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Chemo-mechanical effects of carbonates dissolution on a Carbonate Clay

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Summary

The effectiveness of CO_2 underground storage is strictly connected to the sealing capacity of the caprock, which must necessarily prevent CO_2 leakage. However, its hydro-mechanical behaviour might be affected by the dissolution of CO_2in the brine, which acidifies the pore fluid and triggers chemical reactions with the solid phase, a highly critical aspect for carbonate-bearing rocks.

The results of an experimental campaign aimed at studying the chemo-mechanical effects due to the dissolution of carbonates in a Carbonate Clay (CC) exposed to acidic solutions are presented. Titration tests allowed determining the sequence by which carbonate minerals dissolve upon addition of H^+ in a clay-water suspension, thus exerting a buffering effect on the pH. Calcite dissolved first, followed by ankerite, and finally dolomite. The results of long-exposure tests of reconstituted CC specimens to diffusive or advective transport of an acidic solution also highlight the fundamental role of the transport mechanism, exposure times and concentrations on the extent of geomechanical effects on caprock.

1 Introduction

Carbon Capture and Storage in deep saline aquifers and depleted oil and gas reservoirs should be engineered to retain the CO_2 for a duration up to 10000 years [1]. High entry capillary pressure, low permeability, significant sorption capacity, and limited porosity are required for an effective sealing capability of the caprock. Carbon dioxide can potentially escape through the pore network of low permeability caprocks under several conditions: if the caprock's threshold capillary pressure is exceeded (*e.g.* [2]); if the high pressure used for CO_2 injection exceeds the caprock's shear strength, causing fracturing (*e.g.* [3]); or if geochemical interactions in the acidic environment compromise the caprock's seal and integrity (*e. g.* [4]).

Chemical interactions between the injected CO_2 and the caprock take place at the interface between the reservoir and the sealing layer, whether the CO_2 is in a free phase or dissolved in water. These CO_2-induced chemical reactions can modify the sealing rock's internal structure and mineral content. Consequently, these changes may lead to alterations in its fabric and hydro-mechanical properties.

The goal of this study was to investigate the effects of the geochemical and geomechanical processes on a Carbonate Clay due to the exposure to acidic solution. This material is noteworthy for comprising over 50 % carbonates, a factor that becomes critical when considering the potential acidification of the pore fluid by CO_2. Titration and long exposure tests to diffusive or advective flow of acid solution (10^{-3} M HCL) were conducted to shed light on the effects of carbonate dissolution on caprock behaviour.

2 Material

The material employed in all experimental tests is composed of 50 % carbonates (30 % calcite, 16 % dolomite, 4 % ankerite), 29 % phyllosilicate minerals (9 % illite, 9 % muscovite, 7 % chamosite and 3 % kaolinite), 14 % quartz, 2 % albite and 5 % gypsum (more details in [5]), and it can be traced back to a typical carbonate-clay caprock.

3 Titration tests

The investigation involved titration experiments with the caprock powder suspensions (10 g powder / 50 g H_2O), which were reacted with increasing volumes of concentrated hydrochloric acid. The primary objective was to determine the material's buffer capacity by measuring pH changes as acid was added, reflecting the dissolution of carbonate compounds. Acid volumes of 0.3 or 0.6 ml of 12.07 M hydrochloric acid were repeatedly added, and pH was measured after 10 minutes, following [6] (details reported in [5]).

The tests were divided into three groups based on the total volume of acid added: 7.8 ml (CC_TA, CC_TB, CC_TC), 5.7 ml (CC_TD, CC_TE, CC_TF), and 3.6 ml (CC_TG, CC_TH, CC_TI). The pH change during titration is shown in Figure 1. The titration curves' consistency across all tests demonstrates the repeatability and reliability of the results. Initially, the suspension had an average pH of 8.5. After adding 0.3 ml of acid, the pH rapidly dropped to 6.4. The decline continued gradually until an inflection point occurred at over 3.6 ml of acid, at pH approximately equal to 4.9. After this, the pH dropped gently until a sharp decrease occurred at over 5.7 ml of acid, bringing the pH below 1, indicating the complete dissolution of carbonate components.

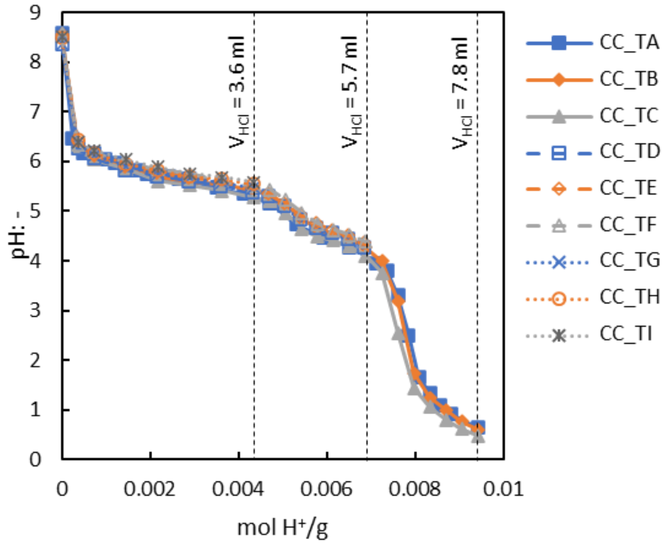

Figure 1: Titration curves of CC. The acid additions are reported per gram of soil

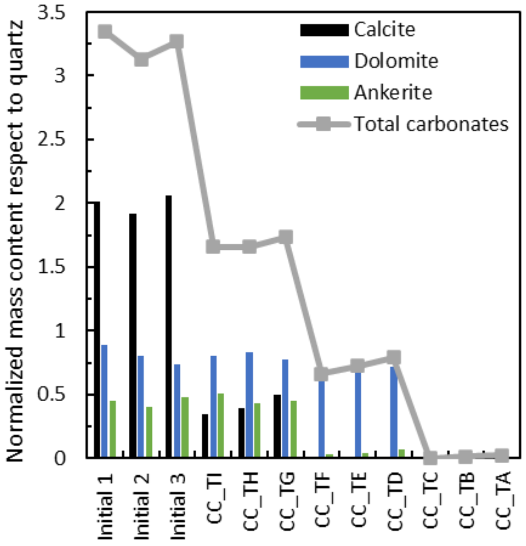

Figure 2: Mass of carbonates in CC as the amount of acid solution used varies

Mineralogical analyses (X-Ray Diffraction) identified the pH ranges at which each carbonate species contributes to buffering. The normalized mass of carbonate minerals relative to quartz mass is shown in Figure 2. These analyses confirm that calcite is the main carbonate buffering the pH early in the titration (up to pH 4.9), due to its lower ionic bond energy compared to ankerite and dolomite. As calcite dissolved, dolomite and ankerite precipitated (e.g., CC_TI, CC_TH, CC_TG tests in Figure 2). At 3.6 ml acid (0.0043 moles of H^+ per gram of solid), calcite dissolution averaged 79.4 %, while dolomite and ankerite precipitation averaged 4.7 %

and 9.8 %, respectively. After calcite dissolution, ankerite became the primary buffering agent until pH reached 4.2 (around 5.7 ml acid), with 88.5 % dissolution of ankerite, as shown in Figure 2.

Further additions of hydrochloric acid solution lead to the complete dissolution of both ankerite and dolomite (specifically tests CC_TC, CC_TB, and CC_TA in Figure 2). This total dissolution of the carbonates is clearly marked in the titration curves by a sudden and sharp drop in pH (Figure 1). This drastic pH change occurs when the ratio of moles of H^+ to grams of the initial dry solid phase mass reaches approximately 0.009. This value aligns with the calculated stoichiometric amount of H^+ required to dissolve all the carbonates present in a 10 grams sample of CC powder. Upon reaching this condition, the mixture loses its capacity to buffer the pH changes caused by the ongoing addition of acid.

4 Exposure tests of reconstituted samples to 10^{-3} M HCl solution

Long-term exposure experiments with a 10^{-3} M HCl solution were conducted to assess the geomechanical impact of prolonged exposure on reconstituted CC specimens. These tests were performed under oedometer constant stress conditions. To investigate the influence of transport mechanisms, two distinct exposure methodologies were implemented: one based on H^+ diffusion from the oedometer basin into the specimen (CC_Diffusion), the other on the advective flow of the solution through the specimen (CC_Advection). To isolate the strains resulting from geochemical reactions and differentiate them from those attributable to viscous behaviour under consistent pore fluid chemistry (distilled water), a parallel creep test was simultaneously performed.

Details on the experimental protocol for reconstituting the specimens using distilled water and on the test apparatus are reported in [5]. The maximum vertical effective stress was 6.3 MPa for the creep and diffusion test, while it was 6.4 MPa for the advection test. In the diffusion test, a target pH = 3 was imposed and maintained in the oedometer basin. In the long-term advection test the inflow of a pH = 3 solution in the specimen was imposed by applying a pressure drop of 0.95 MPa between the specimen's ends. The creep test lasted 197 days, the diffusion test 329 days, and advection test 184 days.

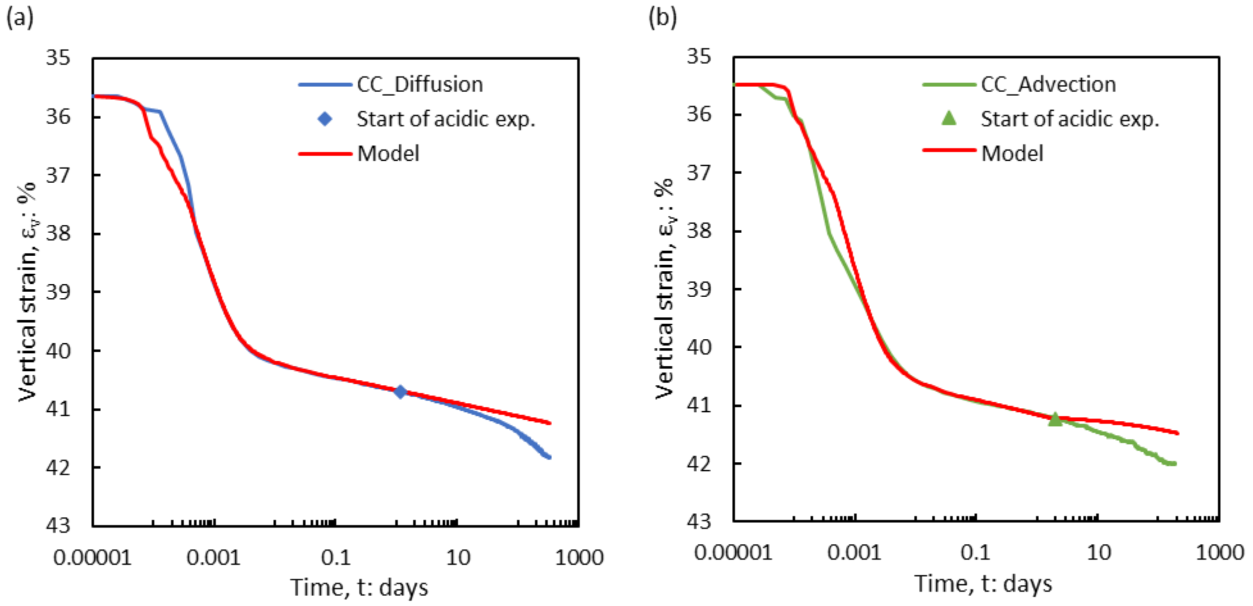

Figure 3: Vertical strain of the last consolidation step and of the exposure stage (CC_Diffusion (a), CC_Advection (b)): comparison between experimental data and numerical results

Given the long exposure durations, creep strains were expected to develop in the samples. In the advection test, a pressure gradient also induced a non-uniform stress distribution, complicating the assessment of geochemical contributions to mechanical strains. To isolate creep effects from geochemical interactions, the final consolidation and acidic exposure stages were simulated numerically using an elasto-viscoplastic model (details in [5]).

Experimental data and numerical results are shown in *Figure 3*. As exposure progressed, a growing discrepancy was noted between the model (which accounts for only the elasto-viscoplastic strains) and experimental data from samples exposed to acid. This discrepancy reflects the combined effects of elastic deformation, creep, and microstructural changes from chemical reactions.

After 185 days of exposure to acidic solution, the vertical strain difference attributed to geochemical effects reached 0.5 %, greater than the 0.4 % observed in the CC_Diffusion test over the same period. Post-mortem X-Ray Diffraction analyses revealed carbonate dissolution in both specimens exposed to H^+ diffusion and advective flow, though with some differences (details in [5]).

5 Conclusions

The role that carbonate minerals have in the buffering action of a Carbonate Clay was identified through titration tests. The results highlighted the dissolution sequence of carbonates, that is correlated to their bonding energy and reaction kinetics (calcite → ankerite → dolomite). These results will be used to validate a reactive transport geomechanical model, which will allow to study in greater detail the chemical reactions that occur in the material exposed to an acidic fluid and to simulate the geochemical effects on the hydro-mechanical behaviour of caprock on the time scale typical of CO_2 storage projects.

The results of the prolonged exposure tests to acidic fluid showed the effect of the different transport mechanism on the time progression of the chemo-mechanical processes, which might lead to a faster onset of strains and possible lost of strength in presence of an advective flow. In the relatively long exposure times (185 days or more) to acidic solution at pH = 3 (acidity equal to that of the pore fluid in the reservoir due to the dissolution of CO_2), the percentage of dissolved carbonates was small (about 0.5%). However, an inherent problem in the experimental study of CO_2 storage related effects, is the very long design times and the slow kinetics of the involved reactions. On the one hand, this might suggests the use of more acidic solutions for future exposure tests to be able to experimentally observe, in reasonable times, the effect of the interaction between a stable amount of H^+ and the solid phase. On the other hand, it might suggest the use of numerical models appropriately validated with representative exposure tests, which might help in planning testing conditions were the relevant reactions are obtained in feasible times.

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