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Technology Information

Immobilization of heavy metals by directed and controlled $BaSO_4$ precipitation

1. FUNDAMENTALS

$BaSO_4$ has a solubility product of 10^{-10} mol^2/L^2 and is a mineral which is stable in most naturally occurring solutions. Due to the extremely low solubility, even traces of Ba^{2+} ions are precipitated in the presence of SO_4^{2-} ions. Only the addition of special precipitation inhibitors offers the possibility of synthesizing solutions supersaturated in $BaSO_4$. The inhibitors prevent spontaneous precipitation during the preparation of the solution (for example by mixing of $BaCl_2$ and $MgSO_4$ solutions) and stabilize the supersaturation for a limited period of time (Fig. 1). A favorable way to prepare "pure" $BaSO_4$ solutions bases on the use of $Ba(OH)_2$ solutions and diluted H_2SO_4. Apart from the inhibitor, the resulting solution contains only Ba^{2+} and SO_4^{2-} ions and no further components are present. It is possible to control the rate of the crystallization process by the composition of the inhibitor and its concentration or as well as by the absolute degree of supersaturation (Fig. 2). The maximum achievable $BaSO_4$ supersaturation lies between 200 and 400 mg/L, depending on the type of inhibitor and its concentration. Decomposition of the inhibitor results in the formation of insoluble $BaSO_4$ precipitates. If $BaSO_4$ forming solutions are used as grout, the precipitates form a protective layer on reactive mineral surfaces and prevent further dissolution processes (Fig. 3). Immobilization of soluble contaminants is achieved by a long time stable mineral.

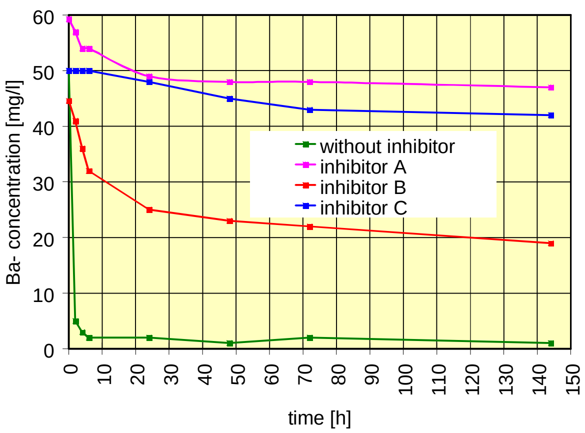

Fig. 1: Course of $BaSO_4$ precipitation depending on the used inhibitor

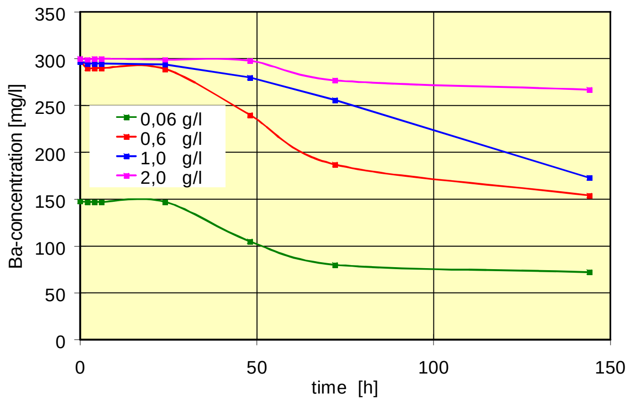

Fig. 2: Course of $BaSO_4$ precipitation depending on the inhibitor concentration

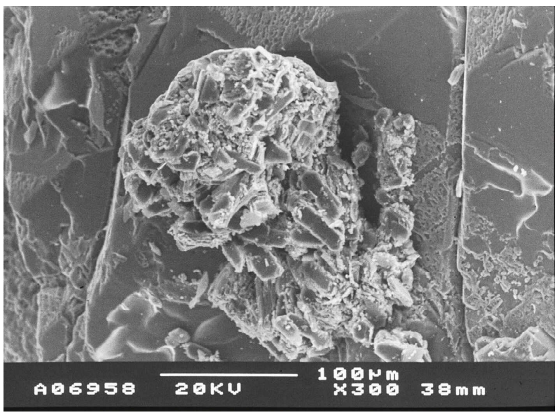

Fig. 3: SEM picture of $BaSO_4$ layers grown on sandstone.

2. FIELD APPLICATIONS

The developed process has been successfully applied in the former uranium mine Königstein of Wismut GmbH, Germany. In this mine uranium was recovered by in-situ leaching of a sandstone formation with highly diluted H_2SO_4. After the end of mining operations large amounts of acidic, contaminated solutions were present in the formation, which have to be treated before flooding the mine. The use of $BaSO_4$ forming solutions to neutralize highly contaminated zones was one of the concepts used to remediate the mine.

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Approximately 255 000 m^3 of $BaSO_4$ forming solutions were injected within three years. The solutions were pumped into the sandstone and after passing the formation the output solution was collected at a lower horizon (Fig. 4). During the injection of the $BaSO_4$ grout a significant reduction in permeability was found (Fig. 5). The dimensions of this effect were surprising because the absolute amounts of $BaSO_4$ brought into the formation were low in relation to the pore volume. The composition of the solutions collected after passing the formation is summarized in Fig. 6. After an output of solutions having low contents of contaminants and a low conductivity, rapid increase and then a fast decrease of all concentrations takes place. This is a result of the flow conditions in the formation.

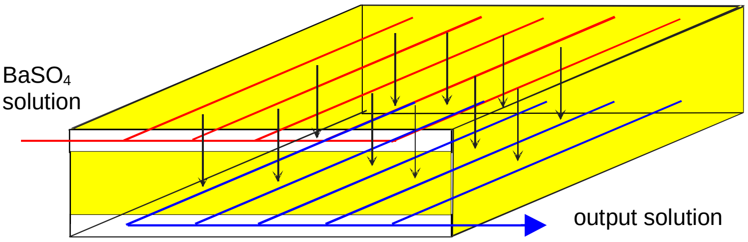

Fig. 4 Schematic view of the test site

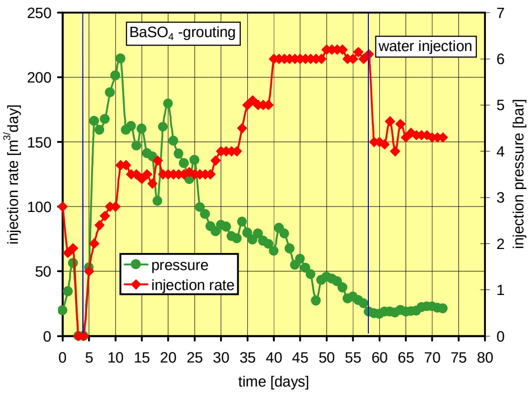

Fig. 5: Development of injection rate and pressure

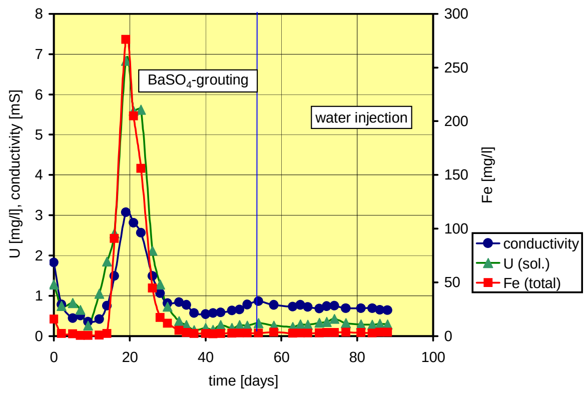

Fig. 6: Course of contaminants in the output solutions

In the first step the injected grout penetrated preferred flow paths with high hydraulic conductivity. With increasing amounts of injected $BaSO_4$ grout, zones with lower permeability were also reached and the maximum of the concentrations in the output solutions reflects pore water which is undiluted or only affected by low amounts of $BaSO_4$ grout. The penetration of zones with lower permeability is supported by a closure of bigger flow paths by newly formed $BaSO_4$ precipitates. Further concentration development is characterized by a rapid decrease in the contents of all components. The $BaSO_4$ grout leads to in-situ precipitation processes and to the formation of protective layers. After finishing the $BaSO_4$ grouting, a test area was treated with fresh water for three weeks. No dissolution processes and no increase in the permeability of the formation took place. The output solution did not contain Ba^{2+} ions. The level of contaminants remained low.

3. CONCLUSION

The directed and controlled crystallization of $BaSO_4$ from supersaturated solutions is a favorable method to fix contaminants by precipitation. Reactive mineral surfaces are protected against leaching by layers of insoluble minerals. The immobilization is connected with a drastic reduction of the hydraulic conductivity of the treated formation. It is not necessary to fill the flow paths with secondary minerals to obtain sealing. Even closure by single crystals leads to a drastic reduction in permeability.

$BaSO_4$ forming solutions can be prepared in a simple way under conditions typical for the mining industry. The total costs of chemicals are low and immobilization and sealing is achieved by minerals naturally present in the rock or soil formation. The method has the essential benefits of mineral crystallization directly from the injection solution as well as multiple possibilities to control both the crystallization and immobilization process.