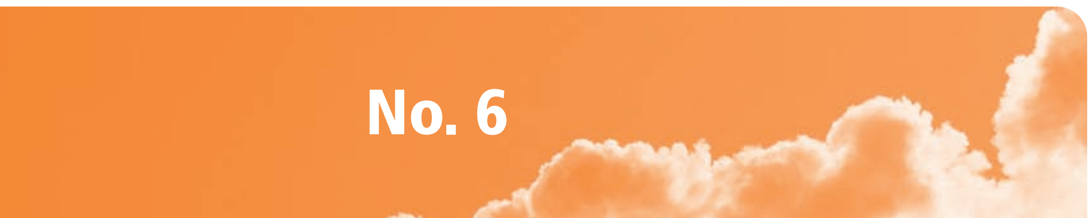
GEOTECHNOLOGIEN

Investigation, Utilization and Protection of the Underground

- CO_2-Storage in Geological Formations
- Technologies for an Underground Survey in Urban Areas

Kick-Off-Meeting
22-23 September 2005

Programme & Abstracts



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Science Report

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Preface

The R&D Programme GEOTECHNOLOGIEN aims at better understanding of the complex processes underlying System Earth and the development of new prevention strategies and negotiation options for sustainable management of Planet Earth. The recently started projects on the »Investigation, Utilisation and Protection of the Underground« focus on two main scientific subjects:

- CO_2 storage in geological formations
- Technologies for an underground survey in urban areas.

The reduction of anthropogenic CO_2-emissions has become highly challenging for science and society. Capture and storage of CO_2 as a bridge in the transition from the age of fossil fuels to that of renewable energies could be a key technology for reaching this target. Consequently, a portfolio of 10 research projects between academia and industry is being funded by the German Ministry for Education and Research (BMBF) under the umbrella of the R&D Programme GEOTECHNOLOGIEN.

The overall targets of the integrated research projects between universities, research centres and SMEs are

- the development of technologies and processes for the safe underground storage of CO_2 in Germany and their implementation in demonstration projects
- providing a profound scientific basis for decision-makers

In the initial phase (2005-2008), a total of nearly € 7,3 Million will be invested by the BMBF. Currently funded projects focus on the following key themes:

- Evaluation of potential storage sites and storage technologies
- Baseline characterisation (e.g. geology, reservoir/caprock features)
- Storage operation (injection technologies, EOR/EGR potentials)
- Development/implementation of reliable short- and long-term monitoring techniques
- Development and evaluation of strategies for the elimination, transformation and permanent immobilisation of CO_2

Currently only one project is focused on the research field »Technologies for an underground survey in urban areas«.

The main objective of the Kick-Off-Meeting at BGR-Hannover was to bring together the scientists and investigators of the funded projects to present their ideas and proposed work plans; several projects are interlinked and could therefore benefit from synergies. All who are interested in the forthcoming activities of the projects - from Germany, Europe or overseas - are welcome to share their ideas and results.

Ludwig Stroink
Peter Blümling

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Carbon dioxide elimination by using acid mine lakes and calcium oxide suspensions (CDEAL)

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Introduction

CDEAL's concept is to combine CO_2 mineral trapping and treatment of acidic mine waters. In the Lausitz (Lusatia) mining district intensive mining during the last century has produced huge deposits of fly ash, carbon slurry, and iron sludge (caused by the treatment of acid mine drainage) in the abandoned and flooded mine pits. One of these former pits is the acidic Burghammer pit which contains large amounts of these substances deposited on its bottom. A treatment of lake Burghammer sediments and water with CO_2 appears thermodynamically feasible using carbonation. Kinetic aspects, the real world phase assemblage, and technical aspects of the dosage, mixing, precipitation, and settling of the carbonate solid will be investigated in the project. CDEAL will perform laboratory experiments in the first stage and in case of a positive evaluation a feasibility pilot scale plant will be constructed and a field scale CO_2-injection plant will be installed at the Burghammer open pit lake.

Overall Goal

Generally, the Kyoto-Protocol requires a reduction in greenhouse gases, especially carbon dioxide. As concerns exist over the effects that such an action might have on the economy of developed countries, a worldwide search for other approaches to reduce carbon emissions has started. Existing engineering alternatives can significantly reduce CO_2 levels, while still allowing to rely on inexpensive energy sources as the cost of renewable energy decreases and their economies grow. One of those alternatives will be studied in the laboratory and then being developed to match field scale needs within the CDEAL consortium.

The overall goal of CDEAL is twofold: reduce the CO_2 emission into the atmosphere and to rehabilitate contaminated, acidic mine waters using carbonation. As the storage of carbon dioxide (CO_2) will be in the form of carbonate it will therefore be sustainable. Thus, CDEAL will positively contribute to the reduction of greenhouse gas emissions by CO_2-sequestration and to the goals described in articles 2 and 3 of the Kyoto-Protocol. Furthermore, as acidic mine waters belong to the largest waste streams in Europe, any significant reduction of such mine waters will result in a reduction of the total waste streams in Germany. CDEAL will only use pre-treated mine water and mine water with elevate CaO-contents due to fly ash deposition, where an excess of CaO exists and can be used to react with CO_2 to $CaCO_3$. In addition, iron-hydroxide sludge is available in great amounts in some parts of the open pit lakes and the waste rock piles, which can be used as reacting material as well.

Main goal of the proposed project is to investigate a sustainable low risk strategy to incorporate CO_2 into the subsurface and thus exclude it from the atmosphere. The precipitation of CO_2 and an alkaline earth metal (M) oxide or hydroxide can be written in the overall equations

$$CO_2 + MO \longrightarrow MCO_3\,(s) \qquad \text{(eq. 1)}$$

$$CO_2 + M(OH)_2 \longrightarrow MCO_3\,(s) + H_2O \qquad \text{(eq. 2)}$$

Using iron hydroxides as cation source for a carbonate precipitation the following redox half reaction can be written

$$Fe(OH)_3\,(s) + CO_2 + e^- \longrightarrow FeCO_3\,(s) + H_2O + OH^-$$
(eq. 3)

These storage mechanisms, the storage in the sediment and in the water phase may be applied in acidic mining lakes. The East German Lignite mining area is well suited for the demonstration of the proposed technology. CO_2 production and acidic lakes are locally concentrated. CaO is produced in combustion power plants. Over the past decades of intensive mining in the Lausitz area large amounts of fly ash and coal slurry from power plants and iron hydroxides from water treatment plants have been deposited in abandoned mines that now form lakes. Lake Burghammer contains sediment layers of these substances of several meter thickness on its bottom and was picked as field location in the proposed project. The Lausitz post mining lakes in general and lake Burghammer in particular yield a high potential for utilizing equations 1 to 3. To utilize equation 3 it has to be investigated if lake internal or external electron donors may be used.

The proposed project comprises of two steps. In a first step the feasibility of the treatment will be investigated in the laboratory and bench scale identifying governing chemical equilibrium and rates. The second step will transform the findings to the pilot and field scale. The thermodynamic possibility for a precipitation of calcite (saturation) is given when the product of the calcium and the carbonate activities reaches the temperature dependant constant K_{sp}. The strong dependency of the appearance of the carbonate ion in solution from pH creates the need of near neutral to alkaline conditions for calcite precipitation. Given an acidic water with a typical high concentration of calcium (3 to 10 mmol/L) a base titration will lead to a saturation with respect to calcite if carbon dioxide is allowed to reach equilibrium concentrations with atmospheric conditions. Calcite precipitation will decrease the calcium concentration as long as saturation is maintained. DIC concentration increases as Ca con-

Figure 1: Aerial view of lake Burghammer (courtesy eta η Aktiengesellschaft engineering Cottbus).

centrations decreases. This shows the high potential of acidic lakes for the uptake of CO_2 into the water if the treatment is combined with a neutralisation of the water. The natural pH-buffer bicarbonate is introduced to the water and improves the chemical condition and the biological potential.

The amount of calcite that can be precipitated if only pH is raised is of course low and depends on the initial calcium concentration. Unlimited amounts of calcite can be produced if calcium and carbonate are delivered to the solution. Precipitated calcite is stored in the sediment. Lake sediments are natural sinks in the geosphere. The storage mechanism consequently is not based on technical elements but on the geochemical conditions. Calcite precipitation should not be used in lakes that have a long-time tendency of becoming acidic. Nevertheless the return to acidic conditions of a lake used for calcite storage will not result in instantaneous CO_2 release. Apart from the surface area that is too small for an effective dissolution (which has been experienced in many unsuccessful liming treatments) dissolution of calcite will be limited by calcite saturation. Iron precipitation occurring during neutralization can produce sediment layers that support a progressing exclusion of the carbonates from participating in lake internal processes as the sediment consolidates. Calcite precipitation is best applied in acidic lakes that will be neutral after an initial water treatment. Lake Burghammer is part of a storage system that will receive high fluxes of surface waters. A water treatment station at its inflow point can be used to maintain neutral conditions if necessary.

The supply of cations (Ca, Mg) is a limiting factor for the utilisation of the storage strategy. A positive effect concerning the overall carbon dioxide budget can be achieved using cations from the ashes of combustion power plants (eq.1). Whereas cations from lime ovens have previously released CO_2 this must be included in the budget.

Scientific and Technical Goals

CDEAL's scientific and technical goals comprise of several steps: in the first project phase the technology and scientific basis for the CO_2-injection into CaO-rich or $Fe(OH)_3$-rich substrate will be developed in the laboratory. In the second phase, this technology will be transported to the field scale, where all the necessary installations to inject CO_2 into the substrate of an open pit lake (exemplified by using the Burghammer pit lake) will be developed. In the same time, other potential sites with a CO_2-source and a CaO-rich mine water or substrate will be investigated and the potential for installing treatment schemes there will be evaluated.

During the first phase, the CDEAL consortium, namely TU Bergakademie Freiberg and DGFZ, will conduct laboratory, bench and numerical studies to develop the proper layout of the CO_2-injection into the lake's substrate. This step's goal will be to find parameters for the correct CO_2-flow or gas composition, contact time between CO_2 and CaO and the type of injection of the gas into the substrate. Furthermore, pressure and temperature dependencies as well as the correct physico-chemical characteristics of the installation will have to be tested. The final scientific goal in this first step will be to get a proper understanding of the reactions involved and the dependencies of the different parameters involved. Furthermore, a pilot scale plant shall prove that the method developed will be suitable for the field scale treatment.

From the results of the first step, the goals of the second step have to be defined. The second step's goal is to construct a field scale plant near the open pit lake. This field scale plant has to consist of a CO_2-receiver station and an injection system. Furthermore, the results of the CO_2-injection have to be monitored continuously throughout the duration of the whole project. At the final stage of the project, a technical installation at the Burghammer pit lake will demonstrate to treat the acidic mine water by using the excess CaO/$Fe(OH)_3$ in the lake's substrate and the CO_2.

The scientific goal of the project will be to show that a waste product (CaO, $Fe(OH)_3$) and a greenhouse gas (CO_2) can be used to treat acidic mine waters and therefore contribute to the environmental protection of Germany's mining landscapes. Furthermore, the method will help to decrease Germany's CO_2 budget and therefore positively contribute to the aims of the Kyoto-Protocol. Such a CO_2-Sequestration system can also be implied in a ZEC (Zero-Emission Certificate) trading system (Kunsch et al. 2004).

The successful mediation of carbonate precipitation using native water from the post mining lake Burghammer and fly ashes and CO_2 from a nearby combustion power plant (or any other source) is dependent on a number of uncertainties that can be addressed as the main scientific and technical goals:

- *Influence of the specific mine lake water on the treatment reaction*

  Water from mining lake Burghammer is characterized by high concentrations of calcium, magnesium and sulphate, a low pH, an electrical conductivity of 2300 µS/cm, total iron of around 0.2 mmol/L and an acidity of around 2-3 mmol/L. In comparison to formation waters from oil fields, the dissolved organic carbon is rather low (around 3 mg/L) resulting in a less pronounced effect of the organic acids on the acid-base system of the waters. The key parameters for the stipulation of any reaction are the activities of the involved species and the rates of the reaction. A sufficient knowledge of the occurring processes will lead to a numerical model that can simulate laboratory experiments. It is one mayor goal to set up such a model.

- *Influence of the ambient conditions on the treatment reaction*

  Carbonate precipitation is strongly dependent on gas pressures and temperature. Depending on the water column that is to be considered for the location of the reaction and the CO_2 fluxes that will be used, partial gas pressures and total pressure may vary. Seasonal temperature variations must be considered as well. The laboratory experiments must adapt to these conditions.

- *Influence of the technical layout of the bench and pilot scale experiments.*

  Transport phenomena in the subsurface compartments will start to be of major importance entering bench and pilot scale experiments. The simulation model then needs to be multidimensional and be supplied with suitable transport parameters. The relevant compartments are the surface water (lake), the sediment and the groundwater.

Scientific and Technological Standard of Knowledge

To our knowledge, CO_2 and CaO have never been used to treat acidic mine water before, though CaO-rich fly ashes are commonly used to increase the pH of acidic mine water (e.g. Hellier 1998, Wisotzky 2001, Zoumis et al. 2000). An intensive literature review using the relevant literature databases (GEOREF, GEOBASE, FIZ-GEOL, FIZ-BERG, and ISI-Thomson) proved that there is no work using those two compounds actively for the treatment of acidic waters. Yet, there were several investigations studying CO_2-sequestration by the use of CaO, MgO and CO_2 in different environments and CO_2 sorption on different materials, there under metal dotted CaO (e.g. Elfving et al. 1996; Anthony et al. 2000; Reddy and Smirniotis 2004).

The carbonate system in natural waters is a complex phenomenon that involves the transfer among three phases: solid, liquid and gas. CO_2(g) dissolves in water to form loosely hydrated CO_2(aq). Only a small part of it is forming carbonic acid H_2CO_3. The dissolved species of inorganic carbon and water are produced by hydrolysis (exclusion of H^+ from hydration sheaths) of carbonic acid to form bicarbonate HCO_3^- and carbonate CO_3^{2-}. Calcite

$CaCO_3$ (s) is formed by calcium and carbonate. The number of unknowns rules the number of equations that have to be solved to describe the equilibrium of this system. As these reactions are simultaneously occurring with the speciation of the other dissolved species in a natural water, geochemical models are inevitable in predicting the effects of stipulated reactions. To the problem of »aquatic speciation« different theoretical concepts and computational strategies can be applied. Theoretical fundaments are described by Nordstrom and Munoz (1987), Stumm and Morgan (1996) or Bethke (1996) among others. Reardon (1994) gives an example of the a priory indeterminate effects of the increase in pCO_2 on the carbonate system:

Assume we have water at equilibrium with calcite at a specified pCO_2. What will happen to the pH, CO_3^{2-}, HCO_3-, H_2CO_3* and Ca^{2+} concentrations if the carbon dioxide pressure in the gas phase of the container is suddenly increased? Starting at the point in the reaction scheme where the perturbation occurs, if the pCO_2 is increased, then most definitely some H_2CO_3* will form. In other words, the effect of increasing pCO_2 will be offset by the dissolution of some of this carbon dioxide into the water phase. This increase in H_2CO_3* will result in some of it dissociating to form H^+ and HCO_3^-. Thus it can be concluded that the pH will decrease and HCO_3^- will increase as a result of an increase in PCO_2. Now what will happen to Ca^{2+} and CO_3^{2-}? To determine this, the direction in which the following reaction will proceed must be determined:
$HCO_3^- \longrightarrow CO_3^{2-} + H^+$. It has been determined that HCO_3^- will increase and pH will decrease (i.e., H^+ increase), what will happen to the CO_3^{2-} concentration? At this point, it cannot be concluded which way the above reaction will proceed. If only the pH decreased as a result of the increase in pCO_2, then the reaction would proceed to the left and CO_3^{2-} would decrease; and if only HCO_3^- increased as a result of the increase in pCO_2 then the above reaction would proceed to the right and CO_3^{2-} would be increased.

For example, the dissolution of calcite can be expressed with CO_2(g) by two overall reactions:

$$\mathbf{CO_2\,(g)} + H_2O\,(l) + CaCO_3\,(s) \longrightarrow Ca^{2+} + 2HCO_3^- \quad \text{(eq. 4)}$$

or

$$2H^+ + CaCO_3\,(g) \longrightarrow Ca^{2+} + \mathbf{CO_2\,(g)} + H_2O\,(l) \quad \text{(eq. 5)}$$

If Le Chatelier's principle is applied to the above two reactions to discern the effect of an increase in pCO_2 on the solubility of calcite, different conclusions would be drawn depending upon which reaction is selected. This merely reflects the indeterminacy of a change in pCO_2 on the solubility of calcite without knowing the chemical composition of the water.

This again underlines the need of geochemical modelling in describing carbonate species in a natural water. Knowing the composition of mining lake Burghammer and considering the fact that both CO_2 and CaO (H^+ decrease) are to be used, it can be concluded that the precipitation of calcite is the thermodynamically favoured reaction.

The following solution composition was analyzed in the epilimnion of lake Burghammer in 2004: pH 3.1, Na 3 mmol/L, Mg 2.5 mmol/L, K 0.5 mmol/L, Ca 9 mmol/L, C 0.2 mmol/L, S(6) 14 mmol/L, Fe 0.2 mmol/L, Cl 2.0 mmol/L.

A stepwise simulation of the equilibrium processes that might occur was performed using PHREEQC2.7. In the first step CaO and CO_2 was dissolved into the water and calcite was allowed to precipitate. CO_2 was introduced by assigning a partial pressure of 2 bar, assuming a treatment in 10 m depth and the use of a pure gas. In the second step this water was equilibrated with atmospheric CO_2 partial pressures to approximate the degassing of CO_2 from the treated water into the atmosphere (Tab. 1).

This rough calculation shows that calcite may precipitate in the same magnitude as CaO is dissolved in the water. The main influence of the partial pressure of CO_2 is the control of pH.

Tab 1: Results of PHREEQC modelling with CO_2 partial pressure of atmospheric partial pressure.

Step	CaO input mmol/L	pCO_2 bar	CO_2 flux mmol/L	Calcite precip. mmol/L	Ca in solution mmol/L	C in solution mmol/L	pH in solution –
0	0	0.006	–	–	9	0.2	3.1
1	1000	2	1078	988	21	90	5.8
2	0	0.0004	-78	12	9.5	0.4	7.8

Tab 2: Results of PHREEQC modelling with CO_2 partial pressure at 0.1 bar.

Step	CaO input mmol/L	pCO_2 bar	CO_2 flux mmol/L	Calcite precip. mmol/L	Ca in solution mmol/L	C in solution mmol/L	pH in solution –
0	0	0.006	–	–	9	0.2	3.1
1	1000	0.1	1006	997	12.5	10	6.5
2	0	0.0004	-6	3	9.5	0.4	7.8

Low pH favours CaO to dissolve, but hinders Calcite to precipitate and CO_2 to dissolve. A second calculation was performed with a pCO_2 of 0.1 bar (Tab. 2). Best results seem to be possible if CO_2 supply is controlled depending on the dissolution of CaO and the pH. The higher the pH will be in step 1 (the lower the partial pressures of CO_2 will be) the less CO_2 degasses unused into the atmosphere after the water equilibrates with atmospheric gases. In these calculation examples the unused fraction of CO_2 ranges from 0.6 to 7 %. Gypsum saturation was not exceeded in these examples.

The control of the mass fluxes during the reaction is a key task to optimize the efficiency of CO_2 turnover into calcite. Furthermore, biological activity is closely linked to the carbonate system. Primary production and respiration transfer carbon to and from its inorganic form into the organic form. Primary production in acidic lakes is very limited. Büttchner und Uhlmann (2004) calculated for the acidic lake 117 (Grünewalder Lauch) a carbon production rate of 78 g C m^{-2} a^{-1}. Lessmann und Nixdorf (2002) have concluded from their investigation of acidic mining lakes that inorganic carbon is a limiting factor for the primary production in these lakes. Biological activity in the lake will increase after neutralization. The uptake of CO_2 by algae will thus increase as well. Natural neutral lakes produce organic material in the order of 100 to 200 g C m^{-2} a^{-1}. This carbon flux is some orders of magnitude smaller than the carbon fluxes that will be introduced by the proposed technique. At this rate no effect on the technical CO_2 flux and the calcite precipitation is expected to be visible. The effects of the CO_2 injection on biological primary production have to be monitored and quantified, yet no negative effect for the environment or the technical process is expected at this point.

Naturally occurring precipitation of calcite in lakes is a widely recognized process. It is often reported to take place as a consequence of increased primary production due to a high nutrient import and subsequent rise of pH (Klapper 1992). The precipitate can be described as a calcareous mud. During the process of precipitation very fine grains are suspended in the water creating a white bleary that is able to eliminate other dissolved constituents from the water by co-precipitation and adsorption. The re-suspension of autochthonous calcite and the dumping of external calcite on the lake surface has been proposed to eliminate nutrients from eutrophicated lakes (Hupfer et al. 2000). These investigations show that the precipitation of calcite creates positive effects for the aquatic environment and that the precipitate is rather inert concerning the ability to re-dissolve into the water.

Description of planned work

Both problems, AMD forming and carbon dioxide emissions occur in areas where lignite mines and power plants are established. Thus, the major idea of this proposal is to solve the problems simultaneously. Since the deficit of mined coal forms open pits with lakes, that are often characterized by low pH and high sulphate concentration mainly stemming from the oxidized waste pile rocks, these water reservoirs are typical brown coal mining remains. If suspended calcium oxide (CaO), calcium-silicate, or iron hydroxide [$Fe(OH)_3(s)$] and CO_2 is added to a lake the CO_3 in the calcite ($CaCO_3$) or siderite ($FeCO_3$) will be formed from the gaseous carbon dioxide (CO_2). Thus, this is a true sustainable solution to decrease the amount of carbon dioxide emission. In particular, CaO, silicates and iron hydroxides are commonly available in waste rock piles and open pit lakes in huge amounts since ash and iron hydroxide sludge were often deposited. In combination with CO_2 from the flue gases, calcite and siderite can be precipitated in the lake resulting in a sustainable deposit of CO_2 in the subsurface and increasing pH and water quality of open pit lakes simultaneously.

Mining lake Burghammer is located 5 km east of the city of Hoyerswerda in Sachsen (Saxony). It is part of the river Spree catchment area. The mining lakes Dreiweibern, Lohsa II and Burghammer are planned to be operated as one storage pond system. The outflow out of this system will discharge from lake Burghammer into the river Kleine Spree which is a tributary to the river Spree. Today the lake is 59% filled at a water level of 104 mNN. Its final water volume will be 36 x 106 m3. During the 1970ies fly ash from the Schwarze Pumpe combustion power plant has been dumped in the abandoned surface mine. During the years 2000 to 2002 a re-suspension of the dumped ashes was tested and demonstrated. An excavator on a floating platform was equipped with a suction tube and a rinsing device to suspend and dissolve sedimented ashes in the lake water. It was shown that this action was successful in neutralizing the acidic lake water. Furthermore, it was shown, that no buffer capacity could be built up in the water by this action. It was decided to postpone a further operation of the suction excavator until lake Burghammer will start to discharge water into public streams (river Kleine Spree) and to keep an instrument of controlling the effluent pH.

In the first phase of the project the feasibility of that concept will be investigated. The second phase of the proposed research project should pick up the threads of the above described re-suspension technology and combine it with the CO_2 carbonate storage technology.

The research work which will be assisted by LUG, a locally experienced consultant company, will be subdivided in two parts: part 1 will be a detailed feasibility study lasting one year. The goal of part 1 is to evaluate the general procedure investigating the thermodynamics and kinetics of the governing processes by means of laboratory experiments. If part 1 is completed successfully, part 2 will focus on the optimization of the procedure and the implementation of a pilot plant.

Thermodynamics and kinetic reaction rates of calcium oxide (CaO), calcium silicate, and iron hydroxide will be determined in laboratory experiments using natural acid lake water and synthetic flue gases with varying CO_2 concentrations between 5 and 95 vol. %. Grain size of CaO and age of iron hydroxide will be varying in the experiments to evaluate the range of reactivity.

To be more realistic, sediments from several lakes in the Lausitz lignite mining area will be sampled from boat or by scuba diving. The amount of CaO, iron hydroxide and other components will be investigated by means of mineralogical and geochemical methods. The sediments sampled will then be used instead of pure CaO and iron hydroxide for further laboratory experiments with CO_2 injections. Besides the formation of calcite and siderite, the possible liberation of trace elements (metals, PAH) will be investigated as well as coatings on the CaO that may create certain passivity and decrease the theoretical reaction rates.

Laboratory experiments will be evaluated by means of geochemical modelling using the numerical code PHREEQC. Thermodynamic data and in particular kinetic reactions rates will be derived from the laboratory experiments in order to enable meaningful prognosis for modelling pilot scale and large scale treatment plants.

With respect to practical application, the amount of CO_2 in flue gases within the Lausitz will be determined. Furthermore, the amount of deposited ash and fly ash and their chemical composition with respect to CaO, Ca silicate, and iron hydroxide as well as trace elements and PAH will be evaluated from existing data. A comparison of distinct sites for the establishment of a pilot plant will be done and a preliminary study about engineering aspects of CO_2 elimination in the area of interest will be performed in order to evaluate the overall performance of the method and acceptance by shareholders. This includes the evaluation of different suspension and CO_2 injection techniques, however, only by means of theoretical considerations and calculations in conjunction with the partner DGFZ.

The second part deals with the optimization of the procedure and investigations in the lake in order to find suitable sites for a pilot plant. Those results will be an input for the necessary permits that will be compiled by DGFZ. Further laboratory and in lake experiments in the second and third year will investigate the CO_2 gas dissolution behaviour with respect to the total pressure, which is a function of water depths and the partial pressure. According to average water depths in open pit lakes, the total pressure will be varied between 1 and 4 bar. Dissolution of carbon dioxide will vary not only with partial pressure and with total pressure but as well temperature and bubble size. Thus, by varying these parameters, optimal boundary conditions will be found. Because formation of carbonate is in particular a matter of pH, this is a master variable controlling the overall performance of the treatment together with the reactions rates. Reaction rates are depending on reactive surfaces. Thus, the surface of the carbon oxide and iron hydroxide available in the open pit lake might be a limiting factor. Investigations will thus focus on this item and simple methods and techniques will be developed to enlarge the surface of the buried carbon oxide and iron hydroxides.

Different redistribution and injections techniques will be tested and evaluated in close cooperation with the DGFZ and the industry partners and based on an already existing fly ash suspension facility. Design and construction of a pilot plant itself will be done within the second CDEAL project (by DGFZ). Laboratory and field experiments will be evaluated by means of geochemical modelling using the numerical code PHREEQC, PHAST (3d reactive transport code) and MODGLUE (a pit lake model). Thermodynamic data and in particular kinetic reaction rates will be evaluated in order to enable meaningful modelling of real world problems taking into account all relevant boundary conditions.

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Recycling of sequestrated CO_2 by microbial – biogeochemical transformation in the deep subsurface (RECOBIO)

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1 Intentions and Overall Objectives

The green house gas concentration in the atmosphere is constantly increasing. To dam that dangerous development, means like efficient energy use and green house gas avoiding energy production are to be taken. The worldwide increasing energy demand, which will be mainly covered by fossil resources, calls for novel ideas for CO_2 removal from the atmosphere by sequestration into the deep subsurface. CO_2 transformation within the storage units by either mineral or microbial reactions could considerably improve sustainability of sequestrations concepts. The overall objective of the joint research project is to study the impact of sequestrated CO_2 on the microbial biocenosis of relevant deep geological formations. Main focus is on the autothrophic methane formation, which provides the possibility of CO_2 recycling to CH_4 as a »fossil« energy resource. Furthermore, other biogeochemical processes, which either stimulate methanogenesis (e.g. hydrogen formation by water reduction at mineral surfaces) or yield a net CO_2 reduction by itself (e.g. autotrophic sulphate reduction and mineral trapping in carbonates) will be investigated.

2 Project structure – Scientific subgoals

The network of project partners is conceived as close collaboration and is divided into three subprojects:

- »Laboratorial investigation of biogeochemical CO_2-transformation including molecular-genetic methods« (TU BA Freiberg)
- »Microbiology and microbial processes of CO_2-Transformation in deep subsurface« (G.E.O.S. Freiberg)
- »Impact of mineral reactions on the microbial-biogeochemical transformation of sequestrated CO_2« (DGFZ Dresden)

The fundamental importance of CO_2 for microbial reduction in reduced subsurface environments is caused by the lack of other electron acceptors / C-sources.
Considering the microbial formation of methane under consumption of CO_2, the »autothropic pathway« and »acetogenic pathway« need to be distinguished. It has been identified that the injection of CO_2 should mainly advance the formation of methane via these two pathways for a variety of formation water types. According thermodynamic – biogeochemical modelling investigations were conducted by ONSTOTT [2003], which is part of the US-research program

»CO_2 Capture Project« (see KERR [2003]). With this background, the CO_2 fixation via methanogenesis/ acetogenesis is one of the 8 »Top Goals« of the US Department of Energy considering novel innovative CO_2-Sequestration concepts (DOE [2004]). Therefore, availability of H2 as electron donator is of primary importance.

The following items outline the fundamentals of the joint research project:

Main questions

- Which significant reservoir formations can prove suitability for bio-geochemical conversion of CO_2 by means of realistic laborative experiments? Which transformation rates are achievable? What is the role of microbial formation of methane?

Associated Subquestions

- Which bio-geochemical material cycles are accompanied by a transformation?
- Which transformation are occurring under differing geochemical conditions?
- How are the autochthonous microorganisms affected by the CO_2-injection?
- Which abiogenic CO_2 induced H2-supply processes are relevant?
- Is H2 co-injection relevant regarding cost-efficient technical measures such as scrap material conditioning?

Investigations will be conducted with materials and fluid samples of the following sites:

- Oilfield reservoir »Gifhorner Trog«,
- Gasfield »Hannover/ Nienburg«,

The sites have been chosen in accordance with Gaz de France Germany (GdF-PEG), the practical partner of the project. GdF-PEG operates the itemised locations. Main focus is placed on the corresponding aquifer structures.

Figure 1 presents the workflow and the organisation of the different work packages within the entire project. As shown on the left, scientific monitoring and advice will be guaranteed by Gaz de France - Production Exploration Germany GmbH (GdF-PEG), Lingen, (former Preussag Energie) and the BGR Berlin.

The workpackages are based on the main questions of the project as explained above:

WP 1 - Selection of appropriate locations

- Interpretation of data supplied by GdF-PEG for the locations (mineralogy/ geochemistry, microbiology and fluid chemistry) fi Pre-selection of sampling locations. (TUBAF)
- Microbial sampling of fluids at the specified locations. (G.E.O.S./ TUBAF).
- Investigations of the autochthonic, microbial biocenosis at the selected locations (culture methods and molecular-genetic, culture independent methods). (G.E.O.S./ TUBAF)

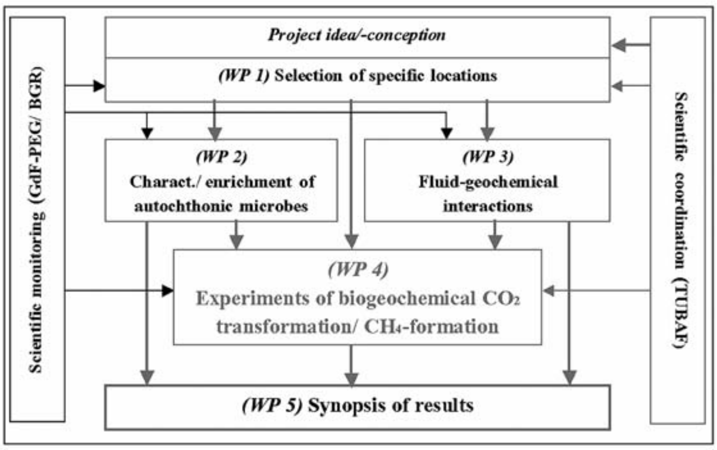

Figure 1: Project structure/-course – Workflow of the different workpackages (WP

- Investigations to the fluid-geochemical interactions in the CO_2 (supercritical) – rock system at representative cores (DGFZ)

Output WP 1 → Determination of 2 promising locations for detailed investigations (*by all partners*)

WP 2 Characterisation and enrichment of the autochthonous, microbial biocenosis

- Detailed microbial investigations of the selected 2 locations (culture methods and molecular-genetic methods). (G.E.O.S./ TUBAF)
- Cultivation/ Enrichment of the autochthonic, microbial biocenosis, supply for experiments in WP 4 (G.E.O.S.)
- Investigation of the impact of CO_2-injection on the microbial biocenosis – characteristically boundary conditions, limiting factors (G.E.O.S.)
- Microbiological monitoring of the main experiments (WP4) (G.E.O.S.)
- Summarising the results (G.E.O.S./ TUBAF)

Output WP 2 → Comprehension of composition/ metabolic pathways/ impact of microbial biocenosis at selected locations. The cultivated microbes are fundamental for the main experiments (WP 4).

WP 3 Fluid-geochemical Interactions (DGFZ)

- Detailed investigation to the fluid-geochemical interactions in the CO_2 (supercritical) – rock system at representative cores of the 2 selected locations (CO_2-extraction unit).
- Impact of CO_2-injection and induced rock interactions on the resulting conditions in the fluid.
- Investigations of the abiogenic/ biogenic H2-supply by CO_2-induced interactions (Silcate weathering, Fe-mineral reactions, formation of clay minerals).
- Fluid-geochemical monitoring of the main experiments of WP4.

Output WP 3 → The results of the CO2-induced impact on the fluid and on H2-supply are a major background for the main experiments of WP 4.

WP 4 Experiments of biogeochemical CO_2 Transformation (Main Experiments) (TUBAF)

- Conduction of preliminary experiments qualifying the laborative equipment & experimental setup/ testing of the measurement system, coupled with the problem of biogenic formation of methane in the system CO_2 (supercritical)/ scrap metal-Fe(0)/ formation water/ halophilic methanogenes.
- Testing of H_2-supply by scrap metal-conditioning.
- The main experiments will be conducted by a three level concept:
  Stage 1 → CO_2- and H_2 co-injection.
  Stage 2 → CO_2-injection taking into account results of WP3 (abiogenic H_2-supply).
  Stage 3 → CO_2 injection taking into account results of WP 2 (microbial limiting factors) and »on-sight H_2-supply« (scrap metal-conditioning, effluents from syngas production).

Output WP 4 fi The experimental results are the essential answer of the main question of the joint research project.

WP 5 Scientific project coordination– synopsis of results

- Coordinating, monitoring the project course by means of the results.
- Concluding the partial results in terms of overall objective of the joint-research project.
- Representation of the project and its partners in relation to the public.

Output WP 5 → Summing-up of the major results of all partners.

3 State of the art in the field of research

3.1 Geological sequestration

Since the early 90's, the idea of sequestrating CO_2 in geologic formations has gained considerable importance. There are four basic concepts (e.g. HITCHON [1996], BENSON ET AL. [2000]):

a)Hydrodynamic trapping: CO_2 is trapped as gas or supercritical fluid in depleted gas reservoirs.

b) Solubility trapping: CO_2 is dissolved in a fluid phase and used for enhanced oil recovery (EOR).

c) Coal bed methane: CO_2 is adsorbed onto coal and thereby methane is desorbed and produced.

d) Mineral trapping: CO2 is trapped in deep brine formations with carbonate mineral formation (driven by silicate dissolution).

The rapid progress in geologic sequestration is illustrated by several ongoing projects. STATOIL operates the well known Sleipner Vest site, where CO_2 has been injected in a brine formation since 1997 (e.g. KONGSJORDEN ET AL. [1997], GALE ET AL. [2001]).

In the US research activity on Enhanced Oil Recovery (EOR) has been increased since 2000 (compilation in KERR [2003]). In Germany the methodology of tertiary recovery was investigated in DGMK/ BMFT projects within the years 1978 to 1988 (DGMK 202-4/1 to 4/4). Investigations focused on detailed theoretical and lab work (KESSEL ET AL. [1989]). Due to cost intensive CO_2 supply, the methodology has not been applied in Germany so far.

Coal bed methane projects were conducted in the US (San Juan Basin, New Mexico), Canada (Alberta Basin) and Europe (TNO co-ordinated EU project »RECOPOL« in Silesian Coal Basin, Poland).

Since 2003, in the project CO_2SINK at the Ketzin test site (Germany) a brine sandstone aquifer underlying a former gas reservoir is used as an in-situ laboratory. The Development of injection technologies, monitoring systems and risk assessment concepts are in focus. The network partner G.E.O.S. Freiberg is involved in this project.

One of the eight top-goals of the novel CO_2-sequestration concept of the US Department of Energy (DOE [2004]) is the use of non-phototrophic CO_2 fixation via methanogenesis/ acetogenesis, which is the objective of our project as well.

Transformation of CO_2 to CH_4 requires large reaction areas, long time scales and the avoidance of leakage to the atmosphere. All these demands are met in the deep subsurface. Therefore, the use of subsurface technologies is favourable compared to surface technologies.

3.2 Potential CO_2 sequestration reservoirs in Germany

Deep saline aquifers and depleted oil and gas fields represent the major potential for underground storage of CO_2. A first overview on the distribution of such reservoirs and their potential in Germany was published by MAY ET AL. [2003]. General compilations of reservoir distribution and properties are given e.g. by BOIGK [1981], DIENER ET AL. [1984], HOTH ET AL. [1997], ROCKEL ET AL. [1997], BANDLOWA [1998], KARNIN ET AL. [1998]. Figure 2 shows the general locations of the major sedimentary basins with deep saline reservoirs in Germany.

The stratigraphic levels of major reservoirs and cap rocks are marked in Figure 3. The majority of the aquifers and reservoirs are formed by sandstones. The large scatter of their reservoir properties is mainly caused by differences in sedimentary facies, burial history and maximum p-T conditions. With respect to petrology it is important to distinguished three major groups for our project:

- feldspar, carbonate, and clay-rich sandstones
- Fe-mineral rich sandstones
- sandstones with a high amount of organic material

Neighbouring rocks of the sandstone reservoirs are mainly shales, siltstones, and marlstones with different concentrations of organic material and in special regions and stratigraphic sections also coals. With respect to hydrocarbon production Rotliegend sandstones are the

Figure 2: Main German sedimentary basins with deep aquifers / reservoirs (after BGR [2004])

most important intervals, followed by Carboniferous-, Jurassic-, and Cretaceous sections.

Important carbonate reservoirs are located within the Zechstein (Northern Germany) and the Upper Jurassic (Northern Alpine Molasse Basin).

The formation water chemistry can be characterised by the following general facts:

- most of the formation waters are high saline (Fig. 4), a major exception is the Northern Alpine Molasse Basin, where fresh and low salinity water occur in deep aquifers of Tertiary and Jurassic age.
- with increasing depth, formation waters are characterised by a more and more reducing environment and high levels of dissolved iron and other metals.
- within clastic reservoirs ph-values are decreasing with depth.
- the sulphate content is generally decreasing with increasing depth too, but shows significant higher values within the Zechstein and in areas close to salt diapers.
- some of the waters are characterised by NH_4^+-concentrations up to 3000 ppm.

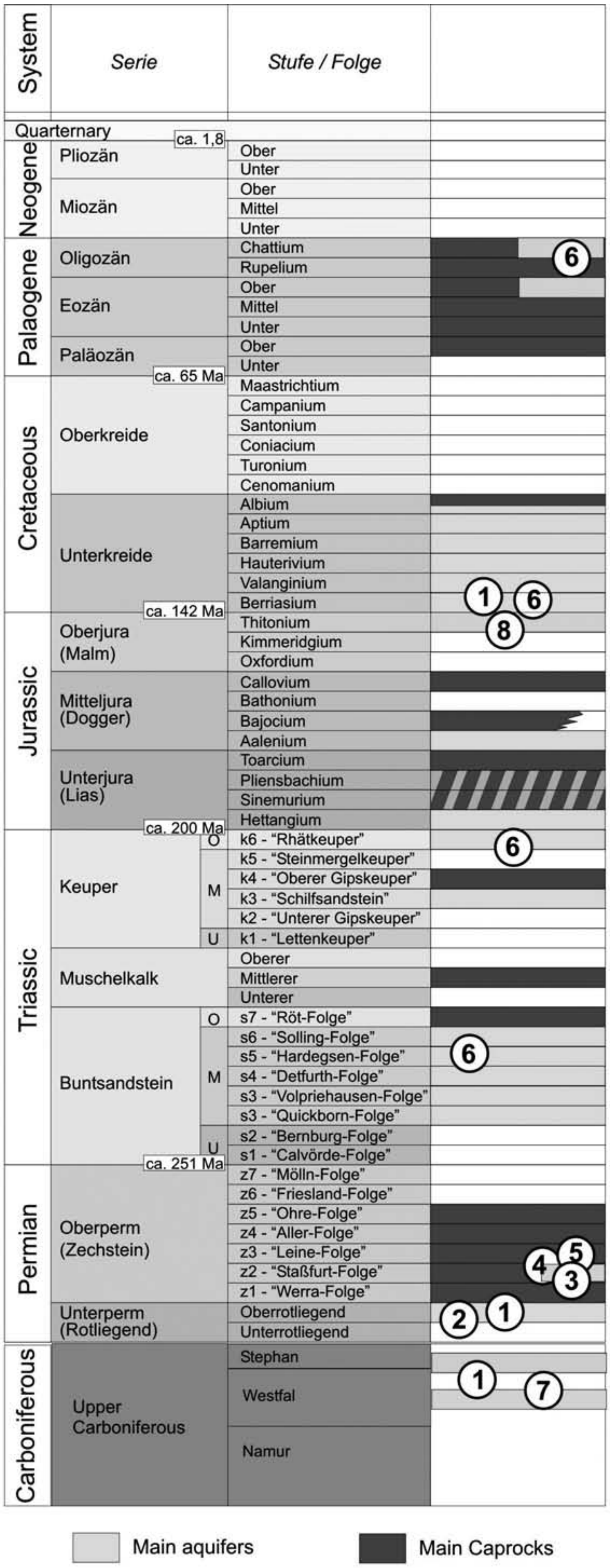

Figure 3: Stratigraphic overview including the most important aquifer and cap rock sequences in the North German Basin (BGR [2004] – modified)

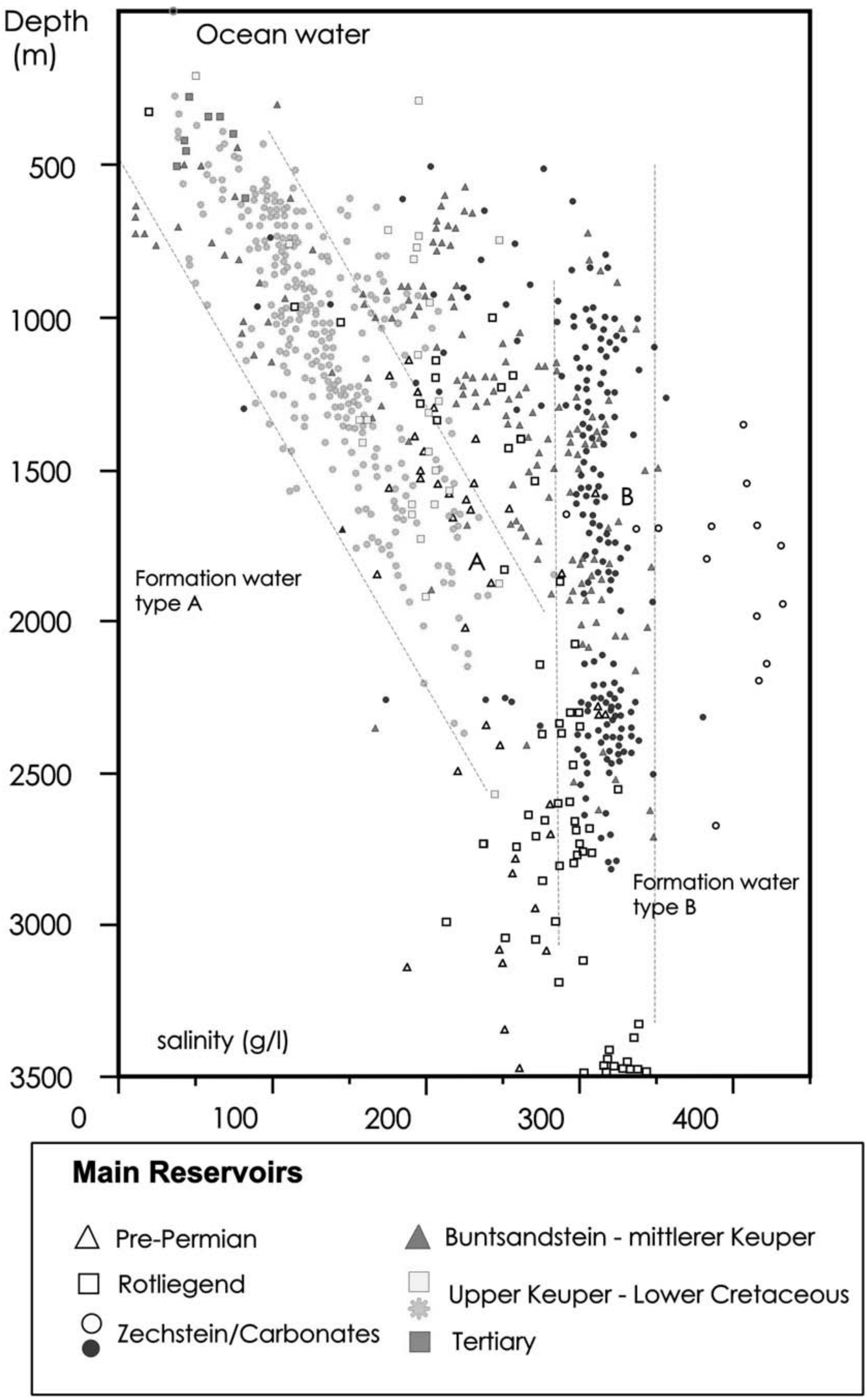

Figure 4: Salinity of the main reservoirs of North German Basin (from ROCKEL ET AL. [1997])

3.3 Methanogenesis and other biogeochemical metabolisms

The fundamental importance of CO_2 for microbial reduction in reduced subsurface environments is caused by the lack of other electron acceptors. Equation 1 (eq. 1) shows the objective process of CO_2-reduction to CH_4 according to the autotrophic pathway.

$$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O \quad \Delta G° = -32{,}4\ \text{kcal} \quad \text{(eq. 1)}$$

Furthermore methane formation can take place by heterotrophic metabolism, like acetotrophic resp. methylotrophic pathway (e.g. BARNS & NIERZWICKI-BAUER [1997], WHITICAR [1999]). A simplified overall equation for the acetotrophic pathway is expressed by eq.2.

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad \Delta G° = -31{,}0\ \text{kcal} \quad \text{(eq. 2)}$$

As indicated by DG0-values the autotrophic pathway is thermo-dynamically favoured under standard conditions compared to the acetate consuming methanogenesis.

Synthrophic effects between autotrophic methanogenes and fermentative anaerobes are expected at fermentation with H2-production (hydrogenic pathway) according (eq. 3). CO_2 would thereby only be net reduced at incomplete fermentation.

$$(CH_2O)_n + n\ H_2O \rightarrow n\ CO_2 + 2n\ H_2 \quad \text{(eq. 3)}$$

The hydrogenic pathway of fermentation may facilitate the autotrophic methanogenes, cause the acetogenic pathway of fermentation may pose synthrophic effects for acetate consuming methanogenes. HOEHLER ET AL. [1999] describe the almost exclusive use of CO_2 by acetogenic fermentative anaerobes for anoxic marine sediments (eq. 4).

$$4\ H_2 + 2\ CO_2 \rightarrow CH_3COOH + 2\ H_2O \quad \text{(eq. 4)}$$

Combination of CO_2 consuming acetogenic fermentation (eq. 4) and acetate consuming methanogenesis (eq. 2) yields with net equation (eq. 1) a second pathway of net CO_2-transformation to methane.

The importance of CO_2-reduction to Methane by CO_2-injection was underlined through the thermodynamic - biogeochemical modelling of ONSTOTT [2003]. The modelling focused on the definition of the energetic most relevant microbial redox reactions for CO_2-injection in various geological formations. ONSTOTT suggests that methanogenesis and acetogenesis are the most favoured biogeochemical processes.

KOTELNIKOVA [2002] summarised by comprehensive literature review and own research the activity of methanogenes of domain Archaea in various deep geological environments by microbiological and isotope-geochemical means. She also pointed out, that molecular hydrogen has been found in a variety of subsurface environments, facilitating chemolithoautotrophic reactions like those of equation (1) and (4). STEVENS & MC KINLEY [1995] showed an active, lithoautotrophic system of methane formation in deep basaltic aquifers of Columbia. Outside of Europe the first considerations of relevant sites for bio-conversion of CO_2 were undertaken by SCHOELL ET AL. [2001]. They showed intensive CO_2-reduction within the San Juan Basin. Furthermore they found a similar subsurface bioconversion process in the Michigan basin which is related to freshwater influx. They conclude that these sites contain bacterial consortia which are able to convert man-made greenhouse gases. The deep subsurface methanogenesis of sequestrated CO_2 was also discussed by KOIDE & YAMAZAKI [2001]. For Japanese sites they discuss the relation between impermeability of the seals and the biogenic conversion of the sequestrated CO_2. They postulate, according to STEVENS & MC KINLEY [1995], the weathering of Fe(II)-silicates as the main source of H2-supply in basaltic aquifers. The evidence of methane formation in oil fields by methanogenic microbes was first shown by BELYAEV ET AL. [1983]. All strains isolated from this Russian oilfield were also capable of growth on CO_2. The kinetic isotope effects (KIE) of the performed experiments range between -32 to -35 ‰ and are lower than expected. SWEENY [2001] concludes that natural

gases (CH_4) from the gulf of mexico are the result of biogenic transformation of the oil phase. Furthermore he refers to analogies found in many contaminated ground water sites. Petroleum decomposition to CH_4 by means of methanogenic processes is well documented for such sites.
With respect to the microbial characterization of German oil fields we refer to the conducted DGMK-projects (345, 441-1, 441-2). BAK ET AL. [1990] identified H_2-consuming methanogenic and homoacetogenic microbes in an oil pipeline in the Hanover area (»Gifhorner Trog«). Thereby the decomposition of the produced acetate occurred by the methanogenic microbes and is related to methane formation. Both the microbial community and the abundance of H_2 determine the extent of the methane formation process. Due to microbial diversity, different physiological types of microbes occur in the subsurface. CO_2 reducing methanogens may compete with or benefit from acetate consuming methanogens, sulphate reducing (SRB) and iron reducing bacteria (FeRB) or fermentative anaerobes, for example.

The importance of SRB for the aquifer systems of German oil fields were demonstrated by CORD-RUWISCH, KLEINITZ & WIDDEL [1986], [1987] and further by KLEINITZ & BAK [1991]. Via isolation series with different organic substrates various types of SRB were present. *Desulfobacter* and an unknown benzoateutilising species were dominant (6*106 – 1*106 cells/ml). Furthermore a large number of lactate or H_2-utilising Desulfovibrio were isolated. Therefore it has to be considered that SRB are the main competitor to methane producing microbes.

After WHITICAR [1999] CO_2 and acetate belong to the competitive substrates, while methylated amines and dimethylsulphides are non-competitive substrates for methanogenic microbes. But the relevance of the last mentioned should be small. For this reason methane formation should take place primarily in locations with low sulphate content. The culture experiments on autotrophic CH_4-formation, performed by WHITICAR [1999] resulted in KIE less than -24‰ . Therefore by a given initial $^{13}C_{CO2}$ signature of close to 0 ‰ PDB a resulting $^{13}C_{CH4}$ signature of nearly -24‰ PDB is possible. Such a signature would match with the thermogenic formation in the classic theory (SCHOELL [1980]). Taking these low KIEs and the latest results for different geologic settings (e.g. POTTER ET AL. [2004]) the classical interpretation of $^{13}C_{CH4}$ signatures has to be discussed.

In addition to the competition of the methane producing microbes by SRB and FeRB also their potential benefit have to be noticed. The degradation products of both physiological types (H_2S und Fe^{2+}) form FeS. The transformation of FeS to FeS_2 by reaction with H_2S was first proved by laboratory experiments from DROBNER ET AL. [1990]. They postulated that microbial CO_2-fixation is coupled with H_2-formation by this reaction. KASCHKE ET AL. [1994] reviewed this H_2-supply process and were able to verify it for the reduction of Cyclo-hexan. It can be summarised that the sulphate- and iron reduction by complete consumption of these terminal electron accepting processes (TEAPs) can be understood as engine of the autotrophic methane formation process. This mechanism is the cornerstone of the theory of non-phototrophic origin of life (WÄCHTERSHÄUSER [1993], [1997]). This is closely related to the metabolism of the methanogenic Archea which are relevant for the project. The coupling between the microbial metabolisms and the carbonate precipitation has been discussed in detail by CASTANIER ET AL. [1999]. They point out that in strongly reduced systems with higher CO_2 – concentrations carbonate precipitation is predominantly related to the non-methylotrophic methanogenesis. Furthermore carbonatogenesis is neither restricted to specific taxonomic groups nor to specific environments.

3.4 H_2-supply and geochemical reactions

3.4.1 Relevant Processes for in-situ H_2-supply

Regarding chap. 2.3, it can be concluded that supply of H_2 is considered to be the most crucial factor for methanogenic conversion of sequestrated CO_2. This is valid for both the autotrophic as well as different heterotrophic pathways.

Although H_2-concentrations in the deep subsurface exceed by far those in surface aquatic environments, the H_2-content in subsurface fluids and the supply form juvenile geogas is small compared to the demand for autotrophic transformation of sequestrated CO_2. But the H_2-concentrations in the deep fluids represent only an »intermediate state« (LOVELY & GODWIN [1988], HOEHLER ET AL. [1998], KOTELNIKOVA [2002]) since H_2 is rapidly transformed. The relatively low H_2 concentrations do not imply low H2 supply rates. Nevertheless LOVELY & GODWIN [1988] and LOVLEY ET AL. [1994] showed that the concentration levels of dissolved H_2 are an indicator to determine the TEAPs in anoxic groundwater systems. CHAPELLE ET AL. [1996], [1997] summarise the results from several sites. According to them, areas with Fe(III)- or sulphate-reduction show a higher H2 affinity then areas with autotrophic methanogenesis. The H_2-content may vary for Fe(III) zones from 0,2 – 0,8 nmol / l, for SO_4 at TEAP from 1 to 4 nmol/l. Contrary to this, H_2-content in methanogenic areas may even reach 5 – 30 nmol / l.

The knowledge about abiotic H_2-sources in subsurface environments is relatively small. For the autotrophic pathway the main process is the reduction of water on mineral surfaces or via mineral transformation. The significance of the system FeS/FeS_2 was already discussed in sec. 3.3. The H_2-production by weathering of ferrous iron silicates is stated by STEVENS & MC KINLEY [1995] for a basaltic deep groundwater system in Columbia. In abiogenic experiments STEVENS & MC KINLEY [2000] provide evidence of olivine minerals as principal supplier. Rates increase with lower pH-values. H_2-production because of the serpentinisation is based on a partial Fe(0)-formation, which causes a reducing potential (RAMDOHR [1967]). NEAL & STANGER [1983] demonstrate the significance of this process for deep ground water systems too. Disproportionation of $Fe(OH)_2$ to Fe_3O_4 , the so called Schikorr reaction, is a second process for the supply of H_2 (e.g. REARDON [1995]). Further on the interaction of clay minerals with thin Corg-interbed layers is discussed in the literature as a potential H_2 supplying process. However, there have been no investigations regarding the impact of supercritical CO_2 yet. It can be supposed that process rates will be significantly increased. The investigation of abiogenic H_2 supply is therefore an important part of the project.

In terms of the different heterotrophic pathways the importance of symbiotic resp. synthrophic metabolisms of methanogens associated with acetogenic resp. fermentative microbes were pointed out in chap. 3.3. Another relevant metabolic syntrophy is the coupling of H_2- supply with nitrogen fixation. After MADIGAN ET AL. [2000] this syntrophy occurs under anaerobic conditions mostly by methanogenic Archea. Therefore the methane formation process is coupled with the transformation of $N_{2(g)}$ to $NH_{3(g)}$ / NH_4^+. This is of special interest in aquifer systems of gas fields, which show high $N_{2(g)}$ / NH_4^+ and CH_4-contents as well as low CO_2-concentrations.

3.4.2 Relevant processes for on site H_2-supply

The concept of H_2 supply by conditioning of CO_2 with scrap is based on the ability of Fe(0) to produce a potentially reducing environment. This ability is used in numerous successful applications of reactive barriers for the degradation of organic pollutants in groundwater. Laboratory tests show that highest corrosion rates occur while the partial pressure of CO_2 is increased (e.g. LOROWITZ ET AL. [1992]). GU ET AL.[1999] demonstrated, that corrosion rates increase when pH is lowered and acidic conditions are reached. Because of very rapid H_2-generation they had to interrupt their tests conducted under sterile, abiotic conditions. In contrast under non-sterile conditions H_2 concentrations declined due to microbial

consumption. After LOROWITZ ET AL. [1992] the corrosion rates increase further on because of biogenic corrosion. This results from the removal of the reaction product H_2 by the microbes, which is accelerating the process.
For this biogenic corrosion process, coupled with the degradation of organic groundwater pollutants, mainly methanogenic microbes play an important role (LOROWITZ ET AL. [1992], WEATHERS ET AL. [1997] NOVAK ET AL. [1998]). High methane formation rates are obtained from methanogenic cultures who are partly thermophilic.

As a second option the utilisation of effluents from the syngas production is considered for the onsight-H_2-supply. These gases have H_2 concentrations of up to 5 Vol%. During gasification of coal/ biomass the produced CO is shifted with water to H_2 and CO_2 (water-gas-shift) via HSD-process[3]. Hydrogen is then separated form the gas through a membrane. The remaining gas[4] still contains residual H_2-concentrations as mentioned above.

4 Cooperation with external partners

As mentioned in chap. 2 there will be cooperation with Gaz de France-PEG, represented by Dr. Kleinitz. He is the head of the research centre of Gaz de France Germany. The focus of the cooperation is on the surface sampling of formation fluids and on the scientific discussion to select appropriate locations by means of available data.
The cooperation with BGR Berlin will enable access to important geological data of Germany and hence, assist with it expertise for selection of appropriate sequestration locations.
A third external cooperation will be with the Department of Energy Process Engineering and Chemical Engineering of TU BAF. This institute provides expertise in the fields natural iron mineral catalysts/reaction carrier and effluents from syngas production. This research group is involved in a variety of projects i.e. in the field of large-scale CO_2-capture techniques. It is a leader group within the BMWA-research program »COORETEC« for low-emission fossil power plant techniques.
Together with this partner the project »RECO-BIO« will be involved in the new Energy Centre of Excellence »CO_2-FREIberg« at the Freiberg university. This network connects different research topics like CO_2 capture, efficient energy generation, efficient energy use in the industry and the sequestration of CO_2.
Furthermore we cooperate with the KU Energy Research Center (ERC) an umbrella organization of the universities of Kansas and the Geological Survey of Kansas for collaborative energy research. An investigation of samples from Kansas by molecular-genetic methods (outside the project) is planed. Many of the shallow gas reservoirs of Kansas are biogenic sourced, especially from coalbed methane production.

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Feasibility Study on the Potential of CO_2-Storage for Enhancing the Recovery Factor in Mature Gas Reservoirs (CSEGR)

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1 Objectives and Concept

The German government aims at a 40% reduction of CO_2 emissions until 2020, provided other European countries commit themselves to significant CO_2 reductions also (Nationales Klimaschutzprogramm 2005). Even though Germany has achieved a remarkable reduction of CO_2 emissions since 1990, a tendency of decreasing annual reduction increments is ob-served. Globally CO_2 emissions are even increasing. Thus, additional measures are needed to achieve the long-term reduction targets. In consideration of the geological conditions in Germany, May et al. (2003) have compared different options for the underground storage of CO_2. According to their qualitative ranking (including criteria like storage capacity, safety, geotechnical suitability, economics and energy balance), gas fields should be the prime choice for CO_2 storage in Germany.

More than 50% of the German gas reservoirs are already in a mature status and operators consider options for future use of the reservoirs. Mature fields offer the opportunity to en-hance residual gas production through CO_2 injection, to extend the production lifetime, and to increase their ultimate gas recovery (CSEGR = carbon storage and enhanced gas recovery, or CO_2-EGR). Finally, after CO_2 breakthrough, production wells could be shut-in and the reservoir could be further used for CO_2 storage. Depleted or mature gas reservoirs have proven their capability for long-term storage of natural gas. The capacity of gas storages in Germany has already reached a strategic 20% share of the annual consumption and a major further increase is not expected at present. Therefore the option of CO_2 storage is gaining interest by the oil and gas industry. CO_2-EGR is a theoretical concept still that has not been practiced yet. It could help to increase the national energy resources and security of supply and to reduce the costs of CO_2 storage in comparison to other options intending underground storage alone. Energy and emission balances could benefit from the production of additional natural gas that could substitute other fossil energy carriers with higher specific CO_2 emissions.

Key factors, to optimise gas recovery and efficient storage of CO_2 simultaneously, are the injection control and the retardation of CO_2 break-through by either separating the fluids in the carrier rock due to the differences in gravity between dense CO_2 and the lighter hydrocarbons, or by reducing the mobility of the CO_2 in layered reservoirs. The tectonic architecture of a gas reservoir and the facies type of reservoir rocks strongly influence CO_2-EGR performance. The feasibility of CSEGR will be studied under different geological conditions of German gas reservoirs. Two prototypes of reservoirs are in principle suited for this task:

- Heterogeneous, fine-scale structured, and anisotropic layered gas carrier rocks, in Rotliegend reservoirs, like those in the Altmark.
- Homogeneous, large-scale-structured, isotropic Bunter sandstone reservoirs.

This study shall investigate likely storage systems including producing gas reservoirs, regional CO_2 sources, and linking corridors of existing pipelines. The geological, technical and economical key parameters that could influence the optimisation of CSEGR will be investigated. Their sensitivity for the planning of future field tests in Germany will be defined.

2 Project consortium

The proposed interdisciplinary project covers civil engineering, geoscientific, environmental and economical subjects. The wide range of interrelated issues addressed requires the integration of scientific research, technical development, and project evaluation. The composition of the project consortium reflects this integration of expertise: two research institutes with expertise in geoscience and reservoir engineering, and industry partners with practical experience in the exploitation of natural gas reservoirs, gas treatment, transport and storage.

The experience in handling and treatment of flue gases is brought into the project by a major power producer leading international CO_2 separation and transport research projects. The project management will be taken by the Technical University Clausthal, represented through the Institute of Petroleum Engineering (ITE). A close co-operation with the other parties and moreover a co-ordinating function of the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) is intended. The industrial parties will work within the consortium using own resources. The interest of these industry partners to reduce the uncertainty in evaluating the future prospects of CO_2-EGR projects is documented by providing source data and geologic models from their assets. Their advice will contribute to the decision making process in the technical project development. Vattenfall AB investigates CO_2 separation and storage technology and will participate actively, providing information on flue gas separation, transport, safety, and cost issues for a case study in East Germany. Reservoir information will be evaluated, updated and provided by EEG. E.ON-Ruhrgas will contribute to the project providing relevant information on CO_2 transport. Wintershall AG will provide seismic and geological information and a numerical simulation model of the Barrien gas field.

Table 1

Participant	Seat	Function
Technische Universität Clausthal (TUC) – Erdgaslagerstättentechnik (ELT) – Erdgasversorgungstechnik (EGV) – Erdölgeologie (IfGP)	Clausthal-Zellerfeld	Project Manager
Bundesanstalt für Geowissenschaften und Rohstoffe (BGR)	Hannover	Project Co-ordinator
Vattenfall AB	Stockholm, Berlin, Cottbus	Industrial Partner
EEG-Erdöl Erdgas GmbH (EEG)	Berlin	Industrial Partner
E.ON-Ruhrgas	Essen	Industrial Partner
Wintershall AG	Kassel	Industrial Partner

2.1 Expertise of the project partners

2.1.1 Technical University Clausthal (TUC)

TUC is a traditional corporate University with a strong focus on industry related research and a competence concentration in petroleum sciences, represented by the chairs Petroleum Geology (Prof. Wolfgang Blendinger), Reservoir Engineering & Simulation (Prof. Guenter Pusch), Oil/Gas Recovery and Gas Supply (Dr. Kurt M. Reinicke).

The Department for Petroleum Geology at the Technical University of Clausthal is engaged in teaching of the multiple aspects of petroleum geology. Research is mainly focussed on reservoir sedimentology and characterization, 3D modelling of outcrop analogues for hydrocarbon reservoirs, and numerical simulation of oil and gas field models.

The Institute of Petroleum Engineering (ITE) at the Technical University of Clausthal is an independent research and industrial development, education, and training centre, active in the fields of oil, and natural gas. Its activities cover:

- Reservoir engineering, drilling, production, natural gas storage and transportation.
- Research and development at ITE aim at supporting the hydrocarbon industry by developing innovative technologies that will allow sustainable development. It is organised around two departments: Reservoir Engineering and Drilling-Production-Natural Gas Supply.

The work of these departments is based on advanced research, conducted alone or in partnership with the scientific, technical and industrial communities in Germany and abroad.

Reservoir Simulation is a traditional research area since more than 20 years with a focal point on using commercial software for solving complex rock process interaction problems. Initial experience started with a unique experimental database on enhanced recovery methods, as for example polymer, surfactant and CO_2 flooding in oil reservoirs. Recently the experimental expertise was extended to so-called tight gas formations (Rotliegend, sandstone and fractured crystalline rocks (Pusch et al., 2000). Within this time ten PhD theses in reservoir simulation were successfully completed.

2.1.2 Bundesanstalt für Geowissenschaften und Rohstoffe (BGR)

(BGR) is the central geoscientific and geotechnical institution to support the German federal government. She consults ministries, the EU, and German industry in all geo-relevant matters. BGR carries out projects of technical and scientific co-operation with developing countries and other European geological surveys. Among others, geotechnical security of (nuclear) waste deposits, research on energy resources, protection of resources and the geoenvironment, and geo-risk assessment are tasks of BGR.

BGR participates in major EU funded CO_2 storage R&D projects: GESTCO, NASCENT, CO_2-STORE, CASTOR, CO2GeoNet. The injection of CO_2 into the Altmark gas field Salzwedel-Peckensen and into the Rotliegend field Alfeld-Elze has been simulated with TOUGHII (Rebscher et al. 2004, May et al. 2004), Geochemical reactions have been studied with PHREEQC (May 2004). CO_2-water–rock interactions in natural analogues have been studied in various locations (e.g. May 2005, Pearce et al. 2005). Another focus of BGR's activities concerning CO_2 storage is safety and monitoring of storage sites.

2.1.3 Vattenfall AB

Vattenfall also runs and participates in several joint venture research development and demonstration programmes concerning CO_2 capture and storage. Vattenfall runs an internal project called the »CO_2 free power plant« over a five year period, with the goal to develop possibilities for a commercial technology for use of fossil fuels with an almost zero emissions, until 2015. As part of this Vattenfall has agreed to take the lead in the EU-sponsored projects ENCAP and to actively take part in CASTOR – projects that complement each other to develop technology for the capture and storage of carbon dioxide from fossilfuel combustion. Both involve many of Europe's major companies and R&D providers. ENCAP aims to develop CO_2 capture technologies that meet the target of at least a 90 % capture rate at a cost lower than 20 € / t of avoided CO_2 emissions. A 30 MW oxyfuel test facility is going to be built in Schwarze Pumpe.

2.1.4 EEG-Erdgas Erdöl GmbH (EEG)

The core area of EEG has been the exploration and production of natural gas and oil. The company's know-how on reservoir characterisation and evaluation which has a good reputation in the industry is marked by comprehensive experience gained in the development and operation of fields in the Eastern part of Germany, in Iraq and in the CIS. Since 1998 EEG has participated in the search for and production of oil and gas in several licenses (P and F blocks) in the Dutch North Sea. In its search for and exploration of gas and oil in Germany the company now focuses on a license area of more than ca. 3400 km^2. EEG has been establishing a new business area with the exploration and development of geological structures appropriate for underground gas storage and the construction of a pilot cavern in the Peckensen salt dome (western Altmark) which began in 1998. The company operates powerful combined heat and power plants. In the power plant of the Steinitz (Altmark), central station of EEG, low calorific gas is used for power generation. With its main German asset Altmark, EEG has an enormous experience in the development of depleted gas fields, including a detailed data base, geological and flow simulations, R&D, practical applications, etc., and is now focusing on EGR projects for the tail end production stage.

2.1.5 Wintershall AG

Wintershall is an international operating oil and gas producing company, operating fields in Germany, Netherlands, Libya and Russia. Other areas with working interests are in Argentina, Caspian area and Middle East. Experience with oil and gas production is available for more than 50 years. Special activities are on and offshore exploration, oil and gas production. In German oilfields enhanced oil recovery (EOR) activities are going on in the Emlichheim oilfield (steam-flooding). Finished EOR projects are steam-flooding in Ruehlertwist, polymer flooding in Bockstedt and caustic flooding in Dickel. In Rehden, Wintershall developed the largest German underground gas storage in a depleted gas reservoir. Underground storage operations are monitored and optimized with appropriate simulation tools. A laboratory for specialized investigations (chemistry, petrophysics and EOR) is located in Barnstorf.

2.1.6 E.ON-Ruhrgas

E.ON-Ruhrgas is the leading company of the German gas industry. E.ON-Ruhrgas stands for a diversified, long-term supply portfolio, proven ties with major gas producers, solid customer ties and substantial experience in gas marketing, a well-developed, efficient pipeline system with integrated underground gas storages in a central position and mid- and downstream shareholdings in Germany and abroad. E.ON-Ruhrgas is the market leader in Germany in gas transportation in terms of both volumes and peaks. E.ON-Ruhrgas and its Project companies operate one of the most efficient systems in Europe for gas transportation and storage. It was extended to 11233 km of pipelines in 2003 and comprises 12 underground gas storage facilities with a working gas capacity of 5.2 billion m^3. E.ON-Ruhrgas is extending the network in line with requirements, making use of all technological advances. Central objectives of its research and development programme focus on improving the competitive position of gas in its field of application and on opening up new market segments for gas. The operation and monitoring of E.ON-Ruhrgas's own pipeline system are also being optimised.

3 Present State of Knowledge

Commercial projects of CSEGR do not exist yet. Tests for CO_2 injection into the small depleted offshore gas field K12-B have begun in

May 2004 (Kreft & van der Meer 2005). The field is operated by Gaz de France. However, EGR presently is not considered to be economical in such small fields and thus, the pilot project is supported by the Dutch government.

CSEGR scenarios have been studied with conceptual (generic) simulations. The first numerical model considered the injection of CO_2 into a 5-layer dipping model, typical for condi-tions of Dutch gas reservoirs (van der Burgt et. al., 1992). Limited enhanced gas recovery effects were predicted due to early break-through of CO_2 to production wells. Another generic simulation study for the Californian Rio Vista gas field performed by the Lawrence Berkeley National Laboratory concluded that sufficient amounts of CO_2 can be injected to produce significant quantities of additional natural gas (Oldenburg et al. 2001). The simulations indicated little mixing of CO_2 and methane because of the large density and vis-cosity differences between the two gas components. However, reservoir heterogeneity accelerates the break-through of the CO_2 and limits the EGR yield. Oldenburg and Benson (2002) stated that the injection of CO_2 at relatively deep levels in a reservoir, while producing from higher levels, attenuates the rise of CO_2 and mixing with natural gas. In June 2005 the US Department of Energy has provided funds for injection tests into the Rio Vista gas field.

Marmora and Seo (2002) studied the displacement of CH_4 by CO_2 in core flooding experiments. Displacement was very efficient, paramount to hydrodynamic dispersion, giving recovery rates of 73 - 87 % at CO_2 break-through. Natural gas mixtures might give different results though. In another conceptional study, researchers from the United States Department of Energy and from the National Energy Technology Laboratory studied the effect of methane displacement by CO_2 in a thin rim reservoir with low permeability, congruent to tight gas formations in North Germany.
Jikich et. al. (2003) investigated the optimal time for starting CSEGR. They have shown that maximum recovery is possible, if the reservoir has been depleted to minimum reservoir pressure, whereas the injection of CO_2 at higher pressures has only the effect of production ac-celeration. Rebscher et al. (2004) have calculated CO_2 breakt-hrough times for CO_2 injection into a generic Altmark Rotliegend reservoir. A comparable study has been performed by Clemens und Wit (2001) based on models of typical Rotliegend reservoirs in The Netherlands.

An inter-comparison of numerical simulation codes for geologic disposal of CO_2 has been organised by the Lawrence Berkeley National Laboratory (Pruess et al. 2003). In 8 benchmark tests different codes have shown their ability to predict the phase behaviour and physical phase properties of CO_2-CH_4-brine-rock systems, chemical reactions of CO_2 with host rock minerals, combined diffusion and advective flow, and miscible displacement of oil by CO_2. Most of the process simulators yielded reasonable results for the complex coupled processes. However, no particular numerical simulator was able to address all problems with the same accuracy and reliability.

The impact of possible geochemical reactions in the reservoir and cap rocks of underground CO_2 storage is a major concern that is being recognised and addressed by geochemical experiments (e.g. Pearce et al., 2001), by numerical simulations (e.g. Johnson & Nitao 2003), and in special scientific symposia. CO_2 can change rock properties due to chemical and physical processes in the reservoir, and in the case of leakage in the overburden. These re-actions can either:

- enhance porosity due to mineral dissolution, which might increase the storage capacity within a reservoir or else increase the risk of leakage in cap rocks, or
- reduce porosity and permeability due to mineral precipitation which could result in long-term storage of CO_2 in the form of solid carbonates (in situ mineralization). But, precipitation also could reduce injecti-

vity and thus storage capacity. Alteration reactions may also be a mechanism of self-sealing for fractures in the cap rock.

Reactions caused by leakage of reservoir fluids or CO_2 into shallow fresh water aquifers may liberate unwanted elements from the rock matrix.

Usually batch reaction, reaction kinetic, reactive transport, or mass transfer approaches are used for predictive geochemical simulations. Reactive transport simulations require a range of necessary input information, usually not completely available for real geologic structures. Reaction kinetic constants are often rather uncertain for solid solutions of complex alumo-silicates and constants derived in lab experiments are often quite different from constants derived from natural analogue studies. Thus, simulations are often used for generic process modelling only. Parameter studies are essential for sensitivity studies and uncertainty assessments. The prediction of likely reactions will be very much site-specific and it has to take into account actual reservoir mineralogy and fluid composition. Thus, for the selected real, geologically complex reservoirs, the available information will be decisive for the selection of the most appropriate simulation strategy.

Several codes are suitable to model geochemical and physical CO_2-water-rock interactions in reservoirs. Transport codes that include geochemical reactions are e.g. CHEMTOUGH (Industrial Research Ltd.), TOUGHREACT (Lawrence Berkeley Na-tional Lab), or SHEMAT (RWTH-Aachen). More powerful geochemical codes restricting to simple transport models of dissolved species like PHREEQC (US Geological Survey) might be more appropriate to model reactions in the overburden, because at low leakage rates CO_2 can dissolve completely in hanging aquifers resulting in single phase fluid transport conditions. All of the above codes are currently under development and have been used for CO_2 injection simulations (e.g. Pruess 2003, Xu et al. 2004, Gauss et al. 2005).

Studies of natural rocks that have been altered by CO_2 rich fluids yield valuable information about slow geochemical reactions involving silicates that can not be studied in laboratory experiments (e.g. Hazeldine 2005, May 2005, Pearce et al. 2005).

CO_2-injection into depressurized oil reservoirs is a common method to enhance oil recovery and was successfully applied in the U.S. in the 70's and 80's and in Hungary in the 80's and has been studied for German reservoirs in a feasibility project for the Sinstorf and Bramberge oil fields. The most important mechanism in this process of dissolving gaseous CO_2 into oil, which swells the oil, is that it improves its mobility and evaporates intermediate compounds from the oil into the gas phase.

Calculations of the economics of the proposed CSEGR project in the Rio Vista field have been published by Oldenburg et al. (2003). Odenberger and Svenson (2003) calculated CO_2 separation, transport and storage costs for case studies in Germany, using the GEST-CO-DSS, developed by Egberts et al. (2003).

4 Case studies

The literature review revealed that the CSEGR-process must be studied for individual reservoir types and the associated peculiar CO_2 supply logistics. Thus, a case study approach has been selected for the present feasibility study. Since most of the German gas fields are hosted either in Buntsandstein or Rotliegend rocks, two gas reser-voirs have been selected, representing these contrasting types of reservoirs. They are part of possible storage systems including industrial CO_2 sources, pipeline corridors, and gas field infrastructure. The feasibility study shall consider real industrial conditions from source to sink.

A modern lignite fired power plant emitting about 10 Mt of CO_2 annually, such as Vattenfall's plant Schwarze Pumpe in East Germany, shall be the source of CO_2 for EGR operations in Germany's largest gas field, in the Altmark. EEG is producing natural gas rich in nitrogen from fractured Rotliegend sandstones in about 3 to 4 km depth. Since 1969 the field yielded more than 200 billion m³ of gas, which would be equivalent to more than about 500 Mt of CO_2 under reservoir conditions. The estimated storage capacity would be sufficient to take up all of the CO_2 emitted during the lifetime of one large lignite fired power station. Declining production rates could be possibly be supported by CO_2 injection, prolonging gas production for a few years, before the reservoir would merely serve as CO_2 storage. The fractured reservoir consists of about 40 different gas-dynamical blokks, separated by low permeable fault zones. The upper Rotliegend sedimentation in the continental North German Basin is characterised by climate controlled regressive, fluvial-lacustrine coarsening upwards cycles (Gralla et al. 1991). Transgressive fine clastic sediments form the base of each cycle, while fluvial sandstones dominate at the top of the cycles. Thick Zechstein evaporites form cap rocks for the Rotliegend reservoirs.

The other type of reservoir consists of coarsely structured, rather isotropic Buntsandstein rocks. Permeability contrasts within the Buntsandstein sedimentary cycles are less prominent than within the Upper Rotliegend, allowing flow perpendicular to bedding. Data of the Buntsandstein field Barrien, operated by Wintershall AG, will be used as an example.

A mature Buntsandstein gas reservoir in Northwest Germany could be used for EGR by the injection of CO_2 separated at an industrial treatment facility for natural gas. Such a facility could emit a few hundred thousand tons of CO_2 annually. Fine clastic and evaporitic sediments of the uppermost Buntsanstein (Röt-Folge) are the cap rock for the sandstone and »Wechselfolge« cycles below.

5 Project organization and work packages

The work is organized in 7 technical work pakkages (WP) and the project administration tasks (WP 8). Information flow and exchange between work packages and project partners involved are shown in the work flow diagram. For this interdisciplinary research project a full duration of 36 months has been planned. Individual work packages last 6 to 36 months. The tasks of the individual work packages are listed in the following chapters. The work pakkage results merge into the final feasibility assessment, carried out jointly by industry partners and research institutes.

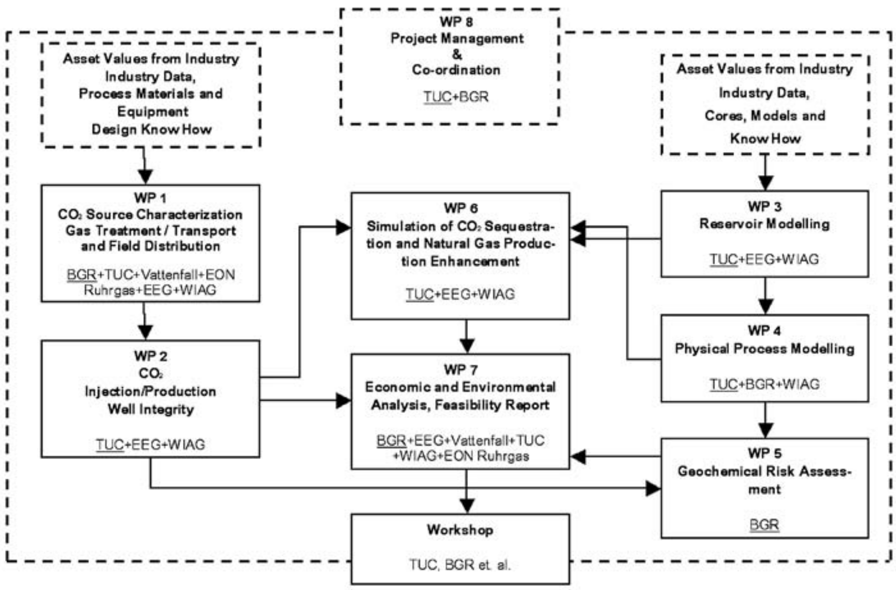

Figure 1:
Project organization and work packages

5.1 CO_2 Source Characterization, Gas Treatment, -Transport, and Field Distribution

The economical, technical, and environmental evaluation of the CSEGR option has to consider the whole supply chain from source to sink facilitating the comparison of CO_2-EGR with other options to reduce CO_2 emissions. The main task of this work package is to provide basic information and characterisation of CO_2 source, transport, and field distribution, which will be needed for overall energy, cost, or emission balances.

Thermodynamic conditions like pressure and temperature, concentrations of impurities, or flow rates are basic data which are needed e.g. for the simulation of gas injection or reservoir recovery processes. They depend on the source characteristics, gas conditioning and transport technology likely to be applied. For both envisaged CO_2 sources fluctuations of CO_2 quantity and quality need to be specified. Likely CO_2 separation technologies shall be identified and expected properties of the gas phase after separation (pressure, temperature, impurities) need to be calculated. The knowledge of these gas parameters is a prerequisite for the technological design of the transport pipelines and eventually necessary gas conditioning measures.

Pipeline tracks shall be proposed, making use of existing pipeline corridors. Possibilities to reuse existing pipelines shall be investigated. Land use, topography, and natural reserves, etc. shall be considered for pipelines that have to be newly built. Pipeline dimensions, material, spacing of safety valves and compressor stations shall be specified.

The purity of the emitted CO_2 stream technically depends on the fuel used in the power plant (or other generation processes), on the chemical or physical approach used for the capture process, and on the effort put into additional cleaning technologies. The requirements on CO_2 purity are defined by technical needs from CO_2 transport and storage, safety requirements and by the economical constraints.

For EGR operations a flexible CO_2 supply to injection wells across the field is required. The suitability of existing field infrastructure shall be tested. Additionally, intermediate storage capacity could be planned in order to balance supply and demand fluctuations. Intermediate storage options might exist in compartments of complex reservoirs or in salt caverns. Injection conditions into compartments of different pressure might require heating, expansion, or compression of CO_2. All issues dealing with the handling of the enhanced produced gas between wellheads and the feed point into the gas transmission network are considered.

In the surface area mainly the following areas of concern exist: potential material and corro-sion problems in the injection and production equipment, processing challenges during com-pression of CO_2, and produced gas processing or blending requirements after CO_2 break-through.

The main building blocks for injection facilities, which are to be reviewed for acceptability or newly designed, are as follows: receiving equipment (manifold), processing/filtering, metering and control, and flow lines to wellheads; for the enhanced gas production: flow lines from wellhead, heating / cooling, water separation, pressure control, processing / humidity control/ blending, and metering.
The feasibility study for CSEGR will build on the published experience gained in applications of CO_2 rich gas production or CO_2 injection schemes (especially for enhanced oil recovery).

5.2 Subsurface equipment for CO_2 injection and well integrity.

CO_2 is known to cause severe corrosion. This is a challenge, in particular, if existing wells with completions not designed for CO_2 service are used for CO_2 injection projects. CO_2 is known to disintegrate the traditional types of cement. The required long term safe deposition in the reservoirs, poses an additional challenge. The cements/sealing materials used to provide a tight seal between casing and formation and to seal abandoned wells must be long-term resistant to a CO_2 rich environment.

This work package addresses the well integrity issues of wells for CO_2 service, in particular completion and cementation. The work will be carried out considering as example the scenarios including the participating industry partners.

It is provided that CO_2 is received at the wellhe-ad. All further injection issues down to the per-forations are addressed in this work package. On the production side, all issues associ-ated with the gas recovered at the perforated inter-val are investigated up to the well head, where the gas is feed into the surface system.

With respect to well integrity and subsurface equipment, the following areas of concern exist:

- potential material and corrosion problems in the injection and production wells,
- durability of well casing cements in the injection phase and long-term as well,
- integrity problems in existing wells and the options for their repair.

The main facility building blocks in the diffe-rent areas, which have to be reviewed for re-use or which have to be or newly designed, are tubing and casing materials, packers, cements and sealing materials.

There are already many applications of CO_2-rich gas production or CO_2 injection schemes (especially for enhanced oil recovery). The fea-sibility study for CSEGR will build on the pub-lished experience gained in these schemes.

5.3 Reservoir Modelling

The geo-model will be build-up with the aid of commercial software: IRAP-RMS/PETREL Work-flow tools. It will be upgraded based on geo-statistical methods considering the facies type of the reservoir, improved data correlations based on logging data, core data interpreta-tion, and well testing analysis.

Geophysical, geological, and engineering pro-vided by the industry partners for each of the chosen reservoirs, are used to define geologi-cal models of the reservoir architecture. The upgraded geo-model will then be introduced into the reservoir simulator ECLIPSE 100 as a fine grid model or as an up-scaled coarse grid model. The simulation study of two candidate fields for CSEGR will be performed within a sector model of the reservoir which is repre-sentative for the location and provides a reaso-nable characterisation of the two storage for-mations. The sector model will then be valida-ted by »history matching« of the previous pro-duction history.

5.4 Process Modelling

The Equations of State (EOS) used in the simu-lator ECLIPSE 300 have been derived from Peng-Robinson modified models. These or others EOS have proven their applicability in practice. The injection of CO_2 into a gas reser-voir, which contains mainly methane in a hy-drocarbon mixture called natural gas (also non-hydrocarbons may be present), differs in 3 respects:

1. The ECLIPSE EOS usually consider quite accurately either low concentrations of CO_2 in a hydrocarbon gas or high concentra-tions (pure CO_2). The accuracy of the deri-ved physical parameters of the mixture must be compared to suitable data or EOS that describe phase behaviour and proper-ties for the entire compositional range of mixtures between CO_2 and natural gas.
2. The injected dense CO_2-phase will presum-ably mix very slowly with the natural gas phase in the reservoir. The efficiency of this process is controlled by the hydrodynamic dispersion phenomenon (Scheidegger model). Dispersion is superposed to the advective velocity of the flowing gas system. The existing simulators must be analysed, if they can, physically correct, model the flow of two gases separated due to high density differences suppressing mixing effects.

3. The hydrodynamic flow properties for multi-phase flow, capillary pressure functions and relative permeabilities may be influenced by the pH-decrease caused by the dissolution of CO_2 in formation water. The impact of pH on the water binding capacity of the different rocks must be studied by capillary pressure measurements and NMR-Relaxometry.

Another aspect of process modelling is the influence of the pore pressure build-up in the res-ervoir on the petrophysical flow properties. For the Rotliegendes formation such correlations have been derived by Häfner et al. (2004). For the Buntsandstein formation such correlations must be searched in literature or provided by the industry partners.

5.5 Geochemical Risk Assessment
Results of this work package shall be qualitative predictions of the likely alteration of reservoir rocks and potential reactions in the overburden and the identification of processes that may cause geotechnical problems in the reservoir, lead to leakage by secondary porosity generation, promote self-sealing of fractures in the cap rock, increase long-term storage capacity and safety by in-situ mineralization of CO_2, or endanger shallow fresh water aquifers.

The hydrostratigraphy and lithostratigraphy of the two reservoirs and their hanging strata has to be compiled from industry data. Fluid and mineral analyses representative for the relevant stratigraphic units are needed to provide information needed to supplement the existing industrial data for predictive simulations of possible geochemical reactions (e.g. composition of solid solutions or relevant trace elements in formation waters. Information from wells in the wider surroundings of the study areas that produce CO_2-rich thermal brines could be useful as natural analogues of relevant stratigraphic units (Rotliegend CO_2 fields in the Vorderrhön, partly studied in the NASCENT project and mineral water wells in Spas at the southern margin of the Norddeutsches Becken). Rock and fluid samples from wells in the case study fields and from natural analogues shall be sampled and analysed in order to supplement the existing limited industrial and published information. These data are the basis for the identification of alteration reactions involving CO_2, either documented in altered rocks, or deduced from geochemical calculations of water-CO_2-rock reactions.
Reactive transport simulators including two phase flow are necessary to study reactions within the reservoirs during CO_2 injection. Quantitative predictions about the velocity of al-teration reactions and the amount of mass transfer shall be derived from the geochemical computer simulations. Reaction conditions fluid and solid phases that have been identified in the natural examples of CO_2-induced water-rock reactions shall be used for the comparison of numerical simulators in order to validate the selected software and the thermodynamic data bases. Parameter variations and sensitivity studies will be performed to identify critical parameters and to constrain ranges of reaction conditions.

The final aim of the natural analogue studies and geochemical simulations is the impact as-sessment of possible CO_2 leakage into aquifers and implications for injection and storage strategies in gas reservoirs. The interpretation of the geochemical results has to consider basic assumptions, uncertainties in simulation results, and the ambiguity of natural analogues in order to evaluate geochemical impact within a more comprehensive risk assessment that is part of the feasibility study of work package 7.

5.6 CO_2 Storage and Enhanced Gas Recovery Simulation
The updated geological model of the two prototype gas reservoirs will be provided by WP 3. For the estimation of the additional gas recovery, a base run for the conventional recovery prediction must be performed with ECLIPSE 300 until the abandonment pressure and rates of the field are reached in the numerical model.

Both CO_2-EGR predictions have to be calculated for the same field life time (some 30 years). After the abandonment of the field (sealing of wells) the pressure build up by continuing CO_2-injection has to be modelled until the maximum working pressure of the storage is reached. Then the operative phase of the CO_2-storage is terminated and the long-term storage performance must be estimated by further simulations of convective and diffusive transport over a period of about 100 years or even more.

The geologic models of the two candidate reservoirs are converted into up-scaled grid models for the ECLIPSE 300 – compositional simulator. A pressure-rate history match will be performed if production data are available. From the structural properties (layering, fine scale lamination, channels, faults, dipping, natural fracturing, aquifer position and size) the proposed injection / production strategies will be derived and selected. The injection/production rates and pressures within the CO_2 storage will be predicted. These data serve as input for the economical calculations in WP 7.

5.7 Economic and Environmental Analysis, Feasibility Report

Chances and risks of CSEGR in Germany shall be quantified, based on two representative storage systems. Uncertainties requiring further research and development shall be identified and discussed. The synopsis of work pakkages 1 to 6 will be an economical, technical, and environmental evaluation of the CSEGR option. It will consider the whole chain from source to sink. Balance equations for the bulk storage system have to be developed in order to calculate energy and emission balances, overall efficiency values, additional natural gas recovery, ultimate CO_2 storage capacity, and CO_2 avoidance costs. The estimation of uncertainties of the calculated balances shall not only rely on results of numerical parameter variations and sensitivity studies performed with the numerical simulators within the respective work packages, but also include published results of other specific research projects. Additionally, Monte-Carlo simulations can be used to predict uncertainties in the balances.

Results of risk assessment studies for other case studies (GESTCO, NASCENT, CO2STORE, CCP, Weyburn), and FEP data bases (FEP = Features-Events-Processes) developed within these projects by shall be used to identify potential storage risks and impact of CO_2 leakage. Potential impact and likelihood of identified risks shall be discussed taking into account the specific features of the two storage systems studied. This discussion shall consider of legal, social, environmental and economic boundary conditions.

A final consideration of all of the different aspects of CO_2-EGR investigated in this project shall facilitate an evaluation of this option for various interested or affected groups:

- for field operators, as a new business chance for continued operation and reuse of mature natural gas fields,
- for power generation and supply industry, as an option to reduce CO_2 emissions when a market for CO_2 emission certificates will persist beyond the Kyoto contract period.
- for the general public, concerning a save, sustainable, socially acceptable, and environmentally friendly energy supply.

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Development and Evaluation of Innovative Strategies for Sequestration and Permanent Immobilization of CO_2 in geological formations (CO_2-TRAP)

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Introduction

The reduction of anthropogenic carbon dioxide (CO_2) in the atmosphere is of paramount importance for the future world climate. Various available options for the sequestration of CO_2 in the subsurface have been proposed and discussed. A possible means of reducing CO_2 emissions is injection into structural reservoirs in deep, permeable geologic formations. Such formations could include aquifers, coal seams, and oil and gas fields. Both, on the international and national level significant progress has been accomplished on this issue. Yet there is a continued need and also still unexploited potential for a judicious combination of carefully designed laboratory experiments and numerical simulations of the physical and chemical processes. The aim of the CO_2Trap project, funded by the German Federal Ministry of Education and Research (BMBF under grant 03G0614A-C, 01.04.2005-31.03.2008) in the framework of the GEOTECHNOLOGIEN special program »Erkundung, Nutzung und Schutz des unterirdischen Raumes«, is to develop, study, and evaluate two alternative approaches for the subsurface deposition of CO_2:

- Precipitation of aqueous CO_2 as calcium carbonate ($CaCO_3$) in formations containing calcium sulphates ($CaSO_4$) and feldspars (Technology I).
- Sorption of CO_2 on (i) residual coal and (ii) waste coal dust or sludge from coal processing plants in abandoned coal mines (Technology II).

The third sub-project covers a comprehensive aspect relevant for all options of underground storage of CO_2 and is entitled:

- Long-term effects of supercritical CO_2 gas and dissolved aqueous CO_2 on the sealing properties of typical cap rocks above potential CO_2 storage formations (Sealing efficiency).

Technology I – mineral trapping: Precipitation of aqueous CO_2 as calcium carbonate in formations containing calcium sulphates and feldspars

The novel approach is to sequester CO_2 not only by physical trapping within a reservoir, but to convert dissolved CO_2 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 geothermal heat or power production. The produced energy can be used and marketed. Due to the geological situation exploitation of geothermal energy in Germany is mainly provided from deep 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 then loaded with dissolved CO_2, and 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 ($CaCO_3$). Injecting aqueous CO_2 at a hydrogeothermal installation has the advantage that the fluid pressure in the aquifer will remain more or less unchanged as the fluid volumes produced from the aquifer roughly equal those injected.

Ultimately, it is one of the prime goals of this project to develop a scientifically and technically feasible new technology in which CO_2 sequestration and geothermal energy use are combined to achieve a safe and economically attractive long-term storage of CO_2 trapped in minerals. Influence factors will be studied in the laboratory, reactive transport is going to be modelled in numerical reservoir simulations, and optimum conditions explored for this process to take place.

State of science and technology

One important potential component of carbon dioxide management is the capture of CO_2 emissions and subsequent emplacement into geologic media. As mentioned one candidate are deep aquifers because they mainly contain highly saline waters and therefore are excluded as source of drinking water. Identifying key issues in connection with CO_2 sequestration is to begin by considering the simple model problem of injecting CO_2 into a closed mineral-fluid system. The main source of uncertainty derives from our inability to entirely specify the thermodynamics and kinetics of the various homogeneous and heterogeneous reactions that take place. CO_2 injection initiates a complex network of reactions that involve aqueous solutions and host rock minerals. First, CO_2 transfers across the gas water interface to become an aqueous ion by the reaction of carbon dioxide to carbonic acid followed by dissociation:

$$CO_2(g) + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2\ H^+ + HCO_3^- \quad (1)$$

The dissolution and dissociation process happens in the reservoir itself in case of pure CO_2 injection or it is forced to happen at the surface within a geothermal plant. It is the task to determine the fate of this aqueous CO_2 from a thermodynamic and kinetic point of view. In the framework of CO_2Trap there are two major ways considered in which CO_2 can be sequestered with regard to the combined process of storage and geothermal energy production. In the first mechanism, pore fluids accumulate dissolved CO_2 through »aqueous trapping«. The pressure, temperature, and salinity (TDS as total dissolved solids) conditions of most subsurface disposal environments limit CO_2 accumulation by thermodynamic constraints. Although solubilities are maximized in formation waters with low salinities, generally speaking, pore fluids can hold only a few percent of HCO_3- regardless of TDS or pCO_2 at injection (Bachu et al. 1996). In a second type, the so called »mineral trapping«, dissolved CO_2reacts with mainly divalent cations to form carbonate mineral precipitates like calcite (2), magnesite (3), or siderite (4).

$$HCO_3^- + Ca^{2+} \Leftrightarrow CaCO_3 + H^+ \quad (2)$$

$$HCO_3^- + Mg^{2+} \Leftrightarrow MgCO_3 + H^+ \quad (3)$$

$$HCO_3^- + Fe^{2+} \Leftrightarrow FeCO_3 + H^+ \quad (4)$$

Overall reaction stoichiometries for the most common minerals show that carbonate precipitation consumes hydrogen carbonate ions while producing acidity. Mineral trapping in such systems is not generally promoted because decreased a pH associated with CO_2 dissolution counteracts the formation of carbonates. However, additional cations can be released by H^+ promoted dissolution of silicate minerals. For example feldspars like anorthite could increase the calcium concentration in solution while buffering pH to higher levels at the same time (5). The overall reaction shows that feldspar dissolution can lead to CO_2 trapping as carbonate minerals.

$$CaAl_2Si_2O_8 + 2\ H^+ + H_2O \Leftrightarrow Ca^{2+} + Al_2Si_2O_5(OH)_2 \quad (5)$$

In view of long-term safety, storage of CO_2 in carbonate minerals is more attractive than a purely physical containment in deep reservoir brines, because in the latter case there is always a risk of failure and escape from such storage.

The novel idea of this project is to convert minerals containing calcium, in particular anhydrite ($CaSO_4$), into calcite ($CaCO_3$). The major focus in Technology I will be on reservoirs containing anhydrite. Such deep aquifers, which are especially abundant in the North German Basin, would also allow using thermal energy.

Equilibrium mineral reactions

The transformation of sulphate minerals (anhydrite and gypsum) to carbonate minerals (calcite, aragonite, and siderite) follows the bulk reaction:

$$CaSO_4 + H_2CO_3 \Leftrightarrow CaCO_3 + H_2SO_4 \quad (6)$$

Calculations with PHREEQC (Parkhurst and Appelo 1999) show that in a closed system the saturation of calcite is not reached due to the formation of soluble hydrogen carbonate species. Calcite only precipitates, if alkalinity is available. Potential host rocks for storage of CO2 combined with geothermal energy production may comprise sandstones with anhydrite, alkali feldspars, micas, dolomite, occasionally siderite and other minor phases (Shiraki and Dunn 2000). The conversion of anhydrite to calcite yields sulphuric acid, which, in turn, is consumed by the forced weathering of feldspar. This shows that weathering of minerals and/or addition of alkalinity are necessary to convert anhydrite into calcite.

The supply of alkalinity is limiting the overall performance of the transformation reaction. In order to provide sufficient alkalinity, the reaction of CO_2 with alkaline fly ashes from the coal burning industry is investigated in Technology I. Fly ashes have a high acid neutralization capacity (ANC). The alkalinity stems mainly from Ca or Mg containing minerals (Meima and Comans, 1997), such as CaO (lime), $Ca(OH)_2$ (portlandite), or $Mg(OH)_2$ (brucite). Neutralization capacities up to 3 mmol (eq) g-1 at pH 7 are quite common. When these minerals react with CO_2, they will transform to carbonates and provide additional alkalinity (7).

$$Ca(OH)_2 + 2\,H_2CO_3 \Leftrightarrow Ca(CO_3) + 2\,H_2O \qquad (7)$$

A lot of knowledge on the carbonation of alkaline material can be inferred from studies performed with municipal solid waste incineration (MSWI) bottom ashes (Johnson et al. 1995, Chandler et al. 1997, Meima and Comans 1997, Yan et al. 1999).

In an initial process of water-ash interaction, many oxides, e.g. CaO, will be transformed into hydroxides. These hydroxides will dissolve together with sulphates in a second step and cause pH-values between 12.5 and 13. The highly alkaline solution leads to dissolution of silicates, mainly glassy, particles of the ashes. Subsequently secondary minerals form, e.g. ettringite ($Ca_6Al_2(SO_4)_3OH_{12} \cdot 12\,H_2O$) and residual silicate minerals like gehlenite ($Ca_2Al(AlSi)O_7$). Such minerals are assumed to play a prominent role in the carbonation process (8) and the generation of alkalinity.

$$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 12\,H_2O + CaSO_4 \cdot 2\,H_2O + 2\,Mg(OH)_2 + 6\,H_2CO_3 \Leftrightarrow 4\,CaCO_3 + 3\,Ca^{2+} + 2\,Mg^{2+} + 2\,AlOOH + 4\,SO_4^{2-} + 26\,H_2O + 2\,HCO_3^- \qquad (8)$$

In this study, we will therefore focus on the reaction of fresh and aged (hydrated) ashes with CO_2. Due to their small particle sizes, fly ashes have a high reactivity, which makes them suitable reactants in a technical process that allows rapid removal of CO_2. The experiments described below shall outline the kinetic and geochemical requirements necessary to operate an engineered system successfully under the desired conditions of high partial pressure of CO_2 and relatively short residence times.

The permeability of aquifers containing anhydrite may not always be sufficient for extracting the required amounts of brines (Lajcsak and Meyn 1999, Baermann et al. 2000). Storage of CO_2 must therefore not deteriorate porosity and permeability. The conversion of anhydrite into calcite could offer positive improvements of both reservoir parameters, since the molar volumes of anhydrite and calcite and their densities correspond to a solid volume decrease of -0.197 $m^3\ m^{-3}$ upon conversion.

The equilibrium scenario outlined above shows that the conversion of anhydrite into calcite is possible given the presence of minerals prone to weathering in the reservoir and/or the addition of alkalinity. Porosity of the reservoir rock is at least preserved, if not increased.

Kinetic considerations

Brines initially in thermodynamic equilibrium with the solids at the reservoir temperature Tr will be cooled to extract the heat, enriched with CO_2 and alkalinity and injected with temperatures $T_i << T_r$. Due to the retrograde solubility of anhydrite with temperature, the injected brine will be undersaturated with respect to anhydrite. A temperature gradient between T_r and T_i induces therefore dissolution of anhydrite. The degree of saturation is given by the saturation index SI which is the logarithm of the ratio of the ion activity product with regard to the mineral under consideration upon its solubility constant. Positive values of SI indicate supersaturation (mineral growth or precipitation), negative values undersaturation (dissolution). The SI of the brines increases with distance from the injection well, and reaches SI=0 somewhere between the injection and production wells. This redistribution of anhydrite has been verified in a column experiment (Bartels et al. 2002) and modelled with SHEMAT (Clauser 2003). SHEMAT uses the following linear rate equation which is going to be revised for the current project:

$$R = k \cdot A \cdot exp\left(E_a / RT \right) \cdot \left(\frac{c - c_{eq}}{c_{eq}} \right) \quad (9)$$

The correct knowledge of the anhydrite dissolution and precipitation kinetic is of utmost importance since it might be the rate-determining step in the dynamic and interactive system of anhydrite and feldspar dissolution and calcite precipitation. With regard to linearity and mechanisms, dissolution studies on anhydrite yielded contradictory results. At high undersaturation, Barton and Wilde (1971) obtained a dissolution constant of 1.9×10^{-4} mol m^{-2} s^{-1} and a linear rate law. They pointed out already that the dissolution reaction might be of mixed control (i.e., between surface and diffusion control). Dove and Czank (1995) derived from dissolution data of isostructural sulphates a dissolution rate and activation energy for anhydrite similar to the values of Barton and Wilde (1971). Kontrec et al. (2002) report a parabolic rate law $(c-c_{eq})^2$ for anhydrite and a linear law for gypsum dissolution. A reaction order of 2 was also found by James and Lupton (1978) in combination with a low reaction constant of 3.5×10^{-5} mol m^{-2} s^{-1}. Measurements of Jeschke (2002) revealed a reaction order of 4 to 5 for anhydrite at high to moderate undersaturation. Such a high order of reaction pinpoints slow dissolution of the mineral close to equilibrium.

The reported values were, except for Jeschke (2002), measured at high undersaturation with respect to anhydrite. In the proposed project, conditions close to equilibrium are expected in the aquifer. Therefore the results reported so far cannot be conferred. A new dataset has to be created taking into account the influence of temperature, foreign ions, and most important the degree of saturation. Lasaga (1998) proposed a rate law considereing all these parameters:

$$R = k_0 \cdot A \cdot exp(-E_a/RT)\, f(\Delta G) \prod_i a_i \quad (10)$$

with the mineral specific rate k0, the reactive surface A, the apparent activation energy Ea and a function f(ΔG), which describes the deviation from equilibrium. The influence of foreign ions ai is considered by the product term. Dissolution experiments are necessary for elucidating the precise form of .

In order to accurately describe the dissolution kinetics of anhydrite all factors of influence, (mentioned above) have to be taken into account. The required parameters for the rate equation will be determined with laboratory experiments (see below). In contrast to the sparse information about anhydrite, calcite precipitation and dissolution kinetics have been investigated by numerous workers (Arvidson et al. 2003, Chou et al. 1989, Liu and Dreybrodt 1997, Morse and Arvidson 2002, Plummer et al. 1978, Svensson and Dreybrodt 1992) with all rate equation parameters available.

Scientific and technical goals

From a geochemical point of view, the conversion of anhydrite into calcite requires both cooling of the reservoir and alkalinity, which may be provided either by the weathering of primary reservoir minerals and/or by adding alkalinity to the injected brines. From the technical point of view, permeability of potential reservoirs is a key parameter. Apart from porosity changes due to dissolution and precipitation of anhydrite (and calcite) within the injected flow volume, conversion of anhydrite into calcite is considered beneficial for improving permeability. Apart from small-scale experiments, modelling is required to achieve this major goal, from small-scale geochemical models to reservoir-scale reactive transport models. Tackling with a highly dynamic system requires precise data on the rates of processes, while at present many of these are only generally known and some of them not at all. Therefore, Technology I focuses on: (1) the dissolution behaviour of anhydrite and the growth kinetics of calcite as a conversion product of anhydrite and (2) reactive transport simulations for reservoir-scale models of the production of hot brines from one borehole, extraction of heat, conditioning of the produced brines with alkalinity and CO_2, and finally re-injection into the reservoir in a second borehole.

Laboratory experiments

For modelling and thus testing the potential of CO_2 sequestration by transforming anhydrite into calcite, the dynamics of anhydrite redistribution within the reservoir as well as the transformation mechanisms and rates need to be known. In detail, three topics will be studied: (i) dissolution rates of anhydrite at near-equilibrium conditions and (ii) at expected variations in solution chemistry. The understanding of the mechanism and rate of the transformation of anhydrite into calcite requires further data (iii) from experiments performed as close as possible to reservoir conditions.

In order to investigate the reaction of CO_2 with fly ashes, a continuously stirred batch reactor is used to study the effects of varying temperature, partial pressure of CO_2, pH and liquid-solid ratios. To determine the chemical and mineralogical composition of the ashes, XRD-, XRF and FT-IR-measurements will be done before and after treatment with CO_2. Particle size distribution determined with laser diffraction technology will be an indicator for available mineral surfaces of specific ashes, which are relevant for their chemical behaviour. Recently the experiments started with flue ashes obtained from the industrial partners. Standard S4 leaching tests (DIN 38414-S4) under different liquid-solid ratios have been performed to quantify the alkalinity generation of the ashes in water and to determine the involved cations. The ANC of these ashes will be determined using pH-stat-experiments before and after CO_2-treatment.

Long-time batch experiments with respect to the kinetics of plagioclase dissolution with high CO_2 pressure at high temperatures will give insights about the possibility of timely supply of alkalinity from feldspars abundant in geothermal reservoirs.

One laboratory flooding experiment will be conducted to study in-situ temperature and pressure conditions with transient monitoring of the brine-saturated core using X-ray tomography. Dissolved CO_2 will be investigated under non-isothermal conditions to study dissolution- and precipitation-patterns of anhydrite and calcite, respectively, in order to estimate the efficiency of various kinds of anhydrite precursors (anhydrite as cementing agent, as nodules, as cloudy nests). New insight gained into dissolution, growth, and transformation kinetics of anhydrite will form a solid base for detailed numerical simulations of a technical scenario, which deals with the input of alkalinity in combination with heat extraction.

Preliminary batch experiments verified the precipitation of calcite from a 0.16 M $NaHCO_3$ solution in contact with anhydrite. After 24 h of reaction 92 % of anhydrite was transformed into calcite. In order to model the evolution of the suspension composition with time, rate laws for dissolution of anhydrite and precipitation of calcite were implemented into PHREEQC. Rate data reported by Jeschke (2002) were fit to the following rate law:

$$R = 4.8 \cdot 10^{-4} \cdot (1 - \Omega)^6 \qquad (11)$$

For comparing purposes a linear rate law, as reported by Barton and Wilde (1971), was used within a second simulation for the dissolution of anhydrite. In both cases the linear rate law reported by Plummer et al. (1978) was implemented to describe the precipitation rate of calcite. Figure I-1 depicts the results of those two simulations. Using high order kinetics for anhydrite dissolution leads to a slow conversion of anhydrite into calcite. In contrast, a linear rate law leads to nearly complete conversion of 74 mM anhydrite into calcite after 15 minutes reaction time. Batch experiment and simulations show that (1) anhydrite can be transformed into calcite, provided alkalinity is present and (2) that the dissolution of anhydrite has to be described with higher order rate laws.

The presented rate law of anhydrite dissolution derived from experimental data of Jeschke (2002) will be refined considering the parameters mentioned above (temperature, degree of saturation, concentration of foreign ions) using a mixed flow reactor. Furthermore, batch experiments, similar to the one described above, will be carried out varying the initial pH and carbonate content of the solution. In a next step anhydrite dissolution and calcite precipitation will be coupled in a mixed flow reactor experiment in order to examine the interaction of the two processes and the kind of precipitate that forms (e.g. coating of anhydrite grains by calcite) under well defined chemical conditions.

Numerical Simulation

Reactive transport will be simulated for injection of a cool fluid, conditioned to contain an optimum amount of CO_2. The simple rate laws currently implemented in the SHEMAT software (Clauser 2003) will be refined and replaced by improved relations derived from the specific laboratory experiments performed in this project (see above). The result will be a realistic simulation which accounts for all of the important physical and chemical processes in this highly non-linear, coupled reactive transport problem. This allows exploring different scenarios in order to provide a ranking with regard to CO_2 storage volume, logistic, or economic feasibility, and to propose an optimum mix between these different criteria.

As yet, the combination of all scales from regional down to micro scale is not feasible in numerical models. The relevant scales studying CO_2 storage in combination with geothermal energy production reach down from the reservoir scale (≈ 10 km) to the micro or thin section scale (≈ 1cm). The idea is to finally provide constraints for smaller scale models from the larger scale and derive functionality from smaller scale models of processes which cannot be

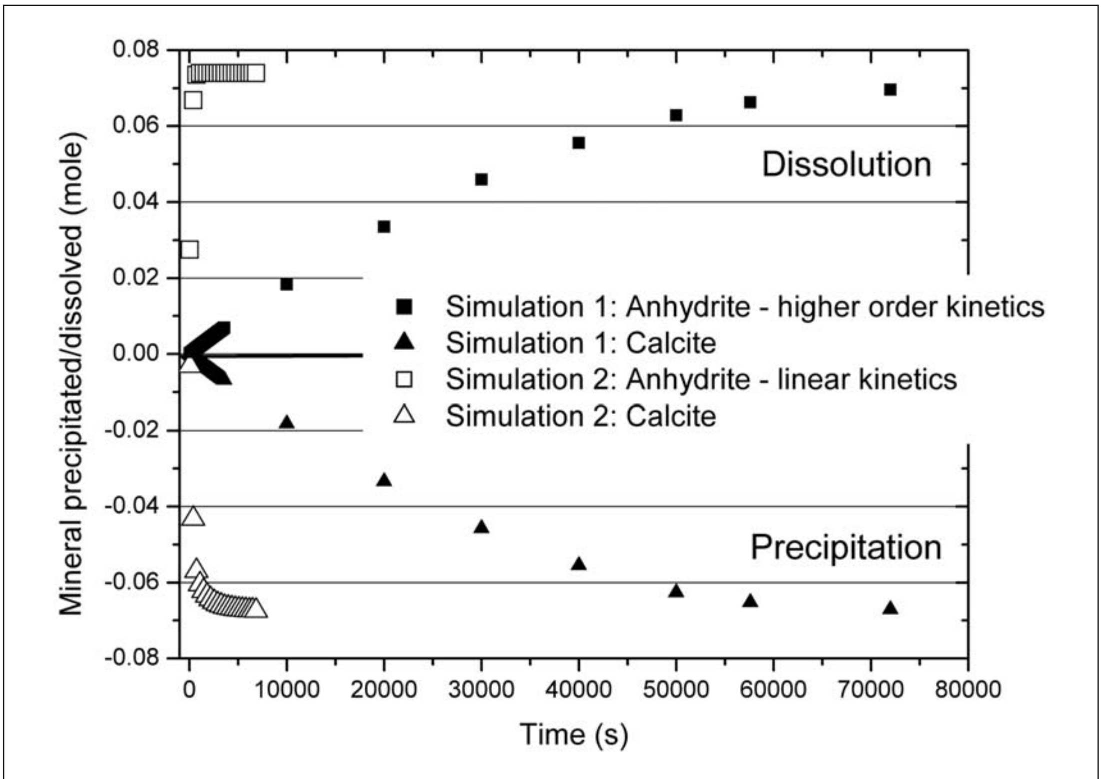

Figure I-1: Amount of anhydrite dissolved and calcite precipitated with time, simulated with PHREEQC.

resolved in larger scale models, due to restrictions of discretization of the applied numerical mesh.

At the Stralsund location a geothermal resource has been investigated and confirmed in previous studies (Bartels and Iffland 2000, Kühn et al. 2002, Kühn 2004) in Buntsandstein layers at a depth of about 1520 m. Stralsund is used here as a first study area to numerically delineate its potential for CO_2 storage. Three wells are already drilled. They tap the Detfurth sandstone with a thickness between 33 and 36 m. From bore profiles and core samples it is yielded that the reservoir consists of a weakly consolidated fine to medium feldspatic quartz sandstone low graded with clay (< 2 % 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^{-1} and a formation temperature of about 58°C. Preliminary simulation results using PHREEQC, conducted as a starting point for further reactive transport simulations with SHEMAT, yield under consideration of thermodynamic equilibrium that 3 times the available amount of anhydrite (0.4 weight % = 76 mol m^{-3} bulk rock), dissolved due to cool water re-injection, can be precipitated as calcite. The deposited amount of calcite is the equivalent of roughly 1 million tonnes CO_2 trapped as mineral.

Data interpretation

Geophysical logs, provided by industry (RWE Dea), of potential targets for geothermal exploitation will be interpreted with respect to reservoir transport and storage properties and content in calcium sulphates. Aim is to locate formations suitable for CO_2 deposition. Combining the information from laboratory testing and log interpretation permits to both calibrate the log interpretation and upscale the laboratory data to the reservoir scale and finally provide mass balance simulations for calculating, how much CO_2 can be dissolved at given pressure, temperature, concentration of solutes and pH and how much CO_2 can be mineralized as carbonate forming calcite, dolomite, siderite, magnesite, or dawsonite.

Preliminary results of the geophysical log interpretation show that various target locations are available with suitable aquifers in Rhät, Buntsandstein, and Rotliegend formations. It is important to note that under specific circumstances all three lithologies are available in one potential area, increasing CO_2 storage capacities significantly. Potential reservoirs require transmissivities above 2000 mD m (milli Darcy meter, permeability times reservoir thickness, 1 mD ≈ 1.0E-15 m^2) to ensure adequate water production rates for geothermal plants to be installed. Generally, the amount of anhydrite in a porous reservoir is inverse proportional with remaining porosity and permeability. The higher the amount of matrix minerals the smaller is the remaining void space of the porous medium and the lower its applicability for geothermal exploitation. However, aquifers are available with anhydrite concentrations in the rock of 10 % or more with remaining porosities above 10 %.

Technology II – physical trapping: Sorptive storage of CO_2 on residual coal and coal dust in abandoned mines

Coal and dispersed organic matter are known to possess a high physical sorption capacity for gases. Considerable amounts of methane originating from the coalification process are commonly associated with coals and released upon pressure decrease during mining operations and the production of coalbed methane (CBM). The fact that the sorption capacity of coals for CO_2 is approximately twice as high as for methane gave rise to the idea to use unminable coal seams for long term CO_2 storage in the subsurface. Furthermore, synergetic effects were expected to arise from a combination of this storage process with CBM production. While the RECOPOL project of the EU has recently documented the perspectives and limitations of CO_2 storage in deep unmined coal seams of Central Europe, the present project aims at the investigation of the feasibility of sorptive CO_2 storage in the void volumes and, in particular, on residual coal and organic matter in the gob and damage zones of abandoned coal mines. Further, and in contrast to earlier studies, the main focus will be on the injection of flue gas instead of pure CO_2 in order to reduce costs associated with CO_2 capturing. Additionally a joint deposition of waste coal dust or sludge and CO_2 in abandoned mines adsorbed to these substances will be examined. This procedure may provide an innovative option for both the deposition of waste coal dust or sludge and a productive future use of abandoned mines.

State of science and technology

Subsurface storage of CO_2 in unmined/unmineable coal seams, partly in combination with coal bed-methane recovery, has been the objective of several research projects worldwide (e.g. RECOPOL, CoalSeq, ICBM). These comprise basic scientific and technical studies as well as field tests. Some of these projects are now in their final stage and on the verge of providing fundamental information on the feasibility of this sequestration approach under specific geological, economical, and social conditions. While the high sorptive capacity of coals for CO_2 is well established, the low permeability of deep, compact coal seams tends to impose limitations on the injectivity and storage rate. Therefore, alternative solutions providing improved accessibility to large volumes of coal or dispersed organic matter need to be explored.

Some fundamental issues of gas (CH_4 and CO_2) storage in abandoned coal mines in Belgium and the USA have been addressed by Piessens and Dusar (2002). This study provides important basic information and will be used as a starting point for the proposed project work.

Scientific and technical goals

Utilization if gob zones of abandoned coal mines for CO_2 storage

The use of gob areas and formation damage zones in and around abandoned coal mines as an alternative to storing CO_2 in coal seams will be explored. These damage zones offer various advantages: (i) they have high permeability; (ii) they provide access to large volumes of residual coal, dispersed sedimentary organic matter and mineral surfaces with potentially high CO_2 sorption capacities; (iii) the geological situation is usually well known; (iv) parts of the existing mining infrastructure (pumps, pipelines, ventilation shafts) may be used for gas injection; (v) long-term gas (methane) monitoring and water management plans are operational in these areas for public safety reasons (little additional investment required for CO_2 monitoring). This project will involve initial laboratory sorption experiments on coals, dispersed organic matter and bedrocks to assess fundamental data on CO_2 storage capacities and kinetics. The main challenge will then consist in the integration of physico-chemical data with engineering and mining information to arrive at a reliable feasibility assessment.

In order to test the feasibility of storing CO_2 from a pure CO_2 or a flue gas stream respectively it is indispensable to define the in situ conditions such as reservoir temperature and pressure, residual coal volumes, residual void volumes, etc. to obtain reliable storage quantities. In general, three different storage options considered to be linked to each other in a dynamic way will be investigated in detail in the course of this study. This mainly depends on the flooding history of the mine, e.g. on the water content available in the coal matrix and in the residual void volumes. The three different storage options are sorptive, free and solubility storage of CO_2. Figure II-1 shows schematically a flow diagram outlining all three storage options and possible ways of obtaining necessary information for calculating the storage capacity of any potential abandoned coal mine. Most information given in Figure II-1 can be obtained from the operating mining companies or the corresponding geological surveys (e.g. mined coal volumes, residual coal volumes, CH_4 contents). Other information, like accessibility of residual coal volumes need to be estimated. Other information, like the selective sorption from CO_2/N_2 or $CO_2/N_2/CH_4$ gas mixtures may only be obtained by precise laboratory measurements. Physico-chemical models for calculating CO_2 solubility in formation waters (Duan and Sun 2003) or CO_2 Equation of State (Span and Wagner 1996) are well established and have yielded reliable results in various publications. Probably the most uncertain fact is the accessibility in either residual coal volumes or residual void volumes. Here best, worst and most probable case scenarios need to be calculated for reasonable estimates.

Figure II-2 shows a comparison of sorption measurements for one coal from the Saar area (Warndt/Luisenthal mine). This mine will be closed by the end of 2005 and might be one possible target for CO_2 or flue gas injection. The experiments have been performed with pure CO_2 on »as received« and moisture equilibrated coal. The "as received" sample is considered to be representative of the coal mine, during or just after active mining. The moisture-equilibrated sample however (moisture-equilibration was performed according to ASTM standard methods at 30°C and relative humidity of 96-97 %), is considered to represent the state when the mine becomes flooded and reservoir pressure approaches hydrostatic pressure. Therefore, Figure II-2 provides information on the amount of CO_2 that can be stored in the dry mine around 3-5 bar (~0.2-0.25 mmol g-1) and the amount of CO_2 that can be sorbed to the coal when the mine becomes flooded (a depth of 1000 m corresponds to a reservoir pressure of ~100 bar which corresponds to a storage capacity of ~0.9 mmol g-1). This observation has implications for the assessment of safety and leakage rates during CO_2-storage in abandoned coal mines. As the mine becomes flooded, the reservoir pressure increases and the CO_2 sorption capacity substantially exceeds the amount of CO_2 injected. This suggests that no or only very little free gas is available that might leak out of the mine and result in safety risks at the surface.

In the further course of this study mixed-gas sorption experiments will be performed to assess the selectivity of CO_2 sorption from flue

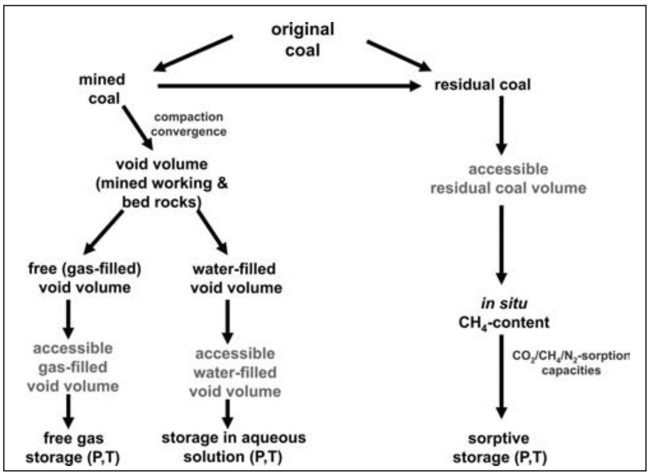

Figure II-1: Schematic flow diagram for he relevant processes associated with CO_2-storage in abandoned coal mines.

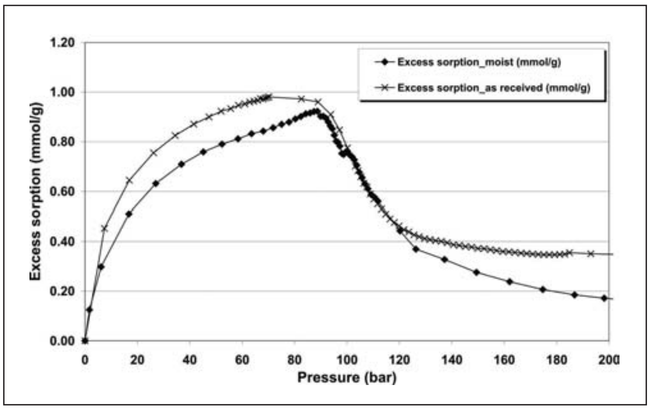

Figure II-2: CO_2 sorption isotherms for coal from mine Warndt/Luisenthal (Saar area), measured in the dry, as received and moisture equilibrated state at 45°C.

gas. Sorption experiments with pure gases document that coal is able to adsorb significantly more CO_2 than CH_4 or N2. Based on single-component sorption data a sorption ratio of CO_2:CH_4:N_2 ~ 4:2:1 is commonly suggested (e.g. Chaback et al. 1996, Stevenson et al. 1991). However, in a recent study, Busch et al. (2005) have documented that, under certain conditions and related to certain coal properties, CH_4 is selectively adsorbed from a CO_2/CH_4 gas mixture. This behaviour needs to be tested for CO_2/CH_4/N_2 gas mixtures for the samples under investigation to be able to obtain a more reasonable estimate on the storage capacity of potential abandoned coal mines.
Molecular diffusion experiments (Krooss et al. 2003) have recently provided evidence that certain shales are able to adsorb significant

quantities of CO_2. Therefore, sorption experiments will be performed on selected shales from coal-mining areas and the results will be related to rock properties, such as carbon content or mineral composition.

Flue gas injection

As a specific feature and timely topic, the injection of flue gas rather than pure CO_2 will be considered. This may have several advantages: (i) it avoids costs for separating CO_2; (ii) it reduces safety risks due to relatively low CO_2 contents and low injection pressures. The concept involves using large volumes of residual organic matter in subsurface mining damage zones as »geologic filters« to remove CO_2 from flue gas. Research will focus on the composition and sorption properties of flue gas, such as: selective sorption of individual flue gas components; rates (kinetics) of adsorption on coals, dispersed organic matter and mineral components under different temperature and pressure conditions. Further, thermodynamic properties (equations of state) and aqueous solubility of flue gas will be studied in detail.

Combination of coal dust or sludge and CO_2 deposition

Another innovative aspect to be studied in the project is the combination of the underground deposition of waste coal dust or sludge with CO_2 disposal. Large amounts of coal sludge are being produced every year as a waste product during the processing of mined hard coal and lignite (brown coal). This material contains significant amounts of organic carbon (>60 % of dry mass), and therefore can be expected to have a high sorption capacity for CO_2. Its small particle sizes correspond to higher sorption rates compared to that in compact coal seams. On the one hand, deposition of coal dust or sludge in abandoned coal mines appears as an attractive way to dispose this waste material while on the other hand it creates additional gas sorption capacity in the underground mines. A combination of those two aspects - disposal of waste coal dust or sludge and underground deposition of CO_2 - generates positive economic and ecologic synergies. We propose to use coal dust or sludge to extract CO_2 on site by adsorption from flue gas. However, an appropriate method should be developed to increase the economical and ecological benefits of the process. In case of success, this new and low-cost CO_2 extraction method could replace existing traditional separation techniques which are uneconomical and deteriorate power production efficiency by currently about 15 %.

The research activities on coal dust and sludge are divided into four major phases: During the first phase samples of coal dust and sludge will be characterized applying standard methods for coal and mineral matter to determine material properties. Furthermore, laboratory sorption experiments will be conducted with the waste products taking into account various conditions of pressure, temperature, grain size, water content, and dwell time. For that purpose a new reactor will be developed based on the technical experience of previous projects to enable the examination of samples with high water contents like coal sludge. The second phase covers the analysis of technologies for underground deposition of coal sludge and dust with regard to flow properties as well as pressure and temperature conditions. Coal sludge and dust injection into underground caverns or mines will be studied in phase three by the use of numerical simulations to examine gas sorption and desorption to be expected during the transport and disposal process. The last phase comprises research about economic feasibility and export potential of the technology as well as a survey of comparable cavities in Europe and world-wide.

So far a couple of product and waste samples from coal processing have been investigated by sorption and geotechnical experiments regarding their potential use for CO_2 sequestration. These have been raw fine coal, two different kinds of coal dust, flotation headings, and flotation waste. The five German hard coal mines West, Saar, Ost, Auguste Victoria, and Prosper-Haniel, owned by the Deutsche Steinkohle AG (DSK) will probably still operate after the year 2012. Table II-1 shows expected quantities for CO_2 sorption, calculated for potential material from coal pro-

Table II-1: Overview of potential CO_2 storage capacity in 5 DSK AG operating German mines for the year 2012 and 5 DSK AG operating German mines for the year 2004.

material	appearance after 2012 (Mg/a)	excess CO_2 sorption capacity (mmol/g)	potential CO_2sorption capacity (Mg/a)	appearance before 2012 (Mg/a)	excess CO_2 sorption capacity (mmol/g)	potential sorption capacity2 (Mg/a)
flotation headings	3.236.025	1	142.385	5.824.845	1	256.293
flotation waste	1.013.992	0,45	20.077	1.825.186	0.45	36.139
coal dust	2.152.600	1.3*	123.129	3.874.680	1.3*	221.632
raw fine coal	453.972	1.3*	25.967	817.150	1.3*	46.741
total	6.856.589		311.558	12.341.860		560.805

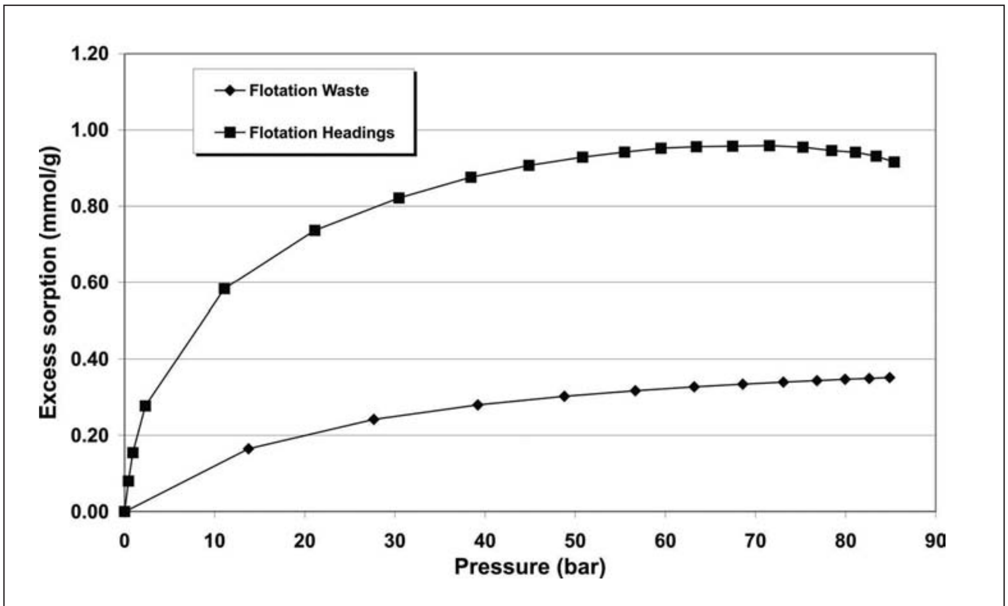

Figure II-3: CO_2 excess sorption on a flotation headings and a flotation waste sample from coal processing in Prosper-Haniel (Bottrop, Germany)

cessing based on the total amount of processed hard coal from those five coal mines.

First sorption experiments on flotation headings and flotation waste (Figure II-3) from the coal processing plant Prosper-Haniel located in Bottrop, indicate significant sorption capabilities for CO_2. The sorption of CO_2 on the examined materials reaches maximum values of approximately 1.0 mmol CO_2 per g flotation headings and about 0.45 mmol CO_2 per g for flotation waste. Based on the knowledge from previous projects the sorption capacity is based on the thermal maturity, the carbon content and the pore size distribution of the processed hard coal. Hence, a relatively higher sorption capability can be expected regarding the coal dust and raw fine coal material due to the higher coal fraction in comparison to the flotation materials. The excess sorption capacity of hard coal can reach up to ~2.0 mmol CO_2 per g coal (Busch et al. 2003). Based on the achieved sorption capacity and the availability of the material from coal processing about 310.000 t CO_2 per year may be disposed by the use of material from coal processing after 2012 (Table II-1).

A higher sorptive storage capacity is available until 2012 due to larger mining activities in the presently exploited nine German hard coal mines of DSK. Based on a mining rate of 25,691 million Mg for the year 2004, the total CO_2 sorption calculates to more than 560.000 Mg CO_2 per year (Table II-1).

Numerical simulations

One of our major goals will be to predict the processes of gas transport and adsorption/desorption in the workings (shafts and passages), gob areas, and damage zones of abandoned coal mines. In this context numerical modelling of gas transport processes in underground mines will be used as an integrative tool to: (a) assess the usefulness of conventional mine ventilation software for modelling flue gas injection and (b) to simulate flue gas injection. Numerical simulations will be performed using the MUFTE_UG simulation software (Helmig 1997, Helmig et al. 1998).

Technology III –Sealing efficiency of reservoir cap rocks over geological time with respect to gaseous and supercritical CO_2

Scenarios for subsurface storage of CO_2 presently encompass saline aquifers, depleted oil and gas reservoirs and coal seams. The long-term sealing efficiency of rock strata (cap rocks) overlying potential CO_2 storage structures is a major concern in the selection and design of adequate storage facilities. Due to its chemical reactivity and physico-chemical properties, CO_2 differs substantially from other natural gas components in terms of transport behaviour and interaction with the mineral/ water system. In this project the sealing efficiency of geological barriers (low-permeability clastic rocks) exposed to CO_2 gas and dissolved CO_2 will be characterised in the laboratory at pressures and temperatures corresponding to in-situ conditions. Experimental methods developed for this purpose during recent years will be applied and refined. Numerical modelling will be applied to analyse and interpret the experimental data and derive an improved understanding of the physical and chemical processes involved. Based on the results of this study and previous experimental work, a scheme for appraisal of the quality and long-term integrity of seal sequences in direct contact with CO_2 will be developed.

State of the art

The occurrence of natural gas reservoirs proves that cap rocks may provide efficient seals which can prevent leakage of gas to the atmosphere over long geological time, i.e., millions of years. Injection of CO_2 into subsurface structures (saline aquifers, exploited oil and gas reservoirs, coal seams) which have not been previously exposed to this gas will affect the geochemistry of the reservoir and its cap rocks. The high CO_2 partial pressures associated with CO_2 injection into the deep subsurface result in a high concentration of carbonic acid (H_2CO_3) and its dissociation products (H^+, HCO_2^-, CO_3^{2-}) in the formation waters. The substantial decrease in pH changes the mineral equilibria and may result in dissolution of formation minerals. In the long run, these mineral reactions may substantially damage the integrity of the top seal and in particular that of fractures contained therein. With respect to this issue, the European NASCENT project has studied naturally occurring CO_2 reservoirs as analogues for future CO_2 storage sites. These systems cover a large spectrum with respect to geological environments, quality of seals, and CO_2 degassing rates. In general, these natural analogues permit to deduce criteria for the selection of structures suitable for a long-term containment of CO_2.

Scientific and technical goals

The principal goal of this study is the quantitative measurement of CO_2 related transport processes in selected fine-grained sedimentary rocks. Commonly this involves the characterisation of the basic petrophysical parameters such as porosity, permeability and specific surface area, and pore-size distribution.

The features and processes of interest with respect to CO_2 storage are the capillary sealing efficiency and the diffusive transport of CO_2 and its hydrolysis products (HCO_3^- and CO_3^{2-}) in water-saturated rocks at elevated pressures (4 – 8 MPa). These two aspects are the focus of the experimental work in this project.

Furthermore, it will be attempted to identify and quantify geochemical, mineralogical and petrophysical changes of the seal rocks as a consequence of exposure to CO_2 at elevated pressures over extended periods of time.

Capillary sealing efficiency

The capillary sealing efficiency determines the height of a CO_2 column that can be accommodated underneath a water-saturated layer of porous rock before the buoyancy pressure results in a displacement of the water and leakage of carbon dioxide across the layer.

Evidently, this parameter is crucial for the judgement of seal quality and, in consequence, considerable efforts have been made to measure it experimentally. Drainage experiments, involving a gradual increase of the CO_2 pressure until displacement of the water (»gas breakthrough«) from a rock specimen occurs, have proven to be very time-consuming and inappropriate for routine tests. In our laboratory an imbibition technique has been developed to assess the minimum capillary gas

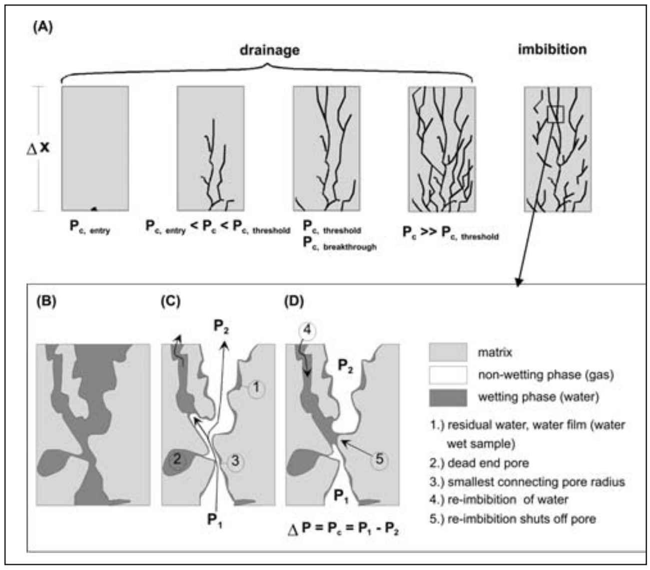

Figure III-1: Scheme of drainage and imbibition processes during gas breakthrough tests. (A) Increasing gas pressure displaces water from the interconnected pore network (B) once the capillary entry pressure (»threshold pressure«) has been exceeded. After reaching the percolation threshold, a pressure-driven gas flow will occur across the sample (C). As the gas pressure gradient decreases, water will re-imbibe into the pore system (D) and shut off the gas flow. The residual pressure difference ΔP is a measure for the capillary sealing efficiency of the rock.

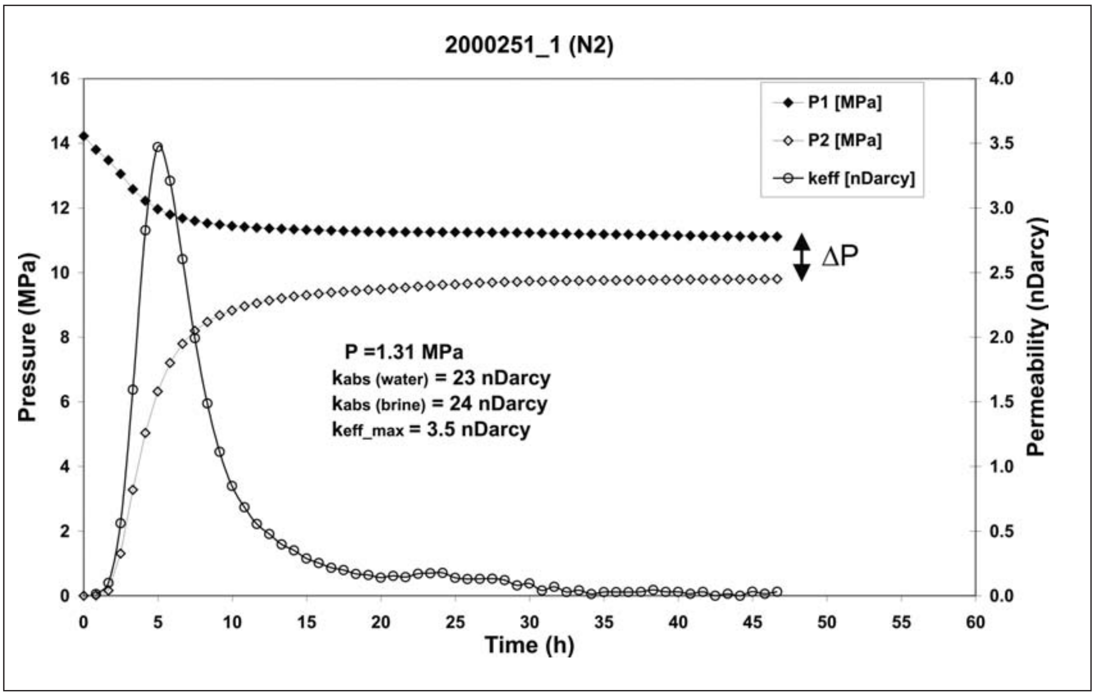

Figure III-2: Results from a gas breakthrough experiment. Upstream and downstream pressures and effective gas permeability as a function of time. k_{abs}: single phase (water) permeability). ΔP is the residual pressure difference interpreted as the minimum capillary breakthrough pressure.

Previous studies (Hildenbrand et al. 2004) have shown that (i) the capillary breakthrough pressures of CO_2 tend to be lower than those for other gases (methane, nitrogen). This could be due to lower water / CO_2 interfacial tensions and/or higher wettability of mineral surfaces for CO_2.

sealing efficiency (Hildenbrand et al. 2002, 2004). The procedure is shown schematically in Figure III-1. It involves a rapid drainage process followed by a re-imbibition step. Experiments are performed by imposing differential gas pressures up to 20 MPa across the sample, and monitoring the decline of the differential pressures (spontaneous imbibition) over time after breakthrough. The residual pressure difference, ΔP, at the end of the imbibition process is interpreted as the minimum capillary breakthrough pressure (Figure III-2).

Diffusion of CO_2 in water saturated rocks

Diffusion is the rate-determining step for many mineral reactions and it controls the redistribution of CO_2 on small and intermediate length scales (cm – 100 m range) in geologic time. An experimental procedure has been developed to measure diffusive transport of CO_2 in water-saturated rocks at pressures up to 10 MPa. Apart from the effective diffusion coefficient, this experimental procedure provides information on the volumetric CO_2 storage capacity of the water-saturated rock sample. Recent experiments have shown that some shales exhibit a relatively high CO_2 storage capacity, usually in combination with low effective diffusion coefficients (Table III-1). This could be indicative for a significant sorption capacity which will be investigated in more detail using the methods of the »Technology II« sub-project (see above).

Numerical modelling

In order to improve the understanding of the complex physical and chemical processes in the CO_2 / water / mineral system, numerical modelling will be applied in the interpretation of the laboratory tests and the extrapolation to natural systems. The numerical simulation tools SHEMAT (Clauser 2003) and MUFTE_UG (Helmig 1997, Helmig et al. 1998) will be adapted for the simulation of the effective physical and chemical processes. Simulations with SHEMAT or other programs (e.g. PHREEQC) capable of handling mineral reactions and reactive transport will focus on an improved understanding of geochemical, rock-mechanical and petrophysical effects of $CO2_2$ injection in reservoir rocks and cap rocks.

Sample acquisition and experimental program

Sample material from seal intervals of different locations in Europe (Greece, France, Belgium, Switzerland, Austria, and Germany) as well as Australia is still available in varying amounts and qualities from earlier projects. Some of these samples have been characterised in great detail and constitute reference samples that are considered for round-robin and inter-laboratory comparison tests. Fresh seal-rock samples from potential CO_2 storage locations in Germany could not be acquired as yet.

The focus in the ongoing project phase is on the refinement of the experimental set-up in terms of data acquisition and leak tightness. Subsequently, permeability, gas-breakthrough and diffusion tests will be resumed on selected samples.

Table III-1: Results of CO_2 diffusion experiments on water-saturated samples.

Sample	coal BRZ 405		cemented sandstone		clay-/siltstone (GR)		shale (AUS)	
Experiment (Temperature)	coal 1 (45°C)	coal 2 (45°C)	cs 1 (50°C)	cs 2 (50°C)	clay/sil 1 (50°C)	clay/sil 2 (50°C)	sh 1 (50°C)	sh 2 (50°C)
D_{eff} (m²/s)	$1.43 \cdot 10^{-9}$	$1.18 \cdot 10^{-9}$	$2.61 \cdot 10^{-10}$	$1.89 \cdot 10^{-10}$	$1.19 \cdot 10^{-10}$	$1.09 \cdot 10^{-10}$	$3.08 \cdot 10^{-11}$	$4.81 \cdot 10^{-11}$
C_1 (mol/m³)	3.3	4.1	9.8	8.3	141	145	389	222
steady state flux (mmol/m²/h)	0.9	1.0	0.7	0.5	5.8	5.4	7.7	6.9

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CO_2-Storage, Monitoring and Safety Technology (COSMOS)

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Abstract

The COSMOS joint project aims at developing novel scientific, technical and regulatory guidelines for maximizing safe geological storage of carbon dioxide (CO_2) in saline formations, for verifying injection and migration processes, and for assessing and mitigating storage risks. Research activities are focused on the capability of saline formations for rapid injection and long-term storage of CO_2.

A major topic is the selection of injection well components under consideration of the specific properties of CO_2 and CO_2-bearing fluids. Well bore investigations will provide guidelines for injection optimization, problem diagnosis, refinement of storage strategies and adjustment of reservoir models. Another major topic is cap rock integrity. Novel geomechanical concepts need to be combined with mineralogical and fabric investigation as well as with existing know-how in order to safely exclude a hydraulic breakthrough.

On-line monitoring provides real-time data on relevant physical parameters. It supports management and control of the CO_2 injection, and of the CO_2 migration and long-term storage. All field measurements are accompanied by small-scale laboratory experiments under simulated in-situ pressure and temperature conditions. Combined petrophysical, geoelectric and seismic data interpretation give insight into the mechanisms of fluid-rock interactions.

The project will be linked to the EU FP6 Integrated Project CO_2*SINK* »In-situ R&D Laboratory for Underground Storage of CO2« (4/2004-3/2009), and will benefit from its strong industrial and scientific partnership. CO_2*SINK* will be of major advantage for COSMOS as a kind of background infrastructure: site with access and facilities, boreholes etc. The objectives of COSMOS are more specific so that the results will be complementary to CO_2*SINK*. The management of both projects by the same coordinator will generate synergies and ensure that no redundancies in research and development will occur.

1. Introduction

According to the commitments of the Kyoto protocol, the EU countries are challenged to reduce the emission of carbon dioxide (CO_2) by 8% in the period 2008-2012. Geological storage of CO_2 in deep saline aquifers and depleted oil/gas reservoirs has the potential to reduce dramatically the release of greenhouse gases into the atmosphere while still allowing for the use of fossil fuels. The development and ample deployment of cost-effective CO_2 capture and storage technology can thus contribute significantly to a sustainable development.

The main barriers for implementing geological storage of greenhouse gases are the additional costs arising from CO_2 capture and the need to prove the reliability of reservoir seals for relevant space and time scales. Storage potential, long-term geological stability, geochemical interactions, cost, public and political acceptance are key issues to be addressed in further research.

Deep saline aquifers are common fluid reservoirs, and large volumes are available worldwide. For CO_2 storage, formations below a depth of approximately 600 m are the most promising targets. Suitable formations are usually filled with highly saline water, and are located across most of Europe. Saline formations have the largest potential capacity and are the most challenging of the potential storage options.

According to a 2003 review of the International Energy Agency Greenhouse Gas Programme (IEA-GHG) on »Leakage from Geological Storage Reservoirs«, focused on underground storage of CO_2, saline aquifers are not as well understood as depleted hydrocarbon reservoirs. Further investigations are needed to safely avoid CO_2 leakage, in particular prior to CO_2 dissolution, but the capability of self-healing is principally recognized for saline aquifers.

For long-term integrity of subsurface storage of CO_2, enhanced surface geophysical methods and borehole measurement techniques are required to quantitative characterization of fluid migration and physical-chemical processes in the reservoir and the cap-rock. Research is needed for realistic up-scaling of parameters and processes measured at laboratory scale allowing these to be incorporated into models at reservoir scales.

2. Objectives

There is little practical experience with CO_2 storage in saline formations. Aquifer storage of natural gas, on the other hand, provides a wealth of experience for important technical issues. From an engineering perspective, operational experience from aquifer gas storage indicates that the main issues for CO_2 storage in saline aquifers relate to the short-term and long-term safety against substantial leakage of CO_2 into the biosphere and atmosphere. More specifically, the sealing capacity of the cap rock has to be assured prior to the start of CO_2 injection. The risk of a breakthrough has to be minimized by geological, mineralogical and fabric investigations, sufficient geomechanical understanding of sealing pelite layers and clay smears, monitoring during and after the injection, and technological tailoring of injection.

A critical issue concerning storage in saline formations is the acceptable leakage rate from the formation to overlying strata. Evaluating general and site-specific acceptable leakage rates is a vital part of any long-term strategy for CO_2 storage. There is a need to develop a comprehensive monitoring and modeling capability. It should not only focus on technical issues. It has also the principal goal of gaining public confidence in geologic storage and to identify crucial factors determining the costs and benefits of the geological storage.

3. Relevance to the objectives of the Programme of GEOTECHNOLOGIEN

Successful and safe geological long-term storage of CO_2 will require monitoring of the pre-injection and post-injection phases to confirm the performance of the cap rock, control the displacement of brine by CO_2 and the CO_2 dissolution in brine, assess leaks and preferential flow paths, and understand the geophysical and geochemical interactions between the CO_2 and the mineral content of the reservoir rock.

COSMOS will contribute to the improvement of the operational and long-term safety of CO_2 storage in deep saline aquifers. It will also focus on the reaction kinetics between reservoir rocks and injected CO_2, and on the petrophysical and mechanical properties of reservoir and cap rocks under in-situ pressure and temperature conditions.

A main goal of the proposal is the development and improvement of injection and monitoring technologies, and the promotion of their commercialization. This should lead to techniques that allow for safe injection and storage of CO_2 at suitable sites. The techniques are transferable to other problems involving fluid-related processes in geological formations such as enhanced oil recovery, environmental monitoring, and natural gas storage.

4. State of knowledge on geological storage of CO_2

Deep geologic formations, such as oil fields, coal beds, and aquifers, are suitable sites for large-scale storage of CO_2. This is already happening in the Weyburn project (Saskatchewan, Canada) and in the Sleipner West field off the coast of Norway, where approximately one million tons of CO_2 are stored per year as part of an off-shore natural gas production project. Developments of CO_2 storage technologies for geologic formations can learn from experience gained over nearly a century of enhanced oil and gas production, natural gas storage, and groundwater management and remediation.

CO_2 can be stored in geologic formations by three principal mechanisms. First, CO_2 can be trapped as a gas or supercritical fluid under a low-permeability cap-rock, hydrodynamic trapping. This will likely be the single most important mechanism for storage in the short term. Second, CO_2 can dissolve into the fluid phase, solubility trapping. The relative importance of solubility trapping depends on the efficiency of displacement of oil or water during the CO_2 injection, the formation of preferred flow paths, and the effects of formation heterogeneity. Efficient solubility trapping will reduce the likelihood that CO_2 gas will quickly return to the atmosphere. Third, CO_2 can react chemically with calcium, magnesium and iron ions to form precipitated carbonates, mineral trapping. Due to the slow reaction rates under natural conditions and possible dissolving processes, mineral trapping may require a stimulation by injection of chemical substances.

Injection of CO_2 into a saline aquifer formation results in displacement of brine by a less dense and less fluid phase. Because CO_2 is soluble in water, a part of the CO_2 will dissolve in the brine during the injection. The physical properties of brine and CO_2 that determine the flow behavior – such as density and viscosity – are well known, as is their dependence on pressure, temperature, and salinity. The rate at which CO_2 dissolves in water depends on the size and shape of the gas-water-interfaces and on the p-T-conditions. All of this, however, is subject to considerable uncertainty.

High-resolution geophysical imaging offers the best potential for cost-effective monitoring of the CO_2 migration and formation of reaction products (mineral precipitation) in subsurface environments. 3D- and 4D- (time-lapse) images of geologic structures and pore fluid distribution can be created with surface, surface-to-borehole, and cross-borehole techniques. The resolution needs to be improved for reliable detection of cap rock seepage, formation of flow instabilities, and preferential pathways.

5. Link with EC FP6 Integrated Project CO_2*SINK*

The CO_2*SINK* integrated project, which commenced on 01 April 2004 within the 6th Framework Research and Development Program of the European Commission (EC FP6), will be a pilot project for injection of CO_2 into a deep saline aquifer underneath the town of Ketzin near Berlin. It involves monitoring of the fate of the injected CO_2 using a wide spectrum of geophysical and geochemical methods, the development and benchmarking of numerical models, and the definition of risk assessment strategies. All these tasks are accompanied by a comprehensive public outreach program.

This pilot project is crucial with respect to
- quality of the seals, including the susceptibility of leakage through overlying strata
- upward migration of gas along artificial pathways, e.g. along the casing of the injection well or in observation boreholes
- migration of CO_2 within the reservoir
- rate at which CO_2 dissolves in brine reservoirs or reacts with the reservoir rock

The Ketzin gas storage site has a number of appealing features:
- The existing surface infrastructure can be utilized for CO_2*SINK* which greatly reduces the need for new developments
- The geology at the site is known and is representative for large parts of Europe, facilitating transfer of results
- The local political community strongly supports the project, and permitting authorities have been involved in the project definition.

The test site, being close to a metropolitan area, provides a unique opportunity to develop a European showcase for onshore CO_2 storage. It will help accelerate the public acceptance of geological storage of CO_2 as a greenhouse gas mitigation option.
CO_2*SINK* will be of major advantage for COSMOS by providing the necessary background infrastructure: test site with, boreholes etc. The objectives of COSMOS are more specific so that the result will be complementary to CO_2*SINK*.

6. Subprojects

The project COSMOS is structured along 3 subprojects (SP), see Fig. 1.

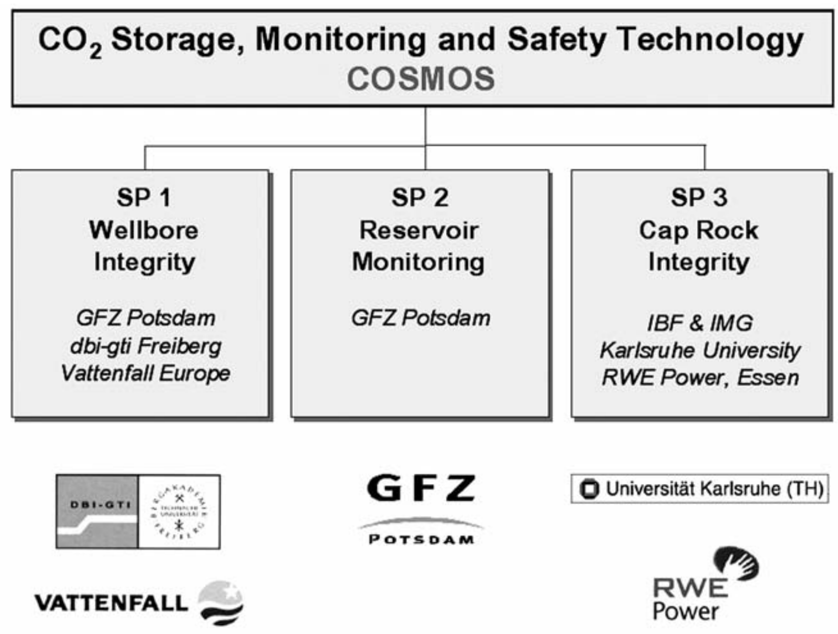

Figure 1:
Project structure

6.1 Wellbore Integrity (SP1)

Compression, injection, drilling, and completion technology for the natural gas industry has evolved to a highly sophisticated state allowing for drilling and completion of vertical, slanted, and horizontal wells in deep formations and multilateral wells, as well as to handle corrosive fluids. Screening of the experience and tailoring of injection wells will be needed for COSMOS. This holds also for design and operating of compressors. Engineering and cost-related issues of transportation and compression of CO_2 will need to be added, alongside with other engineering issues such as effects of contaminants in the CO_2 side stream, before large-scale testing can be started.

Well bore integrity represents a crucial issue with respect to process control and safety. In order to safely operate CO_2 injection and observation wells, the completion needs to be gas tight over a long period of time. The well completion is conventionally made up of a steel casing that is cemented in place. Perforations establish the hydraulic connection to the reservoir. The presence of CO_2 leads to a degradation of the set cement, resulting in strength reduction and gas leakage. In this environment the cementation in the annulus between casing and reservoir rock has to fulfill special requirements especially concerning the installation of sensors in the annulus:

- gas-tightness
- mechanical and chemical sensor protection
- establish a good mechanical bond between rock, sensor and casing
- low electrical conductivity for electrode arrays (electrical decoupling between casing and rock)

The key issue is to find a cement system that combines all of the mentioned properties. New cement types have to be designed and tested under in situ conditions. The testing allows a selection of appropriate cement types and cementing procedures for subsequent field applications.

6.1.1 Safety Conditions of Gas Wells

Wells for geological gas storage (GGS) are exposed to different risk conditions:

Wells in depleted gas or oil reservoirs are sealed in the phase of abandonment with minimum pressure gradient directed into the reservoir. This pressure gradient prevents leakage, i. e. the well integrity is ensured by the reservoir conditions.

Wells in natural gas storages are exposed to pressure variations between maximum and minimum storage pressures. The average pressure value during the operation is approximately at the initial hydrostatic pressure gradient. The pressure equilibrium is achieved between the pressure of the geo-hydrosphere and the reservoir. Leakage can occur only in the high-pressure phase and could be compensated in the low-pressure phase.

Wells in CO_2-GGS are permanently under elevated pressure, i. e. above the initial hydrostatic level, during both the CO_2-injection and the long-term post-operational phase. The pressure gradient is directed toward the geo-hydrobiosphere increasing the risk of gas leakage. These wells are experiencing the most difficult well bore integrity condition.

6.1.2 Components of Well Bore Integrity

The technology of safe CO_2-GGS wells has to consider the following features (see Fig. 2). The results of all these considerations will lead to an »Expert System for CO_2-Well Technology«.

- **Cement** in annulus between casing and rock
  This sealing element is one of the most important unit and under the relatively highest risk. If the cement is sufficiently permeable the well bore integrity is at risk. The CO2 can escape uncontrolled into the geo-hydrobiosphere.

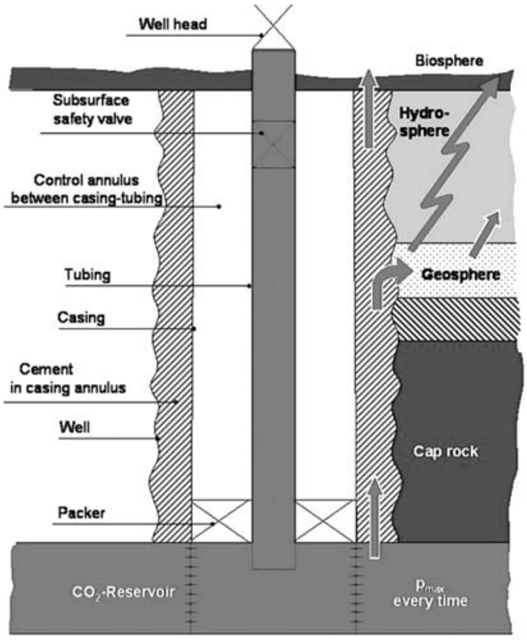

Figure 2: Sketch of well

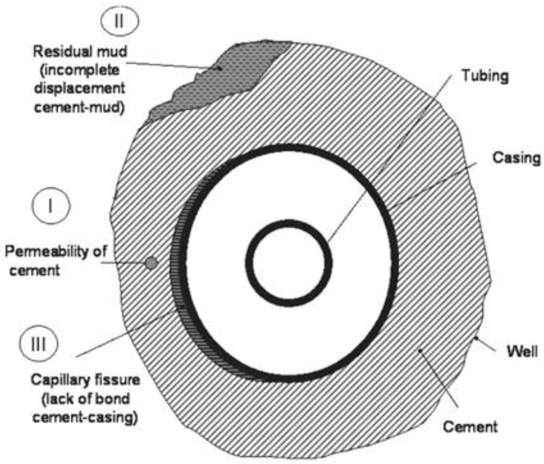

Figure 3: Schematic of well annulus with cement.

The gas-leakage through the cement can occur by:

- **permeable cement** (case I in Fig. 3)
  If porosity and permeability of the cement are relatively high the gas flow can take occur as in a low-permeable reservoir rock. This case is rare since the cement mixtures consider a relatively impermeable cement.

- **mud traps** after cementing the casing due to incomplete displacement of mud by cement slurry in the annulus (case II in Fig. 3)
  This case occurs rather frequently and depends on the quality of the cementing process which is not routine technology in the case of CO_2-GGS wells.

- **capillary fissures** between casing and cement (case III in Fig. 3). The cement shrinks during the hardening phase. Pressure and temperature variations in the well can cause inhomogeneous extensions of the casing. The cement can thus be separated from the casing forming flow channels.

- **Casing** above the packer is completely sealed from the CO_2 and does not require special considerations. The casing inside the reservoir, however, corrodes in the presence of brine and CO_2 and a special design is necessary.

- **Packers** are designed for sour gas conditions, can be made safer by double installation, and the tightness is monitored by pressure control of the annulus.

- **Tubing and subsurface safety valves** are in direct CO_2-contact during the operation phase and need a special design.

- Parts inside the **well head** are in direct CO_2 contact and also need special design.

- **Maintenance and repair techniques** are to be investigated on the basis of similar equipment for sour gas production.

- **Anti-eruption concepts and rules** are to be developed for CO_2-bearing reservoirs based on experiences with natural gas projects.

- **Injection schemes** for CO_2 regarding pressure limitations for head-bottom and well pattern.

- **Monitoring methods** for well bore integrity, their reliability and economy.

6.1.3 Practical Relations to CO2-GGS

The optimum CO_2-well technology is particularly effective in newly drilled wells. This is the case in the EU-project CO_2*SINK* (deep saline aquifer GGS near Ketzin/Germany), the first onshore CO_2-aquifer-GGS worldwide. Storage capacities estimation shows that about 70 % of CO_2-GGS worldwide can be constructed in this reservoir type.

Alternative reservoir types, such as depleted gas or oil fields, have a lower storage potential due to the low safety standard of existing wells that need secondary sealing means after investigation of their integrity state. Another geological storage option is unminable coal seams with a CO_2-GGS storage potential of 10 % to 20 % of CO_2-GGS worldwide. The development of such CO_2-GGS includes the drilling of new wells.

6.2 Reservoir Monitoring (SP2)

Monitoring of CO_2 migration in the subsurface is required for safe long-term large-scale storage of CO_2. Tracking of the distribution of trapped CO_2 in the supercritical, gaseous, dissolved, and solid phases is needed for performance confirmation, leak detection, and regulatory oversight. Existing monitoring methods include well testing, pressure measurements, chemical sampling, surface and borehole seismics and electromagnetics, and geomechanical methods. The spatial and temporal resolution of these methods is unlikely to be sufficient for performance confirmation and leak detection if applied separately. Additional needs are:

- high-resolution multi-method mapping CO_2 migration, such as surface and borehole seismics and acoustic emissions (CO_2*SINK*) together with DC-geoelectric time-lapse imaging (COSMOS)

- remote sensing for CO_2 leaks and land surface deformation (proposed separately)

Permanent monitoring systems provide a novel approach to recording well performance and reservoir behavior. Sensors are placed downhole in the completion string close to the reservoir under investigation and will supply real-time time-lapse data on relevant physical and chemical parameters (instrumented reservoir). Such on-line monitoring provides essential information to manage and control the CO_2 injection, its migration and phase behavior, and storage processes. The systems of permanent captors allow problem diagnosis, injection optimization, refinement of storage development strategies and adjustment of reservoir models.

6.2.1 Development of a Vertical Electrical Resistivity Array (VERA)

The success of geological CO_2 storage projects depends largely on the ability to monitor the state of the reservoir during and after CO_2 injection, in particular in terms of fluid saturation and pressure. This is essential from the reservoir engineering perspective as well as for risk assessment purposes.

Electrical methods are particularly well suited for monitoring of processes involving fluids with a high conductivity contrast, such as brine and CO_2. Time-lapse measurements allow for the assessment of the dynamics of the multi-phase fluid displacement process. They complement the results inferred from seismic methods by adding independent information about the electrical resistivity in the subsurface. This physical parameter is of direct interpretive benefit for the assessment of subsurface structures and processes. In addition, it may be used to constrain and modify the seismic models for better forward predictions.

Downhole geoelectric measurements have the potential for sufficient vertical and lateral resolution, depending on the electrode spacing. They can be operated in profiling and sounding mode. We propose geoelectric DC measurements with permanent electrodes that are electrically insulated from the conductive casing. Electrode arrays offer a high versatility;

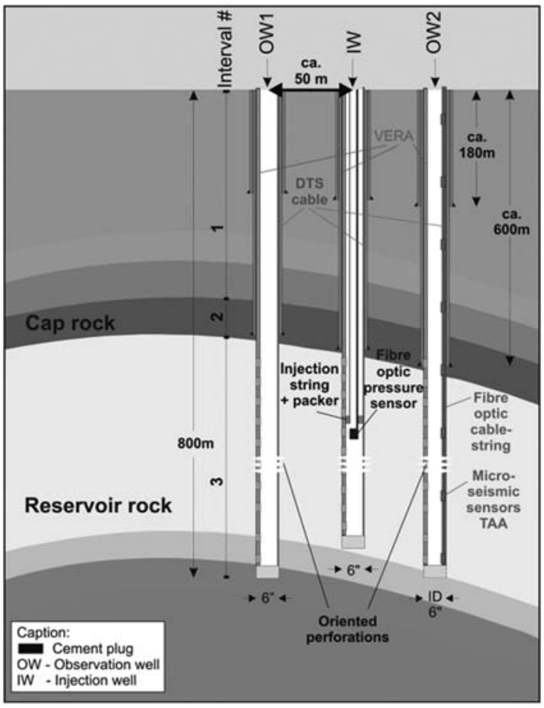

Figure 4: Sketch of permanent downhole monitoring devices at Ketzin. *OW* = observation well; *IW* = injection well; *VERA* = vertical electrical resistivity array (COSMOS); *DTS* = distributed temperature sensing (CO_2*SINK*); *TAA* = triple axis accelerometer (CO_2*SINK*).

they can be designed for optimal performance under specific conditions. The suggested Vertical Electric Resistivity Array (*VERA*) is deployed in the injection well and in monitoring wells.

Because of their high costs, seismic measurements will be performed at larger time intervals whereas geoelectric measurements can be performed almost continuously at reasonable costs. In the suggested monitoring scenario, both seismic and geoelectric approaches are complementary in the following sense: the seismic surveys will provide images of high spatial resolution but sparse temporal resolution of the invasion process. In contrast, geoelectrical images have a lower spatial resolution but can provide data at a high repetition rate. We aim to combine seismic and geoelectric data to constrain and refine reservoir performance models.

A reliable interpretation requires the calibration of the geoelectric and seismic saturation and pressure signature for each reservoir rock in the laboratory. Systematic numerical and experimental analyses of electrical and seismic parameters will be carried out on models simulating the subsurface of the test site. This aims at assessing the resolution of electric mapping and improving the monitoring capability of anomalies related to the CO_2-injection and storage. In addition, this may even lead to a new saturation law for certain rock types, e. g. for high-porosity sandstones.

6.2.2 Laboratory Investigations

A comprehensive and sound petrophysical-geochemical approach to completely understand the CO_2-induced fluid-rock interactions, their influence on physical rock properties, and their geophysical signature is required for a joint interpretation of seismic, geoelectric, pressure, flow, and geochemical data in terms of long-term reservoir processes and their relevance for risk assessment and reservoir management. This approach involves the following research aspects:

- Measurements of physical properties under simulated in-situ conditions for several saturation cycles (electrical resistivity, sonic wave velocities, permeability, etc.). These investigations are required for the quantitative interpretation of geophysical monitoring data and to provide input data for reservoir modeling.

- Experiments to understand the chemistry of the CO_2-induced fluid-rock interactions as well as their dynamics. These experiments are necessary to understand the observed changes in the physical rock properties and to quantify them with respect to the degree of the chemical alteration.

- Investigation of the combined effects of salinity, temperature, pressure, and the amount of dissolved CO_2 on the electrical resistivity of reservoir brine.

This comprehensive laboratory program will help to create reliable long-term reservoir performance models on the basis of multi-method geophysical and geochemical data acquired simultaneously in the same reservoir in the CO_2*SINK* and COSMOS projects.

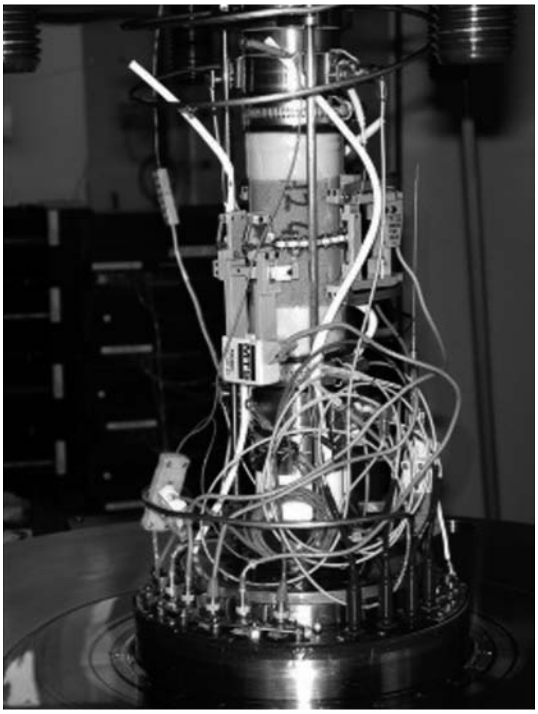

Figure 5: Sandstone sample prepared for a test at reservoir pressure and temperature conditions in the triaxial cell. The sample is equipped with geophysical sensors for seismic velocity and strain measurements.

6.3 Cap Rock Integrity (SP3)

6.3.1 Rock Mechanics

The cap rock in the Ketzin site is a Keuper mudstone with typical slight cementation, slikkensides and a latent crack system. The formation above and below is Schilf sandstone with saline pore water as in the mudstone. A system of normal faults due to salt diapirism in the cap rock is filled with dislocated mudstone. These clay smears have a weaker cementation, almost no slickensides and no latent crack system due to strong shearing. Experimentally produced clay smears with Opalinum shale show kinking and Riedel shears (see 6.3.2). Similar pelitic cap rocks can be found in other sites apt for CO_2 sequestration.

Apart from boreholes the integrity of such a cap rock is principally reduced by CO_2-injection via the following thinkable scenarios (Fig. 6). Depending on the desired rate of injection, the pore pressure in the formation underlying the cap rock increases over a certain area within a certain time. This leads to a very shallow bulge of the cap rock with a smoothly deformed rim. The cap rock is slightly extended along the lower part of the rim, and compressed along its upper part. This can principally reactivate and open an existing crack system along the lower part of the sealing, but not yet to a breakthrough as the upper part is compressed. The clay smears in normal faults are further deformed by the injection; this can lead to new dilated narrow shear bands. The weak cementation plays only a minor role during such deformations and may be neglected therefore in order to be on the safe side. The pore water itself in the cap rock is slightly expanded by the minute opening of a latent crack system and the dilation of shear bands. This happens without filtration of pore water in the otherwise extremely impervious mudstone.

A subsequent hydraulic breakthrough can only occur if the hydraulic gradient reaches a critical amount sufficient for erosion into the adjacent sandstone. The critical gradient is reduced in dilated shear zones, but still very high so that only rather thin clay smears may become critical due to the actual pressure gradient. Erosion channels are formed in this worst case enabling the passage of liquid and gaseous CO_2. This must be safely avoided with a very high probability.

The principal objective is therefore

- to establish sufficient criteria to avoid the loss of cap rock integrity for formations of the indicated kind,
- to demonstrate that these criteria are certainly satisfied in the Ketzin pilot site,
- to outline how these criteria can be applied to comparable CO_2 sequestration sites.

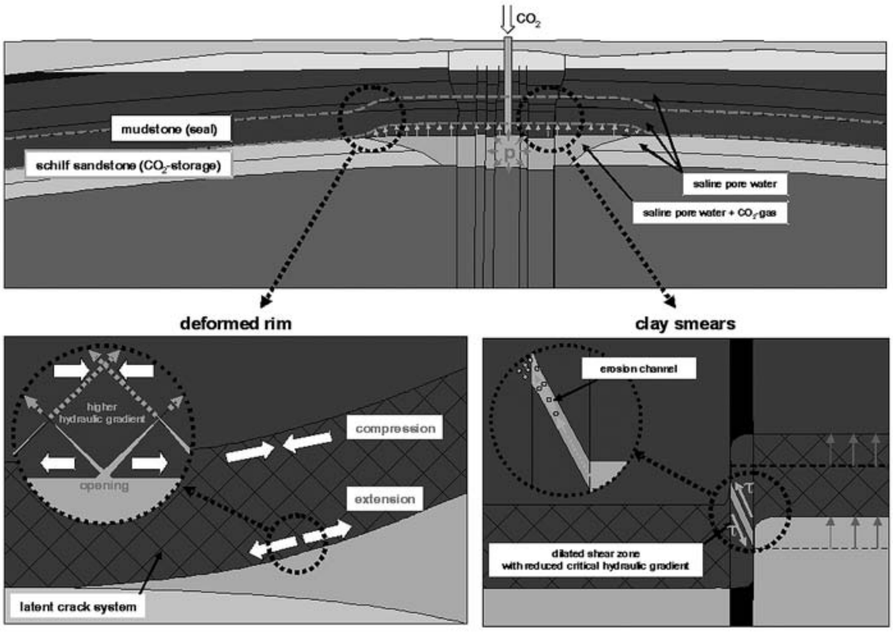

Figure 6: Reduction of cap rock integrity.

More specifically, the following scientific and technological objectives have to be achieved:

- identification and specification of possibly endangered clay smears in cap rocks,
- estimation of cap rock deformations due to CO_2-injection with a simplified numerical model,
- criteria for the formation of reactivated or new patterns of shear bands and cracks in clay smears,
- criteria for opening of a latent crack system in non-remoulded cap rock by lateral extension,
- estimation of critical hydraulic gradients in remoulded cap rock in clay smears and crakked cap rock,
- assessment of safety against hydraulic breakthrough by comparing estimated and critical hydraulic gradients during CO_2-injection.

6.3.2 Reactive Transport of CO_2 in Argillaceous Cap Rock

In order to understand cap rock integrity, the sealing characteristics have to be investigated from nano to macro scale because most processes occur on a molecular scale and can be summarised as reactive transport. The transport takes place either through the pore space of the undisturbed low permeable cap rock or along preferential flow path. Therefore the pore network of mainly argillaceous rock has to be characterized over the full effective length scale which includes major fluid flows in macro-pores such as cracks and open joints, but also diffusion limited transport in narrow pores resulting in a overall permeability driven by different gradients (pressure, temperature, chemical and electrical potential).

In addition, the CO_2 will react with cap rock minerals. This reaction can lead to either mineral decomposition e.g. dissolution or precipitation of secondary minerals. Both influence the fabric and the pore space, hence permeability of seal and thus influences the stability of the storage system. Therefore the description, quantification and understanding of these processes as a reactive transport is essential for the performance and safety of a storage seal.
Furthermore, these processes take place on different time scales and hence a kinetic consideration is mandatory. The chemical reactivity of pressurized CO_2 to the mineral surface area will be investigated with an already running modified HPLC device. With this device the usually separately considered transport and reaction processes can be acquired experimen-

tally as a unique reactive transport. These experiments describe much closer the reality of CO_2 behaviour in cap rock than separate permeability and geochemical reaction studies. The understanding of the underlying chemo-physical processes on micro scale will be achieved by detailed analytical investigation of the fluids at the end of HPLC and the rock material in the column. Finally the evaluation of experimental data, geochemical stability calculations of pore fluid and mineral surfaces should conduct to a performance assessment of the seal.

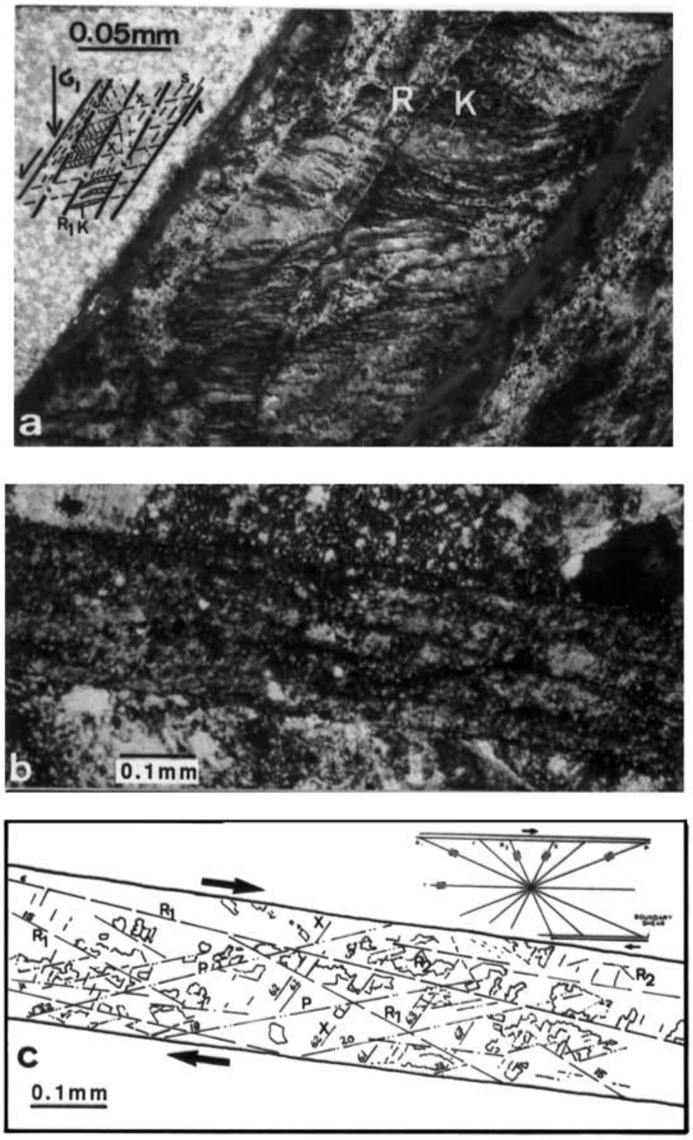

Figure 7: Triaxial experiments with Opalinum clay smears show narrow shear bands and Riedel shears (Nüesch, 1991).

a) Gescherte Probe (Tonfraktion) mit hohem Wassergehalt (30 Gew.%) zeigt kataklastische Mikrostrukturen. b) Stark gescherter (γ= 18), gesinterter Opalinuston (1.8 Gew.% Wasser) bestätigt diese kataklastischen Systeme. c) Skizze der Scherflächen von Figur b, gleicher Massstab, ergänzt mit Figur nach Logan (1979).

Real-Time Observation of the Chemical and Kinetic Behaviour of Carbon Dioxide During Geological Sequestration (CHEMKIN)

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1. INTRODUCTION AND MOTIVATION

The geological storage of carbon dioxide (CO_2) in deep, porous, and permeable reservoir rocks is one of the most promising technologies for a considerable reduction of greenhouse gases entering the atmosphere from stationary point sources such as large fossil fuel power plants. Deep saline aquifers exist worldwide and thus represent the largest potential storage capacity[1]. However, comprehensive research is essential to characterize and map the geological storage structures and to better understand the behaviour of CO_2 during storage [see e.g.[2 3], and literature cited therein]. Therefore the collaborative project, **CHEMKIN**, aims to develop and apply new geochemical monitoring tools for the real time and in-situ observation of CO_2 and additional physical parameters during geological sequestration.

CHEMKIN is closely associated to the CO_2*SINK* integrated project which is largely funded by the EU (started in March 2004). The CO_2*SINK* consortium selected a test site in the vicinity of the town of Ketzin about 20 km NW of Berlin and plans (1) the drilling of one injection hole and two observation holes in the immediate vicinity (50 – 150 m), (2) the massive injection of CO_2 into a 600 – 800 m deep saline aquifer (Schilfsandstein), (3) an intensive monitoring of the fate of the injected CO_2 using mainly geophysical monitoring techniques.

One topic, among many other open scientific questions, which however has not been considered in CO_2*SINK*, is the geochemical real-time observation at depth of the migration of CO_2 within the reservoir and the rate at which CO_2 dissolves in saline aquifers. Therefore, the main objective of CHEMKIN is the development of new, innovative sensor concepts and down hole measuring methods and the practical demonstration of the various benefits of a permanent geochemical monitoring system.

In addition to geophysical measurements, the geochemical real time observation at depth represents the sole method to gain direct and continuous information. The proposed studies will provide critical analyses and samples and will contribute essential guidance for technical decisions. Other commercially viable technologies are not currently available.

2. SUBPROJECTS

2.1. Behavior of Carbon Dioxide in Deep Saline Aquifers Deduced from Ketzin CO_2 Storage Test Site, subproject of GFZ (partner 1)

Objectives

The direct, down hole sampling of fluids and gases and their chemical analysis at the Ketzin sequestration site is essential not only for the calibration and validation of the new sensor technologies to be developed by consortium partners, but also to determine fluid geochemistry in general. Therefore, we propose (1) to pump the encountered formation brine from the drill holes to the surface followed by subsequent analyses of the water and gas, and (2) to apply a phase separating membrane technique combined with real-time mass spectrometrically (MS) gas analysis. Both methods will allow for the determination of other gases e.g. noble gases added to the CO_2-flux as tracers.

Furthermore, during the complete duration of the project, the GFZ will coordinate the various research projects of the consortium partners and is responsible for the logistical needs of the consortium at the Ketzin test site. GFZ will provide logging winches and cables for in-situ tools and will be responsible for the retrieval of data. The collected data will be edited and fed into an information system available for consortium partners.

Planned work

In order to pump deep saline water brine from the aquifer to the surface we plan the installation of a small submersible pump including temperature and pressure sensors within one of the observation drill holes at the Ketzin test site. At the surface, the gas phase will be separated and analyzed on-line for CO_2, H_2, He, CH_4, N_2, Ar, Kr and O_2 with a portable mass spectrometer every minute. A Lucas cell detector will be used to monitor the alpha activity, which is a measure for the radon concentration. Brine and gas flows and the cumulative volume will be recorded in real-time to calculate gas water ratios. In addition fluid temperature, electrical conductivity, pH and redox values of the formation water will also be monitored. Gas and water samples will be taken regularly for subsequent trace element and isotope studies (i.e. to cross-check with the on-site determination of carbon isotopes and in-situ measurements of consortium partner) and for other interested research groups.

Secondly, we intend to develop and apply a phase separating membrane sensor for the downhole extraction of gas from the borehole fluid. This technique will be combined with a mass spectrometer to analyze the gas composition in real-time. The application of gas phase separating membranes has been used for decades in applied sciences, medicine, and industry for gas analysis. The physical model for the permeation process is based on the assumption of adsorption and desorption of the gas on the membrane surface and dissolution and diffusion of the gas through the membrane material (solution-diffusion model). We already tested a combination of a custom made membrane sensor element with a mass spectrometer in a 30 m deep water well, at Ketzin (Figure 1). The gases dissolved in the well water permeated through the membrane and were transported with the applied argon stream via stainless steal capillaries to the surface. Here the gas phase was analysed with a quadrupole mass spectrometer. By considering the different permeation rates of the gases at the temperature and pressure conditions at depth as well as the applied argon flux, the gas contents dissolved in the water could be calculated. The first experiments were successful and showed, that in principal the technique is able to probe the gases physically dissolved in deep saline water. However, further fundamental laboratory and field studies are necessary to adapt appropriate membranes withstanding the high pressure conditions at greater depth and to optimize resolution and detection limits of the method.

Another specific task of partner 1 is to further develop the sensor concepts and sensing methods of the consortium partners for final application. For the implementation at drilling campaigns and field applications, the sensor prototypes have to be mounted in borehole logging tools, which have to be designed and built and which must fulfil the requirements on safety and robustness of modern drilling standards.

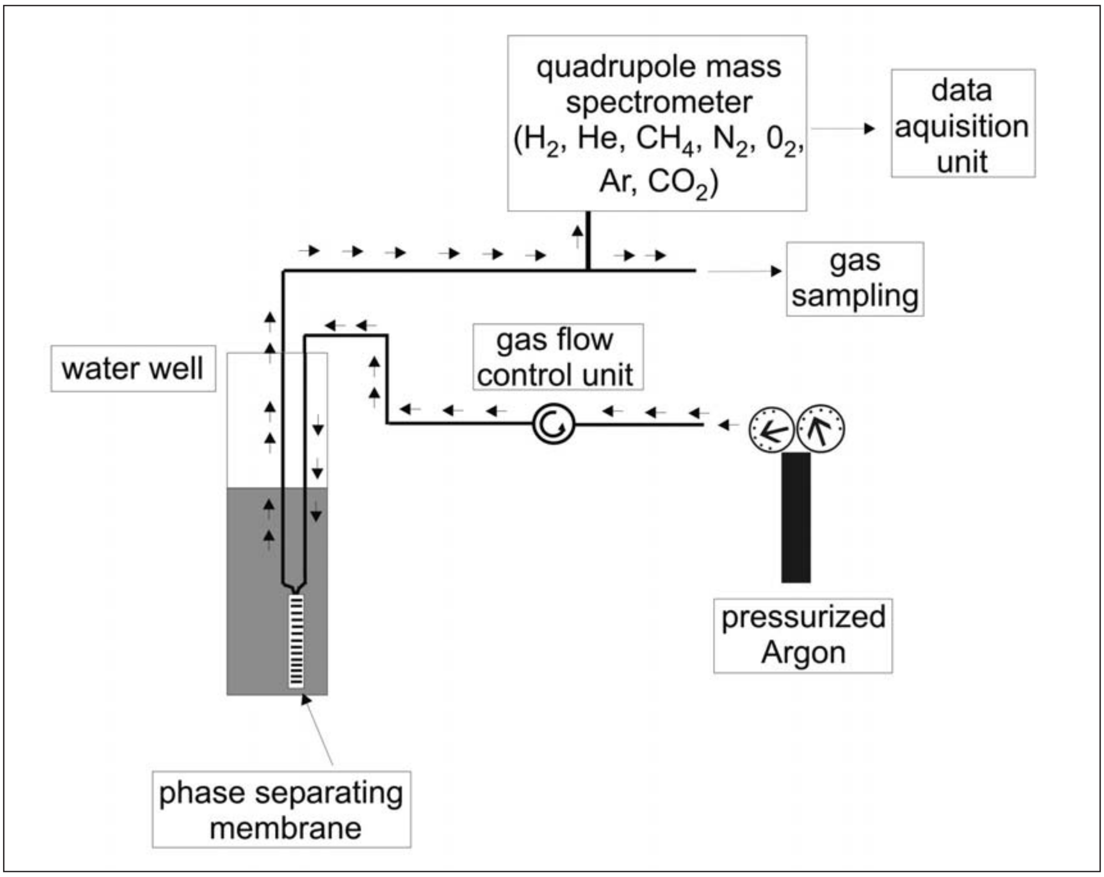

Figure 1: Gas separating membrane system combined with a mass spectrometer at a water well in Ketzin

2.2. Development of a Smart Deep-Well Multisensor Probe for the Measurement of the Parameters Pressure, Temperature, pH-value, Conductivity and Concentration of CO_2 in Ground Water by Electrochemical and Physical Sensors, subproject of Umwelt- und Ingenieurtechnik GmbH (UIT), (partner 2)

General objectives

The foreseen investigation of the geological sequestration of CO_2 demands the monitoring of water quality including CO_2 concentration in deep highly saline aquifers, in order to determine chemical conditions and to quantify migration processes. The sub-project is to develop the methodology, to test and to implement in-situ probes for most essential water quality parameters under the relevant extreme conditions such as high pressure (up to 10 MPa) and high salinity.

The technology of multi parameter probes is applied by several manufacturers in specific modifications for groundwater and surface water (sea, river, lakes) world-wide. However, none of the devices available on the market fulfils the specific requirements of the present project. In summary no suitable borehole monitoring technology is available for the present application of CO_2 sequestration in deep saline aquifers.

UIT is well experienced in developing and manufacturing devices for multi-parameter ground water monitoring as well as in the implementation of large (regional) monitoring networks. UIT is developing a multi-parameter prototype probe, accordingly, focussing on long-term stability and pressure resistance under the physical and chemical conditions characterized above. The scope of work includes:

- Development/adjustment of sensors for the in-situ measurement of relevant parameters

under the given measuring conditions
- Investigation of the long term stability of the sensors
- Investigation of their pressure resistance and optimisation of sensors
- Selection/adjustment of signal amplifiers and data logger system
- Configuring an autonomous power supply
- Design of a measuring probe with an external diameter of 89 mm
- Construction of a prototype
- Implementation of readout data in a geochemical program for the simulation of chemical conditions in the aquifer under such extreme conditions as well as for the investigation/feasibility study of using parameter correlations for direct system control
- Configuring an autonomous power supply

To ensure long term operation of the measuring device, power supply and smart probe operation have to be adjusted to enable continuous operation over at least 3 month. The probe will be set into standby at extremely low power consumption between measurements. The mechanical design of the probe has to be adjusted to the extreme pressure conditions, i.e. the probe and auxiliary units should be water-proof up to 10 MPa.

The following parameters will be measured insitu:
- pH-value
- temperature
- pressure
- conductivity
- CO_2 concentration

The accuracy and resolution for all sensors will be investigated and optimized within the project.

Measurement of pH-value
For the measurement of the pH-value in saltwater, a special sensor design is necessary to avoid inaccuracies caused by the high ionic strength of the water. To minimise these problems a special designed pH-electrode has to be applied. To guarantee for precise measurements a combined sensor consisting of a reference electrode and a pH sensitive glass electrode, both installed in one housing together, will be applied. For the special high-pressure conditions, a double diaphragm for the reference electrode will avoid signal instability during pressure variations. The interface reference electrode is accordingly designed to have a hole-diaphragm. Inside the reference electrode, a KCl-containing gel with a special built-in second diaphragm containing the Ag/AgCl-refence system in a potassium chloride solution will be used. The pH measurement range amounts to 1-14.

Temperature measurement
A standard PT1000 temperature sensor will be used. It is temporarily fed from a 2 mA precision constant-current source during the measurement (to exclude any spontaneous heating effects). The measured signal (voltage drop across the PT1000) is measured differentially (four-wire technology). The firmware of the data logger calculates the measured temperature T from the measured voltage V by a linear calibration function. The tolerances of the temperature probe and of the current source as well as the accuracy of the voltage measurements result in the final measuring accuracy. A precision adjustment incl. offset calibration is recommended to increase the absolute measuring accuracy and to adjust temperature readings from several measuring probes. Measurement range of the temperature sensor is 0-40 °C.

Measurement of the conductivity
The sensor consists of a four-electrode conductivity cell designed for the measurement of conductivities up to 200 mS/cm. The voltage signal output of the accompanying electronics is proportional to the conductivity of the fluid between the electrodes. The calibration function is linear based on zero-point and slope according to data sheets. The measured value will not be normalised by a reference temperature and, thus, will represent the conductivity at the actual measurement temperature. The firmware allows for the calculation of the conductivity for a reference temperature T_{ref} (con-

ductivity Lf_{25} at T_{ref} = 25 °C) according to a standard procedure. The measurement range amounts 0-200 mS/cm.

Pressure measurement

The water level is measured by an absolute pressure sensor. The internal data logger firmware calculates the height of the water column above the probe (level P) from the measured ambient pressure. This calibration function of the sensor has to be adjusted for the conditions of application in the project (possible density effect).

The measurement range is 0-1000 mWs (0-10 MPa).

CO_2 measurement

The electronic measurement system is foreseen to be located within a stainless steel hollow shaft. At the coned point of the sensor a CO_2 permeable polymer membrane with contact to the medium will be mounted. The sensors operating mode is usually based on a potentiometric measurement: CO_2 dissolved in the medium enters through the polymer membrane into the sensor and results in a defined and reproducible change of the pH-value of the electrolyte. This pH change will be measured by a single measuring cell. The voltage signal of the sensor is usually proportional to the concentration of CO_2 in the water. The above measuring principle has to be adjusted to the high water pressure. The measurement range for common sensors is 0-200 mg/l. The measurement at higher concentrations will be investigated.

In Figure 2 the first preliminary design of the device is drafted. For this first concept it is foreseen to store the in-situ measured data in a probes internal data logger.

2.3. Monitoring of CO_2 Stable Isotopic Composition at the Ketzin Sequestration Site with Diode Laser Absorption Spectroscopy, subproject of the Universität Potsdam (partner 3)

The special sub-project issue is to establish a real-time, on-site tool for isotopomere analysis of carbon dioxide. Important geochemical information will be extracted from on-site isotope selective measurements of samples, obtained from the GeoForschungsZentrum (GFZ Potsdam, partner 1) by continuously pumping of small volumes of the brine or using membrane technique. Determination of an element's isotopic composition provides a powerful tool for the quantification of transport paths and efficiencies within complex matrices. Due to its function as a transmitter between inorganic and organic world, the tracer carbon dioxide has already been studied in a variety of applications ranging from the microscopic scale (enzyme mechanics) to mesoscopic (soil dynamics) and even global dimensions (atmosphere and climate). [4,5,6] Excellent summaries of the fractionation mechanisms, including also brine systems, have been presented, e.g., by Criss and Hoefs. [7,8] Based on $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios of the obtained water and carbon dioxide samples, mixing, transport, chemical turnover and seepage processes at sequestration sites can be investigated in detail, as already demonstrated.[7,8]

Isotope ratios are usually expressed in terms of the so-called ∂ (»delta«) notation in per mille (parts per thousand, ‰) normalized to a given standard material. Eq. 1 uses the stable carbon isotope ratio of material derived from the Pee Dee Belemnite (PDB) formation in South Carolina as standard. Typical $\partial^{13}C$ ratios of natural materials cover the range of ca. –50 ‰ to +10 ‰. Positive values relative to PDB are restricted to marine carbonate materials. Organic soil components and plant materials are usually strongly depleted in the heavier isotope. Fractionation due to transport processes or biochemical transformation is generally limited to variations of a few per mile in $\partial^{13}C$. Variation in $\partial^{18}O$ covers a wider range, from +40 ‰ in sedimentary rocks to –50 ‰ in very light meteoric waters.

$$\delta^{13}C = \left(\frac{(^{13}C/^{12}C)_{\text{sample}}}{(^{13}C/^{12}C)_{\text{PDB}}} - 1 \right) \cdot 1000\ [‰] \qquad (1)$$

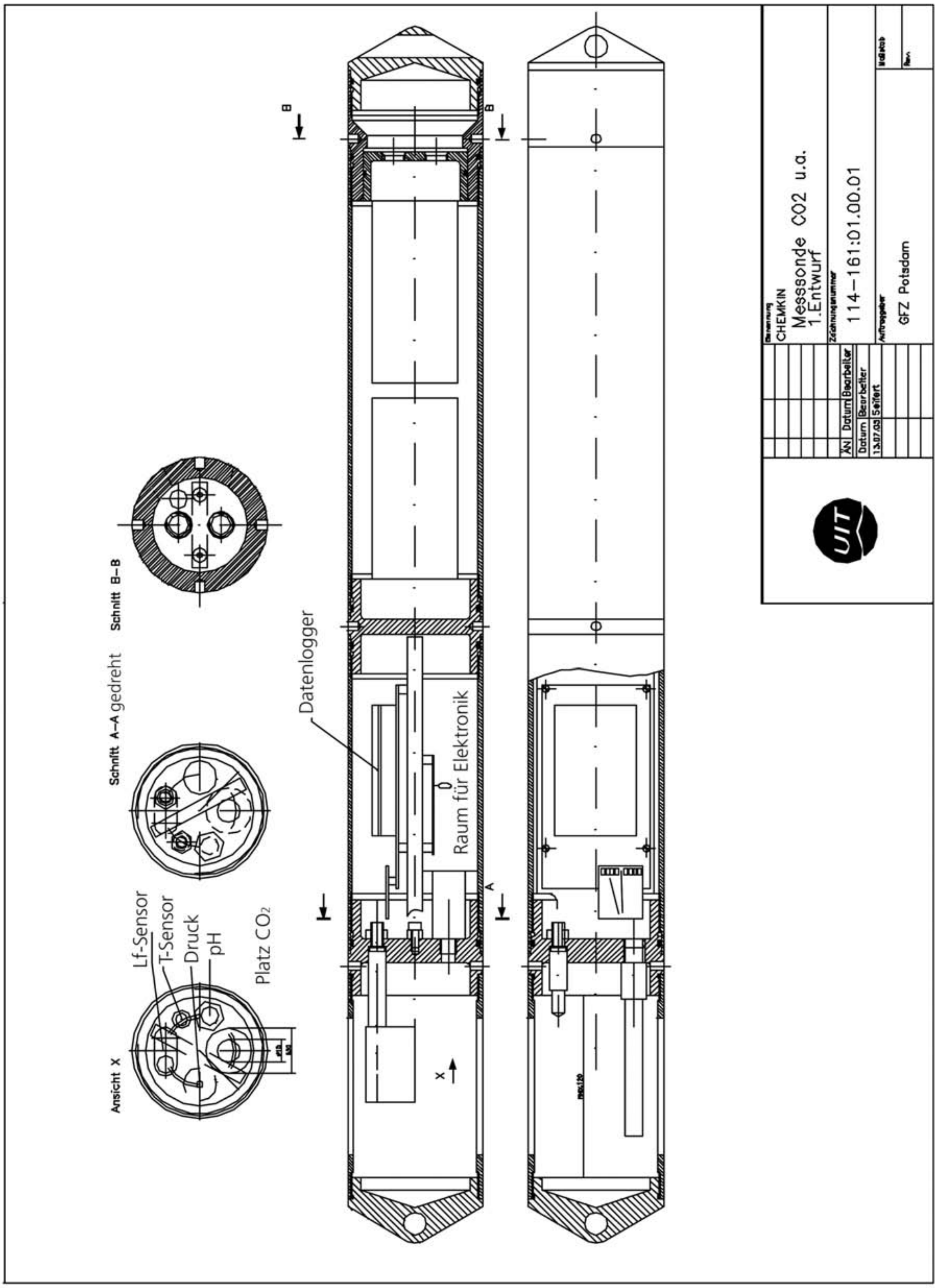

Figure 2: Preliminary design of the sensor probe

Based on our experience in the field of quantitative spectroscopy with tunable diode lasers (TDL), the concept of an ultra-sensitive NIR spectrometer with high spectral resolution was recently developed within a national DFG (Deutsche Forschungsgesellschaft) priority program. [9,10,11] The spectrometer detection scheme is based on wavelength modulation (WM) spectroscopy with detection of higher harmonics in a long-path absorption cell set-up. Usage of an external cavity diode laser (ECDL) guarantees a great versatility of the instrument, due to the strongly enhanced tuning range. Thus, previous studies focused on the performance of our self-built TDL-spectrometer (DLS) to allow for simultaneous multi-line detection of carbon dioxide. [12,13] Employing the spectral range of the $(30°1)_{III} \leftarrow (000)$ band of $^{12}CO_2$ around 1.6 µm, the dominating isotope species $^{12}CO_2$, $^{13}CO_2$ and $^{12}C^{18}O^{16}O$ were resolved and analyzed simultaneously without any interference of water vapor. Detection limits in the low ppm range were obtained for each species. The presented DLS combines flexibility and versatility by allowing sensitive and isotope selective measurements of carbon dioxide in various natural or artificial materials with straightforward and inexpensive equipment. With the same set-up, trace compounds (such as $^{12}C^{18}O^{16}O$ or CO in breath gas) have been identified and simultaneously quantified. Linear calibration plots cover a dynamic range of at least four orders of magnitude. The high precision of the instrument (typically ± 0.8 ‰ and ± 1.5 ‰ $\partial^{13}C$ values for 3 % and 0.7 vol.-% of CO_2, respectively) confirms the performance of the chosen experimental approach and offers a broad range of applications.

Based on the current laboratory version (lab-DLS), a mobile diode laser spectrometer (field-DLS) with isotopic resolution of $\partial^{13}C$ and $\partial^{18}O$ will be constructed and optimized with respect to cross sensitivities, spectral detection limits and isotopic resolution. For field use, temperature stabilization and mechanical stability will be taken into account. In close cooperation with the project partners, gaseous and liquid samples drawn at Ketzin will be characterized in laboratory-based experiments. The obtained results will be validated with mass spectroscopic data from the GFZ Potsdam (partner 1) and compared to the results obtained by other optical (Fa. Optimare, Bremerhaven, partner 5) and electrochemical techniques (Fa. UIT, Dresden, partner 2). Our project will focus on the development and implementation of the field-DLS, capable of high isotopic resolution under field conditions that allows for real-time isotope selective gas analysis at the Ketzin-site. Extended field campaigns will (i) provide real-world feedback for further improvement of the field-DLS and (ii) establish a basis for real-time tracing of carbon dioxide migration, i.e. to determine the origin of the detected CO_2.

The work within this project is divided into two simultaneous sub-sections. The first sub-project will be dedicated to the conceptual design, construction and implementation of a field-DLS capable of isotope selective measurements of water and carbon dioxide. In the second sub-project, the already existing lab-DLS will be used. Analysis of drawn samples will be accompanied by monitoring the results of laboratory-based isotope-exchange experiments. Field campaigns at the Ketzin site will be followed up by a final evaluation of the results within the consortium.

In cooperation with Prof. Dr. Z. Kantor (University Veszprem, Hungary) and Dr. R. Engelbrecht (University Erlangen-Nürnberg), a field-DLS for isotopic resolved measurements will be constructed. The specifications of the spectrometer with respect to resolution cross sensitivities and reproducibility will be defined. In particular, the necessity of a two-wavelength set up with fiber-optical configuration has to be discussed. Since the resulting instrumental resolution is mainly a result of optical back reflection of the individual components, special attention has to be paid to the quality of all optical surfaces and to the mechanical stability of the whole set-up. For field use, the field-DLS has to be stabilized against mechanical interference (e.g. ground vibrations) and, particularly, against temperature variations within the measurement cell.

In the first step, laboratory experiments will be carried out to test the performance of the newly constructed spectrometer and to optimize it by using certified samples. In order to allow for later on-site conditions, the capability and stability under changing environmental conditions (e.g. temperature fluctuations) will be tested. $\partial^{13}C$ and $\partial^{18}O$ values obtained with the field-DLS on real-world samples (drawn at Ketzin) will be compared with the established lab-DLS and a standard isotoperatio mass-spectrometer (IRMS) in cooperation with partner 1.

The carbon dioxide solubility in water and brines will be examined depending on temperature and pressure. The carbon dioxide isotopologues have to be evaluated using the lab-DLS under real-world conditions. The fractionation of isotopes will be studied in laboratory-based experiments. For this purpose, the current lab-DLS will be used. Special emphasis will be placed on kinetic details of isotope-exchange reactions, which are supposed to be of great importance. A transfer port between the reaction chamber and the measurement cell has to be planned and constructed.

Before starting the sequestration of carbon dioxide at the Ketzin site, the existing conditions have to be determined. Partner 1 provides real-world samples from different locations at the Ketzin site. Using the lab-DLS, the isotopic signature of carbon dioxide will be evaluated over months and compared with IRMS data. The obtained isotope ratios of CO_2 at different measuring points will be gathered, subsumed and mapped to localize possible seasonal fluctuations of the three main isotopologues.

After completing the modifications of the field-DLS, the spectrometer will be established at the sequestration site at Ketzin for on-site measurements in field campaigns. Based on the respective infrastructure on-site, a coupling port from the sample reservoir to the measurement cell has to be developed to enable permanent sampling and on-line measurements. The instrument will be run in continuous operation to detect temporal fluctuations of the isotopic signature of carbon dioxide samples during campaigns. The experiences obtained within the field campaigns will offer valuable clues to possible arisen variations of the isotopic ratios.

In conclusion, the results of both laboratory and field measurements will be collected and discussed with the consortium partners, leading to documentation and publication of the gained insights into carbon sequestration. The consolidated findings for monitoring the isotopic ratios of carbon dioxide will certainly apply a new standard for sequestration projects.

2.4. CO_2 Monitoring Inside Boreholes for Real-time Observation of the CO_2 at Ketzin CO_2 Sequestration Site with an Evanescent-field Optical Fibre Sensor, subproject of the Technische Universität Clausthal, (partner 4)

Real time monitoring of a CO_2 storage processes without need of sampling would be desirable. Several optical methods enable in-situ and online monitoring and their applicability has also been shown in harsh environments. Here we propose the use of evanescent-field spectroscopy since it circumvents the need of free optical paths and can be ideally combined with optical fiber cables already used at boreholes.

The specific aims of the project can be summarized as follows:

- Development of a fiber-optic laser sensor based on the principle of evanescent-field spectroscopy
- Development of evaluation-routines for measurements at the high pressure conditions within the boreholes
- real-time measurements of CO_2 in the borehole at different depths

- tracing of the spatial migration of CO_2 in the subsurface aquifer

At the end of the project a functional prototype of the evanescent-field sensor will be available which will have proven it's applicability in measurement-campaigns at the Ketzin test site.

State of research

Within this joint research project, there is a diversity of approaches to meet the requirements of down hole measurements with different sensor configurations. There are two different approaches using optical interactions as sensing mechanisms: fiber-optical chemical sensors (FOCS) and evanescent-field spectroscopy proposed to this application. While the sensing mechanisms are different, the mature fiber optic technology for telecommunication wavelengths can be used by both methods, facilitating the adaptation to the down hole measurements. Evanescent-field spectroscopy does not need free optical paths. This is very valuable, when the measurements are to be performed in highly scattering or optical thick media. When light is incident on the interface between two media with different refractive indices, total internal reflection can take place if the angle under which the incoming beam hits the interface to the optical thinner medium is greater than the critical angle. On a microscopic scale the field penetrates into the surrounding (optical thinner) medium with a decaying amplitude, which in turn results in a loss of energy (light) within the optical thicker medium. This field is called the evanescent-field. Multi-reflection elements are used as sensors in order to increase the sensitivity. Such sensors can be special shaped plates or optical fibers where the cladding has been removed so that a direct contact of fiber core and surrounding medium is possible. The laser light coupled into this sensing element is tuned over an absorption line of the molecular species under investigation which are present in the surrounding of the sensor. In the vicinity of the molecular resonance a change in absorption coefficient as well as in refractive index occurs. This leads to attenuated and frustrated total reflection and therefore to a decrease in intensity of the light within the sensing element.

On the basis of this physical principle a fiber based laser sensor has been developed at the Clausthal University of Technology and successfully used for detection of volcano gases. With the use of silverhalide fibers gases diluted in water have been measured in the mid-infrared spectral range previously. While in general the mid-infrared spectral region is advantageous in comparison to the near infrared because of the higher sensitivity and selectivity (due to the stronger fundamental absorption bands of nearly all molecules in that wavelength range), it can not be used because appropriate optical fibers are not available. Silverhalide fibers can be produced up to a length of several meters and exhibit a large transmission loss. Chalcogenide fibers are not suitable for guidance over 800 – 1000 m as well because of large transmission losses.

On the other hand, there are fiber optical cables available for the near infrared spectral region around λ = 1570 nm, addressing the weaker combination band of CO_2. These telecommunication fibers are relatively cheap and their production has reached a high degree of maturity. Their handling in boreholes is an established technique as well and the material is robust and chemically inert.

While the gas content of a liquid has been determined in the mid-infrared with evanescent-field-spectroscopy, there is no experience on measurements at high pressures. Since there are huge broadening effects, the analysis can not be performed using the line shape of a single absorption line. New routines for data analysis have to be investigated.

Planned work

In this project, the previously in our group developed fiber-based evanescent-field laser sensor for gas analysis will be adapted to the requirements for operation at high pressure conditions in bore holes. This new sensor will then enable online measurements of the dissolved CO_2 inside the holes. Therefore a monitoring of the sequestration process will be possible.

There are the following work packages:

- Theoretical investigation of the near infrared spectral region to identify frequencies which allow the measurement of CO_2 in the presence of water and high pressure conditions.
- Development of an evanescent-field laser sensor for online and in situ monitoring of CO_2 in water
- Laboratory measurements of different CO_2 concentrations in water
- adaptation of the laser sensor design to the application of measurements directly in the borehole
- Real-time measurements of CO_2 concentrations at different depth in the borehole during measurement campaigns at Ketzin.

In the framework of the project, it is planned to set a laser based sensor for measurements in the spectral region to be specified in the first months of the project. The interesting approach is to measure the concentration of the CO_2 dissolved in water directly in the borehole rather than the concentration of the gaseous phase. It has been shown, that a concentration determination is possible in the mid-infrared spectral range for gases dissolved in water. [14] This spectral range is preferable for this approach because the absorption of the gas under investigation is well separated from the absorption of the solvent. However, there are no fiber materials available which could serve to guide the light to a sensor within a borehole. Commercially MIR-fibers are either available in short length only (sapphire) or are chemically not stable enough to withstand the rough environment (silverhalides, chalcogenides). Therefore, the laser-spectroscopic analysis is restricted to the near-infrared spectral region ($\lambda \approx 1.6$ µm) where adequate fiber materials are commercially available. The drawback of this approach is that liquid water has strong absorption in that wavelength region too. In laboratory investigations the feasibility of evanescent-field spectroscopy has to be shown, i.e. single absorption lines of CO_2 have to be found which are not overlapped by water absorption. In the gas phase this is possible as evanescent field spectroscopy has been demonstrated to be a valuable tool as well for industrial monitoring as for gas analysis. [15,16,17] In such a wavelength range where no crosstalk with the solvent occurs, an evanescent-field laser sensor will be designed for application in a borehole. For the robust construction of the sensor and its integration into the logging tool, the expert knowledge of the project partner GeoForschungsZentrum in Potsdam is very valuable. Calibration measurements are performed in the laboratory with different contents of CO_2 dissolved in water. Afterwards, the CO_2 content of the water in the borehole can be determined in different depth and therefore a spatially resolved measurement of CO_2 is possible. This will be done at measurement campaigns at the sequestration site in Ketzin.

2.5 Down-hole CO_2 Monitoring with Fibre-Optic Chemical Sensors at the Ketzin Sequestration Site, subproject of the Optimare GmbH, (partner 5)

Introduction

To any kind of in situ sensor, the underground fluid imposes very harsh conditions, e. g. a pressure of ca. 80 bar, high salinity, low pH etc. Fibre-optical chemical sensors (FOCS) are ideally suited to operate under hostile and hazardous conditions. [18] Such sensors are sensitive, robust and cheap, and they offer the possibility of remote, continuous analysis. For measurement of dissolved CO_2, FOCS usually monitor absorption and/or luminescence changes (stationary or time-resolved) of pH-sensitive dyes embedded in polymer membranes. Such sensors have, e. g., found applications in seawater, marine sediments and the gastrointestinal tract. [19,20,21]

It is pointed out that hitherto down hole analysis is almost exclusively restricted to geophysical methods. The employment of optical techniques to obtain chemical information has remained exceptional. [22] Optical determination of temperature profiles with so-called distributed sensors in bore holes down to depths > 1 km is well established. [23] With the project proposed Optimare makes an important step to implement a laser-based FOCS technology for underground characterization. A challenge for the future is the attempt to apply the concept of distributed sensing to FOCS. It is proposed that the company also participates in integration of the other optical techniques employed by the consortium partners. Planning for a subsidiary at the new technology park in Golm (only ca. 20 km away from the Ketzin site), Optimare is preparing to be able to offer comprehensive optical technology for geophysical purposes.

The specific aims of the project are:

- to design and characterize a FOCS suitable for analysis of dissolved CO_2 under the conditions of the underground fluid in the Ketzin site in cooperation with our partners,
- to define the requirements on a field suited system concerning excitation source, detector and data processing unit, to construct, test and optimize the FOCS in cooperation with our partners,
- to integrate this sensor into the company's OPTIMOS device, based on laser induced fluorescence (LIF) and fibre optical coupling, for environmental analysis and thus to obtain an optical detection unit suitable for field measurements (field-FOCS) in the Ketzin sequestration site,
- evaluate suited algorithms and operating software for quantitative determination of CO_2 concentrations,
- to obtain the analytical parameters, such as detection and cross sensitivities, spectral resolution, stability etc., of lab- and field-FOCS for in situ CO_2 analysis,
- to implement the field-FOCS at the Ketzin site and to perform down-hole in-situ measurements for real-time monitoring, to establish a continuous feedback from the down-hole measurement experiences to improve design, performance and specifications of the field-FOCS,
- to perform, in close cooperation with the consortium partners, a comprehensive characterization of the dissolved CO_2, to evaluate, in close cooperation with the consortium partners, the results obtained by the different experimental techniques
- to understand solvation, phase separation, transport etc. of dissolved CO_2 in the binary carbon dioxide / brine-system at the Ketzin site.

Basic approach and realisation

For the optical detection of CO_2, different types of FOCS are described utilizing different optical techniques for CO_2 quantification. For the application in Ketzin, these different types of FOCS have to be tested concerning their ability to work under the conditions in the sequestration site. The active material of the FOCS consists of a pH-sensitive dye in a polymer membrane, in contact with an aqueous phase where dissolved CO_2 influences the local pH-change, covered by CO_2-permeable membrane. Building the FOCS, this active material has to be combined with a suited fibre optical system and integrated into a housing optimized for the extreme conditions found in the sequestration site.

The FOCS has to be integrated into a field-suited device including light source, detector and data evaluation unit. Optimare has built and commercialized a device family (OPTIMOS)for fast on-site environmental analysis, employing laser-induced fluorescence (LIF) spectroscopy for the analysis of PAH and petroleum products. The OPTMOS family offers high flexibility. A powerful Nd:YAG-laser with nonlinear optical components and a dye laser is employed, providing a wide range of excitation wavelenghts. The detector, an ICCD-Camera, can be used for absorbance measurements as well as for sensitive static and time-resolved fluorescence detection. For CO_2 measurements, the excitation source and the detector of the OPTIMOS will be optimized and the the operating software will be modified. Quantification algorithms will be developed considering the experimental circumstances and the analytical parameters for the CO_2-determination will be evaluated. The data obtained with this field-FOCS will be validated within laboratory experiments as well as within down-hole tests a Ketzin.

Previous experience and preliminary work
Optimare is a high-tech enterprise (SME) with expert knowledge in optical sensing and optoelectronics, and applications thereof in the fields of environmental analysis, remote sensing and oceanography. The company was founded in 1992 by members of laser remote sensing group of the University of Oldenburg.
Optimare has established a well known and widely accepted expertise in airborne remote sensing applied e.g. for surveillance of the german teritorial waters or for airborne polar research in cooperation with the Alfred-Wegener-Institute, Bremerhaven. We employ different types of sensors, e.g. radar systems, infrared and ultraviolet scanners or fluorescence detectors in order to sensitively detect, classify and accurately quantify organic pollutants under extreme circumstances (heights of several 100 m, day and night operation, weather-independent operation).

We have developed analytical devices for fast on-site and in-situ analysis in different environmental applications. [24 – 27] Our OPTIMOS system is able to determine polycyclic aromatic hydrocarbons (PAH) and petroleum hydrocarbons directly in soils without sampling or sample preparation. For the observation of aquifers and surface waters, we have combined this device with fiber optic sensors for the determination of oxygen content and pH applying different techniques, e.g. stationary and time-resolved fluorescence measurements.

In cooperation with our subsidiary, the Optimare Sensorsysteme AG in Bremerhaven, we participate at the ARGO-program observing oceanographic flow and transport processes. With our »NEMO-floats« oceanographic parameters (conductivity, temperature, depth) can be monitored independently over a period of several months up to years. The system operates in a depth of several thousand meters, collect depth profiles and automatically broadcasts the data via satellite after emersion.
Optimare GmbH and it's subsidiary has 30 employees comprised of 10 senior scientists, mainly physicists and chemists, 15 engineers and technicians and as well as 5 member of staff and administration.

3. CONCLUSION

Within the consortium a partnership is formed with institutes and companies interested in developing and applying new methods, some very innovative, for in situ analyses of CO_2 in deep boreholes. Each partner proposes a technique with specific advantages, so that several complementary methods will be developed. The close cooperation and information exchange prevents duplicate of work already being undertaken, and results in synergy and progress.

Each method has its specific advantages i.e., the GFZ technique allows the analyses of all gases dissolved in the brine so that tracers, injected into the CO_2 stream, can be analyzed. Additionally, samples can be drawn for special investigations in the laboratory.

The UIT multi-sensor modules represent the state of the art technology and are well tested and applied in monitoring networks. Based on this experience, UIT will develop a prototype for harsh chemical and physical conditions.

The advantage of an evanescent-field optical fibre sensor of the TUC is to circumvent a free optical path and the possibility to combine it with opticle fibre cables already used in boreholes.

The University Potsdam has a diode laser spectrometer which combines flexibility and versatility by allowing sensitive and isotope-selective measurements of carbon dioxide with relatively undemanding and inexpensive equipment.
The fibre-optical chemical sensors of Fa.

Optimare monitors absorption and/or luminescence changes (stationary or time-resolved) of pH-sensitive dyes embedded in polymer membranes and is ideally suited for operation under hostile and hazardous conditions. The sensors are sensitive, robust, cheap and offer the continuous analysis of dissolved CO_2.

At the end of the project, surface and down hole sensors and optimized methods will be available to permanently observe storage reservoirs. The new tools for cost-effective geochemical monitoring will assist installation of an industrial real-time CO_2 monitoring network to be used during active sequestration of CO_2.

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High-Resolution Images of Subsurface CO_2 Storage Sites in Time and Depth by the CRS Methodology (CO_2CRS)

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1. Introduction

1.1 Climate Protection by reduction of Green House Gases in the Atmosphere

The accumulation of green houses gases like CO_2 from industrial emissions in the atmosphere presents an increasing problem for the climate. The global warming, i.e. the rise of the average athmospheric temperature during the last decades, significantly increased the number and intensity of devastating floods and storms worldwide. Another consequence is the melting of polar ice reservoirs and associated rise of the sea level that endangers lowland countries, e.g., The Netherlands, Bangla Desh, and Pacific island states.

The global warming effect is attributed to the emission of green-house gases, as a result of the increased consumption of fossil energy sources by both, the industrial and the private sectors. A further rise of fossil energy consumption is expected for the growth-oriented global economy, with major increase rates in the developing countries. In view of the disastrous consequences of the global warming, international attempts have been made to stabilize, or even reduce the emission of greenhouse gases. In 1997, an obligatory reduction of CO_2 emission was fixed by the Kyoto protocol. The industrialized countries signed to reduce emission by 5% in 2008-2012 with respect to the level of 1990. Germany committed itself for a 20% reduction.

1.2 Reduction of Green House Gases by CO_2 storage in the subsurface

The strategies for climate protection aim at reducing the CO_2 production by a decreased consumption of fossil energies, and by preventing the produced CO_2 from spreading into the atmosphere. A potential key technology for reducing the emission of CO_2 into the atmosphere is its long-term storage in the subsurface. Such an approach is currently being successfully tested in the Sleipner gas field in Norway in the framework of the »carbon dioxide capture project (CCP)« by Statoil and other partners.

A similar project is planned in Germany, complying with Germanyls intention to take a leading role in the efforts for climate protection. This role cannot be confined to the ambitious target of a CO_2 reduction by 20%, but also requires significant advances in CO_2 reduction technologies. For underground storage of CO_2, it is essential to identify appropriate storage formations in the subsurface and to thoroughly evaluate their long-term safety. In the context of hydrocarbon exploration, reflection seismic surveys have proven to be an appropriate tool for obtaining a structural image of geologic structures and to investigate their properties as storage formations. Modern 4D (or time lapse) seismic measurements have been established as methods to explore and monitor reservoir formations in the subsurface. Corresponding seismic methods are now to be applied at selected locations in Germany to survey the properties of reservoir formations in the framework of a scenario analysis for the potential storage of CO_2. However, the analysis of such 3D seismic data requires the application of specific data processing methods.

2. CRS methodology for analysis of CO_2 storage locations from 3D seismic data

2.1 CRS imaging method

For high resolution imaging of complex 3D subsurface structures, there is a general trend nowadays to use the costly but accurate Prestack depth migration (PreSDM) techniques. The PreSDM method simultaneously performs the focusing and the localization of the reflector images in the subsurface. Alternatively, methods that perform the focusing step already in the time domain allow to separate both steps. In this way, a seismic section with improved S/N ratio can be generated prior to the determination of the velocity model.

One such model-independent stacking method is the so-called Common-Reflection-Surface (CRS) stack method (see, e.g., Hubral, 1999, Mann et al., 1999 and 2004, Jaeger et al., 2001) which was developed at the University of Karlsruhe. In contrast to conventional stacking methods, the CRS stack uses all information contained in the data and, thus, yields seismic images of significantly improved quality. During the past years, this technology was successfully introduced into production in cooperation with several companies involved in hydrocarbon exploration (e.g. Trappe et al., 2001). The cooperation takes place within an industry-supported research consortium, the Wave Inversion Technology (WIT) Consortium.

2.2 Scope of work and proposed developments within the 3D CRS methodology

The proposed research and applications to CO_2 storage locations are entirely based on the CRS technique. They comprise advances both in 3D time domain imaging and 3D depth domain imaging, which will provide superior images of the storage reservoirs. There is good confidence that the proposed targets and quality improvements will be reached within the project, since the advantages of the CRS methodology have already been proven in 2D applications, both in research and industrial environments. Examples of the 2D technique are presented below in this chapter.

The 3D CRS methodology to be developed consists of three work packages (WP), which together deliver a high-quality image of the storage reservoir:

WP 1: 3D CRS imaging for improved time processing (TEEC)

In the first step, the 3D imaging method and software delivers a time domain image with excellent resolution and signal-to-noise ratio. Additionally, it provides densely sampled volumes of CRS stacking attributes which provide access to an abundance of local wavefield information, like wave front curvatures, incidence angle, slowness, spherical divergence, projected Fresnel zone, etc.

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WP 2: 3D CRS tomography software for reliable velocity depth models (UKA)

The 3D CRS attribute information is input to the second step. A 3D CRS tomography method and software inverts these attributes with respect to a reliable velocity-depth model. This velocity-depth model allows to perform poststack depth migration on the CRS stack which transfers the excellent resolution and signal-to-noise ratio from the time to the depth domain.

WP 3: 3D Fresnel volume migration using CRS slownesses (FUB)
The slowness information from 3D CRS attributes of the first step, and the velocity-depth model from 3D CRS tomography of the second step are input to the third step. This allows to determine local Fresnel volumes for an extended 3D Kirchhoff PSDM method and software. Migration noise is reduced, and signal-to-noise ratio of the depth section is increased by restricting PSDM to the physically relevant portions of the data.

The development and test applications of the methods are followed by a final evaluation of the information increase for gas/CO_2 reservoirs with respect to conventional methods (TEEC).

The flow of data and intermediate results in this project implies an intense and precise interaction between the project partners. The 3D CRS Imaging by TEEC in WP I (Work Package I) delivers the attributes for 3D CRS tomography by the University in Karlsuhe. A tomographic 3D model of the interval velocitiy in depth is calculated by the University of Karlsruhe in WP II. Together with 3D CRS attributes from TEEC, this 3D model is delivered to the Free University of Berlin for the specific PreSDM approach in WP III. All results are then returned to TEEC for final evaluation of the information increase, e.g. in structural resolution, or in specific special processing steps like coherency and neural network processing.

2.3 Application of proposed 3D CRS tools to gas / CO_2 storage sites

The present project is designed to transfer the previously mentioned advantages of the CRS technique from the 2D to the 3D case. The improvement of the imaging in time and depth as well as the additional information from CRS parameters are directly demonstrated at two 3D seismic data sets:
1. An initial accuracy test is carried out with synthetic data.
2. The final application comprises primarily a comparison of the new methods and conventional methods at 3D seismic data over a depleted natural gas reservoir or industrial gas storage. Optionally, a 3D seismic dataset from a planned CO_2 storage tests will be incorporated in this project as well, in case that acquisition is finished in time and additional aspects can be covered.

Both, the established technology for subsurface storage of natural gas, and the new approaches for subsurface CO_2 storage utilize the same types of subsurface reservoirs. They impose the same requirements to seismic investigation of the reservoir, and monitoring of the storage process:
- A good resolution of the general geological and tectonic setting of the storage site is the main key to the detection of potential storage and sealing formations, and to the extent and directions of the fault systems.
- Potential storage layers with thicknesses ranging from several meters to small multiples of 10 m have to be resolved, requiring a high signal-to-noise ratio especially at the high end of the seismic spectrum.
- Seismic lithology prediction provides an initial classification of potential storage layers and storage seals, e.g. by impedance inversion.
- A high-resolution fault mapping at storage depth requires seismic images with a high-signal-to-noise ratio and poststack fault enhancement techniques like coherency processing, in order to detect possible leakages in the reservoir seal, and compartment divisions.
- Both, the initial appraisal of exploited natural gas reservoirs for gas / CO_2 storage purposes, and the final monitoring of active storage processes strongly depends on a reliable detection of residual gas, or storage gas by seismic porefill prediction methods like AVO analysis.

Datasets from several planned or operating gas storage locations were investigated with conventional technology in commercial projects by TEEC in the past. From several suitable 3D surveys, an industry dataset over a depleted gas reservoir in Germany was selected for testing the CRS methodology in this project. It is ideally suited for the planned investigations, since it resolves a proven storage site, and has good well coverage for calibration of results derived from seismic data.

2.4 Evaluation of new CRS methods for gas/CO2 storage investigations

The high resolution CRS imaging of the Gas / CO_2 storage reservoir is expected to provide a significant increase of structural and petrophysical information. The information increase is determined in an interdisciplinary evaluation by geophysical and geological techniques.

The following aspects are investigated and compared for both CRS and conventional results:

- The increase in resolution is assessed by structural geological interpretation in the entire time and depth ranges, leading to general geological models of the storage site.
- The depth accuracy is checked against depths measured in injection and reconnaissance wells.
- A coherency processing is carried out, allowing a detailed fault detection and interpretation in the time/depth range of storage reservoir and sealing beds, with implications to reservoir and seal quality.
- An acoustic impedance inversion of the poststack data is expected to benefit from the high signal-to-noise ratio of the CRS imaging for mapping the low-impedance reservoir.
- The gas fill at reservoir level is assessed by AVO analysis, where the traveltime information for CRS-AVO is obtained from the CRS imaging parameters (Pruessmann et al. 2004).

2.5 Objective summary for development, application, and evaluation of CRS tools

The objectives of the project can be summarised as follows:

- Creation of a 3D CRS imaging method in the time domain for production seismic processing, with numerically efficient and stable algorithms for the search for the CRS stacking parameters.
- Implementation of a strongly parallelized CRS computation method on a parallel hardware platform, selected by the criteria of lowest costs and widest use, and allowing to run tests and applications in a reasonable time.
- Creation of a 3D CRS tomography algorithm and software, for the derivation of reliable velocity-depth models from 3D CRS imaging attributes
- Creation of a 3D Kirchhoff PreSDM method that incorporates slowness data from 3D CRS imaging in order to limit migration to the physically reasonable Fresnel volumes.
- Application of the CRS tools to synthetic 3D seismic data, and to real 3D data from industrial gas storage, comprising 3D CRS imaging in time, PostSDM with the velocity model from 3D CRS tomography, and PreSDM based on Fresnel volumes calculated from CRS attributes.
- Demonstration of the increased structural information with respect to conventional imaging in time and depth domain, by various interpretation techniques including poststack processing with coherency methods.
- Demonstration of the increased petrophysical information with respect to conventional imaging by poststack acoustic inversion, and by prestack AVO analysis based on imaging parameters, with calibration to well parameters

Similar to the presently available 2D CRS tools, the proposed 3D tools represent a leading technology that will contribute to the achievement of Germany's ambitious CO_2 reduction target.

3. Present status and applications of CRS related techniques

From the applications of the 2D CRS software by TEEC, an example is given in Figure 1. It displays the 2D CRS stack versus the 2D DMO stack for an overthrust structure from the prolific Assam Shelf Basin in north-east India. The

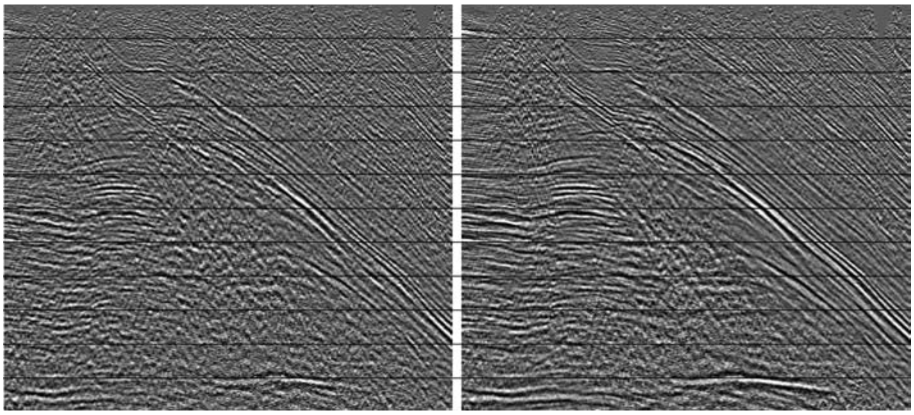

Figure 1: Time domain imaging with NMO/DMO stack (left) in comparison to CRS stack (right).

enhancement of dipping events, and of the signal-to-noise ratio by the CRS technique is obvious.

Whereas a commercial 2D CRS-processing package has already been developed by TEEC, the 3D CRS imaging still requires major work on performance and stability of algorithms in order to provide efficient parameter searches in the huge volumes of typical 3D datasets. Additionally, parallelization would be required to obtain eight CRS stacking parameter for each point of a 3D dataset in reasonable time.

In addition to the imaging result, the CRS stack method automatically provides a set of local stacking parameters, so-called kinematic wavefield attributes, which can be used to determine a velocity-depth model. Recently, a tomographic method for the determination of 2D velocity models based on these parameters has been developed at the University of Karlsruhe (Mann et al., 2003, Duveneck, 2004).

First successful applications of the 2D CRS tomography in an industrial environment have already been reported (e.g. TEEC technical note~#18). Figure 2 compares two velocity-depth models from conventional layer based prestack depth migration (PreSDM) velocity analysis, and from CRS tomography. These models were derived for the overthrust example of Figure 1. The velocity inversion below the thrust fault is very well obtained by CRS tomography.

Figure 3 shows four depth sections for this overthrust example. In the top row, the velocity model derived by conventional PreSDM velocity analysis is used for both PreSDM, and post-

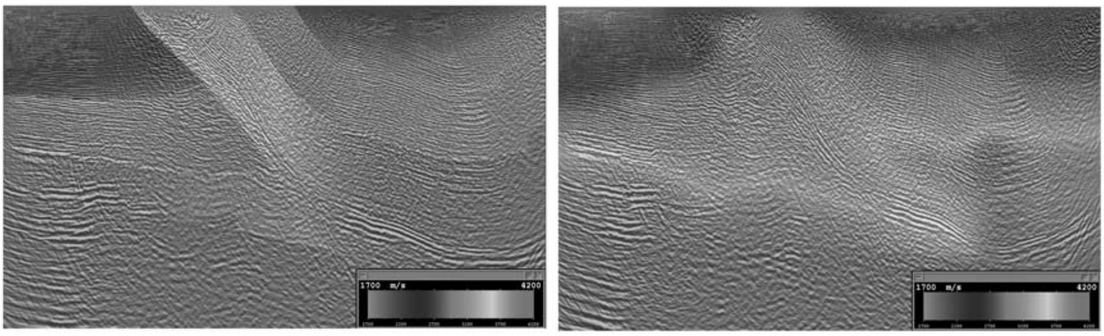

Figure 2: Velocity-depth models from PreSDM (left) and from CRS tomography (right) for overthrust data of Fig. 1. Both models are superimposed on the resulting PostSDM of CRS stack.

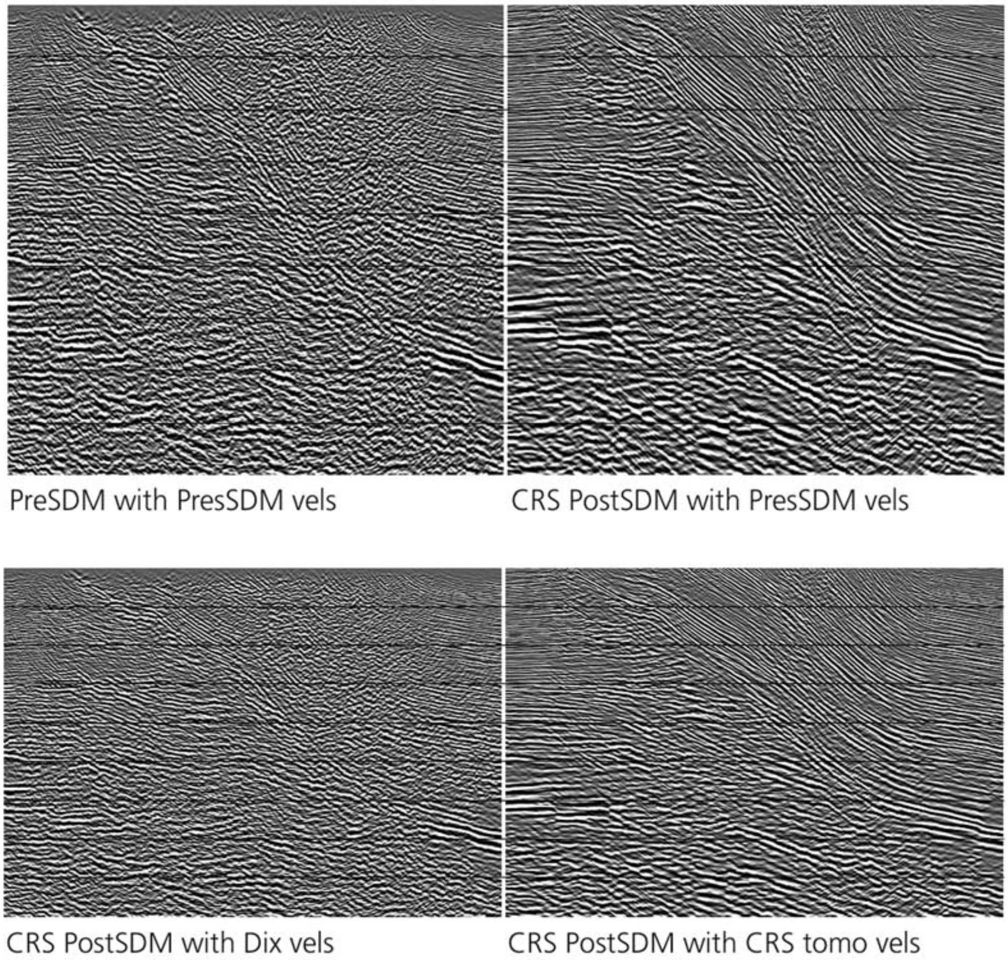

Figure 3: Depth sections from PreSDM with velocities from PreSDM (top left),
PostSDM of CRS stack with velocities from PreSDM (top right),
PostSDM of CRS stack with velocities from Dix inversion of stacking velocities (bottom left),
PostSDM of CRS stack with velocities from CRS tomography (bottom right).

stack depth migration (PostSDM) of the CRS stack. The steeply dipping overthrust layers that pinch out at the surface are much better resolved in the PostSDM of the CRS stack. In this case, the local fit of the CRS stacking surface to the data, and the associated larger stacking fold provide a better signal-to
noise ratio for the CRS depth section. In areas where prestack depth migration suffered from strong noise problems, CRS imaging repeatedly produced superior images.

The PostSDM of the CRS stack from Figure 3 bottom left used a velocity-depth model that was derived by simple Dix inversion of stackin velocities. The deterioration of the depth image shows that the derivation of a velocity model for this overthrust data is no trivial task. PostSDM of the CRS stack with PreSDM velocities, and with CRS tomography velocities are compared in the right column of Figure 3. Though the PreSDM velocities were produced with a much larger effort, the depth sections do not significantly differ in structure and depth. This result indicates that CRS stacking, followed by CRS tomography and PostSDM can be used to produce reliable depth sections with much less effort than PreSDM depth sections. Moreover, the velocity model from CRS tomography can be inserted as an advanced starting model into PreSDM, thus saving some costly iterations of PreSDM velocity analysis.

The CRS processing thus provides two important prerequisites for performing PreSDM more effectively, and more accurately. A reliable initial velocity-depth model is available from CRS tomography, and a slowness field is available from CRS stacking. Kirchhoff PreSDM can be improved by calculating local Fresnel volumes from the CRS slowness information, and restricting migration to these physically relevant volumes.

This strategy has been developed recently for multi-component data where polarisation and slowness data is commonly available (Lueth et al. 2004). It significantly increased resolution in the resulting depth sections since it avoided to collect noise from physically non-relevant portions of the prestack data. The slowness information of the CRS processing now offers an effective possibility to transfer this approach from multi-component data to the usual one-component, or vertical-component data where similar improvements of depth sections can be expected.

The development of the Fresnel-volume migration has been started for the 2D case. Promising results were obtained for synthetic data and saltdome data, using simple methods for slowness determination. The development is now focussed on the extension to the 3D case and on the application of more advanced methods for slowness determination, including the use of CRS attributes.

The presentation of the CO_2CRS project in the kick-off meeting will include an up-to-date status of the ongoing developments.

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Development of the SPIN-Instrument System for Nuclear Magnetic Resonance Exploration and Monitoring of Subsurface Carbon Dioxide Storage (SPIN)

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1 Introduction

Targets

The sequestration of carbon dioxide (CO_2) from industrial exhaust gases and their underground storage in gas and oil reservoirs, coal seams or deep saline aquifer formations can play an important role in decreasing the climate gas emissions.

For a safe and efficient realization of CO_2-storage projects a detailed knowledge of the following geological and hydrogeological properties are a necessary precondition:

- 3D-exploration of reservoir and overburden concerning water and hydrocarbon content, effective porosity and permeability in a stage before CO_2-injection;
- monitoring of the CO_2 fluid extension within the reservoir formation during the injection phase (4D-exploration);
- long-term safety control after termination of CO_2-storage.

The **Sp**ectroscopic **I**maging of **N**MR-Underground (SPIN) is a novel geophysical Nuclear Magnetic Resonance (NMR) technique combined with Time Domain Electro-Magnetics (TDEM) proposed by Geohydraulik Data GdbR. It will provide information concerning subsurface hydrogen distribution, reservoir characterization (water, gas, oil, mixtures) and formation properties, e.g. effective porosity and permeability (Fig. 1). Thus, it will be best suited to give a contribution in solving the above mentioned aims. Furthermore it is expected that commercial exploration services with SPIN is of great interest for the oil and gas industry as well as the geothermal heat and energy suppliers.

Geophysical Surface Nuclear Magnetic Resonance (SNMR) is an established method for the investigation of the first 150 m of the underground. It is expected in accordance with the pre-work studies that greater depths, up to 1.000 m and more can be reached.

Technical and scientific aims are the construction of a SPIN prototype system, the development of new forward and inversion modelling

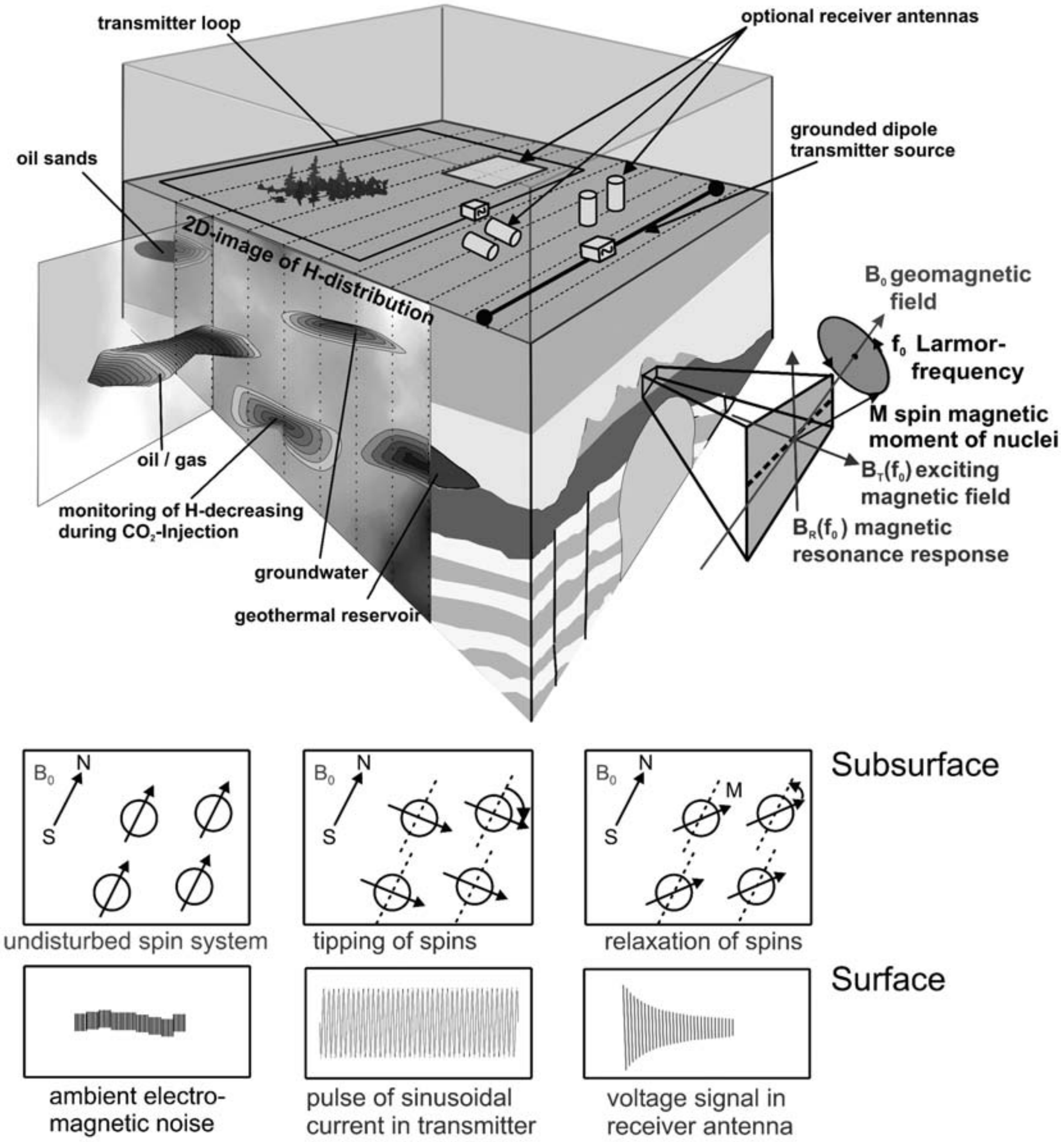


Figure 1: Principles and exploration targets of the SPIN method

software, data processing and analysis and finally the application test at a well-investigated proving site.

Thus, the development of the **SPIN Instrument** System is the main target of the outlined project, which will be performed by the new founded ASIST cooperation group consisting of the institutes of the University of Applied Sciences Gelsenkirchen (UAG), the Technical University Berlin (TUB) and Geohydraulik Data (GHD).

NMR Principle and State-of-the-Art of Geophysical NMR

NMR uses the property of nuclei to possess a spin and a related magnetic moment. In a static magnetic field environment all nuclei magnetic moments of a sample volume will align along or opposite this field, giving a macroscopic net magnetization. Exposed to a transversal magnetic field pulse of a specific excitation frequency, the so called Larmor frequency, these magnetic moments can be flipped out of direction, which results into a synchronous precession movement around the original static field axis. The Larmor frequency depends on the magnitude of the static magnetic field and the gyromagnetic ratio which has a specific value for each type of atomic nucleus.

Right after switching off the excitation source a decaying magnetic field oscillating with the Larmor frequency can be measured, which is from the relaxation - the process of the excited magnetic moments returning into the equilibrium state. The signal amplitude is directly proportional to the number of nuclei that have been excited. Furthermore, the decay curve is characterized by specific relaxation times T1, T2 and T2*, which provide additional information about type and properties of the material. As a third parameter the phase lag between sent and received signal can be used for interpretation.

Beside the classical applications for medical and chemical investigations, the importance of NMR as a geophysical method has arisen from the ability to directly detect and quantify water (hydrogen protons) in the subsurface.

Varian (1962) was the first who proposed in his patent »Ground liquid prospecting method and apparatus« to use Nuclear Magnetic Resonance (NMR) for the non-invasive detection of proton-containing liquids (hydrocarbons and water) in the underground. Nowadays the geological NMR investigation is still a fairly new field of application. Only a few instrument systems are existing.

There is one group, the well logging MRI tools (SCHLUMBERGER-CMR, NUMAR-MRIL), which uses an artificial static magnetic field and gradient fields to measure small volumes (cm^3 – dm^3) in the near well bore zone. They have an increasing application in the oil and gas industry.

The second group are equipments (HYDROSCOPE, NUMIS) based on the Magnetic Resonance Sounding (MRS)-method (Surface NMR) used for groundwater exploration from the earth's surface up to 100 – 150 m depth. The earth's magnetic field is used as the static field and a 150-m-coincident-loop on the surface as the transmitter and receiver antenna.

Developments have been made in the recent years to improve data quality and to extend acquisition and inversion schemes for 2D data, but up to now there is no such system commercially available.

2 The SPIN Method

The SPIN method and technique is a new approach to geological NMR investigation, promising a lot of innovative and advantageous features, as follows:

- rapid data acquisition by using a high-power long-term operating transmitter system with a fixed source (grounded dipole, large loop, etc.) and a plurality of receiver sounding survey sites scanning a large underground area of about 1 - 4 km^2 (excited near field zone of transmitter source)
- high spatial resolution capability by flexible spacing of small receiver units, multi-pass data acquisition strategy and multi-site processing techniques
- great detection depths from surface up to 1.000 m and potentially more
- investigation of 10^5 – 10^7 m^3 of excited underground sample volume
- 1D - 3D imaging results and 4D (monitoring while production or injection)
- spectroscopic analysis of signal response for hydrogen reservoir and multi-component characterization, e.g. identification of water, oil, gas, mixtures as well as effective porosity and permeability estimations.

It is intended by the project partners to design a system which is highly modular and flexible, to best fit the respective survey site conditions. The new system should as far as possible be able to feed different transmitter antenna types and transmit different NMR / TDEM excitation AC and DC pulse sequences.

Since the subsurface resistivity distribution is an important limiting factor (attenuation by skin effect) different types of excitation may be combined and weighted for interpretation. In a high resistivity environment standard NMR might produce best results, while in a low resistive underground stress could be laid on TDEM measurements and special NMR-techniques.

NUMIS / SPIN Comparison
The above mentioned SPIN advantages, especially increased detection depth and providing economically and time-efficient 3D-Imaging, can be achieved by completely redesigning the following system components:

Source Types
Various types of innovative SNMR antenna shapes will be evaluated. The most promising seems to be a grounded dipole, which may be considered as a vertical loop, since the current returns through the earth. Another type of grounded antenna, which includes existing steel casings of deep wells as line electrodes, may have a great potential in increasing detection depth. The site conditions must be considered to decide, which transmitter type is mostly applicable.

Transmitter Pulse Moment
The larger the pulse moment (current * pulse duration), the greater is the maximum depth of investigation. It can be increased either by current amplitude or pulse duration. The power units to be developed will be designed as partially modular units, which can be assembled to provide currents up to 4.000 Amperes and sinusoidal pulses from 40 ms up to 1.000 ms.

Pulse Sequence
By applying a »dynamic« pulse sequence to a nuclear spin it is possible to receive the highest signal-to-noise-ratio per total stakking time. Furthermore different pulse sequence types with varying repetition and recovery times may be used for spectroscopic interpretation and identification of water, oil, gas and mixtures.

Receiver Configuration
The 100 - 150 m receiver square loop used in other systems shall be replaced by a portable flexible receiver unit, using one or several multi-turn coils potentially filled with high permeability material. Many of these units (> 8 for the prototype, potentially > 200) will be distributed within the near field transmitter source area (1 – 4 km^2) in certain arrays, allowing 2D data acquisition schemes and a rapid data acquisition.

Integrated TDEM-Capability

TDEM (Time-Domain Electro-Magnetics; also: TEM) is a common geophysical method to receive information about resistivity distribution in the underground. Since the TDEM system set-up is partly similar to Magnetic Resonance Sounding (MRS) systems, it will take only little effort to integrate a TDEM-system into the SPIN control unit, to get additional information about the underground resistivity and potentially induced polarization (IP) parameters. NMR data interpretation will be much more reliable and be especially helpful in imaging 3D underground structures. Furthermore it is expected that a comparison to the obtained phase lag data will strongly support interpretation work.

The new antenna types will be evaluated for use with TDEM as well. A modelling example of migrating eddy currents produced by a grounded dipole is shown in Fig. 2.

3 Concept, Working Plan & Tasks

Investigation Concept Carbon Dioxide Storage
Exploration and monitoring of subsurface CO_2-storage performed by several SPIN surveys is based on the following conception applicable for abandoned gas and oil fields, enhanced oil recovery, deep coal seams as well as deep saline aquifers:
In all cases the pores, fractures, voids and cavi-

Table 1: New SPIN features and technical comparison of SPIN Instrument System and NUMIS Plus Instrument

Feature		NUMIS	SPIN
Transmitter	Source Type	Moving Horizontal Square Loop, < 150 m	Fixed Grounded Dipole (e.g. deep well earthing) or Fixed Large Loop, >1.000 m
	Loop Area	< 22.500 m^2	> 100.000 m^2
	Excited Volume	-	+
	Attenuation Properties	-	+
	Power Unit Type	Single	Partially Modular
	Current I	< 450 A	< 4.000 A
	Pulse Duration τ	40 ms	40 – 1.000 ms
	Pulse Moment q (I * τ)	< 18.000 A ms	< 4.000.000 A ms
	Exciting Pulse Sequence	1 – 2 options	> 3 options
	Transversal Orientation of Exciting-Field	-	+
Receiver	Antenna Type	Receiver Loop = Transmitter Loop	Separated Receiver Antennas or Receiver Antenna = Transmitter Source
	Effective Loop Area (n * A * μ_r)	< 22.500 m^2	> 100.000 m^2
	Number of Simultaneous Receivers	1	> 8 (prototype), > 200 (covering the whole transmitter source near field zone)
	Delay Time	-	+
	Multi-Site Acquisition and Processing	Not Possible	Possible
	Resolution Capability	-	+
	Data Acquisition Rate	-	+
Other	Resistivity Structure	-	Integrated TDEM-Data
	Long-term Operation	Not Possible	Possible

ties of the rock mass are mainly filled by the hydrogen-containing liquids and gas like water, oil, methane or mixtures.

Because the amplitude of NMR-signals is directly proportional to the number of hydrogen (^1H)-protons, the SPIN method has the capability to detect and quantify the content in the underground.

Under the pressure and temperature conditions in depths of more than about 700 - 800 m the injected CO_2 is a liquid which is removing and substituting the detectable hydrogen-containing water and hydrocarbons within the formation. This process results in a decreasing ^1H proton-saturation and therefore enables the transient change of the CO_2 extension body to

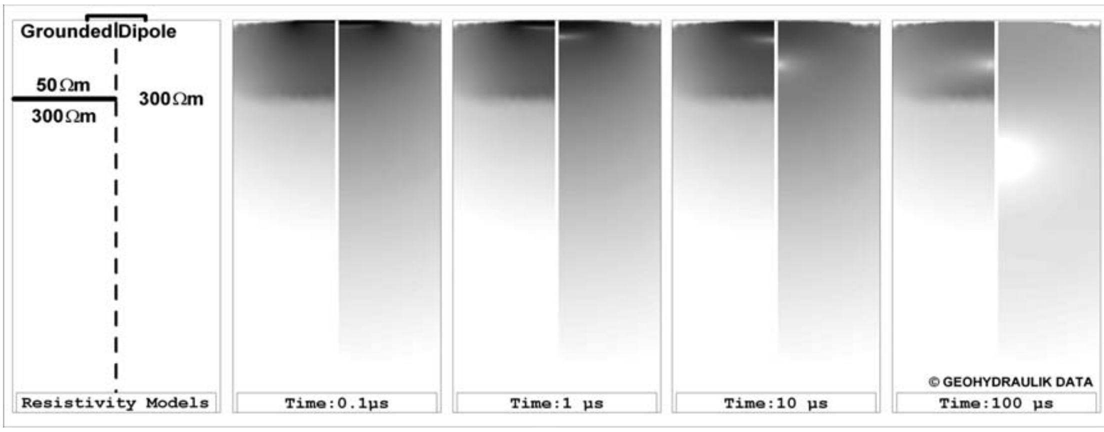


Figure 2: TDEM eddy current propagation using a grounded dipole source (schematically)

be measured by the SPIN method from the earth's surface at different time stages.

A SPIN exploration and monitoring survey from the earth's surface within an area of interest will start before CO_2-injection in order to ascertain the effective porosity and permeability distribution in the storage formation by measuring the NMR-amplitudes and relaxation times.

The near field zone around the fixed transmitter source is covered by a survey grid of receiver antennas. As a result a 3D-image of the underground hydrogen distribution will be obtained.

On the basis of these results optimum injection boreholes can be planned and reference data at zero-time is available, with 100 % water / hydrocarbon saturation in the pore / fracture/ vuggy space volume.

Subsequent survey of the same area during and after the injection delivers the saturation change, which means decreasing ^1H (water/hydrocarbon) quantities and derived increasing CO_2 quantities (4D monitoring).

Furthermore, since the transmitter/receiver configuration is applicable for TDEM measurements, changes of resistivity distribution and IP effects can be monitored as well.

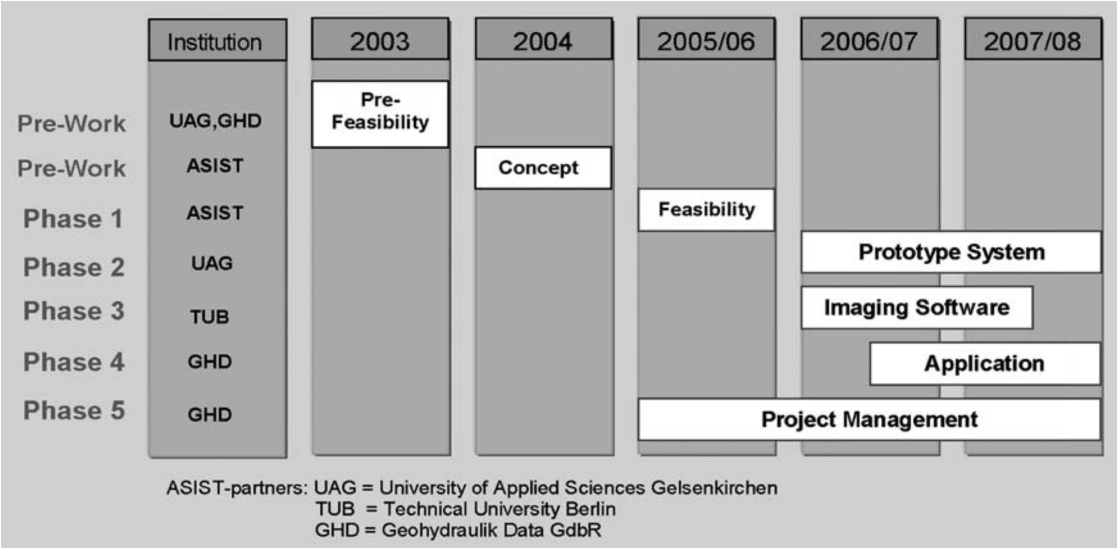
Working Plan
The SPIN Instrument System development project is divided into five task-phases which depend partly on each other subsequently (Table 1). The pre-feasibility study and the project conception were already accomplished within pre-working phases.

In the first step a one year feasibility study has to be carried out which has to prove the milestone criteria, that an investigation depth of 1.000 m can be reached with the budget available. If successful, the main study, including prototype construction, imaging software programming and application test, will follow within the remaining two years.

The main project tasks have been assigned to the partners as follows:
- Geohydraulik Data: Project Management, Choice of Proving Ground, Application
- UAG, Energy Institute: Transmitter system and power supply
- UAG, Department of High Frequency Technology and Digital Radio: Receiver system and signal processing
- TUB, Department of Applied Geophysics: Forward modelling and Imaging Software

Feasibility Study
To prove feasibility, the following queries have to be answered in detail and summarized in a report:
- What are the magnetic field conditions (strength, duration, orientation, local distri-

Table 2: Project schedule



bution) to provoke measurable signal response from a depth of about 1.000m and possibly more?
- What are the technical parameters of the transmitter unit and generator to realize these magnetic field demands?
- In which range is the magnetic field strength to be measured by the receiver at the earth's surface of the proving ground site?
- What are the necessary technical parameters of the receiver system to record this magnetic field?
- Is the expected budget sufficient to realize the whole »SPIN 1.000 m deep NMR-project«, especially the necessary hardware costs of transmitter, power supply and receiver units?

The following tasks have to be solved by the ASIST-partners during the feasibility study:

- Choice of Proving Ground (GHD)
  A hydrocarbon field or abandoned hydrocarbon field has to be found in a depth range of about 1.000 m. The overburden and the water, oil or gas containing formation has to be defined in geophysical-geological terms of resistivity and effective porosity distribution.

- Forward Modelling (TUB)
  The SNMR kernel function for the new suggested transmitter-source-types have to be developed for a numerical modelling of the complete signal path and its intensity. Based on this tool, simulations for different geological-geophysical scenarios and for the discrete proving ground situation have to be carried out.

- Transmitter/Receiver Specification (UAG)
  With a low energy transmitter unit the basic electrical parameters have to be obtained by several field tests. Together with the forward modelling results, a profound assessment of the realization possibilities and technical parameter specification for the transmitter and receiver system with respect to economic aspects will be the result of this task.

Prototype System (UAG)
Based on the feasibility study transmitter and receiver specifications a prototype system will be designed and constructed. It includes several hardware components (transmitter unit, energy supply, source antenna, receiver units) as well as software components for controlling acquisition.

Imaging Software (TUB)
The development of 1D, 2D (potentially 3D) inverse modelling programs for data processing, evaluation, imaging and interpretation shall be accomplished within task-phase 3.

Application (GHD)
Application phase comprises the general evaluation of the geological exploration potential of the SPIN method and the performance of the SPIN investigation test at the chosen proving ground. For the application potential the following tasks have to be carried out.

- Analysis of Exploration Targets
- Geological-geophysical Model Definition
- Synthetic Modelling
- Evaluation and Assessment of Results

Finally the application test will consist of the following steps

- Preparation of Field Campaign
- Field Survey
- Data Processing and Interpretation
- Comparison and Assessment of Results

4 Hardware: Basic considerations and tasks

Transmitter
To generate the variable excitation frequency (2000±500 Hz) a resonant circuit rectifier shall be used. The technology is well known since tens of years and is implemented with good success in the area of inductive heating.

The transmitter shall generate sufficiently high voltages to drive sufficiently high currents (~kA) via a large insulated dipole (~1 km length) grounded at both ends and the ground beyond the dipole antenna. Furthermore the transmitter shall be able to drive the current via a large insulated loop antenna (~1 km radius) positioned directly on the ground.

The voltage/current frequency shall be adaptable between 1500 and 2500 Hz with accuracy between 100 to 500 mHz depending on the changing earth's magnetic field requirements.

The electrical data of the transmitter/loop unit shall be
- power losses < 400 kW
- current level < 4 kA.

The final specification of the electrical data (especially voltage and power level) greatly depends on the findings during the feasibility study about
- the magnitude of the magnetic field necessary to excite the atomic spins sufficiently to generate an electromagnetic response sufficient to be detected at the receiver
- the electrical conductivity and inductivity of the ground
- the type of the antenna (loop antenna, dipole antenna, other antennas)
- the hardware parts to purchase in combination with the foreseen funding

The transmitter shall be constructed as a mobile device with modular loop-capacitor units to be potentially able to increase the power of future exploration systems to values necessary to generate the required magnetic fields at higher exploration depths or larger exploration zones. The main part of the transmitter will be a resonant circuit rectifier with transformer unit and tuneable inductivity. To overtake the reactive volt-amperes medium-frequency capacitors foreseen for serial and parallel connection are required. To get the right current level a medium-frequency transformer is needed. To get the right frequency levels one or more tuning inductivities have to be included. For the mobile device a Diesel generator will be used.

Risks
The technology of resonant circuit converters is well understood for devices in the 10- to 100-kW range. However, the construction of this unique and commercially not available high-power transmitter chain implies a couple of technical risks like the following:
- In-time tuning of the frequency during the operation of the transmitter modules
- Self-safety in the case of a malfunction
- Interaction with the receiver
- Switch-off (high level energy has to be dumped completely in a very short time to avoid interfering with the back-coming signal of the hydrogen atoms)
- Contact between ground and the ends of the dipole or comparable antennas
- Interface to persons, nature and technical

devices (example: weather, vandalism, animal bite, electromagnetic compatibility)

Research Tasks

- Construction, build-up and test of the prototype. The device shall run with the highest possible voltage. This requires some investigations about the voltage strength of the transmitter insulator components at the required frequencies. The question between which values the inductivity has to be tuned and how to construct the tuneable inductivity has to be investigated. Some interface problems have to be solved. After successful tests modular parts of the transmitter will be built-up at a company.
- A feasible switch-off unit has to be specified, to be built-up and tested.
- A supervising unit has to be specified and developed allowing the control of the whole transmitter system (start and stop of the Diesel engines supplying the transmitters; start and stop [dump] of the transmitter; control of the intactness of the antenna).
- The contact between ground and antenna has to be specified and to be investigated.

Receiver

The receiver shall detect the generated narrow-band sinusoidal magnetic field strength from the radiating nuclei below the earth surface. It delivers a measured voltage value, which depends on the active volume of investigation, exploration depth and field strength amplitude of the stimulating magnetic field. The maximum investigation depth is limited by the receiver noise and man made noise.

The receiving system will consist of a collection of individual, autonomous widely spread antenna units that collect the receiving field data and an information centre that processes the data of all antenna units to gain the information of the local distribution of the nuclei. The information link will be radio based or LWL based.

The individual antenna receivers have to sense the local incoming magnetic field from the nuclei and determine the parameters amplitude and time constant of the received damped sinusoidal waveform. They consist of

- antenna array to sense the nuclei response field
- trigger unit: to detect the radiated pulse from the transmitter
- receiver front end: with a low noise amplifier and a time gating circuitry
- signal processing unit: with digital filtering noise reducing algorithms
- data storage unit
- energy management unit: for battery powered operation
- information transmitting unit: sends the collected data to the information centre unit
- information centre unit: collects all data from the individual dislocated antenna units and acts as a data server for the 3-dim data processing.

The following overall characteristics should be achieved

- Frequency range: 1500 – 2500 Hz
- sensitivity: < 100nV
- noise figure <3dB

Risks

The receiver unit has to detect very low level signals from the nuclei and to reject very high level signals in the same frequency band from the transmitter. In contrast to RADAR systems where a similar situation is well known and techniques like directional couplers and mode damping is applied in the gigahertz region, these techniques are not working in the lower kilohertz region. No commercial available single receiver unit is available which is solving the following technical risks:

- low noise amplifier with adaptive input filter
- low noise fast gate circuitry to blend out the time window where the transmitting signal is applied
- digital noise reduction DSP algorithms for noise shaping and adaptive channel estimation pole fitting to detect the decay rate
- wireless/optical synchronisation to the transmitter
- cooling of the LNA (optional)

- symmetric structure to reduce man made noise and magnetic change artefacts due to fluctuations on the ground surface, in the atmosphere and due to sun storms etc.
- low frequency shielding techniques

Research Tasks

- Final specification of the technical data of the receiver: This task requires the definition of the actual 1/f and thermal noise figure, the maximum jitter between the averaging measurements, the frequency jitter of the transmitter and the overall man made noise level. This work will be done by HFD.
- Construction, build-up and test of one proto-type receiver module. This work will be done by HFD. The receiver module includes a autonomous antenna module with antenna, analogue and digital filtering/signal processing unit (DSP), the information centre, that collects the data of the dislocated antenna units and the information server that delivers the data to the 3-dim processing unit. The interface problems have to be solved. After successful tests additional antenna modules will be added.
- Methods to reduce the overall 1/f, thermal and man made noise have to be implemented and tested. These include analogue and symmetrization tasks as well as digital noise shaping and optimal channel estimation algorithms.
- Low frequency EMV means
- Synchronisation tasks between the transmitter and the receiver

5 Modelling and Inversion of Surface-NMR

Modelling and inversion of Surface NMR measurements are meanwhile quite advanced so that various effects can be accounted for reliably (Mohnke and Yaramanci 2005, Braun et al. 2005, Hertrich and Yaramanci 2002, Mohnke and Yaramanci 2002). However, these are only for the standard lay-outs with surface loops as transmitter and receiver. Recently SNMR with separated loops on the surface has successfully applied and can be modelled and inverted (Hertrich et al. 2005, Hertrich et al. 2005a). For non standard lay-outs as they are necessary for the project here new modelling and inversion schemes are to be developed taking all the recent progress and developments in account as for example the effect of resistivity. In particular modelling of new lay-outs is essential to assess their sensitivity to changes at target depths. This is the prerequisite for designing and building the new SPIN equipment. Currently some modelling with coincident surface loops demonstrate the basic difficulties and also the approach.

From the fundamental equation of the SNMR signal (Legchenko 2002, Yaramanci 2000, Hertrich et al. 2005a) response it becomes obvious that the penetration depth of the method can be controlled by the variation of the exciting magnetic field induced by a surface loop. The variation can here be achieved by changing the loop size and the current through the loop. In SNMR applications increasing the current, i.e. the magnetic field strength, does not only increase the penetration depth but also leads to a complex shaped focus depth, where the method shows the maximum sensitivity to stored hydrogen protons. The sensitivity of a sounding, consisting of a set of increasingly strong pulses, versus depth is commonly called the SNMR kernel function. Graphically displayed as contour plots the maximum penetration depth and depth resolution for a given loop configuration be can directly estimated. The distribution of the induced magnetic fields at the given frequency of some 2 kHz is additionally influenced by the Earth's resistivity: a lower resistivity attenuates the magnetic fields and consequently decreases the SNMR penetration depth.

Figure 3 shows the kernel function for loop radii of 1000 m and 500 m respectively, on a 100 Ωm and 1000 Ωm half space. In all subplots the characteristic tail of the sounding sensitivity is visible with increasing excitation intensity. Comparing the two leftmost figures shows the difference in subsurface sensitivity for a wire loop of 1000 m radius. For this loop the depth penetration at 1000 Ωm half space resistivity is about twice as deep as for 100 Ωm, the maximum amplitudes are about constant. The rightmost figures show the same dependency for loops of 500 m radius. Here, compared to 1000 m radius loops mainly the amplitude of the sensitivity function is significantly reduced whereas the penetration depth shows only a minor decrease even though the loops size is halved. The effect of significant attenuation for the 500 m radius loop is also observed comparing the 1000 Ωm and 100 Ωm case, but for the larger loop it is more prominent.

The penetration depth of SNMR soundings is consequently determined by the loop size but is significantly limited by the local settings of subsurface resistivity. The geological settings have thus to be carefully considered for the design of optimal loop configuration to reach maximum target depth. Previous investigations on smaller loops show that resistivity layering additionally influences the depth sensitivity (Braun 2004).

Based on the introduced kernel function, a synthetic sounding can be derived by the multiplication of the kernel function with a water content distribution with depth (Yaramanci 2000). According to the project demands we already evaluated on an exemplary subsurface model the influence of the desaturation of a water i.e. hydrogen-bearing layer on the variation of measured SNMR signals. The initial layer was assumed to spread from 550 – 600 m with a water content of 30% (Figure 4 left). The respective sounding curves for such a layer are displayed as dashed lines in the figures to the right for the loop and resistivity settings above. For the given investigation the layer under investigation was then decreased to a thickness to 5 m spreading from 595 m to 600 m. The corresponding sounding curves are additionally given as solid lines.

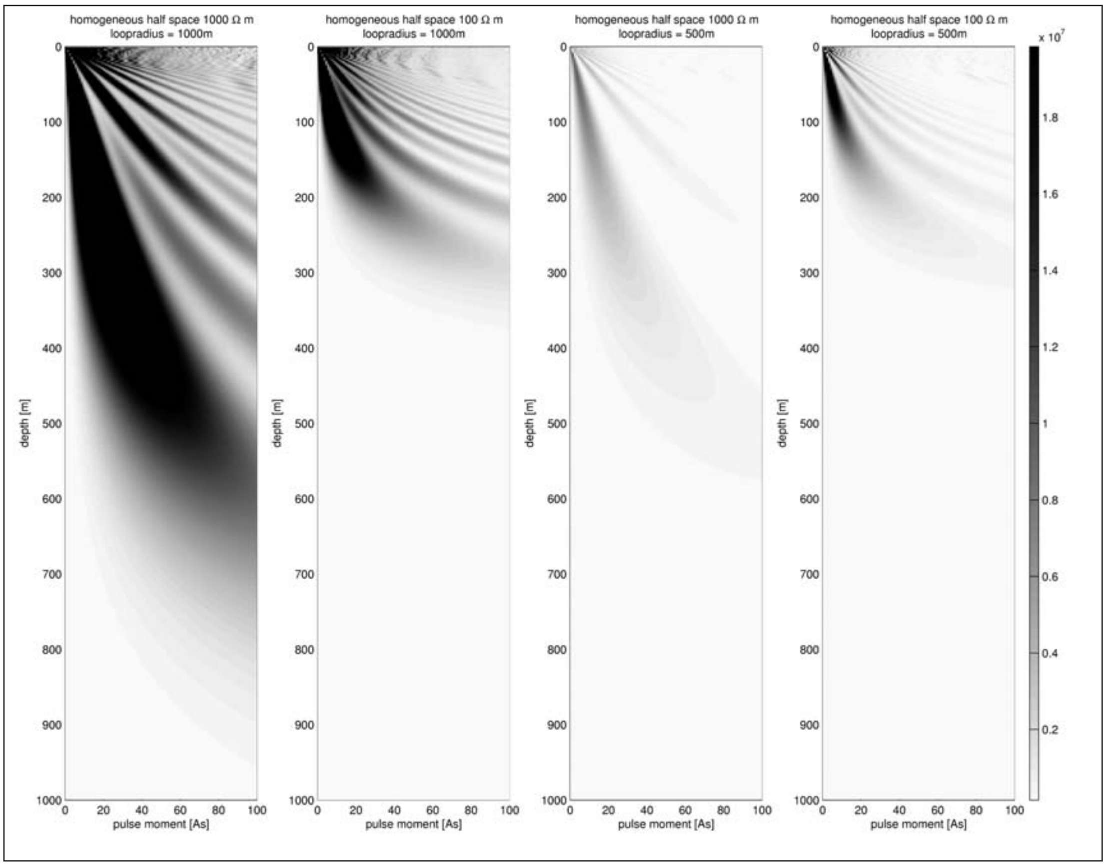


Figure 3: Sensitivities (Kernel functions) for SNMR measurement for surface loops

Interpreting the results a significant difference of the two layer models can be observed both for the 1000 m and 500 m loops in case of resistive ground (1000 Ωm). For a more conductive ground the difference of both soundings is considerably smaller. Note the different scaling of the sounding curves for both resistivities, which indicates that response amplitudes are about ten times smaller for 100 Ωm than for 1000 Ωm. The observed results are in good agreement with the interpretation of the kernel function above. It shows that for more conductive ground the penetration depth is reduced such that the layer under investigation is below the penetration depth, whereas the kernels for higher resistivity still show significant sensitivity in the target depth to measure reliable changes in signal response from that layer. Here, the difference between 500 m and 1000 m loops is mainly given by decreased amplitude of the signals. The relative changes in both sounding curves are about comparable.

To assess the feasibility to render the given layer settings from measured data by inversion the synthetic soundings were artificially noise disturbed and inverted by a Simulated Annealing algorithm (Corona et al. 1987). Due to the statistical nature of the noise samples and inversion algorithm repeated runs of the inversion lead to different optimum models. The variation of the various found models gives additional information on the reliability and reproducibility of the results. Figure 5 shows on the left the two models (from Fig. 4) with the respective set of noise disturbed sounding curves for both layers to the right. For each inversion run a new statistical noise disturbance was used. The found models by the inversion are shown in the two rightmost columns for the models of the initial and desaturated layer respectively. It shows that the layer of 50 m thickness is represented by a set of models ranging in the thought depth region with reliable water content estimations. The inversion of noise affected data of the layer

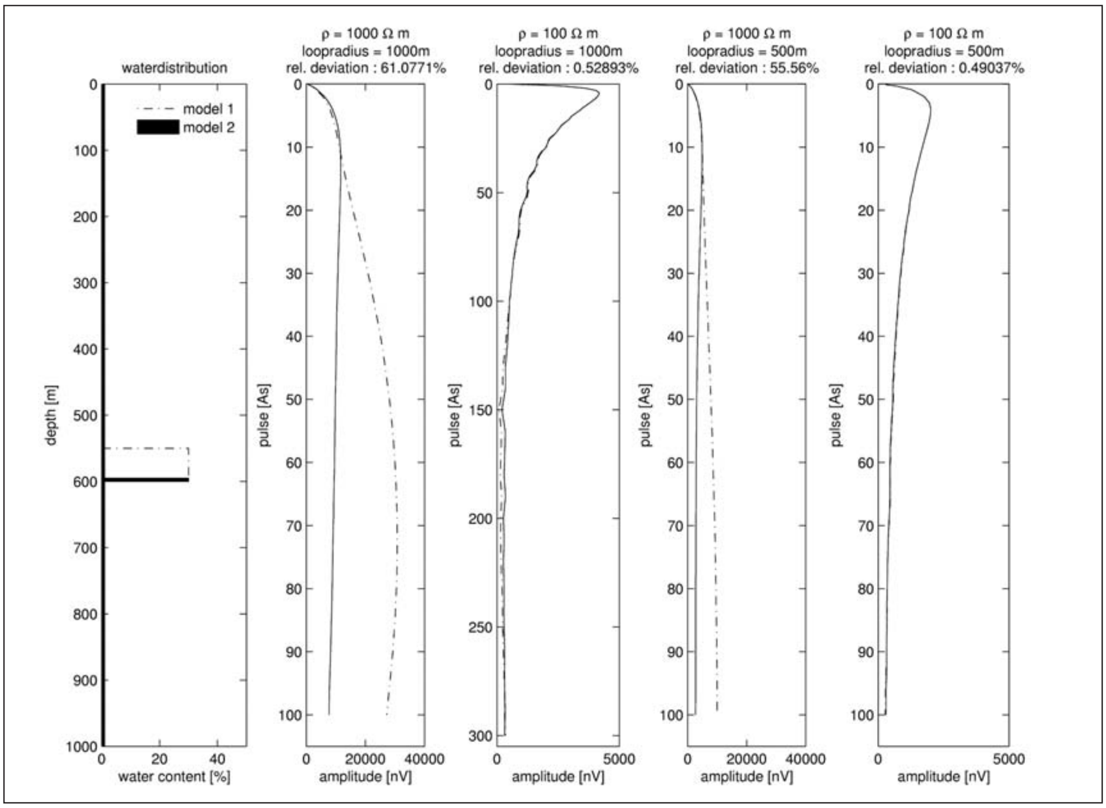


Figure 4: Effect of water removal on SNMR measurements

decreased to 5 m shows a poor rendering of the initial model concerning the correct layer boundaries. In most cases the algorithm converges to models with about equivalent integral water content, but in thicker layers with small water contents. Such small layers in the sought depth can consequently not be reliably recovered concerning location and water content under natural noise conditions. A monitoring of water content variations in a layer of known extension is, however, still feasible.

6 ASIST Partners

The University of Applied Sciences Gelsenkirchen has become ASIST partner with three departments. The High Voltage Technology Department and the Electrical Machines and Power Electronics Department (both part of the Energy Institute) provide excellent experience and equipment for designing and constructing a high power magnetic transmitter source, which is necessary to reach the aimed depth of penetration. The Department of High Frequency Technology and Digital Radio will provide its expertise for the high accuracy receiver design and hardware as well as signal processing.

The Department of Applied Geophysics of the Technical University Berlin has got one of the most active and advanced SNMR research groups worldwide. They provide a unique competence about modelling, inversion, processing and interpretation of SNMR data.
Geohydraulik Data GdbR started to perform geophysical and hydrogeological surveys in 1986. Their activities have covered a wide range of geophysical methods and geological consulting in several countries. Moreover, numerous patents and approved innovative developments of new instrument-systems have arisen over the years.

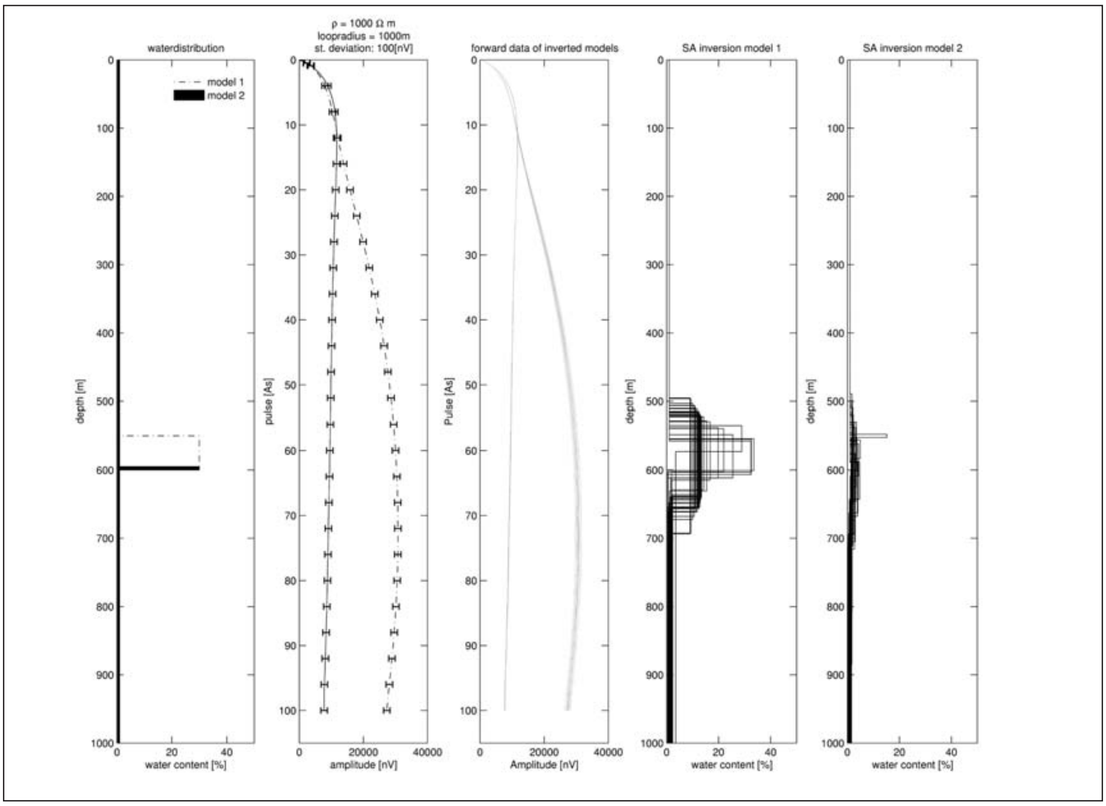


Figure 5: Inversion of SNMR data (from FIG. 4)

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Assessment of the Long - Term Risk and Sustainability of Underground Storage of CO_2 in Germany: Current Practises, Future R&D-Needs and Development of Methodologies (CO_2-UGS-Risks)

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Abstract

The general objective of the project is the development of a common performance assessment methodology for geological CO_2 storage options that shall be applicable for typical sites located in Germany. This will include the adaptation of the Features-Events-Processes (FEP) procedure that is used in assessing the risks associated with the underground disposal of radioactive waste. This approach allows to identify and rank the critical performance parameters for underground CO_2 storage. For each of the three geological storage options in Germany (depleted gas field, saline aquifer, unminable coalbed) a comprehensive set of scenarios, including the normal evolution and the disturbed evolutions, will be derived on the basis of the relevant FEPs and the most important loss of CO_2 containment modes will be identified. Subsequently, for one storage option performance assessment calculations will be carried out for a hypothetical site that resembles a typical geological situation, in order to demonstrate the applicability of the approach. On the basis of this, unresolved scientific and technical questions will be identified and, as far as possible, feasible solutions will be proposed or additional RTD work will be recommended.

Introduction

Capturing CO_2 and storing it underground is one of several CO_2 abatement strategies considered today in several countries. In recent years this option has received increasing public awareness in Germany for the following reasons: (1) about 50 % of the national CO_2 emissions stem from large stationary sources where capturing CO_2 is feasible with available technology, (2) a sufficient capacity for underground storage in different geological settings has been identified in Germany, and (3) cost estimates suggest that CO_2 capture and underground storage could become a cost-effective mitigation option.

There are a number of potential geological reservoirs that can be used to store captured CO_2. in Germany (May et al., 2003): depleted gas reservoirs, deep saline aquifers, and unminable coalbed. Considering R&D needs, available storage capacities and costs for site investigations, the first choice in the short term seems to be CO_2 storage in depleted gas reservoirs and in the mid term also in deep saline aquifers, which represent the largest potential capacity in Germany.

The long-term underground storage of CO_2 is associated with some risks concerning health and safety of man and the environment (HSE-risks), most of which are related to the loss of the containment function of the storage reservoir or aquifer and the subsequent migration of CO_2 back to the biosphere. In the early studies, safety issues were addressed by separately considering the surface system, the injection process, and the storage reservoir. For each of these systems an assessment of possible failures that might result in CO_2 emission to the atmosphere was made. In general, it was concluded that with standard oil industry practices and extra precautions the risks of uncontrolled emissions could be eliminated (van der Meer, 2003). In the late 1990s public acceptance of CO_2 injection projects became an issue, calling for a more structured approach to risk assessment. Systems analysis has proved to be a well suited tool for assessing the performance and safety of geological disposal of radioactive wastes and this approach is now being applied to the long-term geological storage of CO_2.

General safety assessment methodology
According to the terminology commonly used a performance assessment (PA) is an analysis to predict the performance of a system or a subsystem followed by comparison of the results with appropriate standards or indicators. A PA becomes a safety assessment, when the system is the overall system (here: the entire storage site with reservoir rock, overburden and biosphere) and the performance measure is related to some HSE impact. If the performance measure includes the probability of occurrence of the impact, the PA is usually termed risk analysis (RA). PAs can be used to describe the analysis and comparison of systems at a variety of levels and requirements.

In a PA, a certain set of scenarios representative for the storage site is evaluated. A scenario describes the possible evolution of the storage site which is characterised by an assumed set of features, events and processes (FEP). This approach ensures a comprehensive consideration of all potentially significant factors in the assessments. The number of FEPs for subsurface storage identified is in the order of magnitude of several hundreds (Kreft et al., 2003) and thus they have to be reduced to a subset by screening with respect to their potential HSE impact and in case of a risk analysis to the incidence rate, too.

After identification of the most important or at least the worst-case scenarios, the scenarios are transferred into conceptual models which form the basis for mathematical models to quantitatively calculate a performance, safety, or risk measure. The conceptual model comprises a set of assumptions to describe the system. Often, these assumptions are of a simplifying character and they concern the geometry and dimensionality of the system, initial and boundary conditions, time dependence, and the nature of the relevant physical and chemical processes.

Project outline
In order to develop a common performance assessment methodology for geological CO_2 storage options that is applicable for typical sites located in Germany, the project is divided into several tasks, some of which depend on data and information derived in other tasks. The flow of information is schematically shown in Figure 1.

Mainly on the international level a substantial number of research projects have been carried out in the field of geological CO_2 sequestration during the last two decades (Gale & Kaya, 2003), which will be drawn on as far as possible.: In addition, pertinent information will be requested from the other national projects which are carried out in the framework of the national Geotechnology research programme »The utilization of the underground in order to promote global climate protection«. A detailed request form is now being developed and will be sent to the institutions involved in these projects, in order to obtain the required infor-

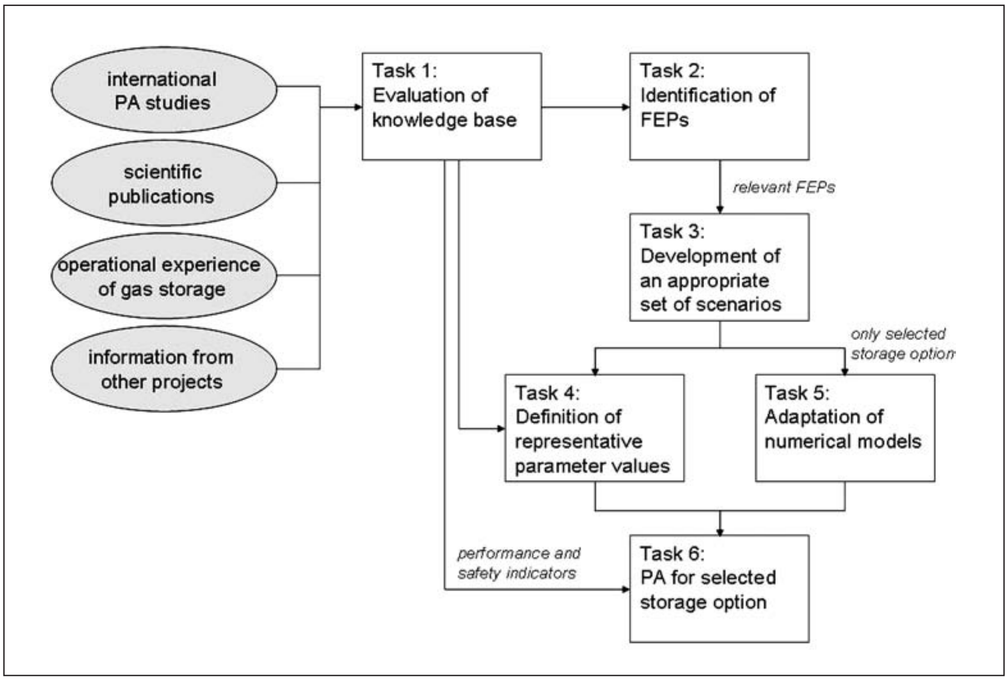

Figure 1: Outline of project tasks and flow of information

mation with particular emphasis on the relevant features, events and processes. All this information will be evaluated, adapted, and documented as necessary in the project.

In a second step the Features-Events-Processes (FEP) procedure will be adapted that is used in assessing the risks associated with the underground disposal of radioactive waste. This approach allows to identify and rank the critical performance parameters for underground CO_2 storage.

For each of the three geological storage options in Germany (depleted gas field, saline aquifer, unminable coalbed) a comprehensive set of scenarios, including the normal evolution and the disturbed evolutions, will be derived on the basis of the relevant FEPs and the most important loss of CO_2 containment modes will be identified. Subsequently, for one storage option performance assessment calculations will be carried out for a hypothetical site that resembles a typical geological situation, in order to demonstrate the applicability of the approach. For this, numerical models will have to be adapted.

In all tasks, unresolved scientific and technical questions will be identified and, as far as possible, feasible solutions will be proposed or additional RTD work will be recommended.

Previous safety assessments

In several R&D projects, risk assessment activities have recently been performed or are currently underway. These projects cover the whole range of potential geological reservoirs, both on-shore and off-shore. In some of these projects performance and safety assessment methodologies are applied that were adapted from respective risk assessment studies related to the storage of radioactive waste (Gale, 2003). One of the objectives in the project is the adaptation of PAs already performed for situations similar to the three potential on-shore storage options in Germany. Based on a survey of the accessible international literature a systematic description of current practices and lessons learnt from performance and risk assessments will be given. In order to round off this information, direct contacts to relevant researchers that are known to be active in this field will be sought to get the relevant information.

The following aspects are documented inter alia

- the type of PA that has been performed, i.e. whether the safety measure is impact- or risk-based, and whether the assessment uses deterministic or probabilistic approaches,
- the storage options that have been investigated and the quantity of available data,
- the underlying features, events and processes
- the treatment of uncertainties in models and data, and
- the safety and performance indicators that have been taken as safety measures.

An important result of this task will be a list of performance and safety indicators to be used in the assessment of HSE-impacts. Among these indicators may be the leakage rate or CO_2-flux, respectively, and groundwater pH changes.

FEP analysis

On the basis of generic FEP-databases made up for radioactive waste disposal issues (NEA-OECD, 2004) and CO_2-sequestration (Savage et al., 2004) a comprehensive set of FEPs relevant to German storage options will be compiled in a database. This will include information derived in task 1. In addition, the operational experience from the 42 German storage facilities for natural gas will be taken into account. With regard to FEPs, also current international CO_2-injection projects such as the SLEIPNER off-shore aquifer of Statoil in the North Sea, the RECOPOL-project of CO_2-injection in Polish coal seams, the ALLISON-USA-project of CO_2-injection in coal seams will be considered as well as the experience of CO_2-production from geological reservoirs by deep wells.

The following FEP's are already known to be especially relevant:

- the wellbore integrity to prevent CO_2-leackage behind the casing,
- the sealing function of the caprock against CO_2-displacement and diffusion,
- the CO_2-tightness of tectonic faults, and
- the areal CO_2-bubble closure to prevent flow across the spill point.

Special emphasis will be laid on the distinction of FEPs between those characterising the normal evolution of the storage system and those describing a disturbed evolution. The normal evolution FEPs are associatied with the functioning of the system as expected. In contrast, disturbed evolutions describe unintended features of the system, including the occurrence of faults due to mechanical stress, human intrusion into the storage horizon, and leakage of CO_2 through undetected pathways or technical seals. The identification of a representative set of disturbed evolutions is of high importance, since such scenarios might lead to more detrimental consequences than the normal evolution scenarios.

The most important objective of this task is to identify the relevant FEPs that have to be considered in performance assessments and to provide scientific reasoning for their selection. In accordance with common practice, a screening technique will be applied, e.g. (Locke & Bailey, 1998), to the comprehensive set in order to omit those FEPs having either low probability of occurrence or low expected impact from further consideration.

Scenario development

A scenario describes a potential temporal evolution of the storage site, taking into account the associated FEPs. Starting with the injection of CO_2 into the host formation, the release of CO_2 into overlying strata and finally to the biosphere has to be considered. All of these processes must be considered for normal and for disturbed evolutions of the site. For each of the three feasible geological storage options in Germany, representative scenarios will be developed taking into account the differences in storage and potential release mechanisms. In the following, the procedure is briefly exemplified for the case that CO_2 is stored in a porous aquifer.

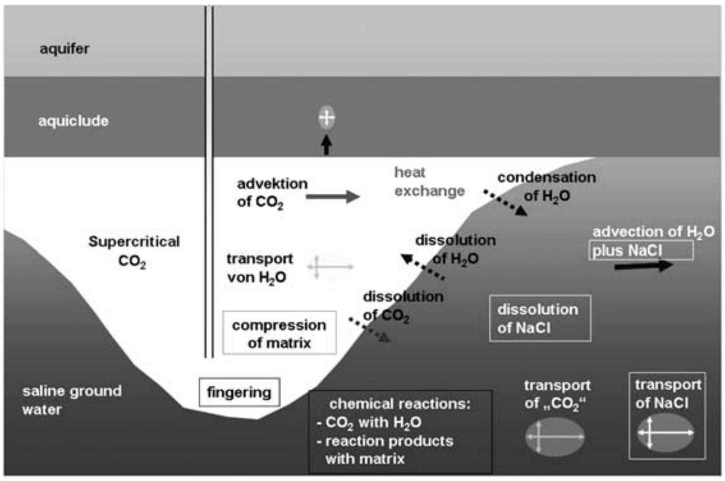

Figure 2: Simplified sketch of possible processes to be considered in the normal evolution scenario of CO_2 injection into a deep porous aquifer which is not of technical interest due to high salinity

It is assumed, that CO_2 is stored in a deep porous aquifer, which is not of technical interest due to high depth or high salinity. Potential FEPs and scenarios to be considered could include:

- CO_2 is injected under high pressure as a fluid (i.e. liquid or gaseous state).Under the pressure and temperature conditions at the storage horizon, CO_2 will undergo a phase transition into the supercritical state.
- The stored CO_2 displaces saline water from the aquifer in horizontal direction.
- Under normal evolution, CO_2 will be stored in the aquifer. The inhibiting layers are poorly permeable to CO_2, thus CO_2 can escape vertically only by slow diffusion and slow advection (stratigraphic trapping). It can not escape in horizontal direction, on conditions that a limiting volume of CO_2 is not exceeded which is determined by the spill point of the structure, and that the ground water velocity is slow (hydrodynamic trapping). Other potential trapping mechanisms include solubility trapping and mineral trapping. Possible processes to be considered in the normal evolution scenario are schematically shown in Figure 2.
- In the case of overpressurisation, uncontrolled lateral CO_2-flow may result.
- Under disturbed evolution, a fault can be assumed to develop by stress or earthquake. The consequence could be a transport of CO_2 along the fault through the inhibiting layers, which would be much faster than the diffusive transport.
- Another disturbed evolution resulting in a loss of CO_2 containment is that the technical seal surrounding the injection borehole deteriorates leading to a direct upward motion of CO_2.

The consequences of CO_2 migration are calculated as CO_2 fluxes into the biosphere aquifer.

In case that a former gas reservoir has been exploited and is now being used for CO_2 sequestration, in principle, the scenarios for that storage option are similar to those described above. Since the reservoir was filled initially with gas or oil, it can be assumed – at first glance - to be impermeable also to CO_2. However, a number of processes have to be considered which may increase the risk of leaking and disruptive events for this storage option. Due to rock movements as a consequence of gas exploitation, the probability of fault opening is relatively high. Also the number of access drillings to the reservoir penetrating the caprock is high and the existence of old wells with leackage problems has to be taken into account. It is technically feasible and economically advantageous to increase the storage pressure above the inital reservoir pressure, since this results in a higher storage volume. Such an overpressure would disturb the pressure equilibrium between reservoir and caprock.

Modelling aspects and data requirements

Scenarios provide the basis for numerical calculations. For the selected storage option to be investigated in detail, therefore, the associated FEPs will be transferred into conceptual models and, finally, into physical and chemical models. These models will be implemented in computer codes to calculate release and transport of CO_2.

For the selected storage option, a model for the storage site will be constructed which resembles a typical geological situation. This model will be used in the following as reference system, for which representative (generic) parameter values will be used in the study. Required data entail e.g. the geometry and stratigraphy of the reservoir rock and overburden. Values for porosity, permeability, and storage coefficient have to be assigned to each rock type. In addition, assumptions concerning the groundwater flow field, fractured zones, the typical number of access boreholes, and other boundary conditions, e.g. pressure distribution and initial temperature field, will be made. For the other storage options, which will not be dealt with in detail, also typical geological situations will be discussed and a summary of necessary data will be given, to allow for further investigations in the future. Performance assessment calculations, however, will not be carried out for these options within this project.

Relevant field data will be provided by the project partner DBI-GTI based on their 35 years of experience in the investigations of all geological types of underground gas storage and their participation in the ongoing CO_2-injection projects RECOPOL (CO_2-injection in Polish coal seams) and CO_2*SINK* (CO_2-injection in aquifer Ketzin nearby Berlin). In addition, further data are required that will be derived from the literature and other sources where possible. For example, in order to model CO_2 storage in a deep saline aquifer, the physico-chemical parameters listed in Table 1 are required to describe the phase behaviour of the system consisting of two phases (CO_2 and H_2O) and up to four components (CO_2, H_2O, NaCl, heat). Most of these parameters show a significant dependence on pressure and temperature, which should be taken into account. Also several parameters depend markedly on the salt concentration in the aqueous phase. However, some of these data and dependencies are not known very well, so that certain simplifying assumptions or extrapolations have to made. Should this be necessary, it will be documented and the possible influence on the modelling results will be estimated.

To calculate the migration of CO_2 in the deep underground, mainly two-phase flow models must be applied. Several established computer codes, e.g. TOUGH2, MUFTE-UG and ECLIPSE 100–300, could be used for this purpose. Possible limits of applicability of these computer codes shall be identified and discussed. This holds especially for disturbed evolution scenarios, such as transport in faults or leakage around technical seals. A real challenge for

Table1: Required physico-chemical input data for modelling CO_2 storage in deep saline aquifers

rock matrices	fluids	dissolved components
porosity	density	solid density
permeability	viscosity	solubilities (NaCl in H_2O)
capillary pressure	specific inner energy	diffusion coefficient (NaCl in H_2O)
relative permeabilities	specific enthalpy	
tortuosity	solubilities (H_2O in CO_2, CO_2 in H_2O)	
heat conductivity	diffusion coefficients (H_2O in CO_2, CO_2 in H_2O)	

modelling such disturbed evolution scenarios is the phase behaviour of CO_2. during its upwards migration. The subsurface temperature and pressure conditions change in such a way, that supercritical CO_2 becomes subcritical with phase transitions into the gaseous or the liquid phase, respectively, depending on the actual boundary field conditions These processes are associated with significant heat exchange which should be taken into account.

For the reference system, performance assessment calculations on the basis of the scenarios identified in Task 3 will be carried out using the models developed in Task 5. The performance assessment comprises the development of a numerical grid for the storage site, two-dimensional Two-Phase Flow calculations for the transport of CO_2 in the saturated zone, and the calculation of applicable performance and safety indicators, as derived in Task 1. Since a generic geological model will be studied rather than a real storage site, no consequence analysis with respect to health risks can be performed. The purpose of these performance assessment calculations is to test the applicability of the methodological approach.

Outlook

This project deals with the development of a performance assessment methodology for geological CO_2 storage options in Germany in a rather generic way. Since this has not been performed before in Germany in such a systematic and broad way, the project provides important basic knowledge for the political and economical decisions which have to be made in the near future with respect to fulfil Germany's obligation to reduce its greenhouse gas emissions. If subsurface CO_2 storage in Germany is envisaged, the methodology derived in this project could be applied for site selection and within the licensing process by using site-specific parameters and geological models and by adapting the existing performance assessment codes as necessary.

From a scientific perspective, the project contributes to an emerging societal discussion of benefits and risks of this new technology to curb CO_2 emissions. In this respect it should be taken into account that, apart from general environmental benefits, underground CO_2 storage has an economic relevance since a market prize is establishing for CO_2 emission certificates.

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Numerical Investigations of CO_2-Sequestration in Geological Formations – Problem-Oriented Benchmarks

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1. Project Coordination and Partners

Coordination

Universität Stuttgart (Holger Class, Rainer Helmig, Anozie Ebigbo)

National Partner

Deutsche Montan Technologie, Essen (Ralph Schlüter, Heribert Meiners)

International Partners (not funded by GEOTECHNOLOGIEN)

- University of Bergen, Norway, Institute of Applied Mathematics (Jan Nordbotten, Helge Dahle)
- Princeton University, USA (Michael A. Celia)
- De Norske Veritas, Oslo, Norway (Todd Flach)

2. Project Description

The technologies that are currently investigated and developed in order to mitigate the greenhouse effect by reducing the concentration of CO_2 in the atmosphere are manifold. Different trapping mechanisms could be utilized for the underground storage of huge amounts of CO_2 (see project CO_2TRAP). However, in the run-up to any large-scale implementation of such a technology, a number of safety, feasibility and economic issues have to be clarified.

Numerical simulators are essential tools in addressing problems and questions arising in the context of CO_2 sequestration in the subsurface. In order to transfer any kind of laboratory results to the scale of application of the technologies it is necessary to understand the relevant physical processes and to implement them in mathematical and numerical models. Accompanying technical investigations with the development of numerical simulation methods helps significantly to understand the coupled physical processes. Furthermore, the models are necessary to quantitatively evaluate long-term scenarios, perform parameter studies and sensitivity analyses, etc.

Within this project, we focus on injection scenarios in deep geological formations. In general, the physical systems can be described by multiphase multicomponent models including non-isothermal effects mainly in the near-field of an injection due to pressure-lowering and expansion of the CO_2. In recent years, there have been different numerical and analytical concepts developed for such kind of problems. Still, the validation of these models is a big challenge since in general the necessary data on the relevant scales are not sufficiently available. For assessing the reliability and accuracy of the different concepts we consider it essential to formulate benchmark problems that can be used for intercomparisons. This project will take and extend the results of recent benchmark studies like, for example, the GEO-SEQ Code Intercomparison Study (Pruess et al., 2003 [1]) initiated at Lawrence Berkeley National Laboratory. The formulation of new benchmarks is necessary due to the sophistication and improvement of the model concepts. Furthermore, we aim at designing specific problem-oriented benchmarks related to the current research in different national and international projects.

The preliminary topics, that we plan to address deal with

- leakage of injected CO_2 through overlying formations or natural and anthropogenic fault zones (fractures, abandoned wells),
- storage capacities in aquifers, depleted oil/gas fields, or coal formations,
- different storage (trapping) mechanisms like, for example, hydrodynamic trapping in deep brine aquifers, solubility trapping in the formation brines, adsorptive trapping in coal seams, etc.,
- enhanced gas recovery (EGR)
- and enhanced coal-bed methane (ECBM). In the last two cases, CO_2 is injected in order to release methane.

Further topics may arise from ongoing discussions with the partners during the project.

Although funded by the national GEOTECHNOLOGIEN program we explicitly place this project in an international context by narrowly collaborating with our partners in Norway and in the USA.

3. Project Partners and their Contributions

In the following, we list our national and international partners and give a short description of their backgrounds. We outline the contributions that we expect and assign these to the context of the research plan.

Partners

- Prof. Michael A. Celia, Princeton University (USA)

Prof. Celia works in the general areas of groundwater hydrology, numerical methods for differential equations, contaminant transport simulation, and multiphase flow in porous media. Many of his modeling efforts are directed toward improved understanding of multiphase flow systems, including upscaling studies, tests of new constitutive relationships, and studies of the effects of material heterogeneities on nonlinear flow phenomena. More recent projects include modeling and upscaling studies for plant-soil-water interactions, with a focus on root uptake models, and deep subsurface injection of carbon dioxide as a partial solution to the atmospheric carbon problem. As far as the latter subject is concerned, Prof. Celia is part of the Carbon Mitigation Initiative (CMI [3]), a joint project of Princeton University, BP, and the Ford Motor Company with the goal of finding solutions for the global problem of climate change. Overall modeling approaches range from pore-scale network models to larger-scale continuum simulators based.

- Prof. Helge Dahle, Dr. Jan Nordbotten, University of Bergen (Norway)

Prof. Dahle is associated with the Laboratory for Industrial Mathematics within the Institute of Applied Mathematics. He has long experience in mathematical and numerical modeling of multiphase flow in porous media. Together with Prof. Björn Kvamme, Department of Physics, University of Bergen, he is currently (2002-2006) running a project named »Model Studies of Safe Long-Term Storage of CO_2 in Aquifers«. This project is funded in part by the Norwegian Science Foundation and in part by Norsk Hydro, and involves the education of five PhD candidates.

The overall research goals of this project are:

1. the development of numerical simulation tools for modeling and analysis of CO_2 sequestration in aquifers and reservoirs;
2. to contribute to understanding the problem

of permanent or long-term sequestration of CO_2 in aquifers and reservoirs.

- Dr. Nordbotten is a young scientist at the Department of Mathematics at the University of Bergen. He finished his PhD studies in 2004 with a dissertation on analytical and semi-analytical solutions for the description of CO_2 plume evolution and leakage through abandoned wells. He and Prof. Dahle cooperate closely with the groups of Prof. Celia, Princeton University, and our group in Stuttgart.

- Todd Flach, De Norske Veritas (Oslo, Norway) Todd Flach is currently developing services in DNV Research related to the risk management of CO_2 storage in geological reservoirs, as well as developing evaluation tools for technologies related to commercializing stranded gas.

- Ralph Schlüter, Dr. Heribert Meiners (DMT) There is a long-standing cooperation between DMT and our workgroup at the University of Stuttgart. Several problems regarding methane migration in the subsurface and the assessment of hazardous gas emissions from the subsurface have been worked on jointly.

Ralph Schlüter (Dipl.-Geol.) has been working in coal exploration for more than 25 years in various countries. Since 1993, he has been involved in CBM and CMM projects in Germany and abroad. His main topics are the structural, lithological, and mining-related preconditions of these projects. Currently, he is co-ordinating DMT's activities in CO_2 sequestration.

Dr. Heribert Meiners has long experience in the gastechnical assessment of coals of different rank. He deals with laboratory experiments on sorption and desorption parameters on coals, the determination of gas contents underground, and the calculation of gas volumes when mining coal. One research interest is the examination of the permeability of coal samples in the laboratory and in situ in coal seams.

In recent years several R&D projects have been carried out that dealt with the determination of cavity volumes, residual gas contents, residual gas volumes, and residual gas fluxes in abandoned coal mines.

We further cooperate with the groups of Prof. Clauser/ Dr. Kühn and Prof. Littke/ Dr. Krooss within the CO_2TRAP project. This concerns essentially the enhanced coal-bed methane (ECBM) topic. Another cooperation exists within the CO_2*SINK* project funded by the EU and coordinated by Prof. Borm, GFZ Potsdam, Germany.

The contributions that we expect from our partners can be summarized as follows:
- discussion during the formulation of questions and issues to be addressed by the benchmarks,
- development of benchmarks, (semi-)analytical solutions, simulation results with other codes,
- evaluation and interpretation of the results.

Who will contribute to what?
- Prof. Celia, Prof. Dahle, Dr. Nordbotten Benchmarks concerning CO_2 plume evolution, leakage through abandoned wells, and storage capacity of aquifers will benefit from the expertise of these partners. With their experience and preliminary work in this field, they will help draw up important questions and issues to be addressed by the benchmarks. Furthermore, they will contribute to numerical and (semi-)analytical results for certain problems, which is necessary for comparisons between different codes as well as for the verification of the codes against the analytical solutions.

- Todd Flach, DNV Since questions concerning risk assessment and risk management play an important role in the design of the benchmarks, the expertise and experience of DNV and Todd Flach are valuable for this project. He will mainly be involved in the development of the benchmarks and the interpretation of the results.

- Dr. Meiners / Schlüter, DMT
  For the benchmarks dealing with CO_2 injection into coal, the DMT is an esteemed partner for the development of problem-specific benchmarks. DMT can further contribute to model input information concerning, for example, hydraulic properties, formation properties, structure of the coal formations, coal swelling and coal adsorption behavior etc.

4. Project Deliverables and Workplan

The ultimate goal of this project is to design new problem-oriented benchmarks and make them and their results available to the scientific community. Accordingly, publications and discussions in international workshops will be appropriate means.

What will be the benefit for the scientific and engineering community from this project?

- Modelers can use the benchmark problems for validating their numerical or analytical concepts. By comparison with the results of the methods applied by the collaborators within this project, they can check the accuracy and reliability of their codes.
- The problem-orientation of the benchmarks will help in creating a common basis for the discussion of the main aspects, open questions, risks, and chances of CO_2 sequestration among experts.
- Parameter studies and numerical sensitivity analysis will improve the basic understanding of how the physical processes are coupled. The dominance and importance of processes can vary dependent on the scale of interest.
- Before the technologies can be applied on large scales, it is necessary to get a positive public opinion. Visualization of the sequestration scenarios by means of numerical simulations are absolutely necessary for that purpose.

How can the products of this project, namely the benchmarks, be specified?

It is planned that a benchmark problem contains:

- A description of the main issues that are addressed with the benchmark example. Each benchmark will be related to a certain scenario and/or technology which is currently worked on in the scientific or engineering community. Thus, the evaluation of the benchmark results and any kind of sensitivity analyses or parameter study will aim at certain practical aspects, for example, concerning safety, risks, feasibility, capacities, etc.
- The description of the model domain as well as the initial and boundary conditions.
- The results of the numerical and mathematical/analytical models applied to the benchmark problem. This includes also the description of the underlying model assumptions, the model performance data, in case of numerical models further the applied discretization schemes, meshes, solvers.
- A discussion of the results and conclusions thereof.

How is the project work structured and what are the steps to be taken?

- The first benchmark example addresses the problem of CO_2 leakage through abandoned wells. Nordbotten et al. (2003) describe a semi-analytical solution for an injection scenario with leakage through an abandoned well into an overlying formation. This example builds the basis for the design of the first benchmark, see also Section »First Results«. The numerical results will be compared with the semi-analytical solutions. It is planned to involve further codes and models such that the intercomparison is founded on a broader basis.
- A workshop on numerical simulation of CO_2 sequestration at Princeton University organized by one of the international project partners in November 2005 will be visited. This gives the opportunity to discuss details of current modeling problems.
- The project partners DMT (Essen, Germany) and De Norske Veritas (Oslo, Norway) will be

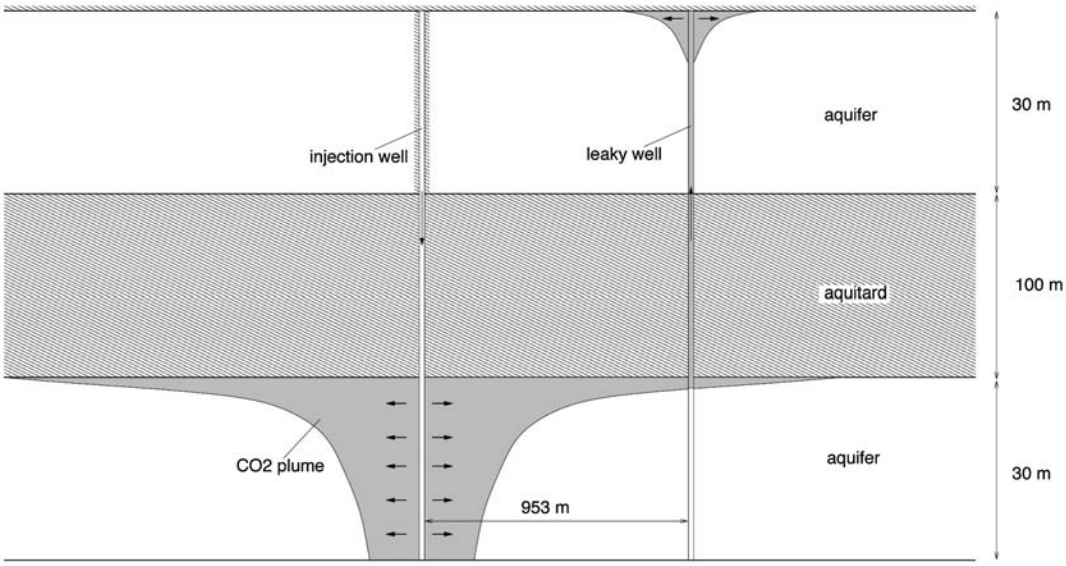

Figure 1: Formation geometry as used for the semi-analytical solution procedure by Nordbotten et al.

involved into the aspects of engineering, risk analysis, and scenario selection. Concerning the ECBM and EGR scenarios, it is planned to shift them to a later stage of the project. The reason for this is that we try to gain benefit from the results of the CO_2TRAP project which also deals with injection of CO_2 into coal and investigates the adsorption/desorption behavior of CO_2 and the release of methane.

- For the year 2007, we plan to prepare the final publication and to get funding for the organization of an international workshop on this benchmark study.

5. First Results and Next Steps

As mentioned earlier (section »Project Deliverables and Workplan«), the first benchmark example deals with the problem of CO_2 leakage from a geological reservoir. The importance of the investigation of such scenarios is obvious. The goal of CO_2 capture and storage in geological formations over long periods of time is undermined if the CO_2 can leak back to the atmosphere. Moreover, CO_2 leaking into the atmosphere in large quantities poses a serious threat to human lives, since high concentrations of CO_2 cause suffocation. Leakage can occur through abandoned wells or through fractures in the formation. In North America, for example, many potential formations for CO_2 sequestration are perforated by between thousands and millions of oil and gas wells. In the following, a well or a fracture will simply be represented as a zone of much higher permeability than in the formation. Since CO_2 is less dense than water (even as a supercritical fluid), it would upon reaching such a well rise towards the surface. The thermal effects involved while the CO_2 is rising are just as important especially if phase changes are involved. The numerical simulation of scenarios involving such leakage is a major part of this benchmark.

Semi-analytical solution

Nordbotten et al. (2003) presented a semi-analytical solution procedure for the prediction of the CO_2 plume evolution during CO_2 injection into a deep saline aquifer and leakage through an abandoned well. Using the procedure, one can calculate both saturation and pressure distribution in the formation. The CO_2 flux through the leaky well is calculated using the multiphase version of Darcy's law, given the relative and absolute permeabilities in the well and the pressures in the aquifers above and below the well.

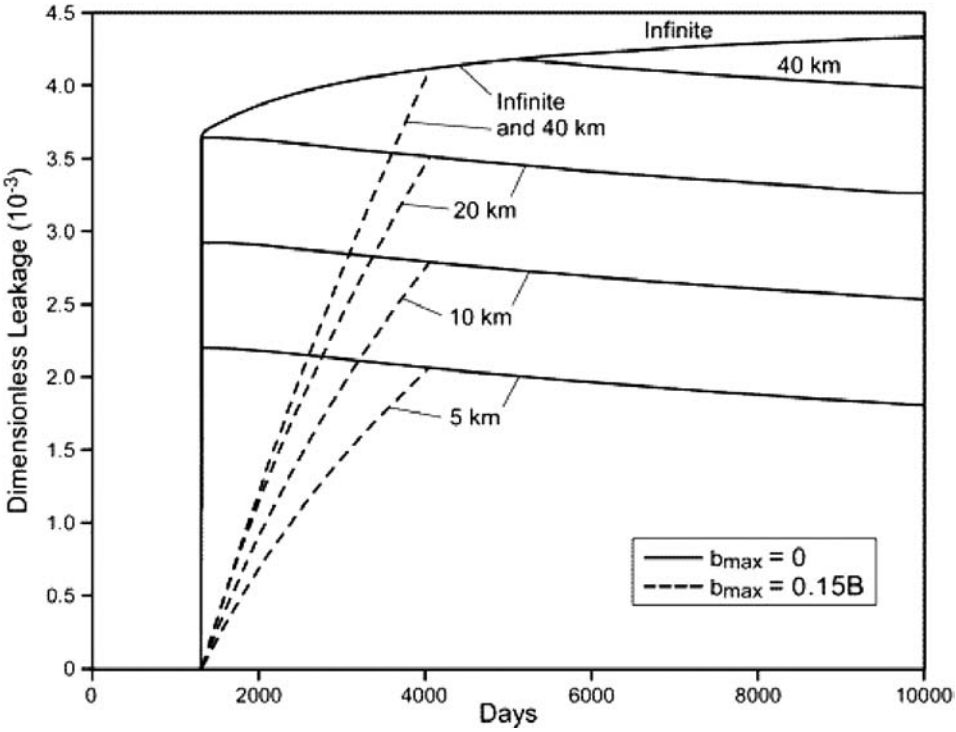

Figure 2: Semi-analytical solution for CO_2 leakage through abandoned well.

Figure 1 shows the arrangement of the injection and leaky well as well as two aquifers and an aquitard. The leaky well connects the two aquifers. The three-dimensional geometry is cylindrical with the leaky well in the center. The bottom of the lower aquifer is taken to be 3000 m below the groundwater level and the injection rate is 1600 m³/d. The radius of both the injection and the leaky well is 15 cm. Physical properties such as fluid density and viscosity are assumed to be constant. Relevant parameters used in the simulations are given in Nordbotten et al. (2003). The semi-analytical solutions in figure 2 shows the leakage rate of CO_2 normalized by the injection rate as a function of time for different domain radii. The parameter bmax is used in the semi-analytical procedure to impose a gradual build-up of the CO_2 saturation in the leaky well. It represents the thickness of the CO_2 plume, measured at the leaky well, that is required to achieve full saturation of CO_2 within the leaky well.

- If bmax is set to 0, the CO_2 saturation in the leaky well is always either 1 or 0.

- if bmax is not zero, then the CO_2 saturation in the leaky well is 0 for b = 0, 1 for b ≥ bmax and linearly interpolated between these values.

b is the thickness of the CO_2 plume measured at the leaky well and B is the thickness of the aquifer.

Numerical simulation

In an effort to compare numerical results with the semi-analytical solution, we use similar formation properties (geometry, permeability) and the same injection rate as Nordbotten et al. (2003) for numerical simulations. The radius of the domain used is 4.5 km. The height of the aquifers is 100 m (as opposed to the 30 m used in the semi-analytical solution). The other parameters are identical to those used in the semi-analytical solution procedure.

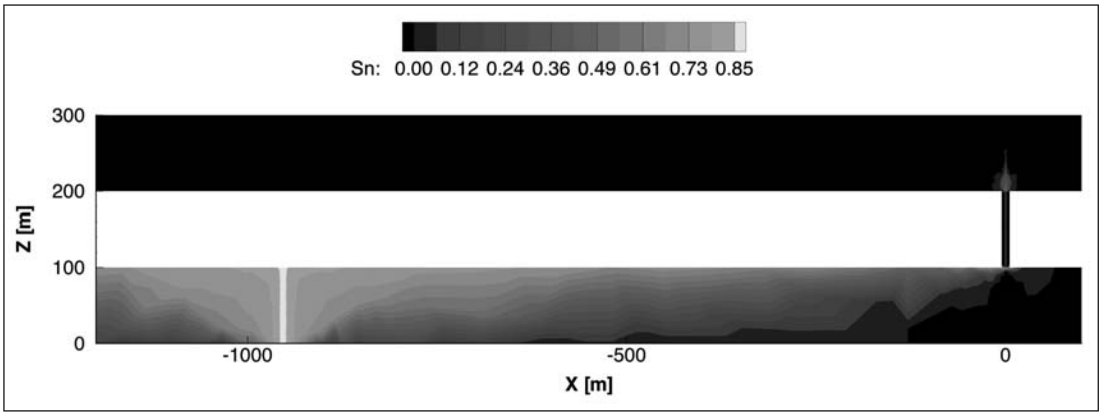

Figure 3: Numerical results: CO_2 saturation

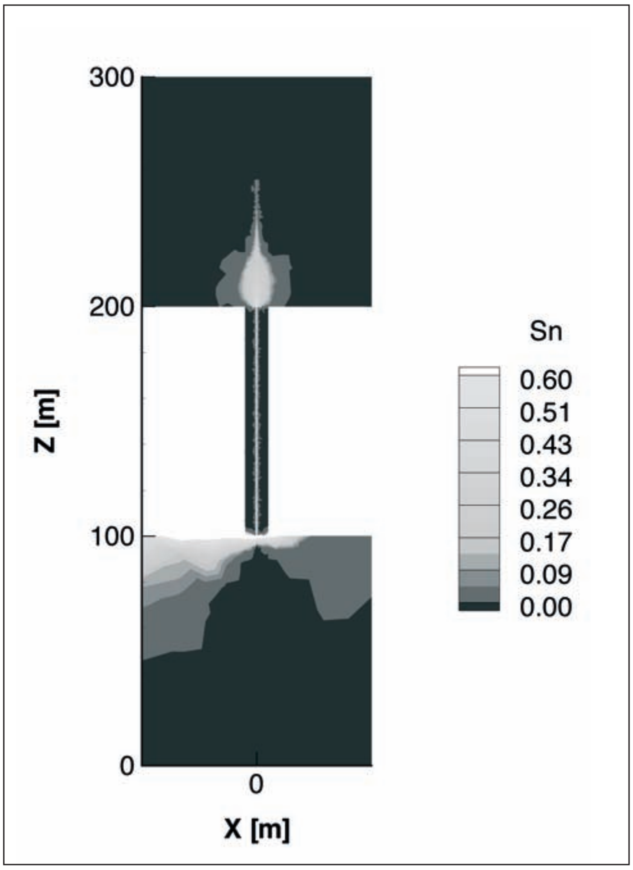

Figure 4: Numerical results: CO_2 saturation near the leaky well

The preliminary results of our numerical simulation are depicted in figures 3 and 4. They show the region around the injection and leaky wells with the CO_2 plume shortly after its appearance in the upper aquifer. Note that figures 3 and 4 are two-dimensional slices taken from the cylindrical, three-dimensional domain.

Future work on this topic will involve:

- Completion of the numerical simulations and comparison with the semi-analytical solution
- Numerical simulation of the same problem with a two-phase two-component model to account for mutual solution of the components water and CO_2.
- Inclusion of thermal effects in the numerical model and numerical simulation of the pro-

blem in shallower depths to find out more about the effects of phase change on the CO_2 leakage rates.

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Hamburg – A Dynamic Underground (HADU) Subsurface Evaluation of Hamburg Based on Analysis and Modelling of Recent Geological Structures and Dynamic Processes

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1 Preface

Large building complexes for industry, traffic or science-technology and residential areas require an extraordinary long-term security, functionality and sustainability. The knowledge of the underground structure and geological situation is crucial for cost optimization during planning, building and throughout operation. Faults, underground cavities or strong geo-material inhomogeneities bear a significant geological risk, especially in deformed and altered sediments and have to be considered for a save and sustainable engineering. Typically, building structures are set up in metropolitan regions where standard geophysical exploration techniques may be impossible as, for instance, the use of explosives (seismics) is either forbidden or very strictly regulated, or the level of noise and artefacts prevents the use of refined techniques.

An interdisciplinary research group with geologists, geophysicists and computer scientists of the Universities of Hamburg and Potsdam is involved in the subsurface evaluation of the City of Hamburg and adjacent areas based on exploration, analysis and modelling of recent geological structures and their dynamic evolution.

In combination with geological methods we develop and apply different passive geophysical exploration methods and low-energetic active methods to estimate the relevant underground geology and geological risk within metropolitan regions built on soft sediments and evaporites. This information is i-portant for long-term planning of infrastructures and buildings as well as to improve cost calculations for single building projects. The metropolitan region of Hamburg locally bears a significant georisk due to several large salt diapirs coming to shallow depths and generating repeated cavity collapses and current vertical creep deformation along geological faults. All obtained data will be geo-referenced, maintained in a database management system and visualized by using Spline interpolation algorithms which will be implemented as software components, utilizing the Common Object Model (COM) component model together with ArcObjects, thus extending ArcGIS, the GIS platform of the market leader ESRI.

Table 1: Involved institutions

Institution	scientificsub-projects	Project-manager	Tel / E-mail
Univ. Hamburg Geology	Geological structures and dy-namics, Paleoseismology Ground Penetrating Radar	Prof. Dr. C.-D. Reuther	040 42838 5018 reuther@geowiss.uni-hamburg.de
Univ. Hamburg Geophysics	Seismology Ambient vibrations Gravimetry, Geoelectrics	Prof. Dr. T. Dahm Dr. A. Dehghani	040 42838 2980 dahm@dkrz.de ali@dkrz.de
Univ. Hamburg Computer Science Information Tech-nologies	Data Integration and Database Management 3D visualisation	Prof. Dr. D.P.F. Möller	040-42883-2436 dietmar.moeller@informatik.uni-hamburg.de
Univ. Potsdam Geophysics	Seismology, Ambient vibrations	Prof. Dr. F. Scherbaum Dr. M. Ohrnberger	0331 977 5257 fs@geo.uni-potsdam.de

Duration of the project
01. 04. 2005 - 31. 03. 2008

Cooperating partners

- Deutsches Elektronen-Synchrotron DESY (Dr. Bialowons, Dr. Ehrlichmann)
- Geologisches Landesamt Hamburg - State ministry of urban development and environment (Dr. R. Taugs)
- System Operators Fachbereich Geowissenschaften Universität Hamburg (Dr. J. Krebs)

1.1 Problem introduction

The metropolitan region of Hamburg with about 2 million inhabitants (fig.1) is geologically situated in the center of a late Tertiary basin with Quaternary and recent deposits comprising a wide range of more or less consolidated sandy, clayey and organic sediments. The extraordinary geological situation of the city of Hamburg is manifested by several large salt diapirs rising from the deeper subsurface and affecting the overburden by deformation. Special georisks are induced by collapses of caverns created by evaporite-solution and karstification of these diapirs. Collapses in minor depths have created at least 30 collapse features represented by morphological depressions in the city area (Niedermayer 1962, Grube 1971 & 1973, Paluska 2002). Collapse-earthquakes in Hamburg were observed since the 18th century; organized records exist since the 20th century. During the last 100 years, 20 collapse-earthquakes occurred, this means averagely every five years, and led to relatively severe damages. The last Hamburg collapse earthquake happened on the 8th of April 2000. Recent creeping vertical surface uplift is observable in several parts of the city and might be related to ongoing salt-tectonics such as faulting and folding. However observable slow-moving recent subsidence can be either salt-tectonically induced by forming rim-synclines around the diapir or by atectonic groundwater lowering. Recent large-scale surface oscillations were monitored in Hamburg in the sixties and seventies by Fleischhauer (1979) and demonstrate maximum uplift of 1.2 mm and maximum subsidence of 3.6 mm per year.

These movements as well as the Quaternary sedimentary pattern govern the behavior of the subsoil which is covered with buildings from small houses to multi-story buildings and large factories, power-plants, large complexes of research institutions, streets, tunnels, rail- and subways. A modern reconnaissance of the subsurface structure and the estimation of potential georisks is an important contribution to the installation control within the existing infrastructure and to an advanced knowledge of the subsoil regarding the realization and surveying of future constructions.

1.2 Methodical approach

The topics of our interdisciplinary project are the investigation and on-site prediction of the geological situation as well as the evaluation of potential georisks in the metropolitan region of Hamburg. The applied techniques and the methods to develop include bistatic and monostatic 400 MHz, 200 MHz and 100 MHz ground-penetrating radar (GPR) for the investigation of near sub-surface structures in the sediment succession (Sub-project GEOLOGY Hamburg: C.-D. Reuther); passive seismological investigations using ambient seismic vibrations technologies with online-processing (Sub-project GEOPHYSICS Hamburg / Potsdam: T. Dahm / F. Scherbaum). Geoelectric, gravimetric and low-active seismological methods are complementing the investigations and are carried out by the geophysic group Hamburg (A. Dehghani). An overlap in detecting sub-surface structures with increasing depth exists by using low-frequency GPR, low-active seismology and ambient vibrations measurements. The IT (COMPUTER SCIENCE Hamburg: D.P.F. Möller) work packages of the interdisciplinary research group will focus onto two main topics, providing an IT framework for data integration and visualisation, and development and integration of methods for data processing, classification and visualization, which will lead to a higher transparency of the heterogeneous data due to less uncertainty and better accessibility and interpretability.

1.3 Target areas

The first target is the examination of effects related with the most prominent subsurface structure of Hamburg: the Othmarschen – Langenfelde Diapir (fig.1). This diapir intruded and deformed the thick Mesozoic and Cenozoic strata of the deeper subsurface and is probably still active. Reflexion-seismic surveys were carried out in 1991/92 (Linke, 1993) and in 2005 by teams of the GGA (Institut für Geowissenschaftliche Gemeinschaftsaufgaben; Hannover) and the GLA HH (Geologisches Landesamt Hamburg) and defines the general position and contours of the Othmarschen – Langenfelde Diapir. The cap rock of the diapir approaches the present surface beneath the Altona Hospital (fig.2). North of the hospital, at Seiffert-Sport-Fields (fig.2), the top of the diapir is in about 70 m depth. The area is affected by roof collapse and has been investigated with Ground Penetrating Radar (see sub-project GEOLOGY) and Ambient Vibration Measurements (see sub-project GEOPHYSICS). In this area are four fifteen-storey buildings and therefore it is relatively sensitive regarding potential georisks.

At Flottbek Market (fig.2) the western rim of the diapir is faulted and affected by roof-collapses. These collapse structures and their border areas have been studied in detail by ground-penetrating-radar and a first 3D modeling of the evolving collapse has been developed (sub-project GEOLOGY). A first ambient vibration survey was carried out in the district of Schenefeld (sub-project GEOPHYSICS).

Origin and formation of further circular structures as well as the rims and the roof of the salt diapir will be studied in the districts of Altona, Bahrenfeld, Blankenese, Flottbek, Krupunder, Othmarschen, Quickborn, Wentorf and Northern Hamburg.

1.4 Aim and scope of the sub-projects

The aims of the geological sub-project are the determination and analysis of near surface structures above and along the Othmarschen–Langenfelde diapir to classify past and recent movements associated with the diapir. To evaluate potential georisks and sub-recent geologic evolution Ground Penetrating Radar (GPR) in combination with structural and sedimentological field investigations are applied.

The two goals of the geological investigation are: (A) to reveal the formation of circular structures and their potential georisks. Several of the »sub-circular depressions« are collapse-structures (sink-holes) and have been formed by ongoing subrosion processes. Sudden collapses occur up to present times. Geo-risks of these areas are moderate to strong and damage of buildings might happen. Other circular structures represented as bowl-shaped depressions are former kettle-holes and originated from buried large dead-ice blocks during the Pleistocene whose final melting away left a hole. These structures imply very low geo-risks. Both circular structures, either collapse features or former kettle holes are forming nowadays many small lakes and depressions infilled by fossil soils and sands in the urban area of Hamburg. Origin and formation of the depressions (lakes) is not always clear and contro-

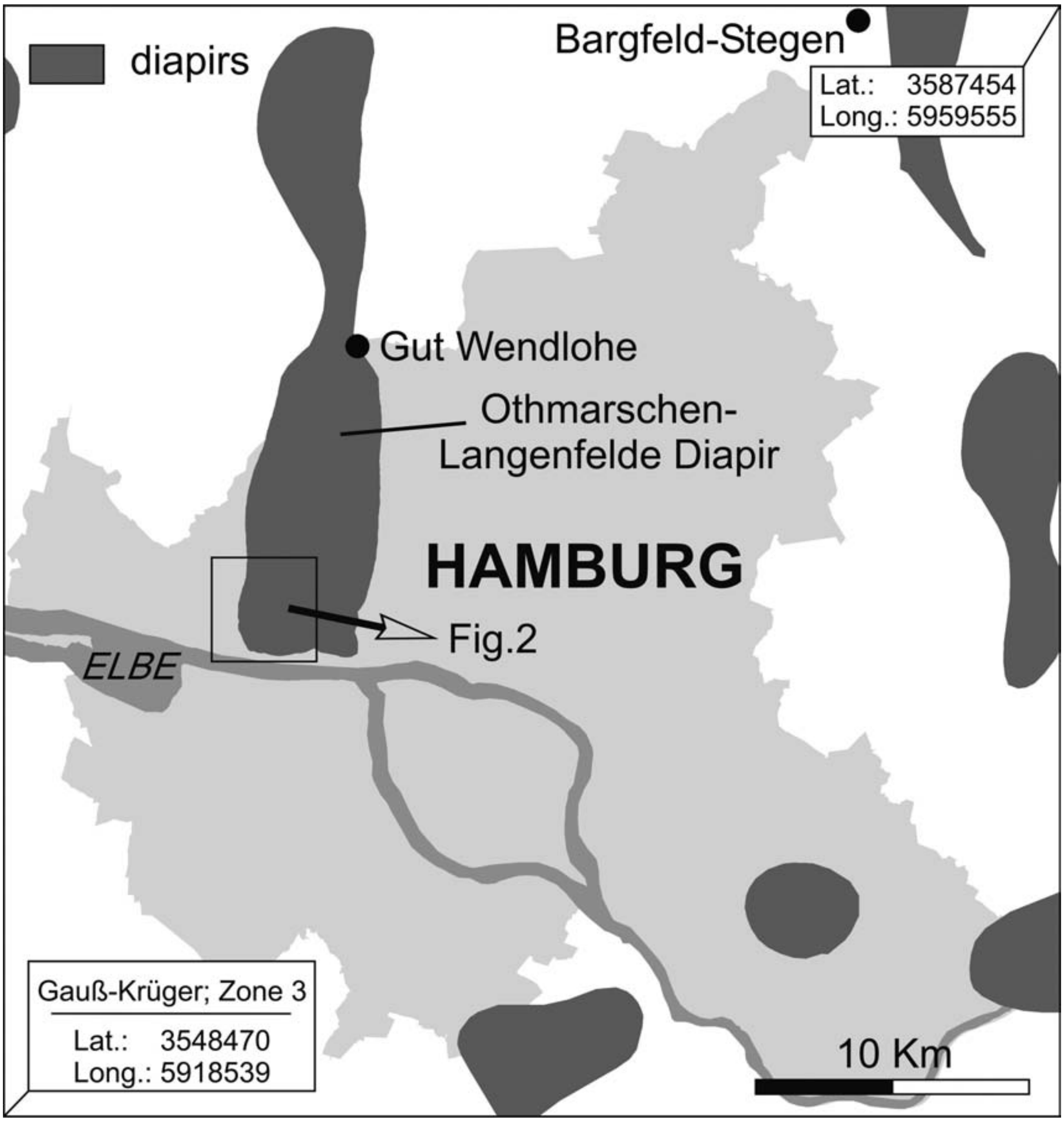

Figure 1: Metropolitan region of Hamburg with location of salt diapirs and georadar test sites

versial discussed. Ground penetrating radar surveying allows clear differentiation of infilled depressions regarding the origin whether they are collapse structures or kettle-holes.

The second goal (B) is to detect areas affected by recent salt-tectonics and / or glacial processes. Thus detailed field studies regarding the formation, dislocation and faulting of sedimentary deposits combined with GPR techniques will be applied. The reconstruction of the geometry of the late glacial and interglacial sandy channels, their infillings and recent fluvial deposits allows insights into palaeo and recent surface changes.

The main goal of the geophysical sub-project is to estimate the 3D-geometry of the top of the Othmarschen – Langenfelde diapir by means of ambient seismic vibration methods and other standard geophysical methods. Both array and single station H/V measurements will be conducted to estimate both the dispersion characteristics (array measurements) as well as the ellipticities of Rayleigh waves (H/V measurement) contained in the ambient seismic vibration wavefield. The information can be used to derive shallow to intermediate deep shear wave velocity structures in a combined inversion procedure.

The methodical innovation of this proposal consists in the development and implementation of an adaptive array configuration measurement strategy for the in-field determination of dispersion curves and averaged H/V ratios and subsequent in-field combined inversion of shear wave velocity structures. The nature of the ambient wavefield in Hamburg, which consists of a strong microseismic component in the frequency range between 0.2 and 0.5 Hz, as well as the expected penetration depth together with the strong impedance contrast between sediment and salt provide excellent prerequisites to achieve the proposed goal.

The inversion of velocity models from dispersion curve data is a highly non-linear and non-unique problem. Any a priori information, which allows to constrain the range of model parameters for the inversion procedure, considerably improves the reliability of the inverted shear wave velocity models. The additional use of other geophysical and geological methods as gravity, shallow seismics, ground penetrating radar or geoelectrical methods will allow to refine the structural information obtained from ambient vibrations.

A combined interpretation of geophysical data and geological structural information is planned in cooperation with project partners, taking advantage of visualisation tools developed by sub-project computer science.

The main focus of the first work package of the computer science sub-project is to establish and configure a customizable and extendible software environment for all sub projects. Additionally, data models will be developed which provide homogeneous access to the heterogeneous data of the different sub projects independent from different scales, distributions or levels of exactness.

The second work package will deliver visualisation methods for spatial and thematic data in 3D, utilizing 3D Splines. This model offers a convenient and stringent way to model thematic, i.e. non spatial data attributes and to bind them to spatial data. The second focus of this workpackage is to handle data uncertainty and embedding it by using Fuzzy Set Theory, which provides simple strategies for rule-based analysis and search in complex data structures based on linguistic statements. Implicit trilinear interpolation will allow the visualization of homogeneous areas in spatial systems, even if the underlying database lacks in quality, quantity or reliability by operating on value intervals rather than scalar values. The implicit representation allows all three basic set operations (and thus any set operation).

2 HADU SUB-PROJECTS

2.1 Sub-project GEOLOGY

HADU: Dynamic analysis of underground deformation and evaluation of potential georisks: Ground Penetrating Radar (GPR) and structural investigations.

Introduction

The objective of the GEOLOGY sub-project is high-resolution determination of near surface deformations above and along diapiric structures to classify their past and recent movements.

The main targets of the geological project are: (A) to reveal the formation of circular structures in order to specify their potential georisks and (B) to detect areas affected by recent salt-tectonics and / or former glacial processes. Of fundamental interest is the recognition of larger underground anomalies with respect to the subsoil stability.

Target A

Several of the »sub-circular depressions« in the metropolitan region of Hamburg are collapse-structures (sinkholes) and have been formed by ongoing subrosion processes. Sudden collapses occur up to present times and sediment infillings show multiple deformations either by rupturing or by ongoing creeping. Georisks of these areas are strong to moderate causing some damage of buildings.

Up to now we focused mainly on the Flottbek market subsidence and collapse structure as the most active feature. This sinkhole system is characterized by two main subsidence centers and was shaken by collapse earthquakes in 1928, 1963 and 2000 (fig. 2). The subsidence structure is elongated in a N-S direction in almost the same manner as the entire Othmarschen-Langenfelde salt diapir and the nearby smaller Bahrenfeld structure (fig. 1,2). E-W trending Ground Penetrating Radar Surveys (fig. 3) carried out in July / August 2005 show the subsurface boundary of the Flottbek market buried crater-like collapse structure. The radar profiles were taken with a 200 MHz antenna as well as with the newly acquired 100 MHz antennas from GSSI, the world leader in GPR-techniques. High-resolution radar imaging (200 MHz) reveals multiple deformations expressed by at least 3 different displaced paleo-surface horizons down to 5 m (3D model) depth and macro-deformations down to 10 m depth. The activity of the collapse feature up to present time is indicated by slight deformation of the uppermost soil-layer. Nearby buildings are damaged, one of it as seriously as it had to be knocked down within the running project phase.

The results of a GPR - pre-survey (200 MHz) in July 2004, north-east of Seiffert-Sports-Fields site (fig.2), provided a first 3D radar interpretation indicating at least 2 different displaced (paleo-) soil horizons down to 5 m depth. Because of the unique characteristics of the

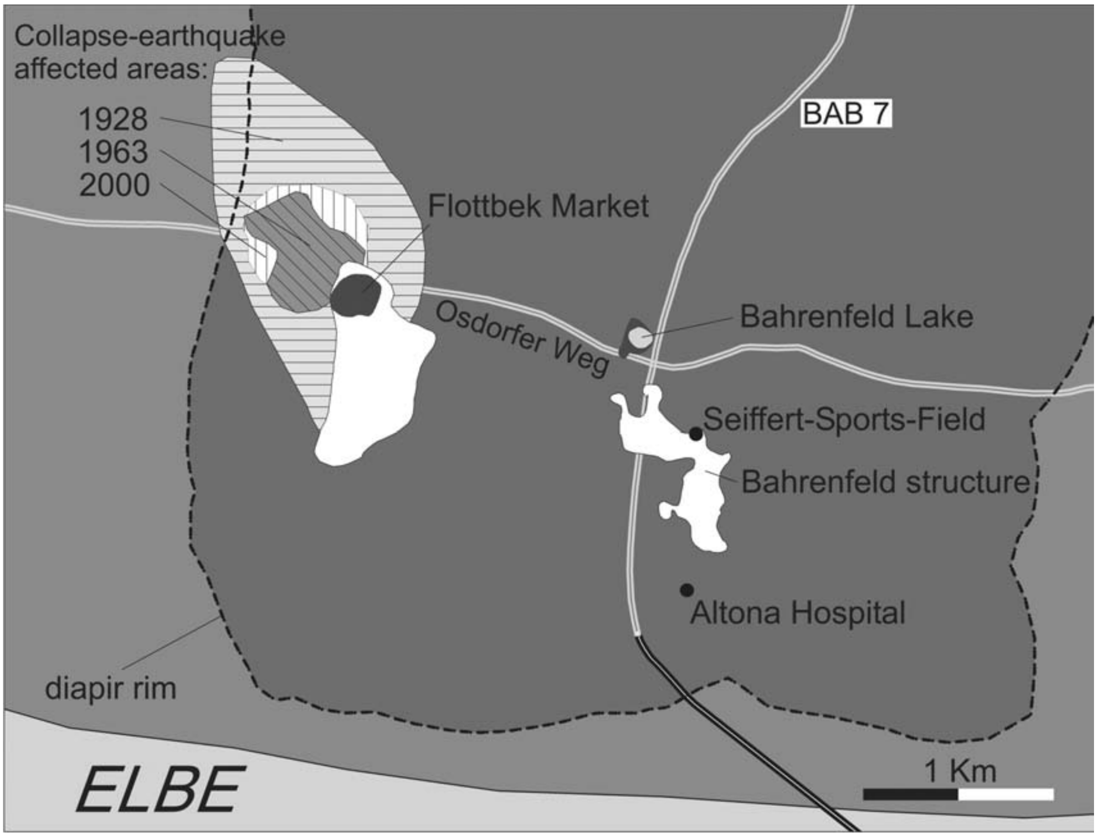

Figure 2: Flottbek Market location (collapse earthquakes) and georadar sites

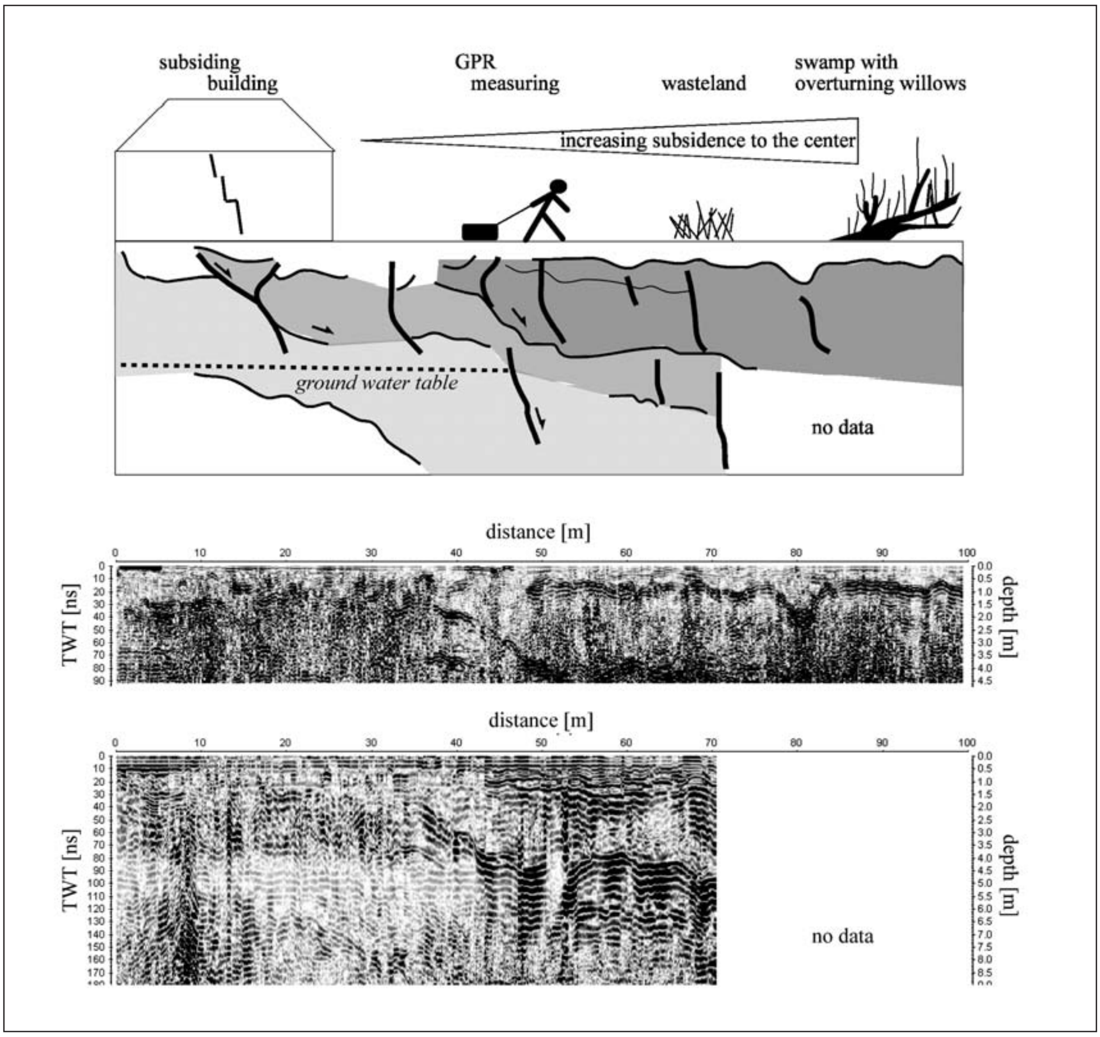

Figure 3: E-W georadar sections across the eastern rim of the sinkhole system. Interpretation (top) reveals at least four different stages of ongoing creeping subsidence phenomena. 200 MHz bistatic GPR section for high resolution (middle) and 100 MHz bistatic GPR section for deep penetration (bottom), vertical exaggeration 3x.

GPR pattern (fractured and faulted rim) these multiple deformations can be regarded geogenetic in origin and caused by collapse events. Meanwhile we achieved W-E trending GPR profiles across the subsidence centre of this depression, revealing both break-off edges with multiple offsets.

Target B

Our second target is the detection of areas affected by recent salt-tectonics and / or glacial processes. Thus detailed field studies regarding the formation, dislocation and faulting of sedimentary deposits combined with GPR techniques supported by the sub-project GEOPHSICS HH are in progress. The reconstruction of the geometry of the late glacial and interglacial paleo-channels, regarding the displacement of their infillings and recent fluvial deposits allows insights into surface changes in diapiric areas.

First GPR surveys above the eastern rim of the Othmarschen-Langenfelde diapir at the »Gut Wendlohe« site (Fig. 1) site revealed promising large-scale polyphase deformed paleo-surfaces, which imply ongoing creeping uprise of the diapir. As soon as the area (grain field) is fully accessible in August 2005, a large 3D survey will be arranged using 200 and 100 MHz GPR in combination with active seismics and geoelectrics.

Surface and shallow subsurface deposits in the metropolitan area of Hamburg are represented by a variety of glacial, interglacial and recent clays, sands, and gravel and can be distinguished by different radar facies. Diapiric activity is reflected in the sedimentary record showing variations in thickness of the deposits and changes in the drainage pattern. Morphological surveys regarding changes within the drainage pattern e.g. the latest geological evolution of the Alster River, imply long-lasting syn-Quaternary and active salt-tectonics in the Hamburg area (Paluska 1976).

In the northern metropolitan region of Hamburg (Bargfeld-Stegen site, fig.1) we used a 100 MHz antenna for deeper penetration in comparison to the 200 MHz antenna. The chosen area is close to a gravel pit exposing sands and gravels down to about 5 m. The sand pit offers excellent ground truth conditions as a channel structure is directly exposed. The adjacent area under investigation was not altered by anthropogenetic activities. The 200 MHz antenna revealed structural information down to 5 m (~ 100 ns TWT) penetration depth and the channel and its infill is clearly visible. The 100 MHz antennas revealed precise structural information down to 17 m (~ 350 ns TWT) penetration depth. Not only the channel within the uppermost 5 m can be recognized but also the anatomy of the front of a push moraine exhibiting different brittle and ductile deformation styles. Beneath a disturbed paleo-channel compressional structures related to a glacial push moraine are clearly recognizable.

Thus GPR-techniques used in this project visualize lateral changes in thickness and facies in continuous subsurface sections. In a later stage of investigation, these areas will be analyzed in detail in order to resolve the controlling factors of structural formation. The data quality and the range of penetration depth strongly depends on the different surface and sub-surface conditions in Hamburg as vegetation, soil, buildings and other anthropogenic alterations, dry or wet sand and gravel, thickness of clay layers and groundwater tables. During the sub-project we will provide high-resolution 3D reconstructions of the structural architecture of the Quaternary and recent deposits.

Ground truth of GPR surveys will be supported by existing borehole reports provided by the Geologisches Landesamt of the state ministry of urban development and environment of Hamburg. Drillings at selected localities will supply samples for age determinations and additional detailed logs of the geological successions to verify the radar interpretations. Within the sub-project we are constructing a Geoslicer (Nakata & Shimazaki 2000), a special tool for soft sediments to get »slice-like« 2D structural ground truth information and samples down to at least 2 m depth.

To optimize field coordination the entire metropolitan region of Hamburg is already integrated by the GEOLOGY sub-project in a detailed geo-referenciated ArcGis data set, which is actualized day by day by all new acquired geological and geophysical information (as e.g. by mapping of damaged buildings or new ground truth). Beside known geological features (mapped features, drillings, hydrology…) also high resolution aerial photographs, geodetic surveys, different digital elevation models, topography (buildings, streets, water) and all new acquired information can easily and directly be plotted in any scale and any cut-off which is needed.

The use of GPR for structural and sedimentological analysis and interpretation of the shallow sub-surface became a widely applied tool in recent years for earth scientists (Bristow & Jol 2003). The experience of the geology group in analyzing subsurface structures has been achieved during different paleoseismological and sedimentological surveys in recent years (Reiss 2004, Reiss et al. 2003, Reuther et al. 2002, Reuther et al. 2004).

2.2 Sub-project GEOPHYSICS
HADU – Ambient vibration array analysis for mapping the Othmarschen-Langenfelde Diapir beneath Hamburg.

Introduction

It has been widely demonstrated (Aki 1957, Horike 1985, Tokimatsu 1997, Okada 2003) that the analysis of ambient vibration wave fields is a valuable tool for characterising the shallow subsurface characteristics in terms of the shear wave velocity structure. The measurements of ambient vibrations with single stations or arrays are attractive alternatives to active measurements due to their generally low cost and their feasibility even in densely urbanised areas. Two main techniques are distinguished and their application for mapping the extent and depth of the Othmarschen-Langenfelde diapir in the city region of Hamburg is subject of this sub-project.

- Single station H/V analysis techniques (Nogoshi and Igarashi 1971, Bard 1999) allow the estimation of the fundamental resonance period of low impedance sediment layers overlaying much higher impedance materials (bedrock or in our case salt). The physical interpretation of this fundamental period is still ambiguous, both reverberating SH body waves as well as the ellipticity characteristics of Rayleigh surface waves may account for the observation of a peak in the H/V spectral ratios. However, it has been shown that for large impedance contrasts in simple structures both hypotheses may explain the observation equally well as response of the subsurface to the seismic excitation (Malischewsky & Scherbaum 2004). The derivation of shear wave velocity structures from H/V measurements alone are topic of current research (Fäh et al. 2001, 2003, Arai and Tokimatsu 2004). However, the trade-off between accumulated traveltimes in the sediment structure and depth of the main impedance contrast suggests the usage of combined inversion strategies from H/V information and dispersion information (Scherbaum et al. 2003, Parolai et al. 2005, Picozzi et al. 2005) obtained from array measurements.

- Array analysis techniques aim at deriving the phase velocity dispersion characteristics of surface waves constituting large parts of the observed microtremor wave field. Although logistically more demanding, array techniques allow the direct estimation of wave propagation characteristics, i.e. apparent wave velocity and direction of the impinging seismic wave front. Frequency wavenumber (f-k, e.g. Capon 1969, Tokimatsu 1997) and auto-correlation techniques (Aki 1957) are widely used in the realm of ambient vibration measurements for obtaining then the apparent phase velocities in narrow frequency bands. The resulting frequency dependent phase velocities are interpreted in terms of dispersion branches of surface waves which permit to invert for the physical quantities (V_s, V_p and ρ) of 1D earth models parameterised as stack of layers with constant properties. Constituting a highly non-linear and non-unique inverse problem, it is of crucial importance to obtain an accurate dispersion curve measurement and a well-founded interpretation of observations in the first place. Thus, considering the resolution capabilities of array settings with only a few sensors, adaptive measurement strategies have to be used to capture the full available wavelength range of the surface waves present in ambient vibration wave fields (Ohrnberger et al. 2004a,b, Ohrnberger et al. 2005). Further, accompanying geophysical measurements (shallow hammer blow refraction seismics, gravimetry) add valuable a priori information for the reduction of non-uniqueness of the inverse problem.

The first phase in the sub-project »ambient vibrations« aims in the development of an optimised small-aperture seismic array system for enabling cost effective and highest quality ambient vibration measurements. This system constitutes the key technological component of this sub-project and is based on the concept depicted in figure 4. Starting with very small

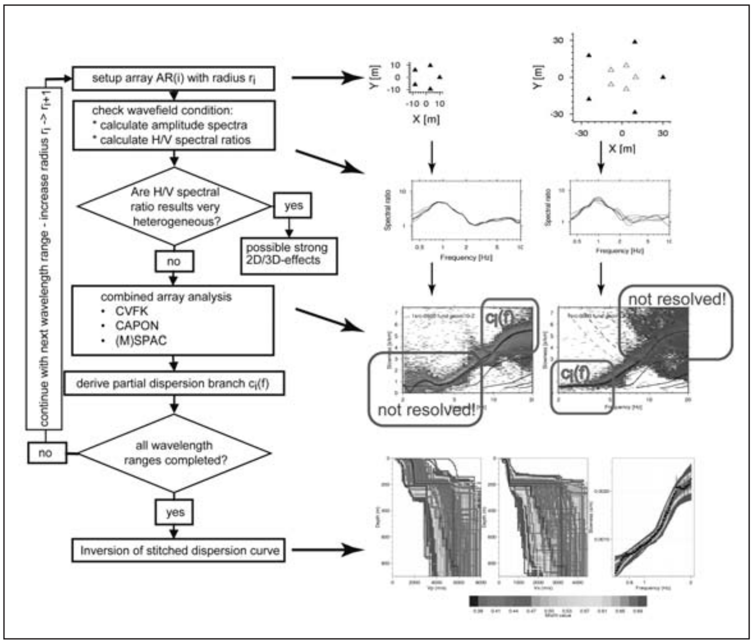

Figure 4: Technological components of ambient vibration concept.

aperture array configurations, the smallest wavelengths of interest can be captured. A first partial dispersion curve branch can be derived and allows estimating the subsequently expected wavelengths for which the next array geometry can be adapted. Thus, the optimization of the adaptive measurement strategy is guided by suitable a priori information at each deployment.

Such a measurement strategy can be only applied effectively for real world field experiments when the analysis results can be obtained insitu during the measurement phase. Therefore, the ambient vibration small-aperture array system to be developed contains wireless data transmission from the array sensors to a central field processing unit. Enabling the real-time data acquisition makes it possible to not only quality control the measurements during system operation but also to process the signal waveforms in-field. It especially allows the operator of the system to determine when the acquired information (dispersion curve) is sufficient stable for submitting it to the inversion procedure.

The technical development of this wireless real-time operating small-aperture seismic array system, which we will refer to as »WARAN« (Wireless ARray ANalysis system) in the following, requires both the adaptation of commercial hardware components for the given purpose as well as adjustments to our existing software package for continuous array processing of ambient vibration recordings (CAP, see also Ohrnberger et al, 2004a,b,c, Ohrnberger et al, 2005).

Status of project phase

The status of this project phase can be considered as being on schedule for the moment. Most of the necessary hardware equipment which has been requested in this project has been purchased and was delivered to University of Potsdam.

The key of the real-time data acquisition system lies in the employed wireless data communication and transmission facilities. Due to the rapid change on the communication market with respect to new developments of WLAN technologies made it necessary to re-evaluate actual available components with respect to the anticipated task of real-time data acquisition and data transmission. On base of this research, we decided to replace the previously sought solution based on ethernet serial conversion equipment offered by Artem GmbH during the proposal/planning

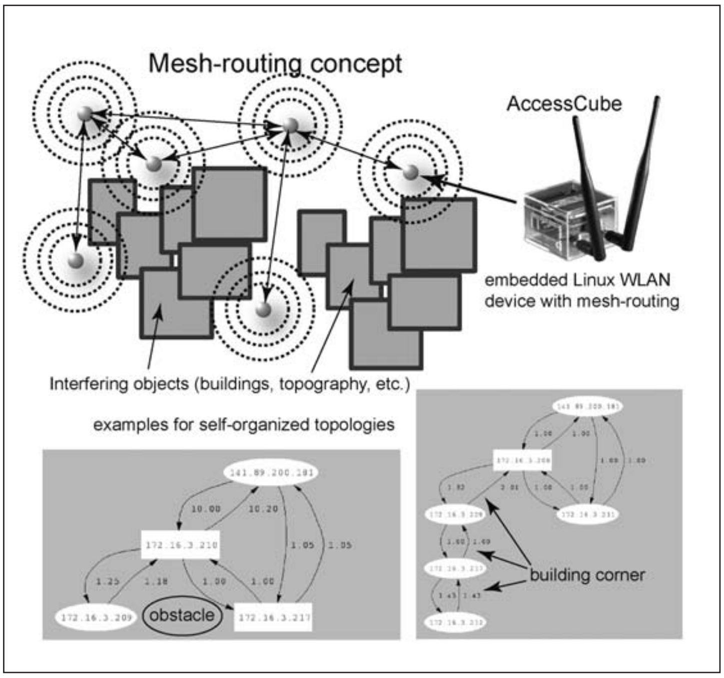

Figure 5: AccessCube and mesh-routing concept and self-organized routing information

phase of this project by an embedded Linux based WLAN device (product name: AccessCube) manufactured by 4G-Systeme GmbH in Hamburg (http://www.4g-systems.de). The advantage of this equipment is many-fold. Mainly important for this project are the following points:

- The equipment is a 400MHz MIPS based embedded Linux platform which allows the direct usage of the Seedlink architecture (see http://geofon.gfz-potsdam.de) to acquire the data in real-time before any WLAN transmission. Thus, in case of temporarily interruption of the wireless communication, no data will be lost as Seedlink provides means for buffering the data in both memory and file buffers.

- Distributing the task of real-time data acquisition to each array sensor, reduces the computational load on the central field processing unit, which then is just concerned with the data gathering and processing.

- The AccessCube includes the newly developed mesh-routing protocol (fig. 5). The mesh-routing allows all invidivdual devices to »talk« to each other in a private self-organized network after deployment. No static routing tables have to be used, all systems operate equally as sender, receiver or repeater. Figure 5 depicts graphically the mesh-routing concept and the self-organized routing information for tests in- and outdoors, just a few seconds after deploying the devices at their respective locations. Wherever line-of-sight between the devices is available a fully connected network is built, whereas isolated devices which are only visible by individual neighbours, a routing chain is created. In any case, all devices can »talk« with all others without any need for the operator to create the network at hand.

- Light weight and low power consumption.

In the very first step, we successfully ported the Seedlink architecture on the MIPS based AccessCube devices. At the current stage, we have tested certain antenna configurations for enhancing the range of communication for the WLAN communication. First tests have been conducted in the vicinity of the Institute of Geosciences at the University of Potsdam. Typical WLAN antenna allowed us to communicate without problems within the 150 m range between devices (with line-of-sight, but interfering small topographical barriers and vegetation). The usage of a high-gain omnidirectional WLAN antenna allowed extending the reliable communication range to around 300 m. The additional usage of an intermediate gain directional antenna (patch-antenna) made reliable communication possible up to (at least) 620 m distance. No farther distances have been tested so far. It is however noteworthy that the transmit power of the devices has been set only to 30 mW in these test. Enhancing the transmit power to the allowed 100 mW may further increase the range of available communication for this equipment. In conclusion, the tests have been very successful and the selected and adapted communication solution works very satisfactorily.

Further equipment tests have been conducted regarding the seismometers (huddle test) and the real-time positioning system for the accurate deployment of sensor in the field. As anticipated, the accurate real-time positioning of array stations will be accomplished with a RTK-DGPS solution with integrated radio communication from the Rover system to the central field processing unit. The radio communication works in the 440 MHz band and the communication range has been tested already successfully at the Institute of Geosciences at University of Potsdam.

In parallel to the equipment tests, we currently are working on the adaption of the software package for array processing as standalone Seedlink clients which enables the real-time processing facility in the system. As the purchased A/D converters have not yet been delivered (expected delivery end of August), we have to wait for the full system test until September/October. An overview of the interplay of system components can be given as follows. The sensors are connected to A/D digitizers whose serial output is captured by the Seedlink architecture for real-time data acquisition on the AccessCube devices. The field processing unit requests data packages from the individual sensor locations via the WLAN network. The routing of data packets within the network is fully automatic (self-configuring) through the usage of the mesh-routing protocol. Transmission ranges are enhanced by appropriate antenna devices. Antenna devices may be switched depending on the logistical constraints like the required maximum transmission distance, building corners, etc.. Finally, the wave-forms acquired in real-time at the central field processing unit will be visualised, analysed and inverted to subsequently improved earth models.

2.3 Sub-project COMPUTER SCIENCE / INFORMATION TECHNOLOGIES
HADU: Data Integration and Database Management

The sub-project work packages of the interdisciplinary HADU research group are focussed on

1. providing an IT framework for data integration and visualisation
2. development and integration of methods for the processing of uncertain data and NURBS based 3D visualisation

This sub project will integrate and visualize the results of the different geophysical exploration methods, thus enhancing transparency and providing homogeneous access.

Providing an IT framework

The main focus of the first work package is to establish and configure a customizable and extendible software environment for all subprojects. Additionally, data models will be developed which provide homogeneous access to the heterogeneous data of the different sub projects, independent from different scales, distributions or levels of exactness.

The ArcGIS 9 platform by ESRI allows us to build and deploy custom desktop applications and to extend the GIS architecture and data model. The most important feature of the ArcGIS is, that it is built and extended using software components (ArcObjects) which are compatible to the .NET-Framework respective Microsoft's middleware specification COM (common object model) component model. It allows using the ArcGIS as an open basis for the development of extended functionality, using Microsoft Visual Studio as development environment.

Development and integration of methods for the processing of uncertain data and Spline based 3D visualisation

This work package will deliver visualisation methods for spatial and thematic data in 3D, utilizing 3D Splines. The suggested model offers a convenient and stringent way to model thematic, i.e. non spatial data attributes and to bind them to spatial data (Kesper et al. 1999). Spline interpolation has certain advantageous properties, especially (Kesper et al. 2000)

- Closed analytical expression, which is e.g. relatively easy derivable.
- Local support: control points have only local importance, i.e. moving a control point position in space only modifies its narrow neighbourhood.
- Strong convex hull property: all points in and on a V-NURBS lie in the convex hull of the control points by which they are determined. In the linear case control points correspond with measured points.

This model combines data modelling, by storing measured data in control points respective by interpreting measured points as control points and model behaviour by providing algorithmic functionality. This allows:

1. Modelling information in 3D, especially supporting underground engineering and geo-sciences.
2. Homogeneous visualization of spatial and non spatial information. This is because the control point vector can easily be extended to representing any attribute, not only geometry, since the components of the control points are linearly independent.
3. Convenient methods for reconstruction of heterogeneous data, based on transforms into one single concise and homogenous model.

Uncertain data

Uncertain data can be embedded by using Fuzzy Set Theory, which provides simple strategies for rule-based analysis and search in complex data structures based on linguistic statements (Haas et al. 1995, Möller 2003). The rule base consists of a description of the situation (IF – part) and its resulting reaction (THEN – part). The IF – part is composed by one or more conditions, which are combined logically by operators (AND / OR, etc.). The evaluation of the definition of the situation is realised by an inference operator that calculates the degree of membership for the chosen fuzzy rules. Finally combining operators lead to conclusions about the system behaviour by evaluating the respective output conditions (fig. 6).
The specific analytical impact is defined by an adequate appending or deleting of rules. To support this complex incident, the content of truth of each rule can be modified by an association factor. This value associates a factor to each rule, which can be used as an individual weighting for certain criteria. It can also be used for the adjustment of rules while calibrating the process model. Several possibilities exist to link fuzzy systems with self learning algorithm to achieve a more optimized solution due to this manipulating factor (Möller 1995).

The application of a fuzzy rule based system (FRBS) leads not only to more realistic treatment of gradual transitions between individual classes; it also supports the consideration and treatment of uncertainty within the determination of individual parameters. The results of one computational step represent the fuzzy input variables for the next step. Hence arithmetic operations can be replaced by fuzzy operators meaning that the fuzzy theory extends the classical arithmetical operation.

Visualization of uncertain data

An essential function of common GIS solutions is the overlaying and merging of thematic maps in varying contexts. Attributes having a spatial distribution are interrelated to provide additional, derived information. This work pak-

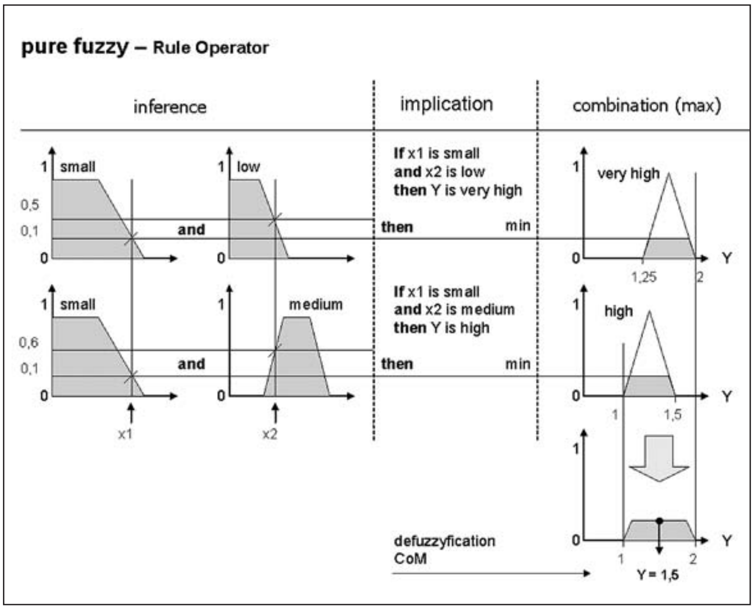

Figure 6: Principles of fuzzy rule based modelling

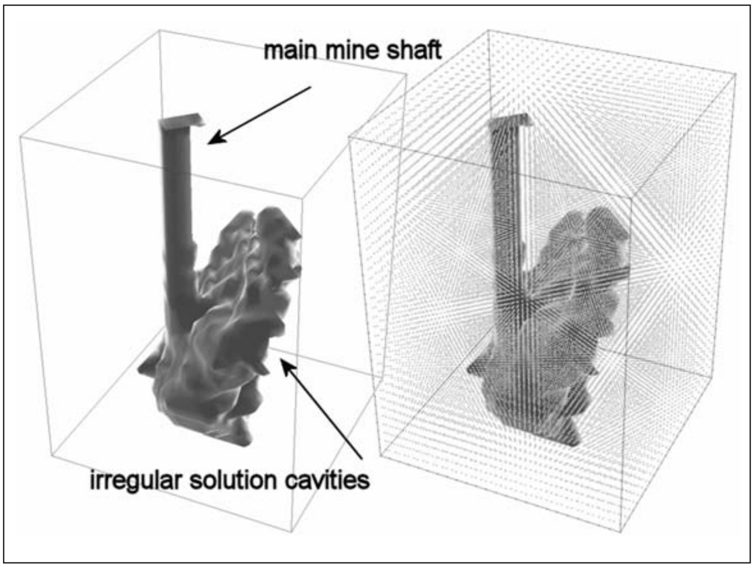

Figure 7: Rendering of complex trilinear geometry showing cavities of a flooded salt mine in a salt diapir (200 m x 200 m x 350 m) near Stassfurt, Germany

kage will extend these operations to 3D Space, particularly considering the visualization and modelling of uncertain data which is especially required by the GEOPHYSICS sub-project.

The NURBS based representation model, and especially the implicit trilinear subtype, developed at the Dept. of Computer Science of the University of Hamburg, easily allows the identification of homogeneous areas in spatial systems, even if the underlying data base lacks in quality, quantity or reliability by operating on value intervals rather than scalar values (Körber et al. 2004, Zemke et al. 2004). The implicit representation allows all three basic set operations (and thus any set operation). This approach is by no means restricted to simple geometries, see figure 7 showing the complex geometry irregular solution cavities and the main shaft of a salt mine near Stassfurt, Germany.

Implicit interpolation is inherently dependent on scale. A large area sampled narrowly will eventually exceed the limits of what is reasonably representable with standard PCs. For this reasons a data model will be developed, together with adequate adaptive algorithmic functionality, as the HADU project must correlate models from highly different size and scale. Because the model resolution ranges from centimeters to several meters it has to prevented that the much larger areas with broad resolution must be modelled with the same resolution as the small narrowly sampled areas.

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No. 2 Information Systems in Earth Management – Kick-Off-Meeting, University of Hannover, 19 February 2003, Projects, 65 pages.

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No. 5 Continental Margins – Earth's Focal Points of Usage and Hazard Potential – Status Seminar, GeoForschungsZentrum (GFZ) Potsdam, 9-10 June 2005, Programme & Abstracts, 112 pages.

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Investigation, Utilization and Protection of the Underground

Despite the growing importance of renewable energy sources, it can be assumed that coal will retain its pivotal role in the German energy supply in the coming decades. However, coal can only be an important part of the sustainable energy scenario if the amount of CO_2 released during its combustion is minimised or does not reach the atmosphere at all. CO_2 capture and storage is one of several options that would achieve this goal. A number of issues, however, still stand in the way of this technology's large-scale application.

Therefore, a portfolio of 10 research projects between academia and industry is being funded by the German Ministry for Education and Research (BMBF) under the umbrella of the R&D Programme GEOTECHNOLOGIEN. The overall aim of the integrated joint projects is an assessment of the various options for underground CO_2-storage in Germany. The research projects comprise established solutions, such as CO_2-injection in depleted oil and gas fields or deep coal seams, as well as new approaches which have received only little attention up to now, for example the recycling of sequestered CO_2 by microbial and biochemical transformation in the deep subsurface environment.

Currently only one project is focused on the research field »Technologies for an underground survey in urban areas.«

The abstract volume contains the presentations given at the »Kick-Off-Meeting« held in Hannover, Germany, in September 2005. They reflect the multidisciplinary approach of the projects, which are expected to provide a substantial scientific basis for decision-makers when assessing this innovative technology.

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