

REPORT

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GEOLOGICAL CO₂ STORAGE AND OTHER EMERGING SUBSURFACE ACTIVITIES: D 1.1

CATALOGUE OF POTENTIAL IMPACTS ON DRINKING WATER PRODUCTION

Project acronym: Cosma-1

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Title

Geological CO₂ Storage and Other Emerging Subsurface Activities - Catalogue of potential impacts on drinking water production

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Chapter 1

Introduction

1.1 Background

Against the background of continuously increasing CO₂ concentrations in the atmosphere, as well as diminishing reserves of fossil fuels, finding new ways for autarkic and “climate friendly” energy production becomes more and more important. Moreover, new solutions have to be found for the mitigation of process-related CO₂ emissions.

A more extensive use of the earth’s subsurface might offer new options to tackle all three of the mentioned challenges. The earth’s heat might be used as a clean and in human timescales endless source of energy (geothermal energy production). Process-related CO₂ emissions from steel or cement production can be stored in specific geological formations (geological CO₂ storage, GCS). Finally, since the technique of horizontal drilling was developed, the exploitation of unconventional reserves of natural gas or oil via hydraulic fracturing (fracking) poses another way for countries to become more energy autarkic.

Nevertheless, all these emerging subsurface activities (ESA) are related to intensive drilling activities and thus intrusions in the subsurface, which is also a major source of freshwater and supplies billions of people worldwide. Therefore, water suppliers are concerned that these emerging activities might have negative impacts on groundwater resources and consequently on the drinking water supply.

The project COSMA-1, a cooperation between the Berlin Centre of Competence for Water, the German Research Centre for Geosciences (GFZ) and the Free University of Berlin (FUB), aims at identifying and assessing potential risks for drinking water supply as a consequence of the named subsurface activities.

1.2 Focus and structure of this report

As a first deliverable of the COSMA-1 project, this report includes background information on risk analysis, including the relevant terminology and methodology (Chapter 2.1). Moreover, theoretical information is given for the three considered subsurface activities (Chapters 2.2-2.4). This will serve as a common base for the forthcoming deliverables of the project.

A qualitative summary of hazards and hazardous events, related to the respective subsurface activity, which might pose a risk for drinking water supply, is provided in the core part of this report (Chapter 3). This information will be then summarized in Chapter 4, with further conclusions and recommendations.

It shall be underlined at this point that in this report “potential impacts” are summarized, not “risks”. “Impacts” are defined as changes in groundwater quality. As it is outlined in Theoretical Chapter 2.1 the term *risk* requires a statement about the *probability* of a certain event. This report rather points out which *impacts* are theoretically thought possible and gives no information on the likelihood of the respective impact. Statements on risks are just provided in general terms or cited from literature.

Chapter 2 Theoretical Background

This chapter aims at providing the necessary theoretical background on risk analysis and its terminology as well as on the regarded subsurface activities.

2.1 Risk analysis

Definitions

The term **risk analysis** “includes risk assessment, risk management, and risk communication” ((Haas, Rose et al. 1999), Chap. 3, l. 9). The single parts in turn include certain methods and objectives (Fig. 1).

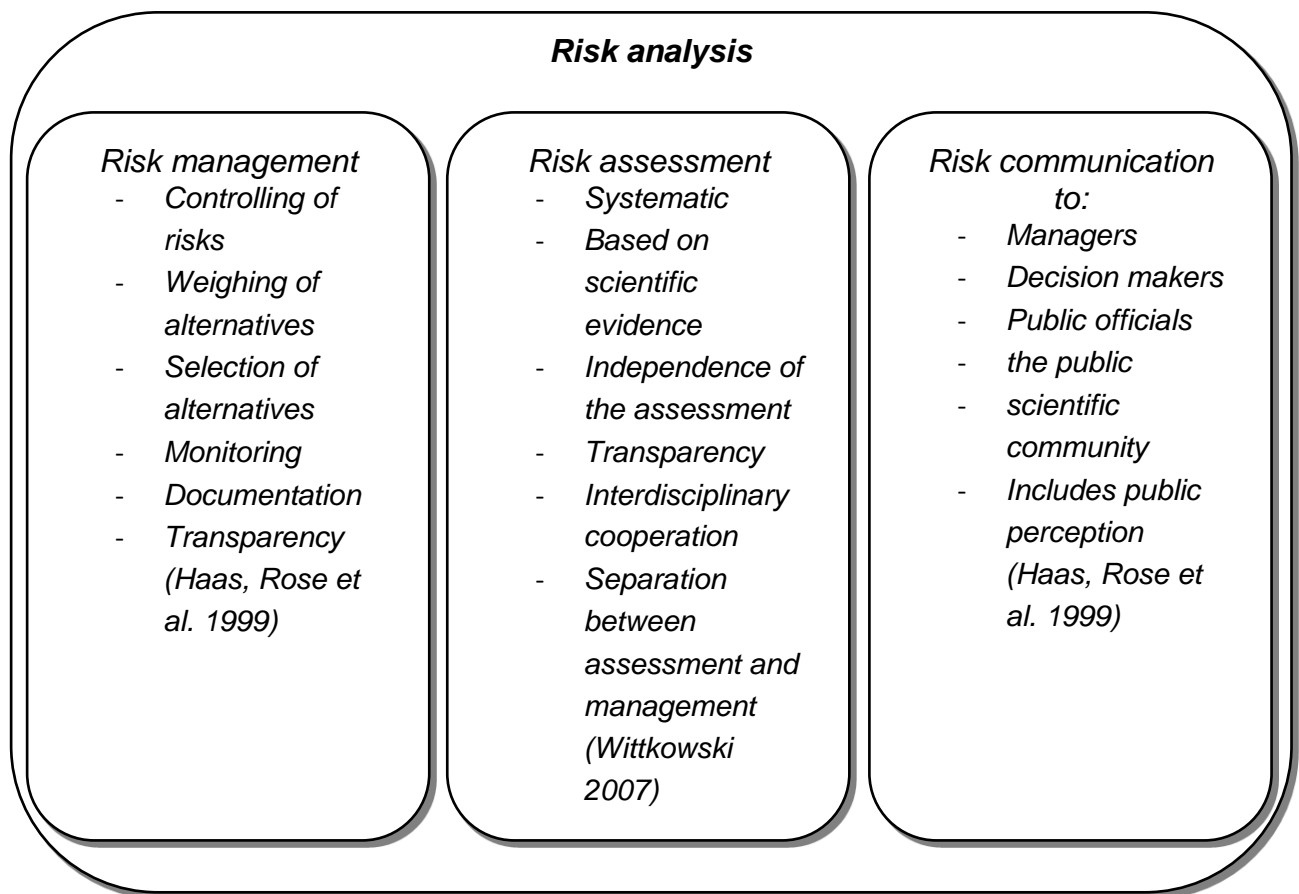


Fig. 1: Different components of risk analysis. Within the three smaller boxes objectives and characteristics for the management, assessment and communication of environmental and human health risks are listed.

Risk assessment is a science-based, systematic approach in order to assess quantitatively or qualitatively risks resulting from specific hazards. As various fields of study are often involved in the assessment of certain risks, risk assessment is dependent on interdisciplinary cooperation. Risk assessment is always part of **risk communication**. Therefore, it has to be written in a transparent and understandable manner, so that the information is accessible to all relevant stakeholders (Wittkowski 2007).

In order to ensure objectivity in risk analysis, risk assessment should be independent from **risk management**. The purpose of the latter one is to select, plan, establish and monitor risk reduction measures. In order to decide if additional risk reduction measures

are necessary the present risks have to be quantified and compared to a level of risk which is considered to be acceptable or tolerable.

In matters of food safety, the European council establishes a legacy in regulation No 178/2002 and considers water as a substance “*ingested [...] like others foods, thereby contributing to the overall exposure of consumer to ingested substances*” ((EU 2002), EC 178/2002).

In areas of food safety and safety engineering, hazards, hazardous event and risk are defined as:

- **Hazards** in food safety, which includes water “*means a biological, chemical or physical agent in [...] (water) with the potential to cause an adverse health effect*” - EC 178/2002 (EU 2002),
- **Hazardous events** can be physical and/or a chemical processes or a pathway which explain the hazard's presence within the water supply (Condor, Unatrakarn et al. 2011),
- **Risk (R)** is the product of the probability (P) of an adverse effect and the severity (S) of that effect, consequential to a hazard (EC 178/2002, (EU 2002, Condor, Unatrakarn et al. 2011)), or mathematically:

$$R = P * S$$

Methodology of risk assessment

The basic structure of any human health or environmental risk assessment consists of four steps (WHO 2006):

- Hazard identification,
- Hazard characterization,
- Exposure Assessment,
- Risk characterization.

Hazard identification

The purpose of hazard identification is to build a causative correlation between a certain chemical or microbiological agent and a certain adverse effect for human health or the environment (disease, eco-toxic effects). This field of study is covered by numerous disciplines, like clinical microbiology, epidemiology, environmental chemistry and toxicology ((Haas, Rose et al. 1999), Chap. 4). The objective is to give a detailed description of the mechanisms and the cause of the actual adverse effect, e.g. the adverse health effect due to an EHEC infection (enterohemorrhagic *Escherichia Coli*) is not due to the infection itself but due to the toxins the organism produces. Furthermore, hazard identification includes the detection of a specific hazard in the system of interest, e.g. a water supply system.

Hazard characterization

After a certain agent is identified as a hazard, the step of hazard characterization collects information on its characteristics, e.g. distribution, physic-chemical properties, main sources of emission (BfR 2010). A crucial point of this step is to determine dose-response relations, or concentration-effect relations. Within this procedure it is determined, at which concentrations or doses an adverse effect occurs and if there is a

threshold level below which no adverse effect will result. Again, numerous fields of research may be involved in this process, like chemistry, microbiology and immunology.

Exposure Assessment

The purpose of the step of exposure assessment is to predict the fate of a hazard from its source to the endpoint of interest and the probable quantity this endpoint is exposed to. Endpoints are points in the modeling process at which the risk is assessed, e.g. the endpoint of human exposure assessments are humans. Concerning the environment, multiple endpoints may be of interest, like surface waters, soil or atmosphere. A main difference between human and environmental exposure assessment is that human exposure assessment calculates the dose a human being is exposed to, whereas environmental exposure assessment calculates concentrations of soil, water or food related to the specific endpoint.

Risk characterization

Risk characterization includes all the information of the three previous steps in order to estimate the magnitude of the human health or environmental risk ((Haas, Rose et al. 1999), chap. 3).

It shall be underlined that a mean or median value, which was used during exposure assessment for any parameter, represents its “most probable value” as it is always subject of variability and uncertainty.

The terms variability and uncertainty refer to the problem of imprecise or not reliable data, which might lead to errors in the overall result. Variability refers to variations within the data, which cannot be improved by further investigation, like human behavior or the analytical error of a specific chemical analysis. Uncertainties on the other hand refer to variations and assumptions within the model, which can be improved by further investigations.

Calculations, which are based on point estimates, thus calculate the result which is expected to be the most probable one against the background of the reliability of the available data.

In order to give a more detailed picture of the expected outcome, more advanced methods of risk analyses try to consider all the variation and uncertainty, which underlies each parameter. One way of doing so is the use of Monte Carlo Simulations which accounts for the whole distribution of the specific parameter. The approach delivers a distribution of results (probability distribution), thus accounting for the present uncertainty and variability.

2.2 Geological CO₂ storage

Process description and technical realization

Geological CO₂ storage (GCS) is the final step of the carbon capture and storage (CCS) technology. CCS consists of the separation of CO₂ from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere (IPCC 2005). For the sake of efficiency, CO₂ is stored at supercritical state ($P > 73.9$ bar, $T > 31.1^{\circ}\text{C}$) and not as gaseous phase. Possible target formations include deep saline aquifers, oil and gas fields (depleted or for enhanced recovery), and unminable coal beds (Fig. 2).

Since the main option for GCS in the Northern German Basin are saline aquifers, this report focuses on these kinds of CO₂ storage formations. Concerning GCS in deep saline aquifers, different trapping mechanisms can be defined (Fig. 3).

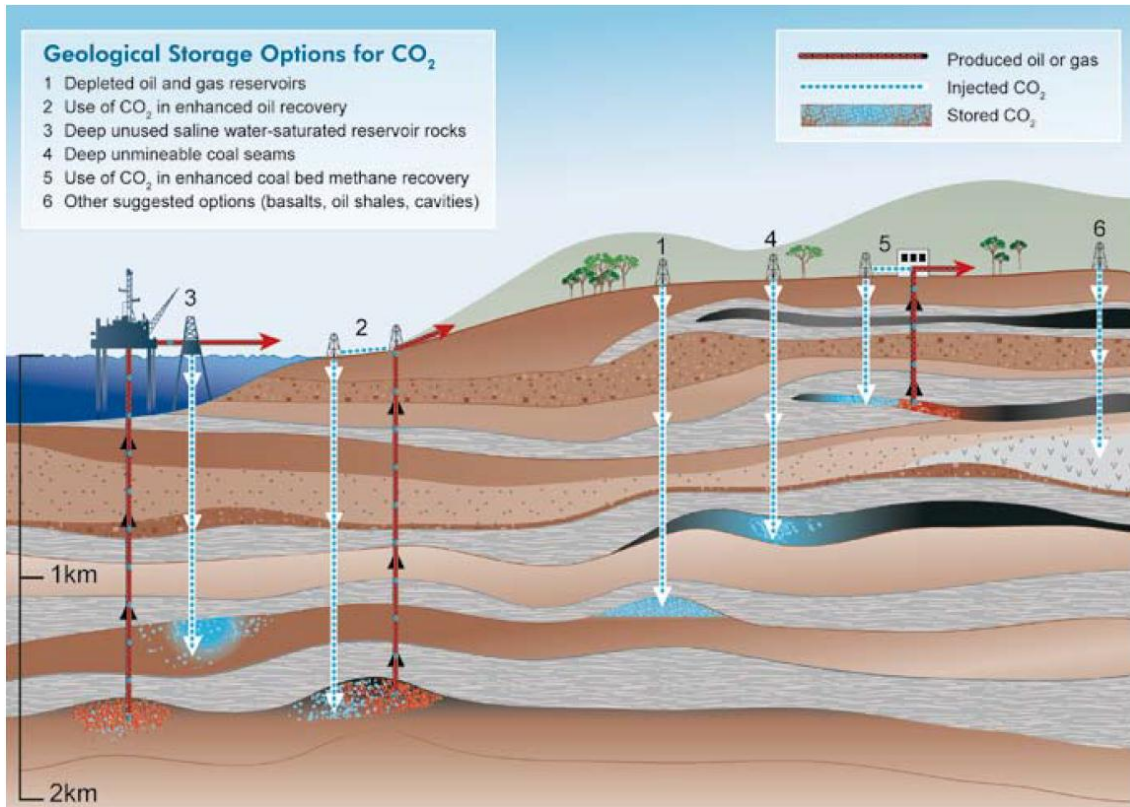


Fig. 2: Illustration of potential storage sites for GCS (IPCC 2005).

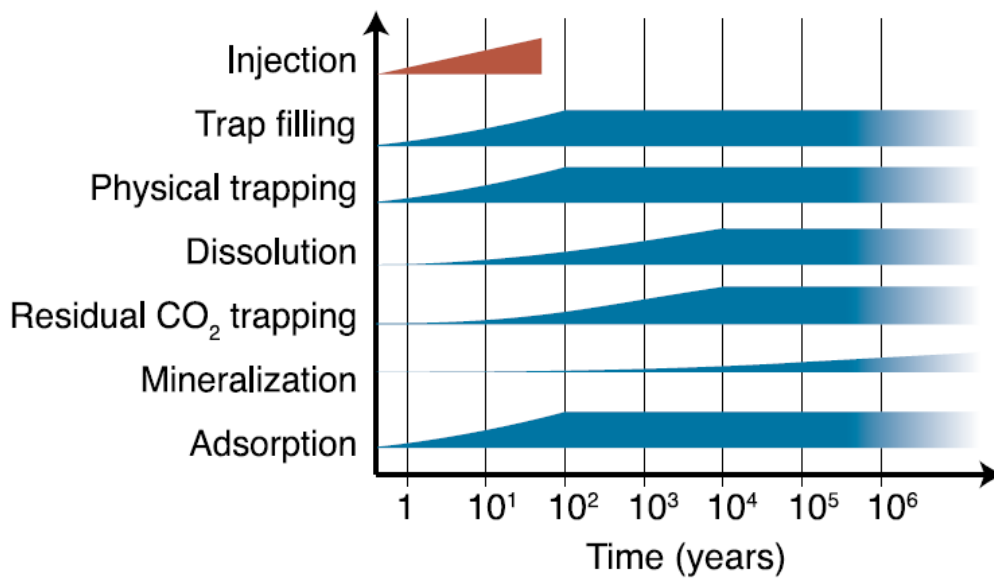


Fig. 3: Phases during CO₂ storage (IPCC 2005). The corresponding phases are marked in **bold** in the next paragraphs.

Phases during CO₂ storage and corresponding main trapping mechanisms

CO₂ is retained in geologic formations via three main mechanisms, namely physical or hydrodynamic trapping, solubility trapping and mineral trapping (Xu, Apps et al. 2004, Gombert and Thoraval 2010, CO₂CARE 2011).

Physical trapping and adsorption effects

Structural or stratigraphic trapping (**physical trapping**) refers to the storage of CO₂ under a low-permeability seal, which prevents it from upward migration (CO₂ has a lower density than saline waters). The difference between a structural and a stratigraphic trap is that in the first case the trap results from a folded or fractured rock formation and in the second one is the consequence of a change of rock type (IPCC 2005). Hydrodynamic trapping on the other hand can occur in saline formations that do not have a closed trap, but where fluids migrate very slowly over long distances. CO₂ is stored as a gas or supercritical fluid during this phase (Xu, Apps et al. 2004). This first trapping mechanism occurs during the first years to decades of storage after **injection** and **trap filling**, and is the most important method of retention in the short term and in the near well area (Farret, Gombert et al. 2010). In coal seams, the CO₂ fixation mechanism involves **adsorption** starting from the injection phase, and thus the storage in coal seams is distinctively different from that in oil and gas reservoirs and aquifers (IPCC 2005). This process depends on the permeability of the coal bed and on ends when the maximum adsorption capacity of the coal is reached, usually around 55-100 kg of CO₂ per ton of coal (Bachu 2007).

Dissolution or solubility trapping

CO₂ can dissolve into the groundwater (**dissolution phase**), a process referred to as a solubility trapping (Xu, Apps et al. 2004). The CO₂ solubility in formation water decreases as temperature and salinity increase. Dissolution is rapid when formation water and CO₂ share the same pore space, but dissolution outside the immediate contact zone is slow since it depends on diffusion as the transport mechanism (CO₂CARE 2011). Over longer time-spans, the increased density of the brine with dissolved CO₂ can create gravitational instability and may cause convection that mixes the different brines and further enhances dissolution. Dissolution trapping increases the acidity of the groundwater and the solubilities of many minerals of the host rock matrix (Xu, Apps et al. 2004). Several studies have concluded that dissolution processes could take up to 1,000-20,000 years, depending on the host rock properties, groundwater properties and anisotropy of the formation (Farret, Gombert et al. 2010, CO₂CARE 2011). In parallel to the dissolution phase, **residual CO₂ trapping** is caused by wettability and capillary effects in porous media (CO₂CARE 2011). CO₂ is trapped in small pores of the host formation and is durably immobilized during the natural equilibration phase after injection stop.

Mineral trapping

When CO₂ reacts directly or indirectly with the host formation minerals, it leads to the precipitation and **mineralization** of secondary carbonate minerals. This is the so-called "mineral trapping" phase, considered to be the safest form of geological CO₂ trapping (IPCC 2005). Mineral trapping is almost negligible during injection phase, and is a long process lasting for several centuries. Mineral trapping capacity can be comparable to that of solubility trapping, e.g. up to 7-10 kg of CO₂ per cubic meter of host formation according to numerical simulations (Xu, Apps et al. 2004, CO₂CARE 2011).

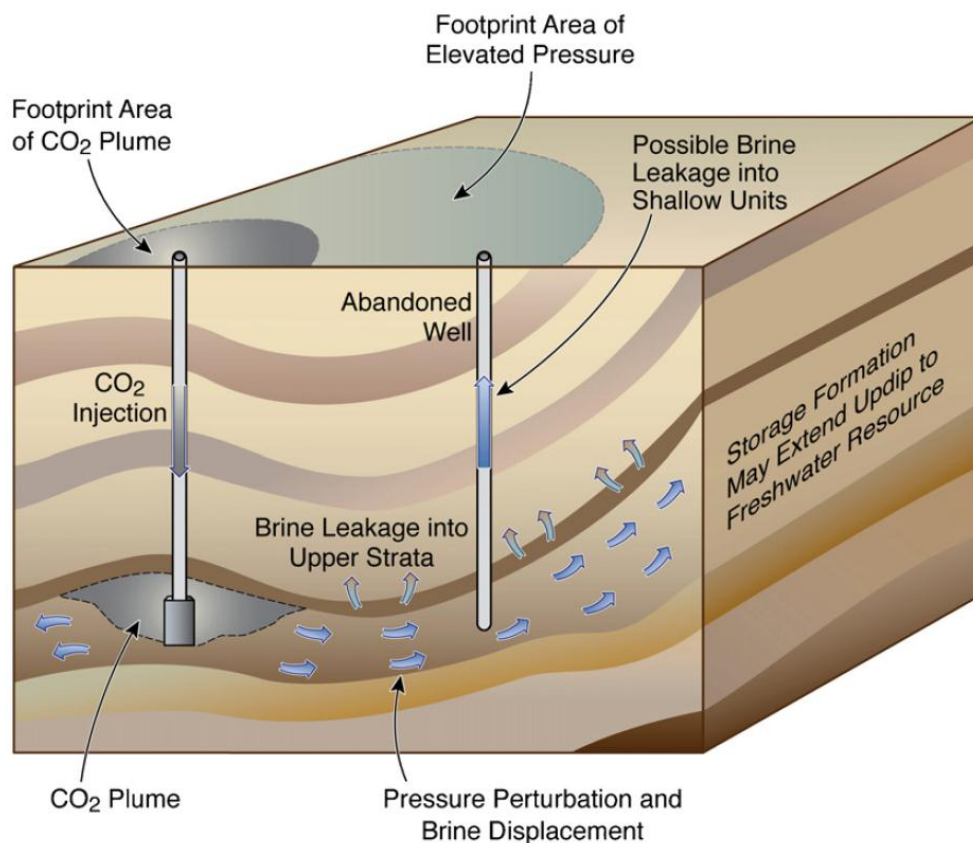
Spatial extent, pressures and relevant time scales

Concerning the spatial extent, one has to differentiate between the two major fluids of concern, namely CO₂ as a free phase and the formation waters in the deep aquifer.

CO₂ as a free phase will influence the subsurface within the boundaries of the reservoir and the surface footprint above. Although some authors refer to this kind of impact as "near-field impact" it does not necessarily mean that it is spatially close to the injection

site, as the footprint area of injected CO₂ might cover an area with a radial extent of several hundred meters around the actual injection site (Lemieux 2011).

Concerning pressure build-up due to CO₂ storage, the pressure regime of the deep aquifer and fluid dynamics might change even in great distances (basin-scale or far-field impacts) (Lemieux 2011). The difference between the footprint area of the CO₂ plume and the footprint area of elevated pressure is illustrated in Fig. 4 (Birkholzer, Zhou et al. 2009). Pressure build-up is site specific depending on various factors like injection rate, the permeability of the caprock, pore compressibility and the potential presence of other injection sites using the same host formation (Birkholzer, Zhou et al. 2009). Reported pressures range from 73 bar (Ketzin, pilot site, 650 m depth) to 270 bar (Alberta basin, 2814 m) and usually lie below calculated opening fracture pressures for extensional stress regime (Massat 2012).



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Fig. 4: Illustration of the footprint areas of CO₂ and pressure elevation (Birkholzer, Zhou et al. 2009).

Since the purpose of GCS is to store CO₂ over very long time scales (ten thousands of years), technical security as well as monitoring has to guarantee long-term safety.

Concerning the issue of pressure build-up, one has to differentiate between various phases of CO₂ storage. The formation pressure will increase during the injection phase of the system. As illustrated in Figure 3 the timescale of the injection phase lies within the range of decades (IPCC 2005). If storage capacities are reached and the injection is stopped, the pressure regime will head towards equilibrium. If geochemical trapping processes occur, the system develops towards a stable state (at higher or lower pressure level).

How long the respective phases last as well as predictions on pressure development in the reservoir over the centuries following injection are the result of complex geochemical and geophysical interactions and currently topic of extensive research. Under favorable

conditions pressure might decrease due to solubility and mineral trapping. The operating phase of GCS sites is estimated to be around 40-50 years, but rough estimates give a monitoring duration of at least 250-1,000 years (Gombert and Thoraval 2010).

2.3 Exploitation of unconventional gas resources

Process description and technical realization

In this report, the term “hydraulic fracturing” or “fracking” refers to the exploitation of unconventional oil and gas resources, although the technique finds application in other mining processes, including geothermal applications (e.g. the hot dry rock technique), too. Oil or gas reserves are considered unconventional when the oil or natural gas is tightly bound within the rock, so that without additional stimulation exploitation would not be possible.

For this kind of stimulation, fracking is used. Significant volumes of fracking fluids are injected into the borehole. The required volume of each stage in a multi-stage fracking process lies between 1,000 and 2,000 m³, and the entire volume of a multi-stage fracking operation between 9,000 and 29,000 m³ (Wood, Gilbert et al. 2011). For example, within the BGR GeneSys project close to Hannover 20,000 m³ of water were injected within five consecutive days to frack the foreseen area (Orzol, Jung et al. 2005).

Via the fluid a pressure is applied to the deep, gas or oil-containing rock formation, which exceeds the lithostatic pressure of the overlying layers as well as the compressive strength of the rock formation. In this manner, fractures are created through the shale or reservoir, and the contained oil or gas, which was tightly bound within the rock before, becomes accessible.

Due to the high lithostatic pressure the created fractures may close directly after the application of the externally applied pressure, depending on the host rock properties and the in-situ stress field. Therefore, the fracking fluid contains so-called proppants, mainly sand (AEA 2012). The sand particles remain inside the created fractures and prevent them from closing.

Moreover, fracking fluids contain diverse chemical additives which fulfill different purposes (De Lary, Fabriol et al. 2011, Wood, Gilbert et al. 2011):

- Gelling agents increase the viscosity of fracking fluids for better transport of proppants (sand),
- Cross-linkers increase the viscosity of polymer emulsions by polymer chain cross linking (also for better transport of proppants),
- Corrosion inhibitors aim at reducing the corrosion of the injection well due to the injected fluids,
- Friction reducers are used for low viscosity fracking fluids injected with high pumping rates to reduce frictions within the fluids,
- Acids are used for cleaning filters and the casing before the hydraulic fracturing and for dissolving minerals in the reservoir in the vicinity of the well,
- Foaming agents facilitate the transport and deposit of sand,
- Surfactants reduce the surface tension of fracking fluids,
- Clay stabilizers are injected in case of shale gas exploration to maintain clay permeability,

- pH-buffers stabilize the pH of fracking fluids,
- Biocides reduce bacterial growth.

Caused by the site specific characteristics, the exact composition of fracking fluids differs from borehole to borehole.

The whole process of unconventional gas exploitation may be subdivided into three phases, namely the drilling phase, the stimulation phase and the exploitation phase.

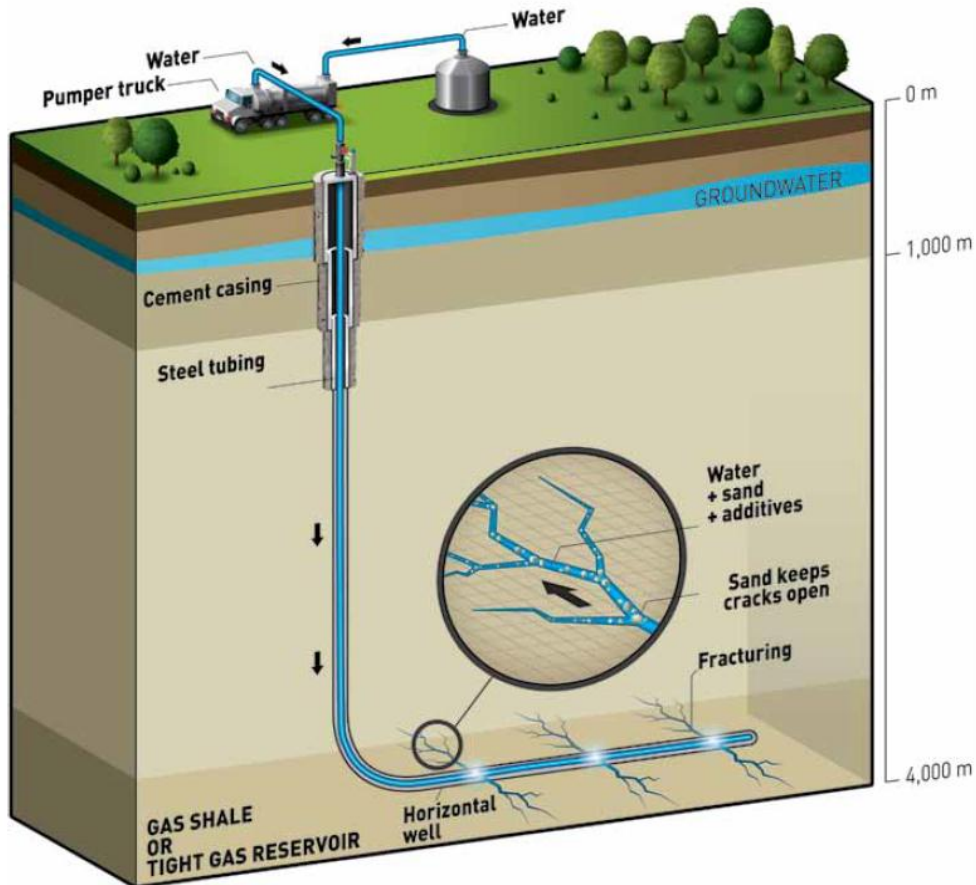


Fig. 5: Schematic illustration of hydraulic fracturing (Total 2011).

Spatial extent, pressures and relevant time scales

The surface area required by a single drilling site lies between 1 and 2 ha (Joseph and Magaud 2012). Due to horizontal drilling, the fracked area in the subsurface can have a spatial extent with a radius of 1-2 km (Neutraler Expertenkreis 2012) around the actual borehole. For the exploitation of a shale-gas containing formations often more than one borehole is drilled. In the United States a density of 3-4 wells per km² is common (Joseph and Magaud 2012).

The actual fracking process, meaning the pressure build-up to create fractures, lasts for several hours. Reported pressures were found to lie in the range of 600 bar for 4,700 m depth (deep geothermal system) (Tischner, Schindler et al. 2007). After the hydraulic fracturing operation pressure levels within the geological formation are highly elevated. The high pressure level is subsequently released leading to a rapid backflow of fluid consisting of the injected fracking fluid, formation waters and gases. The high flow-rate causes a rapid pressure decrease within the formation, leading in turn to a decrease in gas exploitation. In the first year, typical losses of productivity lie between 50-60 % of the

initial one and 40 % in the second year (Lechtenböhmer, Altmann et al. 2011). Thus, the lifetime of a fracked well is not expected to last for more than 3 to 10 years.

2.4 Geothermal systems operation

Process description and technical realization

In geothermal energy production the earth's heat is used for heating up water, which is subsequently used for energy production. Depending on the thermal gradient, it may be used for heating and cooling purposes or electricity may be generated (Lee 1996). The classification of geothermal systems differs internationally. In Germany a difference is made between shallow (<400 m) and deep geothermal systems (>400 m). Other classification systems, like the one used in the United States, are not based on the depth but on the temperature, referred to as low, medium and high enthalpy systems. In Germany, shallow systems generally only suit non-electrical uses (Sanyal 2005), like heating, cooling and storage of thermal energy. In the sector of private housing shallow systems find more and more application for heating purposes using small geothermal gradients (7-12°C) in combination with a heat pump in order to elevate the temperature to the required level. For the realization of such systems usually boreholes between 30 and 100 m depth are drilled (Töpfner and Fritzer 2005).

For the generation of electricity via deep geothermal systems one distinguishes between hydrothermal and petrothermal systems (Fig. 6) (Lee 1996). Hydrothermal systems may be realized at sites where a sufficiently hot deep aquifer is present. Usually, two boreholes are drilled (a "doublet"), one extraction well and one injection well, but more the one production well are also realized. The heat of the thermal water is transferred to a working fluid, which in turn is used to run a steam turbine for power generation. Turbines which use pure water as a working fluid require high temperature levels. Therefore, up to a temperature level of 200 °C ORC systems (Organic Ranking Cycles) are used for power generation, which use other working fluids like Butane or Pentane (Kummer 2010). Currently, such systems show comparably low energy conversion efficiencies (6 % at 100 °C, 13 % at 200 °C) (Bracke 2009). The Kalina process (realized at the geothermal power plant in Unterhaching, Germany), as an example for the generation of electricity from a hydro-geothermal source, uses a mixture of water and ammonia as a working fluid and requires a temperature > 90 °C. The technique promises increases of the energy conversion efficiency of 10 - 60 % in comparison to ORC systems.

In contrast, petrothermal systems do not require the presence of an aquifer. When constructing a petrothermal system, wells are drilled down to a sufficiently hot rock formation. To realize a circulation system in the absence of an aquifer, pathways have to be generated between the injection and the extraction wells by geological stimulation. One way of doing so is hydraulic fracturing, another one the use of acids. Such systems are also referred to as Enhanced Geothermal Systems or Engineered Geothermal Systems (EGS). Thus, during installation of deep geothermal systems, fracking fluids and acids may be involved (see Section 2.3).

The minimum requirements for an economically relevant use of geothermal power generation are presented in Table 1.

Table 1: Minimum requirements for economically relevant geothermal power generation (Bracke 2009).

Parameter	Value
Minimum rock temperature	100 °C
Maximum depth	7 km
Minimum production temperature	100 °C
Injection temperature (power generation only)	70 °C
Injection temperature (power generation with cogeneration)	50 °C
Injection temperature (power generation with cogeneration and heat pump)	30 °C
Minimum flow rate	50 m ³ /h
Maximum pressure difference	80 bar
Minimum permeability	2 mD

Due to the high salinity of the fluids from deep aquifers, the operation of deep geothermal systems is often challenging as a result of corrosion and scaling. It is reported that different chemicals are used, mainly for inhibiting corrosion and scaling (Swisher and Wright 1990, Fridriksson and Thórhallsson 2006):

- pH buffers, like sodium hydroxide,
- Scaling inhibitors like aqueous polyacrylate,
- Biocides, in general commercial solutions (mixture of different substances).

Like for the fracking fluids, the exact composition of additives for geothermal systems is site-specific.

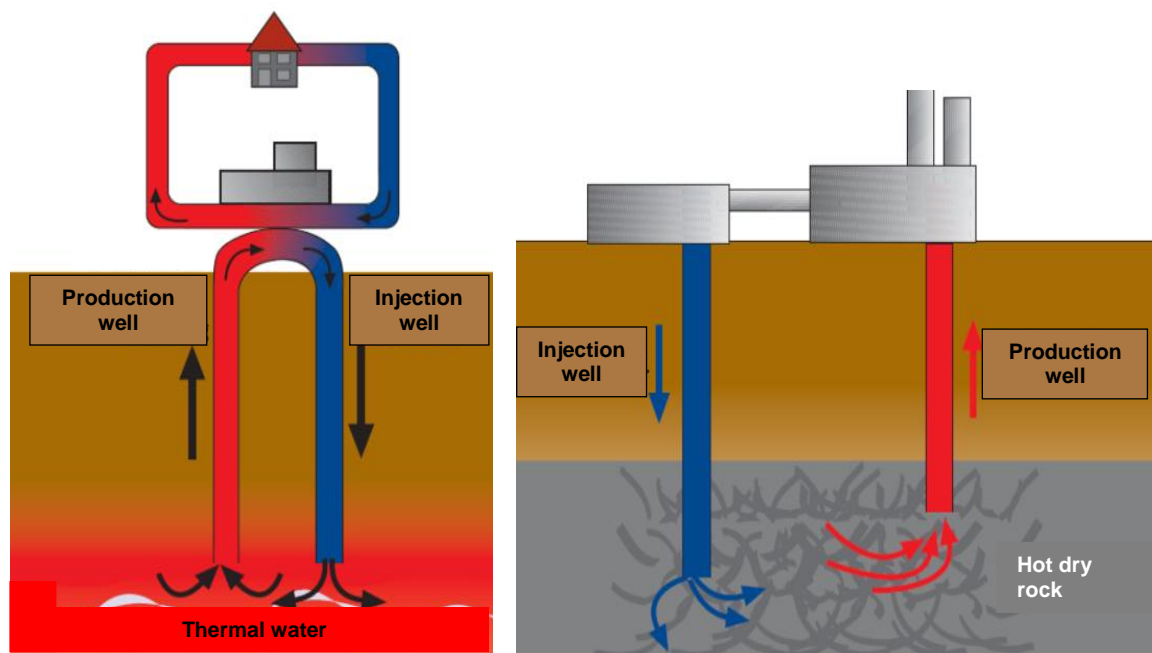


Fig. 6: Schematic illustration of hydrothermal (left) and petrothermal (right) geological power generation systems (adopted from (Bracke 2009))

Spatial extent, achieved pressures and relevant time scales

The spatial extension of deep geothermal systems (distance between the boreholes) lies between several hundred meters and up to 2 km (see Fig. 6) (Bußmann 2008).

As there are no additional fluids injected in order to run the actual circulation process significant pressure build-up within the formation is not expected. However, pressure has to be applied to run the circulation process. To be economically feasible, the pressure difference should not exceed 80 bar as the required pumping significantly influences the overall energy conversion efficiency (Paschen, Oertel et al. 2003).

The pay-back time for deep geothermal systems currently lies between 30 and 40 years (GFZ, personal correspondence). Thus, operation is planned to be at least 40 years.

Chapter 3

Inventory of hazards and hazardous events related to drinking water resources

At this stage of the COSMA project, no quantification of the potential impacts is done. Statements on probabilities will only be given as far as they could be found in literature. This catalogue focuses on providing an overview of potential hazardous events and hazards, the latter meaning chemical substances, which can lead to groundwater contamination and thus might have impacts on drinking water supplies.

3.1 Drilling

Against the background that all established and emerging subsurface activities are connected to drilling, here, focus is put on potential impacts of the activity “drilling” on shallow aquifers. The respective impacts depend of numerous factors like the local geological features, the technical realization of the drilling and the borehole or the depths of the drilling. Impacts on shallow aquifers can result from direct contamination (e.g. leakage of drilling fluids containing hydrocarbons, PAHs and heavy metals), either from the bore-hole itself, or from above-ground storage facilities.

Reported contaminations of aquifers by drilling mud include a wide variety of substances (Sumi 2006): During drilling of an oil / gas well a spring ¼ of a mile downstream an increased turbidity was observed. This was attributed to the mud consisting of bentonite gel, polymer, lime and crystalline silica (cristobalite, tridymite and quartz). At another site observations were made of elevated concentrations of calcium, chloride and total dissolved solids, and concentrations of chlorides that exceeded Colorado water quality standards. The Material Safety Data Sheet (MSDS) document the following additives used for the drilling suspension: ethoxylated nonylphenols, isopropanol, 2-bromo-2-nitropropane-1,3-diol, acrylamide, heavy aromatic petroleum naphtha, and dipropylene glycol monomethyl ether. Additionally, hydrochloric and hydrofluoric acids are used at various stages during the drilling process. As these additives were not measured in the groundwater, no information on their actual concentrations is available.

Impacts of drilling can additionally result from damaging local geological structures. Hydraulic short circuits might be created by the creation of passages and pathways between two under present conditions separated pathways. The drilling in unknown caverns, cavities or caves might make them collapse, impacting the hydrogeological flow regime. Moreover, drilling into gas reservoir or artesian aquifer may lead to blow-out events which might lead to local contamination around the drilling site, which might enter shallow aquifers.

It has to be mentioned that the named hazardous events can be avoided by thorough pre-investigation of the drilling site and a carefully conducted drilling operation. Nevertheless, in risk theory there is no level of zero risk, meaning that there will always be a level of residual risk > 0 . Thus, even if the probability of groundwater contamination of a single drilling is very small, the probability of “failure” increases with the actual number of drilling and boreholes and may exceed tolerable values. Consequently, when assessing a certain technique concerning its risk the number of drillings has to be considered. Shale-gas exploitation, for example, usually requires a higher number of boreholes (up to 3-4 per km²) than the exploitation of conventional natural gas reserves (related to a specific volume of exploited gas).

3.2 Geological CO₂ storage

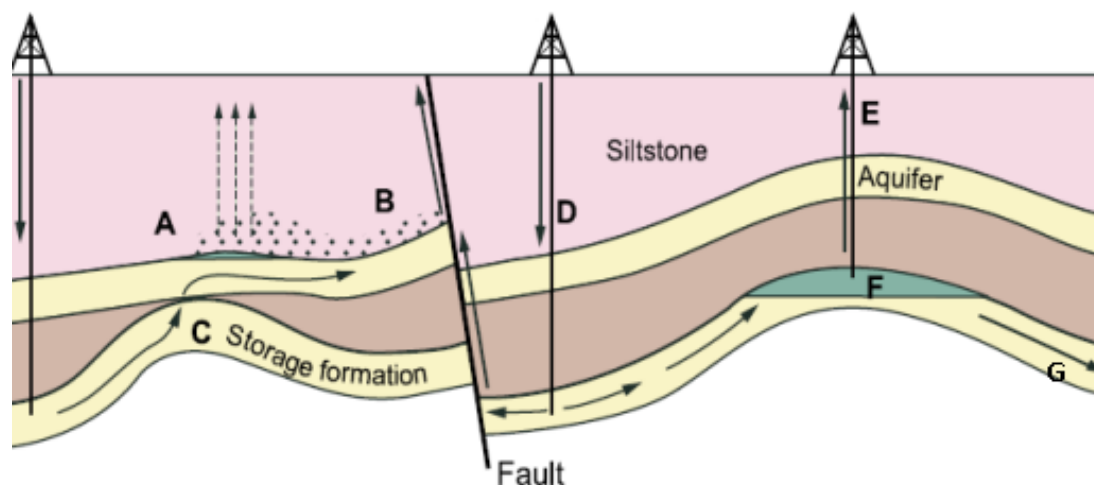
Generally, local and regional negative health or environmental effects due to geological CO₂ storage can be the result of:

- Elevated gas-phase CO₂ concentrations in the shallow subsurface and near-surface environment,
- Change of groundwater quality due to CO₂ intrusion,
- Effects resulting from brine displacement due to CO₂ injection (IPCC 2005).

Impacts resulting from elevated gas-phase concentrations of CO₂ in the near-surface environment (soil and surface) are not considered in this report. The focus lies on groundwater impacts. Thus, only CO₂ intrusion and the intrusion of deep saline groundwater (brine) are considered (IPCC 2005, Section 5.7). The following sections provide information on possible hazardous events leading to the intrusion of the named fluids as well as on the constituents within the respective fluids which pose a hazard to drinking water supply or indirectly trigger the presence of hazards.

Hazardous events of Geological CO₂ storage systems

CO₂ and/or brine intrusion might cause the presence of hazards in shallow aquifers. Lemieux (2011) names different possible pathways via which CO₂ and brine intrusion might take place, namely migration via active and abandoned wells, caprock failure and upward migration along faults and fractures (Lemieux 2011). **Fehler! Verweisquelle konnte nicht gefunden werden.** illustrates possible migration pathways/mechanisms for CO₂ out of the reservoir (IPCC 2005).



- A:** CO₂ gas pressure exceeds capillary pressure
- B:** Free CO₂ leaks from A into upper aquifer
- C:** CO₂ escapes through gap in cap rock into higher aquifer
- D:** Injected CO₂ migrates up dip, increases reservoir pressure and permeability of fault
- E:** CO₂ escapes via poorly plugged old abandoned well

Fig. 7: Possible migration pathways of CO₂ (IPCC 2005).

Abandoned and active wells

Active wells represent a continuous open circuit between the deep subsurface and the surface. During the construction of the borehole, engineered materials are introduced into the subsurface. The replacement of the originally present rock formation with anthropogenic designed materials may pose a migration pathway for injected CO₂ (IPCC 2005). Six different pathways via which CO₂ may migrate along active and abandoned wells were identified:

- Leakage between cement and the outside of the casing (Fig. 8, a)
- Leakage between cement and the inside of the metal casing (Fig. 8, b)
- Leakage within the cement plug itself (Fig. 8, c)
- Leakage through deterioration or corrosion of the metal casing (Fig. 8, d)
- Leakage through deterioration of the cement in the annulus (Fig. 8, e)
- Leakage in the annular region between the formation and the cement (Fig. 8, f)

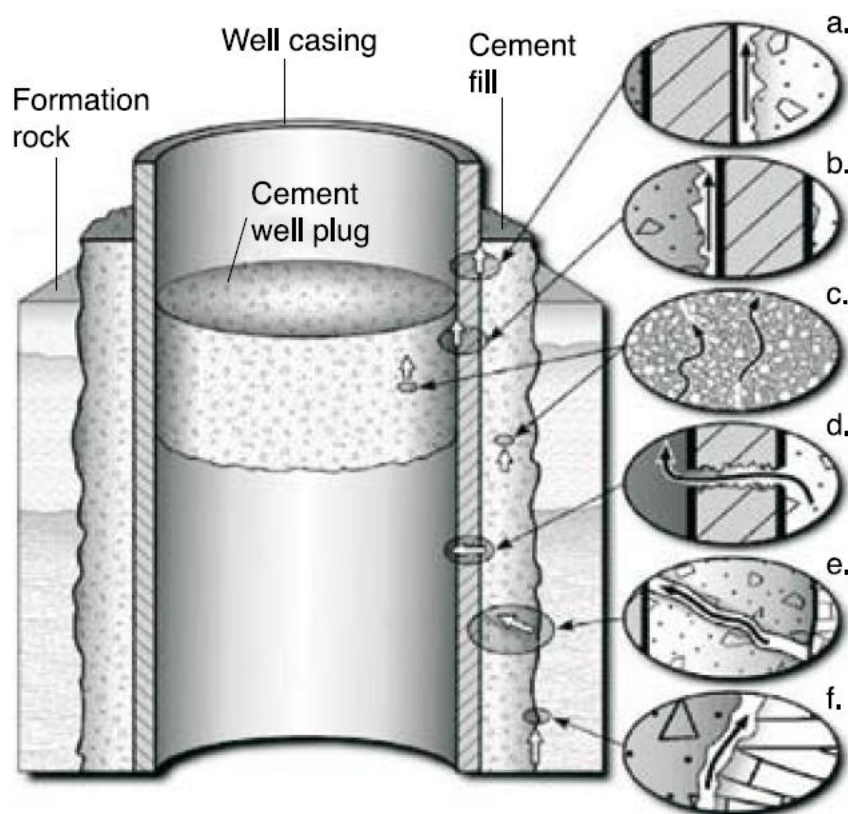


Fig. 8: Potential migration pathways of CO₂ along abandoned wells (IPCC 2005)

Caprock failure and migration along faults and fractures

Caprock failure as an migration pathway may result if the entry pressure of the injected CO₂ exceeds the capillary entry pressure of the low-permeable caprock (IPCC 2005). The capillary entry pressure is the pressure necessary for a fluid to enter the pores of a solid porous media. Migration through the caprock thereby becomes possible.

Moreover, open faults and fractures represent potential pathways between deep subsurface formations and the geological formations above. The presence of a completely open and continuous fault between the deep storage formation and shallow aquifers is unlikely but theoretically possible. For instance, in order to assess impacts resulting from hydraulic fracturing the presence of an open and continuous fault is used as a worst-case assumption (Neutraler Expertenkreis 2012).

Furthermore, in order to inject CO₂ in a deep porous formation the injection pressure has to exceed the pressure of the surrounding formation. A pressure increase of this kind potentially leads to deformations of the reservoir and/or the seal rock, which, in turn might trigger the opening of fractures or failure along a fault plane (IPCC 2005). Thus, new migration pathways might be created by CO₂ injection itself.

Furthermore, “*fault activation can, in principle, induce earthquakes large enough to cause damage*” (IPCC 2005, Section 5.7.4.4, l. 10-12). It is possible that induced seismicity might destabilize sub-surface formations like caverns, cavities or caves. The damage of these structures might have impacts on shallow aquifers, like hydraulic short circuits and might create additional fractures which again might serve as a migration pathway.

Probabilities of hazardous events

There is no long-term experience with CO₂ injection for the explicit purpose of storage. Statements on probabilities are thus based on numeric modeling as well as on experience from other closely-related systems, like Enhanced Oil recovery, engineered and natural gas storage sites or acid gas injection (IPCC 2005).

Concerning the probability of inducing seismic events, experiences from the storage of other gaseous and liquid fluids may be derived. This seems appropriate against the background that seismic events are primarily dependent on pressure perturbations rather than on the quality of the injected fluid (IPCC 2005). According to the IPCC the low numbers of reported cases in which seismic events have occurred due to deep-well injection of fluids (CO₂ for Enhanced Oil Recovery, brines, hazardous wastes etc.) indicate that the probability and thus the risk of induced seismicity associated to CO₂ injection is low (probabilities in terms of expected events per time scale are, however, not given).

Concerning the hazardous events leading to brine intrusion statements are based on the same experience as for induced seismicity. The IPCC report assesses the probability of brine intrusion as low. Again, the report does not give any information on the quantitative meaning of “low”. Within the COSMA project numeric modeling will focus on the probability of brine intrusion into shallow aquifers considering the geological features of the North Eastern German Basin.

Concerning the probability of CO₂ migrating out of the reservoir analytical and numerical models indicate that the fraction of the total amount of injected CO₂ migrating out of the reservoir within a 5000 years’ time period lies below 1.4%, with a mean value of 0.001%, even if the presence of abandoned wells is included in the assessment (IPCC 2005). Abandoned wells were identified of substantial relevance when assessing probabilities of CO₂ release from storage reservoirs (IPCC 2005).

Hazards

Hazards related to CO₂ intrusion

If CO₂ enters shallow aquifers it dissolves and forms carbonic acid and bicarbonate, which are not toxic and thus do not represent a hazard by themselves. However, depending on the local buffer capacity of the aquifer matrix (mainly induced by carbonate minerals) a drop of pH will result, which in turn triggers the mobilization of heavy metals (Scheffer and Schachtschabel 2002). In presence of carbonate minerals, field experiments have shown a drop from pH 7 to pH 5.6 after CO₂ injection (Karakha et al. 2010, cited in Lemieux 2011). Other theoretical considerations for the Paris Basin have predicted a drop in pH by 2.4 (Audigane et al. 2009, cited in Lemieux 2011). Values for unbuffered aquifers, like crystalline or volcanic rocks may reach values below pH 4 if we

suppose a possible CO₂ partial pressure between 0.9 bar (10 m depth) and 9 bar (100 m depth), according to (Carrol, Hao et al. 2009).

The heavy metals cadmium, mercury, lead, nickel, uranium, chromium and arsenic are toxic to humans and priority substances according to the Water Framework Directive. Limit values for heavy metals of the German Drinking Water Directive of presented in Table 4. The metals zinc, manganese, iron and copper are less relevant concerning toxic effects on humans, although copper might be relevant for small children (German Drinking Water Directive value: 2 mg/L).

Cadmium shows high toxicity and the highest mobility of all heavy metals. Mobility already occurs at pH levels below 6.5 (Scheffer and Schachtschabel 2002). For comparison, a pure saturated CO₂ solution will exhibit a pH level of 4.2 (Stumm and Morgan 1996). CO₂ intrusion thus triggers the presence of health related hazards (Siirila, Navarre-Sitchler et al. 2012).

Moreover, CO₂ from power plants is not pure. In aqueous solution impurities of SO₂ and NO_x injected with the captured CO₂ form sulfuric and nitric acid, respectively. Both compounds are far stronger acids than carbonic acid and enhance soil acidification ($pK_a(\text{HNO}_3) = -1.4$, $pK_{a1}(\text{H}_2\text{SO}_4) = -3$, $pK_{a2}(\text{HSO}_4^-) = 1.9$, $pK_{a1}(\text{H}_2\text{CO}_3^*) = 6.3$, $pK_{a2}(\text{HCO}_3^-) = 10.3$) (Stumm and Morgan 1996, IPCC 2005, Jacquemet, Picot-Colbeaux et al. 2010) Jacquemet et al. (2010) calculated a pH shift due to SO₂ and NO impurities of 1 pH unit lower in comparison to pure CO₂. Depending on the kind of fuel used for power generation and the technique used for CO₂ capture different kinds and amounts of impurities may be present in the CO₂ stream (see Appendix 1).

Hazards related to brine intrusion

Brine intrusion from pressure build-up in deep saline aquifers will usually first affect the aquifer in the vicinity of the storage formation. For the Northern German sedimentary basin, multiple different saline aquifers occur in vertical direction between the favoured storage formation "Middle Bunter" and Quarternary freshwater aquifers. Accordingly, the brine which is displaced into the freshwater aquifers will originate most probably from the uppermost saline aquifer (Großmann, Naue et al. 2011). However, this hypothesis is questioned by GCS experts, who postulate that discrete channels in transmissive faults may allow for leakage from deepest saline aquifer directly into a freshwater aquifer without communicating with intermediate aquifers (pers. communication T. Kempka 2012).

The composition of brines and thus the presence and quantity of health-related hazards mainly depends on the composition of the host formation. In the Northern German Basin deep aquifers are highly mineralized. For the purpose of illustration, Table 2 shows typical ion concentrations of Berlin freshwater (from shallow aquifers), seawater and of the aquifer, which is used for GCS at the Ketzin pilot site for CO₂ storage Table 2 (Stuttgart formation) as well as the European limit values for drinking water. The comparably high ion concentrations of the deep groundwater illustrate the high potential of exceeding tolerable salt concentrations concerning drinking water supply in the case of brine intrusion.

Brine intrusion is common in the Northern German sedimentary basin, often related to groundwater abstraction in the vicinity of natural pathways between the deep saline aquifers and the shallow freshwater aquifers. Reported hazards are, however, limited to elevated salt concentrations (e.g. chloride). In Brandenburg, the Federal State around Berlin, specific monitoring is being carried out by the environmental authorities as early warning for saline intrusion in order to act accordingly (e.g. by reducing water abstraction rates) (Hannappel & Hermsdorf 2009). An overview of the current situation in Berlin will be provided in D 2.1 of COSMA-1.

Table 2: Comparison of average ion concentrations and physico-chemical parameters of Berlin freshwater, deep brine in the Stuttgart formation and seawater (Seibt and Wolframm 2003, KWB 2009, Würdemann, Möller et al. 2010).

Parameter	Unit	Berlin freshwater	Brine Stuttgart formation	Seawater	Limit value (EU 2002)
Ba	mg/L	-	0,068	-	0.3
Br	mg/L	-	42	65,0	0.01
Ca	mg/L	98,2	2092	401	
Cl	mg/L	65	134000	18789	250
Fe	mg/L	0,25	7,4	-	0.2
HCO ₃ ⁻	mg/L	196	88	138	
K	mg/L	8,2	412	376	12
Li	mg/L	-	1,8	-	
Mg	mg/L	10,8	814	1256	50
Mn	mg/L	0,31	1,4	-	0.05
Na	mg/L	41,9	87400	10447	200
NH ₄	mg/L	1,4	18,3	-	250
O ₂	mg/L	0,3	-	-	
SO ₄	mg/L	138	3893	2633	
Sr	mg/L		47,9	7,8	
T	°C	11,5	35	-	
pH	-	7,4	6,7	7,5-8,4	6.5-8.5
Density	kg/L	1	1,148	1,03	
Ionic strength	mol/L	0,01	3,4	0,7	

3.3 Hydraulic fracturing

This chapter focuses on hazards and hazardous events for groundwater resources during fracking for the purpose of exploitation of unconventional gas reserves. Other environmental effects like land use or global warming potential via methane emissions were not considered.

Hazardous events of hydraulic fracturing

During shale gas exploitation hazardous events concerning groundwater contamination may occur during drilling, stimulation and exploitation. Moreover, hazard intrusion which cannot be attributed to any of these specific technical steps might occur, like upward migration of natural gas or during the treatment/disposal of wastewater.

Therefore, one of the most recent studies (Neutraler Expertenkreis 2012) concerning the issue of groundwater contamination via fracking, elaborated under the leadership of the Helmholtz Centre for Environmental Research (UFZ) in Germany subdivided potential risks into "risks in the geological system" and "risks in the technical system". The study is based on information provided by Exxon Mobil, who also financed the study. Thus, the experience the named company gathered during fracking operations in the United States, where hydraulic fracturing is already a widely spread technique for the exploitation of unconventional gas reserves, is included within the study. Fig. 9 gives an overview of hazardous events during fracking the study investigated.

As general conclusions the study states that technical risks are more relevant than the risks resulting from the geological system (Farret, Gombert et al. 2010, Neutraler Expertenkreis 2012). The risks concerning the *technical systems* strongly depend on the

reliability of the different technical components, the quality of construction as well as on quality management and human factors. Possible hazardous events include (De Lary, Fabriol et al. 2011, Neutraler Expertenkreis 2012):

- *Traffic accidents during the transport of chemicals:* for the stimulation process high quantities of chemical additives are needed. Via accidents during transport to the drilling site surface or groundwater contamination may occur,
- *Borehole and pipeline leakages:* Depending on the location and the operation phase either fracking fluid, flowback or natural gas may contaminate shallow groundwater,
- *Blow-outs:* if gas reservoirs are encountered during the drilling phase an eruptive spill of drilling fluids and gas might contaminate the area around the drilling site and thus underlying aquifers,
- *Accidents during the storage of chemical additives:* In preparation to the stimulation process the chemical additives are to be stored at the drilling site. Accidental leakages may migrate into groundwater,
- *Unexpected events like airplane crashes or sabotage* may indirectly lead to groundwater contamination by destroying or damaging the existing infrastructure and security measures.

Concerning the geological system, the following hazardous events were derived (Neutraler Expertenkreis 2012):

- *Upward migration of fracking fluids:* fracking fluids might migrate upward along faults and fractures and contaminate shallow aquifers,
- *Fracking fluid in deep groundwater:* Fracking fluids might migrate further with deep groundwater if the created/existing fractures or faults enable a hydraulic connection,
- *Upward migration of methane:* geological faults can function as pathways for methane which was trapped within the shale formation before.

During the investigation of risks concerning the respective pathways in the geological system the scientists followed a scenario-based deterministic approach (Neutraler Expertenkreis 2012) in order to derive statements on the probability of the respective hazardous events. The following conclusions on probabilities were derived.

Migration of fracking additives within the deep groundwater: possible under unfavorable conditions, namely:

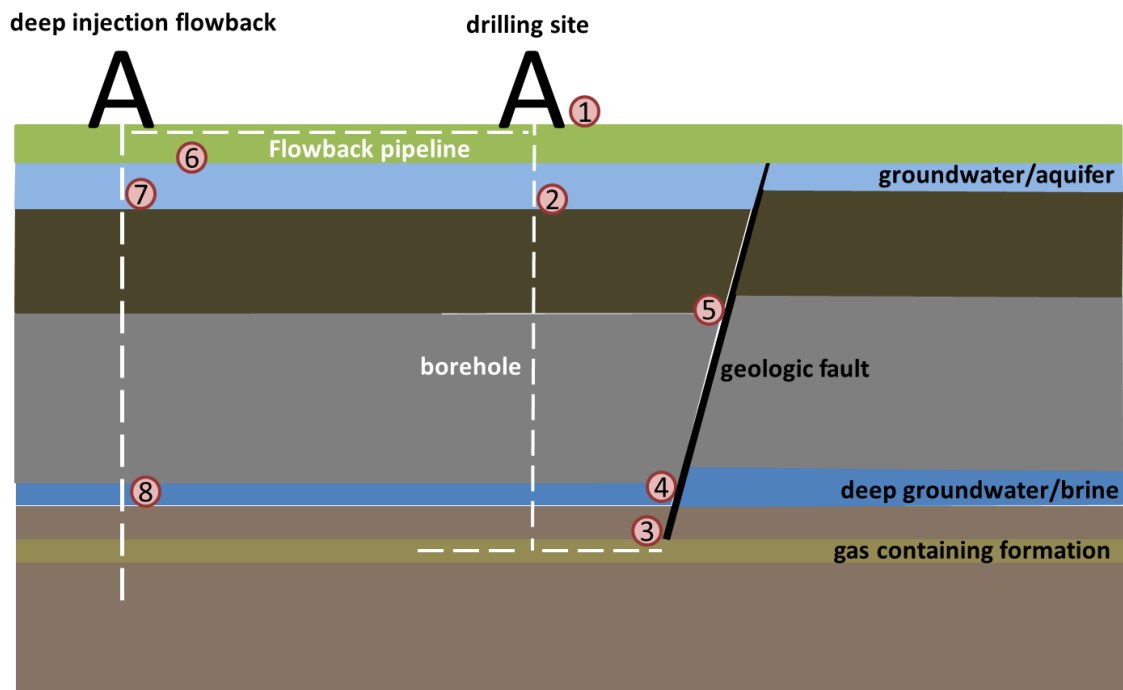
- Fractures propagate beyond expected dimensions

Upward migration of natural gas: possible under very unfavorable conditions namely:

- Presence of a continuous open fault and
- Fractures propagate beyond expected dimensions

Upward migration of fracking additives: theoretically possible, but just under extremely unfavorable conditions, namely:

- Presence of an artesian aquifer and
- Presence of a continuous open fault and
- Fractures propagate beyond expected dimensions



- | | |
|---|--|
| 1 | Spillage of chemicals at the drilling site |
| 2 | Leakage borehole |
| 3 | Upward migration of fracking fluid |
| 4 | Fracking fluid in deep groundwater |
| 5 | Upward migration of methane |
| 6 | Leakage flowback pipeline |
| 7 | Leakage borehole |
| 8 | Upward migration of flowback |

Fig. 9: Illustration of potential hazardous events concerning hydraulic fracturing adapted from (Neutraler Expertenkreis 2012).

Hazards related to hydraulic fracturing

During the fracking process different relevant fluids have to be distinguished, namely, the fracking fluid, the deep formation waters and the so-called flowback.

As mentioned in the previous chapter the exact composition of the fracking fluid differs from borehole to borehole. While fracking fluids during the 1990s contained fractions of chemical additives of up to 15%, the fraction of chemical additives of current fracking fluids lies between 1 and 5% (Ewers, Frimmel et al. 2012).

The percentage of toxic chemical additives related to the overall volume of fracking fluid lies below 1%. Table 3 lists exemplarily the chemical substances of three recent fracking operations in Germany, which are classified as toxic (Ewers, Frimmel et al. 2012). A list of all chemical additives used for fracking operations so far by Exxon Mobil is provided in the appendix of this report.

Formation water is water which is present in the subsurface in its natural composition. It may be freely circulating or adhesively bound within the pore-structure. As the fluid is exposed to high temperatures and pressure over long time scales, it is usually highly mineralized (Neutraler Expertenkreis 2012, Gutachten zur Abwasserentsorgung). Its composition depends on the composition of the host formation and may contain:

- High concentrations of heavy metals
- Hydrocarbons including benzene
- Radionuclides
- High salt concentrations

Concerning shale gas exploitation formation waters are mostly adhesively bound in the pore structure. Maximum values of the chemical components of the formation water present at the drilling site Hegstlage in Germany is given exemplarily in Table 4 (neutraler Expertenkreis 2012, Gutachten zur Abwasserentsorgung).

The term flowback defines the fluid which surfaces after a fracking operation. It is a mixture of the fracking fluid and formation waters. Moreover, substances which were formed by chemical reaction among additives or between additives and formation water constituents as well as dissolved substances originating from the host formation may be present in the flowback.

Table 3: List of toxic chemical additives used for fracking operations in recent years in Germany: concentrations in fracking fluids as well as limit values (Ewers, Frimmel et al. 2012) according to different guidelines.

Substance	Use	Concentration (mg/L)	Limit value (mg/L)
Propan-2-ol	Solvent	141 – 184	8.4 (LW)
Sodium Bromate	Breaker	258 – 410	0.01 (TrinkwV)
Disodium tetraborate, anhydrous		55	1 (TrinkwV)
Tetra-ethylene-pentamin	Stabilizer	173 – 736	0.0003 (GOW)
5-Chloro-Methyl-2H-Isothiazol-3-One, 2-Methyl-2H-Isothiazol-3-One (3:1) Kathon	Biocide	3.6-5.5	0.0001 (TrinkwV)
Zirconium dichloride oxide	Gelling agent	55	0.0003 (GOW)
Citric terpenes	Gelling agent	184	0.0003 (GOW)
Glycoether	surfactant	184	
2-Butoxyethanol	Solvent	4729 – 5440	0.35 (LW)
Amphoteric alkyl-amines	surfactant	193	0.0003 (GOW)
Methanol	Solvent	705	1.75 (LW)
Inorganic Borates		25	1 (TrinkwV)
Acetic acid	Stabilizer	162	
Sodium hydroxide	pH regulator	41	
Tetramethylammonium chloride		502 – 711	0.0003 (GOW)
Distillates (petroleum), hydrotreated light	Friction reducer	208	0.0001 (GOW)
TrinkwV:	Limit value according to German drinking water directive		
GOW:	Health based precautionary value according to the German Federal Environmental Agency		
LW:	Health-based value based on threshold concentration of health impacts		

Table 2 points out that in order to be in accordance with the limit values for drinking water dilutions of fracking fluids of 1:10,000-1:100,000 are necessary. It has to be

mentioned that the GOW values are precautionary values for substances for which health-based limit values based on toxicological investigation have not been derived, yet, or for substances for which an assessment is not or just partly possible (Umweltbundesamt 2003).

In the past few years operators of fracking sites have taken measures to replace additives by less toxic and better biodegradable compounds (Neutraler Expertenkreis 2012). Thus, the toxicological impact is expected to decrease.

Table 4 illustrates the potential of groundwater contamination if flowback or formation water enters shallow aquifers. In addition to the substances in Table 4 formation waters and thus the flowback may contain radionuclides. In the Northern German Basin the radioactive activity of formation waters lies between 2 and 100 Bq/L (Degering, Köhler 2009). At the location Neustadt-Glewe (North-Eastern Germany) the main isotopes are ^{40}K , ^{226}Ra , ^{228}Ra , ^{224}Ra and ^{210}Pb (Degering, Köhler 2009). The guideline value for drinking water is given with 100 Bq/L (Tritium) (TrinkwV 2011). Flowbacks thus represent a major challenge and need to be carefully treated in dedicated treatment plants, in general using high-end treatment processes, or disposed of properly possibly by a controlled re-injection (De Lary, Fabriol et al. 2011). This re-injection however exposes shallow aquifers to significant hazards if the borehole sealing is imperfect.

Table 4: Chemical composition of the formation water at the drilling site Hegstlage. The given values are the maximum values out of ten measurements (Neutraler Expertenkreis, Gutachten zur Abwasserentsorgung 2012)

Parameter	Unit	Maximum value	Limit value (TrinkwV)
PAH (total)	µg/L	368.8	0.1
BTEX (total)	µg/L	26150	1 (benzene)
Antimony	µg/L	5	5
Arsenic	µg/L	73	10
Barium	mg/L	10.2	
Benzene	µg/L	10900	1
Lead	µg/L	4450	10
Cadmium	µg/L	215	5
Calcium	mg/L	19800	
Chloride	mg/L	167200	250
Chromium (total)	µg/L	50	50
Chromate	µg/L	100	
Cyanide (total)	µg/L	10	50
Cyanide (purgeable)	µg/L	10	
Iron	mg/L	84	0.2
Fluoride	µg/L	1530	1500
Bicarbonate	mg/L	158	
Potassium	mg/L	2370	
Cobalt	µg/L	50	
Copper	µg/L	575	2000
Lithium	mg/L	22.5	
Magnesium	mg/L	1100	
Molybdenum	µg/L	50	
Naphthalene	µg/L	250	
Sodium	mg/L	65900	200
Nickel	µg/L	25	20
Mercury	µg/L	55	1
Selenium	µg/L	5	10
Strontium	mg/L	1250	
Sulphate	mg/L	915	240
Zinc	µg/L	218000	

3.4 Geothermal systems operation

Like for any other drilling activity risks result if naturally separated aquifers are connected via drilling or gas reservoirs are encountered (see Section 3.1). Against the background that shallow, low-enthalpy geothermal systems find more and more application also on the level of private housing the overall number of such systems makes these kinds of impacts become more relevant. Moreover, poorly engineered, “cheap” drillings conducted by uncertified companies are reality. A detailed description of impact resulting from low-enthalpy systems will be provided in deliverable D 1.2, which deals with both kinds of geothermal systems. This report concentrates on high-enthalpy (“deep”) geothermal systems.

Hazardous events of deep geothermal systems operation

If the deep geothermal system is stimulated by hydraulic fracturing, hazardous events are comparable those of unconventional gas exploitation (see Section 3.3) except for methane intrusion. However, due to lower applied pressures, less drillings at one location and shorter or missing horizontal extensions, the probability for hazardous events might be lower.

Hot thermal water (high salinity, high temperature) exhibits a high corrosion potential, which increases the probability of casing failures (Fig. 10). Specific to deep geothermal systems might be the creation of fractures and reactivation of faults due to induced seismicity, especially if hydraulic fracturing is used for stimulation. This is due to the fact that areas suitable for geothermal energy production are often found in areas of increased seismic activity, like the German "Oberrheingraben" due to the steeper geothermal gradient. Therefore, the probability of inducing seismic events due to stimulation operation increases in comparison to GCS or shale gas exploration systems. Induced seismicity in turn might create fractures or destabilize present geological formation like caves and caverns, thus potentially creating hydraulic short circuits or new pathways for formation waters.

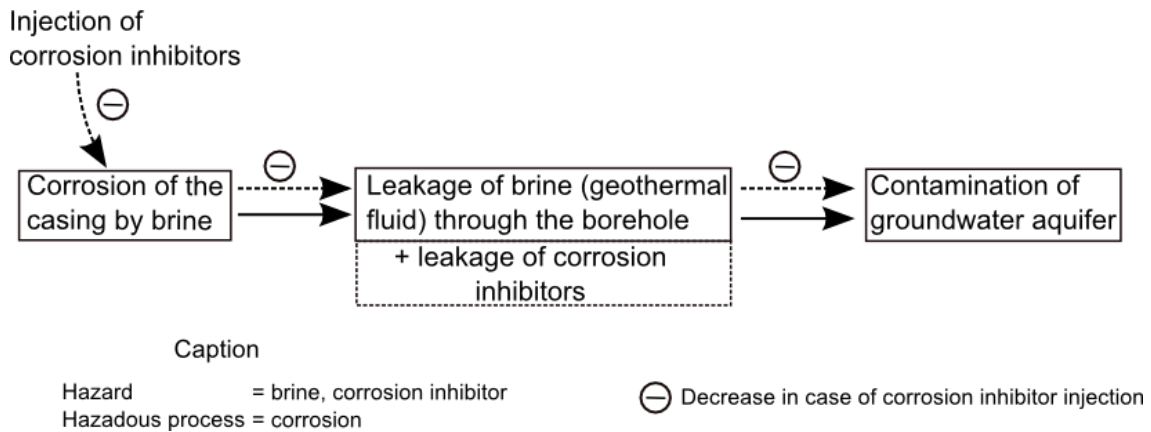


Fig. 10: Fault-tree of hazard release due to corrosion of casing.

Hazards related to deep geothermal systems

As already mentioned in Section 3.2 the composition of deep groundwater depends on the composition of the host formation. For detailed examples of formation water constituent see Sections 3.2 and 3.3. A detailed description of chemical additives within working fluids of deep geological fluids was not found. However, within the GeneSys project (deep geothermal operation) pure water, without chemical additives, was used for hydraulic fracturing (Orzol et al. 2005). A similar case study for shale gas exploitation could not be found. Thus, the quantity of relevant hazards might be lower for geothermal power generation as for shale gas exploitation.

Chapter 4 Summary and Conclusions

The report points out that there are various ways in which emerging subsurface activities might impact shallow aquifers potentially used for drinking water supply. Table 5 summarizes major features of the investigated subsurface activities.

Table 5: Overview of major characteristics related to the different subsurface activities.

	GCS	Fracking	Shallow geothermal systems	Deep geothermal systems
Timescale (years)	>10,000	3-10 (exploitation per frac)	Decades	>30-40
Density of wells	+	++	+++	+
Depth [m]	>800	Several km	<400 mostly 30-100	600-7000
Pressure	> 80 bar $P_{\text{hydrostatic}} < P_{\text{injection}} < P_{\text{fracturing}}$	$P_{\text{fracturing}} < P_{\text{injection}}$		
Major sources of uncertainty	Time scale, long-term reservoir stabilisation	Prediction of fracture dimensions	Quantity of wells	Corrosion

Concerning the timescales, hydraulic fracturing as well as deep and shallow geothermal systems are built for time scales of years and decades, respectively. In contrast, after the injection phase and well abandonment (after 30-50 years) the purpose of GCS is the long term storage of CO₂. A minimum timescale of 10,000 years is named in Table 5 but the overall intension of GCS has to be the permanent storage of carbon dioxide.

The risk of technical failure increases proportionally with the number of drilled wells. Concerning the well density, hydraulic fracturing and shallow geothermal systems are expected to be of most relevance. While shallow geothermal operations should be mostly found in densely populated regions, hydraulic fracturing is more expected to take place in rural areas. Deep geothermal systems are currently of minor importance in central and Western Europe, and the number of wells is currently very limited. The number of required wells for GCS systems is hard to estimate because of the uncertainties on present capacities and of the amount of CO₂ necessary to be stored to have an actual impact on overall CO₂ emissions.

Pressure build-up in the subsurface is especially relevant for GCS and fracking operations. For GCS, a minimum pressure of 80 bar is desirable, because CO₂ is in its supercritical state at this pressure level (T = 31.1°C), and thus the storage efficiency is relatively high. The pressure build-up in the storage formation should not exceed the fracturing pressure of the storage formation and its caprock, in order not to create fractures. Since the purpose of hydraulic fracturing is the creation of fractures, here, the fluid injection pressure has to exceed the fracturing pressure. Since geothermal systems involve fluid circulation, pressure build-up should not be a major issue for this activity, as long as there is no stimulation involved.

Full scale experience is available for all kinds of subsurface activities, but with limited return of experience compared to geological time scales. Currently, any long-term prediction on the behaviour and the capacity or the security of GCS systems are based on numerical modeling and natural and engineered analogues. Although there are plenty of applications from which information on GCS systems can be derived, none of them

covers the timescales relevant for GCS systems. This is also the major source of uncertainty concerning geological CO₂ storage. Against the background of the relevant timescales especially geochemical numerical models can hardly be validated.

Table 6 gives a summary of the reported hazards related to the different subsurface activities. The drilling process is associated with all the regarded subsurface activities although to a different extent. The risk related to leakage of the drilling fluids is elevated for fracking (for shale gas exploration) and shallow geothermal systems due to the high number of drillings associated with them. The drilling fluids may contain hazardous substances like nonylphenols or acrylamide – however, there is little information available on the extent, to which drilling have contaminated freshwater aquifers so far.

Table 6: Summary of hazards potentially resulting from emerging subsurface activities.

Hazard (potentially affecting drinking water resources)	Resulting from			
	GCS	Fracking for shale gas exploration	Geothermal systems shallow	Geothermal systems deep
Drilling fluids	+	++ (high number of boreholes)	++ (high number of boreholes)	+
Brine / formation water	+	+		+
CO ₂ – mobilization of heavy metals	+			
Additives		++ (fracking fluids)	(+)	+ (corrosion inhibitors, anti-scalants)
CH ₄	+	++		(+)

Hazards present in brine or formation water are salts, heavy metals, radionuclides and natural organic contaminants like hydrocarbons and BTEX compounds. Their occurrence and potential mobilization has only been associated to deep subsurface activities like GCS, unconventional shale gas exploration or deep geothermal systems. Shallow geothermal systems usually remain within the zone of freshwater aquifers, at least for the Northern German Sedimentary Basin. Brine or formation water will be mobilized by pressure increase in the subsurface or it is released to the surface environment from flowback (fracking > deep geothermal systems). The pathways can be improperly sealed production wells, abandoned wells without proper sealing or faults open for fluid flow. Among these, abandoned wells have been identified to represent the most probable pathway, but in any case, information on actual contamination is lacking and only theoretical studies are available.

CO₂ intrusion due to GCS might mobilize heavy metals within the aquifer matrix, of which cadmium, mercury, lead, nickel, uranium, chromium and arsenic are toxic to humans and priority substances according to the Water Framework Directive. Impurities of NO_x and SO₂ may enhance this effect. For the other investigated subsurface activities CO₂ intrusion is not expected.

Additives like formaldehyde or nonylphenol may be present in fracking fluids and thus represent a hazard associated with unconventional shale gas exploration. A contamination of drinking water resources has been reported to be possible and a

relevant risk – primarily from above ground handling of these substances (Neutraler Expertenkreis 2012). Stimulation of deep geothermal systems has not been found to include hazardous substances, whereas additives like corrosion inhibitors or anti-scalants are used during operation and might leak into drinking water aquifers. To a lesser extent, additives in shallow geothermal systems (anti-frost additives for instance) may also leak and contaminate the aquifer under unfavourable conditions (e.g. deterioration of the borehole or geothermal probe).

The mobilization of methane is the aim of unconventional shale gas exploration and has been shown also to potentially impact freshwater aquifers (Neutraler Expertenkreis 2012). Methane may also be present in geological formations encountered during GCS or deep geothermal systems in concentrations of up to 14 % (Seibt and Wolfgramm 2003). Its mobilization might therefore also be an issue for these subsurface activities.

Concerning the probabilities of the respective hazardous events of CO₂ intrusion and brine displacement, current estimates and assessments rely on numerical models as well as on natural analogues and closely-related engineered systems like natural gas storage or Enhanced Oil Recovery. So far, referring to the IPCC report on CCS in 2005, against the background of existing security standards and technical experience, risks resulting from GCS are considered manageable or low, respectively. Nevertheless, the behaviour of a storage formation always depends on the site-specific geological boundary conditions as well as on technical features of the injection process. Thus, coupling of shallow and deep hydrogeological models will be carried out within the COSMA-project to derive first conclusions on likelihoods considering aquifer systems in the Northern German Sedimentary Basin and to develop an assessment method transferable to other study areas. In this model faults are determined as the major leakage pathway and are especially investigated.

During the operation of hydraulic fracturing (for shale gas exploration as well as EGS systems) hazards may enter shallow aquifers via various pathways and may be of different origins. Specially designed chemical additives present in fracking fluids as well as the partially toxic constituents within formation waters might enter shallow aquifers both via technical failure or accidents and upward migration within the geological system. Moreover, the upward migration of natural gas to aquifers due to hydraulic fracturing still concerns the public as well as water suppliers. Recent scientific studies, conducted at the Helmholtz Centre for Environmental Research assessed the technical risks and risks concerning the geological system resulting from hydraulic fracturing to be manageable or low, respectively (Neutraler Expertenkreis 2012).

Concerning geothermal systems, the simple quantity of shallow geothermal systems increases the risk caused by drilling operations, like the creation of hydraulic short circuits. Concerning deep geothermal systems for power generation, formation water as well as working fluid constituents may leak into shallow aquifers. No general information was found on the composition of these working fluids, but case studies show that chemical additives are often not used. However, formations suitable for geothermal energy production are often located in regions of higher seismic activity as of the steeper thermal gradient. Thus, the probability of induced seismicity is expected to be higher than for shale gas exploitation or GCS. Also, land subsidence may be induced under given circumstances, which in turn may have impacts on the groundwater resources. Deliverable 1.2 of the COSMA-project will specifically focus on risks resulting from geothermal operations including case studies.

Chapter 5 References

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Appendix 1

Published hazards involved in emerging subsurface activities

In this Appendix, published hazards are listed. It must be underlined however that the published hazardous substances (hazards) are not exhaustive, and depend on the local setting and technology in use.

List of hazards involved in Geological CO₂ sequestration

Table 7: List of impurities published by (Farret, Gombert et al. 2010).

Capture from		Oxyfuel-combustion		Post-Combustion	Pre-combustion (IGCC)	
Case		CO ₂ /SO ₂	CO ₂ -SO ₂		CO ₂ / H ₂ S	CO ₂ +H ₂ S
H ₂ O	vol%	0.141	0.141	0.141	0.14	0.14
CO ₂	vol%	91.611	90.284	99.802	97.845	95.616
Ar	vol%	5.702	5.619	0.021	0.05	0.049
O ₂	vol%	1.601	1.578	0.003	unknown	unknown
SO ₂	vol%	0.076	1.527	-	-	-
NO	vol%	0.248	0.244	0.002	unknown	unknown
N ₂	vol%	0.612	0.603	0.021	0.03	0.03
H ₂	vol%	-	-	-	1.72	1.68
H ₂ S	vol%	-	-	-	0.01	2.28
Hydrocarbons	ppmv	-	-	30	unknown	unknown
CO	ppmv	unknown	unknown	10	1700	1700
CH ₄	ppmv	-	-	-	350	350
Mercaptants	ppmv	-	-	-	220	220
NH ₃	ppmv	Trace	Trace	unknown	30	30
HCN	ppmv	Trace	Trace	-	< 5	< 5
HCl	ppmv	Trace	Trace	Trace	Trace	Trace
Hg	ppmv	Trace	Trace	Trace	Trace	Trace
Particulates	ppm	< 1	< 1	< 1	< 1	< 1
Metals	ppm	Trace	Trace	Trace	Trace	Trace

Table 8: Concentrations of impurities in dried CO₂, % by volume (IPCC 2005).

	SO ₂	NO	H ₂	H ₂ S	CO	CH ₄	N ₂ /Ar/O ₂	Total
<i>Coal fired plants</i>								
Post-combustion	<0.01	<0.01	0	0	0	0	0.01	0.01
Pre-combustion	0	0	0.01-0.6	0.8-2	0.03-0.04	0.01	0.03-0.06	2.1-2.7
Oxy-fuel	0.5	0.01	0	0	0	0	3.7	4.2
<i>Gas fired plants</i>								
Post-combustion	<0.01	<0.01	0	0	0	0	0.01	0.01
Pre-combustion	0	0	<0.01	1.0	0.04	2.0	1.3	4.4
Oxy-fuel	<0.01	<0.01	0	0	0	0	4.1	4.1

List of hazards involved in Hydraulic fracturing

Table 9: List of substances used by Exxon Mobil for hydraulic fracturing (Neutraler Expertenkreis 2012).

Substance	CAS Number
<i>Methanol</i>	67-56-1
<i>Disodium octaborate</i>	12008-41-2
<i>N,N-bis(2-hydroxyethyl)oleamide</i>	93-83-4
<i>Isooctan-1-ol</i>	111-46-6
<i>Diethylene glycol</i>	26952-21-6
<i>2-butoxyethanol</i>	111-76-2
<i>Distillates (petroleum), hydrotreated light</i>	64742-47-8
<i>Stoddard solvent</i>	8052-41-3
<i>Adipic acid</i>	124-04-9
<i>Alcohols, C11-C14-iso, ethoxylated, propoxylated</i>	78330-23-1
<i>Bronopol</i>	52-51-7
<i>Light aromatic solvent</i>	64742-95-6
<i>1,2,4-trimethylbenzene</i>	95-63-6
<i>Xylene</i>	1330-20-7
<i>Ethylbenzene</i>	100-41-4
<i>Potassium chloride</i>	7447-40-7
<i>Glycerol</i>	56-81-5
<i>Acetic acid</i>	64-19-7
<i>Acetic anhydride</i>	108-24-7
<i>Sodium hydroxide</i>	1310-73-2
<i>Sodium chloride</i>	7647-14-5
<i>Propan-2-ol</i>	67-63-0
<i>Quartz (SiO₂)</i>	14808-60-7
<i>Citrus, ext.</i>	94266-47-4
<i>Ammonium acetate</i>	631-61-8
<i>Citric acid</i>	77-92-9
<i>Sodium hydrogencarbonate</i>	144-55-8
<i>Sodium thiosulphate</i>	7772-98-7
<i>D-mannitol</i>	69-65-8
<i>Tributyl phosphate</i>	126-73-8
<i>Sodium chlorite</i>	7758-19-2
<i>Diammonium peroxodisulphate</i>	7727-54-0
<i>Polyvinylidenchlorid</i>	9002-85-1
<i>Fumaric acid</i>	110-17-8
<i>Guar gum</i>	9000-30-0
<i>Ammonium chloride</i>	12125-02-9
<i>Disodium peroxodisulphate</i>	7775-27-1
<i>Carbon dioxide</i>	124-38-9
<i>Kyanite</i>	1302-76-7
<i>Formaldehyde, Polymer with 4-Nonylphenole & Phenole</i>	40404-63-5
<i>Aluminium oxide</i>	1344-28-1

Table 5 continued

<i>Cristobalite</i>	14464-46-1
<i>Titanium dioxide</i>	13463-67-7
<i>Diiron trioxide</i>	1309-37-1
<i>Reaction mass of: 5-chloro-2-methyl-4-isothiazolin-3-one [EC no. 247-500-7] and 2-methyl-2H -isothiazol-3-one [EC no. 220-239-6] (3:1)</i>	55965-84-9
<i>2,2',2''-nitrilotriethano</i>	102-71-6
<i>Tetramethylammonium chloride</i>	75-57-0
<i>Choline chloride</i>	67-48-1
<i>Prop-2-yn-1-ol</i>	107-19-7
<i>Edetic acid</i>	60-00-4
<i>Tetrakis[[2,2',2''-nitrilotris[ethanolato]](1-)-N,O]zirconium</i>	101033-44-7
<i>Polyethyleneglycol-octyl-phenylether</i>	9036-19-5
<i>Propane-1,2-diol, propoxylated</i>	25322-69-4
<i>Propane-1,2-diol</i>	57-55-6
<i>3,6,9-triazaundecamethylenediamine</i>	112-57-2
<i>Formaldehyde</i>	50-00-0
<i>Formic acid</i>	64-18-6
<i>Guar gum, 2-hydroxypropyl ether, depolymd.</i>	68442-94-4
<i>Sodium bromate</i>	7789-38-0
<i>Disodium tetraborate, anhydrous</i>	1330-43-4
<i>Magnesium nitrate</i>	10377-60-3
<i>Sodium thiosulfate·5H₂O</i>	10102-17-7
<i>Potassium iodide</i>	7681-11-0
<i>Hydrogen chloride</i>	7647-01-0
<i>Magnesium chloride</i>	7786-30-3
<i>Calcium chloride</i>	10043-52-4
<i>Zirconium dichloride oxide</i>	7699-43-6
<i>2,2',2''-(hexahydro-1,3,5-triazine-1,3,5-triyl)triethanol</i>	4719-04-4
<i>Dichlorophen</i>	97-23-4
<i>2,2-dibromo-2-cyanoacetamide</i>	10222-01-2
<i>Dibromoacetonitrile</i>	3252-43-5
<i>Tert-butyl hydroperoxide</i>	75-91-2
<i>2-methylpropan-2-ol</i>	75-65-0
<i>Sodium formate</i>	141-53-7
<i>Potassium formate</i>	590-29-4
<i>Xanthan gum</i>	11138-66-2
<i>Disodium tetraborate decahydrate</i>	1303-96-4
<i>Potassium hydroxide</i>	1310-58-3
<i>Sodium carbonate</i>	497-19-8
<i>Calcium carbonate</i>	471-34-1
<i>Bentonite</i>	1302-78-9
<i>Barite (Ba(SO₄))</i>	13462-86-7
<i>Ceramic materials and wares, chemicals</i>	66402-68-4
<i>Triethyl citrate</i>	77-93-0
<i>Sodium dodecyl sulphate</i>	151-21-3

Table 5 continued

<i>Polyepichlorohydrin</i>	24969-06-0
<i>Fuels, diesel, no. -2</i>	68476-34-6
<i>Ethanol</i>	64-17-5
<i>Propan-1-ol</i>	71-23-8
<i>Aliphatic lipid alcohol poly-glycolether</i>	127036-24-2
<i>Oils, vegetable, hydrogenated</i>	68334-28-1
<i>Cellulase</i>	9012-54-8
<i>Potassium carbonate</i>	584-08-7
<i>Sulphuric acid</i>	7664-93-9
<i>Aluminium sulphate</i>	10043-01-3
<i>Acrylamide</i>	79-06-1
<i>Poly(oxy-1,2-ethanediyl),α-hydro-ω-hydroxy- Ethane-1,2-diol, ethoxylated</i>	25322-68-3
<i>Natriumcarboxy-methylhydroxy-ethyl-cellulose</i>	9004-30-2
<i>Calcium dihydroxide</i>	1305-62-0
<i>Zinc oxide</i>	1314-13-2
<i>Montmorillonite</i>	1318-93-0
<i>Feldspar-group minerals</i>	68476-25-5
<i>Calcium sulfate</i>	7778-18-9
<i>Attapulgit/Palygorskite</i>	12174-11-7
<i>Lignosulfonates</i>	9009-75-0
<i>Orthophosphoric acid</i>	7664-38-2
<i>Nonylphenol, ethoxylated</i>	9016-45-9
<i>Sodium polyacrylate</i>	9003-04-7
<i>Polyacrylamide</i>	9003-05-8
<i>Alkylalcohol, ethoxylated</i>	68439-46-3
<i>Hydroxyaluminium distearate</i>	300-92-5
<i>Polyvinylamine</i>	26336-38-9
<i>Sodium-ethene-sulphonic acid polymer</i>	9002-97-5
<i>Cellulose-carboxymethyl ether</i>	9000-11-7
<i>Cellulose</i>	9004-34-6
<i>Starch</i>	9005-25-8
<i>Muscovite</i>	1318-94-1
<i>Pentasodium trihydrogen [ethane-1,2-diy]bis[nitrilobis(methylene)]tetrakisphosphonate</i>	7651-99-2
