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Mineral trapping of CO_2 in operated hydrogeothermal reservoirs

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ABSTRACT

Storage of carbon dioxide (CO_2) 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 CO_2 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 CO_2 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 CO_2 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 subsequently result in the reaction of dissolved Ca and CO_2 to form and precipitate calcium carbonate. We show that anhydrite dissolution with concurrent pore space increase is important to balance pore space reduction by precipitation of calcite and secondary silicates. A core flooding experiment under increased pressure and temperature conditions showed that the average permeability increases continuously. Laboratory experiments prove the feasibility of literally transforming anhydrite into calcite and provide necessary kinetic input data for the modelling.

Suitable geothermal reservoirs exist with anhydrite as matrix mineral and plagioclase supplying alkalinity. Their CO_2 storage capacities depend on their volume and porosity as well as on the chemical and mineralogical composition of the formation brine and reservoir rock, respectively. Mass balance calculations yield that the storage capacity can be estimated from the abundance of anhydrite in the reservoir. Based on an operation time of 30 years this theoretical, quite significant storage capacity amounts to million of tons of CO_2 around geothermal heating plants.

1. INTRODUCTION

Various available options for the sequestration of CO_2 in the subsurface have been proposed and discussed to reduce the amount of anthropogenic carbon dioxide (CO_2) released into the atmosphere. A possible means of reducing these CO_2 emissions is injection into structural reservoirs in deep, permeable geologic formations. The aim of the CO_2Trap project (Kühn et al. 2005), funded by the German Federal Ministry of Education and Research (BMBF under grant 03G0614A-C) in the framework of the GEOTECHNOLOGIEN special program "Investigation, Utilisation, and Protection of the Underground", is to develop, study and evaluate an alternative approach for the subsurface deposition of CO_2. The concept is to sequester CO_2 not only by hydrodynamic trapping within a reservoir, but to convert dissolved CO_2 into the geochemically more stable form of calcite ($CaCO_3$) in a reaction with calcium obtained from dissolution of sulphates and alkalinity from feldspars or fly ashes. The costs for sequestration in deep saline aquifers 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 CO_2. After re-injection into the reservoir, this cold water becomes enriched in calcium e.g. due to dissolution of anhydrite ($CaSO_4$). Subsequently, CO_2 precipitates as calcium carbonate ($CaCO_3$). The following chemical reactions need to be considered with regard to CO_2 storage in geothermal reservoirs:

Due to the decreased solubility of anhydrite with temperature, injecting cold water dissolves the mineral in a region expanding around the well. The concentrations of calcium and sulphate increase in the water with the dissolution of anhydrite:

$$CaSO_4 <=> Ca^{++} + SO_4^{--} \quad (1)$$

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

$$CO_2 + H_2O <=> H_2CO_3 <=> H^+ + HCO_3^- \quad (2)$$

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

$$CaSO_4 + H_2CO_3 <=> CaCO_3 + 2\ H^+ + SO_4^{--} \quad (3)$$

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 CO_2 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:

$$[NaAlSi_3O_8]_2[CaAl_2Si_2O_8] + 4\ H^+ + 10\ H_2O => 2\ Na^+ + Ca^{++} + 4\ H_4SiO_4 + 2\ Al_2Si_2O_5(OH)_4 \quad (4)$$

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.

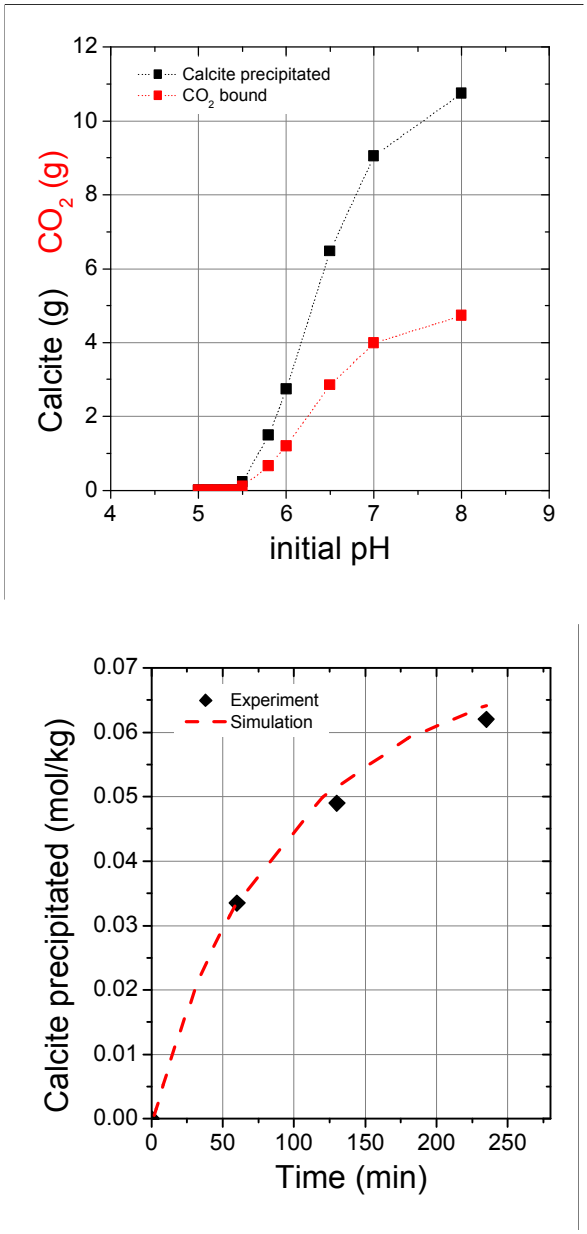


Figure 1: (top) Calcite formed and CO_2 bound versus initial pH of solution as modelled with PHREEQC; boundary conditions: mass of solution = 1 kg, 0.16 M $NaHCO_3$ solution, infinite amount of anhydrite, T = 30 °C, pCO_2 = 1 MPa. (bottom) Evolution of calcite in suspension during a transformation experiment.

The core (length 5 cm, diameter 3 cm) was flushed applying a 1 molar sodium carbonate solution for 1700 hours with 2 mL per hour (Figure 2). Dissolution of anhydrite was determined by measuring the sulfate concentration of the solution at the core outlet. In total, round about 16 g of anhydrite were dissolved and flushed out of the core. The measured sulfate concentration at the beginning of the experiment (about 15 g L-1) corresponds to 10 % of the thermodynamic equilibrium. Hence, the dissolution reaction does not reach saturation within the sandstone sample. The calcium concentration is too small to be measured at the core outlet. The main quantity of calcium is precipitated as calcite within the core.

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.

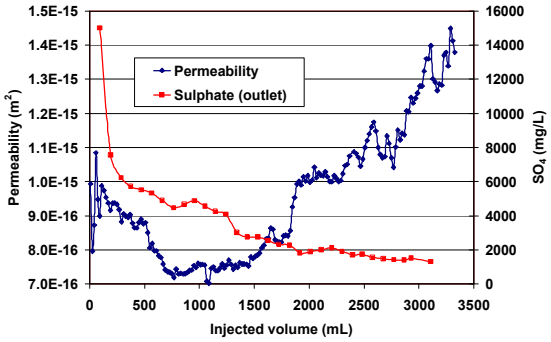


Figure 2: Core flooding of a sandstone sample (length 5 cm, diameter 3 cm) cemented with anhydrite and flooded with 1 m Na_2CO_3 solution at 2 mL per hour. Anhydrite is dissolved and detected by the sulphate concentration at the core outlet. The average permeability across the core length increases with 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 $5.0 \cdot 10^{-4}$ mol CO_2 per kg water (Figure 3).

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.

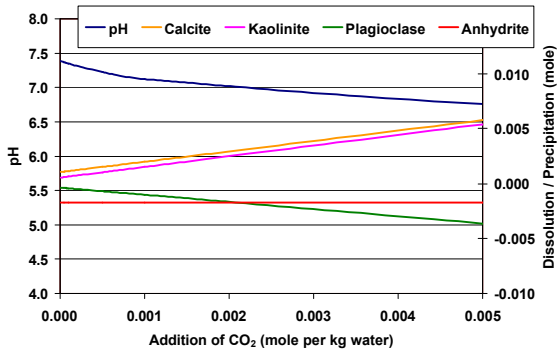


Figure 3: Batch reaction calculation for the Stralsund site. Initial chemical composition of the formation water and the reservoir rock are taken from Kühn et al. (2002). pH decreases with increasing amount of added CO_2. Weathering of plagioclase is a prerequisite for calcite precipitation. For an increased rate of buffering, kaolinite needs to be formed.

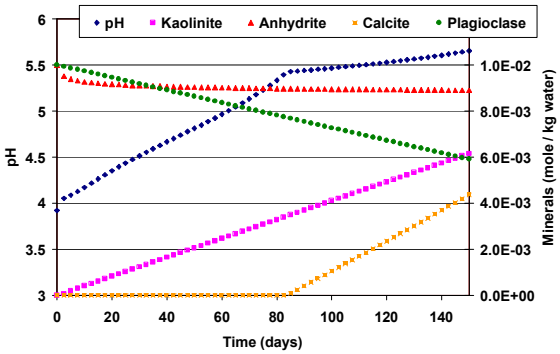


Figure 4: Batch reaction calculation for the Stralsund site. Initial chemical composition of the formation water and the reservoir rock are taken from Kühn et al. (2002). The reaction rates of anhydrite and calcite are determined from the laboratory experiments. All others are taken from Palandri and 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 ($1.1 \cdot 10^{-3}$ 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 $1.7 \cdot 10^{-3}$ 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.

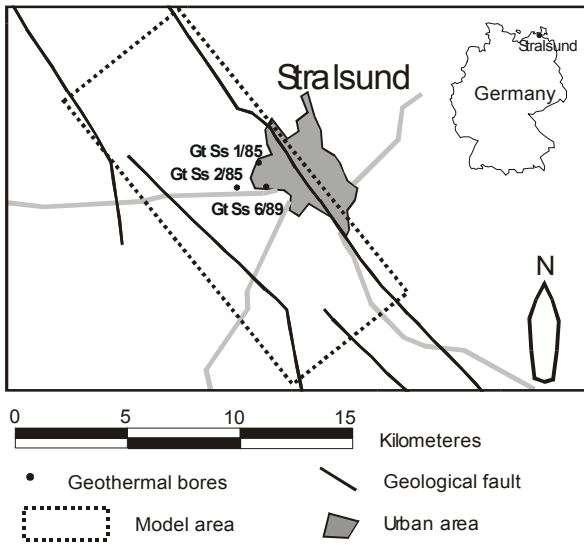


Figure 5: Reservoir model of the Stralsund location.

The wells tap the Detfurth sandstone with a thickness between 33 m and 36 m. Drilling profiles and core samples indicate that the reservoir consists of a weakly consolidated, fine to medium feldspatic quartz sandstone. The sandstone is low graded with clay (< 2 % kaolinite, muscovite, chlorite, illite, and montmorillonite) and cementing minerals (4 % -5 % dolomite, calcite, and anhydrite). The highly saline formation water is of the Na-(Ca-Mg)-Cl type with a solute content of 280 g L^{-1} and a formation temperature of about 58 °C.

The storage capacity of CO_2 in a geothermal reservoir depends on the volume and porosity of the reservoir and on the pumping rates. Additionally, the chemical and mineralogical compositions of the brine and reservoir rock, respectively, determine the amount of CO_2 which can be minerally bound. Mass balance calculations yield that the storage capacity can be estimated from the abundance of anhydrite in the reservoir. The theoretical, quite significant storage capacity amounts to 0.5 million tons for the candidate site. Calculations were performed for the reservoir volume influenced by a geothermal heating plant, based on an operation time of 30 years and the assumption that the entire anhydrite content is transformed into calcite as outlined in equation (3). Apart from the mineral trapping an additional 2.2 million tons of CO_2 can be stored in form of dissolved CO_2 in the brine.

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.

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