A novel technology for sealing and immobilization – the use of precipitation processes from supersaturated solutions

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Abstract. Mineral forming solutions can be prepared by using of special precipitation inhibitors. These are compounds allowing the mixing of solutions which are incompatible under normal conditions, for example $BaCl_2$ and Na_2SO_4 solutions or lime suspensions and diluted sulfuric acid. Clear, temporary stable solutions are obtained. If these are used as grout, directed precipitation takes place in the flow paths. The paper summarizes the fundamentals of the technology and gives an overview about the characteristics of gypsum and $BaSO_4$ forming solutions. Their immobilization effect was proven by column tests, which are discussed in detail.

Introduction

Precipitation processes play an important rule in nature. For example, the generation of acid rock drainage is stopped when formation of hard and insoluble crusts of hydroxides or sulfates takes place. The precipitated minerals protect deeper zones against the infiltration of water and oxygen and prevent the oxidation of sulfidic ores. Such “self healing” processes leading to the closure of flow paths are widely known. They base mainly on coupled dissolution and precipitation processes and need long times because only small amounts of mass are transported (Chermark 1996, Ettner 1999). The aim of this paper is to present the fundamentals of a novel technology for sealing and remediation of porous or fractured formations by using directed precipitation processes. Solutions are prepared and used as grout which are highly supersaturated in respect to slightly soluble minerals. The preparation of these solutions bases on the use of special precipitation inhibitors. These allow mixing of components which are normally incompatible. The resulting solutions are stable for a limited period of time only, depending on the degree of supersaturation, the used inhibitor and its concentration.

Experimental

Preparation of supersaturated, mineral forming solutions

$BaSO_4$ as well as gypsum supersaturated solutions were prepared step by step by mixing solutions containing $BaCl_2$/$CaCl_2$ or $Ba(OH)_2$/$Ca(OH)_2$ with Na_2SO_4 or $MgSO_4$ containing solutions/diluted sulfuric acid, respectively, in the presence of various types of precipitation inhibitors. Barium sulfate forming solutions characterized by reducing properties were obtained by using Na_2SO_3 as source for sulfate generation. The stability of the obtained supersaturated solutions was determined by stirring experiments at room temperature. The temporal change of the barium or calcium concentrations served as a measure for the course of $BaSO_4$ or gypsum crystallization.

Column tests

The columns used to determine the immobilization capacity of $BaSO_4$ producing solutions had a height of 1000 mm and a diameter of 300 mm. They were filled with approximately 60 kg of broken sandstone (from the Koenigstein mine of Wismut GmbH) with an average diameter of 2 cm. 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. A volume of approximately 23 l was required to fill the columns right up. The immobilization tests were carried out with a solution resulting in the formation of 300 mg/l $BaSO_4$. At an inhibitor concentration of 50 mg/l the stability was in excess of 96 hours. In order to increase the immobilization capacity small amounts of sodium silicate were added. Technical grade $Ba(OH)_2*8H_2O$, Na_2SO_3 and sodium silicate solution were used. The feed solution was discontinuously prepared step by step by mixing solutions of the separate constituents.

Results and Discussion

Preparation and properties of gypsum forming solutions

Gypsum has at 25 °C a solubility of approximately 2.5 g/l in water. It has been found, however, that gypsum is able to produce long time stable layers in waste rock dumps and tailings. Gypsum forming processes can be enhanced if solutions are applied which transport higher amounts of dissolved $CaSO_4$ than natural waters. Such solutions can be prepared by mixing of $Ca(OH)_2$ suspensions with diluted sulfuric acid. The presence of a suitable precipitation inhibitor is essential, otherwise fast and almost quantitative precipitation takes place. Precipitation inhibitors are compounds which are able to interrupt the crystallization process temporarily. This effect bases on the adsorption of the inhibitor on formed gypsum nuclei. The growth of the nuclei is temporarily blocked and the solution remains supersaturated for a limited period of time.

Fig. 1 explains the action of precipitation inhibitors. Fast crystallization takes place in the absence of an inhibitor. In the most cases, already few ppm are enough to prevent spontaneous gypsum crystallization. Increasing inhibitor concentrations result in solutions with raising stability. The extent of crystallization in a 0.5 molar $CaSO_4$ solution depending on the inhibitor content is visible in Fig. 2. The amounts of formed gypsum decrease with increasing volumes of added inhibitor solution. High inhibitor concentrations allow complete stabilization of the solution for a limited period of time. After that, crystallization starts as well. Factors influencing the stability of supersaturated solutions are temperature, pH and mechanical agitation as well as the presence of solids. Due to adsorption of the inhibitor on the surface of many solids, faster crystallization takes place in suspensions than in pure solutions. NMR investigations on gypsum formed in supersaturated solutions have proven that the inhibitor is incorporated into the growing crystals. If $CaCl_2$ and sodium or magnesium sulfate solutions are mixed together in the presence of a suitable inhibitor, final $CaSO_4$ concentrations up to 100 g/l are possible. Concentrations up to 45 to g/l $CaSO_4$ can be achieved in the case of using lime milk and diluted sulfuric acid. All solutions are completely clear; their stability depends on the type and the concentration of the used inhibitor. Gypsum forming solutions have a high sealing capacity. If they are used as grout in porous or fractured soil or rock formations, gypsum crystallization takes place in the treated flow paths and leads to a step by step reduction of the permeability.

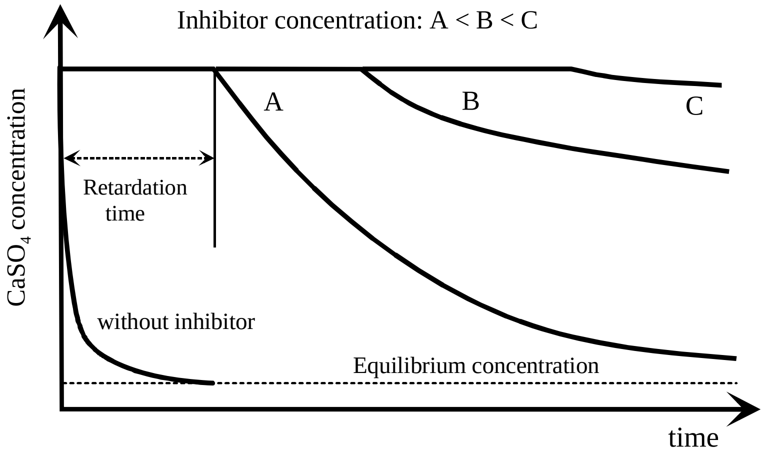
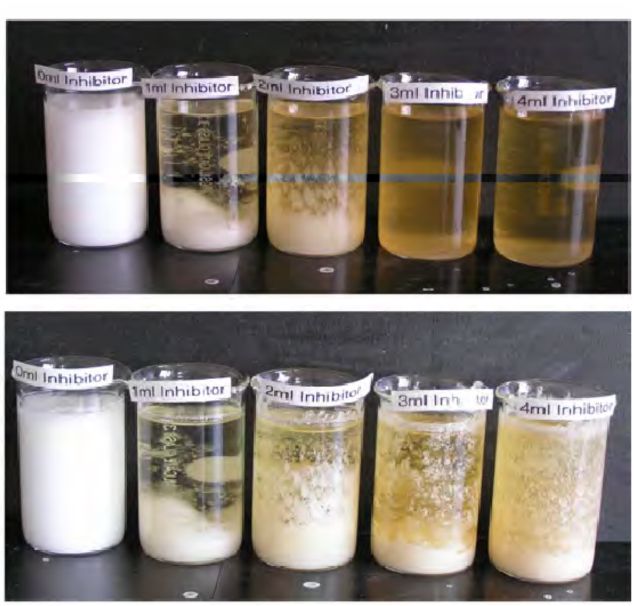


Fig. 1. Course of crystallization from supersaturated solutions in the presence of precipitation inhibitors.



1 hour after preparation

10 hours after preparation

Fig. 2. Gypsum crystallization depending on the amount of added inhibitor solution

Preparation and properties of $BaSO_4$ solutions

Barite ($BaSO_4$) is a mineral with an extremely low solubility. It normally precipitates immediately upon mixing of solutions of barium ions with sulfate containing solutions. The resulting precipitates are capable of binding many ions, mainly Fe^{3+}, Al^{3+}, Cl^- and PO_4^{3-}. In principle, three different options are possible:

- Mixing of $BaCl_2$ and Na_2SO_4 or $MgSO_4$ solutions;
- Mixing of $Ba(OH)_2$ solutions and diluted H_2SO_4;
- Mixing of $Ba(OH)_2$ and sodium sulfite solutions.

In all cases it is necessary to add a suitable inhibitor. While the first option produces a solution containing dissolved NaCl as a by-product, the second results in a solution containing, apart from the inhibitor, only dissolved barite. The third solution has reducing properties. $BaSO_4$ is formed as a result of sulfite oxidation. The solution has an alkaline character and it is possible to add sodium silicate solutions to enhance the immobilization capacity. Temporal stability of $BaSO_4$ supersaturated solutions depends on the overall solution composition, the used precipitation inhibitors (Fig. 3) and the latter's concentration. Fig. 4 shows the course of $BaSO_4$ precipitation as a function of inhibitor concentration. While an inhibitor concentration of 0.8 mg/l suffices to stabilize a solution containing 50 mg/l of Ba^{2+}, 60

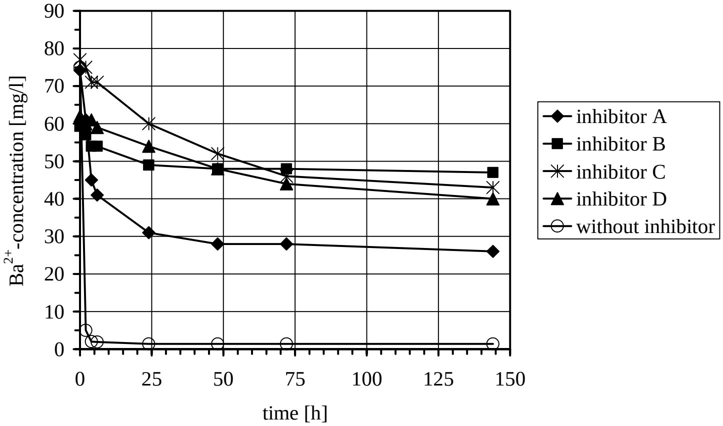


Fig. 3. Stability of $BaSO_4$ solutions depending on the used inhibitor.

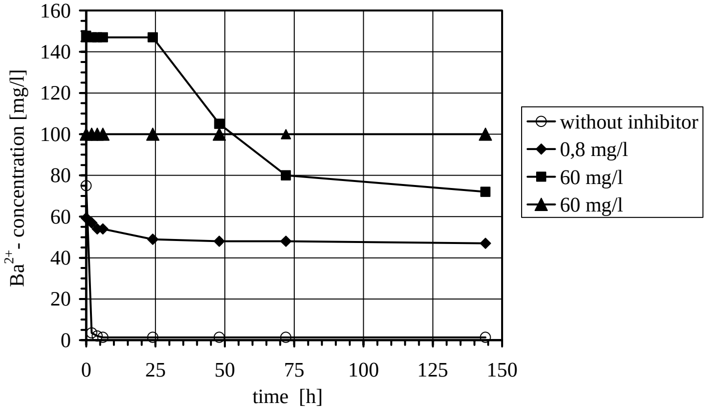


Fig. 4. Course of $BaSO_4$ precipitation from supersaturated solutions depending on the inhibitor concentration.

mg/l of inhibitor are capable of stabilizing 100 mg/l of Ba^{2+} for a period of more than 140 hours. In general, higher supersaturations require higher inhibitor contents. $BaSO_4$ concentrations up to 800 mg/l can be stabilized temporarily. This is approximately 350 times higher than the equilibrium concentration of $BaSO_4$ in water. It is possible to prepare solutions having acidic as well as alkaline character. In general, a higher inhibitor concentration does not only allow the stabilization of higher $BaSO_4$ concentrations, but also leads to a slower crystallization process. While "pure" $BaSO_4$ solutions have an extremely high stability, interactions with reactive mineral surfaces can provoke fast crystallization.

At the same inhibitor level, alkaline solutions prepared on the basis of $Ba(OH)_2$-, Na_2SO_3 solutions are characterized by a higher stability than neutral solutions composed by mixing of $Ba(OH)_2$ and diluted sulfuric acid (Fig. 5).

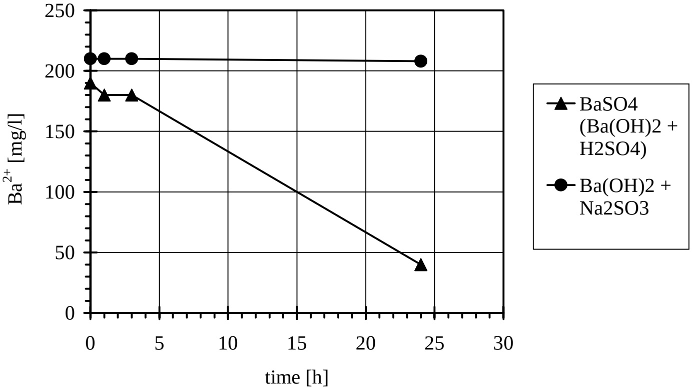


Fig. 5. Course of $BaSO_4$ precipitation depending on the used sulfate source (80 mg inhibitor/l).

Results of column experiments

The first column was treated with water for a period of 56 days. After that period, the water was drained off completely. The sandstone remained in the column for a period of 25 weeks, then followed a second flushing with water. The course of concentrations in the solutions collected after passing the column is summarized in Fig. 6. The first solutions were characterized by high concentrations. They de-

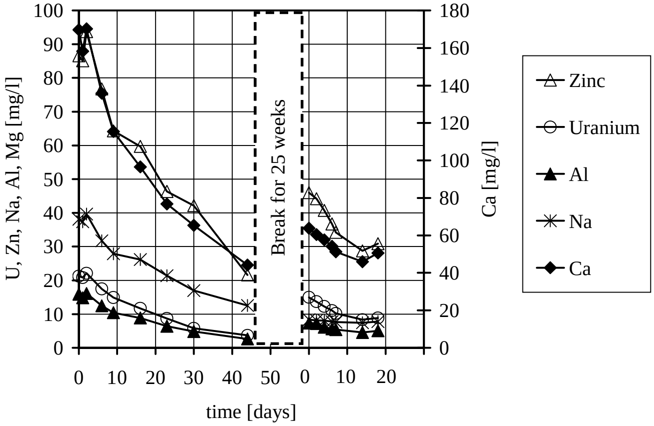


Fig. 6. Change of effluent concentrations during flushing the column with water.

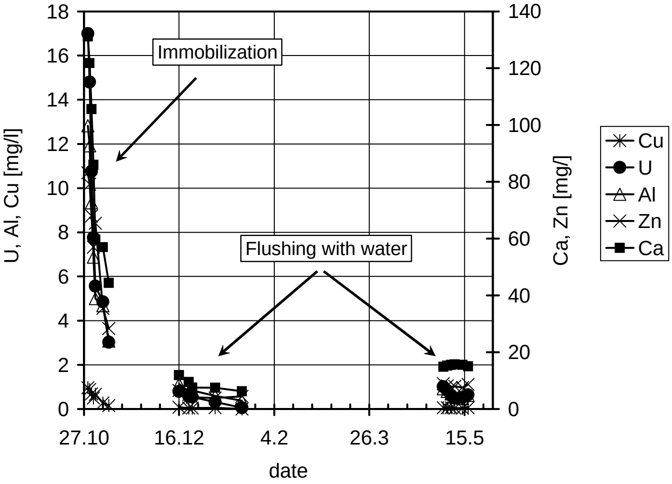


Fig. 7. Change of effluent concentrations during and after immobilization of the column with $BaSO_4$ solutions.

crease over time; however, this is a slow process. The replacement of more than 23 l of solution was necessary to reduce the concentrations by half. As a consequence, pH shifted only slowly. After the outflow of 44 l the solution was characterized by uranium concentrations of 3.8 mg/l while zinc concentration was 21 mg/l. The second treatment with water produced solutions with concentrations similar to the first flushing process. This indicates that oxidation processes have led to the mobilization of further contaminants. In other words, flushing with water results in large amounts of contaminated solutions characterized by only slowly dropping concentrations. No immobilization takes place; and contact with oxygen causes the mobilization of leachable heavy metals.

In contrast, solutions resulting from the treatment with $BaSO_4$ were characterized by rapidly decreasing concentrations (Fig. 7). The used solution had the following composition: 176 mg/l Ba^{2+}, 150 mg/l SiO_2, 102 mg/l SO_3^{2-}, 50 mg/l inhibitor. Fast and almost complete reduction of all main components was observed in the effluents during the $BaSO_4$ treatment of the column. It becomes apparent that $BaSO_4$ forming solutions lead to rapid immobilization. $BaSO_4$ concentrations were detected below the natural solubility of barite. This is an indication of complete $BaSO_4$ precipitation. It was also of great importance to see complete inhibitor adsorption on the sandstone. After 22 l of $BaSO_4$ forming solution had passed through the column the flow was stopped. The column was emptied completely, and treatment with water started a week later. The low concentrations in the output solutions demonstrated the formed precipitates' resistance to water. Flushing with water was stopped after the outflow of approximately 20 l of water. Again, the water was drained off completely. A second flushing with water was carried out 17 weeks later. In contrast to the column treated with water only, the contact with air did not lead to significant oxidation processes. The amounts of discharged contaminants were low in comparison to the flushing process. Stable immobilization was achieved with $BaSO_4$ forming solutions.

As visible from Fig. 8, the treatment with $BaSO_4$ forming solutions produces effluents in which the contaminant concentrations decrease faster than during flushing with water. This means, the use of $BaSO_4$ solutions results in reduced total amounts of discharged contaminants and produces a long time protection against oxidation and leaching.

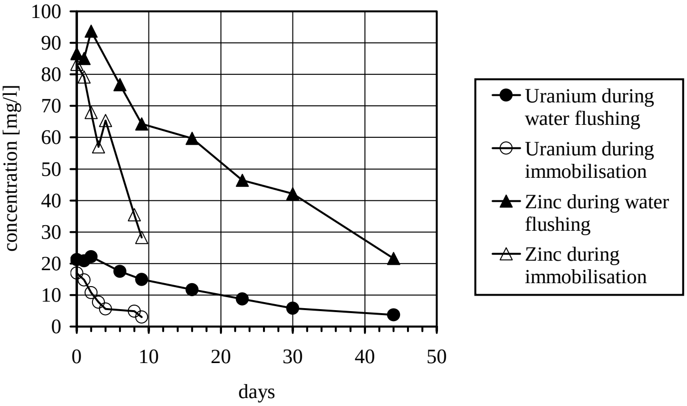


Fig. 8. Comparison of effluent concentrations during water flushing and immobilization.

Conclusions

Solutions supersaturated in respect to gypsum or barite can be prepared by the use of precipitation inhibitors. Systems are obtained characterized by concentrations high above the normal solubility of the minerals. The solutions are temporary stable. If they are used as grout, directed crystallization takes place in the penetrated flow paths. Due to the high amounts of mass that can be transported gypsum forming solutions are favored for sealing purposes. The application of $BaSO_4$ oversaturated solutions is seen as a favorable way to in-situ immobilize heavy metals within porous rock or soil formations. $BaSO_4$ layers covering reactive mineral surfaces as well as secondary precipitates such as hydroxides or hydroxysulfates are formed. Due to the extremely low solubility of barite a long time stable immobilization is achieved.

The described laboratory investigations were the basis for large scale field tests in the Koenigstein mine of Wismut GmbH. These have resulted in the decision to use $BaSO_4$ forming solutions for the immobilization of selected parts of the mine (Ziegenbalg, 1003A, Ziegenbalg 2003B, Jenk 2005).

Further applications of the technology are seen in the remediation of rock formations treated by acidic as well as alkaline is-situ leaching techniques and to stop or reduce the formation of acid rock or mine drainage.

Acknowledgements

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