Chemical and Physical Interaction of CO$_2$ and Carbonate Rock

A GESTCO contribution

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GEOLOGICAL SURVEY OF DENMARK AND GREENLAND
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Introduction

Many rock-forming minerals may in principle react with CO_2 at the pressure-temperature (P-T) conditions of a potential geological CO_2 storage site. In this report we present a literature study, intended to delineate the current knowledge about relevant chemical and physical interactions between CO_2 and carbonate rocks. Because many carbonate rocks have significant contents of silicate minerals, we have included information about the chemical reactions most likely to take place in silicate rocks. Chemical reaction rates and stability regions are difficult to predict with certainty. Therefore, the most significant indication to what extent and at what rate such reactions will take place in CO_2 storage operations comes from CO_2 Enhanced Oil Recovery (EOR) operations, laboratory experiments and natural CO_2 reservoirs. Instances of mineral dissolution or precipitation, changes in mechanical stability, and changes in porosity or permeability are given special attention.

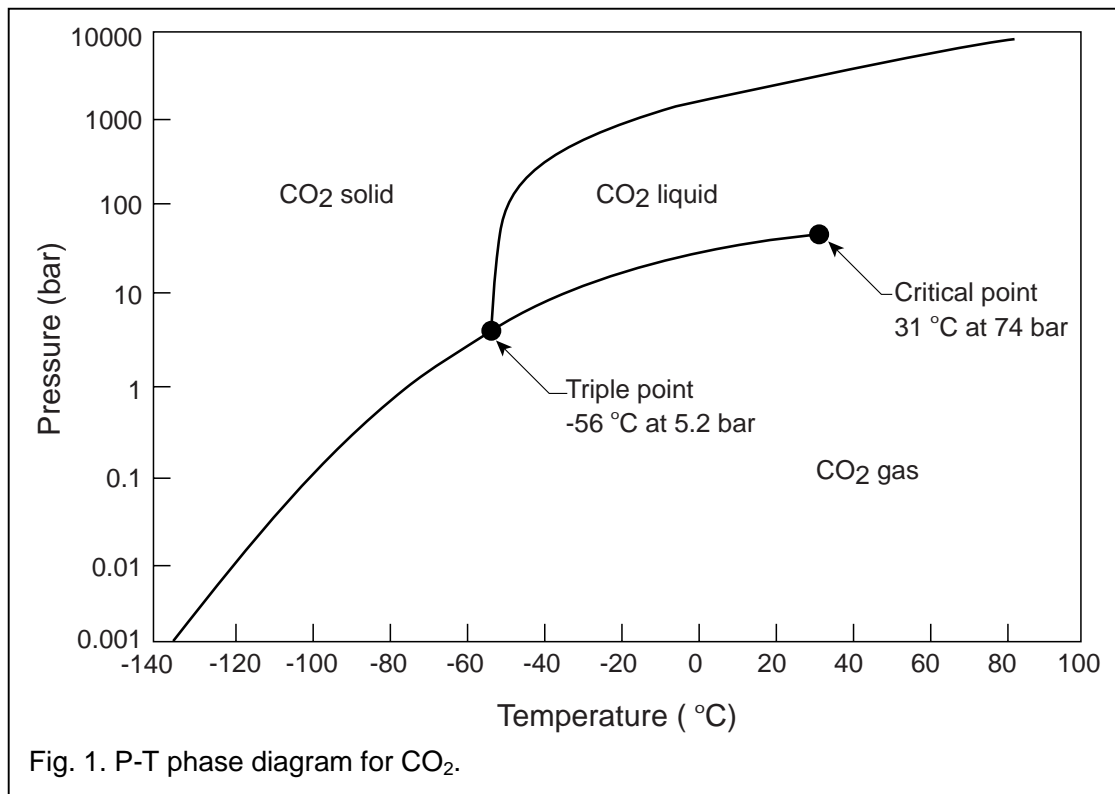This work is part of the EU GESTCO project.
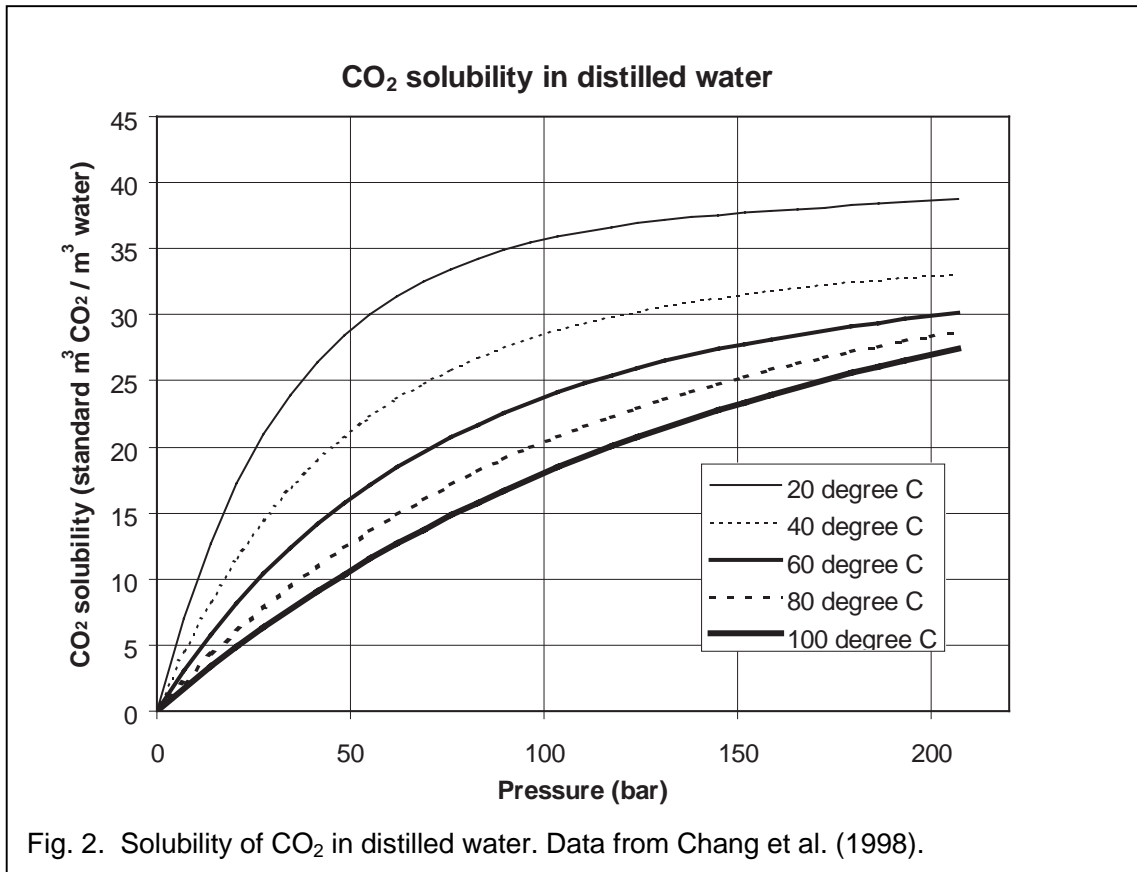
Chemical and physical interactions involving CO_2

Reactions between CO_2 and carbonate minerals

At the P-T conditions considered in this review CO_2 may exist as either gas, liquid or supercritical fluid, cf. Fig. 1. In the region above the critical point, the CO_2 is neither a gas nor a liquid, being more gas-like at lower pressure to more liquid-like at higher pressure. In many potential CO_2 storage reservoirs a free CO_2 phase will occur as a supercritical fluid. CO_2 has a significant solubility in water, the size of which depends on the P-T conditions (Fig. 2) and the amounts of other dissolved components in the water (Fig. 3). For conditions relevant to CO_2 storage the solubility of CO_2 in water will usually be between 1 and 5 weight percent.

The solubility of the $CaCO_3$ polymorphs depends on the lattice structure of the crystals. At the same partial pressure of CO_2 (P_{CO2}), the rhombohedral calcite is the most stable modification showing lower solubility than the orthorhombic aragonite. Both the vaterite and the gel-like amorphous $CaCO_3$ are unstable with water. Dolomite, $CaMg(CO_3)_2$, is less soluble than calcite. Calcite may contain significant amounts of Mg, but contrary to what might be expected from the behaviour of dolomite, the solubility of calcite increases with increasing contents of Mg (Bathurst, 1976).

In an open system (e.g. in the vadose zone, or in the area close around an injection well) the dissolution of limestone and dolostone takes place in the CO_2 - H_2O - $MeCO_3$ system

Fig. 1. P-T phase diagram for CO_2.

CO$_2$ solubility in distilled water

Fig. 2. Solubility of CO$_2$ in distilled water. Data from Chang et al. (1998).

(Me: Ca and/or Mg) and comprises a series of physical and chemical processes in which three states – gaseous or supercritical CO$_2$, liquid water and solid mineral - participate, and they imply a mass transport through the interface gas/supercritical-water and water-rock. Below is given a review of interactions relating to pure calcite, but the behaviour of Mg^{2+} and Fe^{2+} containing calcite is similar. In the CO$_2$ - H$_2$O - CaCO$_3$ system the following essential steps take place (Bögli, 1978; Buhmann & Dreybrodt, 1985):

(1) gas-CO$_2$ diffuses into water

$$CO_{2\ gas} \rightleftharpoons CO_{2\ physically\ dissolved} \tag{1}$$

(2) the physically dissolved CO$_2$ is hydrated (at 4° C and 1 bar up to 0.75 weight %)

$$CO_{2\ physically\ dissolved} + H_2O \rightleftharpoons H_2CO_{3\ CO2\ chemically\ bound} \tag{2}$$
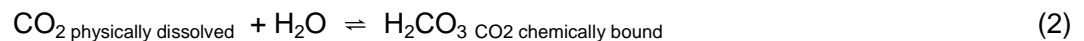
(3) H$_2$CO$_3$ is dissociated:

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \tag{3}$$

(4) at the rock/water contact, ions of the crystal lattice are released (a physical process):

$$CaCO_{3\ calcite} \rightleftharpoons Ca^{2+} + CO_3^{2-} \tag{4}$$

(5) the created CO$_3^{2-}$ associate with the H$^+$ from step (3)

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{5}$$

Fig. 3. Solubility of CO_2 in NaCl brine at 68.9 bar. Data from Chang et al. (1998).
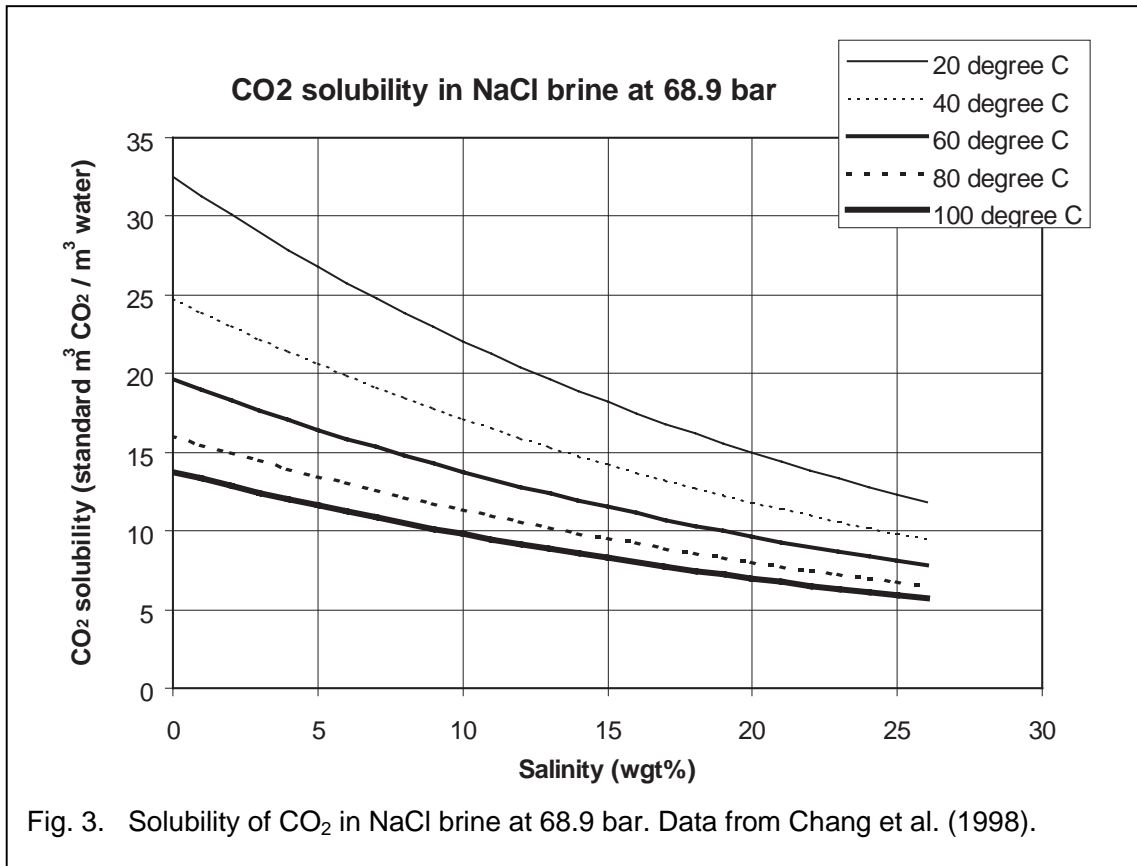
(6) their association impoverishes the water in CO_3^{2-} along the rock/water interface, which disturbs the dissolution equilibrium with the solid $CaCO_3$,and the ion product no more corresponds with the solubility product K (K = $[Ca^{2+}][CO_3^{2-}]$). Therefore more $CaCO_3$ is dissolved (step 4) to bring the ion product to the size of K. K depends of temperature: according to Picknett (1973) K is 4.1×10^{-9} and 3.7×10^{-9} at 5°C and 25°C respectively. By the consumption of H^+ (step 5) more CO_2 get hydrated (step 2) and more CO_2 will diffuse into water. That is: by the association of H^+ with CO_3^{2-} (step 5) all the reaction steps are reactivated until a new equilibrium is brought about. It is thus obvious that high concentrations of artificially added CO_2 (high P_{CO2} in step 1) will strongly force the reactions (step 1 - 5) to the right. A summing up of the five steps results in the commonly used dissolution equation for calcite dissolution:

$$CaCO_{3 \text{ calcite}} + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad (6)$$
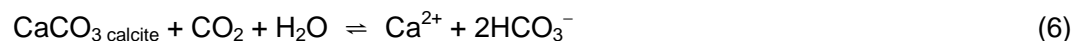
At equilibrium it is assumed that the *rates* of the opposing reactions are equal so that no changes in the mass of solid (the calcite rock) and in the solution composition are observable with time, the equilibrium constant K being equal to the ratio of the forward (k_1) and the reverse (k_2) rate constants, that is: K = k_1/k_2 = [reactant]/[product] (even though minor dissolutions and precipitations may occur all the time). If the conditions in the $CaCO_3$ - CO_2 - H_2O system are not in equilibrium a dominant directional rate R will prevail - the forward or the reverse one. A commonly used equation to estimate the rate of carbonate mineral dissolution (Morse & Arvidson, 2002) is as follows:

$$R = -dm_{calcite}/dt = (A/Vk)(1-\Omega)^n \tag{7}$$

where R is the rate in μmole m^{-2}h^{-1}, m is moles of calcite, t is time, A is total surface area of solid (the calcite), V is the volume of solution, k is the rate constant, n is a positive constant (the "order" of the reaction), and Ω is the saturation state, $\Omega = IAP/K_{sp}$, where IAP is the ion activity product and K_{sp} the solubility product for the solid.

Several *rate-controlling processes* occur during the dissolution of calcite in an open system (the reactions of step 1 - 5 above), at least seven can be included (Bögli, 1978; Morse & Arvidson, 2002):

1. *Diffusion of reactants* through the solution to the solid surface.
2. *Adsorption of the reactants* on the solid surface.
3. *Migration of the reactants* on the solid surface to high-energy sites (dislocations, steps etc.).
4. *Chemical reactions* at the solid surface between adsorbed reactant and solid.
5. *Migration of products* away from the reaction sites.
6. *Desorption of the products* to the solution.
7. *Diffusion of products* away from the solid surface to the bulk solution.

The slowest one of these processes will determine the dissolution rate. When the diffusions of step 1 and 7 are rate-limiting, the reaction can be described as diffusion controlled, and when one of the processes of step 2 - 6 controls the rate, the reaction is surface controlled. Highly soluble minerals usually participate in diffusion controlled reaction. Carbonate minerals, that are relatively insoluble, show surface controlled reaction rates at conditions close to equilibrium and at lower degrees of disequilibrium, but when *very* high degrees of disequilibrium prevail (e.g. the conditions around the injection well during CO_2 flooding) the reaction rates get diffusion controlled (Berner, 1978). The thickness (being in μm scale) of the stagnant *boundary layer*, which is formed in between the surface itself of the solid and the surrounding moving water (laminar or turbulent flow), can also control the rate of reaction, as the water movement is slow in this layer relative to the transport velocity by diffusion.

It is also well-known that the presence of foreign ions in the solution may severely lower the dissolution rates of calcite. Since the fifties the effects from a series of these *reaction inhibitors*, that first and foremost affect the reactions by their interactions with the surfaces of the calcite, have been studied (Morse & Arvidson, 2002). Both the presence of silica, nitrate, phosphate, sulphate, and metal ions like Sr^{2+}, Ba^{2+}, and Mg^{2+} shoved inhibitory influences on the dissolution reactions. However, the utility of these informations from the laboratory experiments may be rather limited for natural waters (brines) in deeper reservoir rocks, as the interstitial solutions can there be chemically very complex, and as the reactions, at least in some distance from the injection well, proceed in conditions very close to equilibrium.
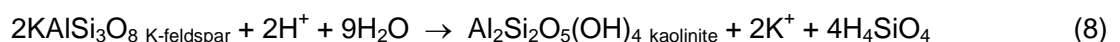
The calcite dissolution kinetics mentioned above assumed $CaCO_3$ - CO_2 - H_2O systems with a free surface open to the CO_2 of the atmosphere or to the gaseous or supercritical CO_2 from an artificial source. However, when the waters percolate through the narrow rock

passages (very narrow fracture joints and stylolitic joints, that may have previously been solution-enlarged) either downwards towards the phreatic zone, or out from an injection well in a reservoir, the CO_2-enriched water flows in completely filled conduits and exchange of CO_2 is therefore no more possible after some time, since the free surface to the atmosphere or the CO_2 source no more exist. In a *closed system* like this, with a theoretic P_{CO2} in equilibrium with the dissolved CO_2, the calcite dissolution rate will be extremely slow, where pore spaces and joint widths are so small (μm scale) that the ion transport takes place by diffusion. Under the surface-controlled conditions near equilibrium it is probably unimportant that the calcite dissolution, with constant P_{CO2}, is lowered with rising temperature. If a laminar flow prevail, or even a turbulent one (when the dimensions of joints are larger than ca. 0.5 cm), some further calcite dissolution may take place by *mixing corrosion*, by which a water regains its aggressiveness by mixing with water of different CO_2 content (e.g. Bögli, 1978). This may take place at the crossing of two joints or conduits. The difference in salinity and/or H_2S content has also proved to be important for the renewed dissolution.

Calcite and dolomite dissolution/precipitation processes may also play some part in sandstone reservoir rocks in which non-carbonate crystals or grains (quartz, feldspars, pyroxenes etc.) are cemented together by calcite and/or dolomite crystals precipitated during the diagenetic history of the original terrigenous sediment. In the process of CO_2 flooding, non-carbonate grains of the rock may be loosened, at least near the injection well, because the cementing minerals get more or less dissolved. This may result in a general lowering of the permeability of the rock as loosened fines can clog up pore throats and narrow joints. The same can, of course, happen if the non-carbonate grains/minerals are cemented together by the relatively more soluble anhydrite crystals, or other soluble salts (e.g. halite).

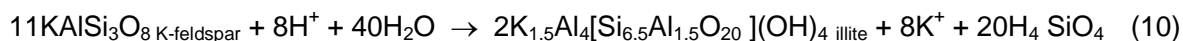## Reactions between CO_2 and silicate minerals

During CO_2 flooding experiments on sandstone samples feldspars are observed to be more or less dissolved. In a study on water–rock interactions on Tensleep Sandstone plugs (at a temperature of 80°C, a P_{CO2} of 166 bars, and using synthetic brines) it was thus observed that K-feldspar was corroded and kaolinite crystals precipitated during the experiments (Shiraki & Dunn, 2000). It was assumed that the following reaction took place:

$$2KAlSi_3O_{8 \text{ K-feldspar}} + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_{4 \text{ kaolinite}} + 2K^+ + 4H_4SiO_4 \qquad (8)$$

the H^+ ion coming from the dissociated H_2CO_3:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (9)$$

An artificially caused weathering like that of the K-feldspar may probably also result in a formation of other types of clay minerals. Both in "normal" weathering and in low-temperature hydrothermal processes are different clay minerals – depending on the climatic/chemical conditions - thus observed to be formed by the alteration of aluminium silicates (c.f. e.g. Krauskopf, 1979): besides kaolinite especially montmorillonite and illites. The formation of the latter may follow the reaction:

$$11KAlSi_3O_8 \text{ K-feldspar} + 8H^+ + 40H_2O \rightarrow 2K_{1.5}Al_4[Si_{6.5}Al_{1.5}O_{20}](OH)_4 \text{ illite} + 8K^+ + 20H_4SiO_4 \quad (10)$$
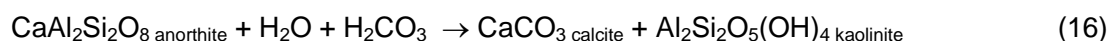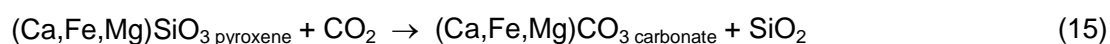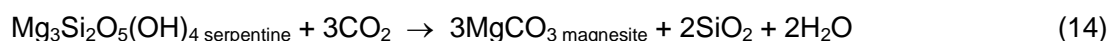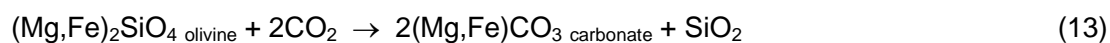
Eq. 10 is only an approximate reaction, because the contents of K, Si and Al vary significantly in illite. Relative to kaolinite (Eq. 8) illite may form at higher activities of SiO_2 and K^+ and lower activities of H^+ (Deer et al., 1992). Such reactions of K-feldspar to form kaolinite or illite will probably occur in some sandstone types in the area close around the injection well for CO_2 flooding or CO_2 sequestration in a reservoir.

In CO_2 experiments on sandstone rocks some silica minerals are observed to be converted to carbonate minerals and silica by *carbonation.* A carbonation is a chemical process during which minerals containing calcium, magnesium, sodium, potassium and/or iron are transformed into carbonates or bicarbonates of these metals by CO_2 dissolved in water. The created carbonate minerals may be stable over very long periods of time. In the laboratory the carbonations are provoked by the injection of supercritical CO_2, but similar processes occur naturally, although very slowly when rocks get weathered. The idea that carbonation could be used as a method for CO_2 storage (sequestration) in a *solid form* was proposed in 1990 (Seifritz, 1990), but several studies have since been initiated, dealing with both technical and economic problems of "mineral sequestration". In some of the studies a "direct mineral carbonation method" is used, in which supercritical CO_2 is dissolved in a slurry consisting of water with additives (e.g. NaCl) and a high concentration of a fine-grained mineral reactant (e.g. olivine). O'Connor *et al.* (2000) used crushed olivine and serpentine as solids in their experiments. For olivine the following reaction equations seem to be valid:

$$Mg_2SiO_4 \text{ forsterite} + 4H^+ \rightarrow 2Mg^{2+} + H_4SiO_4 \text{ or } SiO_2 + 2H_2O \quad (11)$$

$$Mg^{2+} + HCO_3^- \rightleftharpoons MgCO_3 \text{ magnesite} + H^+ \quad (12)$$
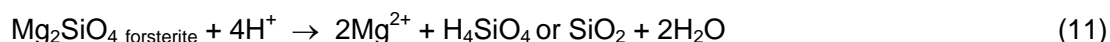
The H^+ ion in Eq. 11 and the HCO_3^- in Eq. 12 derive from the CO_2 dissolved in water, cf. Eq. 9.
The following equations state the carbonation reactions when olivines, serpentine, pyroxene, and anorthite respectively, are transformed:

$$(Mg,Fe)_2SiO_4 \text{ olivine} + 2CO_2 \rightarrow 2(Mg,Fe)CO_3 \text{ carbonate} + SiO_2 \quad (13)$$

$$Mg_3Si_2O_5(OH)_4 \text{ serpentine} + 3CO_2 \rightarrow 3MgCO_3 \text{ magnesite} + 2SiO_2 + 2H_2O \quad (14)$$

$$(Ca,Fe,Mg)SiO_3 \text{ pyroxene} + CO_2 \rightarrow (Ca,Fe,Mg)CO_3 \text{ carbonate} + SiO_2 \quad (15)$$

$$CaAl_2Si_2O_8 \text{ anorthite} + H_2O + H_2CO_3 \rightarrow CaCO_3 \text{ calcite} + Al_2Si_2O_5(OH)_4 \text{ kaolinite} \quad (16)$$

The amount of CO_2 that can be dissolved in water depends on pressure and temperature (Figs. 2, 3). The pH of water saturated with CO_2 likewise depends on pressure and temperature. In the Rangely Field of Colorado, where the reservoir pressure lies in the range 17.9 − 20.7 MPa, the pH of the formation water lies in the range 3.5 − 4.5 (Bowker &

Shuler, 1991). The lowest pH values occur close to the injection wells where the CO_2 saturation is inferred to be highest, and pH decreased towards the production wells.

Transport of CO_2 in a reservoir is governed by the processes of flow and diffusion. In the flow process CO_2 is carried through the pore system of the rock by bulk movement of the fluids. The flow process is governed by pressure gradients, viscosity, rock permeability, wettability, and interactions between the fluid phases present in the pore system. The diffusion of CO_2 is governed by the diffusion coefficient of CO_2 in the relevant fluid phase, the concentration gradient of CO_2, rock permeability, and the spatial distribution of any additional fluid phases. In general, flow processes will dominate the mass transfer of CO_2 when pressure gradients and permeabilities are large, typically close to injection wells and production wells, while diffusion processes will dominate the mass transfer of CO_2 when pressure gradients and rock permeabilities are small, typically in fine grained rocks far from these wells. The diffusion coefficient of CO_2 in water may be estimated from the equation of Grogan & Pinczewski (1987):

$$D_{CO_2,w} = 5.72 \cdot 10^{-12} \cdot \frac{T}{\mu_w} \tag{17}$$

where $D_{CO_2,w}$ is in m^2/s, T is the temperature in $^{\circ}$K, and μ_w is the viscosity in cP. The diffusion coefficient for CO_2 in oil may be estimated from the equation of McManamey & Woollen (1973):

$$D_{CO_2,o} = 1.41 \cdot 10^{-10} \cdot \mu_o^{-0.47} \tag{18}$$

where the notation is similar to Eq. 17.

Mass transfer by pure diffusion is a very slow process. In an idealised case of instantaneous filling of a reservoir with CO_2 it is calculated that it takes about 1000 years before diffusion causes the concentration of CO_2 at a point 20 meters inside the seal to reach a level of 10 % of the concentration in the reservoir. This case assumes that no CO_2 has been used by mineral reactions inside the seal. If CO_2 is used by mineral reactions, the propagation of CO_2 will be even slower.

CO$_2$ effects on rocks – field and laboratory experience

CO$_2$ effects on chalk – evidence from laboratory experiments

Very few researchers have addressed the chalk lithology with respect to CO$_2$ effects. Jensen et al. (2000) mentions laboratory experiments on chalk from the Ekofisk field, which indicates that "immediate and vigorous dissolution reactions with large axial strains and high strain rates" takes place upon introduction of CO$_2$-charged injection water. Unfortunately, no further details are presented. The reference has some weight because the operator, Phillips Petroleum Company Norway, approved the publication of the results.

Schroeder et al. (2001) conducted CO$_2$ flooding experiments at 8-10 MPa and a temperature above 30 °C on chalk samples, and did not find any effect on permeability. Mechanically, the CO$_2$ flooding did not cause any weakening of the rock – in fact it is stated "that the CO$_2$ injection seems to reinforce the chalk" (op.cit.). However, the provenance of the chalk samples, and experimental details like temperature, timing and amount of injected CO$_2$ are not given.

Olsen (1995) found that 5 chalk samples of Campanian – Conacian age from the Linde-1 well, Denmark experienced restricted alterations during laboratory experiments with exposure to supercritical CO$_2$ and saline brine at 50 °C and 14 MPa fluid pressure for periods up to 17 days. The mineralogy of the samples was strongly dominated by calcite. Permeability to brine was reduced with 0 to 36 %, while permeability to gas, after cleaning, was increased with 0 to 10 %. Porosity change ranged from –0.27 to +0.16 p.u. (porosity unit), which was close to the detection limit of 0.12 p.u. for the porosity determination. Fines were produced from all 5 samples, and the reduction in brine permeability was attributed to blocking of pores by fines. The small increase in gas permeability was attributed to preferential dissolution along high permeability conduits in the samples. Investigation with SEM found clear evidence of calcite dissolution close to the inlet of one sample. In the other 4 samples evidence for dissolution was either equivocal or absent. SEM images from sample centres were all classified as unaltered chalk. Chemical analyses of produced brine showed significantly increased contents of Ca^{2+} and Sr^{2+}. Mg^{2+} increased in most experiments, but did decrease in one experiment. Ipsen (1995) found that the brine in this instance initially was supersaturated with dolomite. Investigation with SEM EDS, however, was unsuccessful in finding precipitated dolomite. Ipsen (1995) also found that the experiments did not reach chemical equilibrium.

The reason for the different extent of reactions in the experiments of Jensen et al. (2000), Schroeder et al. (2001), and Olsen (1995) is not clear, but may possibly be related to lithological differences, e.g. different diagenesis and/or different contents of clay minerals and quartz. If true, this indicates that samples for experiments intended for prediction of reservoir behaviour should be selected to match the lithology as closely as possible. P-T

conditions for the Ekofisk experiments were not stated (Jensen et al., 2000), but if Ekofisk reservoir conditions were used, i.e. P ~ 45 MPa, and T ~ 130 °C, the different P,T conditions may also have influenced the different course of the experiments.

CO$_2$ effects on carbonates – evidence from Permian Basin field operations and laboratory experiments

For carbonates in general, the evidence from field operations and laboratory experiments is much more comprehensive than for the rather restricted lithology of chalk. In particular, the CO$_2$ EOR operations in the Permian Basin of Texas and New Mexico, U.S.A. have resulted in a large number of references.

Generally, the CO$_2$ operations in the Permian Basin take place in dolomitized reef complexes of late Pennsylvanian to Permian age. Anhydrite stringers are important in many reservoirs. Reservoir seals consist of dense mudstones and anhydrite of Permian age. Conditions in the reservoirs are mainly supercritical to CO$_2$, with reservoir pressure in the range 10 – 24 MPa, and reservoir temperature in the range 32 – 58 °C. However, close to wellbores the CO$_2$ conditions may be sub-critical (Brownlee & Sugg, 1987). The carbonates of the Permian Basin have experienced tertiary recovery by CO$_2$ injection at least since 1972 (Newton & McClay, 1977). In 1994 the number of active CO$_2$ injection operations reached 33 (Lang & Biglarbigi, 1994).

Several of the CO$_2$ injection operations have experienced significantly increased scales precipitation after commencement of CO$_2$ injection, e.g. the Kelly-Snyder field (Newton & McClay, 1977), the Slaughter field (Stein et al., 1992), Sharon Ridge Canyon Unit (Yuan et al., 2001), and Vacuum field (Brownlee & Sugg, 1987). The increased occurrence of scales is generally taken as evidence of dissolution of carbonate minerals within the reservoir in the case of calcite scales (Newton & McClay, 1977, Yuan et al., 2001), or dissolution of anhydrite in the case of sulphate scales (Brownlee & Sugg, 1987).

From analysis of well tests Graue & Blevins (1978) showed that dissolution of carbonate minerals occurred in the Kelly-Snyder field. In the Levelland field a monitoring project with two observation wells documented large increases in contents of total dissolved solids (TDS), bicarbonate, Ca^{2+}, Cl$^-$ and Na$^+$ ions (Henry et al., 1981), which was interpreted to result both from exposure of connate water to CO$_2$ in an oil-wet reservoir, and from dissolution of carbonate minerals. Mathis & Sears (1984) compared pre-CO$_2$ flood cores with post-CO$_2$ flood cores of San Andres dolostone from the Wasson field Denver Unit. They found that vuggy and sometimes moldic porosity had increased approximately 1 p.u., which was statistically significant, while changes in intercrystalline and fracture porosity were statistically insignificant. Thin section examination and chemical analysis of fluids gave evidence of anhydrite dissolution, but thin section examination found no evidence of dolomite dissolution. The lack of dolomite dissolution was explained by lack of transport mechanisms for residual, dolomite saturated pore water in the situation where the pore system was filled with a CO$_2$-rich fluid. After the CO$_2$ flood, a brine flood flushed the residual, dolomite saturated pore water, but the amount of dissolved solids was too low to cause any measurable porosity increase. Svec & Grigg (2001) made experiments with CO$_2$ floodings on a sample

of San Andres dolostone, and found that WAG flooding with a total of 2086 pore volumes of brine and 1367 pore volumes of CO_2 caused strong dissolution of both anhydrite and dolomite, creating new, vuggy porosity. Dolomite cement appeared to dissolve more readily than dolomite grains. The porosity change was not quantified, but permeability increased from approximately 30 mD to approximately 190 mD during the flooding, indicating a very significant dissolution. A control experiment on the same lithology, but involving a brine flood without CO_2 caused similar dissolution effects on the anhydrite, but did not dissolve the dolomite to any significant degree. The flooding involved large amounts of fresh brine and CO_2 , which was not recirculated through the sample. This setup is not representative of conditions inside a reservoir, but may provide an analogue to conditions close to a CO_2 injection well.

Declines in well injectivity are common in CO_2 flooding operations in the Permian Basin. Patel et al. (1987) ascribed reduced injectivity in the Wasson field Denver Unit to relative permeability effects caused by a change from oil-wet towards more water-wet conditions during CO_2 flooding. Noticeably, they conclude that precipitation of inorganic material probably did not contribute to the injectivity reduction. Potter (1987) made experiments with samples of San Andres dolostone and Grayburg dolostone and found that flooding with a miscible mixture of crude oil and CO_2 did change wettability towards more water-wet states, but only to a small degree. Stein et al. (1992) ascribed reduced injectivity in the Slaughter field to relative permeability effects. Henry et al. (1981) found that reduced injectivity in the Levelland field was caused by unspecified factors deep within the formation, as opposed to wellbore conditions like skin and high gas saturations around the injector.

Precipitation of wax or asphaltenes is a common occurrence in flooding operations (Brownlee & Sugg, 1987, Patel et al., 1987, Pittaway et al., 1986). It mainly occurs in the production equipment after CO_2 breakthrough (Parra-Ramirez et al., 2001). The phenomenon is linked to phase relations between CO_2 and hydrocarbon components, and appears to have no relation to mineral dissolution or precipitation reactions.

It should be noted that many of the CO_2 operations in the Permian Basin do not report any mineral dissolution or scales production, e.g. South Wasson Clearfork Unit (Burbank, 1992), Means field (Magruder et al., 1990), Maljamar field (Pittaway et al., 1985, 1986, Moore & Clark, 1988), and Welch San Andres field (Keeling, 1984). This may indicate that mineral reactions are not considered significant in relation to the operations. Problems related to geomechanical instability of the reservoir rock are not reported in any of the reviewed papers on Permian Basin operations.

CO_2 effects on carbonates – evidence from field operations and laboratory experiments outside the Permian Basin

Svec & Grigg (2001) performed a CO_2 WAG experiment at P=13.8 MPa and T=38 °C on a 50 cm long sample of Indiana limestone. The rock is a bioclastic grainstone of Mississippian age composed mainly of calcite with minor quartz replacements. A total of 250 PV's of brine and 243 PV's of CO_2 were flooded through the sample. The flooding resulted in dramatic dissolution of the rock, creating an open channel reaching 28 cm into the sample

from the inlet end. In the outlet end of the sample carbonate minerals were precipitated, resulting in a permeability reduction of approximately 50 % in this part of the sample. In the inlet end the dissolution obviously created an immense permeability increase.

Beliveau & Payne (1991) reports from CO_2 operations in the Weyburn field of Saskatchewan, Canada, which produces oil from limestone and dolostone of Mississippian age. Precipitation of wax or asphaltenes in the wellbores increased sharply after the onset of CO_2 flooding, but without any indication that precipitation took place in the reservoir itself. No mention of mineral reactions or injectivity variations is made.

Good & Downer (1988) describes CO_2 injection into crystalline dolostone in the Cedar Creek field of Montana, Watts et al. (1980) describes CO_2 injection into mainly dolomitic rocks in the Hilly Upland field of West Virginia, Thakur et al. (1984) describes CO_2 injection into dolomitic limestone and dolostone of the Little Knife field of North Dakota, and Zoltán et al. (1999) describes CO_2 injection into limestone and dolostone of hydrocarbon fields of Hungary. None of these paper reports mineral reactions or abnormal injectivities.

CO_2 effects on sandstone – evidence from field operations and laboratory experiments

The number of mineral reactions that potentially can take place upon exposure to CO_2 are much larger in sandstone than carbonate rocks, because of the more complex mineralogy of most sandstones. Many of the potential mineral reactions in sandstone involve silicate minerals, which have much lower reaction rates than carbonate minerals (Czernichowski-Lauriol et al., 1996). Therefore, equilibrium may take many years to be established in a sandstone reservoir.

Pearce et al. (1996) investigated the Bravo Dome of New Mexico, which consists of a Permian arkosic sandstone with varying amounts of feldspar and clay minerals. A thin sheet (6 meter) of anhydrite provides a seal. The reservoir is naturally filled with CO_2, which probably originated from volcanic activity. It is one of the main sources of CO_2 for EOR operations in the Permian Basin. The filling of the reservoir is interpreted to have taken place less than 50000 years before present. Thus, the Bravo Dome is a natural analogue for CO_2 disposal in a sandstone reservoir. Petrographic evidence indicates that significant amounts of anhydrite, dolomite, and plagioclase were dissolved by CO_2-rich groundwater. It is noticed that the 6 meter thick anhydrite seal has not been breached by the dissolving water. In the vicinity of faults kaolinite, zeolite, and gibbsite appear to have formed by reaction with CO_2-rich water. Experiments on samples of Triassic sandstone and mudstone of similar lithology from U.K. outcrops corroborate the dissolution of anhydrite, dolomite, and feldspar, and suggest the precipitation of calcite, halite, and possibly smectite. The mudstones often experienced strong disintegration from the exposure to CO_2, caused by swelling of smectite clay and dissolution of cement.

The Rangely field, Colorado, utilizes miscible CO_2 EOR in production from the Pennsylvanian-Permian carbonate cemented Weber sandstone (Bowker & Shuler, 1991). The concentration of Ca^{2+}, Mg^{2+}, Fe^{2+}, and Br^- in produced water has increased significantly since

onset of CO_2 injection, which is considered evidence for dissolution of dolomite, ferroan dolomite, and ferroan calcite. Coreflood experiments reveal distinct dissolution of dolomite cement. Net permeability did not change because the permeability enhancement by mineral dissolution was offset by pore blocking by migrating clays. Formation water pH dropped from 7-7.5 to 3.5-4.5 after onset of CO_2 injection. Going from injection wells to production wells pH increased from 3.5 to 4.5, partly because CO_2 was spent in mineral reactions, partly because of changing pressure and temperature. Large amounts of scales were precipitated in the Rangely field, comprising carbonates, sulphates (barite and celestine), and iron sulphide, reflecting the significant amount of mineral reactions that took place in the field. Precipitation of asphaltenes also took place (Wackowski & Masoner, 1994).

Hsie & Moore (1986) report that in the Quarantine field of Louisiana, a miscible CO_2 WAG operation caused significant production of sand from a poorly consolidated Miocene sandstone. Sand production, did not occur previously, and is believed to be caused by dissolution of calcite, dolomite and siderite cement. After loosing the cementing minerals, sand grains were free to move towards the production wells.

Sayegh et al. (1990) performed supercritical CO_2 flooding experiments on Upper Cretaceous Cardium sandstone from the Pembina Cardium field, Alberta, which contained between 12 and 40 volume percent carbonate minerals. All four experiments showed the same behaviour of permeability reduction followed by partial permeability recovery. A significant amount of fines were produced, which explains the permeability behaviour. A control experiment with brine flooding without CO_2 did not show any significant permeability change. Examination by XRD and SEM showed that the CO_2 floods had dissolved calcite, siderite and dolomite, which resulted in enlargement of pore bodies.

Shiraki & Dunn (2000) conducted supercritical CO_2 flooding experiments on Tensleep sandstone from the Bighorn Basin, Wyoming. This rock is cemented by dolomite and anhydrite. The major reactions observed were dissolution of dolomite, precipitation or dissolution of anhydrite depending on conditions, and alteration of potassium feldspar to kaolinite. In general, permeability decreased during the experiments, which is explained by the growth of kaolinite. Thermodynamic calculations showed kaolinite to be stable during the experiments, and SEM examination actually found precipitated kaolinite.

Ross et al. (1982) performed CO_2 flooding experiments on Jurassic Yorkshire sandstone, which contained approximately 20 % ferroan calcite cement. The cement was strongly dissolved during the experiment, preferentially along high-permeability zones. In accordance permeability showed a strong increase. The authors also tested a Rotliegendes dolomitic sandstone from the Indefatigable gas field in the North Sea. The results were much similar to the Yorkshire sandstone, except that the dissolved mineral in this instance was dolomite. The resemblance includes the preferential dissolution along high-permeability zones.

Krumhansl et al. (2002) performed flooding and static experiments with subcritical CO_2 and brine on Permian Queen formation sandstone from New Mexico. The rock was an arkosic sandstone with carbonate cement and diagenetic potassium feldspar, but without any clay minerals. During the experiments calcite cement was dissolved from the rock, and a fine-

grained mineral suggested to be clay or zeolite was precipitated in the pores. In the outlet system of the rig, where the pressure was lower, $CaSO_4$ was precipitated. The experiments were partly corroborated by thermodynamic calculations, that predicted dissolution of calcite, and, under certain circumstances, precipitation of gypsum.

Czernichowski-Lauriol et al. (1996) performed flooding and static experiments with CO_2-saturated brine on Permo-Triassic samples of Sherwood Sandstone, Mercia Mudstone and anhydrite. It was found that dissolution of anhydrite coupled with precipitation of calcite might take place under certain circumstances, which, however, are not further specified.

Summary and conclusions

Many rock-forming minerals may react with CO_2 at the P-T conditions to be expected in a geological CO_2 storage at a depth of 500 to 5000 meters. Carbonate minerals as well as silicate minerals may be dissolved or precipitated. Reactions rates involving carbonate minerals are generally much larger than reaction rates involving silicate minerals. The most significant indication to what extent and at what rate such reactions will take place in CO_2 sequestration operations comes from CO_2 EOR operations. Laboratory experiments and natural CO_2 reservoirs provides additional evidence.

The evidence about CO_2 interactions with dolomitic carbonates comes mainly from the Permian Basin of Texas and New Mexico, but also from several CO_2 EOR operations at other places. The evidence is that some dissolution of carbonate minerals and anhydrite takes place, but not to an extent that seriously affects the operations. Neither have the CO_2 injection operations compromised the geomechanical stability of the reservoirs. The experience from these operations reach at least 30 years back in time.

The evidence from calcitic carbonates is much more restricted and much more inconclusive. Experiments on chalk from Linde, Denmark, indicates calcite dissolution in a restricted manner that do not affect the mechanical stability of the rock. Experiments by Schroeder et al. (2001) on chalk of unspecified origin gave similar results. In contrast to this, experiments on chalk from Ekofisk, Norway, indicates dissolution processes that seriously affects the mechanical stability of the rock, and experiments on outcrop Indiana limestone resulted in large scale dissolution of the rock. The apparent contradiction of these experiments could possibly be caused by the different sample lithology, and, in the case of the Linde chalk and Indiana limestone, certainly the very different CO_2 throughputs of the experiments. An implication is that lithology and P-T conditions in any laboratory or pilot projects should match the potential sequestration reservoir as closely as possible.

Two groups of mineral reactions take place in sandstone exposed to CO_2. Group 1 comprises reactions with carbonate cement and anhydrite, and may result in dissolution of calcite, dolomite, siderite, and anhydrite, with possible precipitation of gypsum. Group 2 comprises reactions with silicate minerals, and may result in dissolution of feldspar and possibly ferromagnesian silicates, and precipitation of clay minerals and possibly zeolites and carbonates. The reactions of Group 1 are similar to the reactions that are recognised in carbonate rocks, but there is a tendency that the extent of the reactions, i.e. the amount of dissolved material, is larger than in carbonate rocks. The extent of Group 2 reactions generally appear to be limited, but it should be noticed that equilibrium probably was not reached in either laboratory experiments or fields operations, because of the slow reaction rate for silicate minerals. Several sandstone experiments and field operations report mechanical failure of the rock upon exposure to CO_2. This corroborates the notion of generally greater extent of mineral reactions in sandstone compared to carbonates.

Examples of breakdown of the seal above a CO_2 filled reservoir have not been encountered. The thin anhydrite seal above the Bravo Dome natural CO_2 reservoir appears to

have stayed tight for several thousands of years, even though anhydrite is known to be a very reactive mineral.

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