Flooding of the Königstein uranium mine - Aquifer reactivity versus dilution

Broder Merkel

Technical University Bergakademie Freiberg, Department of Geology, 09599 Freiberg

Abstract. The Königstein underground and in situ leaching mine was operated from 1967 to the end of 1991. After ten years of tests, research and pre-works the flooding was started in January 2001. Mine water will be pumped and treated at least until the first flush of contaminants has passed. The question is when active treatment will be stopped and passive treatment take over. One option is diverting the mine water without treatment into the Elbe river. Due to an average flow of about 300 m^3/s compared to 0.028 m^3/s of mine water there will be only a minor impact on the river water quality. Another option is using mine voids or the downstream aquifer as reactive treatment zones. Geochemical simulation were performed by means of PHREEQC´s one dimensional reactive transport tool taking into account dilution, double porosity, surface complexation on iron hydroxides and uranium reduction due to degradation of organic matter.

Introduction

The Uranium Königstein mine is situated about 30 km southeast of the city of Dresden close to the Elbe river and the nature resort “Sächsische Schweiz”. Underground operations started at the Königstein mine in 1967 by classical deep mining in the Cretaceous sandstone ore body. Since 1984 a special in situ leaching technique was applied using sulfuric acid as leaching agent. Uranium mining was stopped at the end of 1991 after reunification of Germany (Zimmermann & Schreyer 1995).

The multilayer aquifer is build up from 4 double porosity aquifers and siltstones in between. Aquifers no 1 und 2 are unconfined and only of local interest, aquifer 3 is unconfined as well and used downstream of the mine for extracting potable water for the city of Pirna. Aquifer 4 is confined and the lowermost with the uranium ore body in it. After a ten years period of research, tests and pre-works flooding of the mine was started in January 2001. During the flooding procedure mine water is pumped from the mine and treated on site at least until the first flush has been passed. Pumping is done by means of a control adit which was build at the downstream edge of the mine; ground water and mine water is withdrawn by means of hundreds of small diameter boreholes which have been drilled through the roof of the control adits into the aquifer no 4 forming a dense drainage fan. However, the question is when the active treatment will be stopped and what strategy will then be followed up. As long as the control adit is accessible and all mine water is pumped to the surface for treatment this requires huge quantities of water to be pumped and treated. The amount of water to be pumped and treated in the long run is depended on the permeability of the sandstone of the aquifer no. 4. If the control adit is flooded and used as a horizontal well the cone of depression is much smaller and the amount of water to be pumped and treated is getting much smaller. One option is diverting the mine water without treatment into the Elbe river. Alternatively some adits and mine voids could be filled with permeable and reactive material and finally the downstream aquifer could be used as natural reactor.

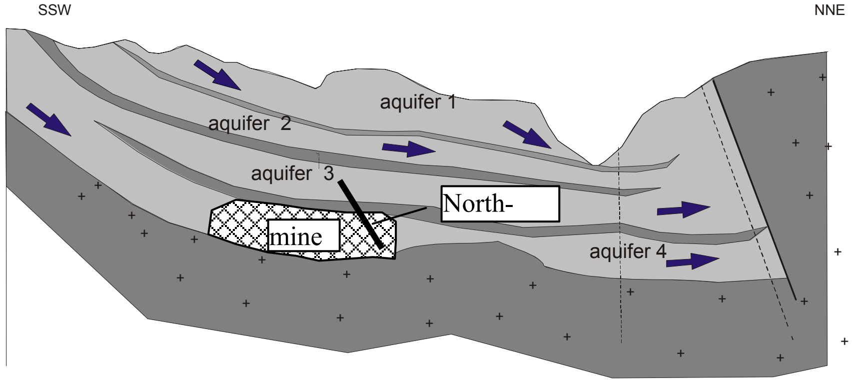

Fig. 1. cross section of the Königstein mine

From two medium scales flooding experiments in the Königstein mine and recent measurements from the ongoing flooding the mine water quality is known considerably well. Average values are given in table 1 for a selected number of elements and parameters.

Table 1. Average concentrations of selected elements in mg/L and key parameters in the flood water of the Königstein mine (first flush)

pH	Temp °C	eH mV	EC mS/cm	Ca	Mg	Na	K	SO_4^{2-}	Cl^-
2	14	650	6.3	130	20	40	10	2700	35
F	U	Cu	Ni	Zn	Sr	Ba	Pb	As	Cd
1.5	200	0.5	4.0	55	0.9	0.03	0.65	1.65	1.4

Dilution

From flooding of other mines it is known that the concentrations (as shown in Table 1) are peak concentrations which will decrease by at least one order of magnitude within a few years. Assuming an amount of 100 m^3/hour (0.028 m^3/s) flowing through the mine and taken into account the average flow of the Elbe with about 300 m^3/s the dilution factor is $9.3 \cdot 10^{-5}$. Thus the uranium increase for the Elbe would be 1.8 µg/L assuming an uranium concentration of 20 mg/l in the mine water respectively 0.18 µg/L, if the mine water contains only 2 mg/L. Compared with average uranium concentrations of 1 to 4 µg/L in the Elbe river an additional increase of less than 1 µg/L sounds negligible. However, taken into account the WHO Uranium MCL of 2 µg/L for drinking water, the Elbe is already at critical quality and thus sensitive for additional loads. Assuming that the concentrations of other elements (e.g. As, Cd, sulfate) are as well decreasing by 1 to 2 orders of magnitude in the mine water, dilution would make the impact of the mine water extremely small for these elements. However, it is in question whether the German regulators will accept dilution as natural attenuation measure since the yearly load would be 1.8 tons of uranium assuming 2 mg/l respectively 18 ton (20 mg/l) of uranium in the mine water diverted to the Elbe.

Backfill of reactive material

Use of zero-valent iron to remove Uranium is a common technique (Farrell et al 1999, Schneider et al. 2001) and lab and in situ field experiments of the Wismut GmbH have shown promising results (personal communication). However several questions are still to be addressed: First of all it is not yet known, whether the removal of uranium is due to sorption or reduction of U(VI) to V(IV) and thus precipitation of uranium oxide (Noubactep et al. 2001). Sorption, as a removal mechanism, is not preferred because uranium will remain in its more soluble oxidation state (i.e., U^{6+}), thereby lending itself to be easily transported by the colloidal iron corrosion products. Another concern is the potential release of soluble uranium back into the groundwater.
Reduction of U^{6+} to U^{4+} is the preferred removal mechanism since the resulting U^{4+} species is less soluble and less mobile in groundwater, assuming that the U^{4+} species is not colloidal. Thermodynamical reduction to U^{4+} is slightly favorable in strongly acidic media as indicated by the modest positive value for the standard cell potential:

$$Fe^0 + 1.5\, UO_2^{2+} + 6\, H^+ \leftrightarrow Fe^{3+} + 1.5 U^{4+} + 3\, H_2O \qquad E^0=+0.17\text{ V}$$

However, results by Wersin et al. (1994) indicate that reduction to the less soluble U^{4+} (e.g., $UO_2{\cdot}xH_2O$) is controlled kinetically. Similarly, reduction of U^{6+} by the ferrous ion (Fe^{2+}) has been reported to be kinetically slow except in the presence of strong acid (Baes 1953).

Then a backfilling technique for getting the iron-sand mixtures into the adits and tunnels has to be developed, since only distinct areas of the underground mine are nowadays accessible. As long as adits are open the preferential flow is through the adits, however, after filling them with a sand-iron mixture the permeability will decrease by several orders of magnitude and the preferential flow might by through the mined parts (conventional and in situ leached blocks). The only adit which can be backfilled with conventional techniques comparatively simply is the control adit. This option has furthermore the advantage that most ground water will pass through as long as the permeability of the backfill is much better than the sandstone. However, the capacity for taking reactive material is limited and an exchange of the reactive material is not possible without development of new techniques.

Aquifer as reactive zone

Another alternative is using the downstream aquifers as reactive treatment zone. Since the aquiclude between the Aquifer 3 und 4 is existing in the entire area the contamination from the mine will flow downstream mainly within the aquifer no. 4 as long as the fault zone between aquifer 4 and 3 in the mine area can be controlled. A certain contamination of the aquifer no. 4 might be acceptable by the German regulators and stakeholders since this aquifer is not used due to natural elevated concentrations of radium in the ground water. What are the controlling processes? Dilution will take place and this will certainly increase the pH, thus distinct minerals might get over saturated and might precipitate. Ion exchange might take place which is strongly dependent on the pH, since uranium species are changing readily with pH. However, solution of minerals (pyrite, calcite) might occur as well. An important reaction might be the decay of organic carbon which is present in the sandstones and was actually triggering the formation of the Königstein uranium ore body at a redox barrier a couple of million years ago. However the organic matter still present in the sandstones seems to have nowadays a considerably low reactivity, since the redox potential of the ground water in aquifer no. 4 is indicating oxidizing conditions.

Distinct potential reactions were modeled by means of PHREEQC using its 1d reactive transport tool. One principle problem linked with 1d transport modeling is that dilution by the surrounding not contaminated ground water is not taken into account. However, within PHREEQC 1d reactive transport tool this can be incorporated. Unfortunately the amount of pyrite and calcite in the Cretaceous sandstone are not known very well. Thus 1% of calcite and pyrite respectively and 2% organic matter were assumed. Kinetic rate constants for calcite and pyrite solution and decay rates of organic matter were taken from the PHREEQC.dat data set (Parkhurst, Apello 1999) and partly modified . Since laboratory tests of permeability show k_f-values of some 10^{-7} m/s and pumping test data on contrary comes up with some 10^{-5} m/s it is proven that the Cretaceous sandstone is a double porosity aquifer. The effective porosity of the sandstones is between 0.1 and 0.2 (Flesch

2000), however, the porosity of fractures is much less and approximately between 0.01 and 0.05. Thus in the PHREEQC 1d transport simulation a primary (fracture) porosity of 0.01 being coupled with 0.15 secondary sandstone porosity were assumed, with diffusion being the major process of exchange between fracture and pore volume. Assuming a k_f of $1 \cdot 10^{-5}$ m/s, a flow gradient of 0.02 and a fracture volume of 0.03 the distance velocity is approximately 210 m/year. A one dimensional array with 20 cells each 40 m in length and a dispersion of 5 m was defined.

Reactive geochemical transport models showed that cation and anion exchange as well pyrite dissolution have only minor impact on concentrations in the contamination plume. On contrary it is clearly shown that calcite dilution, precipitation of iron hydroxides and consequently surface complexation of e.g. uranium and arsenic but as well dilution by uncontaminated ground water are important factors. Fig. 2 shows the breakthrough curves 8000 m downstream the mine assuming that the mine water has the condition described in table 1, which is certainly too pessimistic. Nearly all iron is precipitated as $Fe(OH)_3$ in the first cell and uranium is partly sorbed on the surfaces and thus reducing its concentration roughly by 50%. However, after 10 years the calcite embedded in the sandstone is completely dissolved in the first cell, and thus the pH is decreasing. Due to the decrease of the pH the protons are displacing uranium from the $Fe(OH)_3$-surfaces causing a sharp peak with uranium concentrations exceeding the uranium concentrations of the mine water (200mg/l) by far. Then the system stabilizes again due to still remaining calcite buffer capacities in the next cells of the model. It is important to point out the fact, that precipitation and sorption takes

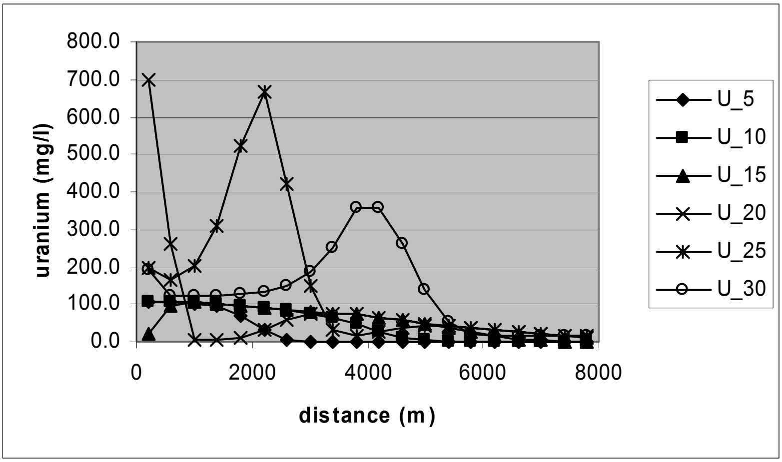

Fig. 2. Breakthrough curve for Uranium for time intervals of 5 30 years assuming concentrations of table 1. Due to iron hydroxide precipitation in the first cell of the model and consequent surface complexation of uranium on the $Fe(OH)_3$ uranium concentration is decreased from 200 to 105 mg/l in the first cell. Further decrease of uranium is due to dilution of the plume. Peaks are due to complete consumption of calcite in the first cell.

place throughout the total model time just in the first three cells of the model which is only 120 m of the aquifer downstream the mine. Besides, this is as well the only cell where gypsum precipitation occurs.

Fig. 3 shows a similar run, but assuming that the peak flush has been pumped off the mine, been treated and the major contaminants are decreased by one order of magnitude. In this case the assumed amount of 1% calcite is sufficient to buffer the mine water to a pH between 6.7 and 7.3. Precipitation of $Fe(OH)_3$ occurs only in the first cell of the model, thus clogging effects might be a problem in reality. However precipitation of $Fe(OH)_3$ was modeled thermodynamically and not kinetically since no kinetic constants were available. Gypsum saturation was not achieved in this run. Assuming double porosity condition the decrease of concentrations in the plume is even more drastic than by dilution and is controlled by the ratio of mobile to immobile pore volume and the pore geometry.

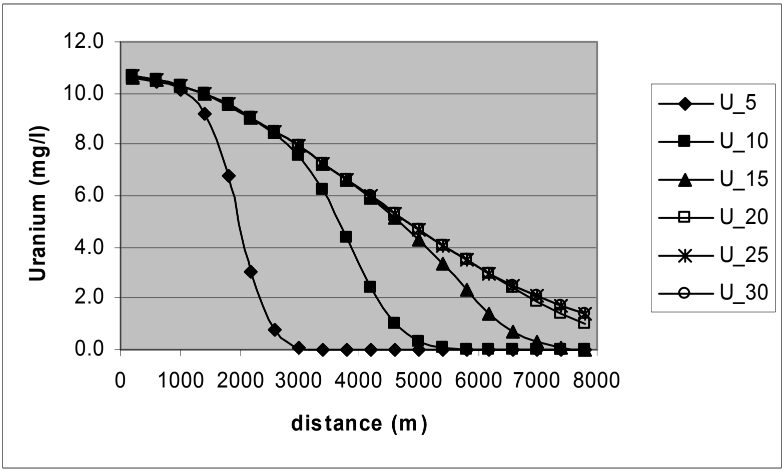

Fig. 3. Breakthrough curve for Uranium for time intervals of 5 … 30 years assuming concentrations 1/10 of table 2. Due to iron hydroxide precipitation in the first cell of the model and consequent surface complexation of uranium on the Fe(OH)3 uranium concentration is decreased from 20 to 10.5 mg/l in the first cell. Further decrease of uranium is due to dilution of the plume.

Fig. 4, 5, and 6 show results of simulations assuming that easily degradable organic matter is available besides calcite and pyrite. In the very beginning pyrite solution lead to an increase of the sulfate concentrations. However, after about 800 days the pe has dropped from 17.6 to 4 and reduction of sulfate to H_2S starts (fig. 4). With decreasing pe redox sensitive elements like iron, arsenic, cupper, and uranium are reduced consequently as well. Fig 5 shows that iron(II) increase and iron(III) decrease start after roughly 200 days. After 490 days more or less no iron(III) is left in the system. A few days later uranium is changing more sharply from uranium(IV) to uranium(VI).

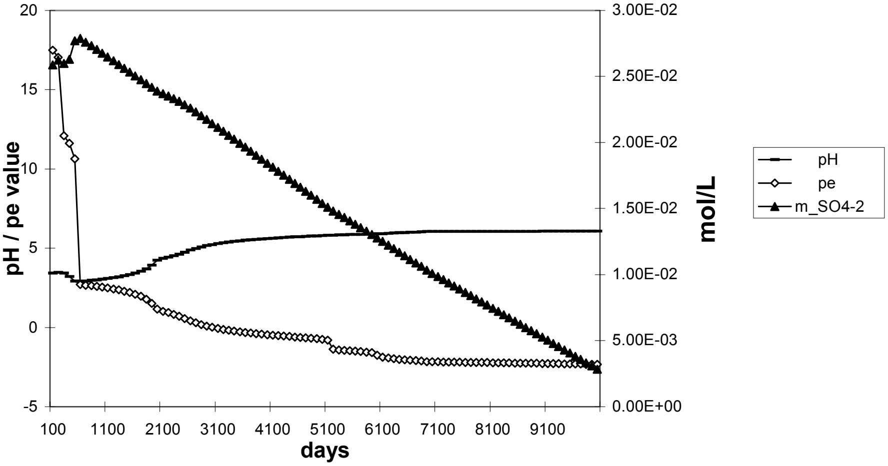

Fig. 4. Redoxpotential (pe) is dropping dramatically during some hundred days at the very beginning. The wrinkle in the pe-line at about 800 days is correlated with the sulfate peak. Decreasing sulfate concentrations is due to further microbial degradation of organic matter.

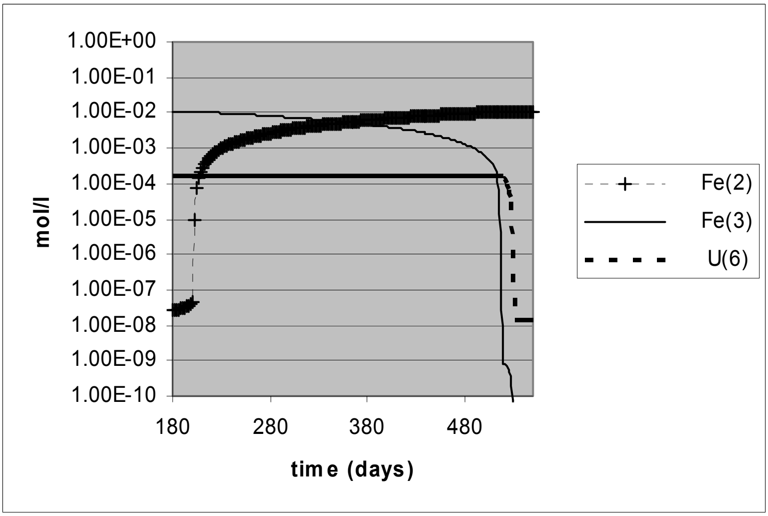

Fig. 5. Speciation change from Fe(II) to Fe(III) and reduction of U(VI) to U(IV) which is precipitated as amorphous UO_2 and thus does not shown up as aqueous species

Fig 6 is enlarging the time period from fig. 5 and displays as well the development of arsenic species. The arsenic(V) decrease line is very close to the iron(III) decrease line and the increase of arsenic(III) is negatively correlated to arsenic(V). Roughly ten days later uranium is reduced form uranium(VI) to uranium(IV) which is readily precipitated as amorphous UO_2. If the thermodynamical data used are reliable and the reactions Fe(III) to Fe(II) respectively U(VI) to U(IV) are not kinetically controlled this is a proof that sorption of uranium on $Fe(OH)_3$ and simultaneous precipitation of UO_2 or Uraninite is not likely to occur.

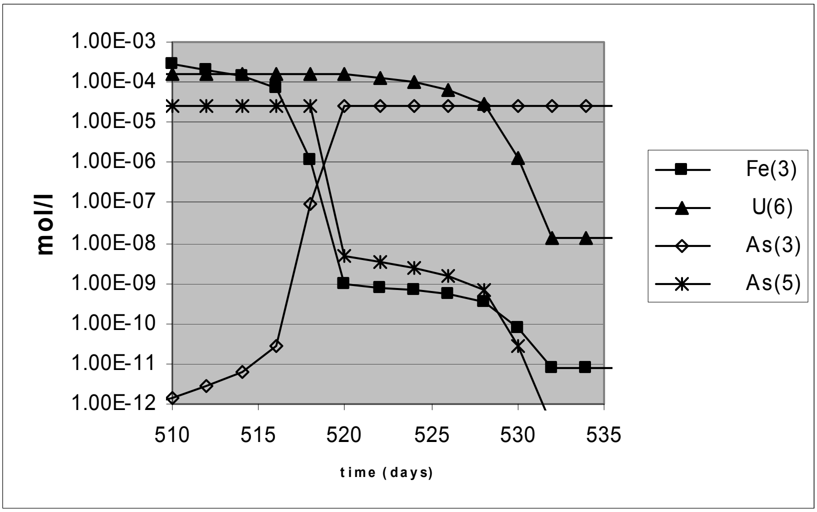

Fig. 6. Distribution of redox sensitive species of iron, arsenic and uranium versus time respectively development of pe due to kinetically controlled degradation of organic matter

However, this simulation was assuming the availability of easily degradable organic matter and there is no evidence from field or lab experiments that the organic matter in the Cretaceous sandstones is that reactive. Therefore reducing conditions in the contamination plume would have to be triggered by adding easily degradable organic matter (e.g. methanol) to the mine water. Theoretically this could be done by means of injecting organic matter into the control adit.

Conclusion

The German government has already spent several hundred millions Euro during the last ten years for rehabilitation work in the Königstein mine and will spent some hundred millions Euro for the Königstein mine in the future. Pump and treat is a suitable option to catch the first flush with high contamination potential. However at the earliest time pump and treat has to be replaced by an alternative technique. One dimensional reactive transport has proven as a handsome tool to evaluate different scenarios and boundary conditions. Dilution and double porosity aquifers can be simulated by means of PHREEQC´s one dimensional transport tool, however, it is not possible to take into account both in one model. Thermodynamically and kinetically reactions can be incorporated as well as limited mineral phases (Merkel, Planer Friedrich 2002). A major problem, as often in modeling business, comes with the lack of reliable data. Gathering these missing data is thus the most important aim.

References

Baes, C. F., Jr. The Reduction of Uranium (VI) by Ferrous Iron in Phosphoric Acid Solution: The Formal Electrode Potential of the U(IV)/U(VI) Couple; Report ORNL-1581; Oak Ridge National Laboratory: Oak Ridge, TN, 1953.

Farrell J., Bostick W.D, Jarabeck R.J., and Fiedor J.N. (1999): Uranium removal from ground water using zero valent iron media. Ground water 34, 618-624.

Flesch (2000) Hydrogeologisches Modell der Sächsischen Kreide. Wiss. Mitt. Inst. Für Geologie, 14, ISSN 1433-1284

Merkel B, Planer-Friedrich B (2002) Grundwasserchemie - Praxisorientierter Leitfaden zur Modellierung von Beschaffenheit, Kontamination und Sanierung aquatischer Systeme, Springer Verlag, 220 S. 74 Abb., 56 Tab.

Noubactep C, Meinrath G, Volke P, Peter H.J, Dietrich P, Merkel B (2001): Understanding the Mechanism of the Uranium Mitigation by Zero Valent Iron in Effluents. Wiss. Mitt Inst.für Geol. TU BAF, Vol 18, 36-44, ISSN 1433-1284

Parkhurst D, Apello C (1999) Users´Guide to PHREEQC (Version 2) — A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigations Report 99-4259

Schneider P., Neitzel P.L., Osenbrück K., Noubacteb, C., Merkel B. Hurst S. (2001): In-situ Treatment of Radioavtive Mine Water using Reactive Materials - Results of Laboratoty and Field Experiments in Uranium Ore Mines in Germany. Acta hydrochim. hydrobiol. 29, 2-3, 129-138

Wersin, P.; Hochella, M. F., Jr.; Persson, P.; Redden, G.; Leckie, J. O.; Harris, D. W. (1994) Geochim. Cosmochim. Acta 58 (13), 2829-2843

Zimmermann U, Schreyer J. (1995) Erstellung experimenteller Daten mittels eines Flutungsexperimentes zur Vorbereitung der Flutung der Lagerstätte Königstein. Uranium Mining and Hydrogeology I, Sven von Loga Verlag: 575-583