# Chapter 6 Safe Operation of Geological CO<sub>2</sub> Storage Using the Example of the Pilot Site in Ketzin

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Abstract Reservoir rocks with the potential for storing  $CO<sub>2</sub>$  are mainly sandstones. In them, four trapping mechanisms facilitate permanent and safe storage: (i) structural trapping below an impermeable caprock, (ii) immobilization via capillary forces in the pore space, (iii) dissolution of  $CO<sub>2</sub>$  in the formation water, and (iv) mineral trapping via carbonization. Because leaks can occur monitoring of  $CO<sub>2</sub>$  storage sites is essential. However, the technological risks appear to be manageable. This is emphasized by the experience from the first continental European field laboratory in Ketzin, Germany. The results show that: (i) the geological storage of  $CO<sub>2</sub>$  is safe and reliable, and poses no danger to humans or the environment, (ii) a well-thought-out combination of different geochemical and geophysical monitoring methods can detect small amounts of  $CO<sub>2</sub>$  and image its spatial distribution, (iii) the interactions between fluid and rock induced by  $CO<sub>2</sub>$ injection at the pilot site in Ketzin have no significant impacts and do not influence the integrity of the reservoir or the caprock, and (iv) numerical simulations can depict the temporal and spatial behaviour of injected  $CO<sub>2</sub>$ . In addition, results from studies at Ketzin provide basic and transferable knowledge which is of value for a new integrated concept of  $CO<sub>2</sub>$  mitigation and utilization in combination with the power-to-gas concept based on a closed carbon cycle approach.

**Keywords**  $CO_2$  storage • Leakage • Trapping mechanisms • Ketzin pilot site • Field experiment • Monitoring • Modelling • Power-to-gas-to-power concept

### 6.1 Introduction and Motivation

Carbon dioxide  $(CO<sub>2</sub>)$  storage research at the GFZ German Research Centre for Geosciences focuses on whether the long-term and safe storage of  $CO<sub>2</sub>$  is possible in geological formations and whether this could help to mitigate greenhouse gas emissions into the atmosphere. Technologies for monitoring and predicting  $CO<sub>2</sub>$ 

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<span id="page-1-0"></span>storage in porous rocks in the deeper subsurface are being tested and new technologies developed. Near the town of Ketzin/Havel in Brandenburg, the first continental European field laboratory for on-shore  $CO<sub>2</sub>$  storage was set up as a pilot site in 2004, and active and continuous injection has been in operation from June 2008 until August 2013.

#### 6.2 Processes of Retaining  $CO<sub>2</sub>$  in Porous Reservoir Rocks

Suitable reservoir rocks are predominantly porous sedimentary rocks in the subsurface. The most important rocks for geological  $CO<sub>2</sub>$  storage are sandstones with sufficient porosity and permeability, allowing the  $CO<sub>2</sub>$  to be injected efficiently into these formations.  $CO<sub>2</sub>$  is injected into the reservoir via wells with the aid of pumps that ensure injection pressure high enough to overcome the flow resistance in the rock, which depends on permeability and other rock properties but also on the flow resistance of the displaced formation fluid in case of saline aquifers.

Different physical and chemical processes ensure that the injected  $CO<sub>2</sub>$  is retained in the reservoir rocks (Fig. 6.1). The relative importance and contribution of these different processes on the overall reservoir's retention potential vary over a logarithmic time scale (IPCC [2005](#page-15-0)). On the shortest time scale of years, during injection and directly afterwards, the injected  $CO<sub>2</sub>$  migrates upwards because it is less dense than the formation fluid initially contained in the geological formation. The  $CO<sub>2</sub>$  accumulates and is physically concentrated below the impermeable caprock, which is usually clay or salt rock (Fig. 6.1).

Within decades, parts of the  $CO<sub>2</sub>$  are retained by capillary forces (Figs. 6.1 and [6.2](#page-2-0)) if the pore necks have such a small diameter that the  $CO<sub>2</sub>$  can no longer migrate



#### $CO<sub>2</sub>$ -injection

Fig. 6.1 CO<sub>2</sub> trapping mechanisms during geological storage in a deep saline aquifer (GFZ 2014)

<span id="page-2-0"></span>upwards despite the density difference compared to the ambient formation fluid. The gas can then only be displaced by other fluids if they flow into the storage formation under elevated pressure.

Over a period of centuries, the major fraction of the  $CO<sub>2</sub>$  dissolves in the formation fluid, and carbonic acid is formed. The binding of  $CO<sub>2</sub>$  to the water remains stable as long as the pressure on the solution does not decrease and/or the temperature does not rise. This  $CO<sub>2</sub>$ -enriched water has a slightly higher density than the original formation fluid and tends to migrate downwards due to gravity (Fig. [6.1](#page-1-0)).

In the long term, on a time scale of some thousand years, the process of mineralization binds fractions of the carbon dioxide in the form of carbonates. Carbonization is the chemical neutralization reaction between the earth alkalines of the rock and the carbonic acid. Thus, mineralization of the  $CO<sub>2</sub>$  leads to permanent trapping in the rock in the form of calcite, dolomite or siderite for example.

Overall, the four trapping mechanisms in the storage formation facilitate permanent and safe storage. Only the fraction of  $CO<sub>2</sub>$  that exists as a free gas phase is driven upwards by buoyancy forces and could escape from the storage complex. The increasing effect of  $CO<sub>2</sub>$  trapping over time via the four trapping mechanisms continuously reduces the fraction of the free gas phase in the storage formation (Fig.  $6.2$ ), which has been verified, for example, by studies of natural  $CO<sub>2</sub>$  reservoirs. These studies show that around 18 % of the  $CO<sub>2</sub>$  mineralizes over a long period of time, and that the major fraction of the  $CO<sub>2</sub>$  is found dissolved in the formation water (Gilfillan et al. [2009](#page-15-0)).





### <span id="page-3-0"></span>6.3 Potential Leakage from  $CO<sub>2</sub>$  Storage

Figure  $6.3$  shows the schematic principle of geological  $CO<sub>2</sub>$  storage, as well as potential risks associated with the technology. The  $CO<sub>2</sub>$  is injected into the storage formation underneath an impermeable caprock (Fig. [6.1\)](#page-1-0). A multibarrier system above the storage complex, as shown in Fig. 6.3, comprises alternating layers of potential reservoir rock and caprock. The largest risk of leakage is location specific but in most cases probably posed by existing wells. Both active and abandoned wells are potential migration pathways because firstly they provide a direct connection between the surface of the Earth and the storage formation, and secondly they contain man-made materials (piping and cementing), which can corrode in the long term.

Considering a multibarrier system containing a large number of passive wells (old wells and observation wells), statistical methods can be applied together with an analytical solution in order to estimate the potential leakage rate (Nordbotten et al. [2004](#page-16-0)). The more barrier units that are present, the smaller the cumulative amount of  $CO<sub>2</sub>$  that can migrate along corroded wells towards the Earth's surface because major fractions of the leaking  $CO<sub>2</sub>$  could be taken up by the formations lying above the storage complex if corrosion connected those layers as well. Calculations show that 10 % of the total amount stored would leak from the storage complex if one caprock layer was present, 1 % if two caprock layers were present (Fig.  $6.3$ ), and 0.1 % if three were present, etc. (Nordbotten et al. [2004](#page-16-0)). If there is only one well 100 m away from the injection well and if this is leaking, then between 0.1 and 0.2 % of the total amount stored in the aquifer is expected above



Fig. 6.3 Schematic principle of the geological storage of  $CO<sub>2</sub>$  with a multibarrier system. Potential anthropogenic and natural leakage pathways for  $CO<sub>2</sub>$  and the mobilization of saline water are also shown (GFZ 2014)

this level (Ebigbo et al. [2007](#page-15-0)). The potential leakage rate essentially depends on the number of (leaking) wells in the vicinity of the storage facility. During the injection of  $CO<sub>2</sub>$  into a depleted oil field in America (West Pearl Queen, New Mexico), the real leakage rate near the injection well was measured using tracers. These studies estimated a leakage rate of about 0.0085 % per year of the total  $CO<sub>2</sub>$  injected (Wells et al. [2007\)](#page-16-0). In this particular experiment, approx. 2,000 tCO<sub>2</sub> were injected over a period of 2 months. In addition to direct measurements of  $CO<sub>2</sub>$  at the surface and in the wells, seismic monitoring can also be used in order to detect  $CO<sub>2</sub>$ migration and potential leakage at an early stage (Bohnhoff et al. [2010\)](#page-15-0) and facilitate countermeasures. As discussed, leaking wells can occur and need to be observed, which makes monitoring of  $CO<sub>2</sub>$  storage sites essential.

In addition to wells, potential natural leakage pathways exist. These are flow pathways along fractures and faults (Fig. [6.3](#page-3-0)). They may be present in the reservoir rock and caprock, as well as in the overlying rock layers, and are more complex than wells because they comprise non-uniform surfaces with variable permeability. Geological faults can be impermeable to fluids, but as natural  $CO<sub>2</sub>$  seeps have shown, they can also be permeable to gases. One of the largest measured degassings at a natural  $CO<sub>2</sub>$  source was in Italy, where an emission flux of 2,000 tCO<sub>2</sub> per day was measured across an area of approx.  $0.5 \text{ km}^2$  (Chiodini et al. [2010](#page-15-0)). The degassing system in this case, however, is located in a mountainous region, and is thus characterized by a very different geological structure than potential  $CO<sub>2</sub>$ storage sites. This region in Italy is tectonically highly active as evidenced by several earthquakes and thus not a prime target for  $CO<sub>2</sub>$  storage. Many fracture and fault systems in sedimentary basins (e.g. North German basin), in contrast, are impermeable to fluids, as verified by the discovery of natural gas and crude oil fields millions of years old. If these systems were not predominantly impermeable, then no hydrocarbon deposits would be found in them.

In case of  $CO<sub>2</sub>$  storage in saline aquifers, another effect that must be investigated in detail for every site is the displacement of saline water (Fig.  $6.3$ ). The CO<sub>2</sub> injected into the reservoir rock displaces the saline water initially present in the pore space. It must be ensured that the saline water does not flow along migration pathways into the drinking water reservoirs of shallow aquifers, and contaminate the drinking water with so much salt that it would be unusable for the drinking water supply. This necessitates a comprehensive and thorough exploration of each potential site. Such data acquisition then provides the basis for precautionary safety analyses. A theoretical study showed that for undisturbed systems (no fractures or faults or other direct fluid flow conduits), there is no risk of saline water migrating upward into drinking water reservoirs despite pressure increases at a distance of tens of kilometres away from the injection zone of the geological storage formation (Birkholzer et al. [2009](#page-14-0)). Similar investigations of disturbed systems show a very low tendency towards possible salinization of near-surface aquifers even for highly permeable fault systems (Tillner et al. [2013](#page-16-0)).

A general evaluation of the suitability of sites in advance cannot be performed effectively. It is therefore essential that a comprehensive exploratory investigation will be performed. This investigation is site-specific, and is the most important and indeed the only possible method of evaluating risks in detail and deciding whether a site is suitable for geological  $CO<sub>2</sub>$  storage in general. To answer the question if long-term and safe geological  $CO<sub>2</sub>$  storage can be realized requires  $CO<sub>2</sub>$  injection accompanied by extensive monitoring.

#### 6.4 Safety of the Geological Storage of  $CO<sub>2</sub>$

The most important question that has to be answered about  $CO<sub>2</sub>$  storage technology is how safe it is for humans and the environment. In order to predict the safety of geological  $CO<sub>2</sub>$  storage at the present time, two 'analogues' are taken into consideration. These are (i) naturally occurring  $CO<sub>2</sub>$  reservoirs and/or sources and (ii) other sites where gas has been stored in porous rocks (Kühn  $2011$ ).

The underground geological storage of  $CO<sub>2</sub>$  is not a human invention but rather a natural phenomenon. Numerous naturally occurring  $CO<sub>2</sub>$  reservoirs have existed throughout the world for thousands or even millions of years, e.g. the Rhon region in Germany, the south of France, and Italy. These naturally occurring reservoirs prove that rocks can store  $CO<sub>2</sub>$  for geologically long periods of time and that caprocks can efficiently retain the gas. If future  $CO<sub>2</sub>$  storage facilities are chosen accordingly and investigated using state-of-the-art methods, then long-term storage of most of the  $CO<sub>2</sub>$  will be possible. Naturally occurring reserves of  $CO<sub>2</sub>$  help us to understand the conditions under which gas can be retained. In contrast, natural  $CO<sub>2</sub>$ seeps show what consequences are to be expected when  $CO<sub>2</sub>$  escapes. With their study of 286 natural  $CO<sub>2</sub>$  sources in Italy, Roberts et al. demonstrate that an appropriate risk management in advance of industrial  $CO<sub>2</sub>$  storage can minimize the health risk associated with the unintended leakage of  $CO<sub>2</sub>$  (Roberts et al. [2011\)](#page-16-0). The calculated risk of death in regions surrounding the natural seeps in Italy is  $10^{-8}$ per year, which is much lower than other everyday risks to human life which are accepted by society. For example, the probability of being killed in a car crash is  $1.8 \cdot 10^{-4}$  or of being struck by lightning in America  $2.3 \cdot 10^{-5}$  (Roberts et al. [2011\)](#page-16-0).

On the shorter technological time scale, experience in gas storage technology provides insights for the geological storage of  $CO<sub>2</sub>$ , such as on the diffusion behaviour of gases in porous rocks. The technology of storing large quantities of natural gas in deep underground rock formations to compensate for seasonal fluctuations in demand has proven its worth over decades in many places in the world. The storage volume of the 23 porous gas storage reservoirs in Germany is around 12.5 billion  $Nm<sup>3</sup>$  natural gas (Sedlacek [2009](#page-16-0)). An example of successful and safe natural gas storage is the underground storage facility in Berlin, which has been in operation since 1992 at a depth of 800 m. This storage facility stretches underneath a protected natural area as well as directly underneath residential areas, sports grounds, and recreation areas.

These two analogues provide important information for the geological storage of  $CO<sub>2</sub>$  and also demonstrate that it is possible to control the process technically and to

operate it safely. They also confirm that large amounts of  $CO<sub>2</sub>$  can be stored for long periods of time in reservoir rocks. Despite this, possible leakage pathways and the risks associated with the technology must be identified in order to ensure that geological  $CO<sub>2</sub>$  storage will not pose any danger to humans or the environment.

Even if  $CO<sub>2</sub>$  would escape to the Earth's surface in spite of all of the safety measures, the dangers associated with it are relatively small compared to other gases (e.g. natural gas) because  $CO<sub>2</sub>$  is non-toxic and neither combustible nor explosive. Depending on the framework conditions such as flow rate, topography, wind speed, and wind direction, fugitive  $CO<sub>2</sub>$  mixes quickly with the ambient air and is diluted to a harmless level. However, it should be noted that continuously inhaling high concentrations of  $CO<sub>2</sub> (TLV = threshold limit value = 5,000 ppm)$ poses a health hazard for humans.

An overview of findings from natural  $CO<sub>2</sub>$  sources and observed leakages from gas storage sites helps us to estimate the hazard potential (Lewicki et al. [2007\)](#page-15-0):

- Carbon dioxide can accumulate in primary and secondary reservoir rocks underneath impermeable caprock layers but it can also permeate these layers under certain conditions and escape at the Earth's surface.
- Many natural releases are directly connected to an event (e.g. earthquakes).
- Permeable fracture and fault systems can act as migration pathways for  $CO<sub>2</sub>$ , allowing the gas to escape at the Earth's surface.
- Wells with construction defects represent the main leakage pathways for  $CO<sub>2</sub>$ .
- The way in which  $CO_2$  is released via leakage pathways and the amount released is always a site-specific phenomenon.
- The hazard potential for humans is mostly small as the population affected has usually been informed and monitoring systems have been installed. Different naturally occurring events, however, have also led to fatalities, e.g. in residential blocks due to elevated concentrations of  $CO<sub>2</sub>$  (Lewicki et al. [2007;](#page-15-0) Chiodini et al. [2010](#page-15-0)).
- Changes in groundwater quality associated with the release of  $CO<sub>2</sub>$  have also been observed, although the respective limits for drinking water were not exceeded in most cases.

As is the case for every technology, there is also a technological risk associated with the geological storage of  $CO<sub>2</sub>$ . However, this appears to be manageable (Roberts et al. [2011\)](#page-16-0), particularly when modern monitoring systems are used.

#### 6.5 Monitoring of  $CO<sub>2</sub>$  Storage

In assessing the surveillance of  $CO<sub>2</sub>$  injected into a geological formation for storage, it must be noted that this is a new technology still in the technical and scientific demonstration phase. Empirical values are currently only available for a few pilot sites. Furthermore, most of these sites are purely scientific projects with

comparatively low amounts of injected  $CO<sub>2</sub>$ . Findings from  $CO<sub>2</sub>$  storage projects on a commercial scale come from the Sleipner project (Norway), where more than 1 MtCO<sub>2</sub> per year has been injected since 1996, the In Salah project (Algeria), where around  $0.7 \text{ MtCO}_2$  per year has been injected since 2004, the Snohvit project (Norway), where about  $0.5 \text{ MtCO}_2$  per year is injected, and the Weyburn Midale project (Canada), which has injected around 2.8 MtCO<sub>2</sub> per year since 2000 within the framework of enhanced oil recovery (EOR). In addition to these projects, recourse can be taken to experience with gas storage technology, as already mentioned. However, the differences between storing natural gas and  $CO<sub>2</sub>$  in terms of chemical and physical properties must be taken into account here. The volumes and objectives are also different. While natural gas storage aims at the best possible recoverability, i.e. a high fraction of working gas,  $CO<sub>2</sub>$  storage aims at the best possible trapping of the injected  $CO<sub>2</sub>$  in the reservoir. This leads to different requirements on geological characteristics in the respective reservoirs. Experience can therefore only be transferred to a limited extent.

A range of direct and indirect methods can be used to monitor the injected  $CO<sub>2</sub>$ . Most of these methods are based on established geophysical and geochemical techniques, which may have to be modified depending on the requirements of  $CO<sub>2</sub>$  storage. Each storage site has very specific monitoring requirements for the injected  $CO<sub>2</sub>$ , which must be precisely defined before start of storage operation within a needs and risks assessment. This definition requires the creation of a comprehensive geological, hydraulic, and geomechanical model of the storage reservoir. Based on the requirements, a monitoring concept must then be developed under surveillance of the responsible authorities in order to combine different monitoring methods in the most appropriate manner.

Based on current knowledge, such a monitoring concept, which is tailored to the individual storage reservoir, will make it possible to reliably monitor and control the injected  $CO<sub>2</sub>$ . It should be noted that the described methods allow a qualitative description of  $CO<sub>2</sub>$  distribution, but that the amount of  $CO<sub>2</sub>$  is difficult to quantify.

A key point for predicting the behaviour of the injected  $CO<sub>2</sub>$ , and for the related risk analysis, is the use of numerical simulations. Modelling and storage site monitoring are iterative processes, and both the modelling results and monitoring concepts can be adjusted accordingly during the storage process and validated. Further, results from monitoring will guide the injection operation in order to allow for a safe storage procedure. While monitoring methods can only reflect the actual situation, numerical modelling can be used to predict long-term behaviour of the storage formation. These predictions can then be used to develop an adaptive monitoring system and to optimize the operation of the storage facility.

In terms of optimal delineation of the storage reservoir and the related determination of the spatial distribution of potential irregularities during storage operation, the spreading of the injected  $CO<sub>2</sub>$  itself must be differentiated from spreading of the pressure increase in the reservoir caused by the injection process. The latter can cover a significantly larger spatial area than the  $CO<sub>2</sub>$  itself. While the distribution of  $CO<sub>2</sub>$  is decisive for the possible leakage of  $CO<sub>2</sub>$  from the storage facility, the spatial distribution of the pressure increase is decisive for displaced saline formation water potentially migrating upwards. Furthermore, it is important to distinguish between spatial distribution or spreading at reservoir depth and spatial spreading of  $CO<sub>2</sub>$  at the surface. Whereas  $CO<sub>2</sub>$  or displaced saline formation water migrates upwards, horizontal migration can occur in overlying rock units, which may extend far beyond the spreading at the depth of the reservoir. Therefore, the underground distribution of the  $CO<sub>2</sub>$  and the pressure increase cannot be directly transferred to the corresponding distribution at the surface. The spatial distribution of the  $CO<sub>2</sub>$  and of the pressure increase at depths of the reservoir can be determined using existing monitoring and simulation methods. The potential spatial spread at the surface resulting from this spatial spread at reservoir level must be individually determined for each storage site as part of a risk analysis.

Not only must the monitoring concept and the spatial distribution and/or limitation be specifically designed or defined for each storage site, but a risk analysis is also only possible on a case-by-case basis. Each storage site is characterized by very specific geological conditions, which often differ from each other considerably. Due to these different geological settings, no generalizable criteria for risk assessments can be defined or applied to all storage sites. Exclusion criteria for a storage site include caprock that has not formed fully, as well as migration pathways, and thus hydraulic connections between the storage formation and the aquifers found above the caprock.

#### 6.6 Experience from the Pilot Site in Ketzin

The underground geological storage of  $CO<sub>2</sub>$  is being studied near the town of Ketzin/Havel (Brandenburg) around 40 km west of Berlin (Martens et al. [2012\)](#page-16-0). The geological target horizons for  $CO<sub>2</sub>$  storage at the pilot site in Ketzin are porous sandstone layers at a depth of 630–650 m (Förster et al. [2006](#page-15-0); Norden et al. [2010](#page-16-0)) (Fig. [6.4](#page-9-0)).

Above the sandstone storage formation are layers of clay, which act as a seal and are more than 165 m thick. From the 1960s until 2000, the Ketzin site was initially used to store town gas and then natural gas in a shallower sandstone formation at a depth of around 280 m. For this reason, the site is well explored. Based on existing knowledge and additional exploratory investigations, in 2007 three new wells were drilled for the geological storage of  $CO<sub>2</sub>$  with final depths of up to around 800 m each. One of these wells (Ktzi 201) is used to monitor and inject the  $CO<sub>2</sub>$ , while the other two (Ktzi 200 and Ktzi 202) are used to monitor the injection and distribution of the  $CO<sub>2</sub>$  (Prevedel et al. [2009\)](#page-16-0). In summer 2011, another well (P300) was drilled at the pilot site to a depth of 446 m in order to observe the geochemical and hydrogeological conditions in the first aquifer above the storage formation. The final well (Ktzi 203) was drilled in 2012 into the reservoir especially to retrieve rock samples which were in contact with  $CO<sub>2</sub>$  for 4 years (Fig. [6.4](#page-9-0)).

<span id="page-9-0"></span>

Fig. 6.4 Schematic profile cross-section of the pilot site in Ketzin with all five wells and an overview of monitoring methods (GFZ 2014)

### 6.6.1 Storage of  $CO<sub>2</sub>$  Is Safe and Reliable

From June 2008 until August 2013, mainly food-grade  $CO<sub>2</sub>$  has been fed into the underground formation via the injection well. Over the entire period, the injection has been safe and reliable. The injection conditions at the injection wellhead are approx. 62 bar and 35  $\degree$ C. The respective injection regime is determined in accordance with the scientific tasks and requirements. Injection began on 30 June 2008, and  $67,271$  tCO<sub>2</sub> had been injected by August 2013.

The injection led to an initial pressure rise in the reservoir from originally 62 bar to 76 bar. Continuous pressure measurements show that pressure conditions in the reservoir have remained stable between 72 bar and 76 bar since spring 2009 (Möller et al. [2012\)](#page-16-0). The allowed maximal reservoir pressure of 85 bar defined in the storage permission, which was approved by the Brandenburg state agency for mining, geology and raw materials (Landesamt für Bergbau, Geologie und Rohstoffe, LBGR), was neither reached nor exceeded at any time during injection. Overall, the measurements verify a stable and reliable storage operation (Liebscher et al. [2012](#page-15-0), [2013\)](#page-15-0).

# 6.6.2 Combination of Geochemical and Geophysical Monitoring Methods for Detecting Small Amounts of  $CO<sub>2</sub>$

At the pilot site in Ketzin, the primary objective is to develop, test and apply geophysical and geochemical monitoring methods. These will provide general information on monitoring of  $CO<sub>2</sub>$  storage reservoirs, and thus facilitate the monitoring of the spatial distribution of  $CO<sub>2</sub>$  injected underground. In this context, the most comprehensive monitoring programme in the world is in place at the pilot site in Ketzin (Giese et al. [2009;](#page-15-0) Fig. [6.4](#page-9-0)). It comprises permanent monitoring methods, such as pressure and temperature measurements (Möller et al. [2012\)](#page-16-0), as well as periodic measurements, such as surface measurements of  $CO<sub>2</sub>$  flows in the upper soil layers (Zimmer et al. [2011\)](#page-16-0), borehole measurements (Henninges et al. [2011](#page-15-0)), deep fluid sampling (Morozova et al. [2011\)](#page-16-0), geoelectric (Kiessling et al. [2010;](#page-15-0) Labitzke et al. [2012](#page-15-0); Schmidt-Hattenberger et al. [2011\)](#page-16-0), and active and passive seismic monitoring (Bergmann et al. [2011](#page-14-0); Kazemeini et al. [2009](#page-15-0); Lüth et al. [2011;](#page-16-0) Yordkayhun et al. [2009a](#page-16-0), [b\)](#page-16-0).

The results of geoelectric and seismic monitoring, in particular, show that even very small amounts of  $CO<sub>2</sub>$  can be determined indirectly in the subsurface with sufficient precision. Geoelectric methods reliably detect approx.  $5,000$  tCO<sub>2</sub>, and seismic methods image the spatial distribution of  $CO<sub>2</sub>$  for an injected volume of around  $22,000$  tCO<sub>2</sub>. The results of both methods also show good agreement with each other.

# 6.6.3 Fluid Rock Interactions Do Not Impact the Storage Integrity

Sandstone samples from the Ketzin storage formation were treated in the laboratory with  $CO_2$  and saline water with near in situ conditions (55 bar and 40 °C). For comparison, samples were studied with and without  $CO<sub>2</sub>$  in contact with saline water. Overall, the dissolution of calcium-rich plagioclase, K-feldspar, and anhydrite was observed, while albite appears to be stable (Fischer et al. [2011](#page-15-0)). The petrophysical properties of the sandstone samples also show changes with a slightly increased porosity (Zemke et al. [2010\)](#page-16-0). The observed chemical reactions occurred on such a small scale that the integrity of reservoir and caprocks is not affected.

# 6.6.4 Numerical Simulations Depict the Temporal and Spatial Behaviour of Injected  $CO<sub>2</sub>$

Static and dynamic modelling complement the monitoring methods at the Ketzin site and provide support to the operational management by delivering predictions.

Dynamic modelling is the only method for predicting the long-term behaviour of a storage site based on the known hydraulic, thermal, chemical, and mechanical processes (Bergmann et al. [2010](#page-14-0); Kempka et al. [2010](#page-15-0); Lengler et al. [2010](#page-15-0)).

Based on new findings obtained during injection operation so far, the underlying geological model was and will be continuously further developed and adapted (Liebscher et al. [2012](#page-15-0); Martens et al. [2012\)](#page-16-0). Numerical simulations performed to date on the basis of this geological model reveal good agreement between simulation results and monitoring measurements. It can therefore be assumed that sitespecific predictions derived for further spreading of the  $CO<sub>2</sub>$  after stop of injection are reliable (Fig. 6.5).



Fig. 6.5 Simulated distribution of gaseous  $CO<sub>2</sub>$  in the storage formation (model di-mensions: 5 km  $\times$  5 km) after 1, 2, 3, and 4 years (from top left to bottom right) and after 5 and 6 years (bottom left and right, prediction) (GFZ 2014)

# <span id="page-12-0"></span>6.7  $CO<sub>2</sub>$  Storage as a Component of Energy Storage for a Closed Carbon Cycle

The geological storage of  $CO<sub>2</sub>$ , however, does not only play a key role for the mitigation of  $CO<sub>2</sub>$  emissions in the atmosphere in the long term, but it could also become a central component in the hydrogen economy as 'dynamic' storage, as proposed in the power-to-gas concept.

If excess electricity is to be converted into methane and stored, a  $CO<sub>2</sub>$  source will be required. According to the German federal government's climate change mitigation targets,  $CO_2$  emissions are to be cut by at least 80 % by 2050 in regard to levels of 1990. In order to achieve this target,  $CO<sub>2</sub>$  from biogas production must be used for any power-to-gas concept because it is not considered to be additional CO2, and is assigned to the natural carbon cycle. Another option is to use processrelated  $CO<sub>2</sub>$  produced in industrial processes.

If we were to go a step further, the power-to-gas concept could be extended to include the separation, storage, recycling and reuse of  $CO<sub>2</sub>$  produced during the energy generation process (e.g. via combined cycle power plants =  $CCGT$ ; Fig. 6.6). If all components are integrated in one site, then a local closed carbon cycle is the result (Streibel et al. [2013](#page-16-0)). This would safeguard the advantages of fossil fuels – the ability to be stored in large quantities and thus supply very



Fig. 6.6 Closed carbon cycle achieved by coupling  $CO<sub>2</sub>$  storage with methane gas storage to store excess renewable wind and solar energy (GFZ 2014)



Fig. 6.7 The closed carbon cycle (GFZ 2014)

energy-intensive industries – in the long term (Kühn et al.  $2013$ ). At the same time, the storage of  $CO<sub>2</sub>$  from biogas combustion gives rise to negative  $CO<sub>2</sub>$  emissions (Fig. 6.7) and thus helps to stabilize the atmospheric concentration of  $CO<sub>2</sub>$ . Figure [6.6](#page-12-0) schematically shows how the individual components can be combined.

This cycle comprises five stages (Kühn  $2012$ , Fig. 6.7). The driving force, which allows the repeated conversion of  $CO<sub>2</sub>$ , is hydrogen, which is produced from excess electricity generated from renewables:

- 1. Preparation of hydrogen via electrolysis.
- 2. Reaction of hydrogen with carbon dioxide from a reservoir.
- 3. Methane is stored temporarily in a geological formation.
- 4. When electricity is needed, the methane is fed back into the cycle and combusted in a CCGT.
- 5. The  $CO<sub>2</sub>$  produced during combustion in the CCGT is then separated and stored.

#### 6.8 Summary and Conclusions

Reservoir rocks with the potential for storing  $CO<sub>2</sub>$  are mainly sandstones, as they are characterized by sufficient porosities and permeabilities allowing  $CO<sub>2</sub>$  to be injected efficiently into these formations. Overall, four trapping mechanisms in the

<span id="page-14-0"></span>layers of the storage formation facilitate permanent and safe storage: (i) structural trapping below an impermeable caprock, (ii) immobilization via capillary forces in the pore space, (iii) dissolution of  $CO<sub>2</sub>$  in the formation water, and (iv) mineral trapping via carbonization.

As demonstrated, leaks can occur and must be detected, which makes monitoring of  $CO<sub>2</sub>$  storage sites essential. A general evaluation of the suitability of sites in advance cannot be performed effectively without a geological site characterization. It is therefore essential that a comprehensive exploration will be performed before a project begins. As is the case for every technology, there is also a technological risk associated with the geological storage of  $CO<sub>2</sub>$ . However, this appears to be manageable, particularly when modern monitoring systems are used.

Near the town of Ketzin/Havel in Brandenburg, the first continental European field laboratory for  $CO<sub>2</sub>$  storage was set up as a pilot site in 2004, and it is in operation until today with active and continuous injection from June 2008 until August 2013. During that period  $67,271$  tCO<sub>2</sub> have been stored. The pilot site in Ketzin was thus the first and is still the only active  $CO<sub>2</sub>$  storage project in Germany. The injection of  $CO<sub>2</sub>$  has been accompanied by one of the most extensive scientific research and development programmes in the world. The results show that: (i) the geological storage of  $CO<sub>2</sub>$  at the pilot site in Ketzin is safe and reliable, and poses no danger to humans or the environment, (ii) a well-thought-out combination of different geochemical and geophysical monitoring methods can detect small amounts of  $CO<sub>2</sub>$  and image its spatial distribution, (iii) the interactions between fluid and rock induced by  $CO<sub>2</sub>$  injection at the pilot site in Ketzin have no significant impacts and do not influence the integrity of the reservoir or the caprock, and (iv) numerical simulations can depict the temporal and spatial behaviour of injected  $CO<sub>2</sub>$ .

Work at the pilot site in Ketzin demonstrates the safety and reliability of  $CO<sub>2</sub>$ storage on a research scale, and is thus an important milestone on the way to decarbonizing society and making an important contribution to using underground geological formations in an environmentally friendly manner. In addition, results from studies at Ketzin provide basic and transferable knowledge which is of value for a new integrated concept of  $CO<sub>2</sub>$  mitigation and utilization in combination with the power-to-gas concept based on a closed carbon cycle approach.

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