Abstract

One of the potential strategies to limit CO_2 emissions in the atmosphere is carbon capture and storage (CCS). CCS is the only option currently available for the so-called hard-to-abate sectors, where a significant proportion of carbon dioxide emissions are linked to the industrial process itself.

The presence of a caprock is a necessary condition for the consideration of underground CO_2 storage. These rocks are distinguished by high threshold capillary pressure, low permeability and porosity, which collectively determine their sealing ability. In order to achieve the purpose of CO_2 geological storage, it is necessary to ensure that there are no CO_2 leaks. Among the ways in which CO_2 can escape through the caprock, one is through the establishment of a mass flow under pressure gradient if the threshold capillary pressure of the caprock is exceeded, or if the sealing capacity of the caprock is compromised due to chemical reactions resulting from the acidification of the pore fluid by CO_2.

In this context, the research focused on the analysis of the chemo-hydro-mechanical effects of CO_2 storage on Italian carbonate clay, grounded caprock from an onshore field in the Ravenna area (Po Valley, Italy). The material is composed of over 40% carbonates, which is a crucial factor given the acidification of the pore fluid by CO_2. The research was conducted in two phases. The first involved experimental simulation of the interaction between the material and different types of acidic environments through exposure tests. The second phase focused on the experimental determination of the threshold capillary pressure of the material using the step-by-step method and, subsequently, through numerical modelling of the dynamic and residual method. These methods are alternative and fast approaches to the step-by-step method but are characterised by assumptions and limitations that affect the estimate of the threshold capillary pressure.

Titration tests allowed to shed light on the pH range in which each carbonate species constituting the material (calcite, dolomite, and ankerite) contributed to the buffering action. Prolonged exposure tests (184 days or more) to water at pH = 3 showed a reduction in carbonate content of 3 ÷ 4 %, whereas exposure tests (74 days) to water at pH = 0 involved a more significant reduction in the carbonate content (≥ 33.7 %). This implicated vertical deformation, dependent on the geochemical process, larger than 8.6 %. Long-term exposure tests (218 days) to water-saturated CO_2 in supercritical conditions ($scCO_2$) brought relevant changes in the mineralogical composition of the samples. Clear difference in the total carbonate mass in the material came from the outermost volume and the one from the core was observed. The former characterized by a carbonate dissolution of approximately 19 % and the latter of just 2.7 %. Specimen subjected to a flow of CO_2-saturated water for 79 days showed an overall reduction

of carbonates of 6.3 %. Significant differences in the mineralogical composition between the inlet layer and the middle and outlet ones were found.

The threshold capillary pressure p_c^* of the Italian carbonate clay was determinate through experimental tests carried out with the step-by-step method. Tests were performed at different stress states and with two pairs of fluids: $scCO_2/H_2O$ and air/H_2O. The results underlined that the ratio $p_{c,air}^*/p_{c,scCO_2}^*$ remains approximately constant (≅ 1.12) over the span of the vertical effective stress analysed. From the comparison between absolute water permeability and void ratio before and after the injection stage, no significant variations were found in any test. The effective permeability to air and $scCO_2$ were about an order of magnitude smaller than the absolute permeability to water. The indirect estimate of the threshold capillary pressure (using MIP tests, tangent method, and the Washburn-Laplace equation), underestimated the actual experimental value (error > 62 %).

The results of the sensitivity analysis regarding the dynamic and the residual method confirm that estimates of the threshold capillary pressure can be obtained in a limited time, ranging from about one day (dynamic method) to about one week (residual method). The results of the two methods are similarly affected by the capillary pressure curve of the sample and by its relative permeability to the wetting and the non-wetting fluid. Depending on the relative permeability to the non-wetting fluid, a greater variability in the threshold capillary pressure is expected for materials with a heterogeneous pore size distribution. The dynamic method estimate is not precautionary, and it tends to the exact value the closer the applied CO_2 overpressure is to the actual threshold capillary pressure. The residual method estimate is influenced by the drainage conditions and the volume of the vessels: it is generally precautionary and tends to increase with the volume of the vessels and the applied pressure. Suggestions for test interpretation and planning are provided.