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THEMATIC ISSUE

The use of tracers to assess drill-mud penetration depth into sandstone cores during deep drilling: method development and application

Linda Pellizzari · Dominik Neumann · Mashal Alawi · Dieter Voigt · Ben Norden · Hilke Würdemann

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Abstract For the utilization of deep saline aquifers in the frame of geotechnical use, such as geological sequestration of CO_2, H_2 or energy storage, a baseline characterization of pristine reservoir rock cores is required to monitor changes in the indigenous microbial communities and pore fluids, and to study alterations in rock characteristics resulting from interaction with geological storage technologies. However, drilling procedures and technical fluids, particularly drill mud, are sources of core contamination. To measure the penetration of drill mud into the cores, three tracers (fluorescein, microspheres, and 4′,6-diamidino-2-phenylindole stained bacteria) were tested under laboratory conditions. The flow of drill mud into core samples was induced by applying uniaxial pressure differentials to the core, and the penetration depth was microscopically determined for each tracer. Fluorescein was extracted from the rock samples and quantified fluorometrically. The results indicate that all tested tracers are suitable for tracking drill-mud penetration. The actual penetration depth seems to be related to differences in mineral composition and texture as well as microfractures. Among all tested tracers, fluorescein labelling is the simplest, cheapest and most accurate method for analyzing the contamination of rock cores by technical fluids. The application of this tracer was successfully applied during two deep drilling campaigns at the CO_2 storage pilot site in Ketzin, Germany. The results highlight that the use of tracers is indispensable to ensure the quality of core samples for microbiological and biogeochemical analysis.

Keywords Fluorescein · Tracer · Subsurface reservoir · Rock core contamination · Drill-mud penetration · Ketzin

L. Pellizzari · D. Neumann · M. Alawi · B. Norden · H. Würdemann (✉)
International Centre for Geothermal Research, Helmholtz Centre Potsdam, German Research Centre for Geosciences (GFZ), Telegrafenberg, 14473 Potsdam, Germany
e-mail: wuerdemann@gfz-potsdam.de

D. Voigt
Institute of Drilling Technology and Fluid Mining, TU Bergakademie Freiberg, Agricolastraße 22, 09596 Freiberg, Germany

Introduction

Due to the increasing geotechnical usage of the subsurface, e.g., aquifers, fossil reservoirs or porous storage media, microbiological and biogeochemical analysis of rock cores are employed for baseline characterization and subsequent long-term monitoring of technical procedures. These studies provide insight to the microbiology and biogeochemical processes of the deep biosphere. However, the recovery of undisturbed pristine rock samples is challenging and the risk of contamination is high, especially when using conventional drilling equipment without devices to reduce the risk of contamination. Drill mud and technical fluids are a major source of biological and chemical contamination during sampling. Organic constituents of the drill fluids may also promote bacterial growth by acting as an energy and carbon source (Zettlitzer et al. 2010; Struchtemeyer et al. 2011). However, the use of drill mud is necessary during coring to lubricate the drill bit, transport cuttings to the surface and stabilize the borehole (Grace 2007).

Several approaches using different dissolved tracers, such as perfluorocarbons (PFTs), or particle tracers, including polyethylene fluorescent microspheres, have

been applied to assess the mud contamination of rock cores during sampling (McKinley and Colwell 1996). Microspheres are particle tracers that are similar in size to bacteria (0.454 μm in diameter). They are internally dyed, allowing them to be observed using a fluorescence microscope. Mimicking microorganisms, microspheres have been successfully utilized during coring operations to obtain samples for microbiological studies (Kallmeyer et al. 2006; House et al. 2003; Smith et al. 2000). Microspheres combined with 4′,6-diamidino-2-phenylindole (DAPI) stained cells have been injected and used as tracers during an Integrated Ocean Drilling Program (IODP) expedition, as part of a pumping experiment intended to test a large volume of basement rock (Fisher et al. 2011). However, the usage of microspheres is expensive when a large volume of drill mud has to be labelled with tracer, to track the mud penetration depth into the core samples.

Fluorescein is one of the first fluorescent dyes, synthesized by von Bayer in 1871 (Sun et al. 1997; Duan et al. 2009). Currently, the water-soluble disodium salt widely known as fluorescein or uranine is among the most-commonly used tracer dyes. It is widely employed in hydrology and hydrogeology to investigate formation permeability and groundwater flow (Goldscheider et al. 2008) and has been used to calculate the contamination effect in formation fluids during hydrologic tests at Cajon Pass, California (Kharaka et al. 1988) and added to the drill mud during the coring of SAFOD wells (Thordsen et al. 2005). Its disadvantage is that it is prone to photodecomposition (Diehl and Horchak-Morris 1987), which can result in the loss of fluorescence due to sunlight exposure in the drill-mud storage tanks. In 2007, fluorescein was added to a KCl/$CaCO_3$/carboxymethyl cellulose (CMC)-based drill mud utilized during the drilling of the cores in the wells designed for geological CO_2 storage in Ketzin, Germany (Wandrey et al. 2010). The concentration of fluorescein in the mud tank was stable during the 3-day testing period. To verify the tracer results, Wandrey et al. (2010) determined the total organic carbon (TOC) concentration in the core samples, which reflects the CMC component of the drill mud. The analyses of fluorescein and TOC revealed that the drill mud penetrated the outer 20 mm of the core samples.

The first part of this study is focused on testing different tracers under laboratory conditions to determine their detection limits and observe differences in the transport and penetration depth of particles using dissolved tracers. The tracers under investigation include fluorescein as a dissolvable tracer and both microspheres and bacteria as particle tracers, to clarify how the physicochemical properties and particle sizes of the tracers influence the penetration rate into the core.

The second part of this study is focused on testing and improving a labelling method in the field to demonstrate the recovery of pristine sandstone cores during two drilling campaigns performed at a CO_2 storage pilot site located in the North German Basin near the city of Ketzin (Würdemann et al. 2010; Martens et al. 2012). The saline aquifer target reservoir for the CO_2 injection is the Stuttgart Formation. It has a thickness of ~75 m, at a depth of 630–700 m (Norden et al. 2010). Three 750–800 m deep vertical wells, the CO_2 Ktzi 200/2007, CO_2 Ktzi 201/2007 and CO_2 Ktzi 202/2007 boreholes (short names: Ktzi 200, Ktzi 201, and Ktzi 202), were drilled in 2007 (Prevedel et al. 2009). In 2011, a shallow hydraulic and geochemical monitoring well (Hy Ktzi P300/2011, short name: Ktzi P300) (Wiese et al. 2013) was drilled into the first aquifer above the CO_2 storage formation. This sandstone aquifer, which is part of the Triassic Exter Formation, was partly cored (404–446 m). One year later, a third deep (~700 m) observation well (CO_2 Ktzi 203/2012, short name: Ktzi 203) was drilled into the Stuttgart Formation. The aim of this well was to investigate the CO_2–fluid–rock interactions in the CO_2 storage formation. Therefore, the Stuttgart Formation, which had been partly in contact with the injected CO_2 for more than 4 years, was completely cored. In all field operations, the drill mud was labelled with fluorescein.

Materials

Tracers

Sodium fluorescein

To visualise the fluorescein (F6377, Sigma–Aldrich, Germany) in the rock, the samples were observed under UV light using a reflected-light microscope (MZ10F, GFP2 filter set, Leica Microsystems, Wetzlar, Germany). Cross-section photographs were taken using a digital microscope camera (Leica DFC 420 C). The photos were assembled using graphic software (Adobe Photoshop CS3 Extended), providing an overall view of the tracer penetration in the sample.

The fluorescein was also extracted from the rock. After the rock sample was ground using a mortar and mixed, 0.250 g of the powder was extracted with 600 μL buffer (50 mM TRIS, pH 9) in a 2 mL reaction tube. The tubes were placed on a vortex and mixed for 30 min at maximum speed. The samples were then centrifuged at 20,800×*g* for 10 min and the supernatant was transferred to a fresh 1.5 mL reaction tube. The extraction procedure was then repeated. The supernatants were combined, centrifuged and transferred to a clean tube. The fluorescein content was measured in triplicate using 96-well plates processed using a filter fluorometer (FLUOstar OPTIMA, BMG LABTECH, Germany).

Microspheres

The microspheres used in this study are Fluoresbrite™ Polychromatic red microspheres (0.5 Micron, Polysciences, Warrington, PA, USA). To analyze the microspheres, 0.5 g of the ground sample was collected in a 2 mL reaction tube and diluted with 500 µL of a 150 g/L NaCl solution. The particle tracer was then microscopically detected using a UV light with a Zeiss Axioskop™ 2 equipped with filters 02 (DAPI), 10 (FLUOS), and 20 (Cy3), a mercury-arc lamp and an AxioCam digital camera. When observed microscopically under UV light, the microspheres show a vivid orange fluorescence.

DAPI-stained bacteria

Pseudomonas halophila was purchased from the Deutsche Sammlung von Mikroorganismen und Zellkulturen (DSMZ), Braunschweig. The bacteria were cultivated in liquid media (300 mL Erlenmeyer flasks), following Fendrich (1988). Cell numbers were estimated by staining aliquots (1 mL) of the culture with 4 µL of DAPI (1 mg/mL stock solution) and counting with a Helber counting chamber using a Zeiss Axioskop™ 2. Cells were collected by centrifugation (10,000×*g*, 20 min, 4 °C) to reach a cell density of $\sim 5 \times 10^6$ cells/mL. For staining, the bacteria pellets were suspended in 50 mL fresh media and subjected to an ultrasonic treatment (mod. Sonopuls™, Bandelin, Berlin, Germany) for 30 s. Then, 35 µL DAPI was added and mixed for 5 s using a vortex. The cells were incubated for 20 min in the dark and added to the drill mud. The same procedure used for microsphere detection was applied to analyze the DAPI-stained cells.

Rock samples

Stuttgart Formation

Two sources of sandstones from the Stuttgart Formation were used in this study. The first sandstone was retrieved from an outcrop at a clay open-pit mine near Erfurt (Gispersleben, Germany). This rock was incubated with drill mud at ambient air pressure or pressure was applied perpendicularly to every surface. These surface samples are strongly weathered, making the preparation of the 40-mm diameter core plugs difficult. The clayey sandstone consists of varying amounts of quartz, feldspar and rock fragments and is reddish in color. The porosities determined from two representative samples are 18.2 and 25.3 % (Kulenkampff and Zemke 2006). The second set of samples originates from Stuttgart Formation rock cores, which were retrieved during the drilling of the third deep observation well, the Ktzi 203 borehole in Ketzin. Similar to the outcrop samples, the sandstones from the Stuttgart Formation are heterogeneous in composition showing variable clay content. Heterogeneous porosity and permeability distributions, related to grain size, facies variation and rock cementation, were observed by Norden et al. (2010) from integrated core-log analysis. The porosity and brine permeability of the sandstone intervals range from ~5 to 35 % and from 0.02 to more than 5,000 mD, respectively. The six core samples investigated in this study were taken mainly from sandy intervals, covering a depth range from ~641 to 670 m below ground level. The sandstone samples are fine-to-medium grained, greyish–green to brownish–red in color, and have varying amounts of cementation. A high amount of clay minerals, mainly Illite [in Ktzi 200 and 201, Norden et al. (2010) measured 13–18 % of Illite, reliable value for Ktzi 203 as well] and organic matter are present in all sandstone samples. The drilled core diameter is 102 mm.

Bentheimer sandstone

In addition to the Stuttgart Formation samples, Bentheimer sandstone samples were used for laboratory flow experiments. This sandstone was selected because it has a porosity and permeability similar to Stuttgart Formation sandstone. The Bentheimer sandstone samples were taken from an outcrop in Lower Saxony. The Bentheimer sandstone (Lower Cretaceous) is a fine-to-medium grained homogeneous quartz sandstone. The selected samples have porosities and permeabilities of ~25 % and 500 mD, respectively.

Exter Formation

During the drilling of the shallow hydrogeological observation well (Ktzi P300) in Ketzin, samples from the Exter Formation sandstone layers above the cap rock of the reservoir for CO_2 sequestration were retrieved for microbiological analysis. The investigated rocks are sandstones to siltstones, with one mudstone. In contrast to the cores from the Ktzi 203 borehole, the drilled core diameter of the Ktzi P300 amounts to 85 mm.

Drill mud

To perform the laboratory experiments, a $KCl/CaCO_3$/CMC-based drill mud was synthesized following the composition data (Table 1) provided by Mi SWACO Deutschland GmbH (Celle, Germany). These data describe the composition of the drill mud used during the Ketzin coring campaign in 2007.

The drill mud used during the coring of the Ktzi P300 borehole consisted of fresh water mixed with K_2CO_3

Table 1 Drill-mud composition provided by Mi SWACO GmbH

Product	Amount/L
Water	920 mL
CMC-LV	25 g
KCl	150 g
M-I Cal SL	60 g
M-I Cide	1 mL
XC-Polymer	2 g

(0.06 kg/L). To avoid the stimulation of sulfate-reducing bacteria (SRB) activity, no organic polymers were added to the drill fluid. For the Ktzi 203 borehole, the use of polymers could not be avoided during the coring due to technical issues. As a result, cellulose-based polymers [CMC, polyanionic cellulose (PAC)] and a natural polysaccharide-based polymer (Biolam) were added in addition to bentonite. Due to the required density of the drill mud (1.21 kg/L) to safely drill the CO_2-bearing reservoir, K_2CO_3 was added ($\sim$0.25 kg/L).

Laboratory test of tracers

During the laboratory experiments, fluorescein, microspheres and DAPI-stained bacteria were tested as tracers. The aims of these experiments were to determine the detection limit of the tracers and to observe differences in penetration depth.

Incubation of samples with drill mud at ambient air pressure or with an applied pressure

Stuttgart Formation samples obtained from the outcrop were cut in 3–4 cm parallelepipeds and saturated with synthetic brine (composition given in Table 2, after Wandrey et al. 2011). To monitor the contamination of the samples, the KCl/$CaCO_3$/CMC-based drill mud was labelled with fluorescein (concentration of 1 mg/L). The samples were wrapped in Parafilm^{TM} such that one side of each sample was not covered. Therefore, the drill mud could only penetrate from one direction into the sample.

Table 2 Synthetic brine composition

Compound	Conc. (g/L)
NaCl	216.59
KCl	0.66
$MgCl_2 \cdot 6H_2O$	6.19
$CaCl_2 \cdot 2H_2O$	7.27
$SrCl_2 \cdot 6H_2O$	0.13
$Na_2SO_4 \cdot 10H_2O$	14.41
NaBr	0.05

The experiments were performed by incubating the samples at room temperature and in the dark with drill mud, either at ambient air pressure or when applying a uniform pressure of up to 90 bar perpendicular to each surface. Ambient air pressure was considered to simulate the field condition after sampling, and verify whether the drill mud would further penetrate the rock core due to gravity. Pressures from 40 to 90 bar were applied to obtain different drill-mud penetration depth with increasing pressure to observe the behavior of different tracers. The incubation time was varied between 1 and 24 h. After every experiment, the sandstone was cut into approximately 3-mm thick layers and the fluorescein penetration was examined microscopically, as described earlier.

Application of a uniaxial pressure difference to simulate coring conditions and induce the flow of drill mud

Because the Stuttgart Formation sandstones are heterogeneous in composition and cementation, the more homogeneous Bentheimer sandstone was used to conduct flow experiments to investigate the influence of uniaxial pressure differences and the related drill-mud penetration into the rock. The samples are 48.6 mm in diameter and 50 mm in length.

The general parameters of the experimental setup are presented in Table 3. Fluorescein was used by itself (in experiments 1, 2, and 3) or combined with microspheres and bacteria. For experiment 1, the synthetic drill mud was labelled with fluorescein at a concentration of 1 mg/L, while 5 mg/L of fluorescein was utilized in the other tests to increase visibility. Two tests were performed with microspheres (concentration of 2 mL/L). In experiment 4, microspheres were combined with fluorescein, and in experiment 5, DAPI-stained cells were also added.

The operating principle scheme of the uniaxial pressure system is shown in Fig. 1. The core sample, located in the core holder, was wrapped in a rubber membrane (Fig. 2) and placed in a vessel filled with oil. Each end of the sample holder was connected to a vessel and filled with water and drill mud. The sample was flushed and saturated with water from the vessel. A containment pressure of $\sim$100 bar was applied to the vessel containing the sample, and the tight membrane guaranteed that drill mud penetrated from only one side of the rock core. The uniaxial pressure was simultaneously raised to force the water and drill mud into the core. The final pressure was 95 bar for the drill-mud vessel and 85–80 bar for the water vessel, resulting in a pressure difference of 15 bar for experiments 1 and 2, and 10 bar for the other experiments. The magnitude of the pressure difference is the same as the pressure between the rock and drill mud during the coring of wells

Table 3 The setup of laboratory experiments using Bentheimer sandstone samples to determine drill-mud penetration by applying a uniaxial pressure difference

Exp.	Difference between drill mud and water pressure	Fluorescein concentration (mg/L)	Microspheres (2 mL/L)	DAPI-stained *Pseudomonas halophila* (10^5 cells/L)
1	15 bar (95–80)	1	–	–
2	15 bar (95–80)	5	–	–
3	10 bar (95–85)	5	–	–
4	10 bar (95–85)	5	Yes	–
5	10 bar (95–85)	5	Yes	Yes

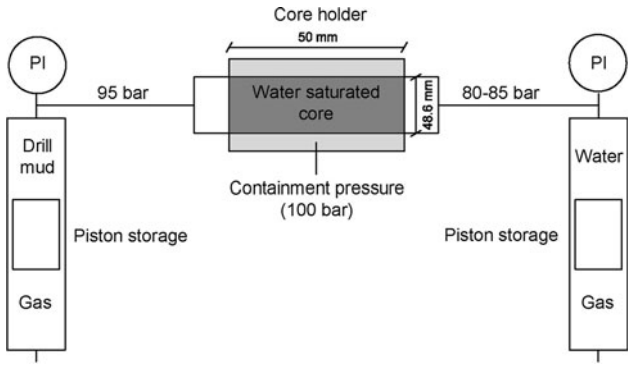

Fig. 1 Principle operating scheme of the uniaxial pressure system

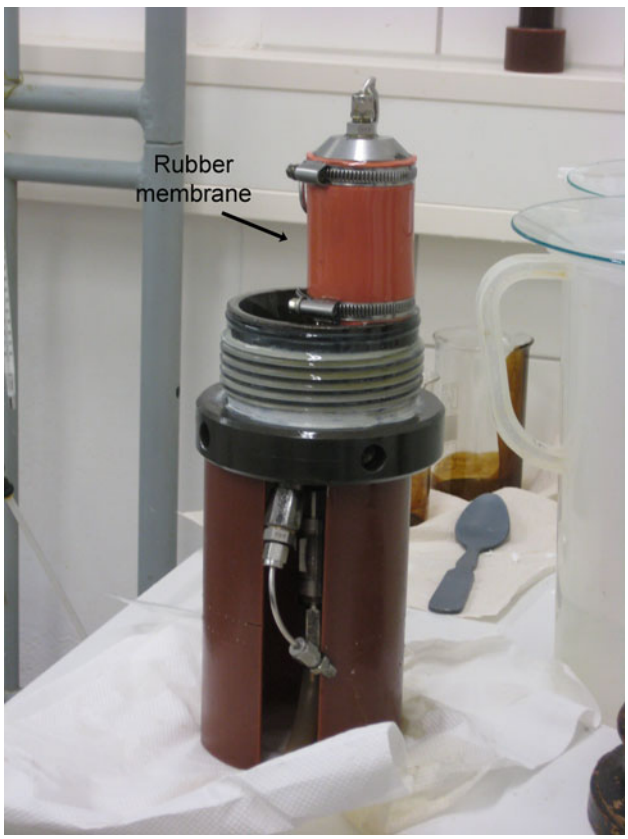

Fig. 2 Core sample wrapped in a rubber membrane and placed in a vessel filled with oil to apply the containment pressure

(Voigt, personal communication) and causes drill mud to flow into the sandstone. After 140 min under these pressure conditions, the sample was removed from the vessel. The sample was wrapped in sterile aluminium foil and cooled until analysis. To observe the penetration of drill mud into the core, the sample was divided into two parts along the direction of the fluid flow using a hammer and a chisel. One part was investigated using a stereo fluorescence binocular to visually detect the fluorescein penetration into the core, while the other half of the sample was cut into 3-mm thick layers and subjected to further analyses, i.e., fluorescein extraction or observation of microspheres and DAPI-stained cells. The layers were sawn using a multi-tool (Dremel™, model 285, Breda, The Netherlands) equipped with a diamond blade. Sawing was started from the bottom, where no drill mud was expected, and the blade was cleaned and flamed with ethanol for sterilization after each cut. Each layer was then ground and homogenized using a ceramic mortar and pestle. The detection accuracy of the method is limited to the size of the rock layers.

Fluorescein, DAPI-stained cells and microspheres were analyzed as described earlier. Fluorescein was extracted and quantified, and DAPI-stained cells and microspheres were microscopically detected using a UV light with a blue/cyan filter for excitation and a red filter for emission.

Field application

Sampling of rock cores using fluorescein as tracer

The application of the fluorescein label method was tested at two Ketzin drill sites (the Ktzi P300 and Ktzi 203 boreholes). At the Ktzi P300 borehole, fluorescein dissolved in water was added to the mud tank during the drilling phase, 3 days before the coring section of the Ktzi P300 well started, allowing adequate homogenization. A total of 40 g of fluorescein was added to 10 m^3 of fluid, resulting in a final concentration of 4 mg/L. The drill-mud tank was not covered and exposed to sunlight, therefore after 4 days the fluorescein concentration was on average 2.8 mg/L (Fig. 3). The first drill-mud sample was retrieved from the surface of the tank 1 day before the coring started,

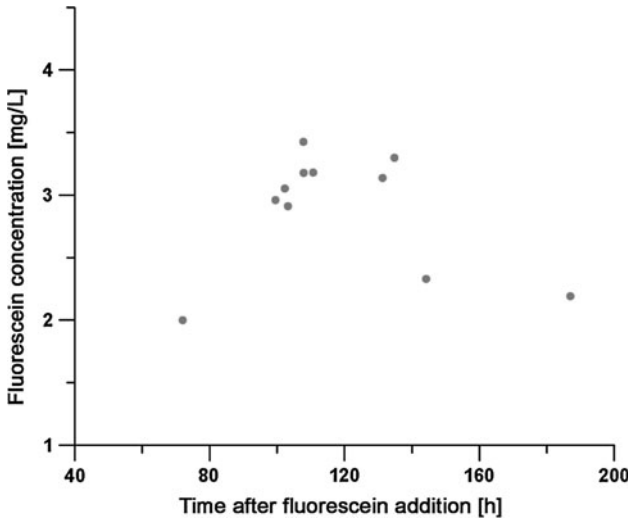

Fig. 3 Monitoring of the fluorescein concentration in the drill mud mixing tank during the coring of Ktzi P300

when the mixing system was not working since 2 days, and therefore it shows a relatively low concentration (2 mg/L). During the coring, new drill fluid was added to the stirring tank in response to losses.

The coring of the third deep observation well (Ktzi 203) was performed in August 2012 and retrieved Stuttgart Formation samples. The Ktzi 203 borehole is located about 25 m from the CO_2 injection well. As expected, CO_2 was observed in the drilled cores of the Stuttgart reservoir. Water containing 380 g of fluorescein was added to the $\sim$50 m^3 drill-mud tank system at the beginning of the coring. For the following 6 days, the concentration was on average 8.4 mg/L.

Sample preparation and incubation

Samples intended for microbiological analyses must be processed as soon as possible to avoid the introduction of oxygen to the inner part of the core and further contamination via diffusion. Therefore, fragments of the samples were immediately observed by microscope to detect the penetration depths of the labelled drill mud and for the cores obtained from the Ktzi 203 well, cross-section photographs were taken. Shortly after core plugs of the inner core, parallel to the borehole orientation, were prepared the same day as the rock core was obtained, or within the following 3 days. A 50-mm diameter drill bit was used to perform the inner coring. Due to the smaller core size of the samples from the Ktzi P300 borehole, the remaining outer core mantle showed a thickness of $\sim$17.5 mm, whereas for the core samples from the Ktzi 203 borehole, showing a diameter of 102 mm, the thickness of the outer core mantle amounts to 26 mm. The tracer was extracted from these remaining outer core fragments and measured by a filter fluorometer. In order to conduct microbiological experiments, the inner core plugs were immersed in sterile synthetic brine and stored in vessels under in situ pressure and temperature conditions (45 bar, 25 °C for samples of the Ktzi P300 borehole and 50 bar, 40 °C for samples of the Ktzi 203 borehole, respectively). Rock and fluid samples were drawn from the Ktzi P300 vessel after 6 months of incubation, and fluid was sampled from the Ktzi 203 vessels after 1 month. The fluorescein concentration was measured in each sample.

In addition to the core investigations, an open-hole pumping test was performed in the Ktzi P300 borehole in January 2012, 5 months after well completion. The pumping phase started with a flow rate of 20 L/min and after $\sim$2 h, the production rate was increased to 24 L/min. At the end of the test, a total volume of $\sim$14 m^3 fluid was produced. To monitor the discharge of drill fluids from the well into the formation, fluid samples were collected during the test and the fluorescein concentration was measured.

Results

Laboratory experiments

During the laboratory experiments in which the sandstone samples of Gispersleben were incubated 1–24 h with drill mud at ambient air pressure, fluorescein could be detected only on the surface of the sample, where the rock has been directly in contact with the mud. Incubation of the samples while applying uniform pressure perpendicular to whole surface resulted in a slightly deeper penetration depth (from the sample surface to 4 mm). In contrast, when using an experimental setup that induced a uniaxial pressure difference, the penetration depth of drill mud was reproducible and could be analyzed in detail under different conditions and using tracers in five experiments (Table 4; Fig. 4). The concentration of all tracers decreased from the surface to the inner section of the sandstone. The fluorescein penetration depths detected fluorometrically ranged from 15 to 33 mm, with an average value of 25 mm. Observed by microscope, the fluorescein could be detected to 16–28 mm depth, with an average of 20 mm. In experiment 2, both approaches revealed similar values. On average, the penetration depth was 5 mm deeper (20 %) when using the fluorometric analysis. The microscopically observed fluorescence signal in experiment 1 (1 mg/L fluorescein) appeared much less intense than in experiments 2–5 (5 mg/L fluorescein). The cross-section pictures (Fig. 5) give an overview of the fluorescein penetration into the rock samples.

The microspheres and DAPI-stained *Pseudomonas halophila* cells were consistently detected at similar

Table 4 Results of the drill-mud pressure experiments using Bentheimer sandstone

Exp.	Difference between drill mud and water pressure	Fluorescein concentration in drill mud (mg/L)	Penetration depth (mm) as detected by			
			Fluorescein (microscope)	Fluorescein (fluorometer)	Microspheres (2 mL/L)	DAPI-stained *Pseudomonas halophila* (10^5 cells/L)
1	15 bar (95–80)	1	16	27	nd	nd
2	15 bar (95–80)	5	17	15	nd	nd
3	10 bar (95–85)	5	20	27	nd	nd
4	10 bar (95–85)	5	19	21	18	nd
5	10 bar (95–85)	5	28	33	36	33
1–5	Average		20	25		

nd not determined

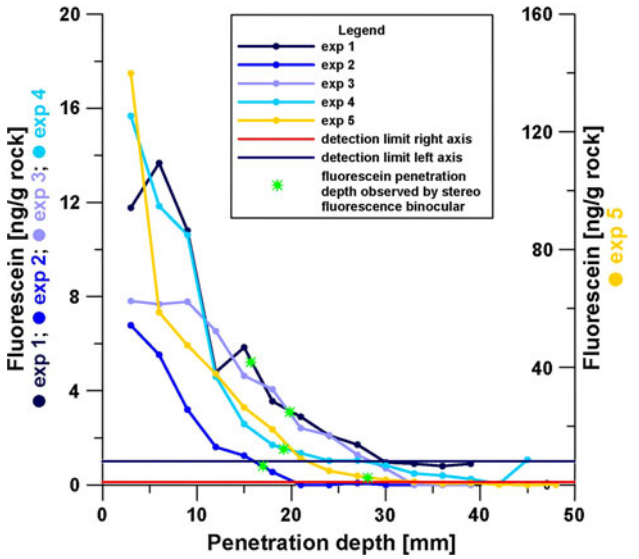

Fig. 4 Fluorescein concentration measured fluorometrically in each sample layer. The *horizontal lines* represent the detection limit

penetration depths as the fluorescein measured fluorometrically (microspheres: 18 to 36 mm, *Pseudomonas halophila* cells: 33 mm).

Field application

The penetration depth of the labelled drill mud varied in the cores retrieved from the two coring campaigns in Ketzin. Some rock fragments were strongly contaminated, whereas in several mudstone rocks, fluorescein could only be detected 2 to 3 mm from the surface, while the formation brine was stored in the inner part of the core. The fluorescein penetration depth for five samples retrieved during the coring of Ktzi 203 is shown in Fig. 6. The results of the fluorescein analyses for the Ktzi P300 and Ktzi 203 samples are shown in Table 5a, b. For the Ktzi P300 vessels, five samples out of eleven (45 %) were not contaminated. For these five samples, fluorescein was detected in neither the rock nor the fluid. Two samples (Mibi 16 and Mibi 19.1) revealed very low fluorescein concentrations in the fluid (corresponding to 0.02 and 0.01 % of drill mud, respectively), and the concentration in the inner rock was below the detection limit of 1 ng fluorescein per g of rock. The control tube containing labelled drill mud showed no significant loss of fluorescein over 6 months. A 40 cm sandstone rock core was retrieved and cut into three equal parts (Mibi 18.1, 18.2, and 18.3) to perform the inner coring. Although these three subsamples originated from the same core, the fluorescein concentrations were remarkably different from each other. The shallowest part (Mibi 18.1) had a high concentration of fluorescein, while it was not detectable in the bottom of the core fragment (Mibi 18.3). Five out of the six incubated Ktzi 203 core samples were free of fluorescein. Only the fluid sampled from one high-pressure vessel (HPV2, MB5) had a very low fluorescein concentration (0.001 % of drill mud).

The fluorescein concentration of the fluid produced during the pumping test of well P300 is shown in Fig. 7. Up to 0.25 mg/L of fluorescein was detected after 6.5 m^3 of production, corresponding to ~8.8 % of the initial concentration in the drill fluid. At the end of the hydraulic test (after 13.5 m^3 of production), fluorescein was still detected at a concentration of 0.2 mg/L, or ~7.2 % of the original concentration.

Discussion

During an earlier coring campaign in Ketzin, Wandrey et al. (2010) detected an average of 15 to 20 mm of drill-mud penetration into sandstone cores by fluorescence microscopy and confirmed these results by TOC analyses, reflecting the carboxymethyl cellulose component of the drill mud. However, an uncertainty for the interpretation of TOC analyses is that even if the concentrations decreased toward the inner part of the core, the background concentrations of the sandstone were unknown. Therefore in this

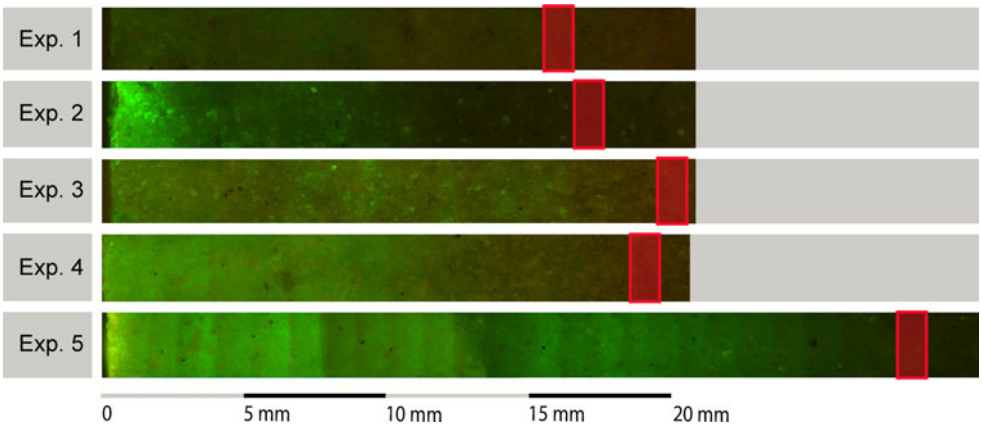

Fig. 5 Cross-section experiments 1–5. On the *left side*, the surfaces of the samples are visible, and the inner parts are shown on the *right*. The *red rectangles* indicate the border between the contaminated and un-contaminated zone (interval of 1 mm)

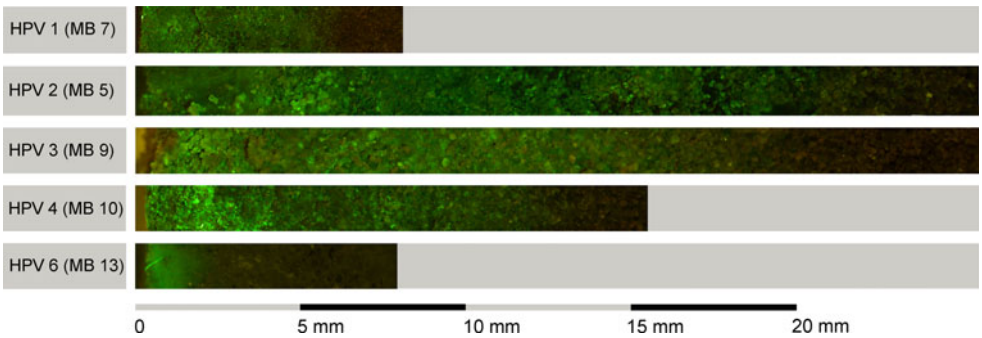

Fig. 6 Cross-sections showing the penetration depth of the fluorescein labelled drill mud for five samples retrieved during the coring of Ktzi 203. On the *left side*, the surfaces of the samples are visible, and the inner parts are shown on the *right*

study, the fluorescein detection was improved through the extraction of rock samples and subsequent fluorometric analysis, resulting in an increase of the detection limit by 20 %. An additional advantage of this method is that it also allowed the quantification of a tracer.

Two outstanding issues are the transport behavior of microorganisms and its comparison to chemical tracers to observe flow processes in soil and rock reservoirs. The migration of bacteria was successfully tracked in several field studies (Hoetzl et al. 1991; Ijzerman et al. 1993). Bacterial tracers were applied to soils or aquifers containing indigenous populations of microorganisms and several methods are employed to distinguish between bacterial tracers and indigenous microorganisms. Molecular or antibiotic (Hoetzl et al. 1991), radioactive (Jewett et al. 1995), and fluorochrome labels (Harvey et al. 1989; Bales et al. 1995) were utilized. An advantage of bacterial tracers is that they realistically mimic microbial contamination through their similar physical and surface properties. Beeman and Suflita (1989) found that bacteria contaminated drilling mud slurries and these bacteria served as a tracer in evaluating the degree of microbial contamination. In this work, DAPI-stained cells of *P. halophila* were applied as a bacterial tracer because they are easy to produce, although bleaching over time and cell lysis caused by high salinity and pH or additives reduce the applicability. Even so, Ijzerman et al. (1993) showed that the cell numbers of DAPI-stained bacteria decreased by only 2–6 % within 48 h and the DAPI staining did not significantly affect the transport of bacteria through porous rock. However, the experimental setup and detection of DAPI-stained cells are cumbersome because the bacteria are similar in color and shape to other naturally fluorescent rock fragments or minerals.

Due to their characteristic orange fluorescence and perfectly circular shape, microspheres were applied as a tracer. They are also easier to detect and distinguish from a fluorescent background. However, microscopic investigation is more time consuming and error prone because only a small area of the sample can be analyzed. The high costs of fluorescent microspheres are another disadvantage, especially considering that drill mud has to be replaced due to losses during coring. In addition, Kallmeyer et al. (2006) reported a surprisingly high loss of microspheres in the field over time.

The penetration depths of tracers into rock cores depend on the applied drill technique, the drill mud composition and pressure, causing drilling induced tensile fractures and the rock characteristics. For the laboratory experiments, Stuttgart Formation samples retrieved from an outcrop and Bentheimer sandstone samples was employed. The main focus of the laboratory experiments was not the observation of the drill-mud penetration depth related to the typology of sandstones, rather the different behavior of the

Table 5 Fluorescein concentration in the Ketzin core samples measured in the outer core mantles and inner core plugs (after incubation in high-pressure vessels)

Ktzi P300 sample	Lithology[1]	Outer core mantle		Inner core plug	
		Outside (ng fluorescein/g rock)	Inside (ng fluorescein/g rock)	In fluid samples % of drill mud	In rock samples (ng fluorescein/g rock)
(a) Ktzi P 300 samples					
Mibi 3	ss	<LOD	<LOD	<LOD	<LOD
Mibi 10	ms	**6**	**6**	<LOD	<LOD
Mibi 12	si, fg, ss	<LOD	<LOD	<LOD	<LOD
Mibi 13.1	fg, ss, si	<LOD	***2***	<LOD	<LOD
Mibi 15	ss	**73**	**66**	**9**	**2**
Mibi 16	ss	<LOD	<LOD	*0.02*	<LOD
Mibi 18.1	fg–mg, ss	<LOD	<LOD	**3**	**9**
Mibi 18.2	fg–mg, ss	nd	nd	**1**	**2**
Mibi 18.3	fg–mg, ss	<LOD	<LOD	<LOD	<LOD
Mibi 19.1	fg, ss	**32**	**27**	*0.01*	<LOD
Mibi 19.2	fg, ss	**44**	**49**	**16**	**40**

Ktzi 203 sample	Lithology[1]	Outer core mantle		Inner core plug
		Outside (ng fluorescein/g rock)	Inside (ng fluorescein/g rock)	In fluid samples % of drill mud
(b) Ktzi 203 samples				
HPV 1 (MB 7)	ss	**44**	**9**	<LOD
HPV 2 (MB 5)	ss, si	**1367**	**285**	*0.001*
HPV 3 (MB 9)	ss, ms–si	**15**	**3**	<LOD
HPV 4 (MB 10)	ss, ms–si	**244**	**51**	<LOD
HPV 5 (MB 16)	ss	**20**	**4**	<LOD
HPV 6 (MB 13)	si, ms	**48**	**10**	<LOD

Values in italics indicate slightly contaminated and values in bold indicates contaminated samples

<LOD below limit of detection indicates un-contaminated samples

nd not determined

[1] *ss* sandstone, sandy; *ms* mudstone, muddy; *si* siltstone, silty; *fg* fine-grained; *mg* middle-grained

[1] *ss* sandstone, sandy; *ms* mudstone, muddy; *si* siltstone, silty

tracers analyzed, therefore the effect of weathering or in situ containment pressure were not studied in detail. In the laboratory experiments performed under ambient air pressure or applying pressures from 40 to 90 bar perpendicular to each surface, fluorescein showed a low penetration depth from 0 to 4 mm. When increasing the pressure from 40 to 90 bar, the fluorescein penetration depth was not measurably increased. The applied pressure did not induce flow through the saturated pores, as the brine could not be displaced. Hence, the drill-mud penetration depth was strictly related to the compressibility of the brine. However, fluorescein labelling of drill mud during the deep drilling campaign at Ketzin in 2007 resulted in penetration depths into sandstone cores between 15 and 20 mm, indicating significant flow during coring. Therefore, laboratory experiments utilizing a uniaxial pressure difference were performed to induce flow and to study the transport behavior of tracers. Differences in the applied pressure slightly affected the penetration depths. Because of their surface characteristics, bacteria can easily bind to clay minerals, iron–oxyhydroxides, and organic matter that constitute the rock and this could influence the bacterial tracer penetration depth. Nevertheless, the results of the laboratory experiments show that the penetration depth of DAPI-stained cells, fluorescein and microspheres labelled drill mud, was in the same range. Despite the differences in physical and chemical properties of the tracers, separation due to different migration velocities in the cores was not observed. Obviously, the flow length of up to 40 mm through the rock core was not long enough to separate the tracers according to their different transport behavior.

As expected, a higher fluorescein concentration (5 mg/L) in the drill mud resulted in better visual detection and increased sensitivity. Since fluorescein is an inexpensive tracer, the usage of higher concentrations in the drill mud does not considerably affect the total operation costs

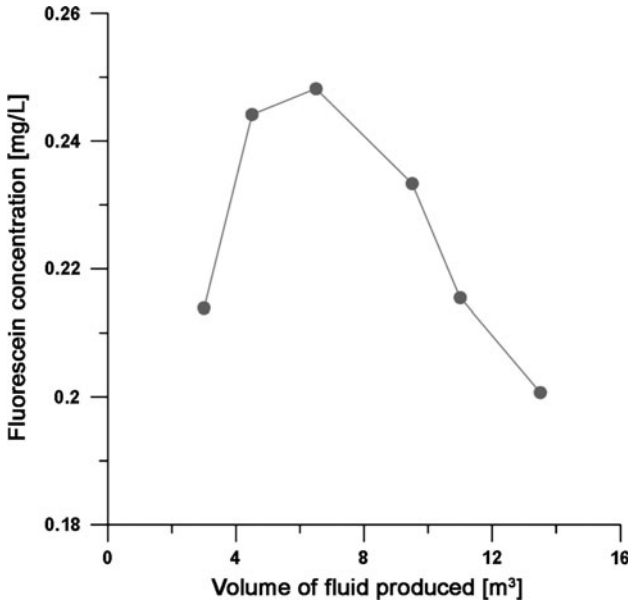

Fig. 7 Fluorescein concentration (mg/L) in the fluid produced during the pumping test at Ktzi P300

and it is recommended for field applications to increase the safety of detection. Moreover, the usage of higher amounts of fluorescein during coring assures detectable concentrations, even if un-spiked drill mud is added during operation. The only disadvantage of fluorescein is that it is prone to photodecomposition, although the tracer concentration in the drill mud was monitored and it showed no significant deterioration within 4 (Ktzi P300) to 6 (Ktzi 203) days of coring. Fluorescein was even detected in the production fluid 5 months after drilling and well completion during and at the end of the pumping test in Ktzi P300 (Fig. 6). This long lifespan of fluorescein in saline fluids was also described by Wandrey et al. (2010). This underlines the suitability of fluorescein to monitor drill-mud contamination in the field, even over longer time periods.

Sampled rock material from cores, especially if used for microbial analyses, should be processed immediately after coring to avoid the further penetration of drill mud or disturbance due to the diffusion of oxygen into the core. Therefore, the evaluation of tracers and detection systems should account for the large number of samples that must be processed in a short period of time. Stressing this point, the results lead to the conclusion that fluorescein measured by a high-throughput filter fluorometer is the most accurate and appropriate method. As heterogeneities and microfractures in cores preclude the exact prediction of drill-mud penetration, a simple contamination control for the microscopic detection of fluorescein helps enormously in the selection of large pieces of pristine core for further preparation. During two coring campaigns in Ketzin, the first steps were microscopic observations of fluorescein in each retrieved sample. Samples with lower penetration depths were chosen for the inner coring, which was performed on the same day as core recovery or up to 3 days after. The inner core was stored with synthetic brine in high-pressure vessels until further analyses. The evaluation of the fluorescein concentration in the brine stored with the rock core allowed an accurate assessment of the sample contamination and served as final proof of the retrieval of pristine rock cores.

Following the described protocol, a sufficient amount of pristine core material preserving the formation brine was collected in Ketzin. The material retrieved during the coring of Ktzi 203 revealed less-contaminated samples than the cores of Ktzi P300. Each sample of Ktzi 203 was microscopically controlled during coring, while only 50 % of the Ktzi P300 samples were analyzed during coring. During inner coring, crowns of 26 mm for the Stuttgart Formation samples and 17.5 mm for the Exter Formation were removed from the outside. A smaller-diameter inner core drill bit, in relation to the total rock core size, increases the chance of obtaining undisturbed samples. Regarding the material retrieved during the coring of Ktzi 203, only one out of the six samples stored in high-pressure vessels was contaminated. After the inner coring the internal part was microscopically observed under UV light and fluorescein was detected. However, the sample was chosen for further experiments because it was obtained from the CO_2 plume in the reservoir, where the pores were partly filled with CO_2. Therefore, the higher compressibility of CO_2 compared to the pore-filling brine may have allowed the drill mud to penetrate deeper into this core. In addition, it needs further investigations how the petrophysical properties of the rocks do influence the penetration depth of the drill mud.

In general, the study shows that the depth of penetration seems to be independent of the drilled core size diameter but sensitive to lithology and petrophysical behavior of the rocks. Concerning the sandstones obtained from the Ktzi P300 borehole, three core samples, originating from a 40-cm sandstone core that was apparently free of fractures, show a remarkably different grade of contamination. Analyses of rock and fluid sampled from the vessels resulted in one part free of fluorescein, while in the other two parts the tracer was detected both in the fluid and in the rock. This high variability of the measured drill-mud penetration depth for one lithotype was described also by Kallmeyer et al. (2006). Because of the heterogeneity of rocks deriving from small differences in lithology (the sample was taken from an interbedded zone of fine-to-medium grained sandstones) or due to invisible microfractures and drilling induced tensile fracture, the penetration depth may not be related directly to the average permeability. The results indicate that every sample, even those from the same core section, should be checked for contamination by drill fluids, as also recommended by Wandrey et al. (2010).

Summary and conclusions

The results of this study demonstrate that the penetration depths of microspheres and DAPI-stained bacteria into a rock core under applied drilling conditions are similar to those of fluorescein.

Fluorescein was successfully evaluated in the field during the coring of two wells as a highly convenient, inexpensive, easy-to-handle and non-hazardous tracer. In comparison, microspheres and bacterial tracers are less advantageous. An easy and reliable procedure of assessing the penetration depth of drill mud labelled with fluorescein in rock cores was established. Inner coring was performed after microscopic observation of the tracer in the sample. As observed during the laboratory experiments, high concentrations of fluorescein in the drill mud facilitate the microscopic detection. The outer part of the sample was microscopically observed again, fluorescein was extracted and fluorometrically measured, and the inner part was stored in a high-pressure vessel containing synthetic brine. After incubation, the rock and fluid were sampled from the vessels and the fluorescein concentration was re-measured. The tracer measurement in the fluid is the most accurate method of assessing if the core sample in the vessel was affected by fluorescein and, consequently, by drill mud. A good number of pristine rock cores were retrieved by applying this enhanced method.

The usage of tracers is necessary to evaluate the quality and the purity of rock cores. The geological characterization is not sufficient to predict the drill-mud penetration depth in rock cores because other factors, e.g., gas content or microfractures have high influence on it.

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