Investigation of efficacy of reactive materials for reduction of pollutants in acid mine water in the former uranium mine of Königstein (Germany)

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Abstract: Mine water in the former uranium mine of Königstein (Saxony, Germany) contains high concentrations of uranium, radium, acid, sulphate, iron, aluminium and various heavy metals. 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 open mine cavities. Underground column tests were conducted by WISMUT GmbH and Deutsche Montan Technologie GmbH with iron and other materials and material mixtures respectively.
Investigation has shown that there are reactive materials which are able to immobilise pollutants enriched in the Königstein mine water effectively. Reactions induced by zero-valent iron (increase of pH, decrease of EH) form a basis for a further improvement of mine water quality by additives. The one-year column tests with zero-valent iron and brown coal show nearly complete retardation of uranium, arsenic, cadmium and most other heavy metals.
The conveyance of reactive materials in open mine cavities of the uranium mine Königstein can be regarded as a supporting measure for reducing pollutant loads in mine water. Long-term effects and accompanying reactions will be investigated further to refine the method for a technological application in the Königstein mine.

1 INTRODUCTION

In the Königstein mine belonging to Wismut GmbH (Federal Republic of Germany, State of Saxony) uranium was mined underground in the period from 1967 to 1991. After the initial application of conventional mining methods, chemical underground leaching has been the main method used since 1984, i.e. the uranium ore has been extracted from the rock using a circulating sulphuric acid solution.

Within the framework of the flooding concept for the Königstein mine, various supportive measures were considered with the aim of attaining the clean-up objective (long-term stable conservation of the mine) more quickly (Schreyer, 1996). To minimise the duration and hence the cost of flooding the mine it is possible, among other things, to reduce the mobile pollutant potential by introducing reactive materials. The notion of "geochemical barriers" as part of the clean-up of the mine assumes the exercise of a controlled influence on the discharge stream, but reactive materials can also be used in the centre of the pollution (i.e. in the mine workings).

2 PARAMETERS

The storage of reactive materials in working cavities at the Königstein mine must take account of the site-related conditions. This relates both to the hydraulic conditions and to the pollutant profile in the mine with the hydrochemical framework.

It is only partly possible to backfill the working cavities in the mine for reasons of accessibility, which is why reactive materials can only have a supporting effect when flooding. It is only possible to guarantee effective through-flow for materials which have excellent long-term water-permeability; otherwise the discharge water flow will probably tend to pass more through other mine cavities.

For the acid flood water in the Königstein mine the materials which are effective in hydrochemical terms are those which lead to an enduring change in milieu in the water towards rising pH values and falling EH values (Parkhurst, 1990) and which have good sorption properties. Components released during the reactions may not lead to the additional mobilisation of pollutants currently bound in the rock and may not have adverse side effects.

3 CONDUCT OF TEST

In connection with an experimental flooding of the mine (Jenk, 1998) underground tests were conducted to establish the action of various potentially effective materials on the quality of the flood water. The column tests were performed in situ, i.e. in an open mine working. PVC columns with a diameter of 30 cm and a filling height of approx. 60 cm were used for the tests. The flow through the columns was upward, i.e. under saturated conditions. After it left the column, the percolate was passed on through a gas-tight hose to a measuring cell, in which – as in the flood water inflow – temperature, conductance, pH value and redox potential were measured, and sampled and analysed at intervals. Reaction gases were collected using separate facilities (Figure 1).

The reactive materials were selected taking due account of the possible reaction mechanisms and the hydraulic properties. In view of the hydrochemical parameters, the use of metallic iron is a preferred variant for the Königstein mine. Iron can be stowed in the mine as a lumpy and hence water-permeable material and it is easy to obtain. The reaction of the flood water with Fe^0 leads to a rise in the pH value and to the creation of reducing conditions (Fiedor et al., 1998). The milieu conditions thus arising facilitate or support the precipitation and greater sorption of heavy metals.

Other potentially effective materials were also tested, among other things to check combined effects: coal, organic residues, baryte-bearing material, brown coal precipitator ash and limestone (Table 1).

Except for a test with brown coal precipitator ash as an additive, the use of fine-grained materials was dispensed with because it was not possible with them to achieve the required hydraulic properties, especially in view of the anticipated formation of precipitation products. A column with washed gravel was also conducted as a blind test.

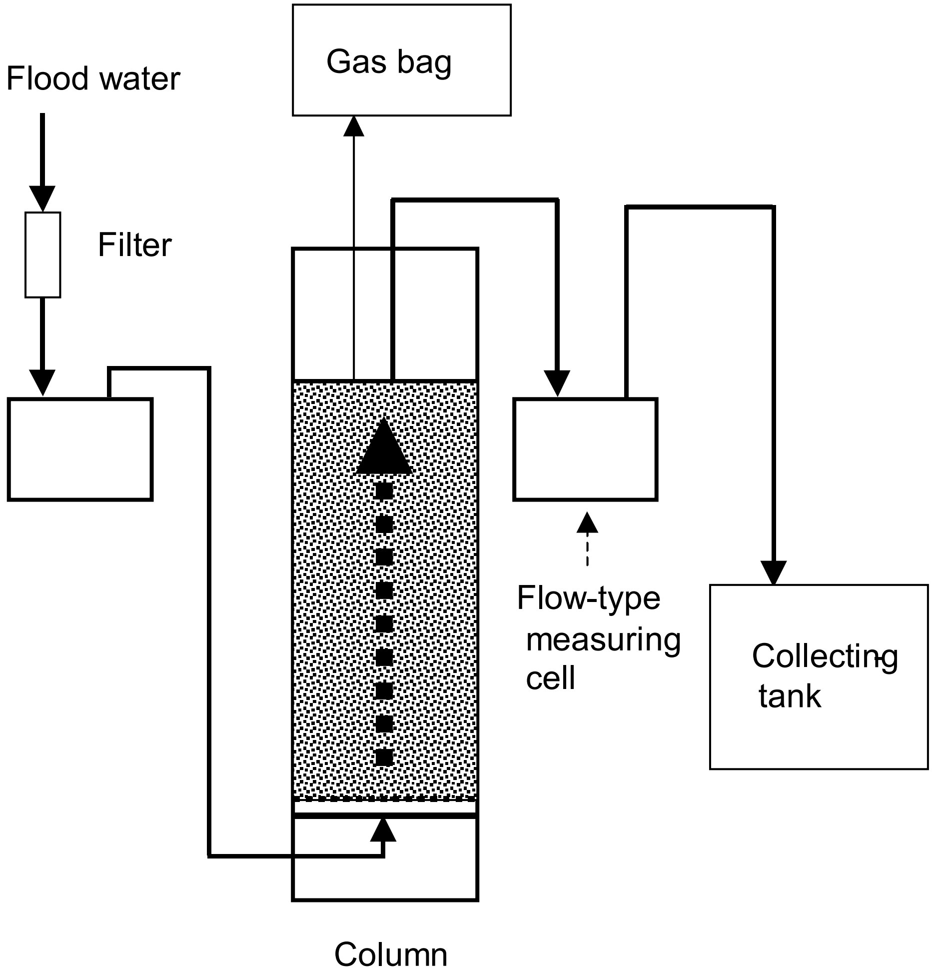

Figure 1 Diagram of a column in the underground testing facility.

Table 1 List of the reactive materials used in the columns

No.	Column filling
Column 1	crushed iron scrap from the Königstein mine
Column 2	iron lathe turnings from the metalworking industry
Column 3	iron turnings* + hard coal
Column 4	iron turnings* + brown coal
Column 5	Gravel
Column 6	iron turnings* + residues from alcohol fermentation
Column 7	iron turnings* + barium sulphate-bearing material
Column 8	gravel + brown coal precipitator ash
Column 9	lime ballast

* as in column 2

The percolation solution (flood water) was taken directly form an area of the experimental flooding. A flood water containing high substance levels was selected: uranium (75 mg/l), radium (12 Bq/l), acid (pH 2), sulphate (7200 mg/l)), iron (2200 mg/l) and aluminium (280 mg/l) and the heavy metals cobalt (2.5 mg/l), nickel (5.2 mg/l), copper (2.8 mg/l), arsenic (3.5 mg/l), lead (0.2 mg/l), cadmium (0.6 mg/l) and chromium (0.9 mg/l). The throughput rates were adjusted to the hydraulic conditions in the mine (1 to 10 days dwell time in the column).

4 RESULTS

The results testify to clear differences in the effect of the materials used on the constituents of the flood water.

In all tests elementary iron displays the expected pollutant-reducing effect on the flood water (Table 2). In all tests with iron a relatively great reaction capacity must be assumed because there was no breakthrough (exhaustion of reactivity) in any of the tests after a term of about 1 year. There is evidence of significant differences in effect between scrap, iron turnings and mixtures with iron turnings.

The mixtures with iron turnings prove to be highly effective. The effectiveness of the metallic iron is enhanced once more with the use of additives. The combination of iron turnings and brown coal immobilises practically all potential pollutants almost quantitatively. Even the relatively mobile elements of U, Co, Zn and Ni are immobilised substantially better with this mixture than with the other material examined. The mixture consisting of iron turnings and brown coal thus proves to be the most effective combination of materials, followed closely by the Fe-$BaSO_4$ mixture, which is merely lacking the effectiveness with zinc, nickel and cobalt. This is caused both by acid buffering, sorptions and the degradation of organic substance. In the columns filled with iron a development of H_2 gas was observed. This gas development lasted up to the end of the test in all columns filled with iron.

Table 2 Immobilised (positive values) or mobilised quantities (negative values) in relation to the loads fed in through the inflow. Immobilised portions > 50 % are given in bold script.

Column Material		**RM 1** Fe scrap	**RM 2** Fe turn-ings	**RM 3** Fe turn-ings + hard coal	**RM 4** Fe turn-ings + brown coal	**RM 5** Gravel	**RM 6** Fe turn-ings + brewing dregs	**RM 7** Fe turn-ings + $BaSO_4$	**RM 8** Brown coal ash + gravel	**RM 9** Lime-stone
As	%	**74**	**91**	**97**	**99**	25	**64**	**97**	36	**92**
Pb	%	**68**	**87**	**87**	**87**	0	**86**	**87**	24	**63**
Cu	%	**68**	**100**	**100**	**100**	2	**94**	**100**	12	37
Ni	%	6	1	1	**68**	4	4	0	5	4
Zn	%	1	0	4	**81**	1	9	-28	4	2
Co	%	-3	-4	-4	40	1	-6	-28	-1	-7
Cr	%	28	**67**	**76**	**54**	15	-66	**79**	20	37
Cd	%	9	21	31	**99**	-4	26	**97**	4	13
Mo	%	**87**	**100**	**100**	**99**	28	**85**	**100**	41	**98**
U	%	41	**52**	**66**	**96**	-2	**50**	**68**	6	38
Ra	%	-20	-28	-45	**67**	-2	-54	**90**	37	11
Al	%	6	30	**66**	**83**	-5	9	**61**	-7	**58**
SO_4	%	0	1	1	3	-2	1	6	3	19

5 CONCLUSION

The investigations showed that reactive materials exist which are capable of effectively immobilising the pollutants enriched in the flood water in the Königstein mine. The reactions induced by metallic iron form an effective basis for improving the quality of the flood water in the Königstein mine with the help of additives. It is therefore justified to subject such a process principle to further examination in order to obtain possibly supporting measures to be taken during the controlled flooding and as a safety component after conclusion of the flooding of the Königstein mine.

The practicability of the process depends to a large extent on the hydraulic and technical parameters. In particular it must be ensured that the reaction capacity of the material up to the onset of more stable conditions in the flooded mine is sufficient to exclude a re-release. The development of hydrogen must be prevented during mine operation.

Essentially, existing mine workings can be used to erect an appropriate barrier system in the Königstein mine. What appears promising at the moment is the backfilling of workings in the downstream flow for the treatment of flood water as a subsequent measure.

More in-depth studies are currently being conducted.

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Badanie skuteczności materiałów reaktywnych stosowanych do redukcji zanieczyszczeń w kwaśnych wodach kopalnianych w byłej kopalni uranu w Königstein (Niemcy)

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Streszczenie: Kwaśne wody kopalniane w byłej kopalni uranu w Königstein (Saksonia, Niemcy) zawierają wysokie koncentracje uranu, radu, kwasów, siarczanów, żelaza, glinu i innych metali ciężkich. Przez kilka lat prowadzono badania mające ustalić do jakiego stopnia można wpływać na redukcję zanieczyszczeń i przyspieszyć ją poprzez nagromadzenie w otwartych wyrobiskach kopalnianych materiałów reaktywnych. Podziemne testy kolumnowe były prowadzone przez WISMUT GmbH i Deutsche Montan Technologie GmbH przy użyciu żelaza i innych materiałów oraz mieszanin materiałów. Badania wykazały, że istnieją takie materiały reaktywne, które są w stanie efektywnie unieruchomić substancje zanieczyszczające wody kopalniane w Königstein. Reakcje wywołane przez zerowartościowe żelazo (zwiększenie pH, zmniejszenie EH) tworzą podstawę do dalszej poprawy jakości wody. Roczne testy kolumnowe z zerowartościowym żelazem i węglem brunatnym wykazały prawie całkowite usunięcie uranu, arsenu, kadmu i większości innych metali ciężkich. Dostarczanie materiałów reaktywnych do otwartych wyrobisk kopalni uranu w Königstein może być uznane za metodę wspomagającą redukcję zanieczyszczeń w wodzie kopalnianej. Długotrwałe efekty i towarzyszące reakcje

będą dalej badane w celu udoskonalenia tej metody dla zastosowania technologicznego w kopalni w Königstein.