

# CO<sub>2</sub> STORAGE THROUGH MINERAL TRAPPING IN GEOHERMAL RESERVOIRS

MICHAEL KÜHN<sup>1</sup>, KATRIN VOSBECK<sup>2</sup>, MARTIN BACK<sup>3</sup>, CHRISTOPH CLAUSER<sup>1</sup>,  
HELGE STANJEK<sup>2</sup>, STEFAN PEIFFER<sup>3</sup>

<sup>1</sup> *Applied Geophysics, RWTH Aachen University, Lochnerstraße 4-20, D-52056 Aachen, Germany*

<sup>2</sup> *Clay and Interface Mineralogy, RWTH Aachen University, Wüllnerstraße 2, D-52056 Aachen, Germany*

<sup>3</sup> *Hydrology, University of Bayreuth, Universitätsstraße 30, D-95440 Bayreuth, Germany*

## ABSTRACT

Costs for carbon dioxide sequestration into deep saline aquifers can be transformed into a benefit when combined with ecologically desirable geothermal heat or power production. The produced energy can be used and marketed. Aim is a scientifically and technically feasible new technology to achieve a safe and economically attractive long-term storage of CO<sub>2</sub> trapped in minerals. We develop, study, and evaluate a novel approach not only to sequester CO<sub>2</sub> by hydrodynamic trapping within a reservoir, but to convert dissolved CO<sub>2</sub> into the geochemically more stable form of calcite.

Due to the geological situation exploitation of geothermal energy in Germany is mainly provided from deep sandstone aquifers. The common arrangement of bore holes 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<sub>2</sub>, and after re-injection into the reservoir this cold water becomes enriched in calcium e.g. due to dissolution of anhydrite (CaSO<sub>4</sub>). Subsequently CO<sub>2</sub> precipitates as calcium carbonate (CaCO<sub>3</sub>), provided that alkalinity is present either by the dissolution of feldspars in the aquifer or by surface water treatment with fly ashes.

The feasibility of transforming anhydrite into calcite has been proved in laboratory experiments as well as by thermodynamic modelling. Although it has been determined from numerical simulations that anhydrite is not the major player from the chemical point of view, its dissolution with resulting pore space increase is important to balance pore space reduction through calcite precipitation and precipitation of secondary silicates in the geothermal reservoir.

Numerical studies on multiple scales, from geochemical batch modelling to reactive transport simulation, has shown that supply of alkalinity is of utmost importance to push the overall reaction towards the products. Buffering capacity is necessary for the transformation of anhydrite into calcite. Both options, in-situ alkalinity through plagioclase or surface water treatment using fly ashes, lead to successful calcite precipitation in the reservoir with significant storage capacities for millions of tonnes of carbon dioxide.

## 1 INTRODUCTION

The novel approach of the so called CO<sub>2</sub>Trap project (Kühn et al., 2005) is to sequester CO<sub>2</sub> not only by hydrodynamic trapping within a reservoir, but to convert dissolved CO<sub>2</sub> into the geochemically more stable form of calcite in a reaction with calcium obtained from dissolution of sulphates and alkalinity from feldspars or fly ashes. The costs for sequestration into deep saline aquifers can be transformed into a benefit when combined with ecologically desirable production of geothermal heat or power. The produced energy can be used and marketed. Due to the geological situation exploitation of geothermal energy in Germany is mainly provided from deep sandstone 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<sub>2</sub>, and after re-injection into the reservoir this cold water becomes enriched in calcium e.g. due to dissolution of anhydrite (CaSO<sub>4</sub>). Subsequently CO<sub>2</sub> precipitates as calcium carbonate (CaCO<sub>3</sub>). Following chemical reactions need to be considered with regard to CO<sub>2</sub> storage in geothermal reservoirs:

- Due to the retrograde solubility of anhydrite, the injection of cold water leads to dissolution of the mineral in a growing region around the well and in turn to increased concentrations of calcium and sulphate in the water:  $\text{CaSO}_4 \rightleftharpoons \text{Ca}^{++} + \text{SO}_4^{--}$
- Before re-injection, brines will be enriched with carbon dioxide generating as a result carbonic acid:  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$
- The overall reaction, the transfer of anhydrite into calcite, outlines the favoured reaction path:  $\text{CaSO}_4 + \text{H}_2\text{CO}_3 \rightleftharpoons \text{CaCO}_3 + 2 \text{H}^+ + \text{SO}_4^{--}$

From the third equation is obvious that a surplus in acid exists which is counterproductive with respect to calcite precipitation in general. However if the increase in Ca is large enough or if alkalinity is available to buffer the reaction the solubility product of calcite is exceeded and CO<sub>2</sub> finally trapped as calcite. Alkalinity to buffer the reaction can be provided from rock forming minerals or by surface water treatment with alkaline fly ashes.

## 2 LABORATORY EXPERIMENTS

### 2.1 Transformation of anhydrite into calcite

The transformation of anhydrite into calcite has been proved in laboratory experiments and numerical simulations. The reaction proceeds at pH values higher than approximately 5 and shows noteworthy calcite precipitation at pH values between 7 and 8. FIGURE 1 displays the result of a batch experiment verifying precipitation of calcite from a 0.16 M NaHCO<sub>3</sub> solution in contact with anhydrite. After 24 h of reaction 92 % of anhydrite has been transformed into calcite. Concerning the dissolution kinetics of anhydrite, experimental results indicate that certain properties of the rock are important. These include the form of crystallisation, intrinsic impurities, and crystal defects.

### 2.2 Alkalinity provided through fly ashes.

Laboratory experiments have confirmed that the uptake of CO<sub>2</sub> 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.

Large amounts of alkalinity in solution are provided immediately after the addition of the ashes.

Lignite fly ash is better suited for CO<sub>2</sub> binding than the hard coal ash because of its higher acid neutralisation capacity. A CO<sub>2</sub> binding potential of 2 mmol CO<sub>2</sub> 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<sub>2</sub> emission of approximately 184.1 Mt. About 10 % of the coal accumulates as fly ash during the combustion process leading to capture of 0.5 % of the CO<sub>2</sub> emissions. 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.

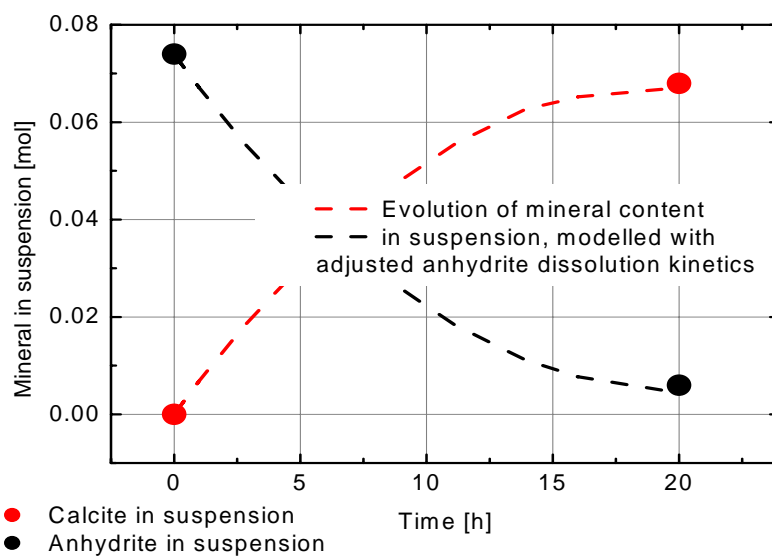


FIGURE 1. Batch experiment verifying the transformation of anhydrite into calcite. After 24 h of reaction 92 % of the initial anhydrite (black dots) in contact with a 0.16 M NaHCO<sub>3</sub> solution has reacted to calcite (red dots).

### 3 NUMERICAL SIMULATION

Numerical simulation is a means to quantify the entire process of CO<sub>2</sub> storage and to provide a deeper understanding of the detailed chemical processes. Simulations are performed on multiple scales, because as yet the combination of all scales from regional down to micro-scale is not feasible.

Programs SHEMAT (Clauser, 2003) and PHREEQC (Parkhurst and Appelo, 1999) have been applied for these simulations. SHEMAT provides two chemical modules: one is based on Pitzer's approach and the other one on the Debye-Hückel theory for ion activity calculations in highly saline brines and dilute solutions, respectively. PHREEQC is based on the Debye-Hückel theory. Although the Pitzer equations currently represent the most accurate approach for calculating ion activities in brines, aluminium is unfortunately not yet represented in the data set due to lacking Pitzer coefficients. Therefore, many rock forming minerals cannot be taken into account. For this reason we have applied both Pitzer equations

(using SHEMAT) and Debye-Hückel theory (applying SHEMAT and PHREEQC) for the following simulations.

### 3.1 Potential location Stralsund.

At Stralsund, situated in Northeast Germany on the Baltic Sea, a geothermal resource has been investigated and 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 potential for CO<sub>2</sub> storage by numerical simulations. The reservoir consists of a weakly consolidated, fine to medium feldspathic quartz sandstone. The sandstone is low graded with clay (< 2 % kaolinite, muscovite, chlorite, illite, and montmorillonite) and cement 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<sup>-1</sup> and a formation temperature of about 58°C.

### 3.2 Batch reaction calculations.

As a starting point for further reactive transport simulations with SHEMAT batch reaction simulations (no spatial scale) have been performed using PHREEQC. Here the aim is to elaborate the thermodynamic background of the transformation of anhydrite into calcite in a geothermal reservoir.

The initial water composition and mineralogy has been set according to chemical analyses of the Stralsund geothermal brine and reservoir rock (Kühn et al., 2002). Under in-situ conditions of 58°C reservoir temperature the geothermal brine is in equilibrium with respect to the minerals calcite, dolomite, and anhydrite.

#### 3.2.1 *In-situ alkalinity source.*

In accordance with the technical process planned for this novel technology, the formation water has been cooled, enriched with CO<sub>2</sub>, and brought into contact with the reservoir minerals again. Results demonstrate that weathering of plagioclase is a prerequisite for calcite precipitation. Without the buffering capacity of plagioclase no CO<sub>2</sub> can be bound. However, plagioclase dissolution itself is insufficient. For an increased rate of dissolution and in turn an increased buffering a secondary siliceous phase needs to be formed, such as albite (FIGURE 2) or kaolinite (FIGURE 3).

FIGURE 2 displays mineral reactions occurring within the Stralsund formation for varying amounts of added CO<sub>2</sub> to the re-injected brine, allowing albite to form as secondary mineral. It can be seen that calcite starts to precipitate for a minimum addition of approximately 0.01 mol CO<sub>2</sub> per kg brine (corresponding to a gas phase of 100 % CO<sub>2</sub> in equilibrium with the brine at 0.1 MPa) while plagioclase, K-feldspar, and anhydrite dissolve. In the case that kaolinite is assumed to form as secondary clay mineral (FIGURE 3) calcite precipitation is observed right from the beginning (blue underneath red line) without a minimum threshold. The amounts of calcite produced and plagioclase dissolved are significantly larger. The maximum CO<sub>2</sub> addition in both cases has been chosen to represent a pure gas phase of CO<sub>2</sub> in contact with the brine at a pressure of 1 MPa (i.e. the maximum operating pressure in the installation aboveground).

Due to the fact that the initial calcium concentration of the brine is high, the additional and small increase resulting from dissolution of anhydrite does not affect the solubility product of calcite. However, anhydrite dissolution is still of importance from the perspective of resulting pore space changes. The break-even point above which porosity is reduced, is reached with

addition of  $1.0 \cdot 10^{-2}$  mol CO<sub>2</sub> per kg water for the first case studied (FIGURE 2) which is below the minimum amount necessary to form calcite. In the second case (FIGURE 3) porosity is already reduced with addition of  $5.0 \cdot 10^{-4}$  mol CO<sub>2</sub> but none the less calcite is produced. Here, the amount of calcite produced ( $1.5 \cdot 10^{-3}$  mol) nearly equals the amount of anhydrite dissolved ( $1.7 \cdot 10^{-3}$  mol).

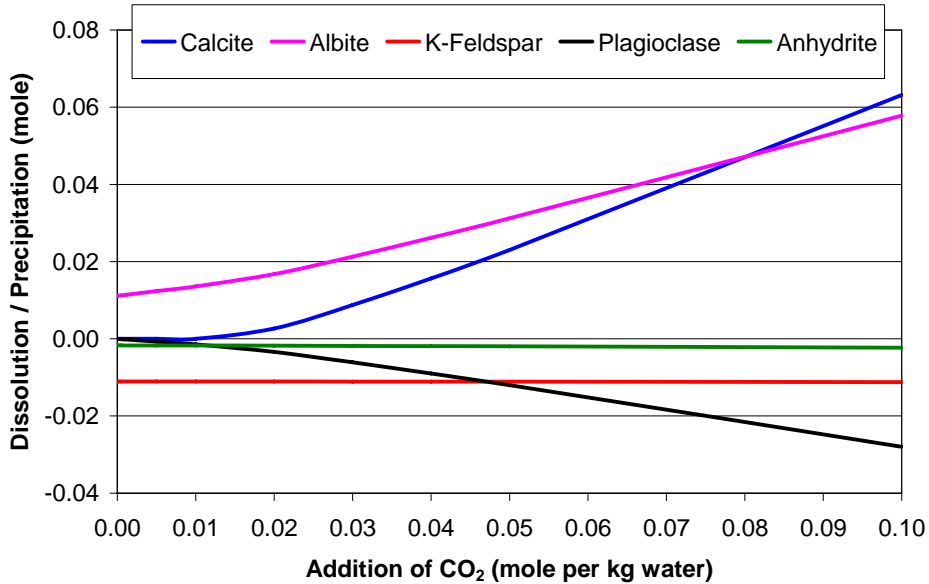


FIGURE 2. Mineral reactions within the Stralsund formation for varying addition of CO<sub>2</sub> to the brine re-injected, taking into account secondary albite.

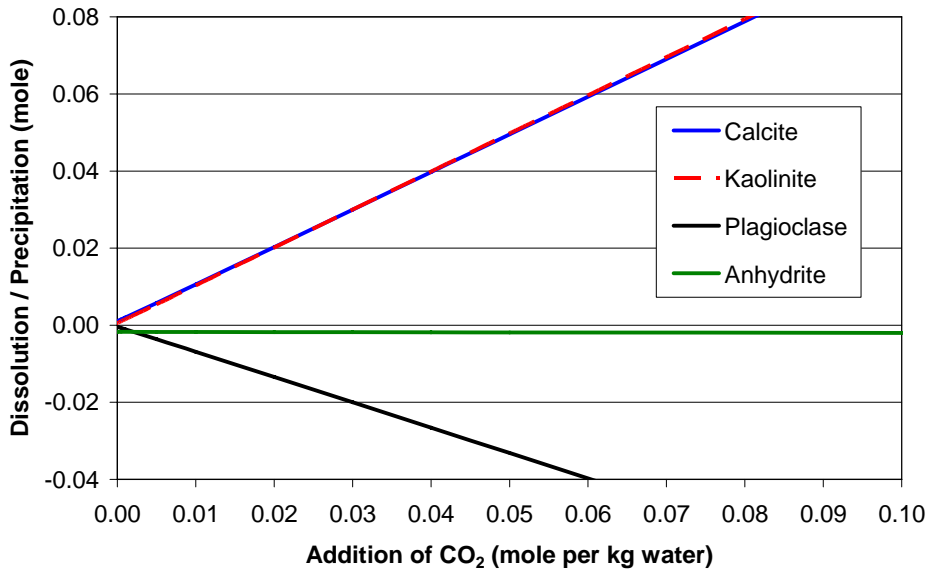


FIGURE 3. Mineral reactions within the Stralsund formation for varying addition of CO<sub>2</sub> to the brine re-injected, taking into account secondary kaolinite.

The storage capacity of CO<sub>2</sub> in a geothermal reservoir depends on the volume and porosity of the reservoir, as well as pumping rates. Furthermore, chemical composition of the brine and the reservoir rock determine the amount of CO<sub>2</sub> that can be minerally bound. If the entire anhydrite content (0.4 wt.%) is transformed into calcite approximately 0.56 Mt CO<sub>2</sub> can be trapped at the Stralsund location. Provided that not the anhydrite content but the in-situ alkalinity source (5 wt.%) is limiting the amount of CO<sub>2</sub> storable in the geothermal reservoir, 1.1 Mt can be captured.

### 3.2.2 Alkalinity provided through fly ashes.

As outlined above the second route to supply alkalinity for transforming anhydrite into calcite 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 CO<sub>2</sub>. 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<sub>2</sub> 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 net porosity increase of the system.

### 3.3 Reservoir scale.

So far, the modelling on the reservoir scale has been limited to the optimization of the hydraulic and thermal conditions of hot water production and cool water re-injection. 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 are used for production and the third one 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. In both cases the thermally and hydraulically affected reservoir rock volume amounts to approximately 220 million m<sup>3</sup> and 370 million m<sup>3</sup>, respectively. This amounts to 2.2 Mt of CO<sub>2</sub> that can be stored in form of dissolved CO<sub>2</sub> in the brine. The life span of the geothermal heating plant, defined by the cold water breakthrough at the production well, is 40 years in both cases.

### 3.4 Borehole-scale

It has been shown in our laboratory experiments that anhydrite can be successfully transformed into calcite. First numerical models on the borehole-scale prove the same. The model measures 50 m by 50 m with the well located in the centre (not shown). The cooled re-injected water spreads radially from the injection well. Due to the retrograde solubility, anhydrite is dissolved around the well. Storage of CO<sub>2</sub> in form of calcite has been detected, resulting from the increase of the calcium concentration in the water and the enrichment of the injected brine with CO<sub>2</sub>.

The numerical simulations on the borehole-scale have been performed with the chemical module of SHEMAT for highly saline solutions. As discussed above this excludes investigation of buffering rock forming minerals like plagioclase. However, a sensitivity study has been conducted defining varying pH values from 5 to 8 for the injected brine (imitated buffering). Results show that no calcite can be produced for pH 5 in contrast to pH

6, 7, and 8 when calcite is precipitated. The entire dissolution of anhydrite in a growing region around the well leads to a moving front of calcite. The lower the pH of the injected brine, the faster the calcite front is moving. As soon as the calcium concentration of the water has decreased, due to a lack of dissolvable anhydrite, calcite starts to dissolve again and is transported away from the well. This effect demonstrates that anhydrite abundance in the rock needs to be sufficiently high to avoid re-dissolution of calcite.

### 3.5 Micro-scale

The numerical experiments on the micro-scale are generic experiments. The idea is that an ion, a water molecule, or a package of mineralized solution can only react with one mineral at a time because it can only be at one location at a time. In “classic” reactive transport simulation space a specific but averaged and homogenised mineral assemblage is considered for one model element or cell. However, the history of a water package getting into contact with distinct minerals in a certain sequence might be important to understand the chemistry of the mineralization process. The applied model is on the scale of 1 cm by 3 cm and discretized into 1 mm by 1 mm cells. Applying the mineral composition of the Stralsund location and based on a random distribution, model elements have been assigned to one distinct mineral (quartz, plagioclase, K-feldspar, or anhydrite).

Two scenarios have been modelled on the micro-scale. The first one as described before with one mineral for each model cell. The second scenario was set up in a way that all initial mineral phases are available in each cell of the model. This is the classic approach in reactive transport modelling. A comparison between both scenarios reveals that the water composition finally is the same after its way through the rock assemblage. However, the resulting rock alteration assemblage shows significant differences between both models. As shown above (Batch reaction calculations) the dissolution of plagioclase is essential for the formation of calcite. It is striking that the classic case produces a planar calcite reaction front moving through the system such as the one observed on the borehole-scale. In the generic model the resulting calcite distribution is heterogeneous and permanent. It has to be concluded that heterogeneity on the micro-scale has important effects for the larger-scale.

## 4 CONCLUSIONS

Costs for carbon dioxide sequestration into deep saline aquifers can be transformed into a benefit when combined with ecologically desirable geothermal heat or power production. Aim is a scientifically and technically feasible new technology to achieve a safe and economically attractive long-term storage of CO<sub>2</sub> trapped in minerals. We investigate the potential of geothermal reservoirs for mineral trapping of aqueous carbon dioxide.

Exploitation of geothermal energy in Germany is mainly provided from deep sandstone 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<sub>2</sub>. After re-injection into the reservoir this cold water becomes enriched in calcium e.g. due to dissolution of anhydrite (CaSO<sub>4</sub>). Subsequently CO<sub>2</sub> will react with the calcium ions to form and precipitate calcium carbonate.

We demonstrate the feasibility of transforming anhydrite into calcite by laboratory experiments and thermodynamic modelling. The reaction proceeds at pH values higher than approximately 5.5. Buffering capacity (alkalinity) from the reservoir rock or provided by

surface water treatment with fly ashes is necessary for the transformation of 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.

The storage capacity of CO<sub>2</sub> in a geothermal reservoir depends on the volume and porosity of the reservoir, as well as pumping rates. Furthermore, chemical composition of the brine and the reservoir rock determine the amount of CO<sub>2</sub> that can be minerally bound. If the entire anhydrite content is transformed into calcite approximately 0.56 Mt CO<sub>2</sub> can be trapped at the potential location Stralsund. Provided that not the anhydrite content but the in-situ alkalinity source is limiting the amount of CO<sub>2</sub> storable in the geothermal reservoir, 1.1 Mt can be captured. Additionally, 2.2 Mt of CO<sub>2</sub> can be stored in form of dissolved CO<sub>2</sub> in the brine.

The chemical reactivity of fly ashes is high due to their chemical instability in aqueous solutions. Large amounts of alkalinity in solution are provided immediately after the addition which is favourable for the technical process of CO<sub>2</sub> storage in geothermal aquifers. Furthermore, alkaline fly ashes have a high CO<sub>2</sub> binding potential. Lignite fly ash is better suited for CO<sub>2</sub> binding than the hard coal ash because of its higher acid neutralisation capacity. A CO<sub>2</sub> binding potential of 2 mmol CO<sub>2</sub> per gram lignite ash was measured leading to capture of 0.5 % of the CO<sub>2</sub> emissions. Taking into account the high amount of earth alkaline elements in the lignite fly ash of around 50 % the maximum, theoretical storage capacity is 5.5 % under the assumption that all Ca and Mg is transformed into carbonate.

The presented study emphasizes that mineral trapping of CO<sub>2</sub> in geothermal reservoirs or using fly ashes provide promising alternative approaches for long-term and safe immobilisation of greenhouse gases. Significant storage capacities are available in geological formations for millions of tonnes of carbon dioxide.

## ACKNOWLEDGEMENT

The CO<sub>2</sub>Trap project is part of the R&D-Programme GEOTECHNOLOGIEN funded by the German Ministry of Education and Research (BMBF) and German Research Foundation (DFG), Grant 03G0614A.

## REFERENCES

- Clauser, C. (Ed.) (2003), *Numerical simulation of reactive flow in hot aquifers - SHEMAT and Processing SHEMAT*, 332 pp, Springer Publishers, Heidelberg.
- Kühn, M., J. Bartels, J. Iffland (2002), Predicting reservoir property trends under heat exploitation: Interaction between flow, heat transfer, transport, and chemical reactions in a deep aquifer at Stralsund, Germany, *Geothermics* 31(6), 725-749.
- Kühn, M., S. Asmus, R. Azzam, M. Back, A. Busch, H. Class, C. Clauser, A. Dengel, T. Dose, J. Ewers, R. Helmig, K. Jaeger, T. Kempka, B.M. Krooß, R. Littke, S. Peiffer, R. Schlüter, H. Stanjek, J. Strobel, K. Vosbeck, M. Waschbüsch (2005), CO<sub>2</sub>Trap - Development and evaluation of innovative strategies for mineral and physical trapping of CO<sub>2</sub> in geological formations and of long-term cap rock integrity, in *GEOTECHNOLOGIEN Science Report: Investigation, utilisation and protection of the underground*, edited by L. Stroink, 42-59.
- Parkhurst, D.L., C.A.J. Appelo (1999), User's guide to PHREEQC (version 2)--A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, *U.S. Geological Survey Water-Resources Investigations Report 99-4259*.