The use of $BaSO_4$ supersaturated solutions for in-situ immobilization of heavy metals in the abandoned Wismut GmbH uranium mine at Königstein

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Abstract. The former uranium ISL-mine at Königstein (Germany) is presently being flooded. To support the flooding process, a new technology to reduce contaminant potential in the source was developed and applied. The application based on the injection of supersaturated BaSO4-solutions to precipitate solved contaminants and to cover reactive mineral surfaces. Since 2002 the technology is applied in the southern part of the mine in order to immobilize contaminants in highly polluted areas before flooding. The article describes the fundamentals of the technology and the full-scale application.

Introduction

Closure of several underground uranium mines is a central issue of the WISMUT project in Germany. A special case is the remediation of the Königstein mine near Dresden. The mine is situated in an ecologically sensitive and densely populated area (Fig.1). Conventional mining started in the sixties and approximately 19,000 t of uranium were produced till 1990.

The ore body is located in the 4th sandstone aquifer, the deepest of four hydraulically isolated aquifers in a Cretaceous basin. 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. In situ leaching was performed on sandstone blocks with volumes of 100,000 to 1,000,000 m³. 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. Remaining pore water in the sandstone water is characterized by pH 2.0, EC 700 mV, 10 g/l SO_4, 2 - 3 mg/l Fe, 200 mg/l Zn, 200 mg/l U 300 mg/l Al.

Flooding of the Königstein Mine

Final mine remediation can only be achieved by flooding the mine. In the case of uncontrolled flooding (walk-away option) it was expected that highly polluted groundwater would rise up into the overlying aquifer through natural or technical hydraulic connections. Thus a concept of controlled flooding was developed. The major element of this approach is a control drift system which allows collection of draining flooding water down-gradient of the deepest part of the mine. The flood-

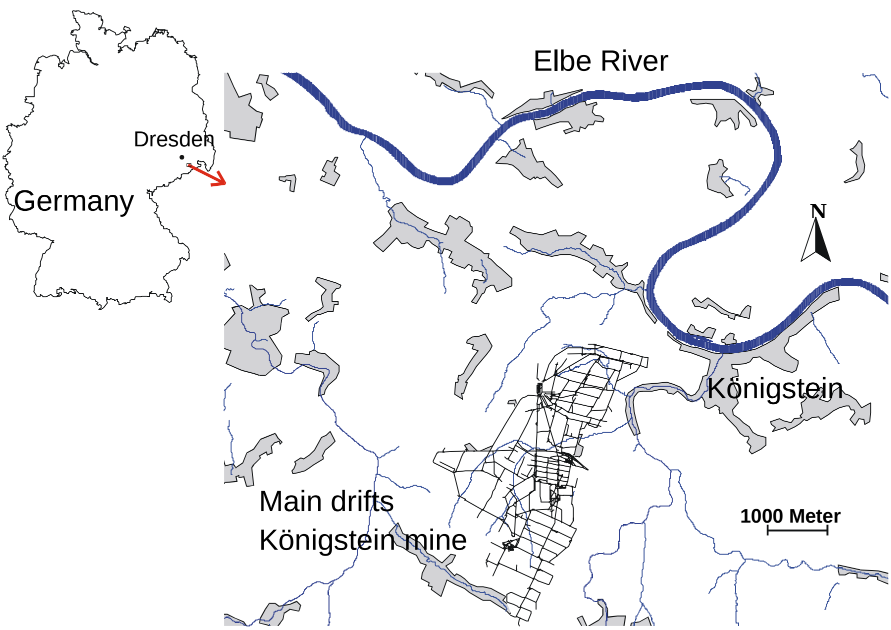

Fig. 1. Location of the Königstein mine.

ing water collected in this control drift system can be treated and discharged to the Elbe river.

To reduce the long term costs of conventional water treatment, two alternative in-situ technologies were developed for full-scale application: (1) direct source immobilization and (2) use 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. The immobilization technology (direct source immobilization by a special solution) was applied in the southern part of the mine as part of the closure plan.

Fig.2. Column tests with white precipitation products on the sandstone surfaces.

Development of the immobilization technology

In-situ immobilization is based on using mineral precipitation or crystallization processes similar to those occurring in nature. First, laboratory experiments ware carried out to create suitable solutions (Ziegenbalg 2003a, Ziegenbalg 2005). $BaSO_4$ supersaturated solutions were prepared by mixing solutions containing $Ba(OH)_2$ with sulphate-containing solutions in the presence of various types of precipitation inhibitors. Solutions characterized by reducing properties were obtained using Na_2SO_3 as a source for sulphate generation.

In a second step column tests were used to determine the immobilization capacity of $BaSO_4$ producing solutions and to investigate crystallisation products inside the sandstone (Fig.2).

In order to increase the immobilization capacity, small amounts of sodium silicate were added. After immobilization, 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.

Field tests were carried out on blocks in the southern part of the Königstein mine (Ziegenbalg 2003a). The average mineral composition as well as the geological and mineralogical situation was similar to the average conditions of the deposit.

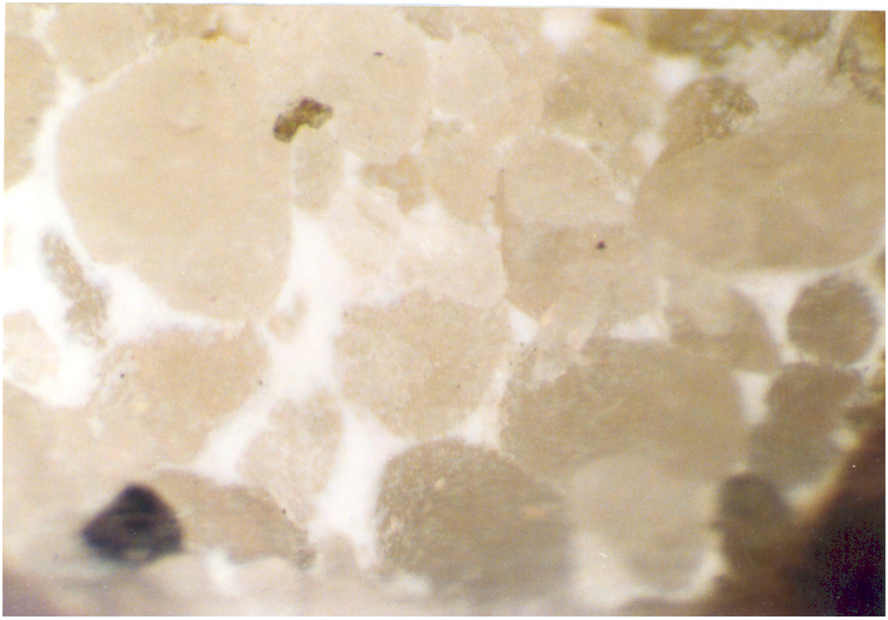

Fig. 3. $BaSO_4$ crystals formed in sandstone pores.

A solution containing $Ba(OH)_2$*$8H_2O$, Na_2SO_3, sodium silicate and a precipitation inhibitor was prepared in a small-size grout plant (Fig. 4). 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 immobilization 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. The amounts of contaminants discharged were between 50 and 70 % lower than would be expected when flushing the block with water.

Full-scale application

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 immobilization solutions were prepared and injected into three different blocks in the southern mine field between December 2001 and May 2002 (Ziegenbalg 2003b, Ziegenbalg 2005).

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 im-

Fig. 4. View of the grout plant used for field tests and first full scale application.

mobilization 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).

Solutions 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. Samples taken from different locations demonstrated the successful use of $BaSO_4$ forming solutions.

In a second step, between November 2003 and May 2005 about 1.1 million m^3 of sandstone have been treated in the southern part of the mine with about 225,000 m^3 solution. For this, a improved grout plant was installed in the southern mine field. To avoid long pipelines, the plant was disassembled and moved to 2 other positions. There were no technical problems to reuse the components (Fig. 5).

Field preparation of the immobilization solutions was trouble-free. Chemical cost of the immobilization solution is about €1/m^3. A grout plant to produce immobilization 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 € and can be run by 2 employees.

The immobilization technology (direct source immobilization) has been applied in the southern part of the mine as part of the closure plan. It is expected that this approach will minimize the source in the final flooding process which will signifi-

Fig. 5. Immobilization grout plant 2005, capacity up to 50 m^3/h, solution vessels on the left site, mixing facilities on the right site, storage vessels in the background.

cantly reduce the costs for conventional water treatment over the long term after ground water rebound has been completed.

In addition, the immobilization 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.

Acknowledgement

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