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Re-Establishment of the proper injectivity of the CO₂-injection well Ktzi 201 in Ketzin, Germany

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ABSTRACT

The onshore CO₂-storage site Ketzin consists of one CO₂-injection well and two observation wells. Hydraulic tests revealed permeabilities between 50 and 100 mD for the sandstone rock units. The designated injection well Ktzi 201 showed similar production permeability. After installation of the CO₂-injection string, an injection test with water yielded a significantly lower injectivity of 0.002 m³/d*kPa, while the observation wells showed an injection permeability in the same range as the productivity. Several possible reasons for the severe decline in injectivity are discussed. Acidification of the reservoir interval, injection at high wellhead pressure, controlled mini-fractures and back-production of the well are discussed to remove the plugging material to re-establish the required injectivity of the well. It has been decided to perform a nitrogen lift and analyse the back-produced fluids. Initially during the lift, the back-produced fluids were dark-black. Chemical and XRD analyses proved that the black solids consisted mainly of iron sulphide. Sulphate-reducing bacteria (SRB) were detected in fluid samples with up to 10⁶ cells/ml by fluorescent *in situ* hybridisation (FISH) indicating that the formation of iron sulphide was caused by bacterial activity. Organic compounds within the drilling mud and other technical fluids were likely left during the well completion process, thus providing the energy source for strong proliferation of bacteria. During the lift, the fraction of SRB in the whole bacterial community decreased from approximately 32 % in downhole samples to less than 5 %. The lift of Ktzi 201 succeeded in the full restoration of the well productivity and injectivity. Additionally, the likely energy source of the SRB was largely removed by the lifting, thus ensuring the long-term preservation of the injectivity.

1. Introduction

A prerequisite for the proper operation of all CO₂-storage sites is a high injectivity of their injection wells because the cost of drilling new wells is very high. Hence, operators tend to keep the number of CO₂-injection wells as low as possible. The Ketzin underground storage laboratory is equipped with one injection well (Ktzi 201/2007) and two observation wells (Ktzi 200/2007 and Ktzi 202/2007), in the following referred without the suffix (Würdemann et al., this issue). It is, therefore, obvious that the success of the whole CO₂SINK project is dependent on the ability of this injection well to perform CO₂ injection at the required rates.

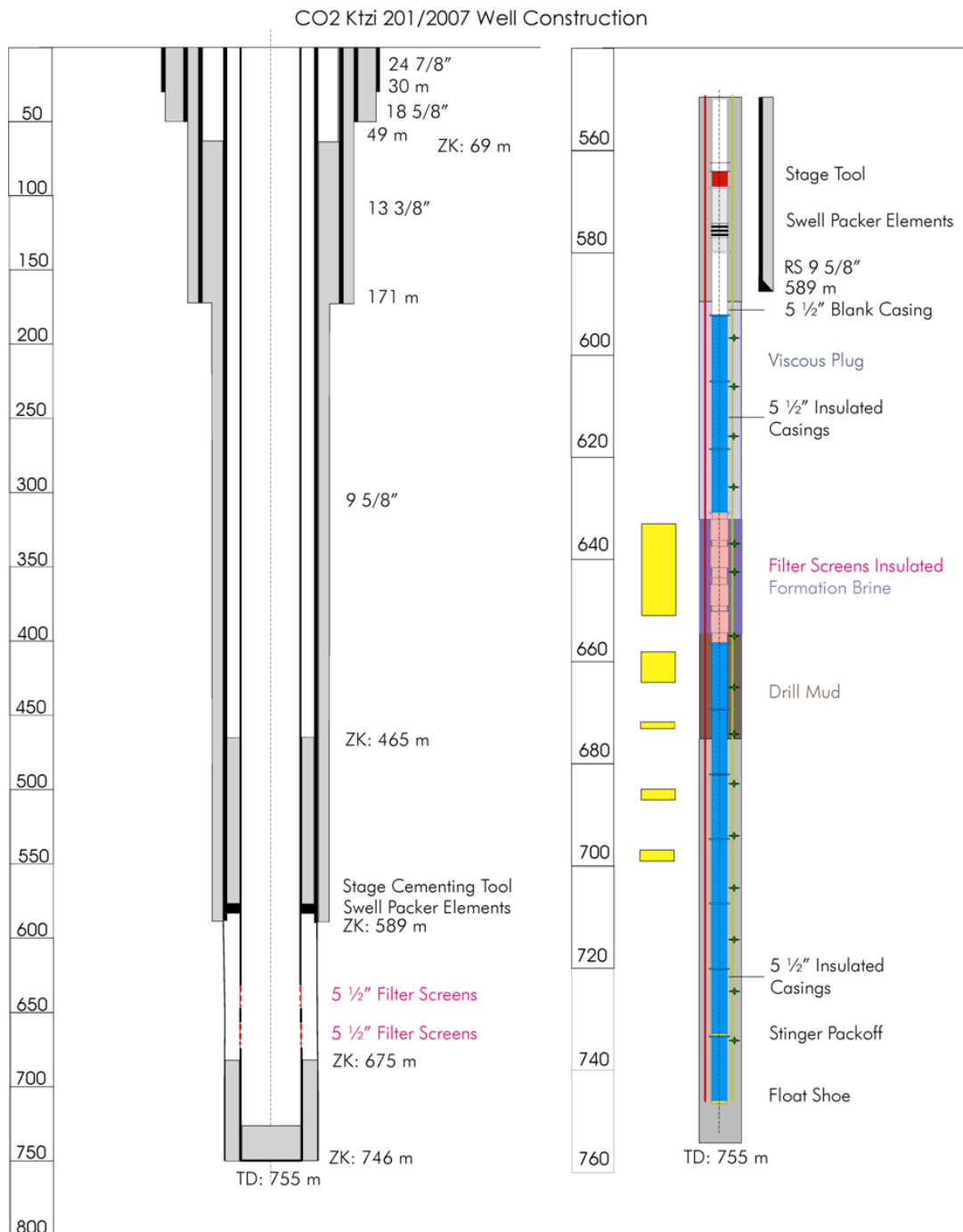


Fig. 1: Drilling design and well completion of the CO₂-storage well, Ktzi 201. The red line indicates the DTS (distributed temperature sensing) and heater cable. The green lines indicate the ERT cable and the location of the ERT (electrical resistivity array) sensors (green stars). Sandstone reservoir intervals are shown in yellow (Prevedel et al., 2009).

All wells are vertical, and the distance between the injector and the observation wells is 50 m for the first observation well and 100 m for the other. The wells are “smart” wells, containing a variety of permanently installed downhole sensors that are located behind casings (Giese et. al., 2009). The underground horizon, in which the CO₂ is stored, is a Stuttgart formation (a permeable sandstone layer).

Quartz, feldspar, and clay minerals predominate in the Ketzin sandstone. The detrital components are often rimmed by thin coatings of ferric oxides and clay minerals. The abundance of feldspar, mica, chlorite, clay minerals, Fe-Ti oxides, and analcime accounts for the reservoir’s richness in Ti, Al, Fe, Mg, Na, and K relative to average mature sandstone (Förster et al., 2006). The sandstone layer is currently filled with highly saline brine with a concentration of approximately 230 g/l of total dissolved solids (TDS). The completion of the injection well Ktzi 201 (Fig. 1) is different from other oil industry wells because it was not perforated in the sandstone layers. All wells were cased with stainless steel equipped with wire-wound filters in the higher permeable zone of the reservoirs (four filters with heights of 4 m each). These filters were wired on the outside with two cables that rich up to the surface. A staged cementation program was performed in combination with the application of a newly developed, swellable rubber packer technology and a stage cementation downhole tool. This approach was performed instead of the perforation work inside the final casing at the reservoir face to protect the sensor cables (Prevedel et al., 2009). Fine-mesh filter screens with a mesh size of 1.5 mm were used because the Stuttgart formation was expected to be weakly consolidated. There were concerns that once the reservoir pressure would rise to higher levels by CO₂ injection, the reservoir rock might destabilise and potentially partially “flow” back into the well bore during interruption of injection CO₂, thus blocking it and preventing further CO₂ injection.

Table 1: Major components of the drilling mud

Well	CMC (carboxymethylcellulose) [g/l]	KCl [g/l]	K+ [g/l]	Chlorides [g/l]	Hardness (Ca ²⁺) [g/l]	Bactericide (Dodigen) [g/l]
Ktzi 201	13	40.5	20.9	39.15	0.14	1

The wells were drilled with a water-based CaCO₃/bentonite/organic polymer drilling mud containing CMC (carboxymethylcellulose). During the completion phase, a viscous pill consisting of a concentrated biopolymer (xanthan gum) solution in comparatively fresh water was used. Further details regarding the drilling mud composition and the biocide are given in Table 1. During the installation of the completion in the Ktzi 201 well, the packer was activated with fresh water to achieve swelling. Because of this procedure, the overall salinity in the borehole and the near-wellbore area was reduced significantly. Technical procedures used to finish the well completion did not allow for a complete removal of technical fluids. To determine the remaining drilling mud content in water samples produced from the reservoir, the drilling mud was spiked with fluorescein (Wandrey et al., this issue). It was observed that there were technical fluids that remained behind the filter screens, in the uncemented area between the casing and the rock above, and below the filter screens that were still in contact with the reservoir horizon.

Productivity/ injectivity of wells between September 2007 and January 2008

As mentioned earlier, the injectivity of the wells in a CO₂-storage site is a key performance factor. The well performance can either be expressed as the productivity or injectivity index (depending on the direction of flow of the fluid) or as the permeability. Soon after completion, all three wells were subsequently equipped with a pump, and 70-100 m³ of water were back-produced to remove the remaining drilling mud and viscous pill from the wells. This back-production of water was also used to determine the productivity of each well during these hydraulic tests. The volumes of produced fluids were kept as low as possible because these highly saline produced fluids required expensive disposal procedures. Table 2 shows the performance for each of the Ketzin wells during production and during a

subsequent short injection phase. In each case, the injection was carried out after the production phase with the reservoir brine that remained in the production string. This was done to avoid contact between reservoir rocks and incompatible water. Hydraulic tests (single-hole tests) revealed well permeabilities between 50 and 100 mD for the sandstone rock units (Wiese et al., this issue). The two observation wells, Ktzi 200 and Ktzi 202, exhibited injection permeabilities up to 109 mD. The designated injection well Ktzi 201 showed similar production permeability, but it barely accepted water in the injection phase. This resulted in a calculated injection permeability of only 0.07mD (Table 2), which is close to that of concrete. It would have been impossible to inject carbon dioxide at such a low permeability.

Table 2: Productivity and injectivity of the Ketzin wells during the end of 2007 and the beginning of 2008. The values are calibrated with no flow boundaries in the vicinity of the wells. The skin factor varies between -3.2 and 4.1.

Well	Test date	Productivity index [m ³ /d*kPa]	Permeability (Prod.) [mD]	Injectivity index [m ³ /d*kPa]	Permeability (Inj.) [mD]
Ktzi 200	01-05.10.07	0.06	63	0.036	40
	22-25.10.07				
Ktzi-201	14-22.09.07	0.06	90	0.0026	0.074
	27.09-1.10.07				
Ktzi-202	07-14.01.08	0.025	109	0.041	81
	14-15.01.08				

Table 3: Productivity and injectivity of Ktzi 201 well during and after N₂-lift in February 2008. The skin factor varies between 0.5 and -0.5. Results are calibrated without no flow boundaries. Assuming the no flow boundaries which were used to calibrate results from Table 2, permeabilities would be almost twice as high.

Well	Test date	Productivity index [m ³ /d*kPa]	Permeability (Prod.) [mD]	Injectivity index [m ³ /d*kPa]	Permeability (Inj.) [mD]
Ktzi-201	26-28.02.08	0.06	54	0.06	47
	28-29.02.08				

Potential reasons for the blockage of the Ktzi 201 CO₂ injector during autumn 2007

Several potential reasons for the blockage of the Ktzi 201 injector blockage are now discussed.

1. The presence of remaining filter cake from drilling mud. As the well was not perforated, it is possible that parts of the filter cake that were formed in the drilling phase at the borehole wall were not removed in the relatively short production test and thus remained inside the filter. If this were the case, they would likely be pushed back to the borehole wall in the injection phase and again block the pore entrances (Parlar et. al., 2002).
2. Gelled polymer. The viscous pill in the annulus remained above the filter elements and thus remained in contact with the reservoir. The Ketzin reservoir bears several iron-containing minerals, including the iron oxides goethite, hematite, maghemite, biotite, clinozoisite, chamosite, Fe-Ti oxide and siderite (Förster et al., 2010). Hence, it is likely that the formation brine contained dissolved iron (ferrous ions Fe²⁺). Upon contact with even trace amounts of oxygen, enough ferric ions (Fe³⁺) would react with the polymers from either the viscous pill or the drilling mud to create a completely impermeable polymer gel. In the oil industry, similar procedures are intentionally used to shut-off undesired parts of the formation (Hurtado et. al., 2005).
3. Formation of ferric oxide-hydrate. Fresh water from a surface well containing oxygen was used to activate the swell packer. The oxygen could react with dissolved ferrous ions to form ferric oxide-hydrate

or ferric hydroxide, which are able to completely block permeable formations even in small quantities (Crowe, 1985).

4. Fine particle migration. Small particles from the weakly consolidated Stuttgart formation could be mobilised into the filter and/or the wellbore and, during the injection phase, could be pushed towards the wellbore side, thus blocking the pore entrances. In the oil industry, similar processes leading to reduced permeabilities are referred to as “fines migrations”.

5. Microbial activity. It is likely that bacteria were either already present in the formation or were introduced into the formation during drilling and completion. Upon replication, these bacteria could either block the formation through the production of bacterial biofilms or by the production of secondary products of their metabolism. For example, iron sulphide (FeS) can be formed in the reaction of dissolved ferrous ions and hydrogen sulphide (H₂S), which sulphate-reducing bacteria produce during their metabolism (Wood and Spark, 2000).

2. Methods

Treatment options to restore the injectivity of the Ktzi 201 well

In the oil industry, there are several options that can be used to treat injection wells with insufficient injectivity. For the Ktzi 201 well, the following possible treatments were considered and discussed.

1. Fracture treatments/ injection with increased wellhead pressure

It is quite common to inject water at high wellhead pressures in a well with the intention of creating certain fractures in the reservoir rock that will increase the overall injectivity of the well (Nainwal et al., 2006). Another option is to intentionally fracture the reservoir using proppants. For the shallow Ketzin reservoir, these two options were deemed unsuitable because the cap rock might fracture during this process, which would damage the primary seal for the injected carbon dioxide and make the reservoir leak.

2. Removal or disintegration of the filters

Regarding the potential presence of gels or remaining filter cake, we considered their removal and/or their disintegration. Filter removal is very expensive, as it would include costly measures such as the removal of the CO₂-injection string and the installation of a new completion. Disintegration of the filters by mechanical means carried the risk of damaging the monitoring equipment that was installed along the wellbore.

3. Perforation

Classically perforating the well is generally considered an excellent way to increase the injectivity of a well (including the Ktzi 201 well) and is one of the most frequently used operations (Ibrahim et al., 2009) in the oil industry to increase injectivity. Many wells are even re-perforated to increase injectivity or productivity. However, the high risk of possibly damaging monitoring equipment in the well impeded the implementation of this option.

4. Acid treatment

Acid treatments are often applied to stimulate wells. The potential success of such treatments is generally higher in carbonate formations than in sandstone formations such as those in Ketzin. Furthermore, for an optimal treatment, information regarding the nature of the blocking material would be necessary to select the type, concentration, and slug size of the acid in addition to further chemicals needed for the acid package. Moreover, the monitoring equipment in the well is sensitive to certain acids, especially organic acids. Organic acids are typically the preferred acid type for acid treatments because they are mild, less

corrosive to iron and have the potential to keep iron that was mobilised by the corrosion processes in solution by chelating it (Kalfayan, 2000).

5. Back-production of the well to remove blocking material

Back-production of the well in order to remove any blocking material is a reasonable approach to take, as long as the blocking material exists in the form of a filter cake at the entrance to the reservoir and has not yet penetrated the pores and formed an internal blockage. However, two valid arguments exist against back-production. First, the well was back-produced before the injection test, and second, another pump could not be installed because of the small diameter of the CO₂ -injection string that was already mounted into the well.

The back-production that occurred during the hydraulic test had not been examined analytically to determine the iron and solid contents. Thus, it could not be determined to what extent the technical fluids, drilling mud, and filter cake had been removed. Thus, it has been decided to back-produce the well by means of a nitrogen lift. If this did not work satisfactorily, a procedure involving acid application would be embarked on as a backup.

The more expensive nitrogen gas was chosen over air as the gas used for the lift because the oxygen content in the air would lead to corrosion and oxidation of dissolved ferrous ions. The lift was carried out with a 1.25 in. string. The tubing volume was approximately 3.5 m³. A production rate of 4.8 m³/h was achieved on average, which was about four-fold higher than the rates achieved in the previously conducted pumping tests. The main criterion for the termination of the lifting procedure was based on the content of solids in the produced water. Based on practical experience (Zettlitzer, 2007), we decided to continue until the water contained approximately 1 mg/l of solids, as determined by membrane filtration.

Analytical investigations of the produced water

The produced water was sampled at the wellhead. At the beginning of the lift, sampling was performed with small time intervals (approximately every 1-2 m³ of water production). Towards the end of the lift, the changes in water quality were expected to be slower, and thus, longer sampling intervals were used.

Several analytical investigations were performed for these samples. Temperature, pH-value, tracer concentration, and the solid content were monitored both onsite and in specialised laboratories. Beyond temperature, pH-value, and tracer concentration measurements, the solid content was monitored onsite by a special filtration method using a 1.2 µm Millipore membrane. The maximum volume of water that we were able to filter prior to the filter blockage by solid content was used to assess the solid content. Cation contents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES), and anions were analysed by ion chromatography. Quantitative solid analyses were carried out in the laboratory by filtration via 1.2-µm Millipore membrane filtrations. The solids were characterised using both a scanning electron microscope (SEM) and energy disperse X-ray (EDX) diffraction. The total organic carbon (TOC) was determined as the difference between the total carbon (TC) and total inorganic carbon (TIC). All carbon analyses were performed in a carbon analyser by means of combustion with pure oxygen at high temperatures followed by infrared spectroscopic detection of the carbon dioxide that was formed. The microbial abundance of the fluid samples was observed before and after the lift using the technique of fluorescent *in situ* hybridisation (FISH). Details of these procedures are available in the work of Morozova et al. (this issue).

3. Results and discussion

Solid content

We observed that water from the bottom of the tubing was completely black and turbid and contained 16.3 g/l of solids. When treated with hydrochloric acid, the solids developed the typical smell of hydrogen sulphide. After a production of 5 m³ of water, the produced water looked clean via visual observation

(Fig. 2), but filtration with membrane filters (1.2- μm Millipore filters) revealed that there still existed a significant content of black solids, even after 50 m^3 of production (Fig. 3). A detailed analytical investigation showed that the solids were produced from the well in at least three slugs (Fig. 4).



Fig. 2: Visual observation of first the 5 m^3 water produced by the N_2 -lift.



Fig. 3: Membrane filtration of produced water from the N_2 -lift.

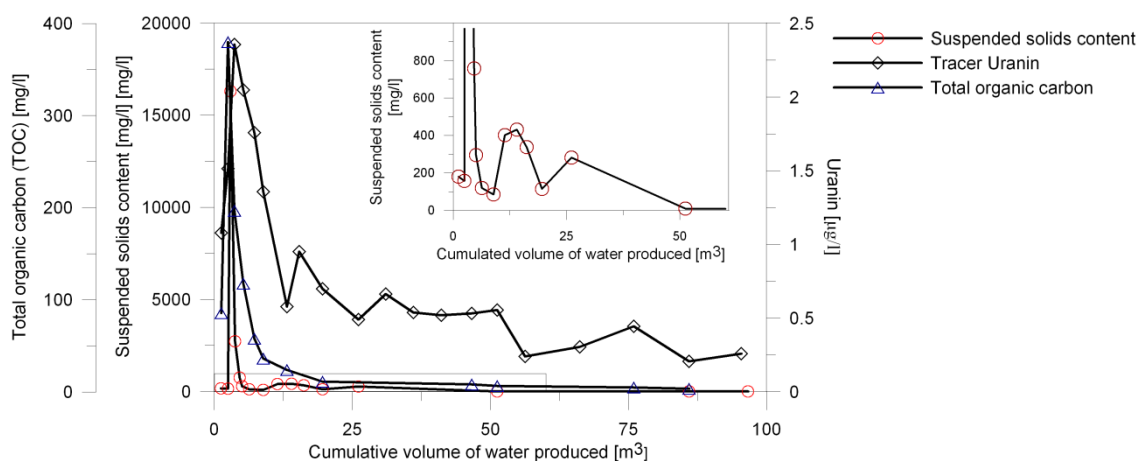


Fig. 4: Suspended solid contents in the produced water from the Ktzi 201 well.

Scanning electron microscope and energy disperse x-ray analyses reinforced the previous assumption that the solids contained large amounts of iron sulphide (Fig. 5). Additionally, some reservoir material was present in the water. It is assumed that iron sulphide was formed by the interaction of ferrous ions, present in reservoir brine, with hydrogen sulphide, which was presumably formed from sulphate by bacterial activity.

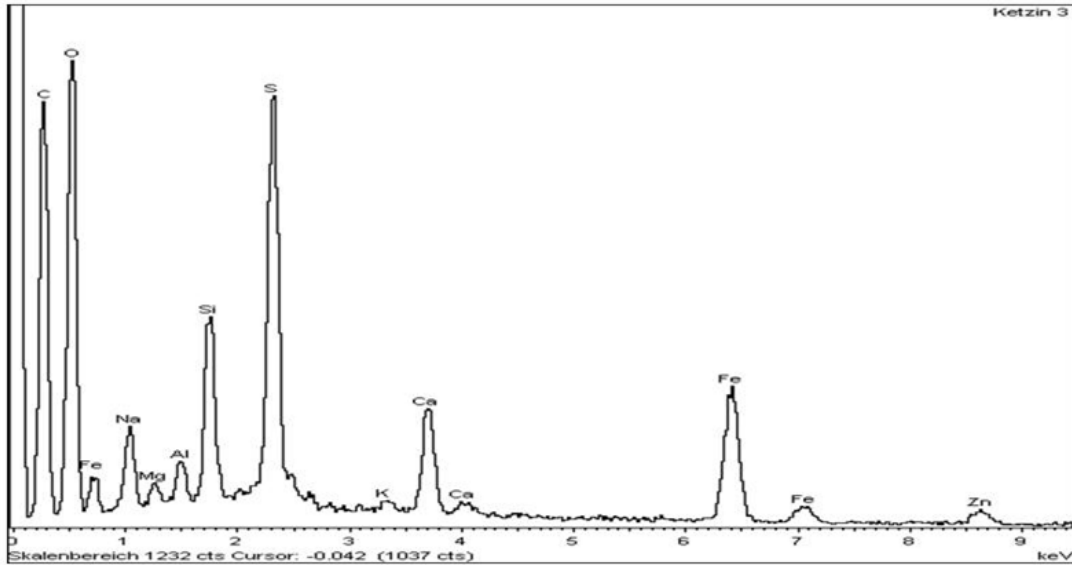


Fig. 5: Composition of the solids in the produced water after 2.9 m³ of water production. Suspended solid content in this sample was 16300 mg/l.

Salinity – total dissolved solids

In the first stage of the production phase, the salinity remained far below the reservoir brine salinity (Fig. 6). The lowest value of 206 g/l total dissolved solids (TDS) was observed after 2.9 m³ of water production, while after about 15 m³ of production, the full reservoir salinity of 231 g/l was obtained. The observed reduction in salinity was a clear indication of the presence of technical fluids. Thus, it has been suspected that the first production phase in September 2007 was not sustained long enough to remove all technical fluids that were pumped into the well. While they remained in the well, their organic constituents may have formed a nutrient base that enabled the fermentation and growth of sulphate-reducing bacteria.

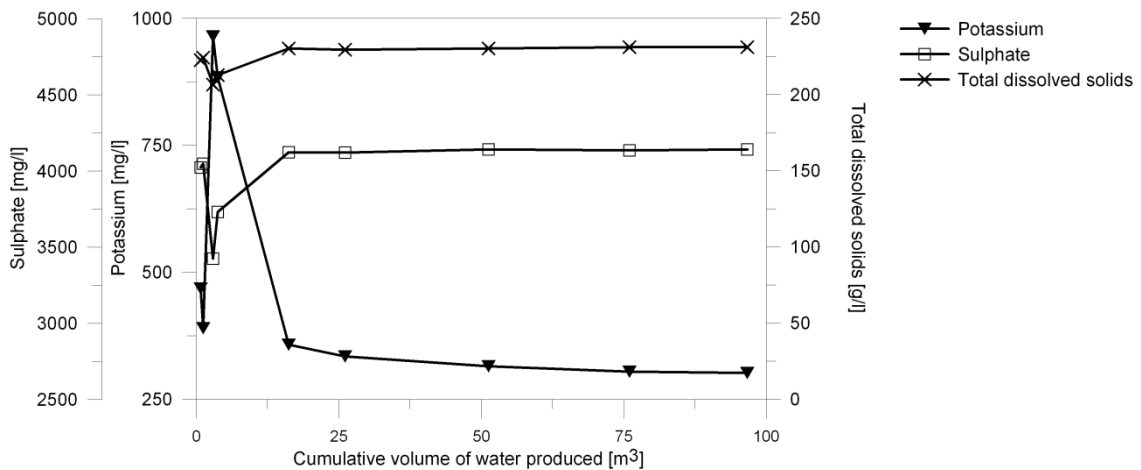


Fig. 6: Salinity, sulphate and potassium concentrations of produced water from the Ktzi 201 well.

Sulphate concentration

The hypothesis that sulphate-reducing bacteria (SRB) were responsible for the observed formation of iron sulphide was supported by the fact that the sulphate content was considerably reduced in those samples with high amounts of iron sulphide (Fig. 6). In some cases, the sulphate concentration was only 82.7 % of the levels observed in the formation water. Specifically, in sample 4, after 2.9 m³ of water production, 3424 mg/l sulphate was present, as compared to a concentration of 4140 mg/l sulphate in the

reservoir brine. This sulphate concentration reduction was even more pronounced than the difference in TDS, as described above.

Potassium concentration

In addition to the changes observed in salinity, a decrease in the potassium concentration during the nitrogen lift (Fig. 6) was another indication that there were leftover technical fluids in the Ktzi 201 well. There was a massive peak consisting of up to 1000 mg K⁺/l after 2.9 m³ of water production. As the lift progressed, the potassium concentration steadily decreased to nearly its normal levels in the formation water. However, because normal, steady levels were never completely reached, it was concluded that the back-production of technical fluids was not fully completed at the end of the lift. If there were no remaining technical fluids, constant potassium levels would be expected. For comparison, BWG (Boden Wasser Gesundheit GbR) performed chemical analyses during the production testing of the neighbouring well, Ktzi 202, in January 2008 and observed decreasing trends that converged to a value near 282 mg K⁺/l by the end of the test. It was assumed that this potassium concentration was close to the concentration of potassium in the formation brine.

Total organic carbon (TOC) content

In the early production phase, TOC was high (almost 400 mg total organic carbon [TOC]/l after 2.9 m³ of water production). The TOC then decreased to low but non-negligible values of 3 mg [TOC]/l by the end of the nitrogen lift (Fig. 7).

There were indications that at least part of the organic carbon originated from the drilling mud that was spiked with the soluble tracer Na-fluorescein. Specifically, a peak in the fluorescein concentration (Fig. 7) occurred in the same samples that exhibited a peak in the TOC (Wandrey et al., this issue).

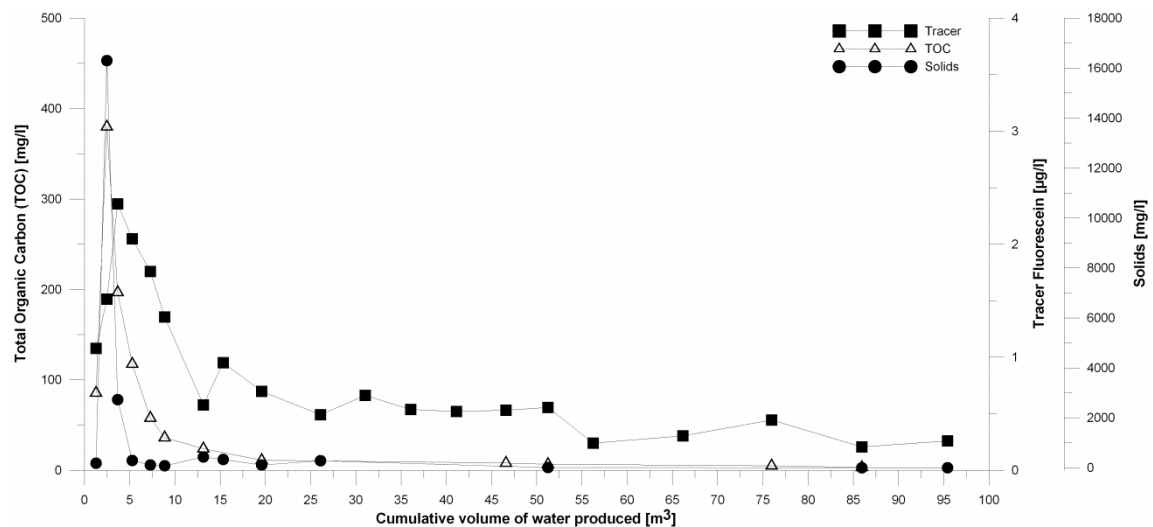


Fig. 7: Total organic carbon, solids, and tracers in produced water from the Ktzi 201 well.

Sulphate-reducing bacteria

The presence of the iron sulphide, the high sulphate concentration, and the high total organic carbon already indicated that sulphate-reducing bacteria were most likely present in the Ktzi 201 well (Würdemann et al., in prep.). The presence of SRB in downhole samples from this well at a depth of 647 m (depth of filters) as well as in samples taken during the lift were examined. Fig. 8A displays the bacterial community in these downhole samples as investigated by DAPI (4',6-diamidino-2-phenylindole) staining, a fluorescent stain that binds strongly to DNA. Approximately 10⁶ cells/ml were detected in these samples. The microbial contents of the fluid samples taken before and after the lift were investigated using FISH. FISH coupled with rRNA-targeted oligonucleotide probes allows for the direct visualisation, identification, and localisation of bacterial cells from selected phylogenetic groups in

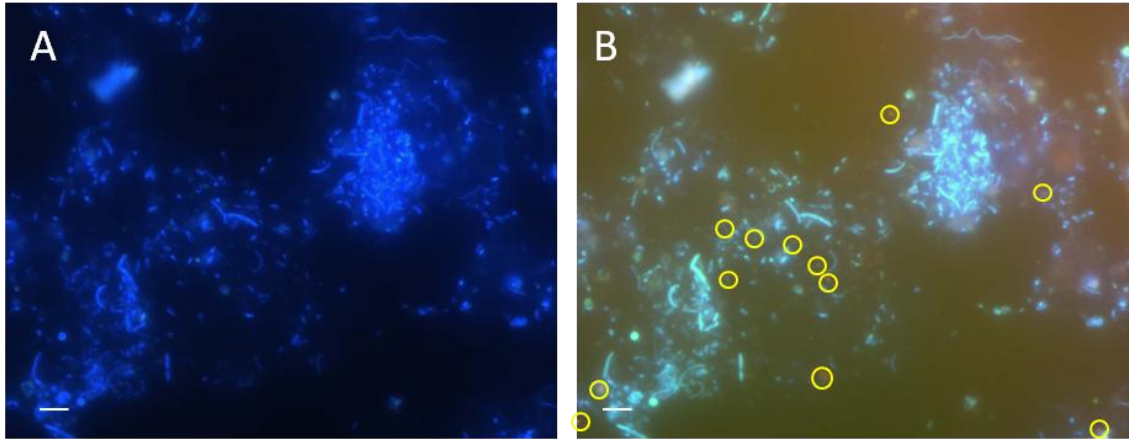


Fig. 8A: Fluorescence microscope image showing DAPI staining (blue) in the downhole water sample from the Ktzi 201 well at a 647-m depth. **B:** Fluorescence microscope image showing DAPI staining (blue) and *in situ* hybridisation of sulphate-reducing bacteria with probe SRB Cy-3 (red). Because of the double staining, SRB cells appear purple. Select SRB cells are marked with yellow circles. Bars represent 10 µm.

environmental samples. A detailed description is given elsewhere (Morozova et al., this issue). The sulphate-reducing bacteria labelled with a special SRB probe were observed in red/purple colour (Fig. 8B). The fraction of SRBs in the whole bacterial community decreased from 0.9×10^6 to 0.02×10^6 cells/ml, which represents about 32 % of all bacteria in the downhole samples taken before the lift and less than 5 % in the downhole samples that were taken 10 days after the lift.

Productivity/injectivity of the Ktzi 201 well in February/March 2008

During the lifting operations, the productivity of the Ktzi 201 well was measured again and similar values to those determined in the first hydraulic lift were gathered (Table 3). In February and March 2008, the injectivity was much higher and was on the same order of magnitude as the productivity. Further, the well experienced similar injectivity values to the other two observation wells (see Table 2). However, downhole samples taken after the lift operations indicated the new formation of iron sulphide. Therefore, a second well clean up using an N₂-lift was conducted. Finally, the lifting operations successfully removed the temporary blockage of the well and re-established sufficient injectivity of the CO₂ injection well, Ktzi 201.

4. Conclusions

Using a variety of analyses, the following conclusions are drawn.

- The temporary reduction of the injectivity of the Ktzi 201 well was most likely caused by bacterial activity.
- Bacterial activity was favoured because of the moderate temperature (approximately 35 °C), reduced salinity originating from the fresh water activation of the packer, and an excess of nutrients from the organic polymers used in the drilling mud and viscous pills.
- Sulphate-reducing bacteria generated hydrogen sulphide that reacted with dissolved iron to form amorphous iron sulphide. This precipitant subsequently blocked the pore throats in the reservoir section, thus reducing access for injections.
- A nitrogen lift succeeded in the removal of large amounts of dark-black iron sulphide and re-established the injectivity of the undisturbed formation.
- Adverse effects on injectivity caused by bacteria cannot easily be excluded in injection wells of other CO₂ storages.

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