

# IN-SITU REMEDIATION OF HEAVY METAL CONTAMINATED SOIL OR ROCK FORMATIONS AND SEALING OF WATER INFLOWS BY DIRECTED AND CONTROLLED CRYSTALLIZATION OF NATURAL OCCURRING MINERALS

Gerald Ziegenbal

Freiberg University of Mining and Technology, Institute of Technical Chemistry  
09596 Freiberg, Germany  
e-mail: ziegenb@server.compch.tu-freiberg.de

## INTRODUCTION

Many processes have been developed for the in-situ remediation of heavy metal polluted areas as well as for the sealing of porous rock or soil formations. In both cases, grouting methods offer a wide range of applications. It is essential to select favourably composed grout materials. Typical grouts are cements, silicate solutions, plastics and clay or bentonite suspensions. Apart from the costs of the materials, a further problem is that fine sealing requires great efforts or may be impossible. In the case of suspensions, a great particle size prevents a penetration of fine flow paths. Many plastics are characterised by a high viscosity and a high injection pressure is necessary to reach microflow paths. A lot of commonly used grouts consist of components which are not present in the natural rock material. Long time stability has to be determined by extensive investigations.

In-situ remediation processes for the fixation of heavy metals often are based on the precipitation of hydroxides or sulphides. The use of alkaline solutions as well as special precipitating agents such as sodium sulphide is described. A further method is the construction of caps containing reactive minerals. Groundwater flow through these materials results in the formation of compounds which react with contaminants during the penetration of the polluted area. In general, all these methods are very expensive and it is difficult to direct the immobilisation process. Especially the homogeneous treatment of large zones is difficult to achieve.

On the other hand many naturally occurring processes are known which lead to a closure of flow paths. Especially the formation of slightly soluble sulphates has been observed both

in tailings and in rocks. In many cases their formation is connected with the precipitation of heavy metals and results in the immobilisation of contaminants. Obviously, the sealing or immobilisation is long time stable.

The main idea of the process summarised in this paper is to use crystallization processes similar to these naturally occurring to seal flow paths or to immobilise contaminants. Solutions supersaturated with gypsum, barite or calcium hydroxide are brought into the soil or rock formation, and a directed precipitation leads to a reduction of the permeability as well as the safe immobilisation of heavy metals.

## FUNDAMENTALS

### Preparation of grouts leading to gypsum or barite crystallization

Mixing of solutions containing calcium or barium ions with sulphate containing waters results in the formation of gypsum or barite ( $\text{BaSO}_4$ ). While gypsum has a relatively high solubility of 2.5 g/l (at 25 °C) barite is a mineral with an extremely low solubility product of  $1.08 \cdot 10^{-10} \text{ mol}^2/\text{l}^2$ . Barite crystallization occurs immediately in the presence of sulphate ions. Gypsum formation requires higher concentrations, however, it takes place spontaneously after reaching the solubility limit.

In both cases, only the use of precipitation inhibitors allows the synthesis of solutions which are temporarily oversaturated with respect to the stable solid phases. The precipitation inhibitors prevent the spontaneous precipitation of the minerals during the preparation of the solutions. For example, in the presence of 100 mg/l precipitation inhibitor it is possible to synthe-

size solutions containing up to 40 g/l dissolved  $\text{CaSO}_4$ . The resulting solutions are completely clear and have a viscosity similar to water. The precipitation inhibitors are only temporarily active. Decomposition and adsorption processes lead to a gradual reduction of their stabilising effect. As a result, gypsum crystallization takes place. The timely course of gypsum crystallization can be directed by the composition and concentration of the inhibitor, the absolute degree of oversaturation and the addition of special chemicals leading to a time-controlled decomposition of the inhibitor. Depending on the composition of the inhibitor, it is possible to stabilise gypsum oversaturations both in acidic and alkaline solutions (Figure 2).

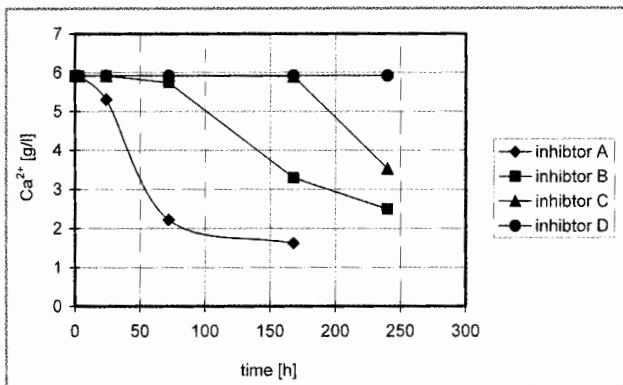


Figure 1. Course of gypsum precipitation depending on the used inhibitor.

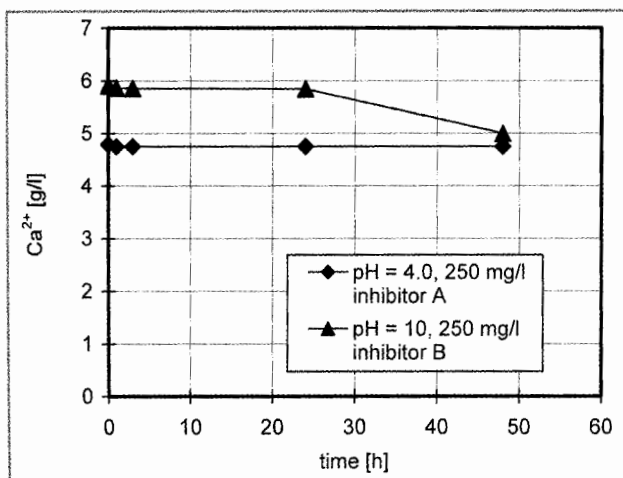


Figure 2. Course of gypsum precipitation depending on the pH value.

The preparation of  $\text{BaSO}_4$  oversaturated solutions is based on the same fundamentals. Mixing of  $\text{BaCl}_2$  and sulphate containing solutions in the presence of an inhibitor results in clear,  $\text{BaSO}_4$  supersaturated solutions. A favourable way to produce solutions containing only dissolved  $\text{BaSO}_4$  and small amounts of a precipitation inhibitor is given if  $\text{Ba}(\text{OH})_2$  solutions and diluted  $\text{H}_2\text{SO}_4$  are mixed. Figure 3 illustrates the stability of the  $\text{BaSO}_4$  solution. At  $\text{BaSO}_4$  concentrations < 200 mg/l precipitation does not take place within 48 hours. Higher oversaturations result in faster  $\text{BaSO}_4$  formation, however, spontaneous

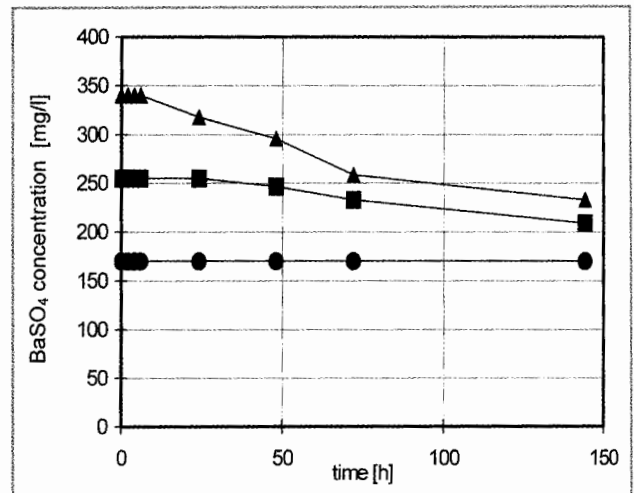


Figure 3. Course of  $\text{BaSO}_4$  precipitation in the presence of 100 mg/l inhibitor.

precipitation is prevented. The oversaturation with respect to the equilibrium concentration is much higher in  $\text{BaSO}_4$  oversaturated solutions than in solutions leading to gypsum or anhydrite crystallization.

### Preparation of $\text{Ca}(\text{OH})_2$ solutions

Lime addition is one of the most widely used method to treat acidic waste waters. The pH increase results in the precipitation of metal hydroxides. Due to the low solubility of  $\text{Ca}(\text{OH})_2$  (at 25 °C approx. 1.8 g/l) solid materials or suspensions are used.

It was found that the solubility of  $\text{Ca}(\text{OH})_2$  can be significantly increased by the use of special chemicals. These chemicals - in the following called dissolver - offer the possibility to prepare clear  $\text{Ca}(\text{OH})_2$  solutions with high concentrations. There are two ways to obtain such solutions:

- Dissolution of  $\text{Ca}(\text{OH})_2$  in a solution containing the dissolver.
- Addition of NaOH or KOH solutions to  $\text{CaCl}_2$  solutions in the presence of the dissolver.

The first method requires high amounts of dissolver and leads to solutions containing up to 30 g/l dissolved  $\text{Ca}(\text{OH})_2$ .

Figure 4 shows the pH development of  $\text{CaCl}_2$  solutions containing different amounts of dissolver during the addition of NaOH solutions. The investigations were carried out by step by step addition of a 2 N NaOH to a solution containing 30 g/l  $\text{CaCl}_2$ . To achieve a molar  $\text{Ca}^{2+} : \text{OH}^-$  ratio of 1 : 2 that is equivalent to  $\text{Ca}(\text{OH})_2$ , it is necessary to add 27 ml of a 2 N NaOH to 100 ml  $\text{CaCl}_2$  solution. As is visible from Figure 4, in the presence of 3 g/l dissolver it becomes possible to add higher NaOH amounts without precipitation. In contrast, in solutions without dissolver,  $\text{Ca}(\text{OH})_2$  precipitation occurs after the addition of 5 ml NaOH. With increasing amounts of dissolver higher NaOH concentrations can be added to the solution without the formation of  $\text{Ca}(\text{OH})_2$  precipitates. If overstoichiometric NaOH contents are added, the final product can be characterised as a  $\text{Ca}(\text{OH})_2$ -NaOH solution.

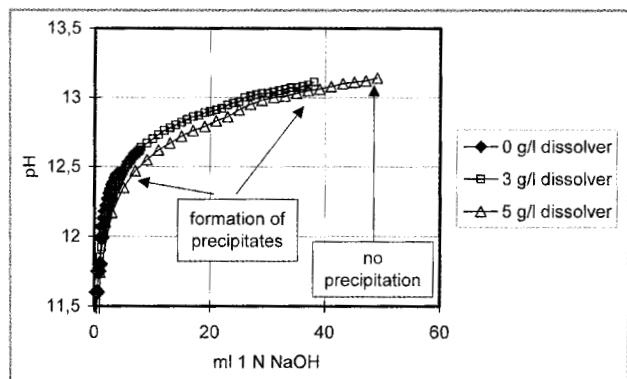


Figure 4. pH-development during titration of  $\text{CaCl}_2$  solutions with 1 N NaOH.

The chemical behaviour of the solutions is similar to pure  $\text{Ca}(\text{OH})_2$  suspensions. Mixing with acidic solutions results in a pH jump leading to the precipitation of metal hydroxides. To increase the precipitation capacity of the solution it is possible to add sodium sulphide. For practical applications, solutions containing between 3 and 10 g/l dissolved  $\text{Ca}(\text{OH})_2$  are suitable in the most cases.

## RESULTS OF TECHNICAL TESTS AND FIRST APPLICATIONS

### Sealing of rock formation

If solutions oversaturated with gypsum or barite are used as grouting agent, crystallization will take place in the penetrated flow paths. Depending on the applied oversaturation, either a very fine crystallizate or slowly growing layers are formed. Additional precipitation is possible by mixing with pore water present in the formation. Due to the higher amount of formed precipitates, the use of  $\text{CaSO}_4$  oversaturated solutions is favoured for sealing purposes.  $\text{BaSO}_4$  grouts are more suitable for the immobilisation of reactive mineral surfaces.

Laboratory investigations showed that the permeability of a sand pack can be reduced from  $1.7 \cdot 10^{-3}$  m/s to  $4.2 \cdot 10^{-5}$  m/s within 48 hours by treatment with gypsum oversaturated solutions. The sand pack was treated continuously with a  $\text{CaSO}_4$  supersaturated solution containing 30 g/l  $\text{CaSO}_4$ . A total of three pore volumes was pumped through the column within the first two days. After 96 hours a permeability of  $4.5 \cdot 10^{-7}$  m/s was measured. The sealing effect is even greater if porous sandstone is treated with a  $\text{CaSO}_4$  supersaturated solution. The flow of a solution with 20 g/l  $\text{CaSO}_4$  reduced the permeability within 24 hours from  $1.45 \cdot 10^{-5}$  m/s to  $1.28 \cdot 10^{-7}$  m/s. A permeability of  $7.26 \cdot 10^{-8}$  m/s was measured after 48 hours. The reduction in permeability is reached by gypsum amounts that are much lower than those necessary for complete filling of the pore volume. This is a result of the specific action of the grout. Single grown gypsum crystals cause the permeability reduction. These crystals prevent the further flow of solutions. Consequently, microfractures and pinpoint porosity can be sealed as the grout solution penetrates these flow paths. Flow routes are not com-

pletely sealed off by a single injection. This holds true as individual crystals grow on the walls of flow routes and consequently flow paths are closed in a step by step process. An optimum propagation of the injection solution is guaranteed. Figure 5 and 6 show typical gypsum crystals formed within sandstone. The crystals are strongly connected with the surrounding rock. Due to a blocking of the flow paths, further solution transport becomes impossible.

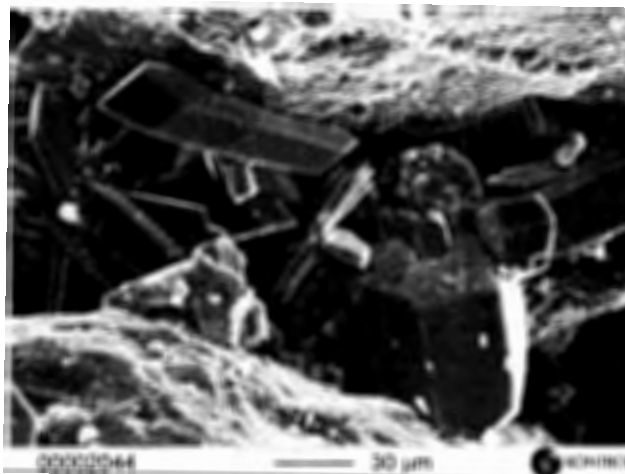


Figure 5. Blocking of flow paths by gypsum crystals.

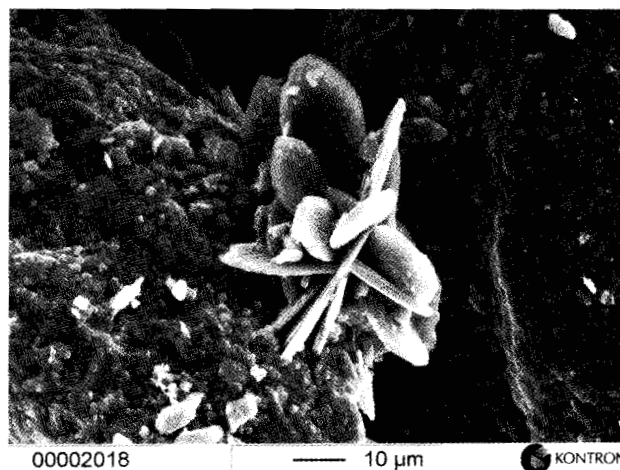


Figure 6. Blocking of flow paths by gypsum crystals.

The stability of the grouts can be changed both by the composition of the used inhibitor and the degree of oversaturation. Solutions with a high stability can be used for penetrating areas far behind the point of injection (Figure 7). This is especially useful for sealing brine or water inflows into mines. The solutions can be injected into main flow paths and then travel through the formation to the inflow point. Gypsum crystallization will lead to a step by step closure of flow routes in a manner similar to natural occurring recrystallization processes.

The use of NaCl saturated,  $\text{CaSO}_4$  oversaturated solutions to seal brine inflows into a potash mine was successfully tested. Further applications are under development.

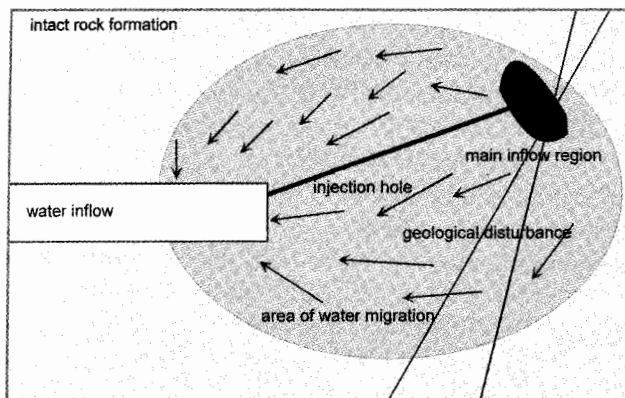


Figure 7. Example for sealing of rock formations by gypsum oversaturated solutions.

### Immobilisation of heavy metals in porous rock or soil formations

There are the following possibilities to remediate soils or rock formations polluted by heavy metals:

- encapsulation of the polluted area by impermeable walls;
- contaminant recovery for example by soil flushing;
- ex-situ decontamination or solidification;
- in-situ immobilisation.

In-situ immobilisation means that the heavy metals are fixed as insoluble, nontoxic compounds. Two aspects have to be regarded. First, the fixation of mobile contaminants present as diluted species in the pore water and secondly, the immobilisation of soluble compounds which can be dissolved by groundwater or other solutions. Soil flushing allows a fast exchange of highly polluted pore water. However, complete decontamination requires very long times. This is a result of secondary dissolution processes as well as of desorption processes. A successful fixation of soluble compounds could reduce the remediation time extremely.

An in-situ immobilisation process has to meet the following demands:

- The immobilisation has to lead to slightly soluble minerals stable under the expected conditions of flooding.
- Immobilisation must not result in an additional input of contaminants into the treated formation.
- The process has to be applicable under field conditions.

If the fixation of diluted contaminants by the precipitation of hydroxides is in the centre of interest, the use of  $\text{Ca}(\text{OH})_2$  solutions offers a wide range of applications, especially for the in-situ treatment of acid rock drainage. In contrast to the use of pure  $\text{NaOH}$  solutions,  $\text{Ca}(\text{OH})_2$  grouts lead not only to the precipitation of metal hydroxides but also to the formation of gypsum. In combination with formed hydroxides such as  $\text{Fe}(\text{OH})_3$ , an additional sealing of the penetrated areas is achieved. Due to the stability of the  $\text{Ca}(\text{OH})_2$  solutions, there are no limits in the injection time resulting from a short set time.

Extensive laboratory investigations and first technical applications demonstrated the favourable use of grouts oversaturated with gypsum or barite. The action of both injection agents is similar. Reactive mineral surfaces are overlaid by insoluble precipitates (Figure 8). These prevent further dissolution processes, and an immobilisation is achieved. Depending on the grout composition precipitation of diluted contaminants can be achieved as well.

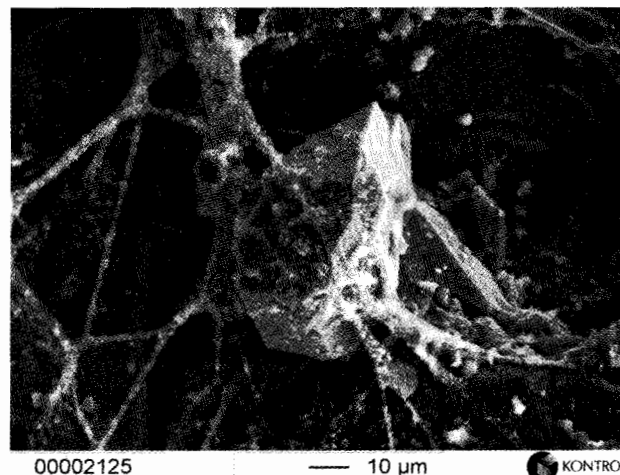


Figure 8. Secondary formed  $\text{BaSO}_4$  precipitates.

It is possible to prepare  $\text{CaSO}_4$  or  $\text{Ba}(\text{OH})_2$  grouts with an alkaline character. In the case of mixing with solutions containing heavy metals, hydroxide precipitation occurs. Additionally, the formation of mixed crystals and the inclusion of contaminants in the  $\text{BaSO}_4$  precipitates has been observed. Further precipitation processes can be induced by the selection of the precipitation inhibitor as well as by the addition of special precipitation agents (Figure 9).

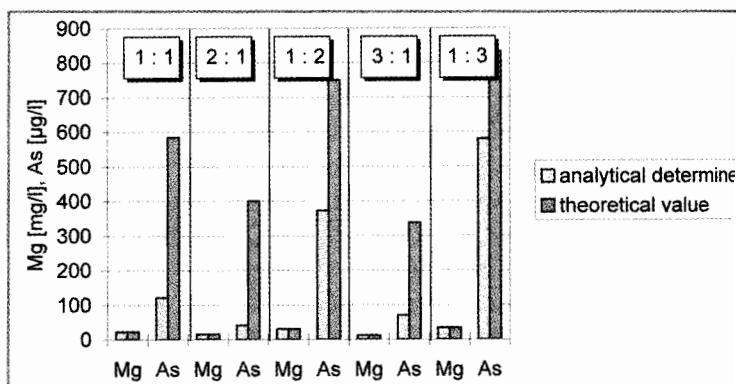


Figure 9. Precipitation of As during mixing with  $\text{BaSO}_4$  oversaturated solutions depending on the mixing ratio.

The successful application of grouts supersaturated in  $\text{BaSO}_4$  was demonstrated in the former uranium mine "Königsstein" of Wismut GmbH (Germany). In this mine uranium was recovered by in-situ leaching of a sandstone formation with dilu-

ted  $H_2SO_4$ . After the end of mining operations it was necessary to develop a strategy for a safe closure of the mine. This was highly important because in large parts of the mine acidic pore waters are present containing high levels of uranium and heavy metals.

In two technical field tests approximately 5000 m<sup>3</sup> of a  $BaSO_4$  solution containing between 100 and 280 mg/l  $BaSO_4$  were injected into a test area of approximately 40.000 m<sup>3</sup> sandstone. The solution was pumped into the sandstone and after passing the formation the output solution was collected at a lower horizon.

The preparation of the  $BaSO_4$  oversaturated grout was based on a step-by-step mixing of  $Ba(OH)_2$  solution, inhibitor solution and diluted  $H_2SO_4$ . The composition of the final mix was controlled by on-line pH and conductivity measurements. A grout composition was selected guaranteeing a stability of the solution for 24 to 48 hours.

During the injection of the  $BaSO_4$  grout a significant reduction of the permeability was found. 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 results of the tests with  $CaSO_4$  oversaturated grouts were confirmed. It is not necessary to fill the flow paths with secondary minerals to reach sealing. Even closure by single crystals leads to a drastic reduction of the permeability.

The composition of the solutions collected after passing the sandstone formation is summarized in Figure 10. After an output of solutions having low contents of U, Fe and a low conductivity, rapid increase and then a rapid decrease of all concentrations takes place. This can be explained by the flow conditions in the formations. The injected grout penetrated in the first step preferred flow paths with a high hydraulic conductivity and led to an immobilisation of contaminants in these flow routes. With increasing amounts of injected  $BaSO_4$  grout zones with lower permeability are also reached

and the maximum of the concentrations in the output solutions characterises 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 the formed  $BaSO_4$  precipitates. Further concentration development is characterised 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 the 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 ions. The level of contaminants remained low.

### SUMMARY

The developed process of directed and controlled crystallization of slightly soluble sulphates is a favourable method both to seal off porous or fractured rock or soil formations and to fix contaminants by precipitation of protective layers on reactive mineral surfaces. The application of grouts leading to gypsum or  $BaSO_4$  precipitation was demonstrated in several field tests. Apart from proving the technical feasibility of injection of  $CaSO_4$  or  $BaSO_4$  oversaturated solutions, the tests showed that the grouts can be prepared in a simple way under field conditions. It is possible to use natural water or inflow brines to synthesise the grouts and only nontoxic compounds are used. The action of the grouts is summarised in Figure 11. The total costs of chemicals are low and sealing or immobilisation is achieved by minerals naturally present in the rock or soil formation.

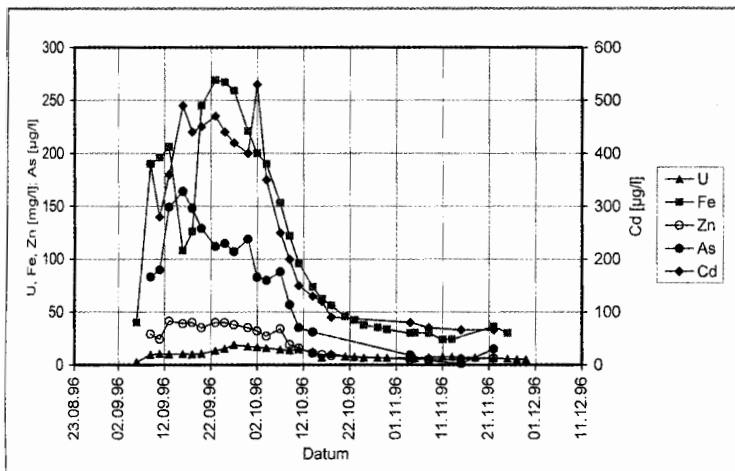


Figure 10. Typical course of solution composition after passing the sandstone formation.

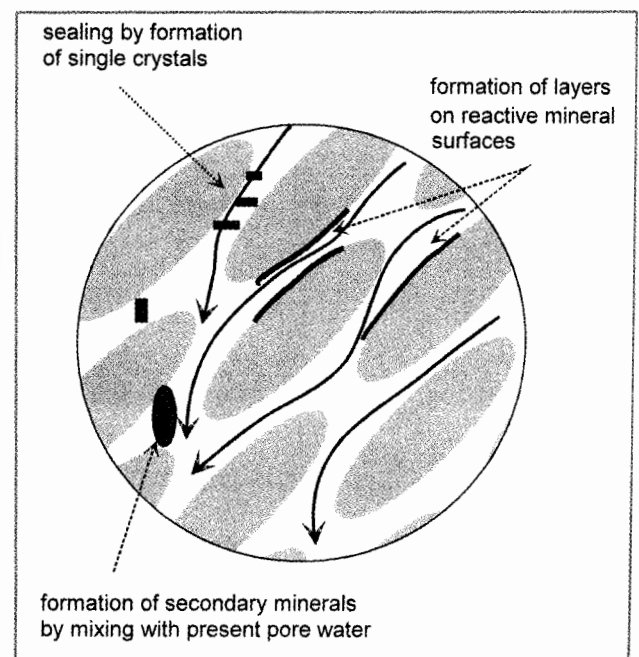


Figure 11. Action of oversaturated solutions during penetration of soil or rock formations.

$\text{Ca}(\text{OH})_2$  oversaturated solutions are a suitable grout material to precipitate slightly soluble hydroxides and gypsum. The preparation procedure is easy and solutions with a high neutralisation capacity are obtained.

The use of solutions oversaturated in gypsum or barite offers the possibility to combine the processes of:

- sealing of porous or fractured rock formations and directed permeability reduction;
- formation of long time stable protective layers on reactive mineral surfaces;
- precipitation of diluted contaminants.

Thus, there are applications both in sealing and reme-

diation projects. Grouting with oversaturated solutions is a possible way to increase the effectiveness of a soil flushing process. In comparison with other technologies, the method has the essential benefits of mineral crystallization directly from the injection solution as well as multiple possibilities for controlling the crystallization process.

## **ACKNOWLEDGEMENT**

The investigations summarised in this paper were partially carried out in co-operation with Wismut GmbH (Germany). The SEM photographs were taken by Dr. K. Stanek.