

Heat and Mineral Mining by adding CO₂ to Deep Groundwater ©

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Abstract

CO₂ can be added to groundwater as an innovative approach to extract valuable elements where in most cases the dissolved mineral concentration would be too low to be considered for economic recovery. Water-rock-CO₂-interactions were investigated under simulated reservoir conditions using carbonate rock from the molasse basin and carbonatite rock from Delitzsch, Germany. This approach can be also joined with geothermal energy production, which – in addition to enhanced in-situ leaching of minerals – would improve permeability in low permeable formations and maintain fluid pathways. Co-recovery of minerals with geothermal energy production can improve the overall economic attractiveness of geothermal energy.

Keywords: Geothermal, carbon utilization, metal recovery, permeability, REE, solution mining

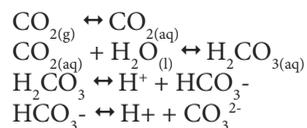
Introduction

In conventional mining, large quantities of rock must be mined and deposited in the form of heaps and dumps. Then, the ore is milled and the metal is extracted from the rock. In case of low grade ores in particular, large amounts of tailings are produced. These tailings are an environmental hazard as well as creating massive pile-ups. Another form of mining is in situ leaching. Currently, chemicals such as sulfuric acid or lye (sodium hydroxide or ammonia) are injected in to the ground which brings a great risk potential for the groundwater and the environment. As a consequence, there are high remediation costs for in situ leaching mining. Minimizing the interference of mining activities with integrity of nature is a necessity which is still very far from ideal.

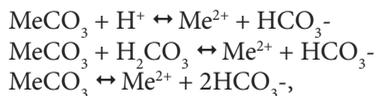
Two vital aspects in geothermal energy production, especially in deep carbonate aquifers such as the Southern German Molasse Basin (SGMB), are adequate permeability and favorable fluid pathways. But very often both criteria cannot be assumed as given. Besides, due to scaling and precipitation, the worsening of permeability in different locations poses a great challenge to maintain constant production. Therefore, preserving and improving these pathways during long-term operation is a key task in deep geothermal energy production. With these in

mind, this research aims to implement using carbon dioxide as an innovative method in the geothermal, mining and ore processing technology portfolio.

Deep groundwater has lengthy interactions with the layers of the earth's crust, resulting in the dissolution of minerals and metals from the aquifer rocks into the geothermal hot water until becoming close to or exactly at equilibrium with respect to certain minerals. These aqueous solutions, especially geothermal waters, can be processed to recover the dissolved valuable elements (e.g. Maimoni 1982, Bakane 2013, Harrison 2014). But often, the concentration of these dissolved elements is too low to be considered for economical extraction. Merkel et al. (2012) suggested a patented method for leaching valuable elements from ore bodies that are not economically feasible using conventional techniques. When CO₂ is added to water, the following steps occur:



According to the mechanistic rate law of Chou et al. (1989) for various carbonates, the elementary steps during the dissolution reactions of carbonates are expressed by:



where Me represents metal ion e.g. Ca^{2+} or Mg^{2+} .

At pH above 3.5, carbonate dissolution becomes interface-controlled as opposed to diffusion-dominated (Buhmann and Dreybrodt 1985) as well as being dependent on the partial pressure of CO_2 . It is worth mentioning that this dissolution happens kinetically which is mainly reliant on on: i) specific surface area of calcite, ii) dislodgement from equilibrium, iii) the purity of the rock, and iv) presence of inhibitors.

When used in geothermal energy production, by increasing the partial pressure of CO_2 in water, the water becomes undersaturated in minerals such as carbonate. This process does not only inhibit unwanted precipitation, but also triggers favorable dissolution and an enrichment of dissolved elements. This dissolution will continue until the formation water is once again in equilibrium with the aquifer rock. Accordingly, even a small increase in porosity has a substantial effect on enhancement of permeability.

Methods

Three experiments were performed using three types of high pressure-temperature (H-P-T) autoclaves, which are named Autoclave 1, 2, and 3 (Table 1 and Table 2) and three rock specimens. Two of the sample rocks were from Kirchweidach, a geothermal field designed for both electricity production and thermal use located in the Malm aquifer system of the Southern German Molasse basin. Kirchweidach is one of the most important reservoirs for geothermal energy production in the south of Germany due to its extensive fault system, water-bearing nature at depth coupled with high permeability from partially karstified limestones and fractured dolomite at favorable temperatures (Seithel et al. 2015). This progressive increment in temperature in the aquifer system, especially towards the Alps, makes areas on this part of the Malm strata potential sites for electricity generation (Ganz et al. 2013). Chemical analysis of the geothermal water from the production borehole in Kirchweidach was

done (Table 3) which showed that it has a total mineral concentration of about 696 mg/L.

X-ray powder diffraction (XRD) based on qualitative and semi-quantitative analysis with the Rietveld method was performed on all the rock samples to obtain mineral compositions. GT1 rock cuttings contained 68 wt % dolomite, 26 wt % calcite and 4 wt % ankerite, while GT2 rock cuttings were composed of 75 wt % dolomite, 14 wt % calcite, 4 wt % ankerite, and 2 wt% quartz. Microscopic examination of samples was carried out before and after the experiments using scanning electron microscope (SEM) for possible changes to the surface of the specimens.

The carbonatite specimen used in this study was sampled before 1989 between 200 m to 550 m below the earth's surface from Storkwitz, Delitzsch in Saxony, which is one of the two most important carbonatite complexes in Germany (Goodenough et al. 2016) and assumed to be the biggest REE reservoir in Europe. According to these authors, carbonatite dykes found in Delitzsch go as far as 1100 m below the surface and rock samples analyzed by earlier investigators have identified some important rare earth minerals such as pyrochlore, bastnäsite, and apatite. The specimen is described as an intrusive breccia which, fits into the geological description of earlier investigators. XRD analyses revealed that the sample consists of 34 wt. % ankerite $[\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2]$, 17 wt. % dolomite $(\text{CaMg}(\text{CO}_3)_2)$, 14 wt. % calcite (CaCO_3) , 13 wt. % anorthite $(\text{CaAl}_2\text{Si}_2\text{O}_8)$, 11 wt. % germanium-phlogopite $[\text{KMg}_3(\text{AlSi}_2\text{GeO}_{10})\text{F}_2]$, 6 wt. % fluorapatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$, and 5 wt. % albite $(\text{NaAlSi}_3\text{O}_8)$. Also, SEM-EDS analysis showed that the rock contained elements such as Na, Mg, Al, Si, S, Ca, Mn, Fe, Sr, F, P, K, La, Ce, Nb, Sn, and Ti. The sample was crushed and the particles with 1 to 2 mm diameter were used.

To determine the change of dissolved elements concentrations over time, sampling was done at predetermined periods during the experiments. For each sampling run, the first 3 mL taken were discarded to account for the water, which was left inside the autoclave tubing from the previous run. Then, the sampled solution was acidified with supra-pure nitric acid so that no precipitation would

Table 1 Specifications of the 3 autoclaves used in the 3 experiments.

Autoclave	Volume (mL)	Type and location	Pressure (MPa)	Temperature (°C)
1	150	Rocking with flexible titanium grade 2 cell, water as pressure medium, gzf Potsdam	40	105
2	1500	Top opening, Static, CO ₂ as pressure medium, TU Bergakademie Freiberg	40	105
3	170	Top opening, Static, CO ₂ as pressure medium, TU Bergakademie Freiberg	15	100

Table 2 Details of experiments GE1, GE2 and GE3

Experiment	Sample	Duration	Type	Autoclave	W:R ratio	Analysis
GE1	GT1	21 days	kinetic	1	20:1	ICP-MS, SEM-EDS
GE2	GT2a	14 days	kinetic	2	13:1	ICP-MS, SEM-EDS
GE3	Carbonatite	28 days	kinetic	3	21:1	ICP-MS, SEM-EDS

Table 3 Chemical composition of groundwater from Kirchweidach, Germany ($\pm 5\%$ relative error).

	Conc. (mg/L)		Conc. (mg/L)		Conc. (mg/L)
Na	109.08	Br	0.397	S	30.4
K	18.82	F	3.802	Al	0.05324
Ca	30.49	I	< 0.05	As	< 0.001
Mg	4.19	Li	0.1242	Pb	< 0.00001
NH ₄	0.498	PO ₄	0.0899	Fe	0.03051
HCO ₃	276.0	Se	<0.005	Mn	0.01214
Cl	82.52	Si	58.80	U	< 0.0001
SO ₄	7.7	Sr	0.8447	Zn	< 0.001
NO ₃	< 0.2	Si	58.80	La	0.00002
NO ₂	< 0.01	Sr	0.8447	Rb	0.05675
Ba	0.1649	Mo	< 0.0001	pH (56°C)	6.33
B	0.6775	Ce	< 0.0001	EC (56°C)	741 μ S/cm


Figure 1 Autoclave systems used in the experiments. Top pictures show autoclave 1, Bottom left and center show autoclave 2 and bottom right shows autoclave 3.

occur in the sampling vials as a result of changes in boundary conditions or degassing. The samples were analyzed by ICP-MS to obtain cation concentrations. Along with measuring the pH and electrical conductivity (EC) during each sampling run, the exact time of sampling was documented on a permanent basis. Due to page restrictions, only element concentrations for the last sampling run are given in this paper and special kinetic aspects accompanied by results from further experiments will be presented in a future publication.

Results and discussion

Electrical conductivity increased rapidly in the first hours for all 3 experiments (Figure 2). In the GE1 experiment, EC decreased to 1500 $\mu\text{S}/\text{cm}$ during the second and third day of the experiments and then rose steadily afterwards. Similar to EC, the pH also rose very rapidly to values around pH 6, which then continued in the further courses to about 6.5 (Figure 2). A methodological problem that exists in such experiments is the measurement of pH, since there are no sensors which provide reliable in-situ values under such P-T conditions. Measurements of the pH after sampling are always associated with some spontaneous degassing and could differ from in-situ pH.

When taken out of the reactor, some of the particles showed a distinct change in color to brick red. Some fine particles and grains were also present, which were smaller than the initial sample particle size. These fine fragments are assumed to be liberated due to the dissolution of the cementing minerals around them. SEM comparison of particles before and after the experiments showed noticeable changes to the surface,

widening of pores and rounding of edges, which in most cases indicate dissolution and weathering of the minerals (Figure 3). Secondary precipitation can also be seen on some of the mineral surfaces, which occurred during the experiments or after the pressure inside the autoclave was relieved.

In all three experiments, elements such as calcium, magnesium, zinc, potassium, sodium, manganese, aluminum, and barium reached (quasi)-equilibrium before the end of the experiments. On the other hand, elements such as sulfur, nickel, silicon, strontium, molybdenum, uranium, and lithium did not reach equilibrium. Extracted mass of elements including REE in experiments GE1, GE2 and GE3 are presented as mg/kg and $\mu\text{g}/\text{kg}$ in order to quantify how much of each element from the rock sample was released into the solution (Table 4). Compared to the initial aquifer water, a noteworthy enrichment of dissolved elements had occurred.

With this method, element separation takes place in situ and thus transport of process volumes and waste is minimized. Several technologies to extract minerals from geothermal waters have been developed over the years (e.g. Brown 1986, Gallup and Ririe 1994, Bourcier 2009). Nevertheless, other methods of element extraction including methods for rare earth elements (REE), e.g. molecular recognition technology, solvent extraction, adsorption, ion exchange, magnetic segregation, microbe technology could also be employed in the geothermal plant or as standalone to process the dissolved elements in the groundwater that has been enriched and brought to the surface. Assuming that a circulation of 10 L/s would be achieved

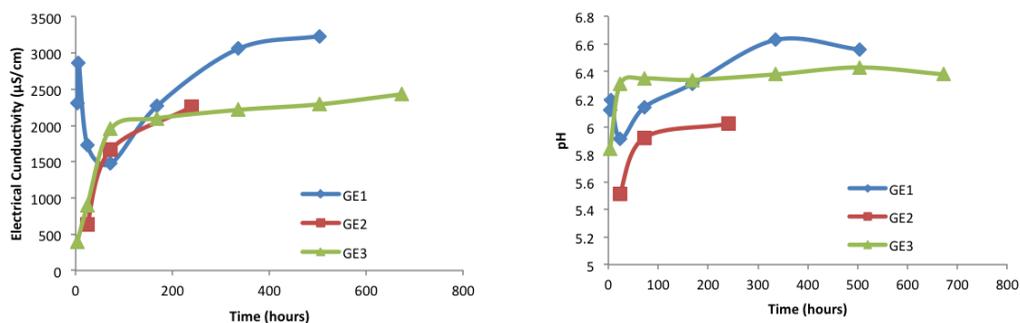


Figure 2 Measured EC (left) and pH (right) during the experiments

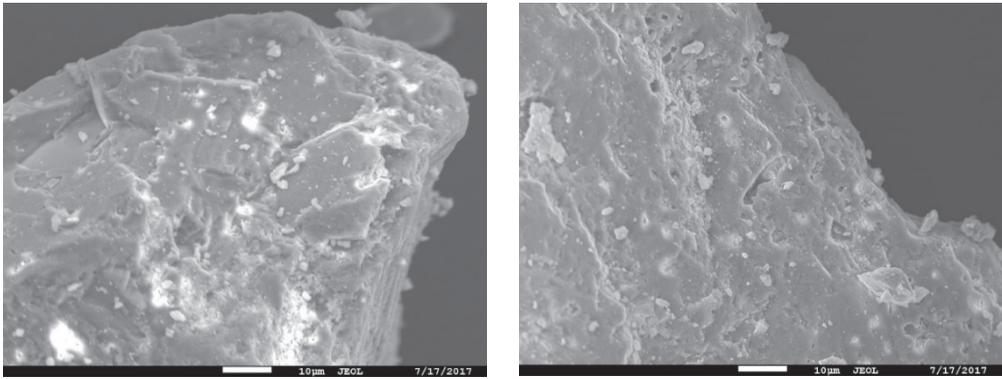


Figure 3 SEM images before (left) and after (right) the experiment shows distinct pits and holes have formed on the surface of the particle as a result of dissolution.

Table 4 Extracted mass of elements in GE1, GE2 and GE3 [mg/kg and µg/kg] ($\pm 5\%$ relative error).

	Unit	GE1	GE2	GE3		Unit	GE1	GE2	GE3
Na	mg/kg	36	14	351	Mn	mg/kg	10.97	2.81	30.32
K	mg/kg	138.6	17.5	1323	As	mg/kg	0.01	0.030	3.98
Ca	mg/kg	11934	7703	11553	Pb	mg /kg	0.05	0.0007	30.32
Mg	mg/kg	477.7	1008.2	979.8	U	mg/kg	0.01	0.087	2.06
Rb	mg/kg	0.61	0.088	3.51	La	mg/kg	< 0.01	0.006	0.05
Mo	mg/kg	0.10	0.006	15.79	Ce	mg/kg	< 0.01	0.009	0.105
Ba	mg/kg	54.39	1.38	9.27	Pr	µg/kg	< 1	1	12.9
B	mg/kg	1.34	0.277	0.7	Nd	µg/kg	2.1	4	52.6
Zn	mg/kg	6.55	0.524	13.98	Sm	µg/kg	0.7	0.5	10
Br	mg/kg	0.8	< 0.3	0.7	Eu	µg/kg	8.7	0.4	4
Ni	mg/kg	2.7	0.627	183.69	Gd	µg/kg	0.8	0.6	11.5
Li	mg/kg	0.23	0.034	0.44	Tb	µg/kg	< 1	0.1	1.7
P	mg/kg	1.3	1.174	801.8	Dy	µg/kg	0.4	0.3	11.4
Si	mg/kg	1198.25	96.76	312.34	Ho	µg/kg	0.1	0.1	2.5
S	mg/kg	-	23.57	1291	Er	µg/kg	0.3	0.2	7.9
Al	mg/kg	0.42	0.44	2.83	Tm	µg/kg	< 1	0	1.2
Sr	mg/kg	18.9	298.8	312.34	Yb	µg/kg	0.2	0.2	9.2
Fe	mg/kg	123.4	6.43	3.98	Lu	µg/kg	< 1	0	1.5

and the solution contains 5 valuable metals at concentrations of 1 mg/L, this sums up to 50 g/m³ and thus 4.32 kg per day. Estimating an average price of 3000 to 8000 € per kg this would result in 13,000 € to 35,000 € value add per day (and 4.7 to 12.6 million € per year, respectively). Therefore, it is rather likely to produce well beyond the costs of conventional mining plus aboveground processing because costs for labor work are substantially lower.

The continuous leaching of minerals will improve permeability and increase the production performance without having to use conventional hazardous and costly

reservoir stimulations (such as acidizing, mechanical precipitation removal, pressure increase and hydraulic fracturing). Co-recovery of minerals with geothermal energy production can improve the overall economic attractiveness of geothermal energy production.

Interestingly, limited geological utilization and storage of CO₂ is another positive by-effect of the approach used in this research. Geological CO₂ sequestration refers to the storage of CO₂ underground in depleted oil and gas reservoirs, saline formations, or deep, un-mineable coal beds (carbon capture and

storage, CCS). The aim of storage of carbon dioxide or other forms of carbon is to mitigate CO₂ emissions caused by fossil fuel usage. CO₂ via dissolution in formation water is one of the approaches, which are used for solubility trapping of CO₂. If during actual geothermal energy production, as low as 0.1 moles of CO₂ is added to one liter of the water that is being re-injected back into the aquifer at a rate of 100 kg/s, around 14,000 metric tons of CO₂ will be used per year per plant. This CO₂ is dissolved in the geothermal water and there is no risk of the gas escaping to the surface. For scenarios of direct introduction of CO₂ inside of the aquifer, much higher amounts than the mentioned weight is used. Such a CO₂ storage by-effect (Carbon Capture, Utilization and Storage, CCUS) requires no additional energy or equipment which adds economic and environmental benefits. However, possible problems related to impurities of the CO₂ used must be considered as well.

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Conclusions

H-P-T autoclave tests showed that adding CO₂ to groundwater leads to economically noteworthy enrichment of dissolved elements in the groundwater, which could then be processed after it has been brought to the surface.

Similarly, by adding CO₂ to the geothermal water, co-recovery of valuable minerals from geothermal water during geothermal energy production can increase the economic attractiveness without the negative effects of conventional mining, e.g. tailings, deforestation, water pollution.

The continuous leaching of minerals will improve aquifer permeability and increase the production performance in low permeable formations.

References

- Bakane P (2013) Overview of extraction of minerals/metals with the help of geothermal fluid. In: Proceedings of the 38th Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, CA, USA, 11–13 February 2013
- Bourcier W, Bruton C, Roberts S, Viani B, Conley S, Martin S (2009) Pilot-Scale Geothermal Silica Recovery at Mammoth Lakes, California Energy Commission: Sacramento, CA, USA
- Brown KL (1986) Gold deposition from geothermal discharges in New Zealand. *Econ. Geol.* 81: 979–983
- Buhmann D and Dreybrodt W (1985) The Kinetics of Calcite Dissolution and Precipitation in Geologically Relevant Situations of Karst Areas. 1. Open System. *Chemical Geology* 48: 189–211
- Chou L, Garrels RM, Wollast R, (1989) Comparative-Study of the Kinetics and Mechanisms of Dissolution of Carbonate Minerals. *Chemical Geology* 78: 269–282
- Gallup DL, Ririe GT (1994) Platinum Recovery. U.S. Patent no. 5290339, 1 March 1994
- Ganz B, Schellschmidt R, Schulz R, Sanner B (2013) Geothermal Energy Use in Germany. European Geothermal Congress 2013, Pisa, Italy, 3–7 June 2013: 1–16
- Goodenough KM, Schilling J, Jonsson E, Kalvig P, Charles N, Tuduri J, Deady EA, Sadeghi M, Schiellerup H, Mueller A, Bertrand G, Arvanitidis N, Eliopoulos DG, Shaw RA, Thrane K, Keulen N (2016): Europe's Rare Earth Element Resource Potential. An Overview of REE Metallogenetic Provinces and their Geodynamic Setting. *Ore Geology Reviews* 72:838–856. doi: 10.1016/j.oregeorev.2015.09.019
- Harrison S (2014) Technologies for Extracting Valuable Metals and Compounds from Geothermal Fluids. California Energy Commission, Sacramento, CA, USA
- Maimoni A (1982) Minerals recovery from Salton sea geothermal brines—A literature review and proposed cementation process. *Geothermics* 11: 239–258
- Merkel B, Bertau M, Mischo H (2012) CO₂-basiertes In-situ-Laugungs- und Aufbereitungsverfahren für den Fluidbergbau. Patent no. DE102012011145B4
- Seithel R, Steiner U, Müller B, Hecht C, Kohl T (2015) Local stress anomaly in the Bavarian Molasse Basin. *Geotherm Energy* 3 (1): p. 77. doi: 10.1186/s40517-014-0023-z