Alternative methods of mine water treatment – Feasibility and technical limitations for a full-scale application at WISMUT's Königstein mine site (Germany)

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Abstract

The rehabilitation of large uranium mining and milling sites in Saxony and Thuringia, which were formerly operated by the Soviet-German company (SDAG) WISMUT, is one of the largest ecological and economical challenges facing the reunited Germany today. The WISMUT remediation project comprises five underground mines to be closed and flooded. The highest priority with regard to environmental impact is the Königstein mine, near Dresden.
At this site, uranium was initially extracted from a sandstone aquifer by conventional mining, and then later by underground in-situ leaching using sulphuric acid. A high level of pollution remains within the deposit from

the leaching operation. The mine water contains high concentrations of uranium, radium, acid, sulphate, iron, aluminium and various heavy metals.

Controlled flooding of the mine began in January 2001. Excess mine water is pumped from the mine and treated in a conventional treatment plant. In order to reduce the long term costs of conventional water treatment, alternative in-situ technologies have been developed since the early 1990s. Two main strategies have been developed for a full-scale application: direct source immobilisation and reduction of contaminant concentrations in the mine water using reactive materials deposited in open mine cavities (reactive barrier)
The immobilisation technology, which is based on the injection of water supersaturated in barite into former leaching blocks, is now used in the southern part of the mine as part of the closure plan. On the other hand, the construction of a reactive barrier in open drifts proved not to be feasible due to problems with air ventilation and mine safety.

Finally, the paper summarizes costs and benefits as well as limitations of the alternative methods.

1 Introduction

In 1947, the Soviet occupation forces in Germany established the state-run company (SAG) WISMUT. After 1954, the new bi-national Soviet-German company (SDAG) WISMUT continued uranium mining. The company’s sole aim was the exploitation of German uranium deposits for the Soviet nuclear programme. During the early years, uranium mining was in complete disregard for the environmental concerns of the densely populated areas, and caused the destructive exploitation of resources. In 1990, the year of German reunification, more than 40 years of intensive uranium mining came to an end, after having produced a total of 231.000 tonnes of uranium in Saxony and Thuringia. In global terms, this ranks Wismut as number three in post-war uranium production, after the USA and Canada. In 1991, the Soviet Union disclaimed its shares under the terms of a state treaty. Under the provisions of the Wismut Act, the former SDAG Wismut was legally transformed into a company under German corporate law (Wismut GmbH). The sole shareholder became the Federal Republic of Germany, represented by the Federal Ministry of Economics and Technology. Mining operations were reorganised to form the nucleus of an environmental restoration company to rehabilitate the impacted areas for the benefit of the local population.

Rehabilitating large radioactively contaminated sites formerly operated by Wismut in Saxony and Thuringia is one of the largest ecological and economic challenges in Germany today. The corporate purpose of Wismut GmbH is to decommission its former uranium mining and milling facilities and to rehabilitate the devastated land for future reuse. This involves a surface area of about 3.700 hectares; of this, more than 2.300 hectares are occupied by waste rock piles and tailings facilities. This tremendous operation is funded by the federal government, which has earmarked a total of 6.2 billion € to conduct an environmentally and economically sound rehabilitation.

The overall project includes abandonment and flooding of underground mines, relocation and covering of waste rock piles, dewatering and geomechanical stabilisation of tailings ponds, dismantling and demolition of structures and buildings, and site clearance and rehabilitation (Federal Ministry of Economics and Technology 2000).

2 Flooding of the Königstein Mine

Within the WISMUT remediation program, the remediation of the Königstein mine near Dresden is a very unique case. The mine is situated in an ecologically sensitive and highly populated area (Fig.1). Conventional mining started in the sixties and approximately 19,000 t of uranium were produced overall.

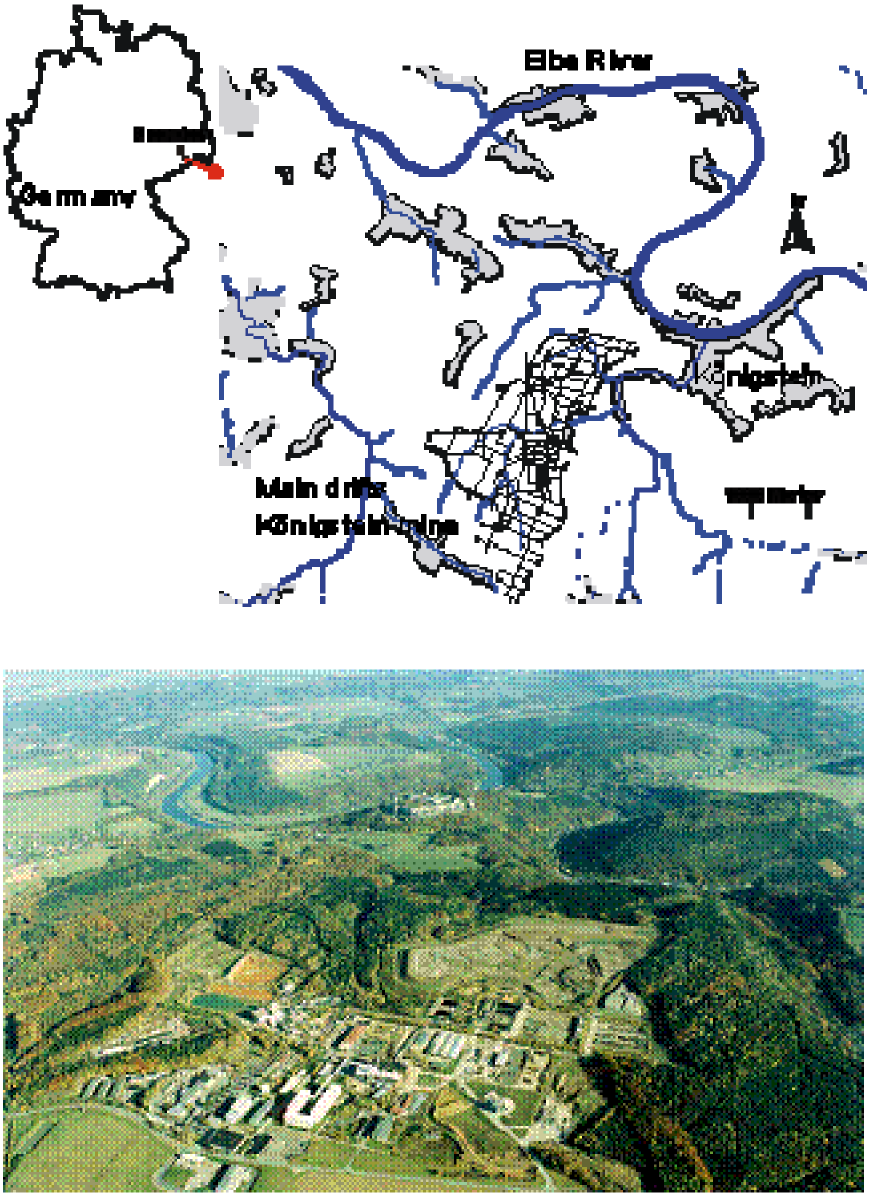

Fig. 1. Location of the Königstein mine

The ore body is located in the 4th sandstone aquifer, the deepest of four hydraulically isolated aquifers in a Cretaceous basin. Between the 3rd and 4th aquifer, a 10 to 30 m thick aquitard is located, which is perforated by

natural faults and technical connections due to mining activities. The 3rd aquifer is an important water reservoir for the Dresden region and is environmentally and economically very significant.
The uranium was extracted from the 4th sandstone aquifer initially using conventional mining methods, but later an underground in situ leaching method using sulphuric acid was implemented. The in situ leaching was performed on sandstone blocks with volumes of 100,000 to 1,000,000 m^3. 104 blocks were leached with solutions of 2 to 3 g/l H_2SO_4. During the in situ leaching period, about 130,000 t of sulphuric acid were applied within the deposit. Additionally, an unknown amount of sulphuric acid produced by pyrite oxidation was released within the mine. Especially due to the reactions of the oxidizing sulphuric acid, the geochemical nature of the deposit was substantially changed, with a high level of pollution remaining within the deposit, mainly sulphate, heavy metals and natural radionuclides.

Final mine remediation can only be achieved by flooding the mine. The development of the flooding concept was based on a huge number of scientific and engineering studies, including a full scale flooding experiment over a period of 8 years within a representative section of the mine (Schreyer 1996). In the case of uncontrolled flooding (a walk-away option) it was expected that highly polluted groundwater would rise up into the overlying aquifer through natural or technical hydraulic connections. This scenario has to be prevented because the overlying aquifer is a major drinking water resource. Instead of uncontrolled flooding, the water will be collected down-gradient of the deepest part of the mine. The flooding water collected in this control drift system can be treated and discharged to the Elbe river (Fig. 2).

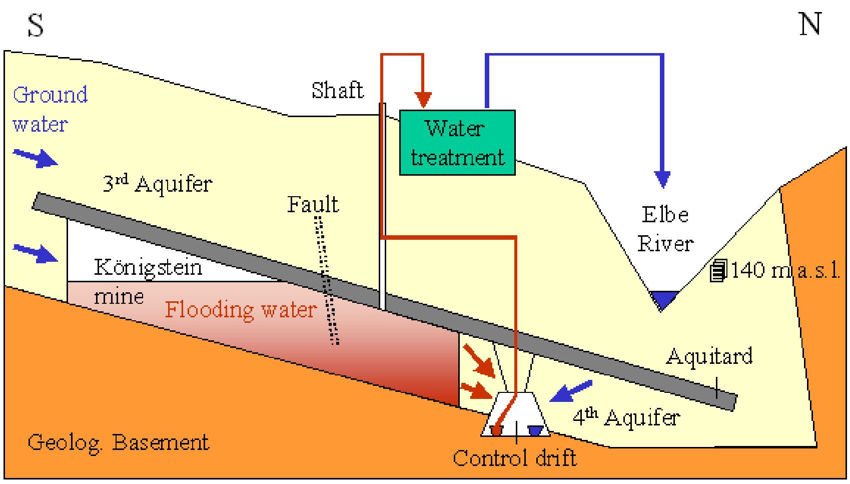

Fig. 2. Schematic cross section of the Königstein mine and the downstream region

The controlled flooding will allow a reduction of pollutant concentrations to acceptable levels, restoring hydraulic conditions to nearly what they were before mining and will prevent pollutant migration into the aquifer lying above and downstream of the mine. The recent quality of the flooding water is characterised in Table 1:

Table 1. Hydrochemical parameters of the flooding water of the Königstein mine, 2004

Parameter	**Concentration**	**Parameter**	**Concentration**
pH	2.5	Al (mg/l)	70
Eh (mV)	650	Zn (mg/l)	24
el. cond. (mS/cm)	3.5	As (mg/l)	0.6
SO_4 (mg/l)	2100	U dissolved (mg/l)	30
Fe (mg/l)	600	Ra-226 dissolved (Bq/l)	8

Flooding of the Königstein mine started January 29, 2001. Excess mine water is pumped from the mine and treated in a conventional treatment plant. The controlled flooding is conceived as a process limited in time. Once residual pollutant concentrations have been reached tolerable levels, the control drift will be abandoned and natural hydrogeological conditions will develop within the mine area.

3 Alternative methods of mine water treatment

Based on scientific investigations, the post-mining pollutant release from the mine was predicted. Given the high level of mobile and readily leachable contaminants, it was clear that contaminated water will be generated over an extended period of time (Jenk and Schreyer 2001), requiring that the flooding water would have to be treated over a period of decades. Both from an ecological as well as from an economic point of view, it is crucial to reduce the time span required to achieve compliance with water standards and to minimize levels of released contaminants. In order to achieve this, alternative in-situ technologies were considered, and two main strategies were developed for a full-scale application: direct-source immobilisation and reduction of contaminant concentrations in the mine water using reactive materials deposited in open mine cavities (reactive barriers).

3.1 Source immobilisation

In-situ immobilisation is based on using mineral precipitation or crystallization processes similar to those occurring in nature. A technology was developed to cover reactive mineral surfaces by targeted $BaSO_4$ precipitation from supersaturated solutions.

$BaSO_4$ supersaturated solutions were prepared step by step by mixing solutions containing $BaCl_2$ or $Ba(OH)_2$ with sulphate-containing solutions in the presence of various types of precipitation inhibitors on a laboratory scale. Solutions characterized by reducing properties were obtained using Na_2SO_3 as a source for sulphate generation. Stability of the obtained supersaturated solutions was determined by stirring experiments at room temperature. The temporal change of the barium concentrations served as a measure for the course of $BaSO_4$ crystallization.

Column tests were used to determine the immobilization capacity of $BaSO_4$ producing solutions. The columns were filled with approximately 60 kg of crushed sandstone. To assess the effectiveness of $BaSO_4$

producing solutions, a second column was flushed with water. The solution or water, respectively, was pumped from bottom to top at an average rate of 1.2 l/d. The immobilization tests were carried out with a solution that would result in the formation of 350 mg/l $BaSO_4$. At an inhibitor concentration of 80 mg/l, the stability was in excess of 96 hours. In order to increase the immobilization capacity, small amounts of sodium silicate were added.

After immobilisation, the sandstone was investigated by chemical and mineralogical methods. $BaSO_4$ layers filled pores and covered reactive mineral surfaces and secondary precipitates, such as hydroxides or hydroxysulfates, were found as reaction products (Fig. 3). Because of the extremely low solubility of barite, long-term stable immobilization was achieved.

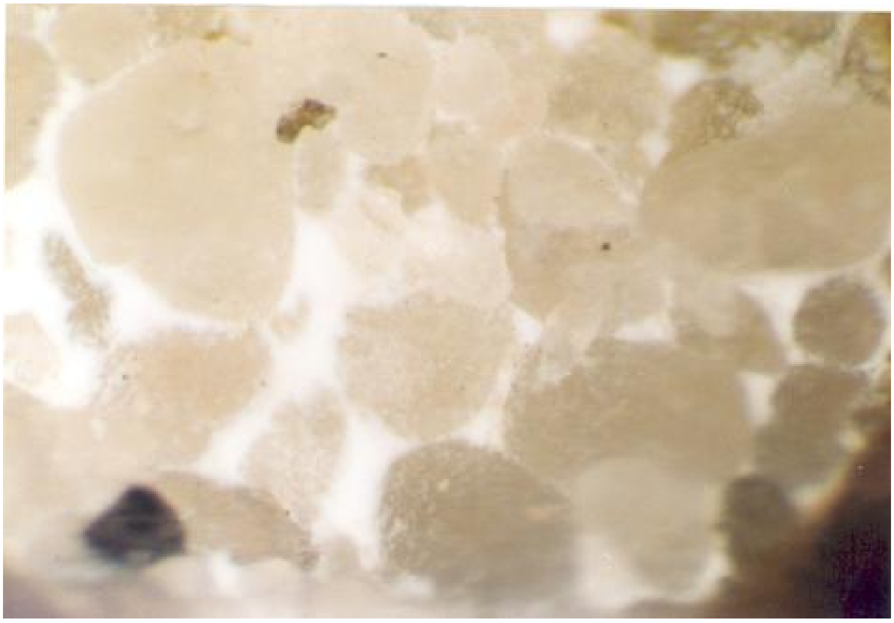

Fig. 3. $BaSO_4$ crystals formed on a sandstone surface

Field tests were carried out on blocks in the southern part of the Königstein mine. The average mineral composition as well as the geological and mineralogical situation was similar to the average conditions of the deposit.

A solution containing $Ba(OH)_2 \cdot 8H_2O$, Na_2SO_3, sodium silicate and a precipitation inhibitor was prepared in a small-size grout plant. The grout preparation was based on the simultaneous addition of a $Ba(OH)_2$ solution and an inhibitory-Na_2SO_3-sodium silicate solution into a water-bearing pipe.

The field test was characterized by different stages during which a block was alternately treated with $BaSO_4$-producing solutions and small amounts of water. At the end, the block was flushed with water in order to determine the stability of the achieved immobilization.

It could be shown that it is feasible to prepare large quantities of $BaSO_4$-forming solutions under typical mine-site conditions without any problem. Following a short training period, the miners operated the grout plant without trouble. After six days, the block was filled with 3,540 m^3 of $BaSO_4$ supersaturated solution. Total consumption amounted to 1,575 kg of $Ba(OH)_2*8H_2O$ and 700 kg of Na_2SO_3. No significant amount of $BaSO_4$ precipitated in the pipes or pumps.

To assess the effectiveness of the immobilization, the amounts of contaminants discharged have to be compared withthose that could be expected in the case of flushing the test field with water. For this experiment, a block situated close to the test site was filled several times with water and subsequently emptied. In both $BaSO_4$ immobilization stages, the amounts of contaminants discharged were between 50 and 70 % lower than would be expected when flushing the block with water (Ziegenbalg et al. 2003a).

In the light of the results of the laboratory, column and field tests, the decision was made to apply the newly developed technology to selected areas of the Königstein mine. In a first step, approximately 100,000 m^3 of immobilisation solutions were prepared and injected into three different blocks in the southern mine field between December 2001 and May 2002.

The blocks had been prepared for uranium leaching, but the operation had to be suspended when uranium mining was terminated. As the rock had been in contact with air and moisture for more than 10 years, flooding of the mine would have caused the formation of highly concentrated acidic solutions. Treatment with $BaSO_4$- and SiO_2-forming solutions was aimed at precipitating contaminants, inhibiting oxidation processes, and reducing contaminant discharge during the flooding process at a later stage.

As in the test fields, the solution was based on $Ba(OH)_2*8H_2O$, Na_2SO_3, water glass, and a precipitation inhibitor. Preparation of the solution was carried out in a grout plant similar to that used in the field tests (Fig. 4).

Fig. 4. View of the apparatus used for the preparation of 100,000 m³ $BaSO_4$ forming solution

Solutions containing $Ba(OH)_2$ were mixed within a pipe with water and an inhibitor-sodium-sulphite-sodium-silicate solution; up to 50 m^3/h of supersaturated solution could be prepared. About 500,000 m^3 of sandstone were treated (Ziegenbalg et al. 2003b).Samples taken from different locations demonstrated the successful use of $BaSO_4$ forming solutions.

Currently, about 1 million m^3 of sandstone have been treated in the southern part of the mine with about 200,000 m^3 of $BaSO_4$-and SiO_2-forming solution (finished December 2004). It is expected that this approach will minimize the source in the final flooding process significantly.

3.2 Reactive barrier

Extensive research has been conducted for several years to establish the extent to which reduction of pollutant concentrations can be positively influenced and accelerated by storage of reactive materials in mine cavities. Investigations were made at different scales to test and select materials with respect to a maximum immobilisation of contaminants (underground column tests), to examine hydraulic effects (underground large-scale column tests), and to optimise material properties (laboratory tests) (Jenk et al. 2003, Fig 5).

Fig. 5. View of underground column tests to find and check suitable reactive materials to treat flooding water

The investigations have shown that a mixture of Fe-chips and lignite is capable of efficiently remediating contaminated acidic mine water. The material studied is easily available and compatible with the environment. A number of feasibility studies were carried out assessing the feasibility of a large-scale application of such a reactive barrier using the control drift down-gradient of the mine. For this reason, a. However, the construction of a reactive barrier in open drifts of the control drift system proved not to be feasible. The main problems were:

- Emplacement of the reactive material would require single face and auxiliary ventilation systems but the dimensions of the mine workings inhibit use of sufficiently sized ventilation equipment (vent pipes); waste air return (and Rn in particular) was not ensured (radiation protection measures).
- The control drift acts as a drainage element for the flooding water. Safe drainage of this flooding water (ca. 300 m^3/h) would not be ensured when backfilling of the barrier material takes place.
- Upon contact with reactive material, acidic flooding water may produce hydrogen. This could lead to potential risks (firedamp),

given the possibility of limited ventilation and the resulting lack of workplace protection.

Since placement of reactive materials from above ground once flooding of the control drift is completed would inevitably incur disproportionately high costs, this option did not materialise at the Königstein mine site.

Conclusions

The former leaching mine of Königstein is remediated by a controlled flooding process. To reduce the long term costs of conventional water treatment, two alternative in-situ technologies were developed for full-scale application: direct source immobilisation and using of reactive material deposited in open mine cavities as a reactive barrier.

Construction of a reactive barrier in open drifts proved not to be feasible due to problems with air ventilation and mine safety. It might be possible to use the developed reactive material in a solid bed reactor on the surface for water treatment at a later state of flooding. Corresponding applications will be investigated in the framework of the final flooding concept.

The immobilisation technology (direct source immobilisation) was applied in the southern part of the mine as part of the closure plan. Field preparation of the immobilisation solutions was trouble-free. Chemical cost of the immobilisation solution is about €1/m^3. A grout plant to produce immobilisation solution for underground conditions with a capacity of about 200,000 to 300,000 m^3/a year would cost between 100,000 and 200,000 €. Such a plant can be run by 2 employees. It is assumed that the time required for flooding and water treatment can be reduced to 3 to 6 years. This would significantly reduce the costs for conventional water treatment.

In addition, the immobilisation technology has other potential applications beyond remediation of acid-contaminated rocks; it could also be used for other contaminated rock formations or for inhibition of acid rock drainage generation. The technology is environmentally friendly, stable, and can be easily adapted to local site and field conditions.

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