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Petrophysical characterization of in situ cores after CO₂ injection and comparison with batch experiments of the German Ketzin Pilot site

Kornelia Zemke, Axel Liebscher*

*GFZ German Research Centre For Geosciences
Telegrafenberg, 14473 Potsdam, Germany*

Abstract

At the Ketzin pilot site for geological CO₂ storage in Germany, about 67,000 tons of CO₂ were injected. Here we compare porosity and permeability from samples recovered prior to CO₂ injection with core data drilled after 4 years of injection. Further batch experiments on Ketzin material under in situ p-T conditions over various time periods investigated by NMR relaxation and mercury injection porosimetry (MIP) complement the real in situ data. However, the observed changes between the different pre-injection and post-injection well of the heterogeneous formation are only minor and have no effects on the injection behavior. The pore size related measurements of the batch experiments show only minor deviations. The results are consistent with the logging data and confirm the data for the recovered in situ rock cores. Based on present data, the siliciclastic rocks of the Ketzin are not significantly affected by the injection of pure CO₂ within this time.

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* Corresponding author. Tel.: +49-331-288-2816.
E-mail address: zemke@gfz-potsdam.de

1. Introduction

Petrophysical properties like porosity and permeability of reservoir and cap rocks are key parameters for a safe long-term storage of CO₂ but also for the active injection operation itself. These petrophysical parameters may change during and/or after the CO₂ injection due to geochemical and mineralogical reactions in the reservoir system, which are triggered by the injected CO₂. Change of porosity and/or permeability may affect storage capacity and influence the injectivity or can also affect reservoir and cap rock integrity.

Data on these CO₂ triggered reactions and their effects on petrophysical rock properties may be gained from observations of natural analogues, which may be taken as equilibrium systems that, however, typically lack any information on initial status, from laboratory experiments, which are typically performed in simplified systems, or from numerical modeling, which depends on quality and quantity of the input values.

Here we present both, comparison of petrophysical pre-injection data from core samples recovered prior to CO₂ injection and recovered after 4 years of CO₂ injection at the storage site Ketzin in Germany and further results from batch experiments at the Ketzin rock material.

2. Background

CO₂ was injected into an Upper Triassic sandstone reservoir at the Ketzin site and the influence of carbon dioxide on the reservoir and cap rock formations was subject of multidisciplinary research over several years. The Ketzin pilot site is located 25 km west of the German capital Berlin, approximately 1.5 km south of the top of a double anticline structure formed during halokinetic uprise of salt. The 10 to 20 m thick target reservoir represent the typical channel facies of fluvial deposits of the Stuttgart Formation and its top is at about 620 to 630 m depth. The channel sandstones are immature, dominantly fine-grained and well to moderately-well sorted. They consists of 22 to 43 wt% quartz, 19 to 32 wt% plagioclase and 4 to 13 wt% K-feldspar with subordinate white and dark mica, illite, mixed-layer silicates and meta-sedimentary and volcanic rock fragments [1]. Fine siltstones and thinner sandstone layers interbedded with thin mudstone and coal layer below the main reservoir represent the flood plain facies. The directly overlaying cap rock is formed by an about 165 m thick sequence of mud and claystones of the Weser and Arnstadt Formations. The geological setting of the storage site has been described in detail in various publications [1, 2, 3, 4].

At the injection site, one combined injection-observation well Ktzi 201 and two observation wells Ktzi 200 and Ktzi 202 have been drilled prior to start of injection to depths of about 750 to 800 m with distances of 50 m (Ktzi 200) and 112 m (Ktzi 202) between injection and observation wells. The whole injection phase of the Ketzin site lasted from June 2008 until August 2013 and a total of about 67,000 tons of CO₂ were injected. After 4 years of injection and ~ 61,000 t of food-grade CO₂ a fourth observation well Ktzi 203 has been drilled through the CO₂ reservoir and nearly 100 m core material were recovered [3, 4, 5]. The new core samples allow studying the impact of CO₂ on reservoir properties at field scale.

3. Comparison of in situ cores to baseline core data

Because the new well Ktzi 203 with a distance of 25 m to the injection well has a lithology similar to the injection well Ktzi 201, core data from these two nearby wells can be used to study changes due to CO₂ injection.

3.1. Baseline measurements Ktzi 201

Baseline characterizations for all three pre-injection wells are reported by Norden et al. [2]. A comprehensive logging program was performed for the wells complemented by a NMR-logging campaign in the injection well Ktzi 201.

Routine core analysis of recovered reservoir and caprock was done on plugs drilled with simulated formation brine, especially gas porosity and gas permeability was estimated. Helium porosity was determined from direct measurements of grain and bulk volume of cleaned plugs, oven dried at 95°C and ambient humidity to a constant weight. Klinkenberg corrected Nitrogen permeability was estimated and converted to brine permeability by using a

multiplier of 0.633 estimated from brine permeability determined for same cores. The core baseline measurements are consistent with the porosity logging data of corresponding wells and show a great range of variation within the heterogeneous lithology.

The core data will be related to the results of the commercial NMR-logging campaign (Combinable Magnetic Resonance tool recorded by Schlumberger, 2.2 MHz) of the injection well Ktzi 201. Basic output of the tool is the NMR amplitude related to the total porosity and the T_2 relaxation time distribution. The T_2 distribution is related to the pore size and can further processed to give bound- and free fluid volumes. Standard formation permeability will be provided by two semi empirical permeability models using the spectral porosity data. Norden et al. [2] calculated the NMR permeability according to the Timur-Coates model with a changed cutoff time of $T_2 = 10$ ms derived from the mean T_2 time in the overlying caprock to match the estimated brine permeability from the core data.

Here in this study, we use the total porosity spectrum and the range >3 ms, which excludes the clay-bound fluid. The baseline measurements of 91 core samples of Ktzi 201 (Helium porosity, converted brine permeability from Nitrogen permeability) published by Norden et al. [2] was supplemented by further NMR core measurements and by brine porosity after Archimedes of some core plugs.

3.2. Measurements after 4 years of CO_2 injection at Ktzi 203

The 100 m recovered core material (Figure 1) of the new well Ktzi 203 span 19 m of mudstone cap rocks and the complete Stuttgart Formation. For NMR core measurements 81 samples were taken, 39 of these come from the main sandstone reservoir horizons. The influence of the potash-containing drilling fluid of the well Ktzi 203 with an added fluorescent tracer to control penetration depth could be seen by porosity investigation on 20 twin samples from inner and outer parts of the cores. Especially for porous outer core samples NMR core measurements show a reduced fraction of larger pores together with lower porosities and so only inner core samples were used for further investigation.



Figure 1: Recovered core material of well Ktzi 203 and prepared plugs for Nitrogen permeability

For Helium porosity plugs were cleaned with distilled water and oven dried at 50°C for 48 h. The Klinkenberg corrected Nitrogen permeability was measured on 20 additional plugs from ten core samples, which were drilled both parallel and normal to bedding. After this, the dried samples were vacuum saturated with brine for estimation of Brine porosity after Archimedes principle. NMR measurements of brine saturated core plugs were recorded in a Resonance Instrument Maran Ultra (7 MHz, 0.1 ms echo spacing, 5 s relaxation) with a slightly shifted T_2 spectrum. The porosity was also determined from whole signal and from T_2 spectrum > 3 ms to exclude the clay bound water, and NMR permeability calculated like for the NMR logging data.

3.3. Results in situ data

To allow for direct comparison between pre-injection baseline results for Ktzi 201 and post-injection data for Ktzi 203 both data sets are plotted together in Figure 2. As well Ktzi 203 is located up-dip of well Ktzi 201, the depths of corresponding lithology are about 2 m shallower in Ktzi 203 than in Ktzi 201. To allow for direct comparison, the data for Ktzi 201 were therefore shifted by 2.7 m. Figure 2a shows the different porosity value from NMR log and core data of well Ktzi 201 in blue before the injection and in red after four years CO₂ injection.

As is evident also from the lithological description by Norden et al. [2] the reservoir section consists of two main sandstone horizons below 630 m. A thin strongly cemented layer separates both sandstone horizons and was used as the marker to overlay the pre-injection well Ktzi 201 with the new well Ktzi 203. A third sandstone horizon is below 655 m with an increasing porosity with depth. These three sandstone horizons corresponds to the permeable channel sandstone within the open filter screen position in the injection well between 632.2m to 641.6m and between 644.8m and 654.2m [5].

The porosity data of helium pycnometry of Ktzi 201 before injection show significant higher values for the whole reservoir sandstone. Porosity determined by NMR measurements is generally slightly lower than Helium or brine porosity, because the different measurements methods reflect different porosities. The results from Helium porosimetry reflect the total porosity and depend on drying temperature, humidity and cleaning process and their effects on the clay fractions and the cements.

The direct comparison of the corresponding pre injection and post injection data show no clear difference beyond the natural background variability. NMR porosity determined on core samples of the Ktzi 203 borehole are very similar to those recorded by the open-hole NMR log of the Ktzi 201 borehole. However, in the upper sandstone horizon the porosity determined in the Ktzi 203 borehole are consistently slightly lower than the Ktzi 201 logging data (about 2%). The transition from the sandy reservoir to the muddy caprock is reflected in both data sets. But the new measured Helium pycnometric data of Ktzi 203 reflect also the same effect like the NMR data: The upper sandstone horizon has slightly lower porosity than in Ktzi 201 and the helium porosity of the lower horizon agree well between Ktzi 201 and Ktzi 203.

Figure 2b shows the different permeability values from NMR log and core data of well Ktzi 201 in blue before the injection and in red after four years CO₂ injection. The permeability data measured with nitrogen of Ktzi 201 before injection shows significant higher value for the whole reservoir sandstone. The NMR Timur-Coates model with the Ketzin specific cut-off of 10 ms after Norden [2] was adapted to brine permeability and we used the original Nitrogen values for the core plugs to compare with the Nitrogen value of the new well Ktzi 203.

For the upper sandstone horizon, where the free CO₂ is present after the four years, the corresponding permeability determined for Ktzi 203 (NMR lab data and measured with nitrogen) is consistently lower than the permeability determined for Ktzi 201 (NMR log data and measured with nitrogen). Like for porosity, the corresponding permeability data for the lower sandstone horizon agree well and seems unaffected by the injected CO₂.

Given the natural heterogeneity of the reservoir sandstone, it is not entirely clear whether the observed small effects of lower porosity and the more pronounced difference of permeability of the upper sandstone horizon in well Ktzi 203 is due to the injection of CO₂. Probably is it only an effect of residual gas saturation, because this part is above the fluid level and CO₂ is present as a free gas phase. It may also simply reflect an a priori difference between wells Ktzi 201 and Ktzi 203; an influence of the drilling operation can also not fully excluded. The different sample treatment (cleaning with organic solvent, humidity drying at 90°C to weight constancy and cleaning with distilled water and then drying at 50°C for 2 days) influences especially the shaly sample.

The mineralogical investigations on the Ktzi 203 samples also show no significant dissolution or precipitation of minerals and find only minor quantities (usually < 2 vol-%) of various species of newly precipitated carbonates with three potential carbonate sources: dolomite dissolution, reactions of injected CO₂ with the formation fluid, and the drill mud [6].

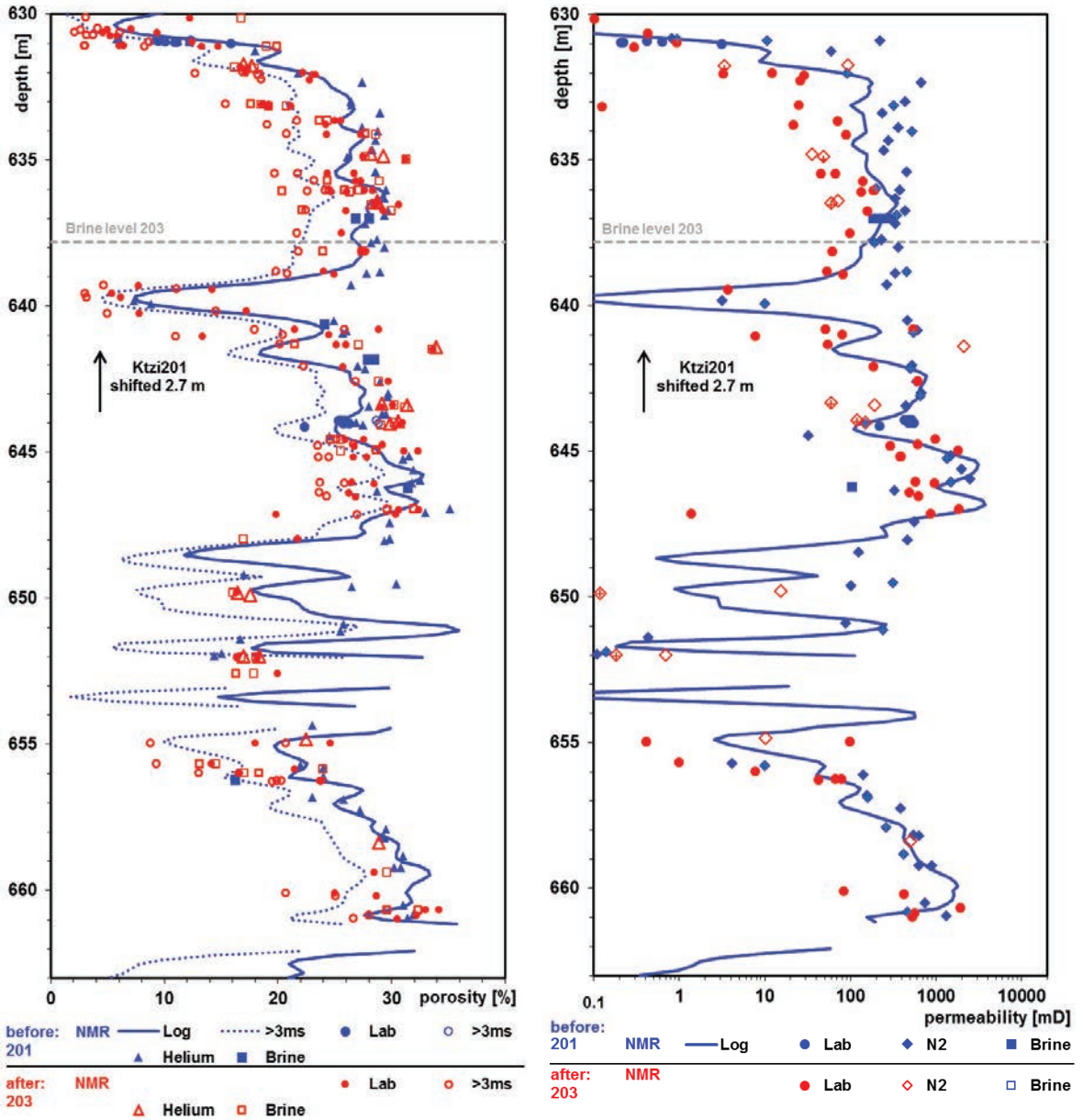


Figure 2: Cross plot of neighboring wells with similar lithology – blue Ktzi 201 before the injection of CO₂, red Ktzi 203 after injection.

- a) Porosity:
 - NMR data from Logging campaign:
 - Log - Total Porosity and >3ms Porosity without shale
 - from Core measurements:
 - Lab - Total Porosity and >3ms Porosity without shale
 - Core data:
 - Helium porosity and Brine Porosity after Archimedes princip
- b) Permeability:
 - NMR data from Logging campaign:
 - Log - Permeability after Coates Modell with 10 ms cutoff time
 - from Core measurements:
 - Lab - Permeability after Coates Modell with 10 ms cutoff time
 - Core data:
 - Nitrogen permeability and Brine permeability

Depth was shifted by 2.7 m to overlay the cemented sandstone at 640 m, 201 NMR Log and Helium porosity and Nitrogen permeability after [2].

4. Batch experiments

Two series of batch experiments were performed in separate autoclaves (Table 1). Rock samples of the observation well Ktzi 202 were characterized prior to and after reactions to investigate the resulting effect of reactions between the rock and CO₂-brine system on the petrophysical properties. Series I investigates the interactions of reservoir rock with CO₂ dissolved in reservoir brines. Series II investigates the directly overlying cap rock.

Table 1: Experimental details of long-term CO₂ exposure experiments

| Series | I | | | | | | | II | | | |
|--------------------------------------------------------|------------------------------------------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------------------------------------------------------------|------|----------------|------|
| Logging depth [m] | 627.6 | 627.5 | 628.6 | 629.8 | 631.3 | 632.1 | 633.2 | 626.9 | | | |
| Autoclaves | 7 Steel V4A high-pressure vessels (Ø 60 mm x 140 mm) | | | | | | | 4 Teflon coated high-pressure vessels (Ø 60 mm x 120 mm) | | | |
| Rock material | 1 core + fragments Ø 50 mm x 100 mm | | | | | | | 1 rectangular block 33 mm x 33 mm x 90 mm | | | |
| Brine | 75% of Original TDS | | | | | | | 99% of Original TDS | | | |
| T [°C] | 40 | | | | | | | 40 | | 40 | |
| p [MPa] | 5.5 | | | | | | | 7.5 | | 7.5 | |
| Gas | CO ₂ | | | | | | | CO ₂ | | N ₂ | |
| Runtime [months] | sampling after 15, 21, 24, 40 and then reloaded with CO ₂ and heated again | | | | | | | 4 | 2 | 6 | 6 |
| Rock Volume [cm ³] | 200-270 | | | | | | | 100 | | | |
| Ratio rock / fluid [cm ³ /cm ³] | 1.9 | 1.5 | 1.5 | 1.3 | 2.0 | 1.2 | 1.0 | 1.7 | 1.79 | 1.71 | 1.79 |

4.1. Series I: interactions of reservoir rock - CO₂ dissolved in reservoir brines

Rock cores (Ø 50 mm x 100 mm) and cm-scaled fragments freshly recovered from the reservoir sandstone (627 - 634 m) with residual trapped formation fluid were used for seven experiments [7, 8]. The rock material is completely capped with 110-130 ml of synthetic NaCl rich brine (~180 g/l TDS) in stainless steel vessels and is exposed to CO₂ partial pressures of 5.5 MPa and 40°C. The experiments ran for 40 months and the autoclaves were opened after 15, 21, 24 month for sampling of 40-60 cm³ rock and brine and after that reloaded. The chemical composition differed from that of original Ketzin formation water (75% of TDS) and so a chemical equilibrium will be formed between the added brine and the trapped formation water in the pores.

Nuclear magnetic resonance (NMR) analyses were used to estimate the NMR-porosity and to characterize pore size distribution of the degassed, brine saturated samples, because many samples disintegrate rapidly in distilled water. Mercury injection capillary pressure (MIP) was measured at one oven dried part piece to estimate MIP porosity and pore throat diameter distributions. Figure 3 show the pore distribution related results by NMR and MIP.

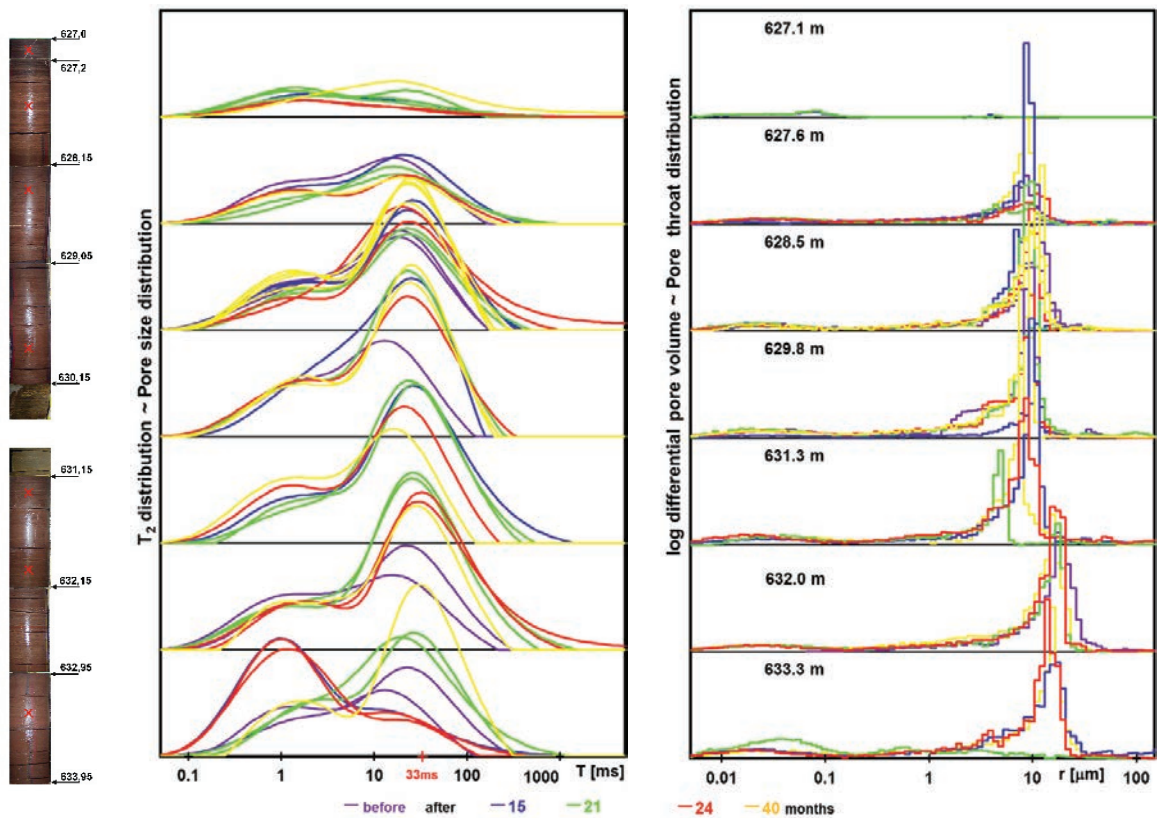


Figure 3: Series I Sandstone, NMR T_2 distribution and Pore throat data from MIP.

This first batch experiments integrates also analysis of chemical change of fluids, porosity analysis of core material, and investigation of mineralogical and microbial changes [7, 8, 9]. Fluid analysis shows an equilibrium reaction in the first months between synthetic brine and formation fluid and an exceeding of the calculated equilibrium for some metal ions through CO₂ in line with the observed minor dissolution processes of anhydrite, plagioclase and K-feldspar grains on grain surfaces. The corresponding calculated porosity change to the changed ion contents in the fluid result in very small effects within the heterogeneity of the samples and below the error limit of the porosity methods. Identified mineralogical changes are generally minor and show no definite trend. In summary, possible CO₂ induced changes in the total porosity, which can be derived from a change in mineral content, are so marginal that they are below the limit of error of the porosity measurement. The average data of NMR and MIP analysis reflect a trend towards larger porosities. Some core sections show a systematic shift of the pore radii equivalent to NMR relaxation time. The variation of the experimental core data reflects also the lithological variation in this section, for these reasons, parallel core pieces obtained from the inner whole core was used in the following experiment.

4.2. Series II: interactions of cap rock - CO₂ dissolved in reservoir brines and water dissolved in CO₂

In a second run, three parallel siltstone samples were placed in separate Teflon coated autoclaves and exposed to brine at 40°C loaded with CO₂ pressure of 7.5 MPa with run durations of 2, 4 and 6 months; a fourth sample was exposed to N₂ for 6 months and served as blind-run. The 3 years old core material from directly overlaying cap rock from the well Ktzi 202 (626.86 and 626.94 m) was sawed in four parallel rectangular blocks of 33 x 33 x 90 mm³ and blocks were saturated with a synthetic brine with comparable fluid chemistry of the Ketzin downhole samples. The lower half of block is exposed to CO₂ dissolved in brine and the upper half of block to supercritical CO₂. After the experiments, each block was sawed in four sample aliquots, three for geochemical-mineralogical analyses [9] and the fourth divided in 5 pieces for the petrophysical analysis.

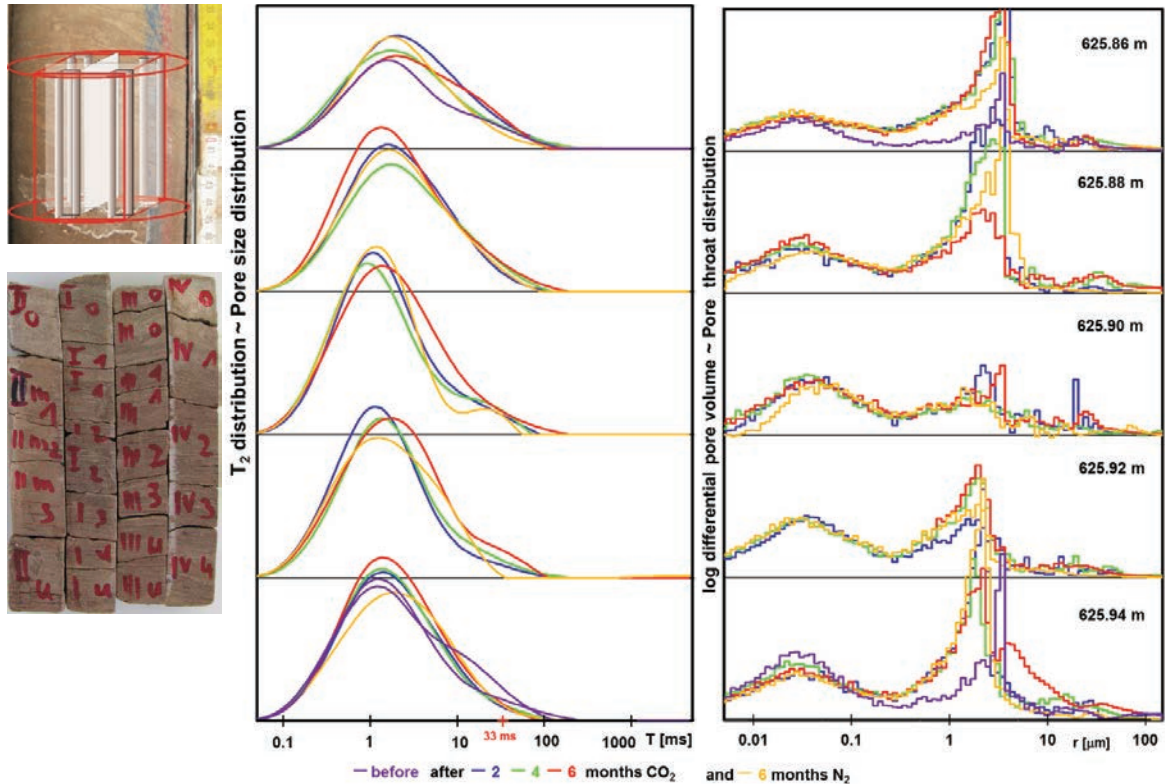


Figure 4: Series II Siltstone, NMR T₂ distribution and Pore throat data from MIP.

Figure 4 show the results of petrophysical analysis by NMR and MIP of the sampled rock before and after 2, 4 and 6 months runtime with CO₂ and for the 6 months blind experiment with Nitrogen for all pieces depending of depth. The data before the treatment are referring to core pieces directly above and under the core segment. The maximum of NMR relaxation time is below the classical cut off time of 33 ms for sandstone. There is no clear trend for porosity evolution within reaction time for all samples. The average data reflect a trend towards larger porosities and no measurable effect for the Nitrogen experiment. There is also no clear context between sample positions in relation to brine level. Only the top sample piece corresponding to the depth of 685.86 m, which is above the fluid level, show porosity decrease with CO₂ treatment time. These sample data show that despite the refined material selection probably still sample heterogeneities superimpose the relevant measuring parameters.

5. Conclusion

The core baseline measurements are consistent with the porosity logging data of corresponding wells and show a great range of variation within the heterogeneous lithology. The determined porosity and permeability data are comparable between pre-injection and post-injection core samples. The lower part of the reservoir sandstone is unaffected by the injected CO₂. Post-injection data of the upper part of the reservoir sandstone shows consistently very slightly lower NMR porosity and permeability, probably only an effect of residual gas saturation, because this part is above the fluid level and CO₂ present as a free gas phase. An influence of the drilling operation can also not fully excluded. However, the observed changes between the different pre-injection and post-injection well of the heterogeneous formation are only minor and have no effects on the injection behavior.

The data of the batch experiment with Ketzin reservoir sandstone indicate only small changes of the pore size related properties. The differentiation between natural, lithostratigraphic variability and experimentally induced, CO₂ related changes is difficult. The second dataset on parallel siltstone samples shows also only very small changes in values over time and no effect at the N₂ experiment. Unfortunately, also in these experiments observed mineralogical and petrophysical changes were within the natural heterogeneity of the Ketzin reservoir. The results of batch experiments are consistent with the logging data and confirm the data for the recovered in situ rock cores.

The natural variability of the rock parameters is greater than the changes observed in the experiments and therefore only limited conclusions regarding the influence of CO₂ can be made from the experiments.

Based on present data, the siliciclastic rocks of the Ketzin reservoir and cap-rock are not significantly affected by the injection of pure CO₂ within this time. This is also in line with the continuously recorded injection operation parameter and it is reasonable to assume that the potential dissolution-precipitation processes appear to have no severe consequences on reservoir and cap rock integrity or on the injection behavior [4].

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