Mineral trapping of CO₂ in operated hydrogeothermal reservoirs

Michael Kühn*, Martin Back**, Christoph Clauser*, Helge Stanjek*** and Stefan Peiffer**

* Applied Geophysics - RWTH Aachen University - Lochnerstr. 4-20 - D-52056 Aachen, Germany.
** Hydrology - University of Bayreuth - Universitätsstr. 30 - D-95440 Bayreuth, Germany.
*** Clay and Interface Mineralogy - RWTH Aachen University - Wülflingstr. 2 - D-52056 Aachen, Germany.

**CO₂ storage, mineral trapping, geothermal energy, anhydrite**

**ABSTRACT**

Storage of carbon dioxide (CO₂) by precipitation of carbon-bearing minerals in geological formations is, on the long run, more stable and therefore much safer than direct storage or solution trapping. Furthermore, options for CO₂ sequestration which offer additional economic benefits besides the positive effect for the atmosphere are attractive. Both arguments motivate us to study the novel approach of storing dissolved CO₂ as calcite in geothermally used aquifers.

Geothermal energy in Germany is mainly provided from deep sandstone aquifers by a so called “doublet” installation consisting of one well for hot water production and one well for cooled water re-injection. After re-injection of CO₂ enriched, cold brine into the reservoir, anhydrite abundant as matrix mineral dissolves. As a consequence, the water becomes enriched in calcium ions. Numerical simulations demonstrate that alkaline buffering capacity provided by plagioclase in the reservoir rock or through surface water treatment with fly ashes can be transformed into a benefit in combination with the production of ecologically desirable geothermal heat or power.

Due to the geological situation, geothermal energy in Germany is mainly provided from deep aquifers. The common arrangement of boreholes is the well doublet, consisting of one well for hot water production and one well for cooled water re-injection. The cooled water is loaded with dissolved CO₂. After re-injection into the reservoir, this cold water becomes enriched in calcium e.g. due to dissolution of anhydrite (CaSO₄). Subsequently, CO₂ precipitates as calcium carbonate (CaCO₃). The following chemical reactions need to be considered with regard to CO₂ storage in geothermal reservoirs:

1. CaSO₄ ⇌ Ca⁺² + SO₄⁻² (1)

Before re-injection, the produced and cooled brines will be enriched with carbon dioxide generating, as a result, carbonic acid:

CO₂ + H₂O ⇌ H₂CO₃ ⇌ H⁺ + HCO₃⁻ (2)

The overall reaction, the transfer of anhydrite into calcite, describes the favored reaction path:

CaSO₄ + H₂CO₃ ⇌ CaCO₃ + 2 H⁺ + SO₄⁻² (3)

From equation (3) it is obvious that a surplus in acid exists which tends to inhibit calcite precipitation in general. However, if the increase in Ca is large enough (equation 1) or if alkalinity is available to buffer the reaction, the solubility product of calcite is exceeded and CO₂ will be trapped as calcite. Alkalinity can be provided either by surface water treatment with fly ashes or in situ through the weathering of feldspars. The reaction of oligoclase to kaolinite is given here as an example:

[NaAlSi₃O₈]₄[CaAl₂Si₂O₈] + 4 H⁺ + 10 H₂O ⇌ 2 Na⁺ + Ca⁺² + 4 H₂SiO₄ + 2 Al₂Si₂O₅(OH)₄ (4)
With regard to the feasibility of this new technology the chemical reactions outlined above give rise to the following three key questions:

1. Does the transfer of anhydrite into calcite work at all and what are the reaction rates?
2. What are probable sources of alkalinity and how fast can they be made available?
3. Where are the suitable geothermal reservoirs with anhydrite abundant as matrix mineral?

2. TRANSFORMATION OF ANHYDRITE INTO CALCITE

The transformation of anhydrite into calcite is critical for the feasibility of this new technology. As mentioned earlier two aspects of the reaction are vital: Firstly, the acidity produced in the system which limits the reaction; secondly, the velocity of the transformation, i.e. the dissolution kinetics of anhydrite and precipitation kinetics of calcite.

Batch reaction calculations with PHREEQC (Parkhurst and Appelo 1999) have been performed to deduce the limiting pH of the brine and to prove the theoretical feasibility of the transformation. The reaction of anhydrite with a 0.16 M solution of NaHCO$_3$ has been studied under varying pH conditions assuming a pCO$_2$ of 1 MPa and a temperature of 30 °C. Figure 1 (top) depicts the mass of calcite formed and the amount of CO$_2$ bound in calcite depending on the initial pH of the solution. Theoretically, the reaction of interest proceeds down to a pH of 5.5. Hence, the transformation is not limited to extremely high pH values but occurs also under boundary conditions that can be achieved with the targeted technology.

In order to study and prove the feasibility of the transformation of anhydrite into calcite we performed batch experiments in the laboratory in which 200 g of a 0.16 M NaHCO$_3$ solution reacted with 15 g of anhydrite for different periods of time. The initial pH was varied between 7 and 8. Anhydrite dissolved and the calcium concentration of the solution increased. Because of the high HCO$_3^-$ concentration, the solubility product of calcite was exceeded and calcite precipitated. After termination of the experiment the suspension was freeze dried and the mineral phases quantified with X-ray diffraction (XRD). The black dots in Figure 1 (bottom) display the amounts of calcite that were formed during the experiments. In order to model numerically the entire process and to describe the transformation of anhydrite into calcite quantitatively, it is necessary to describe the velocity of the reactions, i.e. to formulate rate laws for mineral precipitation and dissolution reactions.

In the kinetic simulation using the program PHREEQC a rate law has been assumed for the dissolution of anhydrite and the precipitation of calcite. The dashed line in Figure 1 (bottom) represents the simulated amount of calcite precipitated, reproducing the laboratory data (diamonds) very well. The fit was achieved by applying a non-linear rate law for anhydrite dissolution and a linear rate law for calcite precipitation. Our experiment proves that the formation of calcite occurs under different boundary conditions.

Original core material of a reservoir sandstone was used for a flooding experiment conducted under increased pressure and temperature conditions. A sandstone sample cemented with anhydrite was used in order to examine the entire process of dissolution and precipitation and resulting pore space changes during CO$_2$ storage in geothermal reservoirs.
As an important result it was observed that the average permeability across the core length increases continuously with flooding time after a short initial period of a slight permeability decrease (Figure 2). As expected, the combined reaction of anhydrite dissolution and calcite precipitation yields a porosity increase. However, it is striking and promising that also permeability is increasing.

We performed additional simulations to take into account kinetic reactions and incorporated reaction rates with respect to anhydrite and plagioclase dissolution and calcite precipitation. We used reaction rates for anhydrite and calcite as determined in the laboratory experiments. Plagioclase weathering is assumed to be 3 to 4 orders of magnitude slower than the calcite and anhydrite reaction rates, respectively (Palandri and Kharaka 2004). Figure 4 displays changes of pH and the mineral composition versus time. It can be seen that the initial pH of 3.9 (due to saturation of the geothermal water with CO$_2$ for a pressure of 0.1 MPa) is increasing (diamonds) with the amount of dissolved plagioclase (dots). Kaolinite (squares) precipitates with a slightly higher rate. After 80 days, at a pH of 5.4 calcite precipitation kicks in. The reaction continues until the buffering capacity of plagioclase is exhausted.

Figure 2: Core flooding of a sandstone sample (length 5 cm, diameter 3 cm) cemented with anhydrite and flooded with 1 m Na$_2$CO$_3$ solution at 2 mL per hour. Anhydrite is dissolved and detected by the sulphate concentration at the core outlet. The average permeability across the core length increases with time.

3. PROBABLE SOURCES OF ALKALINITY

Numerical studies on multiple scales - from geochemical batch modelling to reactive transport simulation - using PHREEQC and SHEMAT (Clauser 2003) have shown that supply of alkalinity is of utmost importance to push the overall reaction (equation 3) towards the products. Buffering capacity is necessary for transforming anhydrite into calcite. Both options, in-situ alkalinity through plagioclase or surface water treatment using fly ashes, result in calcite precipitation in the reservoir.

3.1 In-situ alkalinity source

Numerical batch simulations were performed for the potential site at Stralsund with its confirmed geothermal resource (Kühn et al. 2002). At first, the thermodynamic equilibrium of the chemical reactions was studied under consideration of the technical process planned for this technology. The formation water was cooled, enriched with varying amounts of CO$_2$, and brought into contact with the reservoir minerals again (chemical compositions taken from Kühn et al. 2002). As expected, the pH decreases with an increasing amount of added CO$_2$. Furthermore (Figure 3), the results demonstrate that weathering of plagioclase is a prerequisite for calcite precipitation. Without the buffering capacity of plagioclase no CO$_2$ can be bound. But plagioclase dissolution by itself is still insufficient. For an increased rate of dissolution and in turn increased buffering, kaolinite needs to be formed as a secondary siliceous phase. Anhydrite is not a chemical driver of the reaction due to the fact that the initial calcium concentration of the brine is high. The additional and small increase in Ca ions resulting from dissolution of anhydrite does not affect the solubility product of calcite. However, the dissolution of anhydrite is still important with respect to the resulting changes in pore space. The break-even point above which porosity is reduced is reached with an addition of 5.0·10$^{-4}$ mol CO$_2$ per kg water (Figure 3).

Figure 3: Batch reaction calculation for the Stralsund site. Initial chemical composition of the formation water and the reservoir rock are taken from Kühn et al. (2002). pH decreases with increasing amount of added CO$_2$. Weathering of plagioclase is a prerequisite for calcite precipitation. For an increased rate of buffering, kaolinite needs to be formed.

Figure 4: Batch reaction calculation for the Stralsund site. Initial chemical composition of the formation water and the reservoir rock are taken from Kühn et al. (2002). The reaction rates of anhydrite and calcite are determined from the laboratory experiments. All others are taken from Palandri and Kharaka (2004). After 80 days, at a pH of 5.4 calcite precipitation kicks in.

For the purpose of comparing results this time span of 80 days can be transformed into a saturation length: Assuming an average flow velocity between injection and production well (100 m per year assuming a distance of 1000 m between the wells) the saturation length is 22 meters.
Hence, the area where calcite is precipitated begins at least 22 meters away from the injection well, what is far enough not to endanger well injectivity. Even though plagioclase weathering rates have been assumed to be very small they are fast enough to finally produce calcite between the wells.

3.2 Alkalinity provided through fly ashes

Laboratory experiments have confirmed that the uptake of CO$_2$ by fly ashes is a rapid reaction. The chemical reactivity of fly ashes is high due to their chemical instability in aqueous solutions and due to their small grain sizes corresponding to large reactive surfaces. The fast neutralization process (10-20 minutes) of lignite fly ashes is favorable concerning the technical realization. Large amounts of alkalinity in solution are provided immediately after the addition of the ashes and are not entirely consumed during the experiments (3-4 h).

Alkaline fly ashes have a high CO$_2$ binding potential. Lignite fly ash is better suited for CO$_2$ binding than the hard coal ash because of its higher acid neutralization capacity. A CO$_2$ binding potential of 2 mmol CO$_2$ per gram lignite ash has been measured in reactor tank experiments. The total amount of lignite coal used for power combustion in Germany was about 165.3 Mt in 2003 resulting in a total CO$_2$ emission of approximately 184.1 Mt (DIW 2004). About 10 % of the coal accumulates as fly ash during the combustion process leading to capture of 0.5 % of the CO$_2$ emissions. This value can certainly be increased by optimizing the process, in particular by varying temperature and stirring rate. Taking into account the high amount of earth alkaline elements in the lignite fly ash of around 50 % the maximum, theoretical storage capacity accumulates to 5.5 % under the assumption that all Ca and Mg is transformed into carbonate.

As outlined above the second route to supply alkalinity for transforming anhydrite into calcite in operated geothermal reservoirs is the surface treatment of the geothermal brine with fly ashes. It has been shown in our laboratory experiments that alkalinity is available and that reaction rates are high. Now, batch reaction simulations show that calcite is precipitated from a mixture of geothermal formation water treated with fly ashes and formation water enriched with the technologically maximum amount of CO$_2$ (0.1 mol). In this case calcite is produced even without alkalinity supplied from rock forming minerals. Again, anhydrite dissolution is important to keep the pore space in the reservoir open. The application of different mixing ratios shows that calcite precipitation is maximized (1.1⋅10$^{-3}$ mol) by mixing the CO$_2$ enriched formation brine with only 0.1 wt% of the water treated with fly ashes. At the same time 1.7⋅10$^{-3}$ mol of anhydrite is dissolved resulting in a porosity increase of the system.

4. SUITABLE GEOTHERMAL RESERVOIRS

The stratigraphic horizons, suitable for the storage of CO$_2$, are identified by the analysis of borehole data. Selection criteria are: the occurrence of anhydrite, adequate thickness of potential storage layers, and a pool of petrophysical data which is required to deduce representative input parameters for numeric models.

One candidate site is at Stralsund, situated in Northeast Germany on the Baltic Sea, where a geothermal resource was confirmed in previous studies in Buntsandstein layers at a depth of about 1520 m (Kühn et al. 2002). Stralsund is used here as a first area to demonstrate the potential for CO$_2$ storage by numerical simulations. Three boreholes are available at Stralsund location (Kühn et al. 2002) and two different constellations are conceivable: (1) the two wells nearest to the town (Gt Ss 1/85 and Gt Ss 6/89, Figure 5) are used for production and the third one (Gt Ss 2/85) for injection to minimize transport distances for the hot water; (2) the two boreholes nearest to town are used for injection and the third one for production (Figure 5). In both cases the thermally and hydraulically affected reservoir rock volume amounts to approximately 220 Mio m$^3$ and 370 Mio m$^3$, respectively. The life span of the geothermal heating plant, defined by the cold water breakthrough at the production well, is 40 years in both cases.

![Figure 5: Reservoir model of the Stralsund location.](image-url)
5. CONCLUSION

Our study emphasizes that mineral trapping of carbon dioxide in geothermal reservoirs provides an alternative approach for the long-term and safe subsurface immobilisation of CO$_2$. Furthermore, sequestration of carbon dioxide combined with geothermal heat or power production offers an additional economical benefit.

The feasibility of transforming anhydrite into calcite was proved by laboratory experiments as well as by numerical modelling of the associated chemical processes. Additionally, a core flooding experiment under increased pressure and temperature conditions was used to study the entire process of dissolution and precipitation and resulting pore space changes during CO$_2$ storage in geothermal reservoirs. It was observed that the average permeability across the core length increases continuously with flooding time.

Buffering capacity (alkalinity) derived from the reservoir rock or through surface water treatment with alkaline fly ashes is essential for transforming anhydrite into calcite. Although it turns out that anhydrite is not the major player from the chemical point of view, its dissolution with concurrent pore space increase is important to balance the pore space reduction by precipitation of calcite and secondary silicates in the geothermal reservoir.

Significant storage capacities are available in geological formations for millions of tonnes of carbon dioxide. Further studies to be carried out in the future will yield extensive and accurate process parameters to enable the development of innovative strategies for the realisation of a pilot field test on the technological scale.

ACKNOWLEDGEMENTS

The authors wish to thank Volker Meyn who performed the core flooding experiment.

This is publication no. GEOTECH - 275 of the R&D-Programme GEOTECHNOLOGIEN funded by the German Ministry of Education and Research (BMBF) and German Research Foundation (DFG), Grant (03G0614A-C).

REFERENCES


DIW: CO$_2$ -Emissionen in Deutschland im Jahre 2003: Witterungsbedingt leichte Steigerung. Wochenbericht des DIW Berlin, Oktober 2004 (in German)


