GEOCHEMICAL INTERACTIONS BETWEEN CO_2, PORE-WATERS AND RESERVOIR ROCKS

Lessons learned from laboratory experiments, field studies and computer simulations

Isabelle Czernichowski-Lauriol[1], Chris Rochelle[2], Irina Gaus[1], Mohamed Azaroual[1], Jonathan Pearce[2], Pierre Durst[1]

[1]BRGM, French Geological survey, 3 avenue Claude Guillemin, BP 6009, 45060 Orleans Cedex 2, France (Email: i.czernichowski@brgm.fr); [2]British Geological Survey, Kingsley Dunham Centre, Keyworth, Nottingham, United Kingdom, NG12 5GG.

Abstract: The degree of reactivity between CO_2, pore-waters and minerals may have significant consequences on CO_2 storage capacity, the injection process, and long-term safety and stability. Geochemical reactions are highly site-specific and time-dependent. They need to be assessed on a site-to-site basis according to best practises by combining numerical modelling and observations from laboratory experiments, field monitoring, and natural analogues. A selection of lessons learned from three European projects about the reactivity of CO_2 with reservoir rocks and cap rocks is presented here for three sites: Sleipner (Norway) and Weyburn (Canada) where more than 1 Mt of CO_2 per year has been injected underground since 1996 and 2000 respectively, and Montmiral, a natural CO_2 field in France.

Key words: CO_2 geological storage, geochemical studies, reactivity, reservoir, cap rock, experiments, modelling, CO_2 trapping, Sleipner, Weyburn, Montmiral.

1. INTRODUCTION

The capture and geological storage of CO_2 is increasingly seen as a viable strategy to reduce the release of greenhouse gases to the atmosphere (IPCC, 2002; OECD/IEA, 2004). The injection of a relatively reactive substance such as CO_2 into the deep subsurface will result in chemical disequilibria and the initiation of various chemical reactions. This paper gives an overview of the potential impact of geochemical reactions, based on work carried out jointly by BRGM and BGS in several European projects since 1993. Both institutes belong now to the CO_2GeoNet European Network of Excellence on CO_2 geological storage that was initiated in 2004 within the EC 6th Framework Programme.

2. WHY IS GEOCHEMISTRY IMPORTANT WHEN ASSESSING CO_2 STORAGE

Depending on the nature and scale of the chemical reactions, CO_2 interactions with reservoir rocks and cap rocks may have significant consequences, either beneficial or deleterious, on injectivity, CO_2 storage capacity, sealing efficiency, and long-term safety and stability (Czernichowski-Lauriol et al., 1996 a,b; Rochelle et al., 2004).

As well as being trapped as a buoyant supercritical CO_2 'bubble' (physical trapping), reaction with formation water can trap CO_2 as a dissolved phase (solubility trapping). Furthermore, reaction of this dissolved CO_2 with minerals in the host formation can result in pH buffering, enhancing solubility trapping due to the formation of dissolved bicarbonate ions and complexes (ionic trapping). Reaction of dissolved CO_2 with certain non-carbonate calcium-rich (or Fe- and Mg-rich) minerals can even trap the CO_2 as a solid carbonate precipitate (mineral trapping), essentially immobilising the CO_2 for geological time periods (Bachu et al., 1994; Gunter et al., 2004). Table 1 summarises trapping mechanisms associated with the deep underground storage of supercritical CO_2 and their relative importance with time, up to long timescales measurable in thousands of years.

Table 1. Possible trapping mechanisms associated with the deep underground storage of supercritical CO_2.

> **Physical trapping**
  - CO_2 'bubble': dense supercritical CO_2 phase

> **Chemical trapping**
  - Solubility trapping: $CO_2(aq)$ or $H_2CO_3^0$
  - Ionic trapping: HCO_3^-, $CaHCO_3^+$, $MgHCO_3^+$, $NaHCO_3^0$, …
  - Mineral trapping: $CaCO_3$ (calcite), $CaMg(CO_3)_2$ (dolomite), $MgCO_3$ (magnesite), $FeCO_3$ (siderite), $NaAlCO_3(OH)_2$ (dawsonite), ...

Increasing importance with time ↓

All the mineralogical reactions, which are induced by the dissolution of CO_2 into the pore-waters of the reservoir rocks and cap rocks and the resulting pH decrease, are highly complex. They are the result of interdependent thermodynamic, kinetic, flow and transport processes and can occur in the bulk of the reservoir rock or cap rock, but can also occur in fractures. They result in modification of porosity and permeability, which can either hinder the actual injection of CO_2, or aid its migration out of the storage volume. For example, rapid calcite dissolution around the injection well might increase injectivity while rapid mineral precipitation might block flow pathways needed to maintain high injection rates. Dissolution of minerals in the cap rock might result in the formation of flow pathways that might aid CO_2 migration; equally, a self-sealing mechanism could occur which would aid containment. The geomechanical consequences of the chemically-induced changes in fractures and bulk rock petrophysical properties need to be assessed as they will have an effect on long term storage stability and security.

A recurring theme is that geochemical reactions are highly site specific, depending on the precise mineralogy, fluid chemistry, pressure and temperature of the host formation. They are also strongly time-dependent, due to the wide range of reaction kinetics. So it is important to recognise that geochemical investigations need to be carried out on a site-to-site basis.

3. BEST PRACTISE FOR ASSESSING THE GEOCHEMICAL EFFECTS OF CO_2 STORAGE

General recommendations for assessing the geochemical effects of CO_2 storage can be found in the SACS Best Practise Manual (IEA-GHG, 2003), with specific examples being based on experience gained during the SACS and SACS2 projects investigating CO_2 storage at Sleipner.

3.1 Determination of baseline geochemical conditions prior to CO_2 injection

A good geochemical understanding of the system will require knowledge of the ‘baseline’ conditions of mineralogy and fluid chemistry prior to CO_2 injection. Only with this information can changes due to the presence of CO_2 be assessed. It is important therefore, that sample acquisition be implemented prior to CO_2 injection operations.

As a minimum requirement, the first prerequisite is to have core material from a well intersecting the reservoir formation and the cap rock formation. Core and cuttings from additional wells will improve characterisation, particularly if vertical and lateral heterogeneity is suspected. The second prerequisite is to have at least one formation water sample, carefully collected from the borehole at either the surface or downhole. A special effort should be focused on obtaining both fluid and rock samples from the same location as it is essential to relate fluid chemistry to mineralogy for a good assessment of baseline conditions. Accurate measurements of reservoir temperature and pressures are also essential for accurate experimental and modelling simulations.

3.2 Determination of the geochemical impact of injected CO_2

There are a variety of approaches that can be used that combine numerical modelling and observations from laboratory experiments, field monitoring, and natural analogues. Hence observations can be made at different spatial and temporal scales: from an individual sample scale to field scale; from hours to millions of years; from direct study of the selected injection site to indirect study through natural analogues. Constrained by these three types of observations, numerical models can make predictions from shorter to longer timescales, which is essential for assessing long-term geochemical processes associated with CO_2 storage.

3.2.1 Observations from laboratory experiments

Direct observations of reactions can be achieved through well-controlled laboratory experiments reacting samples of reservoir or cap rock with CO_2 and formation pore-water under simulated reservoir conditions. Geochemical changes can be followed in detail through direct observation and careful sampling. Such investigations are particularly useful for the study of shorter-term processes. Although limited in scale and timeframe, laboratory experiments have the advantage that they can help identify the key geochemical reactions on actual rock material under simulated reservoir conditions, which is very important as such reactions are known to be highly site-specific. They are also helpful to test the ability of geochemical codes to reproduce the experimental observations before using them to make long-term predictions over timescales of up to thousands of years.

Both static batch experiments and dynamic coreflood experiments are useful. Batch experiments can highlight the potential for reaction of samples of reservoir rock or cap rock when in contact with CO_2 and formation pore-water at reservoir temperature and pressure, over different timescales. Coreflood experiments are aimed at reproducing open systems where the rock is continuously flooded by pore-water rich in injected CO_2, which represents more closely actual reservoir conditions, especially during injection. They may elucidate inter-relationships between geochemical and hydrodynamic processes, and overall geochemical impact may be higher than in batch experiments.

3.2.2 Observations from field monitoring

The most obvious way to obtain direct geochemical information is by direct sampling of a CO_2 injection site. This approach requires observation boreholes with repeat fluid sampling and permanent in-situ sensors to monitor fluid chemical changes. Sidewall coring, or the drilling of boreholes through the CO_2 'bubble' would be necessary to obtain samples of rock that had been in contact with CO_2 for a variety of timescales. Such an approach is useful in providing highly relevant 'real time' information about a large-scale system.

3.2.3 Observations from natural analogues

This approach utilises relevant information from large-scale sources other than the selected injection site to generate a better understanding of the CO_2 injection system. Natural accumulations of CO_2 exist in many parts of the world and have many analogous features to a CO_2 storage operation, although these may not be directly comparable. As such, these 'natural analogues' can provide much useful information, especially for long-term processes as the CO_2 can, in many cases, be shown to have been trapped for thousands or millions of years. Study of natural accumulations of CO_2 has the advantage of similar physical size and timescale of reaction. This can build confidence in models that predict likely responses of reservoirs to geological storage.

3.2.4 Numerical modelling

Computer simulations are a very useful way to rapidly scope a range of different scenarios. They can predict the effects of adding CO_2 to formation pore-waters, and the subsequent changes in fluid chemistry and reservoir mineralogy. Some codes only deal with static (i.e. not flowing) systems, whereas others couple geochemical reactions and solute transport to produce simulations where mineral precipitation has a direct impact on fluid flow. A wide variety of different geochemical models are available, but they are generally based on the same underlying mathematical expressions. They do differ however, in their emphasis, and the way they handle input and output files. Many come with their own underlying thermodynamic data files, though kinetic data usually have to be supplied by the user. An important benefit of such codes is their ability to make predictions from shorter to longer timescales, which is essential for the long-term assessment of CO_2 storage. However, their output is crucially dependent on the reactions considered and the underlying data files, as well as on the reliability of the conceptual model chosen (which requires a good expertise in geochemical processes). Uncertainties resulting from this can be minimised by carrying out a wide range of sensitivity runs and by comparing modelling results with observations from laboratory experiments, field monitoring and natural analogues, which serve as useful validation test cases.

4. CASE STUDIES FROM THREE EUROPEAN FP5 PROJECTS

A selection of lessons learned from three European projects (5th Framework Research Programme) about the reactivity of CO_2 with reservoir rocks and cap rocks are presented for the following sites:

- Sleipner, North Sea, Norway, where 1 Mt of CO_2 per year has been injected into a deep saline aquifer since 1996 (Research carried out as part of the SACS and SACS2 projects).
- Weyburn, Saskatchewan, Canada, where 1.8 Mt of CO_2 per year has been injected into a depleted oil reservoir since 2000 (Research carried out as part of the European contribution to the IEA Weyburn CO_2 storage and monitoring project).
- Montmiral, Southeast basin, France, where a natural CO_2 field (98% CO_2) has been exploited since 1990 for CO_2 production for various industrial uses (Research carried out as part of the NASCENT project).

The main characteristics of these sites are summarized in Table 2.

Table 2. Main characteristics of the Sleipner, Weyburn and Montmiral sites

	Depth (m)	**T°C**	**Sal. (g/l)**	**Reservoir**	**Caprock**
Sleipner	800	37	35-40	Sand	Shale
Weyburn	1400	60	35-110	Carbonate	Evaporite/shale
Montmiral	2400	100	>85	sandstone	Clay/marl

4.1 Long term predictions of clay cap rock reactivity at Sleipner

CO_2 is being injected into the Utsira sand, which is overlain by the 250 m thick Nordland shale acting as a cap rock. Due to buoyancy effects the injected CO_2 moves upward from the injection point and accumulates under the overlying cap rock - under the current conditions CO_2 is in a supercritical state. The CO_2 will partially dissolve into the cap rock formation water and may thus subsequently diffuse upward into the cap rock. It is likely that this will lead to reaction with minerals present in the cap rock. Studies of CO_2 migration in low-permeability caprocks indicate that diffusion is an extremely slow process (e.g. Hildenbrand et al., 2002)

Numerical modelling was used to predict the long term effects of geochemical reactions on the porosity of the cap rock (Gaus et al., 2005). A conceptual diagram for the modelled scenario is shown in Figure 1. The upward diffusion into the cap rock has been modelled via 1D reactive transport modelling combining reaction kinetics and diffusive transport. The code used for the modelling is PHREEQC (V2.6) (Parkhurst and Appelo, 1999).

Figure 1. Conceptual model of dissolved CO_2 diffusion and reactivity into the base of the cap rock at Sleipner (Gaus et al., 2005).

At the time of the modelling study, no cap rock core was available. The mineralogy of the Nordland shale cap rock used for the modelling was based on the composition of a selection of cutting samples taken at the base of the cap rock. As no porosity measurements were available, a porosity of 5% was assumed based on observations from the Nordland Shale in UK Quadrant 16, northern North Sea. The initial chemical compositions of the cap rock pore-waters were assessed by equilibrating the water chemistry of the Utsira formation with the caprock mineralogy by means of geochemical modelling. In the absence of more accurate data, this is a common procedure to reconstruct the pore-waters chemistry of argillaceous rocks, given the long time scale over which this equilibrium could be established.

Figure 2. Profiles of impact of dissolved CO_2 in the cap rock after 3000 years at Sleipner. A) diffusion of dissolved CO_2 into the caprock. B) dissolution and precipitation of minerals. C) porosity changes (Gaus et al., 2005).

The diffusion of dissolved CO_2, the major mineralogical changes and the porosity changes after 3000 years are shown in Figure 2. The main results can be summarized as follows:

- Diffusion of CO_2 in the cap rock is predicted to be a slow process. After 3000 years, only the lower 10 meters of the 250 m thick cap rock have elevated dissolved CO_2 concentrations. Depending on the reactivity of the cap rock, diffusion can be further retarded because the dissolved CO_2 is consumed by feldspar alteration reactions.

- The calculated porosity change is small and limited to the bottom few metres of the cap rock. A decrease in porosity is predicted, with a maximum of 3% for the most reactive cap rock composition modelled. This will reduce the rate of diffusion and therefore improve the cap rock sealing capacity.
- At the very bottom of the cap rock some carbonate dissolution is expected to occur, leading to a minor porosity increase. However, this is predicted to not migrate further into the cap rock.

These conclusions are based on the assumption that the cap rock is a homogeneous medium and that diffusion is the only mass transport mechanism in the cap rock causing the displacement of dissolved CO_2.

Further investigations should aim to reduce uncertainties and strengthen confidence in the predictions. A core sample of the base of the cap rock is needed to obtain an accurate mineralogical and chemical characterisation and to initiate a series of laboratory experiments. The presence of any fractures that might lead to preferential pathways has to be studied. Information about the behaviour of similar clay cap rocks in natural CO_2 fields has to be searched for. Once information from these studies has been obtained, then numerical simulations need to be revised and a detailed sensitivity analysis should be carried out. Part of this work is currently being achieved through the CO2STORE European project (2003-2005) carried out within the 5th Framework Programme.

4.2 Reactivity of carbonate reservoir rocks at Weyburn

CO_2 is being injected into the Midale Formation carbonate reservoir as part of an enhanced oil recovery project at the Weyburn oilfield, Saskatchewan, Canada. As this is an active and mature oil field, a lot of wells are present, core samples are available and fluid samples can be taken at almost any time. A three-pronged approach has been used by the North American and European teams as part of the IEA CO_2 monitoring and storage project (Wilson and Monea, 2004) to study the impact of CO_2 upon reservoir geochemistry: monitoring changes in actual reservoir fluids from deep boreholes; laboratory experiments to simulate in-situ conditions within the reservoir; and predictive modelling of evolving conditions within the reservoir over the short to long term. A selection of results is presented below.

Figure 3. Batch thermo-kinetic modelling reacting a CO_2-rich Weyburn brine (1 molal CO_2) with reservoir minerals at 50°C over 1000 years: Evolution of pH and total amount of carbon

in dissolved and mineral forms, expressed in mol/REV (Durst et al., 2003). A REV is a Representative Elementary Volume of 3.85 l corresponding to 1 l of fluid and 2.85 l of rock.

The potential for long term mineral trapping in the Weyburn reservoir has been assessed by numerical modelling. Figure 3 presents the results for the case where a typical Weyburn brine (50°C, salinity 81 g/l) saturated with 1 mole of dissolved CO_2 reacts with the reservoir minerals in a closed system over 1000 years. Calculations were carried out using the PHREEQC code. Key results from this modelling are as follows (Durst et al., 2003):

- A rapid thermodynamic re-equilibration of the CO_2-rich saline solution with respect to carbonates, sulphate and sulphide is predicted. The resulting quick dissolution of carbonates induces an increase in dissolved carbon, whilst the amount of carbon in mineral form decreases.
- slow dissolution of alumino-silicates (Fe-chlorite, illite and K-feldspar), allowing the precipitation of dawsonite and siderite which trap CO_2 in mineral form. After about 3 years of simulated time, the predicted carbon concentration in solution continuously decreases while more and more carbon is trapped in mineral form.
- as the system is closed, the total amount of carbon in the system is constant.
- it is predicted that 50% of the CO_2 initially dissolved in the brine will be trapped in mineral phases (siderite, dawsonite) after 1000 years,
- however, thermodynamic equilibrium is still not reached after 1000 years.
- no significant variation of porosity was predicted as the system was closed (batch calculations). However for open systems with significant advective flow, carbonate reactions could lead to noticeable porosity changes.

Extrapolation to the reservoir scale was attempted by Perkins et al. (2004). Planned CO_2 injection is on the order of 20-25 million tons. In the long term, the Weyburn Midale reservoir has the potential to store all of the injected CO_2 through solubility and mineral trapping mechanisms, but assuming that every part of the reservoir is in contact with dissolved CO_2.

A series of laboratory experiments has been undertaken where samples of well-characterised borehole material from the Midale Formation were reacted with both CO_2 and synthetic reservoir formation waters under simulated in-situ conditions (60°C, 15-25 MPa). The duration of the experiments ranged from 1 week to 6 months. Changes in fluid chemistry, mineralogy, porosity and permeability were measured. The basic layout of the batch experiments is reproduced in Figure 4. Core flooding experiments with a fluid velocity of 15–29 cm/day were also carried out. Interpreted results of these experiments, based on observed changes and numerical modelling using the SCALE 2000 and PHREEQC codes, are described below (Azaroual et al., 2004; Riding and Rochelle, 2005).

Figure 4. Basic layout of the batch experiments used to react rock samples with CO_2-saturated brines under reservoir temperature and pressure conditions. Vessel volume is 100-150 ml.

In the closed system batch experiments the Midale lithologies (limestones, dolostones and anhydrite) showed variable amounts of carbonate mineral dissolution, some precipitation of gypsum incorporating the Ca released from carbonate minerals (Figure 5), ‘inhibition’ of anhydrite dissolution, and poor reactivity of alumino-silicate minerals over the timescale of the experiments.

Figure 5. Gypsum crystals up to 2.5 mm long after 8 weeks reaction of Weyburn reservoir rock with CO_2 in batch experiments under reservoir conditions (60°C, 15 MPa) (Riding and Rochelle, 2005).

In the CO_2 flooding tests observed dissolution features were confined to the inlet end, where CO_2-saturated brine entered the sample (Figure 6). Calcite and dolomite showed various states of corrosion. Porosity and matrix gas permeability increased. No precipitating minerals were observed in the CO_2 flooding experiments.

The 1D PHREEQC reactive transport code was used to simulate the long-term evolution of Midale material under CO_2 injection conditions in the Midale Formation of the Weyburn reservoir (150 bar and 54°C). The effect of mineral dissolution / precipitation reaction kinetics coupled to advective / diffusive / dispersive transport processes was predicted over a simulated 10,000 year time period. Varying flow rates were considered, from the undisturbed natural aquifer flow (0.25 m/year) up to higher values close to the injection zone (50 m/year). Simulations show that main reactions occur close to the injection zone. Calcite dissolves at the very entrance of the system whereas a calcium sulphate phase (anhydrite or gypsum) precipitates. Feldspars dissolve over a long distance while dawsonite precipitates. Clays show two reaction fronts, dissolving close to the injection zone but precipitating further on. Chalcedony, a silica phase, has the opposite behaviour. Finally, as a consequence of these dissolution / precipitation reactions, the porosity is predicted to increase. In the case of a flow rate of 0.25 m/year, the initial 20% porosity is expected to increase in the first 10 meters of the 1D column by up to 20.3% after 1000 years, and by up to 25% after 10,000 years.

Figure 6. Inlet end of the Weyburn reservoir rock sample after the CO_2 flooding experiment carried out at GEUS. Numerous small pits are present in the sample surface after the experiment. They represent dissolved calcite grains. (Riding and Rochelle, 2005; photograph reproduced with kind permission of GEUS)

Further investigations will be carried out in the Weyburn Phase II project. More accurate estimates coupling the CO_2 plume displacement, the CO_2 dissolution process as well as the geochemical interactions will be necessary to investigate the ultimate fate of the injected CO_2.

4.3 Long term reactivity of sandstone reservoir rocks at Montmiral

At Montmiral, supercritical CO_2 has accumulated in Triassic sandstones below 2400m depth (Czernichowski-Lauriol et al., 2002; Pearce et al., 2004). Based upon the tectonic setting and the results of petrographic studies, this accumulation occurred in post-Pyrenean times about 15 million years ago. The reservoir is sealed by Domerian and Callovian clay and marl. The Montmiral CO_2 field (98% CO_2) was discovered during gas and oil exploration in the 1960’s and is currently used for industrial CO_2 production. The availability of core material and access to reservoir fluids through the CO_2 producing well have allowed determination of the geochemical processes occurring as a result of CO_2 emplacement. This has been achieved through diagenetic studies, fluid inclusion analyses, isotopic analyses, numerical modelling, and has also been supported by a detailed reconstruction of reservoir evolution (Gaus et al., 2004).

Observed dissolution and precipitation reactions that can be attributed to interactions with injected CO_2 are, in diagenetic order: K-feldspar dissolution; extensive anhydrite cement removal; infilling of secondary porosity in K-feldspars by kaolinite (Figure 7); barite precipitation; mica splaying in open porosity; dolomite/ankerite development as a major pore-filling cement in some horizons; and the corrosion of ankerite. All these processes created an additional secondary porosity of about 2.4%.

Figure 7. Observed chemical reactivity at Montmiral: large secondary pore in corroded K-feldspar that is part of a coarse lithic grain, which is infilled by fine grained moderately

developed kaolinite books (Q = quartz, F = feldspar, D = dolomite, k = kaolinite, Fe = Fe oxyhydroxides, S = siderite, M = mica) (Riding and Rochelle, 2005).

Batch and flow-through geochemical modelling using PHREEQC was applied to reproduce the observed effects, to identify their driving parameters and to assess their impact in terms of potential mineral trapping and porosity changes. It has proved unnecessary to consider reaction kinetics; in the case of Montmiral, elevated temperatures and long contact times between the CO_2 and the rock allowed an assumption of local thermodynamic equilibrium to be used.

The modelling reproduced most of the observed changes that can be attributed to CO_2 ingress. However, in the batch modelling the extent to which these reactions occurred was not reproduced. The modelled reactions do not have a large impact on the mineralogy of the reservoir and an insignificant porosity increase was predicted (0.02 %). The observed reactivity implies that the sediment has been flushed intensively with CO_2-rich pore waters (open system) and that a flow regime in the reservoir must have been in place at a certain point in the reservoir's geological history. 1D reactive-transport modelling showed that an increase of secondary porosity of 2.4% requires that the pore water of the reservoir must be renewed 6000 times with CO_2-rich brine. This means that if we consider flow velocities between 0.1 and 100 meters per year, this would require between 100 and 100,000 years of flushing.

Mineral trapping can therefore be insignificant when considering certain closed systems. However, the presence of a flow regime can enhance mineral trapping, and a mineral trapping capacity of 8 kg CO_2 per m^3 of reservoir rock was modelled. In the case of Montmiral, the predicted trapping phase is dolomite. However, the precipitation of tiny amounts of dolomite is very difficult to confirm by observations. Dawsonite (another potential secondary carbonate mineral) was neither observed nor modelled at Montmiral.

5. CONCLUSIONS

Further knowledge on CO_2 reactivity with reservoir rocks and cap rocks has been gained through studies of three CO_2 storage sites, Sleipner and Weyburn ('industrial' sites), and Montmiral (a natural site).

Modelling of long timescale upward diffusion of dissolved CO_2 through the thick clay cap rock at Sleipner shows that diffusion is a very slow process, and is potentially retarded further by geochemical reactions. The overall net result is that only the bottom few meters of the cap rock adjacent to the reservoir is exposed to chemical reactions. As a consequence, the overall performance of the caprock seal is likely to be good. That said, however, migration of CO_2 may still be possible through pre-existing or newly formed fractures, or via the well bore. Indeed, for the latter, there is still a question regarding the chemical reactivity of CO_2 with borehole completions and the consequent impact on sealing.

Laboratory experiments, modelling and field monitoring at Weyburn show that the carbonate reservoir undergoes mainly dissolution reactions and an increase of porosity, especially close to the injection zone. However, mineral trapping could play a significant role in the long term due to the predicted precipitation of dawsonite. A full 3D dynamic modelling study still needs to be undertaken, where flow, transport and chemical processes are coupled in order to quantify the temporal and spatial changes in CO_2 solubility and mineral trapping, and consequent porosity changes.

Although CO_2 has accumulated over millions of years in the Montmiral sandstone reservoir, observed chemical reactivity is low. Detailed mineralogical and fluid characterisation combined with numerical modelling show that the dissolution of feldspars is the main reaction and that the porosity has increased by less than 3%. Mineral trapping is very limited and is restricted to minor precipitation of dolomite. Dawsonite was neither observed nor modelled at Montmiral, although often referred to in the literature as an important CO_2-trapping mineral.

Overall, therefore, CO_2 reactivity is highly site-specific and time dependent. Investigations need to be based on a very precise characterisation of minerals and fluids from the host formation. They also benefit from the combined outputs of laboratory investigations, numerical modelling, field monitoring and comparisons with natural analogues.

Reactivity can be minor for certain types of reservoirs or cap rocks, but significant for others. It is worth noting that chemical reactions are accelerated by high reservoir temperatures, and can be amplified in the presence of a flow regime. The impact of reactivity, either minor or significant, on the geomechanical properties of the reservoir and cap rock needs to be assessed to investigate long term storage stability and security.

ACKNOWLEDGEMENTS

This paper highlights a selection of lessons learned from several European research projects: '*The underground disposal of carbon dioxide*' (Joule II project, 3rd Framework Programme, 1993-1995), 'SACS' (4th Framework Programme, 1998-1999), 'SACS2' (5th Framework Programme, 2000-2002), NASCENT and WEYBURN (5th Framework Programme, 2001-2004). We thank the European Commission and the industrial and research consortia of the SACS, NASCENT and WEYBURN projects. We thank also the whole consortium of the international 'IEA Weyburn CO_2 Monitoring and Storage Project'.

BGS staff published with permission of the Executive Director, BGS (NERC).

REFERENCES

Azaroual, M., Kervévan, C., Durance, M.-V., and Durst, P., 2004, *SCALE2000 (V3.1) User's Manual; Software for thermodynamic and kinetic calculations*. BRGM Editions, ISBN2-7159-0939-X, 70 p.

Azaroual, M., Durst, P., Czernichowski-Lauriol, I., D., Olsen, D. N,. Springer, N., Rochelle, C. A., Pearce, J., Bateman, K., and Birchall, D., 2004, Geochemical reactions resulting from CO_2 injection into the Midale formation, Weyburn oilfield; a laboratory experimental and modelling study. *GHGT7- 7th International Conference on Greenhouse Gas Control Technologies*, Vancouver, Canada, 5-9 September 2004, 4 p.

Bachu, S., Gunter, W.D., and Perkins, E.H., 1994, Aquifer disposal of CO_2: hydrodynamic and mineral trapping. *Energy Conversion and Management*, **35:**269-279.

Czernichowski-Lauriol, I., Pauwels, H., Vigouroux, P., and Le Nindre, Y.M., 2002, The French carbogaseous province: an illustration of natural processes of CO_2 generation, migration, accumulation and leakage. *Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), Vol. I*, J. Gale and Y. Kaya (Eds), p. 411-416, Kyoto, Japan, Oct. 1st-4th 2002. Elsevier Science Ltd.

Czernichowski-Lauriol, I., Sanjuan, B., Rochelle, C., Bateman, K., Pearce, J., Blackwell, P., 1996a, Analysis of the geochemical aspects of the underground disposal of CO_2: scientific and engineering aspects. in: *Deep Injection Disposal of Hazardous and Industrial Waste*, J.A. Apps and C.F. Tsang, ed. pp. 565-583, Academic Press.

Czernichowski-Lauriol, I, Sanjuan, B, Rochelle, C, Bateman, K, Pearce, JM, and Blackwell, P., 1996b, Inorganic geochemistry. In: *Final Report of the Joule II Project No. CT92-0031: The Underground Disposal of Carbon Dioxide*, S. Holloway, ed., pp. 183-276, British Geological Survey, Keyworth, Nottingham, UK.

Durst, P., Azaroual, M., and Czernichowski-Lauriol, I., 2003, Weyburn database validation problem for predictive geochemical modelling. *Report BRGM/RP-52375-FR*, 46 p. Restricted.

Gaus, I., Le Guern, C., Pauwels, H., Girard, J.-P., Pearce, J., Shepherd, T., Hatziyannis, G., Metaxas, A., 2004, Comparison of long term geochemical interactions at two natural CO_2-analogues: Montmiral (Southeast Basin, France) and Messokampos (Florina Basin, Greece) case studies. *GHGT7 - 7th International Conference on Greenhouse Gas Control Technologies*, Vancouver, Canada, 5-9 September 2004, 9 p.

Gaus, I., Azaroual, M., and Czernichowski-Lauriol, I., 2005, Reactive transport modelling of the impact of CO_2 injection on the clayey cap rock at Sleipner (North Sea). *Chemical Geology,* **217**:319-337.

Gunter, W.D., Bachu, S., and Benson, S., 2004, The role of hydrological and geochemical trapping in sedimentary basins for secure storage of CO_2. in: *Geological Storage of Carbon Dioxide,* S.J. Baines and R.H. Worden eds., Special Publication of the Geological Society of London n°233, pp. 129-145.

Hildenbrand, A., Schloemer, S., and Krooss, B.M., 2002, N_2 and CO_2 gas breakthrough experiments on fine-grained sediments. in: *Poromechanics*, Auriault et al. (eds). Swets & Zeitlinger, Lisse, 445-450.

IEA-GHG, 2003, Saline Aquifer CO_2 Storage project (SACS) Best Practice Manual. *Report Number PH4/21*, 53 p.

IPCC, 2002, Proceedings of the IPCC Workshop on carbon dioxide capture and storage, Regina, Canada, 18-21 November 2002.

OECD/IEA, 2004, Prospects for CO_2 capture and storage. IEA Publications, *ISBN 92-64-10881-5*, 249 p.

Parkhurst, D.L., and Appelo, C.A.J., 1999, User's guide to PHREEQC (version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: *U.S. Geological Survey Water-Resources Investigations Report* 99-4259, 312 p.

Pearce, J., Czernichowski-Lauriol, I., Lombardi, S., Brune, S., Nador, A., Baker, J., Pauwels, H., Hatziyannis, G., Beaubien, S.E., Faber, E., 2003, A review of natural CO_2 accumulations in Europe as analogues for geological sequestration. in: *Geological Storage of Carbon Dioxide,* S.J. Baines and R.H. Worden eds., Special Publication of the Geological Society of London n°233, pp. 29-41.

Perkins, E., Czernichowski-Lauriol, I., Azaroual, M., Durst, P., 2004, Long term predictions of CO_2 Storage by mineral and solubility trapping in the Weyburn Midale Reservoir. *GHGT7 - 7th International Conference on Greenhouse Gas Control Technologies*, Vancouver, Canada, 5-9 September 2004, 4 p.

Riding, J.B., and Rochelle, C.A., 2005, The IEA Weyburn CO_2 Monitoring and Storage project: Final report of the European research team. British Geological Survey, *Research Report RR/05/03*, 54 p.

Rochelle, C.A., Czernichowski-Lauriol, I., and Milodowski, A.E., 2004, The impact of chemical reactions on CO_2 storage in geological formations: a brief review. in: *Geological Storage of Carbon Dioxide,* S.J. Baines and R.H. Worden eds., Special Publication of the Geological Society of London n°233, pp. 87-106.

Wilson, M., and Monea, M., 2004, IEA GHG Weyburn CO_2 Monitoring & Storage Project Summary Report 2000-2004. *Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies*, *Vol.3*, Vancouver, Canada, 5-9 September 2004, 273 p.

Figure 1: Conceptual model of dissolved CO_2 diffusion and reactivity into the base of the cap rock at Sleipner (Gaus et al., 2005).

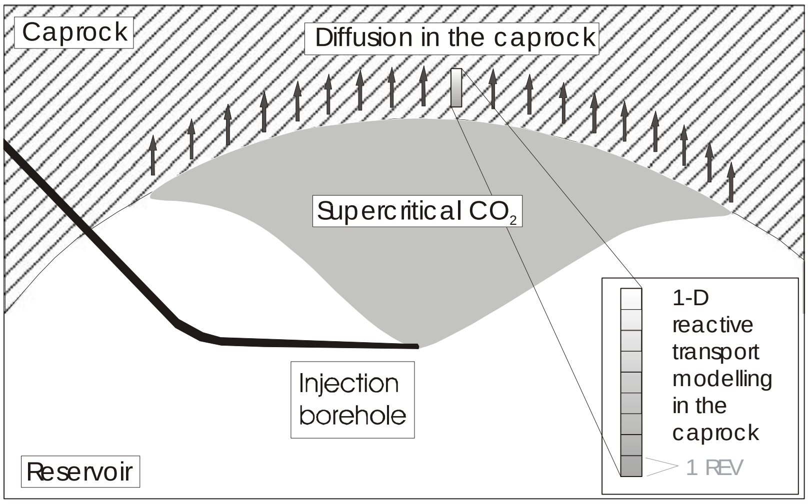

Figure 2: Profiles of impact of dissolved CO_2 in the cap rock after 3000 years at Sleipner. A) diffusion of dissolved CO_2 into the caprock. B) dissolution and precipitation of minerals. C) porosity changes (Gaus et al., 2005).

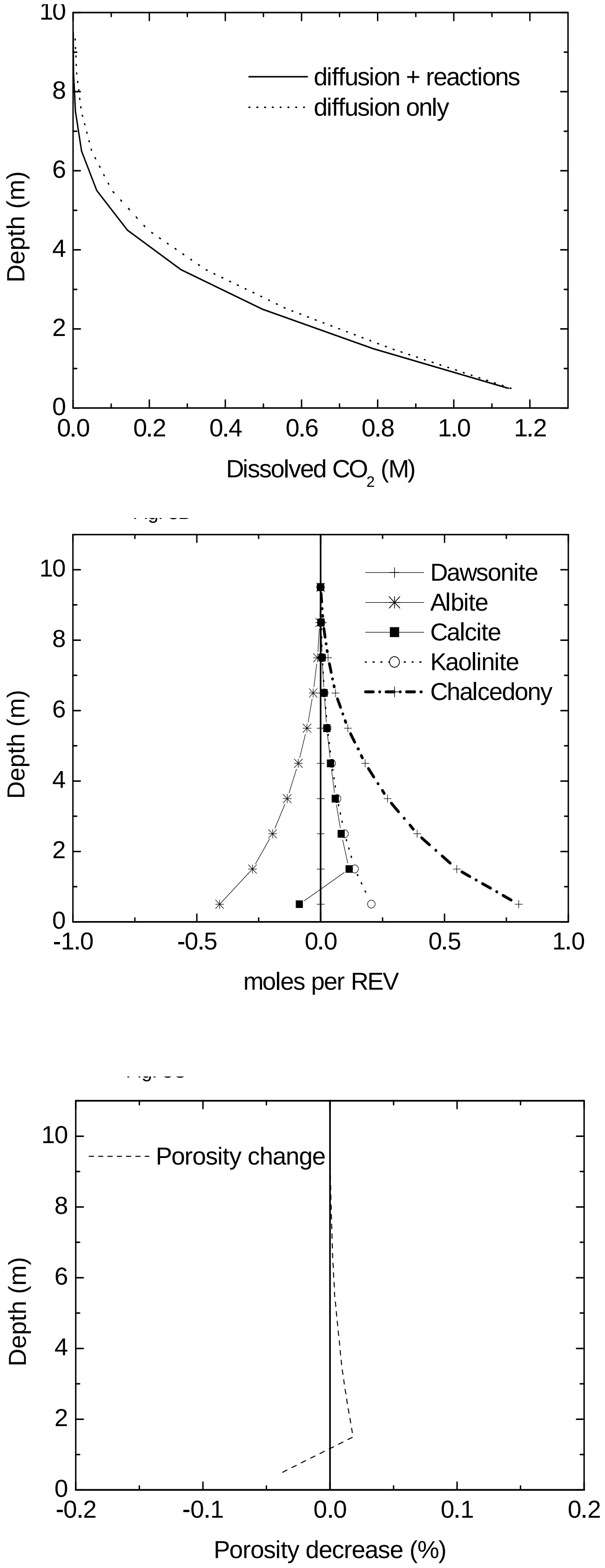

Figure 3: Batch thermo-kinetic modelling reacting a CO_2-rich Weyburn brine (1 molal CO_2) with reservoir minerals at 50°C over 1000 years: Evolution of pH and total amount of carbon in dissolved and mineral forms, expressed in mol/REV (Durst et al., 2003). A REV is a Representative Elementary Volume of 3.85 l corresponding to 1 l of fluid and 2.85 l of rock.

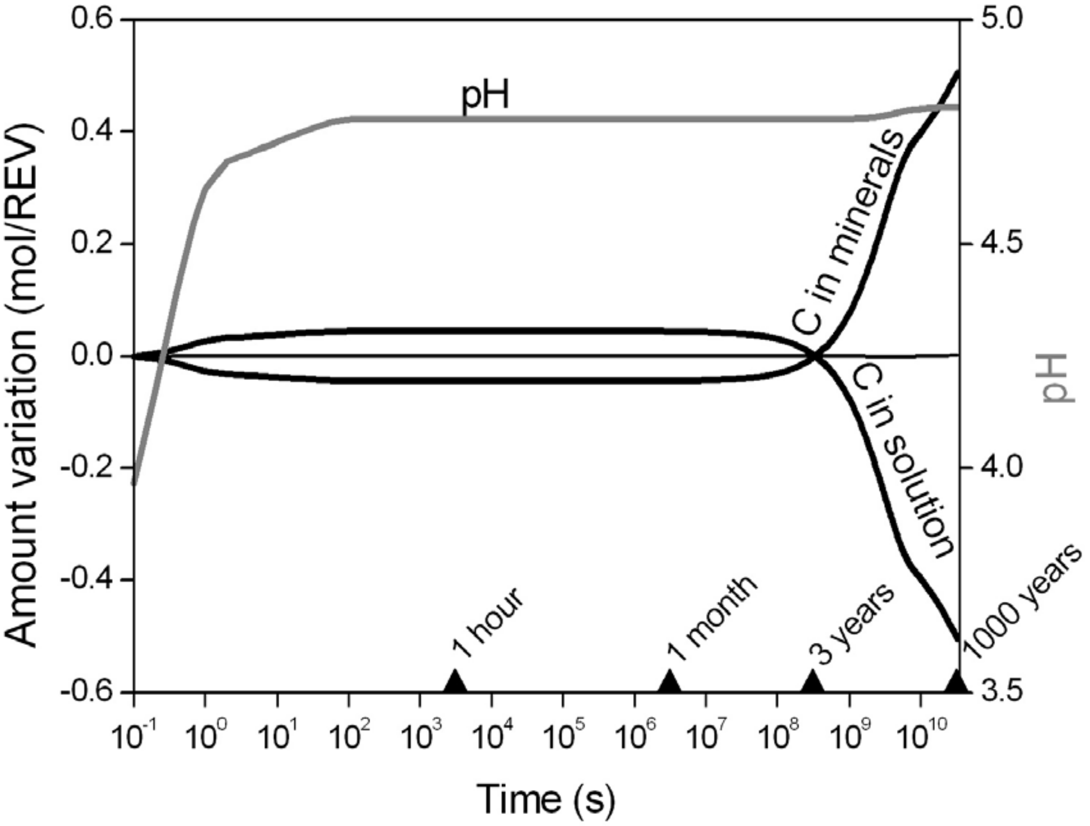

Figure 4: Basic layout of the batch experiments used to react rock samples with CO_2-saturated brines at temperature and pressure reservoir conditions. Vessel volume is 100-150 ml.

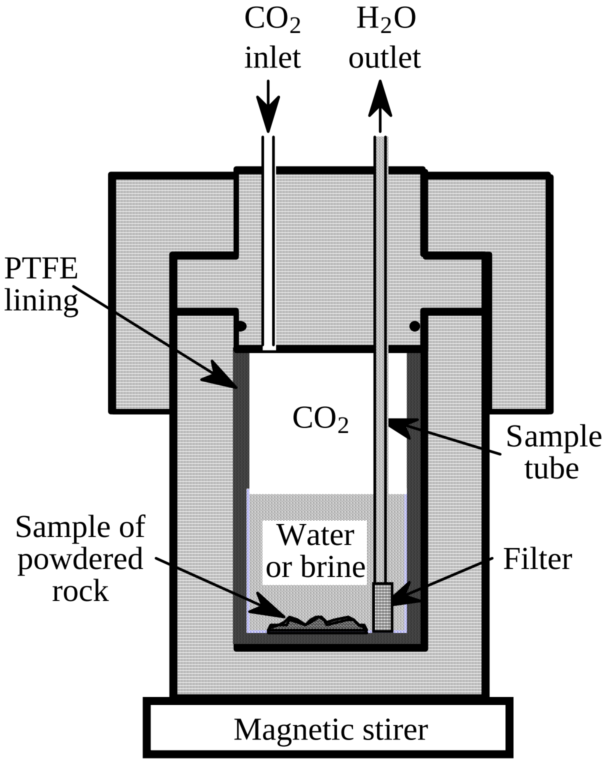

Figure 5: Gypsum crystals up to 2.5 mm long after 8 weeks reaction of Weyburn reservoir rock with CO_2 in batch experiment at reservoir conditions (60°C, 15 MPa) (Riding and Rochelle, 2005).

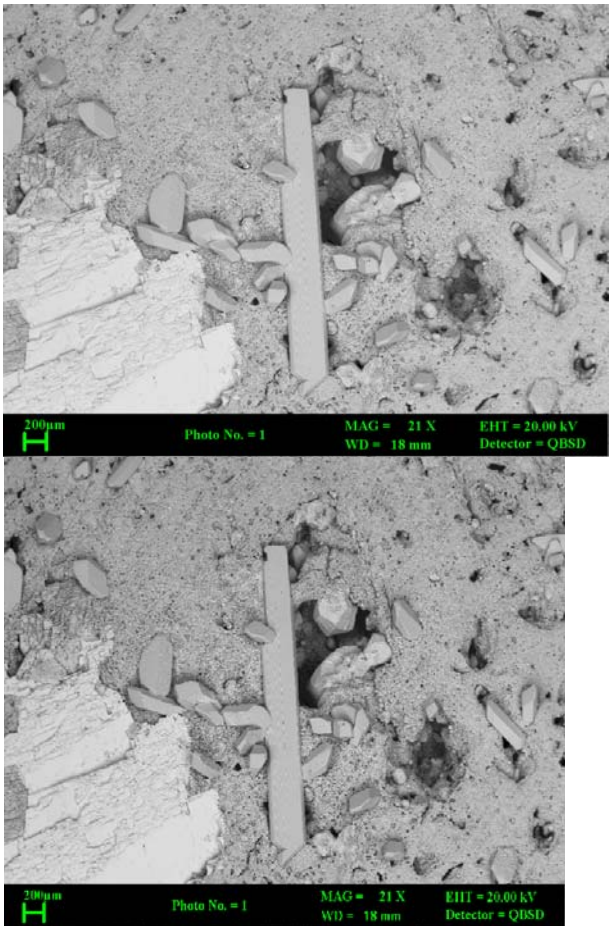

Figure 6: Inlet end of the Weyburn reservoir rock sample after the CO_2 flooding experiment carried out at GEUS. Numerous small pits are present in the sample surface after the experiment. They represent dissolved calcite grains. (Riding and Rochelle, 2005)

Figure 7: Observed chemical reactivity at Montmiral: large secondary pore in corroded K-feldspar that is part of a coarse lithic grain, which is infilled by fine grained moderately developed kaolinite books *(Q = quartz, F = feldspar, D = dolomite, k = kaolinite, Fe = Fe oxyhydroxides, S = siderite, M = mica)* (Riding and Rochelle, 2005).