Directed and Controlled Crystallisation of Slightly Soluble Minerals - a New Technology to Seal Water Inflows and to Immobilise Contaminants

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Abstract

The paper summarizes a novel technology for sealing of soil or rock formations by directed crystallisation processes. Supersaturated solutions are used as grout. They are prepared by mixing of solutions which are normally incompatible, for example $CaCl_2$ and Na_2SO_4 solutions or $Ba(OH)_2$ and diluted sulphuric acid. Spontaneous crystallisation is prevented by the addition of precipitation inhibitors. The obtained solutions are temporary stable. When they are used as grout, crystallisation takes place in the treated flow paths. Both sealing and fixation of contaminants can be achieved. It is possible to synthesise solutions containing up to 600 mg/l $BaSO_4$ or 100 g/l $CaSO_4$. The paper summarises the fundamentals of the technology and gives an overview about properties and applications of mineral forming solutions.

Key words: crystallisation, supersaturated solutions, grouting, immobilisation, gypsum, barite, brine inflow, sealing fractured and porous rock

Introduction

Crystallisation processes play an important role in nature. They can change the hydraulic properties of large areas completely. Especially in waste rock dumps, the formation of hard crusts, consisting mainly of gypsum, could be proven in many cases [1-2]. Gypsum layers cause significant reductions of the permeability. Deeper horizons are protected against the infiltration of water and oxygen. Although the gypsum solubility is relatively high, long time stability has been proven. Normally, coupled dissolution – precipitation phenomena have induced such processes. Limestone is dissolved by sulphuric acid and gypsum crystallisation takes place from the resulting calcium sulphate containing solution. Based on that, the idea was born to develop a technology using directed crystallisation processes for sealing of rock and soil formations as well as to immobilize contaminants. One such possibility is to use supersaturated solutions as grout. These can be prepared by using precipitation inhibitors which allow the preparation of solutions characterised by concentrations high above the normal solubility of slightly soluble minerals such as gypsum or barite. The solutions are temporarily stable, only. When they are used as grout, crystallisation takes place in the treated flow paths. Step by step closure is achieved.

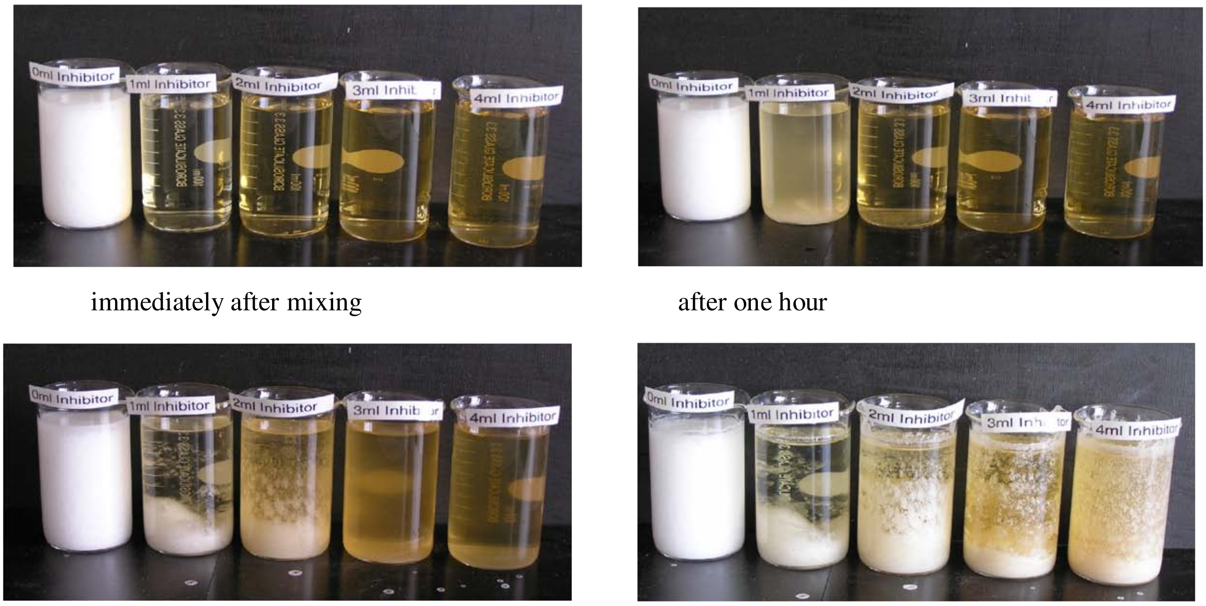
Experimental

Isothermal stirring experiments at 25 °C were carried out in order to determine the course of gypsum or barite crystallisation from supersaturated solutions. The change of the calcium or barium concentrations in the solutions served as indicator for the course of crystallisation. Complexometric titration with EDTA was used for their analytical determination. Stock solutions prepared from analytical grade chemicals ($CaCl_2$, $Ba(OH)_2$, H_2SO_4, $MgSO_4$) were used in the laboratory experiments. The solutions were mixed in stoichiometric ratios. Before adding the second component, for example Na_2SO_4 to $CaCl_2$ solutions, the inhibitor was added in form of a diluted aqueous solution. Typically, the final solutions contain inhibitor contents between several ppm and 500 mg/l. Both organic and inorganic polymers were used as inhibitor. The sealing capacity of gypsum forming solutions was determined by tests in columns with a length of 1000 mm and a diameter of 6 cm. They were filled with sea sand. The solution was pumped from the bottom to the top of the column. Large columns (300 mm diameter and 1000 mm length) containing approximately 60 kg of broken, heavy metals containing sandstone were used to investigate the immobilization capacity of $BaSO_4$ forming solutions. The origin of the material was the former uranium mine "Koenigstein"of Wismut GmbH, Germany.

Results and Discussion

Figure 1 demonstrates the action of precipitation inhibitors. Mixing of pure, one molar $CaCl_2$ and $MgSO_4$

***Figure 1** Timely course of gypsum crystallisation depending on the inhibitor concentration*



immediately after mixing — after one hour

after three hours — after 24 hours

solutions results in spontaneous gypsum crystallisation. In the presence of a suitable precipitation inhibitor, however, timely delayed gypsum crystallisation takes place. The higher the inhibitor concentration the longer the solution is stable. Gypsum has at 25 °C a solubility of approximately 2.5 g/l Mixing of one molar solutions results in final concentration of 68 g/L. That means, the total supersaturation is 65,5g $CaSO_4$/L. Approximately 83 g gypsum can be produced from one Liter solution. This is several times higher than in natural processes.

The stability of the solution and the course of crystallisation are determined by many factors. Important are pH, temperature, the presence of other ions or suspended solids as well as the used sulphate source (Na_2SO_4, K_2SO_4 or $MgSO_4$). Fig. 2 shows the course of gypsum crystallisation from solutions containing different inhibitor concentrations. The stability of the solution and thus the timely course of gypsum crystallisation can be adjusted by concentration and type of the inhibitor.

The results of injection tests in a column filled with sea sand are given in Fig. 3. Due to the high stability of the used solutions, gypsum crystallization did not take place during the first injection period. The effluent concentrations are only little lower than the input concentrations. Thus, it is possible to bring the solution in areas far away from the point of injection. Standing overnight, however, results in significant gypsum precipitation. Further injection of $CaSO_4$ solutions is connected with gypsum crystallisation. The already formed crystals act as seeds and thus, accelerated break down of the supersaturation takes place. As result, the k_f value decreases from 12 m/day to 2 m/day.

If gypsum forming solutions are brought into denser material than loose sand, a permeability reduction down to k_f values of 10^{-5} cm/s or lower can be achieved with few injections. Another way to prepare gypsum forming solutions is the neutralisation of lime suspensions with diluted sulphuric acid. Solutions result containing, apart from the inhibitor, only dissolved $CaSO_4$.

Gypsum forming solutions were used successfully for sealing inflows into salt and potash mines. Due to the high solubility of all salt minerals also small inflows have to be stopped. The danger of flooding the whole mine is substantial. Large scale tests and applications in the Merkers mine of K+S Kali GmbH (Germany) and the K-2 mine of Mosaic Potash Esterhazy Ltd. (Canada) have proven the possibility to seal fractured rock by directed gypsum crystallisation from supersatured solutions. In all cases, solutions saturated in NaCl were used for that. Underground injections from the mine level were carried out in the Merkers mine. At K-2 of Mosaic, the solutions were injected from the surface into a limestone formation at an approximately depth of 900 m. In both cases, solutions with stabilities between few hours and days were used. The preparation process based on step by step mixing of $NaCl$-$CaCl_2$ and $NaCl$-$Na_2SO_4/MgSO_4$ solutions in the presence of different inhibitors.

Figure 2 *Gypsum crystallisation depending on the inhibitor concentration.*

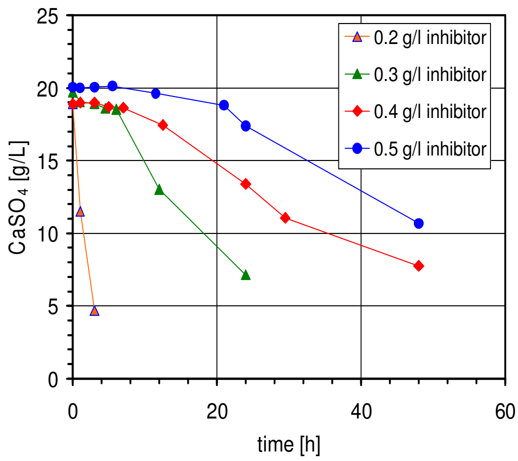


Figure 3 *$CaSO_4$ outflow concentrations and k_f values during treatment a sand column with gypsum forming solutions*

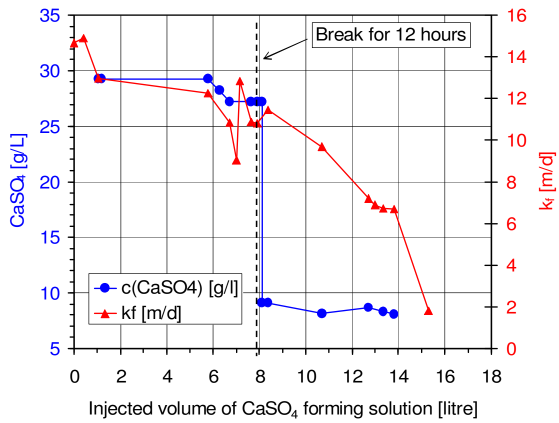


Figure 4 *Timely course of $BaSO_4$ crystallisation from Supersaturated solutions*

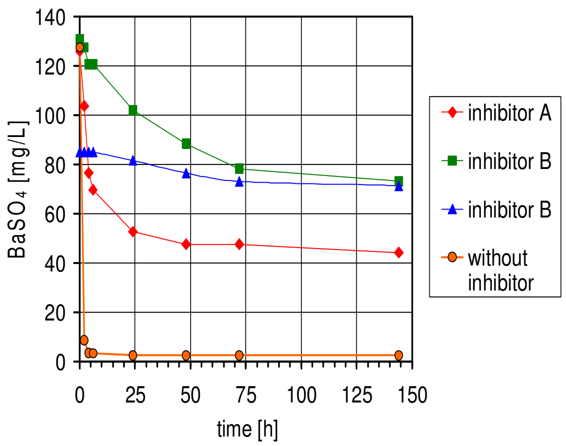
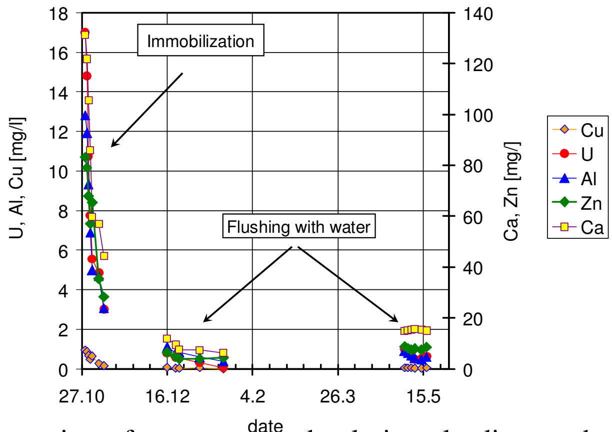


Figure 5 *Outflow concentrations in column experiments to characterise the action of $BaSO_4$ solutions*



The use of precipitation inhibitors allows the preparation of supersaturated solutions leading to the formation of $BaSO_4$, $CaCO_3$, $CaSO_4$ (anhydrite) or $BaCO_3$. Fig. 4 summaries the course of barite formation from solutions prepared by mixing $Ba(OH)_2$ and diluted H_2SO_4. Solutions with a stability varying between few hours and days can be prepared. Column experiments on highly polluted sandstone from the former uranium mine "Koenigstein" of Wismut GmbH have demonstrated the efficiency of grouting with $BaSO_4$ solutions. The immobilization tests were carried out with solutions resulting in the formation of 350 mg/l $BaSO_4$. At an inhibitor concentration of 80 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 $Ba(OH)_2 \cdot 8H_2O$, Na_2SO_3 and sodium silicate solution were used. Na_2SO_3 gave the solution reducing properties. Oxidation of sulphite produces sulphate which was stabilised by the present inhibitor. The feed solution was discontinuously prepared step by step by mixing solutions of the separate constituents. An alkaline solution with reducing properties has resulted. In the case of mixing with acidic, heavy metal containing solutions precipitation of slightly soluble hydroxides or hydroxysulphates took place, depending on the mixing ratio. In contrast to water flushing, fast reduction of the all outflow concentrations was observed (Fig. 5). Four weeks after the permeation with $BaSO_4$-forming solutions, the column was also flushed with water. The concentrations remained at a low level. Obviously, oxidation processes were prevented due to the formation of insoluble layers consisting of $BaSO_4$, hydroxides and other secondary minerals. The same

was observed during a second flush with water, five months later. $BaSO_4$ crystals have formed a dense layer on the sandstone surface protecting reactive minerals against dissolution (Fig. 6).
After large scale field tests $BaSO_4$ forming solutions were applied between 2003 and 2005 for in-situ immobilisation of large parts of the Koenigstein mine (Fig. 7). Approximately 300000 m³ solution were prepared and brought into the formation [3-5].

Figure 6 *$BaSO_4$ crystals formed on sandstone*

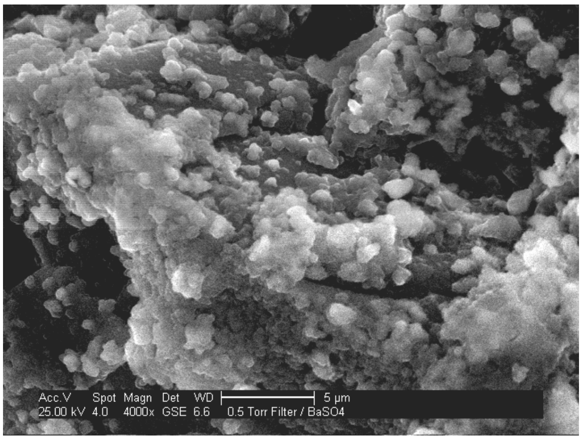
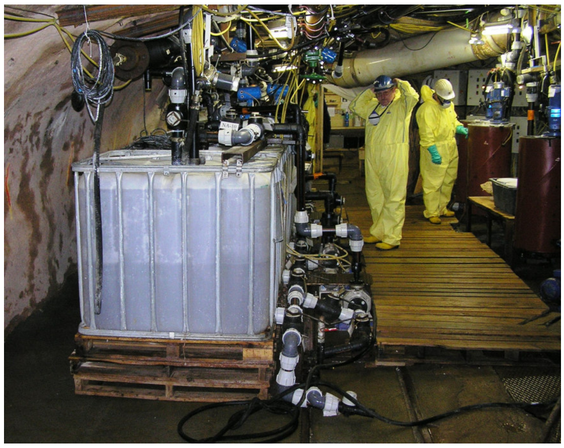


Figure 7 *Grout plant in the Koenigstein mine*



Conclusions

The technology of sealing and immobilisation by controlled crystallisation processes can find many applications, both for the remediation of contaminated areas and for solution of geotechnical problems. The technology combines many advantages such as:

- Sealing and immobilisation is achieved exclusively by naturally occurring minerals. The immobilisation process typically is coupled with a permeability reduction.
- There are many options to direct the precipitation of the minerals and thus to control sealing and immobilisation.
- Different technologies such as spraying, penetration grouting, pressure grouting, infiltration from ponds or reservoirs can be used to transport the mineral forming solutions into the area that is to be treated.
- All grouts or penetration agents are pure solutions with a viscosity similar or equal to natural groundwaters. A good penetration or infiltration even of soils with a low permeability is given
- It is possible to construct reactive barriers within polluted areas by an in situ technique.

The preparation of the solutions is simple and can be carried out both on surface and under conditions typical for underground mining. The total costs of chemicals are low and only standard equipment is necessary. Only non-toxic, environmental friendly compounds are used. The inhibitors are incorporated into the formed minerals and do not cause any new pollutions.

References

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