The effects of impure CO\(_2\) on reservoir sandstones: results from mineralogical and geomechanical experiments

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Project and Methodology:
Within the German project COORAL\(^*\) the behaviour of potential reservoir rocks during the injection and geological storage of CO\(_2\) with inherent impurities such as SO\(_2\) and NO\(_x\) is studied in laboratory experiments. A combination of geochemical and geomechanical studies are performed as autoclave experiments and subsequent tests in a triaxial pressure cell with dry and brine saturated sandstone samples. For a comparative study controlled altered rock samples (with supercritical (sc)CO\(_2\) + SO\(_2\) + NO\(_x\) in an autoclave system) were loaded in a triaxial pressure cell under in-situ PT-conditions (Fig. 1), to study changes of the mineralogical, geochemical and geomechanical rock properties. Working materials are sandstones of possible reservoir formations of the North German Basin (Fig. 2).

Results:
- Silicate Bunter sandstone samples show decreased rock strength under enhanced pore fluid pressure (from 60% to 80% \(\sigma_2\); Fig. 3 A).

- A clear dependency of chemical fluid composition and confining pressure (lithostatic) on the maximum differential stress (effective stress) especially on carbonate sandstones (Fig. 3 B) is obvious according to the experimental results.

- Decrease of rock deformability (strain softening) due to the alteration with pure scCO\(_2\) (Fig. 4).

- Increase of rock deformability (strain hardening) during the alteration under the influence of CO\(_2\) + 1000 ppm SO\(_2\) (Fig. 4).

- Contents of dissolved metals in the reaction fluid during the autoclave alteration experiment depends on the impurities (SO\(_2\) and NO\(_x\)) in the CO\(_2\) gas stream (Fig. 5 A).

- Dissolution rates (Fig. 5 B) of bulk rock (sandstones) as well of single minerals varies with the carbonate fraction. Rates are calculated according to the formula:

\[
\text{rate} = \frac{d}{t} = \frac{V}{A \cdot M}
\]

\(r\): dissolution rate (mol m\(^{-2}\) s\(^{-1}\))

\(A\): inner surface (BE) (m\(^2\)/g)

\(m\): molar concentration

\(t\): time (s)

\(V\): fluid volume (l)

\(M\): mass (g)

Conclusions:
- The strength behaviour of different types of sandstones varies with the degree of sample saturation, the pore fluid pressure, pore fluid chemistry and temperature.

- Various types of fluids cause different maximum differential stresses (effective stresses) at changing pressure conditions. This may be due to different pore space geometries and permeability.

- Different impurities in the reaction fluids in the autoclave (pure CO\(_2\) + SO\(_2\) or NO\(_x\)) showing variable but generally increasing element dissolutions from the rocks (Ca, Si, Al, Ba) during the experimental course.

- The experimental determined differences in rock strength and elastic deformability of altered samples demonstrates clear trends of chemically induced mechanical weakening of the studied sandstones.

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Fig. 1: The experimental flow autoclave samples were contained airtight in a autoclave system (with brine + scCO\(_2\) = NO\(_2\) + SO\(_2\) under 100°C and 100 bar, 2-4 weeks) and then loaded in a heatable triaxial pressure cell (under 5°C to 80°C and up to 30 MPa confining pressure, 35 MPa pore fluid pressure and a maximum of 107 MPa axial pressure) with CO\(_2\) + up to 500 ppm NO\(_2\) and up to 1000 ppm SO\(_2\) as pore fluid. Also untreated samples were tested in the triaxial cell.

Fig. 2: Three types of sandstones from the North German Basin (samples with Ø3-7 mm, L=140 mm):
A: Silicate sandstone "Müller Bunter Sandstein" (lower Triassic: porosity ~ 72%)
B: Carbonate sandstone "Müller Bunter Sandstein" (lower Triassic: porosity ~ 16%)
C: Silicate and carbon "Rottländer sandstone" (lower Permian: porosity ~ 8%)

Fig. 3: Differential stress diagrams showing the influence of rock saturation, confining pressure (\(p_s\)), pore fluid composition (CO\(_2\) with SO\(_2\) and NO\(_x\)) and pore fluid pressure (p) on the maximum effective stress \(\sigma_1\), \(\sigma_2\), \(\sigma_3\) - effective confining pressure \(p_c = \sigma_2 - p\) for silicate (A) and carbonate bound (B) Bunter sandstones. The differently coloured polygons connect sample points of equal pore fluid chemistry. A total confining pressure of 25 MPa corresponding 1000 m reservoir depth.

Fig. 4: Variation of elastic deformation properties (modulus of deformation) of silicate sandstone samples due to CO\(_2\)-alteration and the pore fluid chemical composition

Fig. 5: Development of chemical fluid composition during alteration experiments in silicate sandstones (A): dissolution rates of bulk sandstone types and single minerals (B)

Fig. 6: SEM-images of silicate and carbonate bound Rottländer sandstone samples after the treatment with brine and scCO\(_2\) + 500 ppm NO\(_x\) in the autoclave. Images A and B shows dissolution effects on the carbonate matrix and C and D demonstrates secondary calcite precipitation axis-oriented on dissolved calcite tops (C) and on a carbonate surface (D).