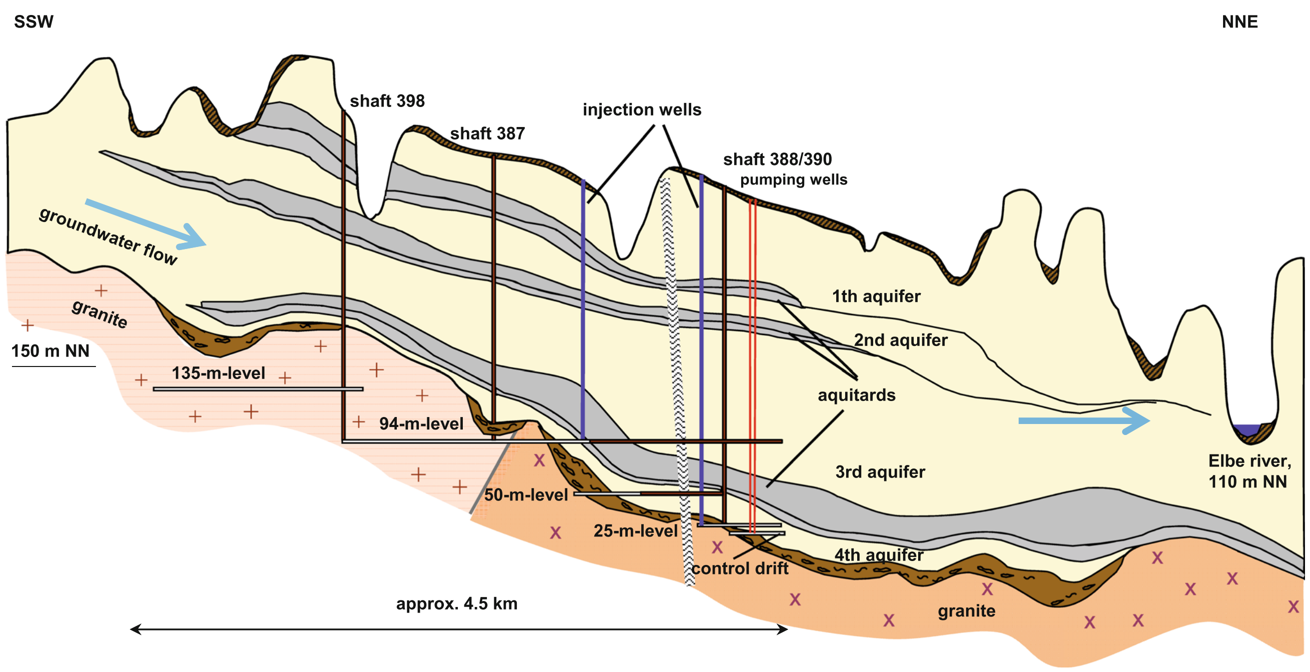

Fig. 1 Regional setting of the Königstein mine site (FBL: pumping wells)

changed and uranium and other metals, especially iron, were mobilized. Simply expressed, mobilization of uranium, which exists in the ore in a reduced oxide form (UO_2), occurs by oxidation (Eq. 1) and acidic dissolution (Eq. 2):

$$UO_2 + 2\,Fe^{3+} \rightarrow UO_2^{2+} + 2\,Fe^{2+} \tag{1}$$

$$UO_3 + 2H^+ + SO_4^{2-} \rightarrow UO_2^{2+} + SO_4^{2-} + H_2O \tag{2}$$

in which iron is re-oxidized by the dissolved oxygen of the leaching liquor. In the sulphate-rich leaching liquor, the uranyl-ion predominantly exists as sulphato-complexes ($UO_2[SO_4]^0$, $UO_2[(SO_4)_2]^{2-}$, $UO_2[(SO_4)_3]^{4-}$).

When uranium production was terminated in 1990, the mine had produced about 19,000 t of uranium, including some 6,000 t by in situ leaching. More than 50 million t of sandstone had come into contact with the acid leach liquor. Due especially to reactions with the oxidizing sulphuric acid, high levels of soluble contaminants remained in the mine, especially inside the leaching blocks. The pore water in the sandstone before flooding was characterized as pH 2.0, EC 700 mV, 10 g/L SO_4^{2-}, 2–3 mg/L Fe, 200 mg/L Zn, 200 mg/L U, and 300 mg/L Al.

The mine closure and rehabilitation plan involves flooding the mine workings up to the natural level of groundwater rise. Following comprehensive preparation, stepwise controlled flooding of the mine was initiated in 2001. While flooding proceeds, the challenge is to maintain control of water-soluble contaminants in the context of restoring natural groundwater conditions and hydraulically isolating the mine from the surrounding aquifers using conventional pump and treat technology. Water level control was implemented using two pumping wells (FBL), which are connected to the northernmost and deepest mine workings, which are known as control drifts (Fig. 2). Given

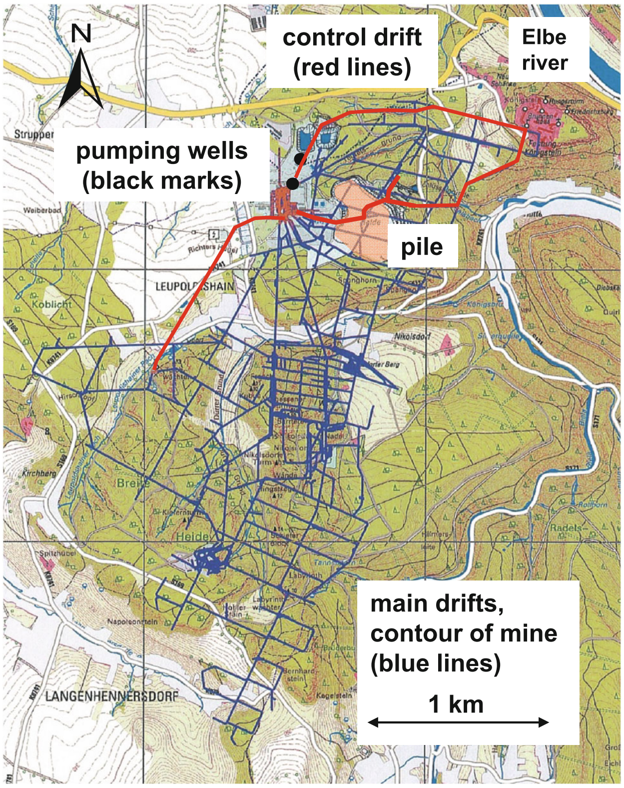

Fig. 2 Schematic geological profile of the Königstein mine (FBL: pumping wells)

that the hydrochemical environment is strongly acidic and oxidizing, the mine water has to be completely captured and treated in the mine water treatment plant (AAF). Furthermore, experience gathered from the flooding process and prognostic calculations indicate that the flood water will likely require water treatment for decades to come.

Final rehabilitation of the Königstein underground mine poses a major challenge, mainly due to the underground leaching technology used. To optimise remediation and shorten the period of conventional water treatment, several approaches for at-source control and in situ water treatment were investigated and a large-scale field experiment was carried out. This paper describes the general technological, hydraulic, and geochemical results of that field experiment.

Approaches to In Situ Remediation

From 2003 to 2005, an in situ immobilization approach based on covering reactive minerals with stable barium sulphate precipitates was investigated in mine areas that were still accessible. This immobilization approach, which is based on the injection of supersaturated barium containing solutions into former leaching blocks, was used in the southern part of the mine as part of the closure plan (Jenk et al. 2004). Since that time, R&D was carried out to improve the quality of flood water from the almost completely inaccessible mine using in situ remediation technologies, e.g. by injecting reactive substances or materials via boreholes. The intent was to alter the geochemical environment so as to precipitate dissolved contaminants in the flooded mine and thus prevent further mobilisation from the solid phase (sandstone). Two alternative approaches were considered:

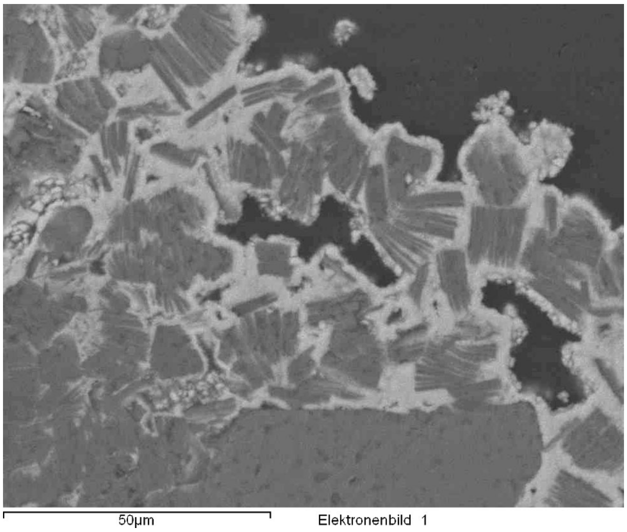

Fig. 3 Sandstone particles analysed after the test and REM micrographs

1. Stimulation of natural sulphate reduction processes in the flooded mine, investigated under a joint project by Wismut GmbH and the Grundwasserforschungsinstitut GmbH Dresden, Germany.
2. Neutralisation of the acidic flood waters by designing an injection technology for chemical buffering, in cooperation with the Brandenburgische Technische Universität Cottbus, Germany.

With regard to the first approach, we investigated bacteria-catalysed long-term processes as well as the potential of stimulating natural attenuation processes (Wismut GmbH 2010). As part of the second-mentioned approach, the effectiveness of reducing alkaline solutions was investigated in laboratory tests.

Uranium, iron, and other metals have been dissolved from the sandstones by the strongly acidic and oxidizing conditions caused by the leaching technology and natural pyrite oxidation. At the end of 2012, the flood water had the following parameters: pH 3.0, redox potential 700 mV, EC 2.1 mS/cm, sulphate 900 mg/L, Fe 70 mg/L, Al 11 mg/L, Si 9 mg/L, U 10 mg/L, Zn 5 mg/L, and Ra-226 10 Bq/L). Uranium can be removed on a large scale from acidic mine water via co-precipitation/adsorption to Fe-hydroxide or aluminosilicates produced by increasing pH, as is done in large-scale water-supply treatment facilities (Langmuir 1978; Porcelli and Swarzenski 2003; Reynolds et al. 2003). Other metal contaminants are conventionally removed in a water treatment plant using milk of lime.

A bench-scale column test was run from March 2007 to Feb. 2010 in a container unit at the Königstein site (Jenk et al. 2010). The test unit (reactor) consisted of a 10 m long horizontal flow-through tube loaded with crushed sandstone and filled with flood water from the mine. In the course of the three test phases, differently alkaline as well as unconditioned mine water passed through the reactor. The column test had three phases:

1. Testing of sodium sulphite solutions
2. Testing of sodium hydroxide—sodium sulphite solutions
3. Remobilisation test due to the ingress of unconditioned acid flood water into a formerly treated reactor section

Iron hydroxide sludge generated after neutralisation was separated before reaching the column inlet area to simulate a sedimentation space within the mine. Upon termination of each test, the sandstone was sectionally removed from the reactor and analysed.

The addition of sodium sulphide to establish anoxic conditions (test phase 1) diminished the redox potential; however, the effect of neutralisation was nullified by sulphite consumption.

In test phase 2, sodium sulphide was once again added, but this time alkalinity (NaOH) was also added. In the course of this test, hydrolysis reactions removed almost all of the iron and aluminium and reduced contaminant levels for Co, Ni, and Cd by 30–50 %, Zn by 60 %, U in excess of 90 %, and Ra by about 50 %.

Loading of unconditioned flood water ($pH < 3$, test phase 3) represented an extreme scenario and led to partial remobilisation of some precipitated materials. Remobilisation of precipitated iron was considerably reduced at $pH > 3$, and under conditions of neutral groundwater inflow, virtually no redissolution took place.

Analysis of rock samples taken from the reactor revealed that sandstone particles located at the intake area had been surface-coated with clay minerals sheathed with iron and aluminium hydroxide. The latter blocked access to the pore system within the sandstone. This type of pore system sealing occurred throughout the entire flow path (Fig. 3).

The hydrolysis of iron and aluminium and their co-precipitating and sorptive action was the most essential mechanism. Significant quantities of secondary mineral phases were detected on the crushed rocks, which in addition to the co-precipitation of contaminants, apparently also contributed to the sealing of pore openings.

In general, the bench-scale test demonstrated the potential of improving the environment and reducing contaminants by injecting appropriate alkaline solutions into the flood water of the Königstein mine. Correspondent neomineralisation found on the rock surfaces corroborated this finding and gave reason to expect probable long-term stable conditions, once there was adequate pH buffering in the flood water body (Jenk et al. 2011).

Use of NaOH instead of hydrated lime ($Ca(OH)_2$) was necessary because a couple of tests in the 1990s showed that neutralisation of acid mine water inside the mine using milk of lime caused massive precipitation of gypsum, which was unstable (resoluble) and decreased transmissivity.

Implementation of a Field Experiment

The experiment was subsequently scaled up to a field test in the flooded mine to prepare for full-scale implementation. The alkaline solution was injected into the Königstein mine site from July to Dec. 2010, with a focus on engineering the method to the mine's specific conditions (Fig. 4). The field experiment concept had been conceived in cooperation with GIP Groundwater Engineer Planning GmbH Dresden (Engineering and Hydraulic) and BTU Cottbus (Chemistry) and submitted for approval to the regulatory bodies in late March 2010. The experiment was subdivided into three partial tests (TV), with varying injection points receiving NaOH (see Table 1).

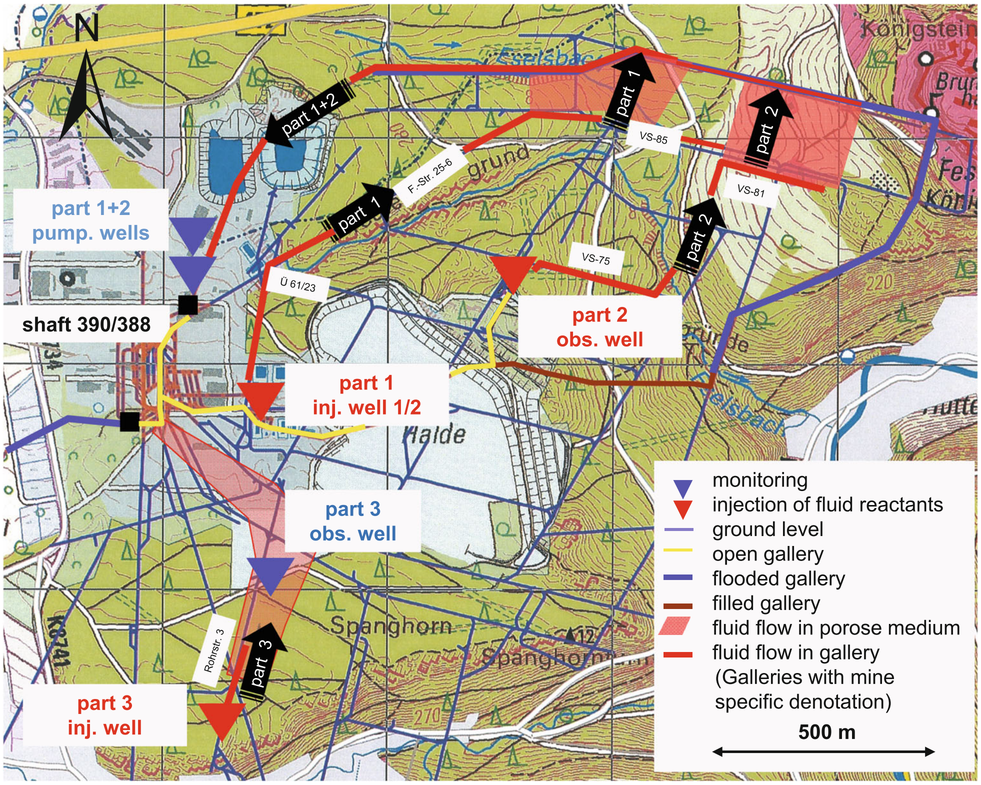

Fig. 4 Overview of partial tests and anticipated flow paths

Injection of alkaline solutions was always made from above ground. Different injection systems (groundwater observation wells and injection wells) were used during the three partial tests and various reaction spaces (drifts, cretaceous sandstones, blasted rock) were investigated. While the experiment was running, the basic flow pattern through the mine was kept unchanged to ensure proper interpretation of the findings of the partial tests. The experiment was integrated into the on-going mine flooding procedure.

Dimensioning and Sizing

During planning of the field experiment, flow paths and reaction space were identified for each of the three partial tests to ensure proper dosages of alkaline solutions. The experiment was run while flooding continued so stability was critical, which made the calculations and predictions extremely important. In the case of under-dosage, the effect of injecting alkaline solutions would have been unquantifiable and the experiment would have been worthless. In the case of over-dosage, there would have been the risk of negatively affecting the water treatment operation, which was of crucial importance for the ongoing mine flooding procedure.

Prediction of flow paths was based on an in-depth investigation of the mine workings as they now existed. Flow paths were predicted based on the updated mine layout, with due regard given to backfilled mine workings, dams, and drainage boreholes.

In addition, the duration of flow had to be predicted from the point of injection to the measurement point as well as to the main flood water collector in the northern control drift. Prognosis of flow duration was established based on anticipated flow paths using simplified calculation approaches. Given the heterogeneity of hydraulic conditions and the insufficiency of specific data on the flooded mine, the use of more sophisticated calculation approaches would not have yielded more accurate results.

Injection of alkaline solutions into connected drifts and drift systems was performed via injection wells and groundwater monitoring wells, respectively. Due to the presence of underground backfilling and dams, the flow also passes through naturally fissured rock (sandstone) and blasted rock (e.g. blasted leach blocks, drainage boreholes, pillars, etc.). These flow sections significantly influence the rate of spreading. As a consequence, the conceptual approach to the flow processes had to be based on distinct sections.

Flow along the Drifts

Laminar flow was assumed in the open drifts as well as in the roof areas of blasted rock. Therefore, the transport velocity in the drifts (v_{drift}) was calculated in an analogous way to fluid mechanics of pipe-systems, from the quotient of cross-section area (A) and volumetric flow (Q).

$$v_{drift} = \frac{Q}{A}$$

For this approach, an average infiltration rate of 100 m^3/h was adopted as the volumetric flow and 10 m^2 as the uniform cross-section area of the drift. In doing so, the flow from the mine into the drift has been disregarded, since that flow would be repressed by the elevated infiltration rate. The ensuing maximum flow rate was on the order of 10 m/day.

$$v_{drift} = \frac{100\ m^3/h}{10\ m^2} = 10\ m/day$$

Flow duration in the drifts was estimated based on past measurements.

Flow in the Cretaceous Sandstone

Flow through the Cretaceous sandstone v_Q (between the 25 m level and the north control drift as well as in the area

Table 1 Selected data regarding the experimental design and key numbers from realization of the three partial tests

Test number	TV1	TV2	TV3
Reaction space	Cretaceous sandstone	Cretaceous sandstone	Blasted rock
Impacted flood water volume, estimated (m^3)	82.500	74.250	104.650
Anticipated flow duration (days)	114	112	47
Calculated amount of alkalinity*	46.3 t KOH	29.7 t NaOH	41.9 t NaOH
	1.9 t Na_2SO_3	1.9 t Na_2SO_3	2.7 t Na_2SO_3
Total water injection (m^3)	24.200	24.200	48.300
Injection time (days)	11	10	10
Composition of reactive solution	1.4 g/L KOH	1.4 g/L NaOH	0.9 g/L NaOH
	0.1 g/L Na_2SO_3	0.09 g/L Na_2SO_3	0.05 g/L Na_2SO_3
	pH 12.2	pH 12.0	pH**

* Calculated for constant water volume of 100 m^3/h for 10 days of injection

** pH measurement not possible due to design of borehole

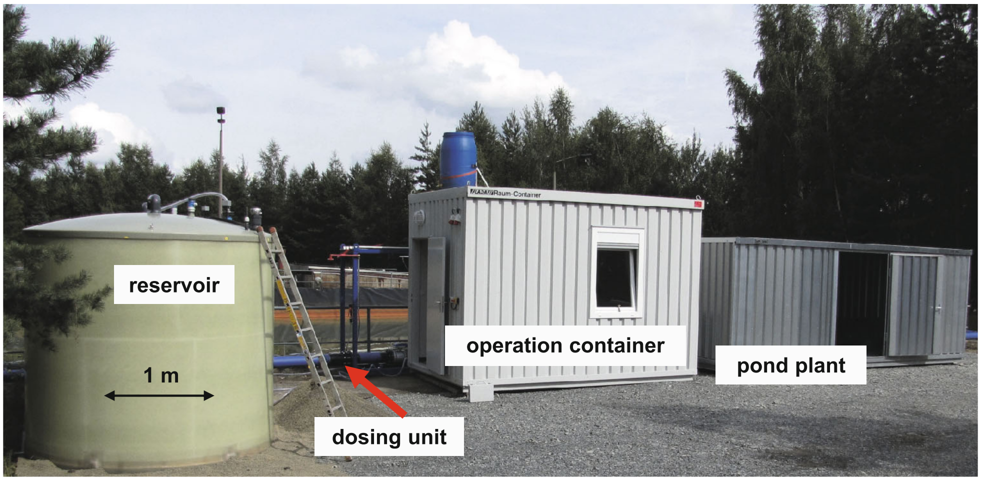

Fig. 5 Dosing station as used for partial test #1 at basin #8: dosing container, metering unit, moistening unit, and storage tank

of pillars) was modelled as flow in a porous medium. Given a corresponding size of the representative elementary volume (REV), this approach was also used to simulate fracture flows.

$$v_Q = -k \cdot grad\,h \approx -k \cdot \frac{\Delta h}{\Delta x}$$

The quotient of the difference of potential heads (h) and downstream travel distance (Δx) was chosen as the hydraulic gradient. From the water balance, the average hydraulic conductivity (k_f) of the Cretaceous sandstone was determined to be 3.3×10^{-5} m/sec, which matched the results of previous conductivity tests.

The selected model approach treated the flow as block flow. Based on theoretical considerations, a factor of 2.5 was assumed to consider hydrodynamic dispersion. This implies that a 2.5 fold pore volume exchange rate would have been required to have the totality of water stored in the pore void replaced. Colloidal transport was not considered in this simplified model.

The hydraulic conductivity for the flow between the 25 m level and the north control drift was assessed based on monitored flood water levels and water balance to provide the basis for further computations. The values were in the same range as in (Jenk et al. 2004).

Technological Implementation

Injection of alkaline solutions was performed exclusively from above ground, using any available injection wells and one groundwater monitoring well (Uhlig et al. 2010). Dosage of alkaline solutions was implemented by a mobile dosing station, designed to ensure precise dosage and speedy transfer between injection locations. Furthermore, the use of sodium sulphite required the use of a moistening unit.

The dosing station (Fig. 5) consisted of a dosing container, which housed the PC-based central control board (SPS), a staff room, hose pumps, and the electrical distribution box. Sheltered at the dosing container's rear were the metering unit, volume flow meter, volume flow controller, feeder pipes for the potassium or sodium hydroxide and sodium sulphite solutions, a static mixer, an immersion tube for the pH probe, and the sampling unit. In addition, the dosing unit contained a chemicals container, housing the moistening unit, and two 10 m^3 storage tanks to stock the alkalinity carrier (Table 1) and sodium sulphite solutions. The design of the mobile unit proved successful; moving the unit to a different site was completed during a single work week without any problems.

Results

Chemical effectiveness was demonstrated in all three partial tests. During partial tests 1 and 2, the flow distance between the injection and measuring points were about 1,500 m. Existing pumping wells (FBL Aneu and B), which were part of the mine dewatering scheme, were used as measuring locations. This configuration allowed us to monitor the effect of the injected solutions on the overall mine discharge. Since the amount of water treated during the partial tests represented less than 30 % of the total, the considerable dilution within the control drift due to the inflow of water from other sections of the mine as well as groundwater had to be considered. The injection and measuring points were only about 250 m apart in partial test 3, so the chemical effectiveness was only observed in the active area.

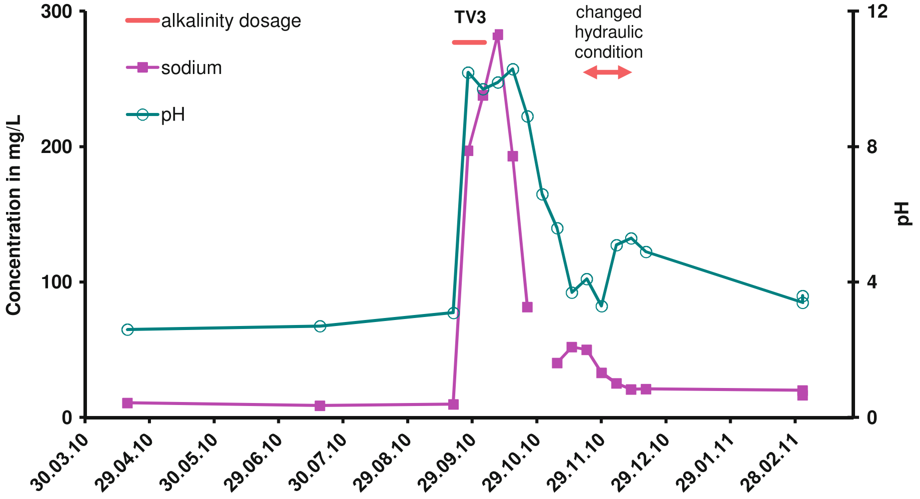

Fig. 6 pH and redox potential at GWMW 7037

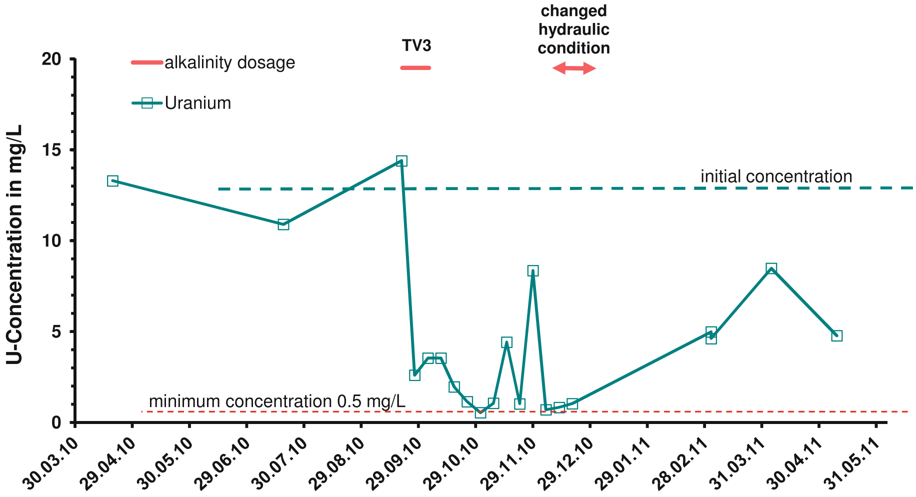

Fig. 7 Trends in uranium concentration at GWMW 7037

Chemical Effectiveness in the Active Area—Partial Test 3

Injection of alkaline solutions (Table 1) in partial test TV 3 was performed via injection well Aufg.-Brl. 4, which is part of the standard mine flooding scheme. With the onset of the mine flooding process, pH-neutral groundwater had been fed via well Aufg.-Brl. 4 for a couple of years. The measuring point, GWMW 7037, is screened within blasted sandstone at a distance of ca. 250 m downstream. Prior to the start of the partial test, water samples taken from this site showed typical flood water quality ($\mathrm{pH} < 3$, $\mathrm{U} > 10$ mg/L). A pump was installed at this measuring point for continuous sampling and was operated until the end of December 2010.

Seven days after the injection, there was a rapid tracer breakthrough and an increase of pH to ≈ 11 (Fig. 6). This demonstrated that the blasted sandstone, which had been subjected to in situ leaching, still had excellent hydraulic conductivity.

Starting with an initial U concentration of about 13 mg/L, a rapid drop was apparent at the end of the test, with concentrations as low as 0.5 mg/L. After continuous pumping was stopped at GWMW 7037, U concentrations levelled off at values between 0.7 and 1.0 mg/L (Fig. 7). Samples taken later revealed that concentrations were still below 5 mg/L. Other metals showed similar trends over time, with an even more rapid drop in concentrations compared to uranium (Fig. 8).

Due to maintenance work performed on the water treatment plant, the injection of groundwater at injection well #4 was temporarily interrupted from Nov. 09 to 13, 2010, during which time acidic water from the southern part of the mine flowed into the already treated zone. Consequently, pH levels dropped for a short period to pH 3, after which they rose again to about pH 5 without any further action being taken (Fig. 6). Uranium and metal concentrations behaved similarly, though the decrease lagged behind the rise in pH (Figs. 7 and 8).

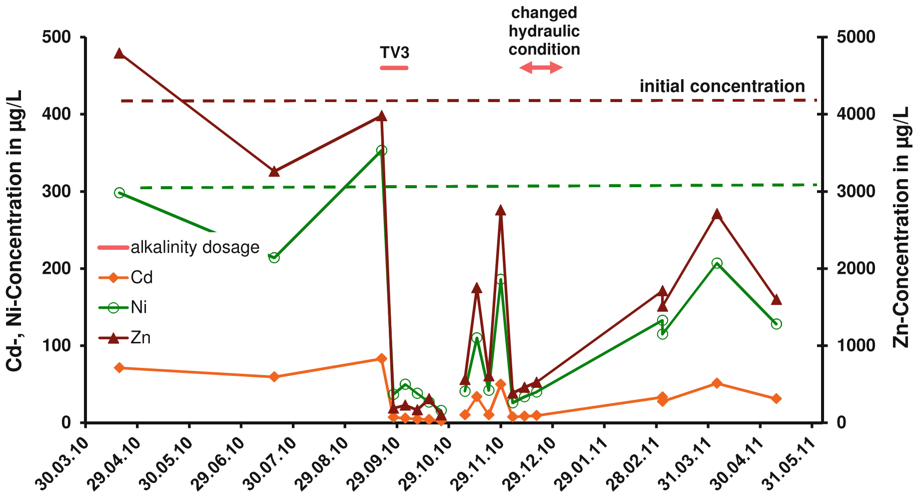

Fig. 8 Trends in concentration of other selected metals at GWMW 7037

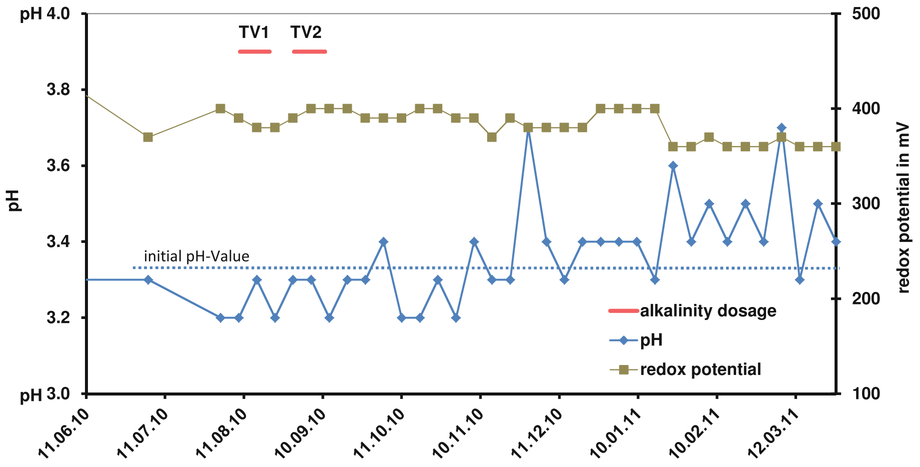

Fig. 9 pH and redox potentials at FBL B

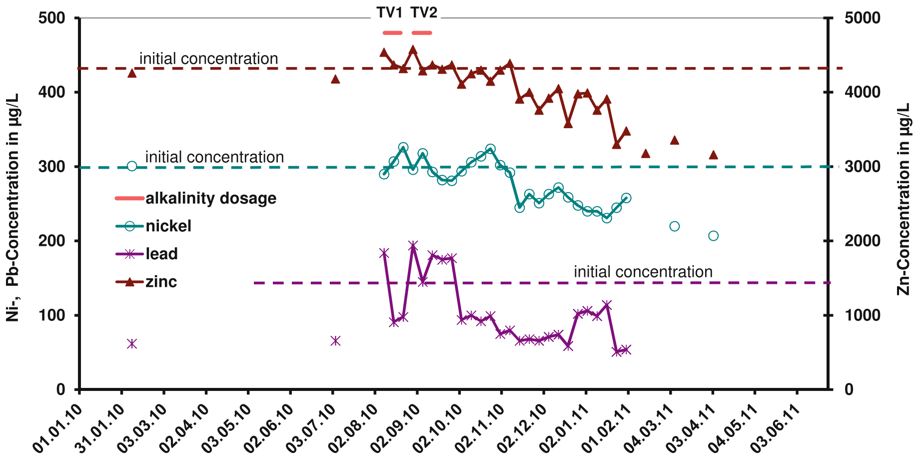

Fig. 10 Trends in concentration of selected metals at FBL B

Chemical Effectiveness in the Downstream Area—TV 1 und 2

The pH and redox potential showed only a slight response at the pumping well (Fig. 9). During the period of tracer breakthrough, pH slightly rose to 3.7 on Nov. 29, 2010, compared to an initial pH of 3.3.

However, despite this, uranium concentrations decreased significantly, from ≈5 to ≈3 mg/L by the end of the test. Significantly lower uranium levels would be anticipated if it wasn't for the background dilution rate of 77 %. Similarly, concentrations of zinc decreased from 4.5 to 3.2 mg/L and nickel decreased from 300 to 250 mg/L. Trends in the concentration of lead are a bit more difficult to interpret, given that they varied considerably before the test (Fig. 10).

The decreased concentration levels of these contaminants proceeded simultaneously with the tracer breakthrough. As hydraulic boundary conditions were to a large extent constant during that period, the reason for diminishing concentration levels during these partial tests is likely to be found in the injected alkaline solutions.

Since April 2011, the water level in the mine has been allowed to rise again. For this reason, concentration levels analysed at the pumping well can no longer be used as a reference for further test evaluation because hydraulic boundary conditions have changed and flushing has reached the areas of elevated acidity and contaminant potentials.

Technological implementation, dosing of alkalinity (NaOH) into the water flow, and injection of the generated buffer fluid via existing boreholes (such as injection wells and groundwater measuring points) into the mine demonstrated the technical feasibility of the approach at full-scale. No decrease of transmissivity and/or injection rates was observed.

Conclusion

The results of the field experiment demonstrated significant neutralisation and induced immobilisation of contaminants and sealing of pollution sources. Iron hydroxide precipitated by the neutralisation of pore water immobilised contaminants within the mine workings. Either sodium hydroxide or potassium hydroxide solutions may be employed as alkalinity carriers, but the use of the more costly potassium hydroxide solution is only recommended when potassium is to be used as tracer. Chemical effectiveness was demonstrated in all three tests.

The targeted dosage of the alkaline solution, their injection via the injection wells, and the performance of the groundwater monitoring wells went smoothly, with trouble-free operation of the dosing station in all three tests. This demonstrated the technical feasibility of injecting buffer fluids in full-scale operations. Also, the approach chosen to predict flow paths, reaction spaces, and duration of flow proved to be fundamentally appropriate and expedient. Tracer breakthrough curves of the partial tests illustrate that the anticipated flow paths were, to a large extent, realistic.

Based on the results of the field experiment, a technological concept for a site-specific technology applicable to the mine as a whole was designed and conceived as a supportive measure to enhance further mine flooding. This technology is aimed at altering the geochemical milieu of the area to be flooded by the injection of alkaline, sodium sulfite solutions and extensively immobilising contaminants at their source. The scaling up of the field experiment results to the entire mine was based on the rate of the underground propagation of alkaline solutions, known data about the mine layout, and the model calculations.

During the licensing process, it became clear that controlled flooding of the Königstein mine up to a steady state water level without additional in situ mine water treatment would not be acceptable. Therefore, in situ mine water treatment constitutes a key element of the submitted documentation, proposing the flooding of the Königstein mine to its natural decant level. It is anticipated that the time period for water treatment can be shortened by years depending on final target values, with annual cost savings on the order of some million €.

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