Abstract

This dissertation deals with the effect of CO_2 and acid exposure on the hydromechanical behaviour of Italian carbonatic clayey caprocks. The sealing capacity and integrity of the caprock can be affected by the geo-chemo mechanical processes involved in CO_2 storage. The injected CO_2 might react with the caprock altering its mineralogical composition and ultimately affecting its mechanical properties.

In this context, the effects of CO_2 and acid exposure on the hydromechanical behaviour of caprocks were investigated in laboratory experiments. The caprocks studied in this study are structured, carbonatic Italian clays from different formations and depths. The exposure to CO_2 and acid was carried out through two different types of tests. In the first type of tests, samples were first exposed to different forms of CO_2, namely dry $scCO_2$, wet $scCO_2$ and CO_2-saturated brine. Mechanical, microstructural, and mineralogical tests were conducted on exposed samples and on twin non-exposed samples. The results were compared to outline the possible effects of CO_2 exposure. The mechanical tests included consolidated undrained triaxial and oedometer tests. The triaxial tests were conducted in high and medium pressure triaxial cells whereas oedometer tests were conducted up to a vertical stress of 25 MPa. The microstructural and mineralogical study involved the determination of equivalent calcite content, mineralogy, pore size distribution and fabric structure. In the second type of tests aimed at studying the short-term effects of CO_2 injection, reconstituted and intact samples were exposed to low pH water solution by diffusion and advection under oedometer conditions, while monitoring induced displacements and determining the induced changes in equivalent carbonate content.

Exposure to dry $scCO_2$ was found to induce specimen drying. The combined effects of geochemical reactions from CO_2 and water evaporation increased the carbonate content. Changes in mineralogical composition were coupled with fabric effects observed through pore size distribution, as a decrease was noted in the frequency of large pore sizes. Mechanically a slight increase in the strength of specimen exposed to dry $scCO_2$ was observed. Some intact samples exposed to wet $scCO_2$ for 30 days showed a reduced peak

strength compared to non-exposed samples. This might be due to micro-fractures detected through post-exposure CT scans. The exposed specimen that did not have micro-fractures showed a peak strength similar to that of the non-exposed specimen although the failure was not that brittle. It also showed higher residual strength compared to non-exposed specimen.

Acid exposure of reconstituted and intact samples was carried out in oedometer cells to investigate the short-term effects of CO_2 injection. The response of specimens after exposure, either induced by diffusion or by flowthrough, was compared to that of control specimens, where only mechanical load histories, with some creep stage, were imposed. The acid-exposed reconstituted specimens showed an increase in compressibility attributed to the dissolution of carbonates. Vertical strains due to the chemical reaction were about 0.58% and 0.48% in the advection and diffusion tests respectively after around one month of acid exposure. In case of acid-exposed intact samples, a rather insignificant reduction in the void ratio was observed during the acid exposure, both in the case of diffusion and advection tests. The dissolution of carbonates was rather modest compared to one of the reconstituted specimens tested in similar conditions. This can be attributed to the structured and tight fabric of the intact specimens which retards transport of dissolved species. The structured fabric not only ensured stiffer behaviour but might also affect the effective diffusivity of the sample.

The flowthrough experiments were carried out in an advanced oedometer developed for this study. It can be engaged for electrical resistivity tomography and ultrasonic wave measurements. Initially, the setup and calibration of the advanced oedometer was carried out. A protocol optimizing the sequence of measurements for significant electrical resistivity reconstructions was defined on the basis of lab and numerical measurements. For reconstruction of electrical conductivity maps, ResIPy, an open-source code was used. Overall, the advanced oedometer was effective in monitoring changes in pore fluid using electrical resistivity tomography and ultrasonic wave velocity during flowthrough experiments.