In-situ immobilisation of heavy metals in the former uranium mine Koenigstein of Wismut GmbH by large scale application of BaSO₄ forming solutions



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Fundamentals

Uranium production by in-situ leaching with diluted sulphuric acid has resulted in large acidified areas within the former uranium mine Koenigstein of Wismut GmbH. In order to reduce the amounts of heavy metals released during flooding of the mine, a new in-situ immobilisation technology was developed. Areas containing highly concentrated pore waters were treated with BaSO₄ forming solutions. Slightly soluble BaSO₄ layers were formed protecting underlying minerals against leaching. Additional, hydroxides as well as hydroxysulphates were formed. Heavy metals were fixed by inclusion and adsorption.

$Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O$ $k_1 = 10^{-10} \text{ mol}^2/l^2$ ⊆ 250

fast and quantitative precipitation



Results of column and field tests

Washing porous, heavy metal containing sandstone with water results in long time discharge of polluted solutions with concentrations dropping only slowly. In contrast, treatment with BaSO₄ forming solutions causes in-situ immobilisation and solutions are discharged with fast decreasing concentrations (Fig. 2).

Areas in which uranium was produced by the block leaching technology were selected for field tests (Fig. 7). A reduction of the discharged amounts of contaminants between 50 and 70% was proved in respect to flushing with water (Fig. 3, 4). Formed BaSO₄ precipitates protect reactive mineral surfaces against leaching (Fig. 5).







depending on the inhibitor concentration

 $BaSO_4$ forming solutions can be prepared by mixing $Ba(OH)_2$ solutions with diluted sulphate containing solutions such as sulphuric acid or sodium sulphate in the presence of suitable precipitation inhibitors. While normally spontaneous and complete formation of BaSO₄ occurs, the presence of the precipitation inhibitor leads to temporarily stable, clear solutions. The timely stability of the solution can be adjusted by the composition of the used inhibitor and its concentration. The use of sodium sulphite as sulphate source gives solutions characterised by reducing properties.

Treatment of contaminated areas with BaSO₄-forming solutions results in crystallisation processes within the flow paths. In-situ fixation of diluted contaminants and protection of reactive mineral surfaces by long time stable minerals is achieved.

Large scale application

In order to reduce the amount of discharged heavy metals during flooding with water approximately 250000 m³ of BaSO₄ forming solution were injected into different blocks between November 2003 and June 2005. Solutions composed by mixing of $Ba(OH)_2$ with Na_2SO_3 and small amounts of water glass were used. Spontaneous BaSO₄ formation was prevented by the addition of precipitation inhibitors.

Fig. 2: Course of contaminant discharge during washing with water and immobilisation with BaSO₄ solutions (column test)



Fig 3: Discharge of uranium during flushing with water and immobilisation (field test)



Fig. 4: Comparison of uranium output during immobilisation and flushing with water (field test)



Fig. 5: BaSO₄ precipitates formed in porous sandstone

Approximately 140 t BaSO₄ were formed in the treated areas.



Fig. 8 - 12: Views of the grout plant

Fig. 6: Scheme of the grout plant for the preparation of BaSO₄ forming solutions

Fig.7: Scheme of filling leached blocks with BaSO₄ forming solutions

Conclusions

Treatment of contaminated areas with BaSO₄- forming solutions allows in-situ fixation of heavy metals.

> Reactive mineral surfaces are covered by insoluble precipitates.

- > Mixing with pore water present in the formation results in precipitation of insoluble minerals.
- > BaSO₄ forming solutions can be prepared under conditions typical for mining.
- > Long time stable fixation is achieved by an environmental friendly technology.