

## Analysis of Chemical and Biological Processes in Geothermal Systems – a Case Study

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### ABSTRACT

The physical, chemical and biological processes taking place in geothermal systems due to changes of pressure and temperature can reduce the system's efficiency. In the case of injection into sandstone reservoirs, these processes can cause serious technological problems and can lead to the non-functioning of the system. The familiarization with, and, handling of, chemical and biological processes characteristic for a given geothermal system may be necessary for the sustainable operation of the injection phase. Our research was carried out in a porous sandstone reservoir in Hungary. We used two different sandstone samples from drillings near operating reinjection wells, and carried out water-rock relationship analyses. For the analysis of the bonding of grains and the eventual suspension, we used sediment volume calculation. The core samples were ground and the prepared samples were analyzed by means of XRF and XRD spectroscopy. We examined original and oxygen-treated water samples. Each treatment was carried out three times; the photos of the sediments were evaluated afterwards. We determined that besides the interaction of the mineral matter the presence of biological components is of high importance during water injection. There is a large number of species of bacteria in the extracted thermal water whose metabolism does not raise a problem during production as they are present in the form of spores. However, as the water becomes colder at later stages of the geothermal system, conditions become ideal for mesophilic microorganisms. Around 90% of mesophilic bacteria present in the system studied were able to form biofilms on different spots of the injection system, especially on the filters, reducing the efficiency of the whole operation. We collected samples from the filter material of the injection wells and carried out metagenomic analyses of the bacteria. This way, we were able to collect the DNA of the bacteria from the analyzed sample, and define the most efficient water treatment processes accordingly.

### 1. INTRODUCTION

One of the most common problems of producing geothermal energy from porous reservoirs is the occurrence of formation damaging caused by various chemical, physical and biological processes. Formation damages are negative interactions in the recipient reservoir due to production and reinjection, as well as drilling and well construction activities and result in the deterioration of the rocks' permeability. The damaging of sandstones is mainly caused by the migration of fine particles and the swelling of clays (Civan, 2007). The fine particles can be external particles, suspended in the injected fluid (these get into the geothermal reservoir during injection), or they can be particles existent in the reservoir that mobilize from the rock surface due to the operation. The external particles can be micrometer-sized parts of rocks, corrosion and precipitation products, material from bacterial activities, and chemicals used in well drilling and construction (Ungemach, 2003).

The bonding of grains depends largely on the pH of the water and on other factors as well. The pH of the water brought to the surface changes due to the interaction with structural materials and air. Acidification occurs due to the oxidation caused by dissolved oxygen, and alkalization occurs due to the escaping of a great amount of carbon dioxide dissolved at high pressure. The magnitude of these effects depends on the composition of the water and the treatment method.

The objective of the research was to determine what happens to the thermal water while in the geothermal system. For the analysis, we looked for a method that allowed the modelling of the chemical-physical modification of water on the surface, and the water-formation interactions.

#### 1.2 Study area

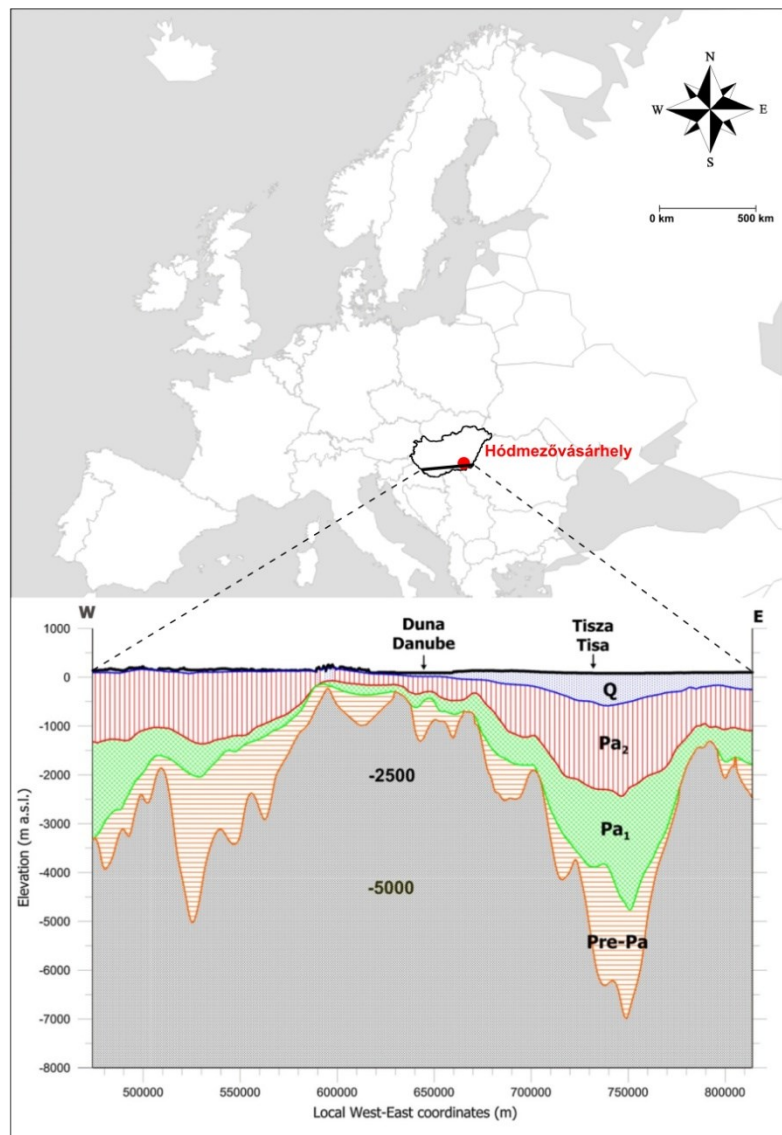
Our research was carried out in a porous sandstone reservoir of the 15 MW Hódmezővásárhely geothermal system which is the largest geothermal energy based district heating systems in Central Europe. The system provides domestic hot water for 3,000 apartments, several large communal buildings (city hall, schools, libraries, swimming pools and sport halls) and the water is also used for medical purposes and balneotherapy.

Hódmezővásárhely is located in the Great Hungarian Plain in the South-East part of Hungary. From geological point of view the Hódmezővásárhely area belongs to the Makó-Hódmezővásárhely Through, where the pre-neogene basement is at 6,000 m depth and was filled with high porosity sedimentary sequences during the late miocene-pliocene Pannonian period. The Upper-Pannonian water-bearing reservoirs mainly consist of sandstone, aleurite and clay marl layers usually have a permeability of 1,000-2,000 mD. The Pannonian layers are followed by young quarter sediments with 550-600 m thickness, with important role in the drinking water supply of Hódmezővásárhely and in hydrodynamic connection with the thermal water reservoirs (Figure 1.).

From a geothermal aspect the city is in one of the most favorable parts of the country. On the basis of the temperature measurement data of the Hód-1 exploration well at 1,000 m depth 50-55 °C, at 1,500 m 70-75 °C, at 2,000 m 90-95 °C, while at 2,500 m depth 105-110 °C can be expected. The geothermal gradient is 40 °C/km between 1,000-3,000 meters.

The thermal waters of Hódmezővásárhely belong to the alkali hydrocarbonate group of waters. The total dissolved solid content increases with the depth and the concentration varies between 700-1,400 mg/L in the Upper-Pannonian layers. According to Varsányiné (2001) the waters are paleometeoric origin and recharged during the last ice age period. The geothermal system consists

of ten thermal wells producing 50-90 °C thermal water from 1,200-2,500 m depths and two 1,700 m depth reinjection wells. The operation of reinjection well No.1 was started 17 years ago, and reinjection well No.2 was started 6 years ago. From the point of view of operational experience, the system in Hódmezővásárhely offers a unique set of reinjection-related data. As an excellent reference for the permanent and cost-effective reinjection into Pannonian sandstone, more than 3.1 million m<sup>3</sup> of cooled fluid have been reinjected successfully into reinjection well No.1 during its operation since 1998. The injection pressure is 3 bar and the specific injection flux is about 15 l/s/bar (Szanyi and Kovács, 2010). Well maintenance is needed every 2 years. The pressure measured at the filter during operation is 4-6.5 bar, depending on the actual clogging of the filter, but at the wellhead, 3 bar injection pressure is maintained. Reinjection well No.2 operated without failure for 5 years but a sudden plugging of the surface system was experienced a year ago due to biological processes.



**Figure 1: Location of the study area with geological cross-section**

## 2. METHODS

The measurement of the sediment volume is an excellent and simple method to analyze the bonding of grains in different solutions and the eventual suspensions. This consists of mixing the same amount of rocks into identical quantities of water in identical vessels, shaking them up and leaving them to deposit, and finally measuring the height of the sediment. The increase of the sediment volume implies the increase of the binding force of grains, while the decrease of the sediment volume implies the opposite. The particles not bonding completely are depositing independently, and the Brown movement can place them into all the free places, resulting in a compact sediment. If the particles tend to bond, they bond during deposition into different grains that cannot fill every place, resulting in unconsolidated sediment and a greater sediment volume.

The rock samples were taken from drillings near the reinjection location and from the reinjection depth. The core samples were ground, and the powder analyzed by means of XRF and XRD spectroscopy.

We used two water samples: Sample I was taken from the production well, Sample II from the buffer tank of the reinjection well. We carried out two water treatments with both water samples:

A. The reduction treatment. The vessel with the original water sample was completely full when taken into the lab, and it remained so until its application. The objective of the process was to avoid the contact of the water sample with air, i.e. to avoid gas exchange on the water surface.

B. The oxidation treatment. For two hours we bubbled air through the original water sample. The experiments were carried out from freshly bubbled samples thus reducing the disturbing effects of long-term slow reactions. With this method we modelled the common practice of geothermal utilization in Hungary, which allows the contact of thermal water and air during degassing.

For the pH analyses water samples adjusted to pH values of 2, 4, 6, 8 and 10 were used for our sedimentation analyses. The sediment volume tests were carried out in 20 ml test tubes, with 2 g of rock sample and 10 ml of water in each tube. After an intensive shake-up and two hours of deposition, the tubes were placed on a rack and photographed.

To investigate biological activity, samples were taken of two filters and were prepared to get the entire genomic DNA without impurity. For this purpose, the collected samples were extracted with 800  $\mu$ l of extraction buffer (100 mM Tris HCl, pH 8.0, 100 mM EDTA, pH 8.0, 1.5 M NaCl, 100 mM sodium phosphate, pH 8.0, 1% CTAB). After proper mixing 4.3  $\mu$ l of proteinase K (20.2 mg/ml) was added. All eppendorf tubes were incubated horizontally at 37 °C with shaking for 45 minutes, after that 160  $\mu$ l of 20% SDS was added and mixed by inversion of several times with further incubation at 60 °C for 1 hour. The sample in each eppendorf was mixed thoroughly after a 15 minute interval. The samples were centrifugated at 13,300 rpm for 5 minutes. The supernatant was transferred into new eppendorf tubes. The remaining pellets were treated with 400  $\mu$ l of extraction buffer, 60  $\mu$ l of SDS (20%) and kept 60 °C for 15 minutes with intermittent shaking after every 5 minute time. The supernatant collected. All extractions were mixed with equal quantity of phenol chlorophorm and isoamyl alcohol (25:24:1) and extracted three times. The aqueous layer was separated and precipitated with 900  $\mu$ l of isopropanol (at room temperature). After centrifugation at 13,300 rpm for 15 minutes, the DNA pellet was washed with 900  $\mu$ l of 70% ethanol, dried at 30 °C in vacuum centrifuge and was dissolved in 60  $\mu$ l of TE (10 mM Tris HCl, 1 mM EDTA, pH 8.0). Its quantity was determined in a NanoDrop ND 1,000 spectrophotometer (NanoDrop Technologies, Washington, USA). DNA purity was tested by agarose gelelectrophoresis. This method yielded a pure (A260/A280 = 1.8) and sufficient amount of total DNA (Wirth et al., 2012). This extracted, purified DNA is not only the DNA of the living microbes, but the total DNA found in the samples (living and dead also). This DNA was sequenced using Ion Torrent sequencing platform. The 23 most abundant species of each filter are presented in Figure 3. After defining the dominant flora of the filters, the location of their appearance was detected.

### 3. RESULTS

#### 3.1 Core sample analysis

Two ground materials were used for the sediment analyses; their symbols:  $\alpha$ ,  $\beta$  rock samples. The two rock samples proved to be very similar in the distribution of elements. There was a significant difference in the Ca-content, its concentration in rock sample  $\beta$  was twice as high as in sample  $\alpha$ . Based on the XRD spectroscopy the dominant components of both samples are quartz, muscovite and dolomite while albite in sample  $\alpha$  and chlorite in sample  $\beta$  are the most important.

From the point of view of deposition, the two samples were significantly different. In sample  $\beta$ , we found one deposition phase, and two well-separable deposition phases in sample  $\alpha$ . The reason for this is that sample  $\alpha$  is the mixture of two rocks with significantly different surface characteristics. We analyzed the phases separately ( $\alpha_1$ ,  $\alpha_2$ ) and together as well.

#### 3.2 The impact of aeration on the water's pH

Both wells show that the pH value of the aerated sample is significantly higher than that of the original water sample. The explanation for this is that the intensive bubble aeration eliminates a great amount of carbon dioxide from the sample, resulting in the reduction of carbonic acid and hydrogen ion concentration.

The original pH of the reinjection well is lower, explained by the fact that the sample oxidizes while contacting the surface, in a way that a much smaller amount of carbon dioxide leaves the system compared to the intensive bubble aeration method. The acidifying effect of oxidation can predominate beside the effect of carbonic acid generating a much bigger alteration of the pH.

#### 3.3 The impact of rock samples to the sediment volume pH dependence

Production well, reductive conditions (Figure 2/a)

- In the case of rock sample  $\alpha$ , we experience a small increase of the sediment volume in relation to the pH for the lower sediment layer, meaning that the increase of the pH value results in the increase of the binding force in reductive conditions, in the production well.
- In the case of rock sample  $\alpha$ , we experience a decrease of the sediment volume in relation to the pH for the upper sediment layer and therefore along the plateau between the weak pH values 4 and 8 on the cumulative curve. This means that in the production well, in reductive conditions, the increase of the pH value results in the decrease of the binding force in the alkaline range in the case of a very smooth fraction.
- In the case of rock sample  $\beta$ , we experience a small increase of the sediment volume in relation to the pH in an alkaline range by a peak of 4 pH. This means that the increase of the pH value results in the increase of the binding force in alkaline range in the production well, in reductive conditions, but it shows a minimum at neutral values.

Production well, oxidative conditions (Figure 2/b)

- In the case of rock sample  $\alpha$ , for the lower sediment layer and the complete sediment, and in the case of rock sample  $\beta$ , we experience a categorical maximum in the sediment volume at 4-5 pH. This means that in the production well, the binding force shows a maximum value in a slightly acidic range in oxidative conditions.

- In the case of rock sample  $\alpha$ , we experience a decrease of the sediment volume in relation to the pH for the upper sediment layer. This means that in the production well, in oxidative conditions, the increase of the pH value results in the decrease of the binding force in the alkaline range in the case of a very smooth fraction.

Reinjection well, reductive conditions (Figure 2/c)

- In the case of rock sample  $\alpha$ , we experience a small increase of the sediment volume in relation to the pH for the lower sediment layer above the minimum of 4 pH, meaning that the increase of the pH value results in the increase of the binding force in reductive conditions in the reinjection well.
- In the case of rock sample  $\beta$ , we experience a small increase of the sediment volume in relation to the pH, meaning that the increase of the pH value results in the increase of the binding force in the alkaline range in reductive conditions in the reinjection well.
- In the case of rock sample  $\alpha$ , we experience a decrease of the sediment volume in relation to the pH for the upper sediment layer and therefore along the plateau between the weak pH values 4 and 8 on the cumulative curve. This means that in the reinjection well, in reductive conditions, the increase of the pH value results in the decrease of the binding force in the alkaline range in the case of a very smooth fraction.

Reinjection well, oxidative conditions (Figure 2/d)

- In the case of rock sample  $\alpha$ , we experience a small increase of the sediment volume in relation to the pH for the lower sediment layer, meaning that the increase of the pH value results in the increase of the binding force in oxidative conditions, in the reinjection well.
- In the case of rock sample  $\beta$ , we experience a small decrease of the sediment volume in relation to the pH, meaning that the increase of the pH value results in the decrease of the binding force in the alkaline range in oxidative conditions, in the reinjection well.
- In the case of rock sample  $\alpha$ , we experience a decrease of the sediment volume in relation to the pH for the upper sediment layer and therefore along the plateau between the weak pH values 4 and 8 on the cumulative curve. This means that in the production well, in reductive conditions, the increase of the pH value results in the decrease of the binding force in the alkaline range in the case of a very smooth fraction.

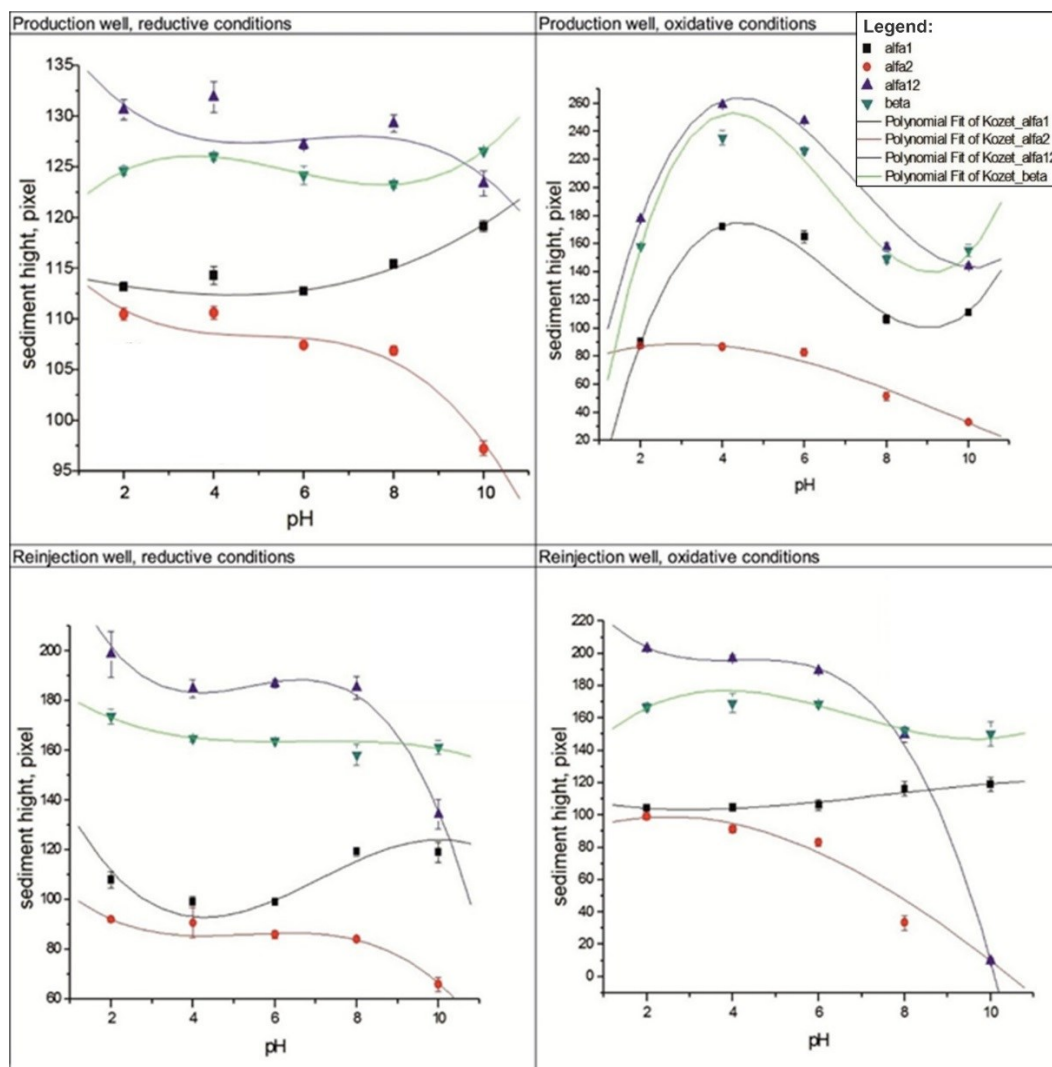


Figure 2: Sediment volume curves for different rock samples

### 3.4 Results of the biological aspects

The microbial floras of the two reinjection systems' surface filters were significantly different. The quickly clogged system's highly dominant genus was *Magnetospirillum*. According to the metagenomic sequencing, on this filter, genera were found in a narrow spectrum, but those genera were much abundant. Conversely, on the control (slowly-clogged) system very wide spectrum of bacteria was found, but none of them was particularly dominant. Chemical water analysis showed that, the quickly-clogged system's water includes two orders more phenol and BTEX compounds than the slowly-clogged system's water.

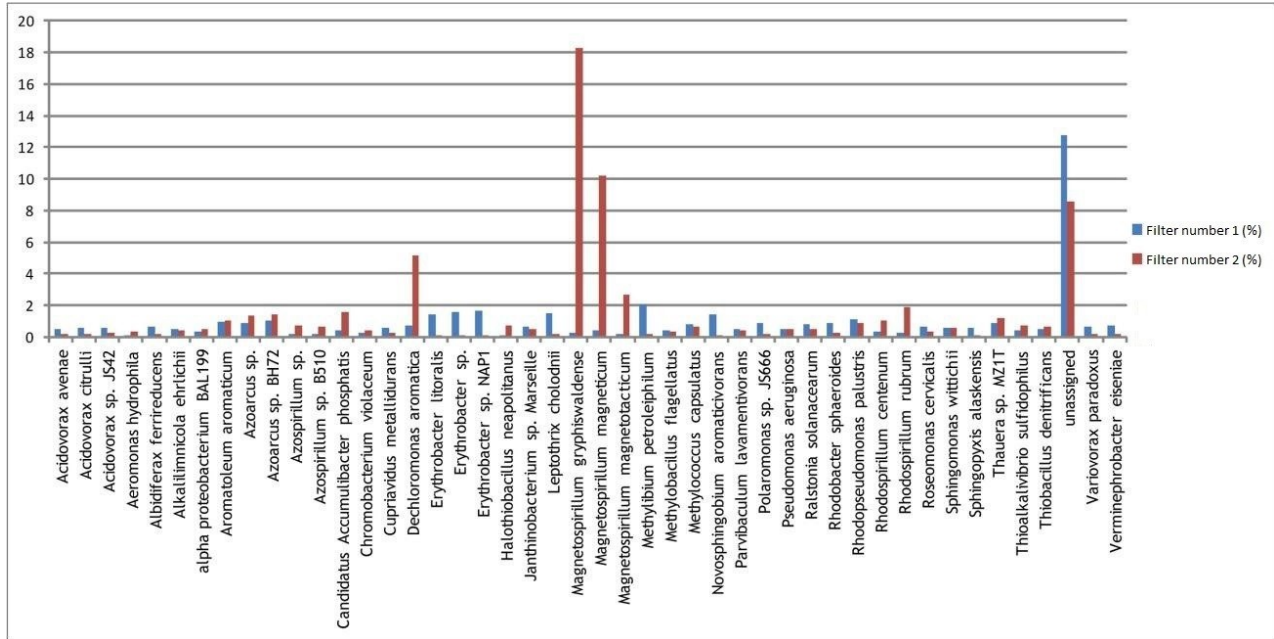


Figure 3: Result of the metagenomic sequencing

Most of the bacteria identified with metagenomic sequencing are able to form biofilms. A biofilm is made of well-organized bacterial colonies in wet environments that provide enough nutrition for them. It is a wet, slimy and adherent association that sticks well to the surface. It is clear that this is a favorable relation for microorganisms, so we see similar slimy substances in practice, mainly sticking to filters. (In fact, biofilm occurs at stagnant pipeline parts and tank as well, but we cannot observe them, since these places are hard to access.)



Figure 4: Filter before (on the left) and after (on the right) usage – with biofilm



#### 4. CONCLUSIONS

Based on the results we found that the reinjected water's chemical oxygen demand, phenol index and BTEX composition determine the appearing flora on the filter surface. When the concentration of these compounds in the thermal water is significant, certain bacteria become dominant, and are able to form a biofilm which plugs the surface equipment. (Figure 4) In our case, the control system was not totally plugged, because none of the bacteria present could become particularly dominant; however, the spectrum of its bacterium flora was wide. Decontamination with UV or with ozone can be a good solution to the problem posed by the presence of bacteria; but chemical disinfection is not recommended.

With the increasing pH, we obtain a decreasing sediment volume, meaning that alkalization decreases the binding force of grains. At the same time, we found extreme values in the analyzed range, which means that there are pH ranges that produce maximally and minimally adhesive particles. More analyses on more rock samples would be necessary in relation to the pH for the deduction of generalities. The details were evaluated separately when discussing the different treatments. These details show that reinjection is a complex process with many parameters, where the surface and subsurface processes together define the successfulness of the operation.

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