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Published in *Proceedings of the 4th annual conference on carbon capture and storage*, Alexandria, VA, May 3-6, 2004.

Long term interactions between minerals and reactive fluids - Stability of dawsonite

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Abstract

Because carbon dioxide (CO₂) is a major greenhouse gas, sequestration of CO₂ in saline aquifers is being explored as one possible approach to limit the accumulation of greenhouse gases to the atmosphere. As CO₂ is injected, it will migrate as a gaseous or supercritical fluid in the reservoir, and gradually dissolve and be dispersed into the formation water. The increase in activity of aqueous CO₂ leads to acidification of the formation waters, and increased reactivity with the host mineralogy. The interactions between the reactive fluids and host rock minerals are a complex interplay between thermodynamic stabilities, reaction kinetics, and fluid flow. To simulate these interactions, reliable thermodynamic and kinetic data are essential. In addition, site-specific parameters like mineralogy, formation water chemistry, temperature, and pressure, will strongly influence the simulations.

Even though large differences exist between different systems, most environments have shown that dawsonite (NaAl(OH)₂CO₃) is an important product of the geochemical interactions at elevated CO₂ pressures. In addition, temperature, associated mineral assemblage, and reaction kinetics also strongly affect its stability.

1. Introduction

Increasing atmospheric concentrations of greenhouse gases are suspected of causing a gradual warming of the Earth's surface and potentially disastrous changes to global climate. Because carbon dioxide (CO₂) is a major greenhouse gas, sequestration of CO₂ in saline aquifers is being explored as one possible approach to limit the accumulation of greenhouse gases to the atmosphere. Mineral disequilibria induced by injection of CO₂ leads to dissolution of primary reservoir minerals, and precipitation of new phases that are stable at elevated CO₂ pressures. A main goal of the current project "Model studies of safe long term storage of CO₂ in aquifers", is the development of Athena, a reactive transport simulator, that is capable of large volume (e.g., the Utsira Fm.; Zweigel et al., 2001) and long time-span (1000s of years) simulations. To gain information *in-situ* information regarding flow behaviour of CO₂, as well as reservoir sand properties and possible geochemical reactions, the Utsira Fm., where Statoil and partners are currently injecting CO₂ from the Sleipner facility, is used as a frame for the project. This site is especially useful because of the ongoing 4D seismic monitoring (Arts et al., 2002).

One mineral phase that commonly precipitates out as a reaction product in sequestering simulations, and is expected to form in the Sleipner injection project, is dawsonite (NaAl(OH)₂CO₃); e.g., Gaus et al., 2002; Xu et al., 2003). The simulations show a steady growth of dawsonite coupled to aluminosilicate dissolution at elevated partial pressures of CO₂. Some natural occurrences of dawsonite have also been linked to CO₂ seepage into groundwater (e.g., Baker et al., 1995). Nevertheless, dawsonite is a rare mineral even in areas that has been exposed to CO₂ seepage. This suggests that dawsonite is only thermodynamically stable at elevated CO₂ pressures, and will tend to decompose as soon as the CO₂ pressure drops below a critical level. This study is motivated by the need to better understand the potential role of dawsonite in CO₂ sequestration scenarios. This study starts with an introduction to the Utsira Sand, and the ongoing

injection, and seismic monitoring, before presenting dawsonite phase stability, and the role of differences in relative kinetics on formation and dissolution.

2. The Utsira Sand

At the Sleipner field in the North Sea, CO₂ is extracted as a by-product of gas exploitation and has been injected into the Utsira saline aquifer at a rate of 1 MT per year since 1996. The multi-institutional SACS (Saline Aquifer CO₂ Storage) project has provided valuable information through their publications, especially with regard to the fate of the injected CO₂ through 4D “time lapse” seismic surveys of the reservoir (see “<http://www.iku.sintef.no/projects/IK23430000/>” for a list of publications).

The Utsira Sand is situated close to the UK/Norway median line and covers an area of more than 2.6×10^4 km². Two key reflectors, interpreted on the basis of well logs, separate the lower- and upper boundary of the sand body, i.e. Base Utsira Sand and Top Utsira Sand respectively. In the southern depocentre, where the CO₂ is being injected, the top of the sand lies between 600 m and 1150 m depth reaching a maximum thickness of 300 m. Base Utsira Sand has been interpreted to consist of mounds caused by mud volcanism and mud diapirism, which was

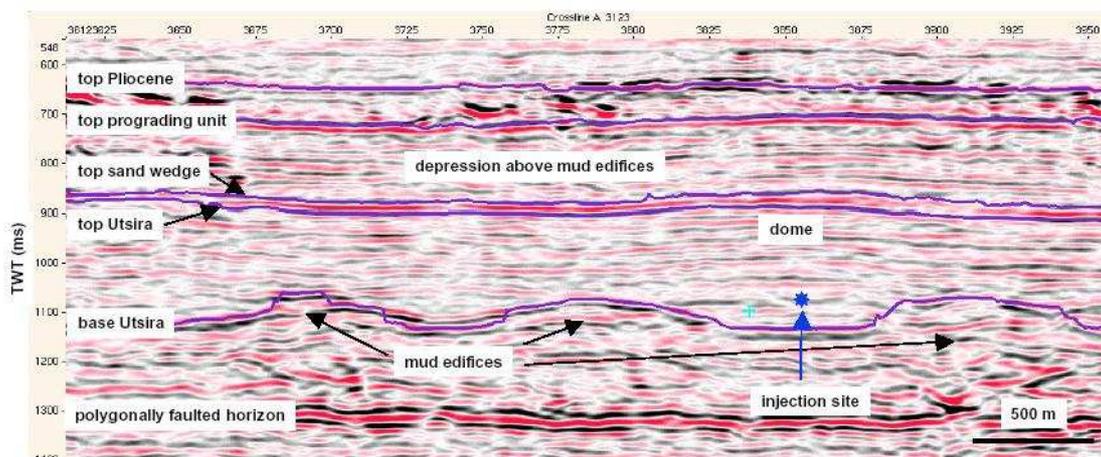


Fig. 1: Seismic section through the injection site; survey ST98M11 (Zweigel et al., 2001).

active during deposition of the lower part of the sand (Fig. 1). The presence of these mounds might have a significant influence on the flow patterns in the reservoir, with the possibility channeling of high-density CO₂ saturated aqueous solutions. The Top Utsira Sand displays a weakly undulating topography with local domal and anticlinal structures, interpreted to have formed as a consequence of mud volcanism and diapirism (Arts et al., 2000). The Utsira Sand is overlain by the several hundreds meter thick Pliocene Nordland Shales, believed to act as an effective seal.

Wireline-log analysis suggests the presence of several thin (<1 m) shale horizons within the Utsira formation. These shales have been predicted to affect the short-term CO₂ migration paths (Lothe and Zweigel, 1999), an effect that has been verified through comparison with seismic time-lapse data (Zweigel et al., 2001). In most wells the lower part of the Utsira Formation is represented by Middle Miocene sandy deposits, whereas the upper log-units are of

Middle- to Late Miocene (>5.2Ma; Gregersen et al., 1997). The sands consist mainly of fine grained, moderately to well sorted, poorly cemented and highly permeable sand. The mineralogy is dominated by quartz with minor amounts of K-feldspar, plagioclase, carbonates (calcite and aragonite) and bioclastic debris. Some detrital grains are coated with a thin (<10 µm) clay layer of mainly smectite with minor illite and chlorite. Variable amounts of glauconite and shell material suggest deposition in a marine environment, while lignite and well-rounded, matured quartz sand suggest that parts of the sediments are derived from nearshore/land areas and subsequently transported towards the basin center (Gregersen et al., 2000).

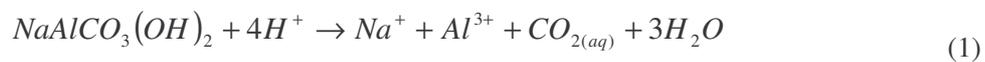
At the 1999 seismic survey, high reflection amplitudes directly underneath the Top Utsira reflection indicates that the CO₂ had reached, but not penetrated the roof. Two years later in the 2001 survey, reflections indicate that the CO₂ had reached the sand wedge, and spread out laterally underneath the Top Utsira reflection. Both seismic surveys in 1999 and 2001 confirm the presence of clay layers, as indicated previously in gamma-ray logs. These reflections occur at up to nine depth levels both on the 1999- and the 2001 survey.

3. Carbonate stability with special focus on dawsonite

The standard state adopted in this study is that of unit activity for pure minerals and H₂O at any temperature and pressure. For aqueous species other than H₂O, the standard state is unit activity of the species in a hypothetical 1 molal solution referenced to infinite dilution at any temperature and pressure. For gases, the standard state is for unit fugacity of a hypothetical ideal gas at a 1 bar pressure. All thermodynamic calculations on the present study were performed using geochemical code PHREEQC-v2 (Parkhurst and Appelo, 1999) together with the LLNL database.

High partial pressures of CO₂ leads to a potential of precipitating carbonates like calcite, siderite, dolomite and magnesite. However, even with elevated activity of carbonate in solution, the formation of these carbonates requires their respective divalent cations, i.e., Ca²⁺, Fe²⁺, and Mg²⁺. The abundance of divalent ions is however generally low in typical formation waters (Egeberg and Aagaard, 1989; Bjørlykke et al., 1995). Thus, the ions have to come from interactions between the aqueous solution and minerals in the sediment, like oligoclase. To quantify the sequestering potential of a host rock, knowledge of the abundance of minerals that contain the ions is essential. Generally, the mineralogy is dominated by quartz and aluminosilicate minerals, which provide little or no divalent cations to the solution. Exceptions are glauconitic sands, like the Utsira Sand, and typical gulf coast sediments with high abundance of oligoclase (Xu et al., 2003). Thus, dawsonite, that only requires sodium and aluminum that are both abundant in formation waters and minerals respectively, may be the major carbonate product in most sequestration scenarios.

Dawsonite dissolution and precipitation can be described by



An increase in aqueous CO₂ activity, leads to a shift in the reaction towards left, stabilizing dawsonite. The relation between CO₂ fugacity and aqueous activity can be approximated through the Henrys constant for CO₂

$$a_{CO_{2(aq)}} = K_H f_{CO_{2(g)}} \quad (2)$$

where a_{CO_2} and f_{CO_2} denote activity and fugacity of CO₂ respectively. The relative stability of dawsonite with respect to other Na and Al bearing phases can be assessed using logarithmic

activity-fugacity diagrams like Fig. 4.

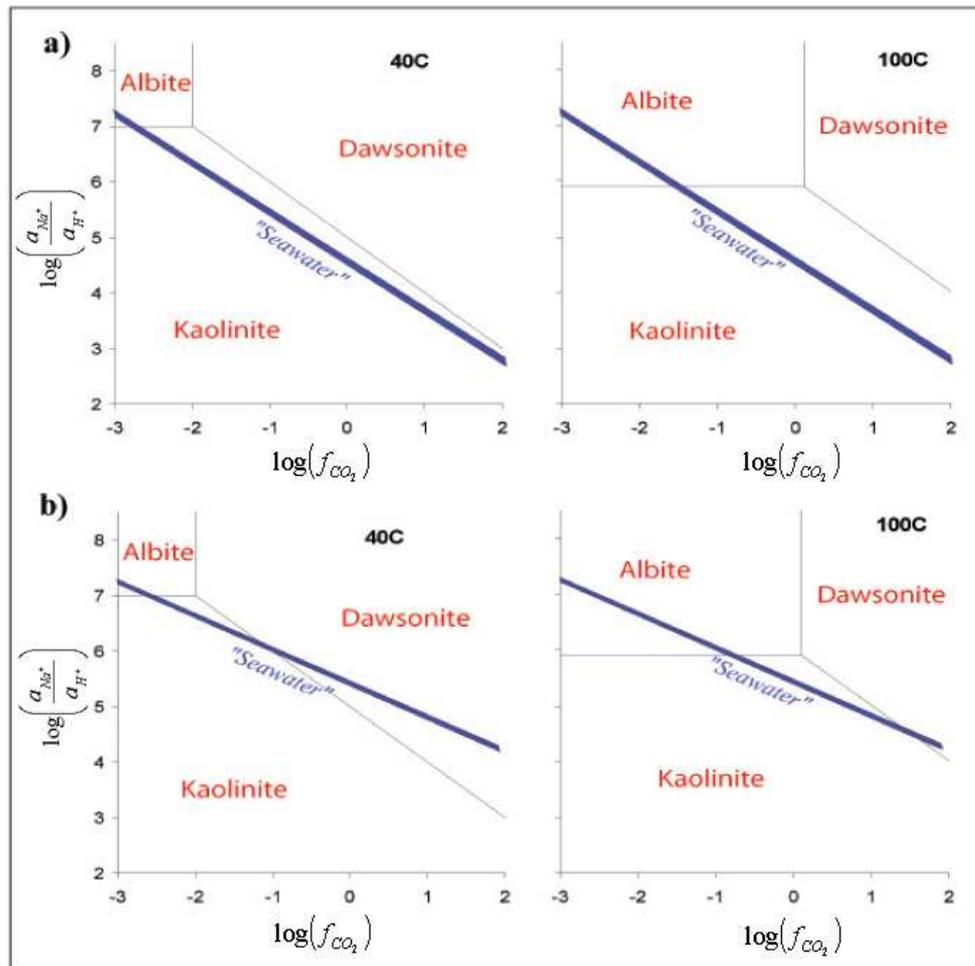


Fig. 4. Activity-fugacity diagram showing the stability fields of albite, kaolinite and dawsonite. An aqueous solution representative of the lower salinities found in typical formation waters is illustrated as a broad line crossing each diagram.

The diagram illustrates phase relations in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CO}_2-\text{H}_2\text{O}$ balanced on aluminium at SiO_2 activity fixed by saturation with quartz at 40 (Fig. 4a) and 100°C (Fig. 4b). As equations (1) and (2) suggest, dawsonite occupy the high CO_2 pressure stability field. The temperature effect can be read as a substantial increased stability at lower temperatures. The activity-activity type of diagram illustrates what phases are stable at different fluid compositions. The broad lines crossing the diagrams illustrates typical $\log(a_{\text{Na}^+}/a_{\text{H}^+})$ at different $\log(f_{\text{CO}_2})$ for a seawater-like solution, which is close to the lower salinity range of typical off-shore formation waters (Egeberg and Aagaard, 1989; Bjørlykke et al., 1995). Fig. 4a and b illustrates the seawater-like solutions, whereas Fig. 4c and d illustrates solutions that have been pH-buffered by the presence of calcite in the system. By comparisons, the buffered solutions are seen to enter the stability field of dawsonite at substantial lower CO_2 fugacities than the non-buffered solutions. This may suggest that the presence of carbonates like calcite increase the stability of dawsonite and the amount that can form in formations. However, the addition of phases to the assembly

change the activity-fugacity diagram from two dimensional to multidimensional, and since a mineral like calcite may compete with dawsonite for carbonate, it may actually affect the formation of dawsonite negatively.

As soon as dawsonite is thermodynamically stable, it will start precipitating out. The amount that precipitates per time unit is a function of the precipitation rate of dawsonite relative to other phases in the system that contains a common limiting component. If the dawsonite dissolution rate is relatively fast, the amount that precipitate per time unit will be determined by the change in the solution activity of the limiting component, which is determined by the release and uptake of the component from competing phases with time

$$v_j \int_{t=t_0}^t r_j^+ dt = \sum_{i \neq j} v_i \int_{t=t_0}^t r_i^{+,-} dt \quad (3)$$

where r^+ is the precipitation rate of dawsonite, $r^{+,-}$ is precipitation (+) and dissolution (-) rates of phases i that exhibit the limiting component, and v is the stoichiometric number of moles of the limiting component in the phases. On the other hand, if the rate of dawsonite precipitation is slow, the amount that precipitate out may be limited by the dawsonite kinetics itself. Similar reasoning may be used to see how fast dawsonite will dissolve if the CO₂ pressure drops below dawsonite stabilization (Fig. 4). Since no dawsonite kinetics has been reported in the literature, sequestering simulations have used a variety of methods to estimate these rates. For example, Gaus et al. (2002) used an intermediate rate between calcite and dolomite, whereas Xu et al., (2004) assumed that dawsonite dissolution rates are equal to that of K-feldspar. This shows that to fully understand the importance of dawsonite during CO₂ sequestration, both the thermodynamics and kinetics has to be known.

4. Conclusions

The general idea when considering geological sequestration of CO₂ in formation waters is that it will dissolve gradually, be dispersed into the formation water, and form carbonates that are stable for geological timescales. To assess this qualitatively and quantitatively, knowledge of thermodynamics and kinetics of the phases present in the system are essential. Because of general low abundances of divalent cations in solution, dawsonite may be the major carbonate forming in most sequestration scenarios. The thermodynamic stability of dawsonite is a function of abundance of coexisting phases in the system, temperature, CO₂ pressure, and relative kinetics of the phases. Thus, to fully understand its potential in CO₂ storage, all the above information must be known. At the moment, the kinetics is unknown, whereas the thermodynamic stability, especially in relation to the activity of ions in multi-dimensional systems, has to be examined further.

5. Acknowledgements

The authors would like to gratefully acknowledge financial support from the Norwegian Research Council, and Norsk Hydro.

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