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CO₂SINK – From Site Characterisation and Risk Assessment to Monitoring and Verification: One Year of Operational Experience with the Field Laboratory for CO₂ Storage at Ketzin, Germany

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ABSTRACT

The CO₂SINK pilot project at Ketzin is aimed at a better understanding of geological CO₂ storage operation in a saline aquifer. The reservoir consists of fluvial deposits with average permeability ranging between 50 and 100 mDarcy. The main focus of CO₂SINK is developing and testing of monitoring and verification technologies. All wells, one for injection and two for observation, are equipped with smart casings (sensors behind casing, facing the rocks) containing a Distributed Temperature Sensing (DTS) and electrodes for Electrical Resistivity Tomography (ERT). The in-hole Gas Membrane Sensors (GMS) observed the arrival of tracers and CO₂ with high temporal resolution. Geophysical monitoring includes Moving Source Profiling (MSP), Vertical Seismic Profiling (VSP), crosshole, star and 4-D seismic experiments. Numerical models are benchmarked via the monitoring results indicating a sufficient match between observation and prediction, at least for the arrival of CO₂ at the first observation well. Downhole samples of brine showed changes in the fluid composition and biocenosis. First monitoring results indicate anisotropic flow of CO₂ coinciding with the “on-time” arrival of CO₂ at observation well one (Ktzi 200) and the later arrival at observation well two (Ktzi 202). A risk assessment was performed prior to the start of injection. After one year of operations about 18,000 t of CO₂ were injected safely.

Keywords: CCS, CO₂ storage, CO₂ monitoring, CO₂ modelling, saline aquifer, microbiology, risk assessment, Ketzin

1. Introduction

The development of strategies for sustainable and safe technologies to substantially reduce emission of greenhouse gases to the atmosphere is one of the major challenges of the next century. Geological CO₂ storage is identified as one of the most promising technologies to effectively reduce anthropogenic greenhouse gas emissions to the atmosphere (IPCC, 2005). Different storage technologies are under development and are tested at large scale experiments. As part of the Norwegian Sleipner project, off-shore storage of CO₂ in a saline aquifer with high permeability is tested at an industrial scale and primarily monitored by 4D seismic and gravity measurements (Arts *et al.*, 2004a, b and Chadwick *et al.*, 2007). The use of enhanced oil and gas recovery as a storage technology for CO₂ is currently being tested at the Weyburn (Chadwick *et al.*, 2006, 2009) and K12B (van der Meer *et al.*, 2006) field sites. Improving monitoring and verification, and the efficiency of storage operations in saline aquifers is the focus of the on-shore projects in USA (Frio), Australia (Otway), Japan (Nagaoka), and Algeria (In Salah) and Germany (Ketzin) (Michael *et al.*, 2010).

The CO₂SINK (CO₂ Storage by Injection into a Natural Saline Aquifer at Ketzin) project is the first pilot project for on-shore geological CO₂ storage into a saline aquifer in Europe. CO₂SINK aims to enhance the understanding of the underlying physical, chemical and biological processes involved in geological CO₂ storage in saline aquifers, to gain practical experience with monitoring and verification of CO₂ storage, to test the predictability of different coupled models, and to verify technologies required safe long-term underground storage of CO₂ (Borm and Förster, 2005). The main focus of the project is the development, testing and benchmarking of monitoring techniques, using a broad range of geophysical, geochemical and microbiological methods.



Fig. 1: Location of the pilot experiment CO₂SINK at Ketzin (Germany)

Geophysical monitoring tools are deployed to observe CO₂ migration in the subsurface and to provide a tomography of the CO₂ evolution in the reservoir. Here we apply surface and downhole measurements to test and optimise the resolution of different methods and to follow the developing CO₂-plume. The use of complementary approaches will help to verify the

detection limit of different monitoring tools. Time-lapse crosshole seismic monitoring has proved to be a sensitive tool to track CO₂ migration at the Frio and the Nagaoka projects (Spetzler *et al.*, 2007, Onishi *et al.*, 2009). 4D seismic surveys were successful tools for monitoring CO₂ evolution in two large scale projects: Sleipner and Weyburn (Arts *et al.*, 2004, Li, 2003, Chadwick *et al.*, 2006, 2009). The feasibility of monitoring CO₂ migration due to electrical resistivity changes in field applications has been evaluated by Ramirez *et al.* (2003) and Christensen *et al.* (2006). Joint evaluation of geophysical and geochemical monitoring results is expected to help reduce non-unique images of tomographic inversions.

1.1 Project Setup at Ketzin

The storage site is located near the town of Ketzin in the state of Brandenburg, about 20 km west of Germany's capital Berlin (Fig. 1). At this site, natural gas has been stored for thirty years gas at a depth of 250 to 400 m until the operation was abandoned due to commercial reasons. The Rupelian mudstone served as cap rock and has demonstrated its suitability for gas storage operation successfully. The former gas storage formation is separated by an additional 200 m thick clay-rich caprock from the CO₂ storage formation at 600 m depths. The site included industrial land and infrastructure and a gas storage permission that enabled easier development of a testing site for underground injection of CO₂. The operation of the CO₂ underground storage is regulated under mining legislation of the state of Brandenburg. A maximum of 60,000 t of food grade CO₂ is targeted to be injected, with the total amount to be adjusted according to scientific and site-specific requirements. A project internal and an external evaluation of the storage activities will be carried out after injection of every 20,000 t CO₂ as part of a risk assessment review.

The CO₂SINK project started in April 2004. Pre-injection preparation included obtaining regulatory approvals, a public outreach program, and the operational work at the Ketzin site – drilling of wells (see 4.1), coring and logging, installation of downhole monitoring tools and building the injection facility (Prevedel *et al.*, 2008, Schilling *et al.*, 2009). CO₂ injection commenced at the end of June, 2008. CO₂ is injected into Upper Triassic sandstone (Stuttgart Formation) at a depth of 650 m. The principal structural trap consists of a double-anticline that forms a classical multi-barrier system. The CO₂ is injected into the reservoir at temperatures and pressures above the critical values.

The geophysical monitoring of CO₂ migration is complemented by geochemical and microbiological investigations of rock cores and water samples taken during drilling, testing and storage operation to study the influence of microorganisms on precipitation, mineral alteration and corrosion processes.

Industrie best-practice for well completion in geological storage projects were enhanced by new technologies for CO₂ monitoring via Ketzin wellbores using a smart casing concept of such extent for the first time. An intensive well bore logging program is applied to control well integrity.

Gaseous and water soluble tracers were applied to better follow the migration of CO₂ within the reservoir. A gas membrane sensor (GMS) was used to monitor changes in the reservoir gas composition in the observation wells in near real time, as a low cost, high resolution alternative to U-tube sampling performed in Frio and Otway (Freifeld *et al.*, 2009, Dodds *et al.*, 2009).

After injection of about 18,000 t of CO₂ into the saline aquifer at Ketzin, the first results of monitoring and storage operation are presented here and discussed in conjunction with predictions given by the numerical models.

2. Site Characterization

The target reservoir for CO₂ storage at Ketzin is the 80 m thick Triassic Stuttgart Formation. High permeability sandstone channel facies of good reservoir quality ranging up to 20 m alternate with muddy flood plain facies rocks of poor reservoir quality (Förster *et al.*, 2006). The distribution of the aquifer within the matrix is highly heterogeneous (Frykman *et al.*, 2006). The temperature of the formation is around 35 °C at the depth of injection (650 m). The subsurface site exploration comprised investigations at different scales prior to and after the drilling of the wells. Förster *et al.* (2009), Norden *et al.* (2008) and Norden (2010) show results from the integration of past and new exploration data used to delineate (1) the freshwater aquifer / aquitard system and the flow conditions that would alter the water chemistry in the case of CO₂ leakage and (2) the local geological structure including fault systems that could act as fluid conduits during storage.

Mud gas analysis, using a procedure described by Erzinger *et al.* (2006), revealed very low gas concentrations in the storage horizons. Substantial mud losses were observed in the formation of the former gas storage horizon, indicating the hypo-hydrostatic pressure in the abandoned, shallower storage site.

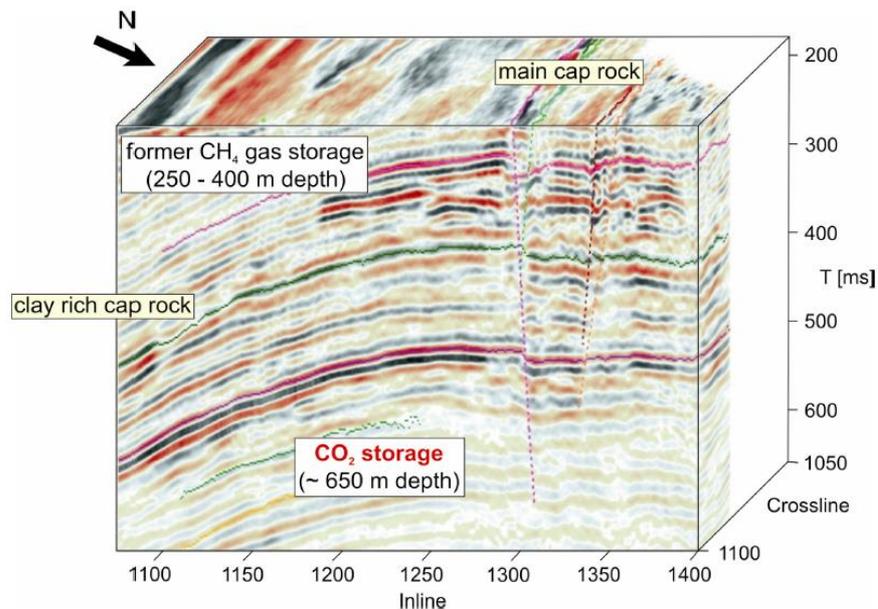


Fig. 2: Cross-section derived from 3D seismic tomography showing the abandoned gas storage, the fault structure, cap rock, and reservoir (modified from Juhlin *et al.*, 2007)

A 3D reflection seismic survey was performed in 2005 to image the geological structure of the site down to depths of about 1,000 m (Fig. 2). In addition to constrain the geological structure of the site, the 3D seismic data serve as baseline for seismic monitoring of CO₂ injection. Details of the data processing and interpretation are described by Juhlin *et al.* (2007). In order to better characterize the shallow subsurface, additional 3D travelt ime tomography was applied to data from the top of the Ketzin anticline, where faulting is present (Yordkayhun *et al.*, 2009, Kazemini *et al.*, 2009). The laboratory petrophysical and petrological characterization of the drill cores, together with the results of the 3D reflection seismic survey (Juhlin *et al.*, 2007) and geological models, provided the basis for stratigraphic imaging of the geological structure at Ketzin (Fig. 2). For the risk assessment an important question was how deep the faults in the more central part of the anticline extend. Reprocessing of the 3D seismic revealed mainly NW-SE striking features within the Stuttgart formation. The reflection data

indicate at least one east-west striking fault zone was observed to extend into the Tertiary unit. The vertical displacement of the fault appeared to be much smaller than the thickness of the cap rocks. This indicates that the former gas storage formation and the CO₂-reservoir are effectively separated.

A number of production, injection, and slug tests were conducted in the injection well (CO₂ Ktzi 201/2007) and the two observation wells (CO₂ Ktzi 200/2007, CO₂ Ktzi 202/2007), in the following referred to without the prefix and the suffix. Test objectives were to derive the test zone transmissivity and to deduce permeability and the static formation pressure (Wiese *et al.*, 2010, this issue).

Tab. 1: Physico-chemical properties of the fluid samples during pump test taken after 30, 55, 61 and 79 m³ of cumulative produced volume (Ktzi 202)

	KTZI 202 No. 10	KTZI 202 No. 18	KTZI 202 No. 20	KTZI 202 No. 26	Method
Date	8.1.2008	9.1.2008	9.1.2008	10.1.2008	
Vkum [m ³]	30,2	54,7	60,8	78,7	
x times of borehole volume	2,6	4,7	5,2	6,8	
Temperature [°C]	26,3	27	27,1	27,3	
pH-value	6,7	6,5	6,5	6,4	DIN 38404-C5
Lf ref. 25°C [mS/cm]	219	222	222	223	DIN 38404-C6
Eh against Ag/AgCl [mV]	-126	-163	-163	n/a	
Acid capacity KS (4,3) [mmol/L]	1,51	0,96	1	n/a	DIN 38409-H7 titration
Base capacity KB (8,2)[mmol/L]	1,36	1,28	1,26	n/a	DIN 38409-H7 titration
Density [g/cm ³]	1,148	1,151	1,151	1,151	pycnometer/density bottle/gravity bottle

Element/ion	c (m) mg/L	c (m) mg/L	c (m) mg/L	c (m) mg/L	Method
cations					
Lithium, Li	1,8	1,8	1,8	1,8	HV-LU 04: Li-AAS
Sodium, Na	87.400	90.400	88.400	90.400	DIN 38406 E14
Potassium, K	412	297	294	282	DIN 38406 E13
Magnesium, Mg	814	835	852	842	EN ISO 11885
Calcium, Ca	2.092	2.059	2.133	2.090	EN ISO 11885
Strontium, Sr	47,9	47,6	48,8	48,9	HV-LU 04: Sr-AAS
Manganese, Mn	1,4	1,4	1,4	1,4	EN ISO 11885
Iron (total), Fe	7,4	6,7	6,4	5,56	EN ISO 11885
Ammonium, NH ₄	18,3	18,5	18,6	18,9	DIN 38406 E5
Barium, Ba	0,068	0,072	0,069	0,082	DIN 38406 E5
anions					
Chloride, Cl ⁻	134.000	139.000	136.000	139.000	DIN 38406 D1-4
Bromide, Br ⁻	42	45	46,5	44,9	DIN EN ISO 10304-1 (D19)
Sulphate, SO ₄ ²⁻	3.893	3.676	3.638	3.744	DIN 38405 D5
Hydrogencarbonate, HCO ₃ ⁻	88	57	56	58,7	DIN38409 H7
TDS (calc.)	228,8 g/L	236,4 g/L	231,5 g/L	236,5 g/L	
Silicic acid, H ₂ SiO ₃	11,6	10	9,2	8,8	EN ISO 11885
Boric acid, HBO ₂	35,9	35,6	35,8	36,2	EN ISO 11885

The recovery of the permeability in the wellbore vicinity was achieved by an N₂-lift clean up procedure and a KCl-slug injection, to establish the anticipated injection regime and to prevent halite scaling in the near well area, respectively. The success of the clean-up procedures of wells, i.e. removal of residues from drilling mud and helper agents like CMC (Carboxymethylcellulose) and xanthan (polysaccharide consisting of monomers of C₃₅H₄₉O₂₉), was verified by a production, injection and slug test procedure and an intensive monitoring of production water.

Hydraulic testing evaluated as single-hole tests revealed formation productivities of around $0.05 \text{ m}^3 \text{ day}^{-1} \text{ kPa}^{-1}$ and $0.1 \text{ m}^3 \text{ day}^{-1} \text{ kPa}^{-1}$. Based on the thickness of 20 m of the permeable zones of the formation, this translates into permeabilities between 50 mDarcy ($0.05 \cdot 10^{-12} \text{ m}^2$) and 100 mDarcy ($1 \cdot 10^{-12} \text{ m}^2$) for the reservoir (Wiese *et al.*, 2010, this issue). Early analysis of hydraulic tests prior to injection indicated a “low-flow” boundary located somewhere between the injection and the observation wells. The monitoring results and the timing of arrival (compared to the modelling results) of CO_2 in the second observation well (Ktzi 202) depict to a “no-flow” boundary which is most probably located North of Ktzi 202, striking NW-SE. This effect is possibly further enhanced by a strong anisotropy of permeability as a result of the fluvial sedimentation within the Stuttgart formation.

During a pumping test after completion of Ktzi 202, the total dissolved solid content (TDS) was about 235 g/l with a pH value of 6.5 subsequent to production of 80 m^3 of fluid, which corresponds equal to a seven-fold exchange of the volume of the borehole. The concentration of fluorescein, which served as a tracer for the drill mud, was at the detection limit. Chemical analysis revealed that the principal constituent of the saline fluid is sodium chloride, with noticeable amounts of calcium. Other ions important to be considered for reliable long-term operation of the CO_2 storage were sulphate (SO_4^{2-}) and iron (Fe^{2+}), with concentrations of about 3,500 to 4,000 mg/l and 5 to 6 mg/l, respectively (Tab. 1). More detailed investigations of minor components revealed no toxic heavy metals in reservoir brine samples taken during lift tests (Zettlitzer, pers. comm., detection limit for heavy metals $\leq 1 \text{ mg/l}$ due to high salinity).

The near borehole formation permeability derived from the injection tests was three orders of magnitude lower in the injection well than the permeability derived from the production tests. The observed differences in permeability were indicative of borehole and / or formation damage at the injection well. After lifting about 100 m^3 of formation water using a nitrogen lift, injectivity was increased close to the value expected from the production tests. The formation of fine-grained solids around the filter screens was observed during the N_2 lift. This is most likely a result of a microbiological reduction of sulphate (Zettlitzer *et al.*, 2010, this issue). The precipitation of iron sulphide can be regarded as the main reason for the temporary loss of injectivity in the injection well.

3. Risk assessment: A multi-fold independent assessment

Risk assessment for gas storage is usually based on expert knowledge. Due to the limited number of CO_2 storage sites and the lack of long-term experiences with geological CO_2 storage, expert knowledge of the oil and gas industry will remain an important pillar for risk assessment. Different risk assessment approaches were applied to evaluate the risk of storage operations in Ketzin involving two teams of experts that worked independently:

Det Norske Veritas (DNV) and Untergrundspeicher- und Geotechnologie-Systeme GmbH (UGS) performed independent risk assessments. The operator (Verbundnetz Gas AG, VNG) and the project leader (Deutsches GeoForschungsZentrum GFZ) were not involved in the risk assessments.

Part of the risk assessment and risk management plan involves hazardous operation identification, repeated incident reporting, post-job analysis, and risk management, which was approved by independent authorities and certified specialists who were not permitted to be partners in the project.

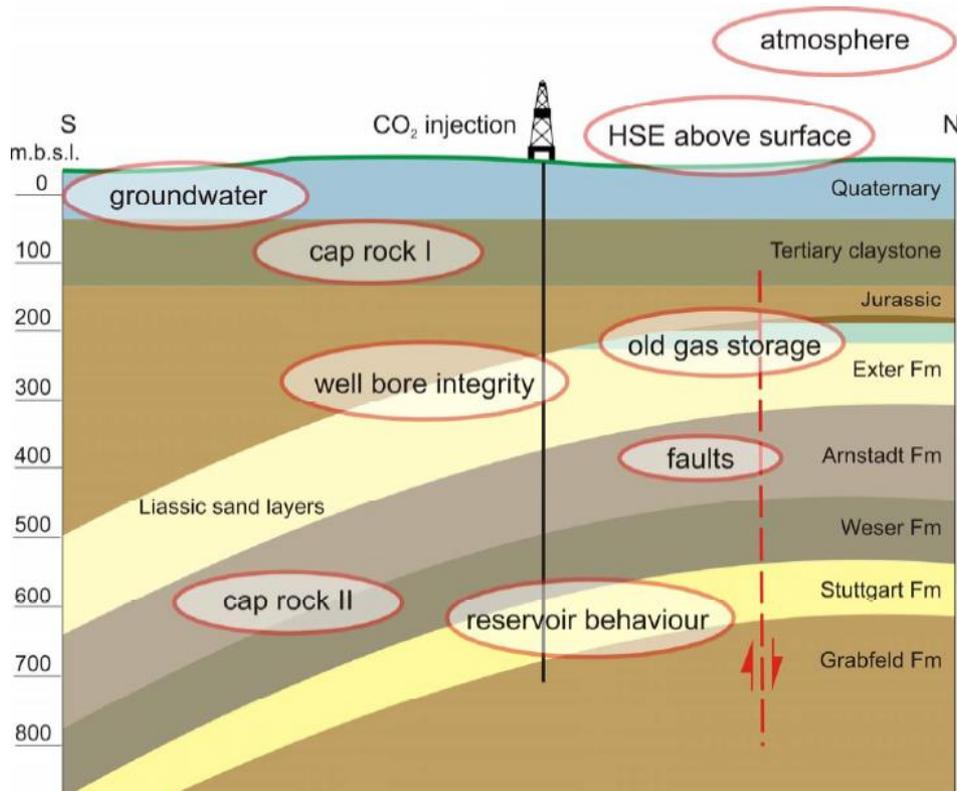


Fig. 3: Compartments addressed during risk assessment

The results of the multi-independent risk assessment were compared. After all assessments were in agreement with respect to Health, Safety and Environmental (HSE) issues, wellbore integrity, reservoir and cap rock (multi-barrier system) the site was given authorization for CO₂ injection. This decision procedure was defined by the operational and scientific board of the project prior to the assessments. The procedure was developed to reduce the risks introduced by an expert knowledge-based risk assessment. All risk assessments for the Ketzin project are based on worst-case scenarios and take into account at least the risks outlined in Fig. 3 and interactions and relations between the compartments.

The following risks were addressed:

A) Public Acceptance

Local public acceptance was recognised as a major issue for CO₂SINK. A forward relation was build up to the major of Ketzin and the council. The people in the neighbourhood of the test site and journalists were informed ahead of all operations and involved in the operations whenever possible. Local requests and local press were always considered first. The local community generally held accepting attitudes toward to the technical usage of the underground due to decades of experience with natural gas storage. The Ketzin site was previously used for thirty years as seasonal gas storage and experienced a well failure during the installation of the storage in the 1970's. Thus, the residents were well informed about the technical processes of gas storage and the involved risks. The close cooperation with the local authorities, e.g. with the mayor of the town of Ketzin, helped to communicate the benefits of the research projects for Ketzin to be a pilot project for long-term storage of CO₂ to the majority of inhabitants e.g. enhanced visibility of Ketzin in the public press and attractiveness for interested citizens, scientists, journalists and politicians.

B) Reservoir Safety

The risks associated with the old seasonal natural gas storage site and the sealing capacity of the secondary seal (Tertiary Clay Stones) and primary seal (Cap Rock) were addressed. Special emphasis was put on well integrity and the nature and behaviour of the crestal faults. Furthermore, interactions between the different compartments were taken into account. A worst case scenario of CO₂ storage performance was established to estimate the consequences of a pressure communication between the Stuttgart Formation and the abandoned Natural Gas storage (NG) reservoir through crestal faults that can be clearly seen on seismic data collected during CO₂SINK.

Therefore, an open fault with a high permeability was considered in the worst case scenario (Frykman and Flach, 2010). This model showed that although about 15-23% (depending on the assumptions of initial conditions at the start of injection) of the CO₂ injected into the Stuttgart Formation may reach the abandoned natural gas storage in a period of about 50 years, the pressure increase in the abandoned NG reservoir will result in a maximum pressure significantly smaller than the reservoir pressure during active seasonal gas storage as much smaller volumes are used for CO₂ storage compared to the former natural gas storage site. The sealing property of the Rupelian mudstone, the cap rock of the former NG is well known and proven from decades of natural gas storage operations at the testing site. This experience was the basis for the permission to operate the CO₂ storage by the mining authority (Landesamt für Bergbau, Geologie und Rohstoffe Brandenburg). Since all three wells are under continuous surveillance, any potential leakage through the wells would be detected and mitigation measures could be taken.

C) Groundwater contamination, health safety and other environmental risk

The abandoned natural gas storage reservoir above the CO₂ storage is characterized by low pressures. Hence, due to the negative pressure gradient within the depleted former gas storage site, if CO₂ might cross the first barrier, it would migrate into the pore space beneath the secondary seal, without approaching the surface. Due to the small total amount of CO₂ to be stored within the research project health safety and environmental risks are considered to be minor by internal and external assessment.

D) Failure of the injection facility with CO₂ release to the atmosphere

The risk of a failure of the injection facility is based on standard risk assessment applied in chemical industry. The facility was planned and erected by specialized companies and audited by TÜV Nord (service provider for technical safety assessment). The injection facility fulfilled the highest safety standards. Therefore, this risk is considered to be minor.

E) Probability of stored CO₂ escaping back to the atmosphere.

Since the project did not apply for CO₂ emission allowances and because it is a science driven project the economical risk was neglected.

The different independent risk assessments as well as the approval by mining authorities, the project coordination team, and the site owner came to the same conclusion: the Ketzin site can be operated without intolerable risks. After the approval by the mining authority, the storage operation of CO₂ was permitted in June, 2008.

4. Experimental Setup

4.1 Site Preparation and Injection Facility

The layout of three wells (Ktzi 200, 201 and 202) in close proximity was planned to obtain high resolution in both, ERT and crosshole seismic experiments (Fig. 4). Furthermore, the CO₂ should arrive at the observation wells within the lifetime of the CO₂SINK project.

From March to September 2007 one injection well and two observation wells were drilled to a depth of 750 m to 800 m (Prevedel *et al.*, 2008) one completed as injection and two as observation wells. They formed a right-angled triangle with a leg length of 50 m and 100 m from the injector. The wells are equipped with a large number of sensors and cables cemented behind the innermost (5 ½”) casing (smart casing installation). The reservoir casing section was externally coated with a two-component material (Ryt-Wrap™) consisting of an epoxy matrix and a polyphenylene sulfide membrane for electrical insulation of the ring-shaped electrodes in the open hole section (Giese *et al.*, 2009). The pressures in the well annuli are recorded permanently to monitor tightness, especially for the last cementation covering the smart casing sensors.

In order to connect the wells with the reservoir, and to protect the cables and filter screens, a staged cementation programme was applied using a newly developed swelling rubber packer technology and a stage cementation downhole tool (Prevedel *et al.*, 2009). All cementations fulfilled the required quality for gas storage operations, assessed with Cement Bond Logs (CBL) and pressure and temperature monitored during and after solidification. Special emphasis was put on the two cementations between the well and the Rupelian mudstone (secondary seal) and between the well and the Weser Formation (primary seal, cap rock directly above the reservoir). To determine the maximum injection pressure for the operation of CO₂ storage, a reservoir integrity test, was implemented next to casing and cementing at each casing shoe during the drilling process. Reservoir integrity tests were only performed in the primary seal resulting in values between 115 bar and 118 bar. The reservoir integrity was not tested on the secondary seal, as this was well known from decades of gas storage operations. The typical procedure in the petroleum industry is to reduce the pressure value by 10 % to 15 % to increase the safety margin. However, to further enhance the high safety standards in Ketzin, this value was further reduced to 82 bar until more experience on the reservoir and fault behaviour is available. Actual results on logging data and geomechanical modelling reveal a maximum bottom hole injection pressure between 129 bar and 138 bar (Sinha *et al.*, 2010). Experiments on well-rock samples show an elasto-plastic behaviour of the rock and a self sealing behaviour of faults. Geomechanical models based on the observed rock properties indicate that no fault reactivation should occur if a smooth pressure increase is applied (Mutschler *et al.*, 2009, Rübel *et al.*, 2008).

During and after the cementation procedure, water of lower salinity than the formation water (brackish and saline water) was injected through the filter screens to start swelling of packers. In order to reduce the risk of clogging due to possible clay swelling in the near well area 3 % KCl solutions were used for most of the procedures, which is a standard procedure in the petroleum industry.

A 6 % KCl slug of 30 m³ was applied to reduce the risk of clogging due to desiccation of the saline brine caused by the injection of dry CO₂ in the area most proximal to the well. The slightly higher ion concentration was chosen in order to achieve a similar electrical conduction in the slug compared to the formation fluid to reduce interferences of the slug with the geoelectric monitoring program. Finally, the well was flushed with N₂ to push the slug from the wellbore into the storage formation before initiation of CO₂ injection. The purpose of the N₂

flush was to lower the water content in the near-well area. A similar N₂-routine was applied during every operational shut-down. This procedure is applied to avoid the formation of multiple phases during shut-down within the injection well which may cause undesired pressure conditions in the reservoir because of different kinetics of condensation and volatilization of CO₂. To date, this course of action assured continuously controllable pressure-temperature conditions within the injection well and avoided possible corrosion effects due to back-flushing of wet CO₂ during shut-in phases.



Fig. 4: CO₂SINK Field-Laboratory at Ketzin

The CO₂ injection facility consists of five main plunger pumps (0 - 1,000 kg h⁻¹), a heating device (305 kW_e) and two intermediate storage tanks (50 t, each). The facility was designed to handle a CO₂ stream of 300 kg h⁻¹ to 3,250 kg h⁻¹ (200 kg h⁻¹ stepwise) at 50 °C at the heater outlet, resulting in a maximum injection of 78 t of CO₂ per day. During commissioning the control parameters were optimised, and an additional air-heater was installed between the CO₂ pumps and the electrical heater to pre-heat the cooled and liquid CO₂ to ambient conditions in order to reduce the required amount of electrical power for gas conditioning and to ensure a smooth injection regime. Additionally installed air heaters reduced significantly energy consumption and variation in CO₂ flux during injection.

An overall control and automation system is used for controlling the injection process and for monitoring the relevant injection parameters: CO₂ flow, temperature along the injection string, pressure data from the formation, and the pressures at the wellheads. All emergency shut-down (ESD) functionality is software independent and has been certified by TÜV and the technical control board of the project. Furthermore, the mining authorities acknowledged the emergency and operation plans of the plant.

The CO₂ flux is measured using a coriolis gas flow meter two meters away from the well head. The well head and the annuli pressures of all three wells are recorded continuously using pressure transducers connected to the overall control and automation system. In the injection

well, temperature and pressure are additionally monitored with a bottom hole sensor. Following the same standards used in the gas storage industry, surface and subsurface safety valves are operated independently from the control and automation system with a hydraulic single-well control panel close to the well. Additional manual valves act as further safety equipment.

4.2 Monitoring CO₂ Migration

CO₂ migration is monitored using a broad range of geophysical, geochemical and microbiological methods (Fig. 5). A smart casing installation – permanently installed sensors outside the innermost casing – is used to enhance the reproducibility of measurements due to constant coupling conditions and to allow for measuring with a high repetition rate. Distributed Temperature Sensing (DTS) cable and electrodes for electrical resistivity measurements are installed behind the casing in the partly cemented annulus of the wells.

The high electrical conductivity of the saline brine in comparison to the low conductivity of CO₂ allows the use of electrical resistivity as a sensitive CO₂ saturation proxy. Hence, geo-electrical measurements are applied together with laboratory investigations under simulated *in situ* conditions for calibration (Kießling *et al.*, 2010). The measurements are carried out using 15 circular electrodes distributed along the casing in each well as part of the smart casing installation together with fibre-optic cables. The electrodes are fixed to the casing at 10 m intervals. Electrical surface-surface and surface-downhole measurements extend the resistivity imaging to regional scale. At the surface, sixteen electrical dipoles are installed. They form two concentric circles around the three wells with radii of 800 m and 1500 m, respectively. The dipole length is 150 m.

DTS temperature measurements from the surface to the bottom of the well are used to determine if CO₂ is in the gaseous, fluid or supercritical state, and to indicate latent heat and fluid flow induced processes within the wells. DTS was installed using fibre optic cables behind the casings of all three wells over the entire length of the well. This technique enables temperature measurements as a function of depth and time with relatively high spatial, temporal and ΔT resolution (for details see Hennings *et al.*, 2005). An electrically insulated cable was successfully deployed for active heating (A-DTS) outside the innermost casing of the injection well to increase the sensitivity of fluid flux measurements (Freifeld *et al.*, 2007).

An optic pressure sensor (bragg-gratings) is deployed for real-time measurements of the wellbore pressure and temperature in the injection well (approx. 550 m depth) into which CO₂ is injected. The fibre optic cable connected to the sensor is used as an additional DTS temperature sensor close to the injection tube to follow the heat evolution triggered by CO₂ injection. Since this fibre-optic cable is installed in direct contact with the injection string and the additional DTS cable of the smart casing is mounted outside, the combination of two DTS cables – one outside the casing, one inside the casing close to injection string – allows for heat flow measurements into the formation using the injected CO₂ as a heat source.

In addition to the permanently installed sensors, an extensive well bore logging program is applied to control well integrity using pressure-temperature measurements (pressure temperature logs), Schlumberger Reservoir Saturation Tool (RST), Cement Bond Logs (CBL), Ultra Sonic Imaging (USIT) and Magnetic Inductive Defectoscopy (MID) measurements.

Bottom hole pressure at the injection well as well as well head pressures at the observation wells are continuously monitored. The data will be used for history matching of the pressure evolution within the reservoir and in that way will deepen our understanding of the reservoir behaviour.

Planned seismic monitoring includes 3D surface measurements before the start of injection (baseline) and repeated measurements during injection and after abandonment. In addition,

Vertical Seismic Profiling (VSP), Moving Source Profiling (MSP), and crosshole seismic tomography were or will be applied at shorter time intervals compared to the 3 D seismic in order to image CO₂ migration in more detail during injection. To reduce the noise and to reduce the enlargement of the CO₂ plume, the injection of CO₂ was interrupted three times for crosshole seismic experiments after one, two and twelve months since injection startup. These interruption times corresponded to 660 t, 1,700 t and 18,000 t of cumulative amount of CO₂ injected, respectively. Therefore, data-logging operations and fluid sampling were performed prior to the several-days-long repeat seismic surveys. This helped to reduce the noise of seismic data and slows the expansion of the CO₂ plume.

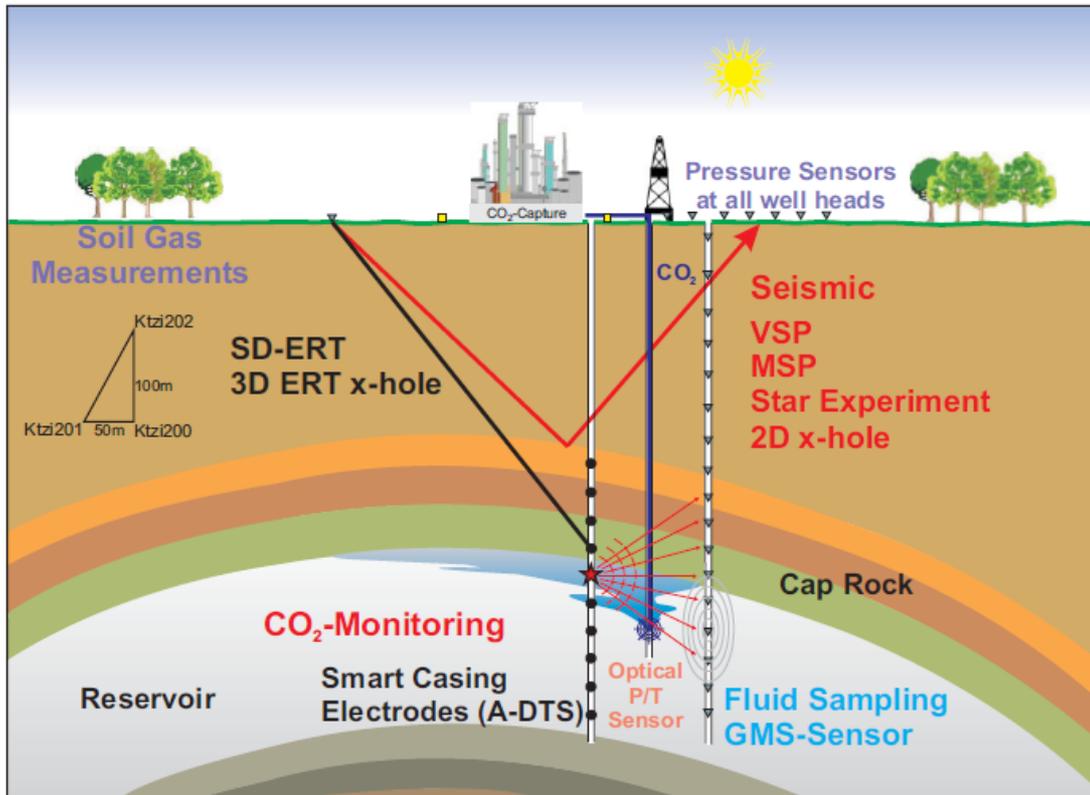


Fig. 5: Overview of installations and monitoring activities at the CO₂SINK Storage Site at Ketzin: Soil Gas Monitoring, pressure sensors at all wellheads (including casing pressure determination to control the cemented annulus), pressure-temperature monitoring using Bragg-grating optical sensors in the injection well. The smart casing includes DTS and A-DTS as well as 15 electrodes outside all three wells. Seismic and geoelectric surveys from the surface to the surface (seismic 3D, 2D line, Star experiment) and from the surface to the borehole (VSP, MSP, SD-ERT) as well as 2D crosshole seismic and 3D crosshole ERT. Fluid sampling was conducted with a downhole sampler for biological and geochemical monitoring. A long-term installed Gas Membrane Sensor (GMS) in each observation well and a profound logging program in all wells complements the monitoring program at Ketzin.

Prior to CO₂ injection, two water-soluble tracers (fluorobenzoic acid and naphthalenedisulfonic acid) were injected together with the KCl slug to learn more about the reservoir, specifically with respect to effective porosity, migration paths of CO₂, hydraulic connectivity of the injection and observation wells, and their perfusion during the storage operation.

Furthermore, krypton was injected as a gaseous tracer prior to the start of CO₂ injection, directly after the KCl slug. Technical fluids were also used as tracers. Gas composition in the fluid measurements by deep fluid sampling are expensive, complicated and provide limited

sampling opportunities. Therefore, a Gas Membrane Sensor (GMS) was developed to sample and analyse gases in deep boreholes with a high repetition rate (Zimmer *et al.*, 2009). The method uses a membrane between a carrier gas inside a tube and the borehole fluids. Argon was used as a carrier gas to conduct the collected gases through capillaries to the surface, where the composition of the gas phase was analyzed in real-time with a portable mass spectrometer. GMS units were deployed in both observation wells for detailed monitoring of the gas composition and the arrival time of tracers and CO₂.

4.3 Monitoring Geochemical and Microbiological Effects

To determine the original brine composition, including the baseline geochemistry, $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, and to characterize the autochthonous microbial biocenosis, production and lift tests were used to obtain water samples less affected by bacterial and chemical contamination from the drilling operation (Morozova *et al.*, 2010, this issue). Samples were taken using a flow through sampler and double ball liner sampler.

To evaluate sample quality, a contamination control method of spiking the drill mud with fluorescein was established by Wandrey *et al.* (2010, this issue). The detection of small concentrations of fluorescein in downhole samples revealed only minor contamination. This indicated an effective clean up processes in the wells that removed most of the drill mud by water production and N₂ lifting. The results of microbiological analysis of downhole samples compared to investigations of water samples taken during pumping and lifting showed the same dominant microorganisms in the biocenosis, independent of sampling procedure. This strongly suggests that the cleaning procedure after drilling allowed the collection of reservoir samples free of, or less affected by contamination from the drilling operation. Before and during injection, downhole samples of fluids were taken using a double ball-lining and flow-through sampler (PNL 64) to monitor changes in the fluid composition and biocenosis at the depth of the filter screens. The results were compared to the results of samples taken during cleaning and hydraulic testing of the wells. Furthermore, core samples from the drilling operations were examined to reveal the autochthonous biocenosis of the reservoir and to quantify metabolic activity. Deoxyribonucleic acid (DNA) fingerprinting analyses of amplified 16S ribosomal ribonucleic acid (rRNA) genes (Single-Strand-Conformation Polymorphism, (PCR-SSCP), Dohrmann and Tebbe, 2004) and Fluorescence In Situ Hybridisation (FISH) (Amann *et al.*, 1995) were used to investigate biological processes involving the injected CO₂, the rock substrate, the formation fluid and the microorganisms. Possible minor contamination effects caused by using a flow-through sampler – which could not be sterilized for aseptic sampling – can be neglected due to the relatively high numbers of microorganisms (up to 10⁷ cells/ml) found in the well compared to other investigations of the deep biosphere (Stevens *et al.*, 1993, Pedersen *et al.*, 1997).

4.4. Numerical simulation

Various numerical simulations were performed to achieve a deepened process understanding, to predict the arrival of CO₂ at the observation wells and to match the monitored pressure data measured bottom hole in the injection well. The applied geological models do either reflect simplified 2D axis symmetrical models or the full 3D models deduced from seismic surveys, well logging data and assumptions with regard to the regional geological setting (Förster *et al.*, 2006). The predicted plume evolution was used as a basis to organize monitoring campaigns before the arrival of the CO₂ within the observation wells. With regard to the EU directive for large-scale CO₂ storage sites (EU 2009) the history matched models are of particular interest

because in the future it needs to be shown for every site that monitoring and numerical simulations coincide before responsibility can be transferred from industry to the government.

A simulation exercise was performed prior to the start of injection to predict the arrival of CO₂ at the observation wells based on the planned injection rates (Kempka *et al.*, 2010, this issue). Data from the actual injection operation served later as input data for a first history match with the unchanged geological model initially used for prediction. Geochemical observations of the arrival time of the CO₂ in the observation wells, determined with the GMS Sensor, were applied to evaluate the simulation results. Three computational codes (ECLIPSE 100, ECLIPSE 300 and MUFTE-UG, Class *et al.*, 2002, Helmig, 1997) were tested within this exercise. A commercial streamline simulator was used for dynamic simulations (Pamukcu and Hurter, 2009). The simulation also yields the time of arrival of the CO₂ at the observation wells. These results are comparable to simulations described above.

Lengler *et al.* (2010, this issue) applied the TOUGH2 (Pruess *et al.*, 1999) code to study the impact of unknown spatial variability in the petrophysical properties of the storage formation using a stochastic Monte Carlo approach. The effects of halite precipitation caused by injection of supercritical CO₂ in the near-well region and accompanying formation damage, due to clogging of the pore space, was investigated applying TOUGH2 and a streamline-based simulator (Muller *et al.*, 2009).

5. Results and Discussion

5.1 Storage Operation: Experiences of the First Year of Storage Operation

Since the start of injection, the facility has been operated without major technical problems. Intentional interruptions occurred to meet the needs of seismic monitoring, logging, and fluid sampling. To ensure stable injection, and to study the injectivity of the reservoir, variable injection rates and fluid temperatures have been applied and tested to adjust injection parameters (Fig. 6 and 7).

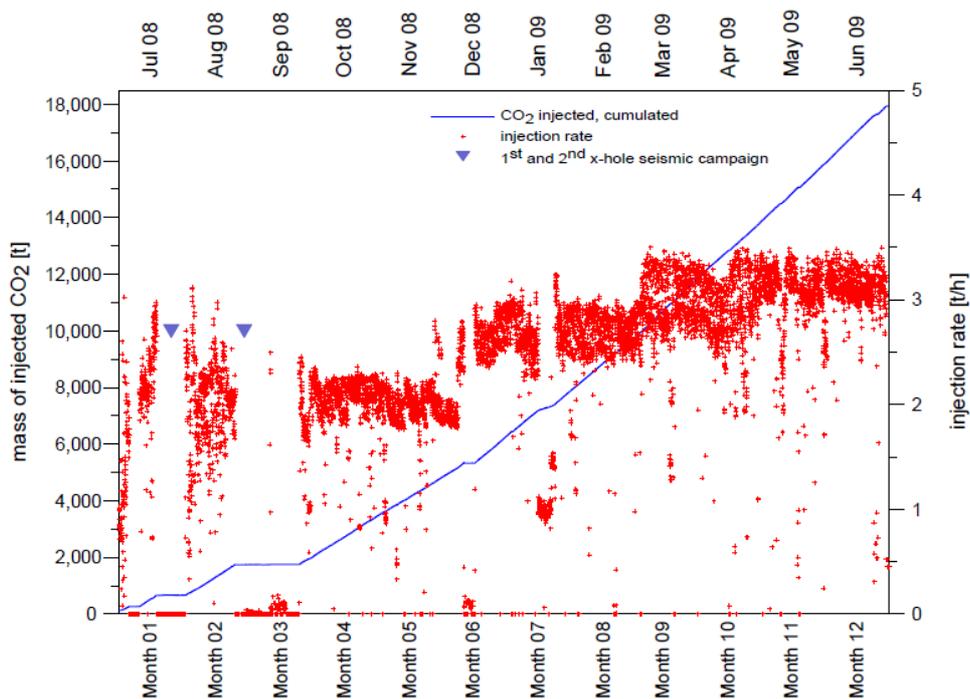


Fig. 6: Injection rate (red dots) and cumulative injected CO₂ (blue line)

The CO₂ flux has been successively enhanced up to the maximum value of 3.25 t/h. The injection facility now operates on a routine basis with an injection rate of approx. (3t/h).

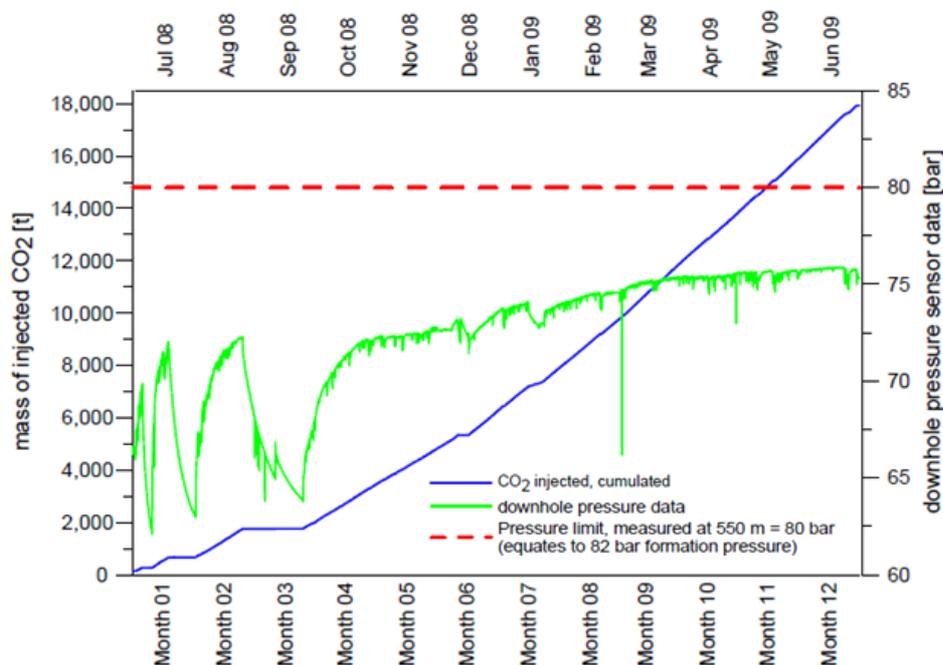


Fig. 7: Injection pressure and cumulated amount of injected CO₂ within the first year of injection operation

Fig. 7 shows the pressure development with increasing amount of injected CO₂. The sensor is about 80 m above the storage formation; therefore the formation pressure at the depth of injection is a few bars higher, depending on the flow rate and pressure-temperature and phase conditions downhole. The injection pressure increases with increasing injection rate which is in accordance to the expected behaviour based on reservoir properties. At the time of writing, there has been no indication that the injectivity has been reduced significantly due to halite scaling.

The reservoir pressure was reduced when the injection ceases during pauses of injection. While comparing the relaxation phases, a reduction of the pressure relaxation with increasing amount of stored CO₂ is observed. The injection pressure and pressure response in the observation wells is in accordance with expectations. If the injection is stopped, the pressure is reduced significantly within the whole reservoir under observation. To enhance the resolution during monitoring experiments a nearly complete stop of the expansion of the CO₂ plume during the measurements is required. This is accomplished by stopping the injection of CO₂.

5.2 Well Monitoring

Temperature measurements with the DTS system started with well completion. The cementation process was monitored successfully using the induced temperature changes (Henninges *et al.*, 2008). The emplacement of the cement was observed as a low temperature signal, whereas a temperature increase clearly showed the process of cement curing and gave early hints about the cement quality that were in close correlation with the cement bond logs procured afterwards (Henninges *et al.*, 2008). Since the start of CO₂ injection, DTS monitoring has been performed with a high repetition rate. The DTS measurements allowed for *in situ* observations of fluid flow due to the different heat transport capacity of the formation fluids,

CO₂ and solid rocks. The results showed the evolution of temperature within the injection well and flow processes close to the first observation well Ktzi 200 (Giese *et al.*, 2009). The evaluation of baseline measurements with active heating allowed for estimation of the *in situ* thermal conductivity of the formation prior to the start of injection (Freifeld *et al.*, 2009). Thermal conductivity is expected to change with increasing CO₂ saturation during injection. The baseline measurements of *in situ* thermal conductivity are in agreement with thermal conductivities measured on core samples.

5.2.1 Monitoring of CO₂ arrival with the Gas Membrane Sensor (GMS)

About three weeks after commissioning and official start of the storage operation, the GMS monitored the arrival of injected gases in the first observation well after injection of ~500 t of CO₂. It was demonstrated that the GMS system allowed online determination of all dissolved and free gases in borehole fluids under extreme pressure conditions on a long term basis with high temporal resolution (minutes). Quantification of the dissolved CO₂ concentration was possible by applying calibration factors determined in the laboratory (Zimmer *et al.*, 2010). The arrival of the Kr gas tracer, technical N₂, H₂, CH₄ and CO₂ were detected, and the direction-dependent relative arrival times of the injected gas to the two observation wells were evaluated (Zimmer *et al.*, 2010).

Arrival in the second observation well Ktzi 202 was nine months after the start of injection, after injection of ~11,000 t of CO₂. As in the first observation well, the gas tracers nitrogen, krypton, H₂ and CH₄ were observed in advance of CO₂ arrival. A detailed analysis of arrival times for the different gases at both wells reflected the technical procedures conducted in the injection well, e.g. injection of gaseous and liquid fluids (Zimmer *et al.*, 2010).

5.2.2 Pressure-temperature logging – Change of density due to CO₂ arrival

Five and nine months after start of CO₂ injection, two repeat pressure-temperature logs were performed to deduce the density gradient in the wells and to gain additional insight into physico-chemical processes within all three wells (Fig. 8). After five months, the main focus of logging was to search for the water table in the three wells, therefore a smaller section, relevant for this purpose has been logged. In the injection well (Ktzi 201) the water level was lowered to the bottom of the filter screens at the start of CO₂ injection, as the entire injection string was filled with gas due to the CO₂ arriving through the reservoir. The CO₂ had already reached the observation well Ketzin 200 prior to the first repeat logging. The logging run nine months after start of injection covering the entire well showed a decrease of density down to 640 m in Ktzi 200, which indicated that the observation well Ktzi 200 well was filled with CO₂ from the surface down to the upper filter screens. From the upper filter screen at 650 m to 580 m depth, the density gradient, pressure and temperature are in accordance with the supercritical state of the CO₂ (density between 0.51 and 0.35). Density continuously decreased with increasing depth resulting in an inverted density profile. Liquid CO₂ was detected between 560 and 300 m due to the temperature within the well that is below the critical temperature of CO₂ (31.1°C) above a depth of about 580 m. The inverse density gradient is the result of a stronger thermal expansion compared to the pressure induced compaction. Above 320 m, pressure, temperature and the density measurements indicated a gaseous CO₂ phase. Beneath the upper filter screens, the fluid in the well was recognized as the original formation fluid with a density of 1.16 g/cm³. This shows that the CO₂ had reached the observation well mainly through the upper filter screen since no increased density of the fluid was observed close to the lower filter, as would be

expected if CO₂ had migrated through the lower filter screen leading to the dissolution of CO₂ in the saline brine and, thus, to an increased density of the brine.

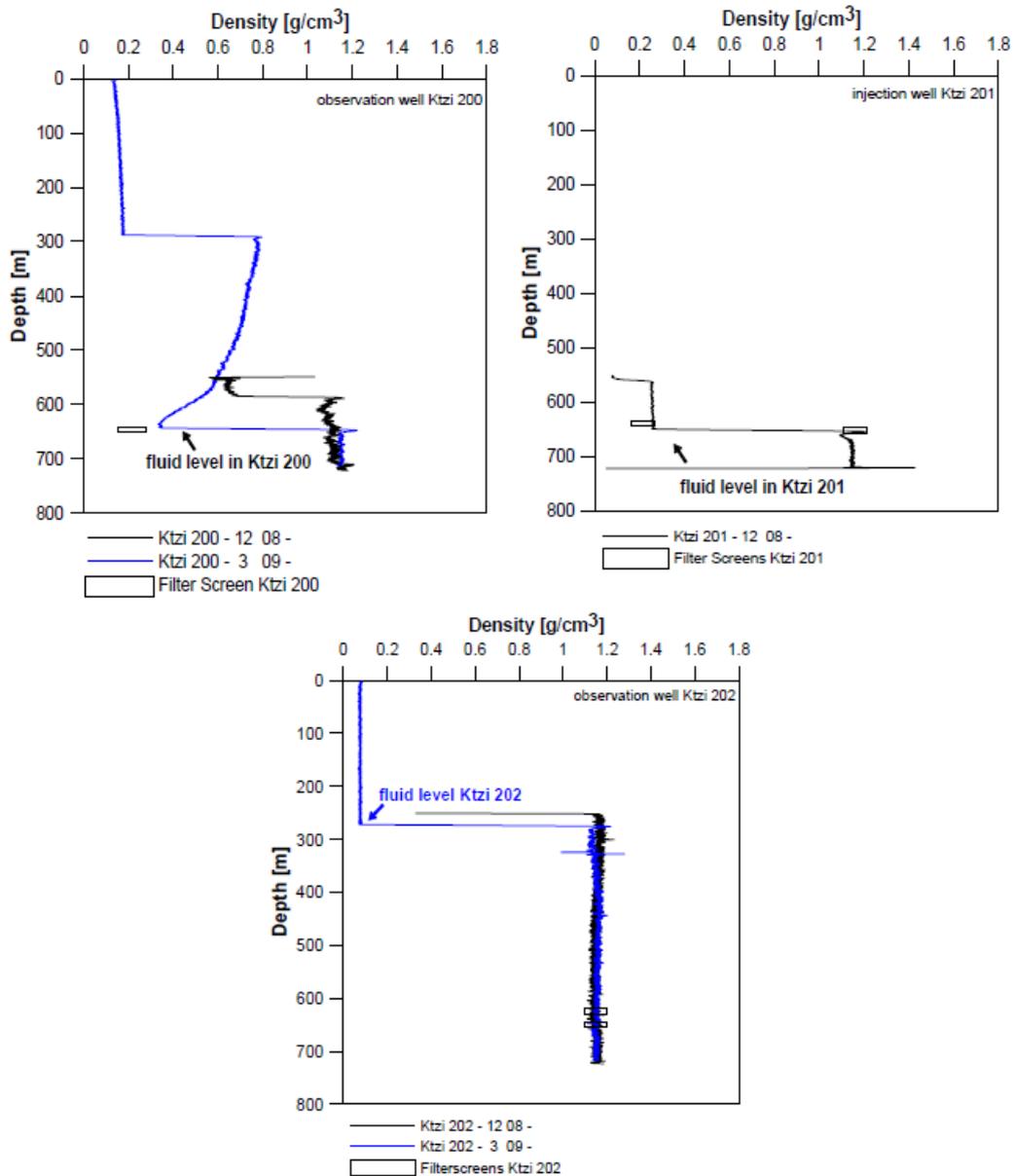


Fig. 8: Pressure-temperature logs and calculated density in the three Ketzin wells six and nine months after the start of injection

Shortly after the arrival of CO₂ in Ktzi 202 the second repeat logging was performed. Even if some CO₂ in the uppermost part of the well above ca. 270 m depth could not be ruled out, the majority of the well fluid (between 280 m and 750 m depth) was interpreted as original formation fluid because of the nearly unchanged density. The arrival of the CO₂ and the resulting ascent of CO₂ within the well led to increased pressure and, in some parts of the fluid column, to the dissolution of CO₂ into the brine. Both led to a main flow direction of the brine from the observation well into the uppermost part of the formation. However, temperature signals in the well and the rising CO₂ show that there was, for a short time period, a more complex flow path of CO₂ through both filter screens into the observation well.

5.3 Monitoring Geochemical and Microbiological Effects: Results from Fluid Sampling

After the arrival of CO₂ at the first observation well, downhole samples showed a significant decrease of $\delta^{13}\text{C}_{\text{DIC}}$ (Myrntinen *et al.*, 2010, this issue). The surface-measured pH value was 5.5 after depressurizing of the water samples to atmospheric pressure. The iron concentration (Fe²⁺) increased from ~6 mg/l to values above 200 mg/l. A coinciding effect was observed after CO₂ arrival at the second observation well. Downhole sampling in the sump of the observation well yielded iron concentrations in the same range. Most of the increase of iron concentration in the observations wells is hypothesized to originate from corrosion processes, because the sump of the injection well was not connected to the reservoir after commencement of CO₂ injection because the water level was lowered below the filter screens due to pressurising of the well (see 5.2.2). The representativeness of downhole samples for processes within the reservoir was dependent on the hydraulic connection between the wells and the reservoir. The fluid needed to pass the well through the filter screens to enable monitoring of geochemical and microbiological processes within the reservoir. Pressure-temperature logging in the wells showed a decrease of the water table caused by the increase of wellhead pressure in all three wells. This limited the significance of chemical composition of downhole fluid samples to monitor reservoir processes. However, the detection of low concentrations of the water-based injection tracer fluorobenzoic acid (FBA) in the observation wells indicated a hydraulic connection between well and reservoir. Immediately after CO₂ arrival in the observation wells, substantial temperature anomalies were observed. The DTS showed an increase of temperature imaging the inflow of reservoir brine. Initially, a temperature decrease of up to 5 °C was recorded at the base of the anomaly, which at the beginning extended down to the depth of the reservoir (Henninges *et al.*, 2010).

DNA fingerprinting and FISH were used to investigate the microbial biocenosis and the related biological processes in the underground. About 10⁶-10⁷ cells ml⁻¹ fluid were detected in downhole samples before N₂ lifting by FISH (Morozova *et al.*, 2010). DNA fingerprinting indicated that the biocenosis was dominated by anaerobic haloalkaliphilic fermentative bacteria. This was expected within the reduced conditions of the reservoir (very low oxygen fugacity), relatively high concentrations of dissolved organic carbon and acetate originating from the drill mud and high salinity. Additionally, sulphate reducing bacteria (SRB) were detected, which corresponded to the observed iron sulphide formation and the decrease in sulphate concentration in the near wellbore area (Würdemann *et al.*, in prep.). FISH analysis revealed decreasing SRB in fluid samples after the N₂ lift, reflecting the effectiveness of the well lifting technique for drill mud removal, which served as an energy and carbon source for microorganisms to produce iron sulphide (Zettlitzer *et al.*, 2010, this issue). Elevated numbers and activity of microorganism after five months of exposure to CO₂ indicate the high adaptability of the microbial biocenosis under extreme changes of environmental conditions (Morozova *et al.*, 2010, this issue). As a consequence, CO₂ injection in the supercritical state changed the biocenosis but did not suppress biological activity.

5.4 Monitoring CO₂ Migration: Geophysical Baseline Measurements and First Results from Repeat Measurements

Interpretations of seismic and geoelectrical measurements provide indirect information on physico-chemical processes in the reservoir. To interpret the geophysical field observations, laboratory investigations in combination with *in situ* observations in deep boreholes were performed. One goal of the CO₂SINK geophysical monitoring experiments is to reveal the spatial resolution limits of the different monitoring methods. In contrast to the storage sites in

Nagaoka (60 m) and Sleipner (250 m), the Ketzin site is a location with thin, complex geological layers and therefore ideal to study the spatial resolution limit of different monitoring techniques.

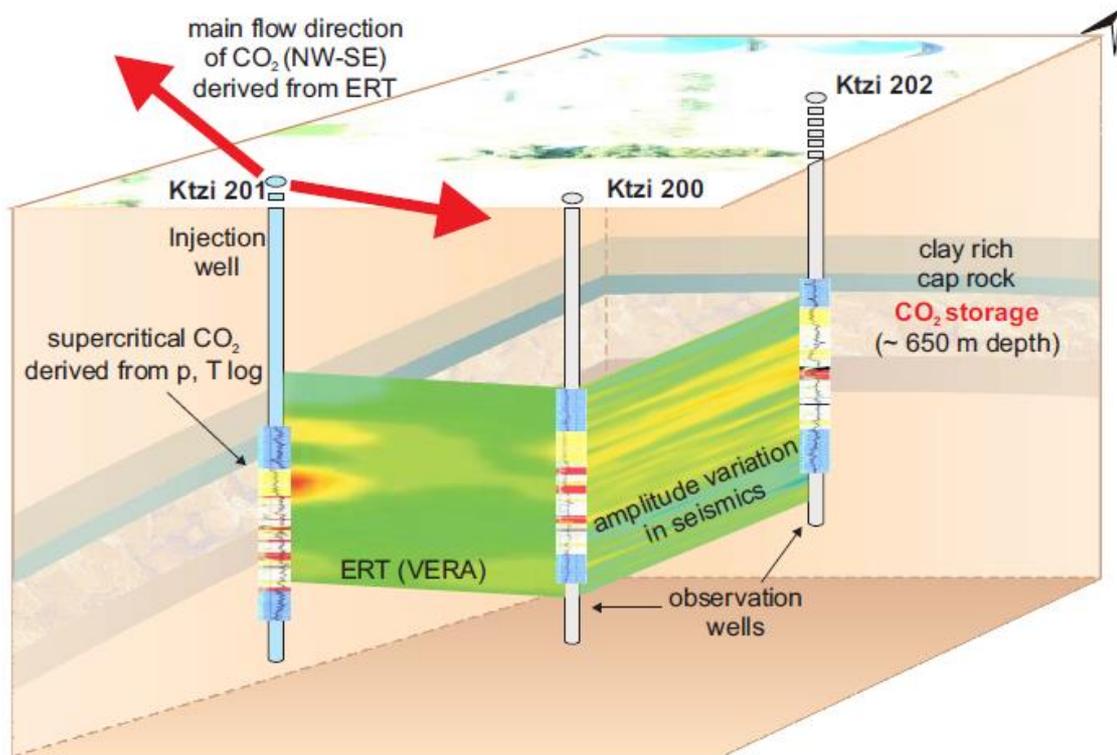


Fig. 9: Preliminary monitoring results. The main NE-SW striking flow direction of CO₂ within the reservoir was deduced from surface-downhole Electrical Resistivity Tomography (ERT). Between the wells, the Vertical Electrical Resistivity-Array (VERA) show higher resistivity within the permeable sandstone layer – indicating the CO₂ distribution. The seismic image (amplitude variation in crosshole seismic) shows no clear indication of the CO₂-plume distribution. Pressure-temperature logs (P/T logs) show that CO₂ is in a supercritical phase within the reservoir. The probable boundaries of permeable sandstone layers are drawn as orange lines – interpolating core sample analyses. At Ktzi 200 and 201 the reservoir sandstones are found at similar depths. To the North (Ktzi 202) the reduced depth of the sandstone layer follows the anticline structure.

At the time of writing, geoelectric monitoring, 4D crosshole ERT measurements and surface to borehole experiments (Fig. 9), have revealed significant changes due to the developing CO₂ plume. The resistivity contrast of more than 50 % between the saline brine and a partially CO₂-saturated sandstone allows determination of injected CO₂ within the reservoir, both between the observation wells (crosshole ERT) and beyond the observation wells (surface to downhole ERT) (Kießling *et al.*, 2010). The resistivity experiments reacted with high sensitivity after small volumes CO₂ were injected. However, as known for potential methods, the inversion to structures gives non-unique solutions, whereas a reasonable sensitivity is obtained close to the well-electrodes.

A systematic change in apparent resistivity of surface to downhole monitoring was observed. The electrodes within the reservoir layer show strong variation in apparent resistivity whereas the other electrodes remain nearly unaffected (Fig. 10, for details see Kießling *et al.*, 2010). Surface downhole experiments in NW-SE directions show a significant increase of the apparent

resistivity, whereas in NE-SW direction an apparent resistivity decrease is observed. This can be explained by a predominantly SE-NW flow of the CO₂.

The electric current preferentially chooses the path of highest conduction not necessarily the shortest distance. The CO₂ leads to a significant increase in the resistivity within the good conductor (saline brine) of the reservoir horizon and a smaller resistivity increase perpendicular to the main CO₂ flow direction. The saline or two phase saline-CO₂ fluid in the reservoir layers have a much higher conductivity than the surrounding mudstones, conduction pathways are focused within the reservoir layer. As long as the CO₂ cloud is within the area represented by the surface electrodes the described simple method can be applied easily. In the main CO₂ migration direction the conduction pathways are more hindered compared to the perpendicular ones, resulting in a higher apparent resistivity in the main flow direction and a reduced apparent resistivity perpendicular to the main CO₂ migration. More detailed investigations are underway.

Time-lapse seismic data showed no considerable change in seismic velocity between the two observation wells within the first two repeats after injection of 660 t and 1,700 t of CO₂, respectively. However, after injection of 18,000 t CO₂ the third repeat survey revealed a clearly visible travelt ime delay in the observations, indicating a velocity reduction in the reservoir due to the injected CO₂ (Lueth *et al.*, 2010). Though there was no clear sign of velocity changes in seismic propagation for the first two repeat experiments, the attenuation of seismic waves due to scattering of seismic energy at small scale heterogeneities may allow observation of the early plume development (Giese *et al.*, 2009). Standard seismic inversion methods are not able to detect the arrived CO₂ after the first two crosshole repeat measurements. However, there are some indications that advanced inversion results will allow for an enhanced detection limit while focusing on the attenuation of seismic waves beside travelt ime inversions.

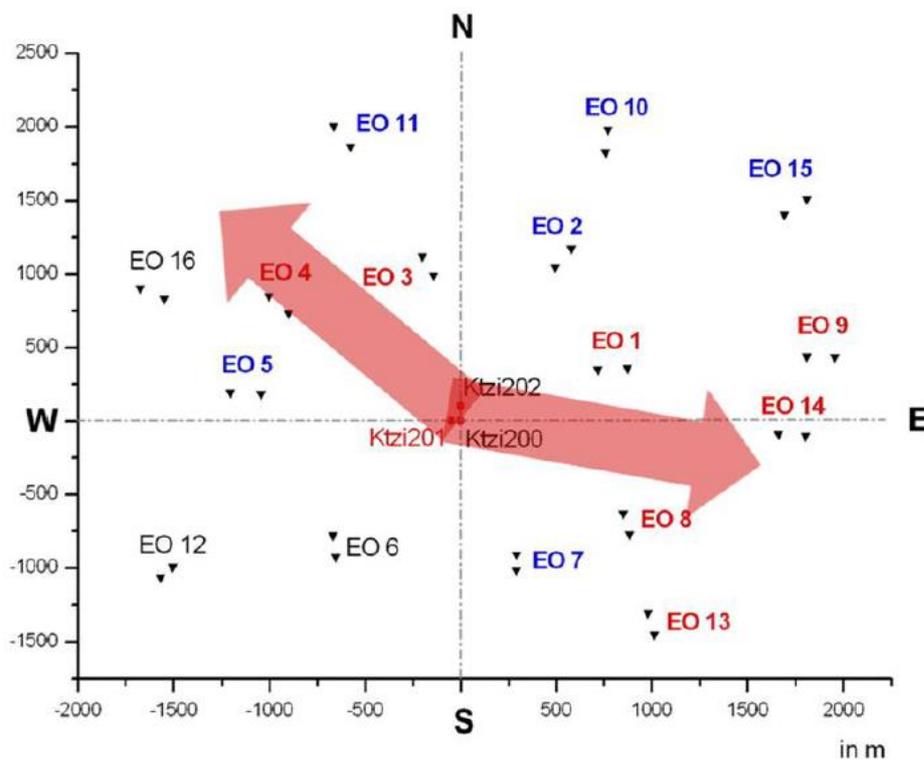


Fig. 10: Main flow direction of the CO₂ cloud derived from first order inversion of geoelectrical surface to borehole experiments (modified after Kiessling *et al.*, 2010). Red stations indicate an enhanced resistivity due to CO₂, black ones apparent enhanced conductivity due to second order effects, black ones no change. Main flow direction is given by the red stations. For details see Kiessling *et al.* (2010).

A reasonable assumption is that during the first few months, part of the CO₂ migrated into thin, highly-permeable, sandstone layers. The thickness of the CO₂ layer was most probably further reduced in size due to gravity override and fingering processes of the two phase fluid flow (CO₂-dominated fluid, H₂O-dominated fluid). Numerical models of wave propagation for standard 3D seismic with a sampling rate of 0.5 and 1 ms indicate that the resolution for 3D seismic experiments should not be sufficient to detect the expected thin layers during the first phase of injection – thinner than five to ten meters (Verdon and Campman, 2009). Therefore, crosshole seismic experiments using higher frequencies were used to enhance the resolution limit. Nevertheless, the thickness of the CO₂ plume seems to be still much smaller than the wavelength of the applied seismic waves for crosshole seismic during the first phase of the injection. A clear change in seismic wave velocities was detected after injection of 18,000 t of CO₂. This demonstrates that crosshole seismic is capable of following the CO₂ plume migration – if the thicker channels are sufficiently filled by CO₂.

Both ERT and seismic investigations have shown their capabilities and limitations to follow the developing CO₂ plume in Ketzin. More detailed analyses and joint seismic and ERT inversions are underway to more precisely quantify and locate the distribution of the injected CO₂.

5.5 Numerical Simulation

Based on the geological model that incorporated all well data and assumptions about the heterogeneity for a fluvial system, arrival of CO₂ to the observation wells Ktzi 200 and Ktzi 202 was estimated by reservoir multi-phase-flow simulation prior to injection using the codes ECLIPSE 100, ECLIPSE 300 and MUFTE-UG (Kempka *et al.*, 2010, this issue). Compared to the measured arrival of CO₂ gas within the wells, the simulations overestimated the required mass of CO₂ based on a too high injection rate which was foreseen prior to operation up to +46%. Applying the variable injection regime results in matched arrival times of the gaseous CO₂ at the first observation well (Ktzi 200) in fair agreement (8-18% deviation) with the field observations considering the uncertainty in input parameters (Kempka *et al.*, 2010, this issue) or an anisotropic behaviour of the subsurface, and most probably a combination of both. Important to note is that operational changes of the injection regime lead to inaccurate estimation of CO₂ migration and masses of CO₂ required to reach the observation wells, because size and shape of the plume and migration velocity are strongly pressure dependent.

Arrival of CO₂ in the second observation well Ktzi 202 was underestimated by a factor of three by all computer codes. Instead of the predicted 3,000 – 4,000 t of CO₂, 11,000 t were needed for the gas to arrive in the second observation well. Reason for that is still unresolved but is expected to be the result of structural geological heterogeneities related to the fluvial system in the Stuttgart formation (Kempka *et al.*, 2010, this issue).

A history match of the observed pressure data downhole in the injection well can be achieved by adjustments of the porosity permeability relationship (Lengler *et al.*, 2010, this issue) applying values in close agreement with the results from hydraulic testing (Wiese *et al.*, 2010, this issue). These simulations were carried out with simplified two-dimensional, axis-symmetrical models and were able to predict the correct arrival time and mass of CO₂ for well Ktzi 200 with a homogeneous geology. Currently the late arrival of CO₂ at well Ktzi 202 is not understood.

Further tests with heterogeneous models based on stochastic methods provide results on the impact of spatial variability for CO₂ storage projects (Lengler *et al.*, 2010, this issue). Under the applied geological constraints, effective storage capacity of the reservoir increases with increasing heterogeneity, whereas the injectivity decreases. This effect is due to an increased net to gross ratio of volume of the reservoir which is reached by the injected CO₂ as well as an

increased dissolution of CO₂. However, this depends strongly on the ratio between viscous and buoyant forces and is therefore supposedly a location specific effect, closely linked to the reservoir rock properties. Nevertheless, implied parameter heterogeneity is not able to explain the late arrival of CO₂ in the second observation well. The arrival time for Ktzi 202 is significantly underestimated in these heterogeneous models as well (Lengler *et al.*, 2010, this issue).

A comparison of the reservoir section of the stratigraphic columns in the two wells Ktzi 201 and Ktzi 202 shows that they have no obvious similarity, although channel facies sand is present in both wells in the very top part. A qualitative assumption of heterogeneity in the reservoir to explain for reduced connectivity between these two wells is the facies pattern found in typical fluvial systems. A possible explanation could be that the upper sand layer could be disconnected by having an abandoned channel located in between the wells. A channel filled with more fine-grained sediment as a result of the main river changing its course to another location could certainly function as a reduction of the connectivity between the two wells. Although there are up to now no additional data to support the existence of such an abandoned channel, it is geologically a plausible reason which could occur as a feature within the length scale of the inter-well distance of 112 m. Repeat geophysical examinations underway will help to better constrain the CO₂ filled structures in the reservoir.

A full reservoir-scale CO₂ injection simulation into saline aquifers is computationally expensive and time-consuming. Therefore, an approach using a streamline model was tested. The model showed that estimates for the arrival time (as before only for Ktzi 200) can be gained at a fraction of the time needed by conventional simulation approaches, although the streamline models are somewhat less accurate (Pamukcu and Hurter, 2009).

In addition to the previously described numerical simulations, models to deepen our process understanding of the reservoir were performed by Muller *et al.* (2009). Due to the process of desiccation of the formation brine by the dry injected CO₂, halite scaling could lead to reservoir impairment in the close vicinity of the injection well. This was studied and shown in a system representative for the Ketzin site (Muller *et al.*, 2009). Potential halite scaling, predicted by the simulations and verified by lab experiments (Wang *et al.*, 2009), led to the decision to inject a KCl slug prior to CO₂ to reduce the risk of halite and clay mineral clogging in the near well area. At the time of writing, no impairment of injectivity has been observed.

6. Conclusions and Outlook

The CO₂SINK storage project at Ketzin is based on an extensive geological, geophysical, petrophysical, geochemical and microbiological exploration. It uses sophisticated downhole installations and includes an intensive public outreach program.

Within one year of injection about 18,000 t CO₂ were injected safely. The reservoir reacted to the injection as expected. The GMS sensor monitored the arrival of CO₂ in both observation wells with a high temporal resolution separating the arrival of different gases, stripped from the formation water or brought into the reservoir by injection. The different gases will be applied as tracers within further calibration of the numerical simulations.

The arrival at the first observation well (Ktzi 200) was in good accordance to the predictive reservoir model; however, the arrival at the second well (Ktzi 202) could not be predicted as well. Deviation between simulation and observed arrival time of CO₂ at the observation wells indicates complex reservoir behaviour. The deviation is most likely the result of an inherent heterogeneity and/or anisotropic permeability behaviour within the fluvial environment. Due to the limited number of exploration wells in CO₂ storage projects, uncertainty will remain.

Accordingly, site characterisation is a continuous iterative process during storage operation and has to include results of geophysical monitoring as well as history matching of reservoir behaviour. Future modelling activities will focus on the improvement of the geological model based on monitoring observations.

Microbial biocenosis showed a high adaptability to the change of conditions due to exposure to supercritical CO₂. Therefore, microbial activity may play a significant role for the long-term behaviour of the reservoir while acting as biocatalysts, e.g. well impairment or enhanced mineral grow rates.

During well completion and one year of storage operation, the smart casing installation operated successfully. ERT measurements showed very promising early results, giving an idea of the anisotropic flow underground coinciding with the “on-time” arrival of CO₂ at the first well and the “late arrival” at the second well.

The combination of site-specific geophysical (seismic, geoelectric, thermal), geochemical and biological monitoring techniques provide new insight into the evolution of the CO₂ plume in space and time. A joint inversion of the different field observations in conjunction with laboratory results will enhance our knowledge of the processes within the CO₂ storage site at Ketzin.

The CO₂ field laboratory at Ketzin offers comprehensive geophysical and geochemical monitoring which provides an opportunity to independently test different reservoir models, to better constrain reservoir and fluid behavior during and after CO₂ injection, and to develop abandonment procedures including long term monitoring concepts. After the first phase of injection of food grade CO₂, the stepwise adjustment towards power plant CO₂ quality is planned. In the coming years, the field laboratory CO₂SINK at Ketzin will be used to test additional monitoring techniques such as an enhanced microseismicity monitoring and Interferometric Synthetic Aperture Radar (InSAR), to improve reservoir modelling tools for CO₂ storage operations, and for field tests of abandonment strategies and post closure monitoring.

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References

Amann, R.I., Ludwig, W., Schleifer, K.-H., 1995. Phylogenetic identification and *in situ* detection of individual microbial cells without cultivation. *FEMS Microbiol. Rev.* 59, 143-169.

Arts, R., Eiken, O., Chadwick, A., Zweigel, P., van der Meer, B., Kirby, G., 2004a. Seismic monitoring at the Sleipner underground CO₂ storage site (North Sea). Geological Society, London, Special Publications 233, 1, 181-191.

Arts, R., Eiken, O., Chadwick, A., Zweigel, P., Van der Meer, L., Zinszner, B., 2004b. Monitoring of CO₂ injected at Sleipner using time-lapse seismic data. *Energy* 29, 1383–1392.

Borm, G. and Förster, A., 2005. Tiefe salzwasserführende Aquifere - eine Möglichkeit zur geologischen Speicherung von CO₂. *Energiewirtschaftliche Tagesfragen - Zeitschrift für Energiewirtschaft, Recht, Technik und Umwelt.* 8, 15-20.

Chadwick, A., Noy, D., Lindeberg, E., Arts, R., Eiken, O., Williams, G., 2006. Calibrating reservoir performance with time-lapse seismic monitoring and flow simulations of the Sleipner CO₂ plume. GHGT-8: 8th International Conference on Greenhouse Gas Control Technologies. Trondheim, Norway, Oxford, Elsevier, 1-6.

Chadwick, A., Arts, R., Bernstone, C., May, F., Thibeau, S., Zweigel, P. (Eds.), 2007.

Best Practice for the Storage of CO₂ in Saline Aquifers—Observations and Guidelines from the SACS and CO₂STORE Projects. British Geological Survey, Nottingham, 267 pp.

Christensen, N. B., Sherlock, D. and Dodds, K., 2006. Monitoring CO₂ injection with cross-hole electrical resistivity tomography. *Exploration Geophysics.* 37, 44-49.

Dohrmann A.B. and Tebbe C.C., 2004. Microbial community analysis by PCR-single-strand conformation polymorphism (PCR-SSCP). *Molecular Microbial Ecology Manual.* 1 and 2, 809–838. Kluwer Academic Publisher, Dodrecht.

Dodds, K., Daley, T., Freifeld, B., Urosevic, M. and Kepic, A., Sharma, S., 2009. Developing a monitoring and verification plan with reference to the Australian Otway CO₂ pilot project. Special Section: Unconventional resources and CO₂ monitoring. *The Leading Edge; Society of Exploration Geophysicists.* v.20 no. 7; p. 812-818; DOI: 10.1190/1.3167783.

Erzinger, J., Wiersberg, T., Zimmer, M., 2006. Real-time mud gas logging and sampling during drilling. *Geofluids.* 6, 3, 225-233.

EU, 2009. DIRECTIVE 2009/31/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 April 2009 on the geological storage of carbon dioxide and amending Council Directive 85/337/EEC, European Parliament and Council Directives 2000/60/EC, 2001/80/EC, 2004/35/EC, 2006/12/EC, 2008/1/EC and Regulation (EC) No 1013/2006. Official Journal of the European Union

Freifeld, B.M., Kryder, L., Gilmore, K., Henniges, J., Onstott, T. C., Lisa, P., 2007. The distributed thermal perturbation sensor: A new tool for *in situ* estimation of formation thermal properties and geothermal heat flux. AGU 2007 Fall Meeting (San Francisco 2007).

Freifeld, B.M., Daley, T. M., Hovorka, S. D., Henniges, J., Underschultz, J., Sharma, S., 2009. Recent advances in well-based monitoring of CO₂ sequestration. *Energy Procedia*. 1, 1, 2277-2284.

Frykman, P. and Flach, T. (2010). Importance of faults and leakage to shallow gas reservoir, included in: Safety Case for Long Term Storage Containment (CO₂SINK project internal report), 2010.

Förster, A., Norden B., Zinck-Jørgensen, K., Frykman, P., Kulenkampff, J., Spangenberg, E., Erzinger, J., Zimmer, M., Kopp, J., Borm, G., Juhlin, C., Cosma, C., Hurter, S., 2006. Baseline characterization of the CO₂SINK geological storage site at Ketzin, Germany. *Environmental Geosciences*. 133, 145–161.

Förster, A., Giese, R., Juhlin, C., Norden, B. Springer, N., 2009. The Geology of the CO₂SINK Site: From Regional Scale to Laboratory Scale. *Energy Procedia*. 1, 1, 2911-2918.

Frykman, P., Zink-Jørgensen, K., Bech, N., Norden, B., Förster, A., Larsen, M., 2006. Site characterization of fluvial, incised-valley deposits. *Proceedings, International Symposium on Site Characterization for CO₂ Geological Storage – CO₂SC 2006* (Berkeley, California 2006), 121-123.

Giese, R., Henniges, J., Lüth, S., Mozorova, D., Schmidt-Hattenberger, C., Würdemann, H., Zimmer, M., Cosma, C., Juhlin, C., CO₂SINK Group, 2009. Monitoring at the CO₂SINK site: A concept integrating geophysics, geochemistry and microbiology. *Greenhouse Gas Technology Conference 9* (Washington, USA). *Energy Procedia*. 1, 2251–2259.

Kiessling, D., Schmidt-Hattenberger, C., Schuett, H., Schilling F., Krueger, K., Birgit Schoebel, B., Danckward, E., Kummerow, J. the CO₂SINK Group. 2010. Geoelectrical methods for monitoring geological CO₂ storage: First results from cross-hole and surface–downhole measurements from the CO₂SINK test site at Ketzin (Germany). *International Journal of Greenhouse Gas Control*. This issue.

Henniges, J., Zimmermann, G., Büttner, G., Schrötter, J., Erbas, K. and Huenges E., 2005. Wireline distributed temperature measurements and permanent installations behind casing, in *Proceedings of the World Geothermal Congress 2005, Antalya, Turkey* [CD-ROM], edited by R. Horne and E. Okandan, paper 1021, International Geothermal Association, Reykjavik, Iceland.

Henniges, J., Prevedel, B., Loizzo, M., 2008. Echtzeit-Beobachtung von Bohrlochzementationen und Sondenbehandlungen mit ortsverteilten Temperaturmessungen. *Tagungsbericht 2008-1, Beiträge der DGMK/ÖGEW-Frühjahrstagung des Fachbereiches "Aufsuchung und Gewinnung" am 10. und 11. April 2008 in Celle*, pp. 47, Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V., Hamburg.

Henniges, J., Liebscher, A., Bannach, A., Brandt, W., Hurter, S. Köhler, S. Möller, F. and CO₂SINK Group 2010. P-T-ρ and two-phase fluid conditions with inverted density profile in observation wells at the CO₂ storage site at Ketzin (Germany). Submitted abstract to GHGT-10, 10th International Conference on Greenhouse Gas Control Technologies.

IPCC, 2005. Special Report on Carbon Dioxide Capture and Storage: Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge and New York, 442 pp.

Juhlin, C., Kim Zinck-Jørgensen R. G., Cosma, C., Kazemeini, H., Juhonjuntti, N., Lüth S., Norden, B. and Förster, A., 2007. 3D baseline seismics at Ketzin, Germany: The CO₂SINK project. *Geophysics*. 72, 5, B121–B132.

Kazemeini, H., Juhlin, C., Zinck-Jørgensen, K., Norden, B., 2009. Application of the continuous wavelet transform on seismic data for mapping of channel deposits and gas detection at the CO₂SINK site, Ketzin, Germany. *Geophysical Prospecting*. 57, 1, 111–123, doi:10.1111/j.1365-2478.2008.00723.x.

Kühn, M., Kempka, T., Class, H., Frykman, P., Kopp, A., Nielsen, C.M., Probst, P., 2010. Predictive modelling of Ketzin - CO₂ arrival in the observation well. *International Journal of Greenhouse Gas Control*. This issue.

Lengler, U., De Lucia, M., Kühn, M., 2010. The impact of heterogeneity on the distribution of CO₂: Numerical simulation of CO₂ storage at Ketzin. *International Journal of Greenhouse Gas Control*. This issue.

Li, G., 2003. 4D seismic monitoring of CO₂ flood in a thin fractured carbonate reservoir (in Carbonate geophysics; an introduction). *Leading Edge*. 22, 7, 690-695.

Lüth, S. Bergmann, P., Giese, R., Götz, J., Ivanova, A., Juhlin, C., Cosma, C., 2010. Time-Lapse Seismic Surface and Down-Hole Measurements for Monitoring CO₂ Storage in the CO₂SINK Project (Ketzin, Germany). Submitted abstract to GHGT-10, 10th International Conference on Greenhouse Gas Control Technologies.

Michael, K., Golab, A., V. Shulakova, V., Ennis-King, J., G. Allinson, G., Sharma, S., T. Aiken, T. 2010. Geological storage of CO₂ in saline aquifers—A review of the experience from existing storage operations. *International Journal of Greenhouse Gas Control*. 4, 659-667.

A. Myrntinen, A., V. Becker, V., R. van Geldern, R., Würdemann, H., Morozova, D., Zimmer, M., Taubald, H., Blum, P., Barth J.A.C., 2010. Carbon and oxygen isotope indications for CO₂ behaviour after injection: First results from the Ketzin site (Germany). *International Journal of Greenhouse Gas Control*. This issue.

Mutschler, T., Triantafyllidis, T., Balthasar K., 2009. Geotechnical Investigations of Cap Rocks above CO₂-Reservoirs, *Energy Procedia*. 1, 3375-3382.

Morozova, D., Wandrey, M., Zimmer, M., Pilz, P., Zettlitzer, M., Würdemann, H., and the CO₂SINK Group, 2010. Monitoring of the microbial community composition in saline aquifers

during CO₂ sequestration by fluorescence *in situ* hybridisation. International Journal of Greenhouse Gas Control. This issue.

Muller, N., Qi, R., Mackie, E., Pruess, K., Blunt, M. J., 2009. CO₂ injection impairment due to halite precipitation. Energy Procedia. 1, 1, 3507-3514.

Norden, B., Förster, A., Vu-Hoang, D., Marcelis, F., Springer, N., Le Nir, I., 2008. Lithological and Petrophysical Core-Log Interpretation in the CO₂SINK, the European CO₂ Onshore Research Storage and Verification Project. SPE Reservoir Evaluation & Engineering - Formation Evaluation, *subm.*

Norden, B., 2010. Modelling of the near-surface groundwater flow system at the CO₂SINK site Ketzin, Germany. Z. geol. Wiss., Berlin *subm.*

Onishi, K., Ueyama, T., Matsuoka, T., Nobuoka, D., Saito, H., Azuma, H., Xue, Z., 2009. Application of crosswell seismic tomography using difference analysis with data normalization to monitor CO₂ flooding in an aquifer. International Journal of Greenhouse Gas Control. 3, 3, 311-321.

Pamukcu, Y., Hurter, S., 2009. Simulations of Breakthrough Time for CO₂ Injection at Ketzin. Geophysical Research Abstracts. 11, EGU2009-9637, EGU General Assembly 2009.

Pedersen, K., 1997. Microbial life in deep granitic rock. FEMS Microbiology Reviews. 20, 3-4, 399-414.

Prevedel, B., Wohlgemuth, L., Henniges, J., Krüger, K., Norden, B., Förster, A., CO₂SINK Drilling Group, 2008. The CO₂SINK boreholes for geological storage testing. Scientific Drilling. 6, 32-37.

Prevedel, B., Wohlgemuth, L., Legarth, B., Henniges, J., Schütt, H., Schmidt-Hattenberger, C., Norden, B., Förster, A., Hurter, S., 2009. The CO₂SINK boreholes for geological CO₂ -storage testing. Energy Procedia. 1, 1, 2087-2094.

Ramirez, A. L., Newmark, R.L. and Daily, W.D., 2003. Monitoring carbon dioxide floods using electrical resistance tomography (ERT): Sensitivity studies. Journal of Environmental and Engineering Geophysics. 8, 3, 187-208.

Rübel, S., Mutschler, T., Balthasar, K., Hauser-Fuhlberg, M., Triantafyllidis T., 2008. Cap Rock Integrity during and after CO₂-injection. Report of GEOTECHNOLOGIEN Statusseminar 2008.

Schilling, F., Borm, G., Würdemann, H., Möller, F., Kühn, M., 2009. Status Report on the First European on-shore CO₂ Storage Site at Ketzin (Germany). Energy Procedia. 1,

Sinha B.K. Ouellet, Bérard T. 2010, Estimation of principal horizontal stresses using radial profiles of shear slownesses utilizing sonic data from a CO₂ storage site in saline aquifer in Germany, SPWLA 51st Annual Logging Symposium

Spetzler, J., Xue, Z., Saito, H., Nishizawa, O., 2008. Case story: time-lapse seismic crosswell monitoring of CO₂ injected in an onshore sandstone aquifer. *Geophysical Journal International*. 172, 1, 214-225.

Stevens, T., O., McKinley, J., P. and Fredrickson, J. K., 1993. Bacteria Associated with Deep, Alkaline, Anaerobic Groundwaters in Southeast Washington. *Microb Ecol.* 25:35-50

Van der Meer, L.G.H., E. Kreft, E. C.R. Geel, C.R., D. D'Hoore, D., J. Hartman, J. (2006). CO₂ storage and testing enhanced gas recovery in the K12-B reservoir. 23rd World Gas Conference, Amsterdam 2006.

Verdon, J. and Chapman, X. 2010, Seismic monitoring at CO₂SINK -- a feasibility study, 72nd EAGE Conference & Exhibition incorporating SPE EUROPEC 2010 Barcelona, Spain, 14 - 17 June 2010.

Wandrey, M., Morozova, D., Zettlitzer, M., Würdemann, H., 2010. Aseptic sampling of rock cores and fluid samples at the CO₂ storage site Ketzin using Fluorescein as a tracer. *International Journal of Greenhouse Gas Control*. This issue.

Wang, Y., Mackie, E., Rohan, J., Luce, T., Knabe, R., and Appel, M., (2009). Experimental study on halite precipitation during CO₂ sequestration. International Symposium of the Society of Core Analysts held in Noordwijk, The Netherlands 27-30 September, 2009.

Wiese, B., Böhner, J. Enachescu, C., Kühn, M., Martens, S., Möller, F. Rohs, S., Wöhrl, T. Würdemann, H. Zemke, J. Zimmermann, G. and CO₂SINK Group, 2010. Hydraulic characterisation of the Stuttgart Formation at the Ketzin test site. *International Journal of Greenhouse Gas Control*. This issue.

Würdemann, H., Morozova, D., Wandrey, M., Zettlitzer, M., Vieth, A., Zimmer, M. and the CO₂SINK Group, 2010. Temporary loss of injectivity due to microbial processes creating iron sulphide in Ketzin. in prep.

Yordkayhun, S., Tryggvason, A., Norden, B., Juhlin, C., Bergmann, B., 2009. 3D seismic travelttime tomography imaging of the shallow subsurface at the CO₂SINK project site, Ketzin, Germany. *Geophysics*. 74, 1, G1–G15, doi:10.1190/1.3026553.

Zimmer, M., Erzinger, J., Kujawa, Chr., CO₂SINK Group, 2009. *In situ* Down Hole Gas Measurements During Geological Storage of CO₂ at Ketzin, Germany. EGU2009-5003, 2009.

Zimmer, M., Erzinger, J., Kujawa, Chr. and CO₂-SINK Group (2010). The Gas Membrane Sensor (GMS): A new Method for Gas Measurements in Deep Boreholes applied at the CO₂ SINK Site. *International Journal of Greenhouse Gas Control*. Subm.

Zettlitzer, M., Moeller, F., Morozova, D., Lokay, P., Wuerdemann, H., CO₂SINK Group, 2010. Re-Establishment of proper injectivity of the CO₂-injection well Ketzin-201. *International Journal of Greenhouse Gas Control*. This issue.