

Calcarenite as a possible host rock for CO₂ sequestration

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ABSTRACT: Deep saline aquifers have a great potential for geologic carbon dioxide (CO₂) sequestration and proper assessment of host and cap rock is needed to guarantee that the procedure is safe. Temperatures and pressures at which most of the possible host rocks exist dictate that CO₂ is present in a supercritical condition, having both gas and liquid properties. Hence, rock-fluid interaction has to be studied and measurements of poroelastic parameters are necessary. Sandstone formations are mostly considered as the possible host rock. However, in some countries only calcite-rich formations can satisfy the requirements for safe geologic CO₂ sequestration.

This paper deals with measurements of poroelastic parameters of calcarenite (or Apulian limestone), which is 95-98% calcite. Jacketed and unjacketed hydrostatic compression experiments and undrained plane strain compression tests provided the full set of poroelastic parameters. Additionally, the specific storage coefficient was calculated. Inability to obtain constant values of Skempton *B* coefficient even at high pore pressures (~ 4 MPa) and the decrease in P-wave velocity with water injection revealed partial dissolution of calcarenite in water at high pressures. This phenomenon, as well as the mechanical behavior of rock in contact with supercritical CO₂, are currently under consideration.

1. INTRODUCTION

Geologic CO₂ sequestration is considered to be the most promising technique to reduce the concentration of greenhouse gases in the atmosphere. Among all the storage options, deep saline aquifers have the greatest potential and due to their worldwide occurrence can play a major role in reduction of carbon dioxide emissions. In sedimentary basins at depths below 800 meters, CO₂ usually exists in a supercritical condition (scCO₂), which means that its temperature and pressure are above 31.1° C and 7.4 MPa, respectively, and it has a liquid-like density (500-800 kg/m³). Carbon dioxide then can be trapped in pore space of the storage formation and by reacting with minerals that form it, as well as dissolve in the *in-situ* fluids. Choice of a host rock is crucial for proper retention of scCO₂, and sandstone reservoirs, which mostly are single-porosity systems, are usually considered [1]. However, in some countries (*e.g.* Switzerland, Italy, and Canada) limestone aquifers are widespread and have to be examined for the possibility of storage [1,2]. The injection of significant amounts of CO₂ into a limestone reservoir has to be carefully treated

because it is usually a multiple-porosity system with wide permeability variations. Also, due to the dissolution reactions, large pores can be created in calcite-rich limestones, which increases their permeability and significantly decreases capillary trapping of CO₂ [1,3].

For the proper assessment of carbon dioxide storage in calcite-rich formations, its interaction with water has to be characterized first. This paper describes experiments aimed at measurements of poroelastic parameters of calcarenite – limestone that contains up to 98% calcite.

2. BACKGROUND AND METHODS

2.1. Poroelasticity relationships

Poroelastic theory introduced by Biot [4] and developed by Biot and Willis [5] is used to characterize the elastic behavior of fluid-saturated rock. The parameters that govern its response and can be measured experimentally were first described by Rice and Cleary [6] and are related to three limiting conditions: drained, undrained, and unjacketed.

A drained condition means that the pore fluid is allowed to leave the rock during loading and pore pressure p is maintained at a constant level: $dp = 0$. Here, “ d ” represents an infinitesimal increment. For an undrained case, the mass of the fluid inside the rock does not change: $dm_f = 0$. The third possible limiting condition for fluid-rock interaction is called “unjacketed,” and it is related to the case when the increase in the mean stress $P = (\sigma_1 + \sigma_2 + \sigma_3)/3$ is equal to the increase in fluid pressure: $dP = dp$. The parameters that govern the poroelastic response are drained and undrained bulk moduli K and K_u , respectively:

$$K = \left. \frac{dP}{d\varepsilon} \right|_{dp=0} \quad (1)$$

$$K_u = \left. \frac{dP}{d\varepsilon} \right|_{dm_f=0} \quad (2)$$

where ε = volume strain, and two unjacketed bulk moduli K_s' and K_s'' :

$$K_s' = \left. \frac{dP}{d\varepsilon} \right|_{dP=dp} \quad (3)$$

$$K_s'' = V_\phi \left. \frac{dP}{dV_\phi} \right|_{dP=dp} \quad (4)$$

where V_ϕ is the pore volume expressed in terms of porosity ϕ and total volume V : $V_\phi = \phi V$.

The introduced bulk moduli are related to each other through the following set of equations [6]:

$$\alpha = 1 - \frac{K}{K_s'} \quad (5)$$

$$K_u = K + \frac{\alpha^2 K}{(1-\alpha)\alpha + \phi K \left(\frac{1}{K_f} - \frac{1}{K_s''} \right)} \quad (6)$$

$$B = \left. \frac{dp}{dP} \right|_{dm_f=0} = \frac{\alpha}{\alpha + \phi K \left(\frac{1}{K_f} - \frac{1}{K_s''} \right)} = \frac{K_u - K}{\alpha K_u} \quad (7)$$

where α is sometimes referred to as the Biot coefficient [4,5], K_f is the bulk modulus of the pore fluid, and the Skempton coefficient B characterizes the increase in pore pressure due to the applied loading under undrained condition [7].

Furthermore, the following inequalities must be preserved [6]:

$$0 < K \leq K_u \quad (8)$$

$$0 \leq B \leq 1 \quad (9)$$

$$0 \leq \alpha \leq 1 \quad (10)$$

Additionally, the hydrologic parameter, specific storage S_s , can be introduced, with g = gravity [8]:

$$S_s \equiv g \left. \frac{dm_f}{dp} \right|_{d\sigma_{33}=0, \varepsilon_{11}=\varepsilon_{22}=0} \quad (11)$$

S_s is the fluid volume released from storage per unit decline in hydraulic head, per unit bulk volume, under conditions such that there is no strain in two orthogonal directions, and the total normal stress in the third direction is constant. It is the coupling coefficient that relates changes in fluid mass to changes in fluid pressure and governs the fluid mass diffusion in a representative elementary volume [6]:

$$\frac{S_s}{\kappa} \frac{\partial m_f}{\partial t} = \nabla^2 \cdot m_f \quad (12)$$

where t = time and κ = hydraulic conductivity. Green and Wang [8] have shown that the specific storage can be calculated from other poroelastic parameters:

$$S_s = \frac{\rho^f g}{K} \left[\alpha \left(1 - \frac{12G\alpha}{3K+4G} \right) + \phi K \left(\frac{1}{K_f} - \frac{1}{K_s''} \right) \right] \quad (13)$$

where ρ^f = density of the pore fluid. In hydrogeology, drained moduli of low-permeable formations are difficult to measure, and hence are estimated from the specific storage, which can be obtained from modified slug tests [9]. Thus, S_s can be used as one of the four constants in the general constitutive poroelastic equations relating three-dimensional aquifer stress and strain to fluid pressure and dilatation (e.g. [6]). Furthermore, specific storage is the single poroelastic coefficient controlling slow compressional wave propagation in the low-frequency regime [8].

2.2. Experimental methods

For the proper characterization of a material's poroelastic response, tests under all three limiting conditions are needed. Drained or more specifically dry ($p = 0$) and unjacketed boundary conditions were achieved in hydrostatic ($\sigma_1 = \sigma_2 = \sigma_3 = P$) compression experiments similar to the procedure described in [10]. Prismatic specimens ($50 \times 35 \times 35$ mm) with strain gage rosettes on their sides were first covered with polyurethane (Figure 1), loaded to $P = 30$ MPa (jacketed test) and unloaded. Then, part of the jacket was removed and the confining fluid (hydraulic oil), which seemed to have no chemical effect on the rock in the short-term, was allowed to saturate the specimen. After 24 hours of saturation at 5 MPa pore pressure, unjacketed loading (P

$= p$ and $dP = dp$) to 30 MPa and unloading was performed. Measurements of 3D strains at different pressures provided the data to determine the material's anisotropy and jacketed (dry) andunjacketed bulk moduli.

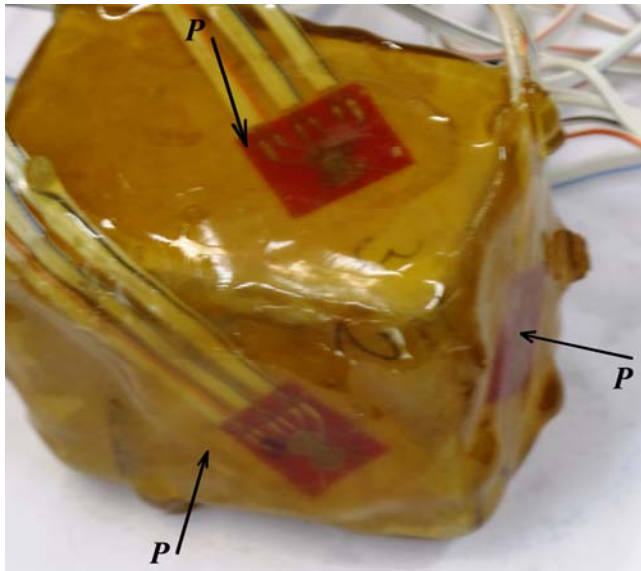


Fig. 1. Prismatic specimen with attached strain gage rosettes on its sides covered with polyurethane and used for hydrostatic compression experiments.

Undrained compression experiments were performed with the University of Minnesota plane-strain apparatus [11] specifically modified for testing fluid-saturated rock [12]. Prismatic specimens ($100 \times 87 \times 44$ mm) were covered with polyurethane (Figure 2) and wedged inside the stiff frame, such that intermediate principal strain was two orders of magnitude smaller than axial strain. The apparatus allows accurate measurements of all principal stresses and strains [13] at different mean stress and pore pressure levels. Additionally, two acoustic emission (AE) sensors were attached to the specimen sides opposite to each other, such that P-wave velocity and AE activity of the rock could be measured at different stages of loading.

3. RESULTS AND DISCUSSION

In order to study the peculiarities and consequences of CO_2 injection and storage in calcite-rich rocks, calcarenite (Apulian limestone) was tested for full characterization of its poroelastic response under drained, undrained, andunjacketed conditions.

3.1. Dry parameters and index properties

Calcarenite is a pale orange to grayish glauconitic fossiliferous limestone comprised of calcite (95 – 98%) with traces of quartz, plagioclase, glauconite, and iron oxide. Rock's interconnected porosity is equal to 33%,

and permeability was measured to be 3-5 mD (at $P' = 5$ MPa). The following P- and S-wave velocities (c_p, c_s) in km/s were measured on the block of rock: (2.57, 1.56), (2.52, 1.56), and (2.56, 1.54), which means that the limestone possesses less than 2% elastic anisotropy.

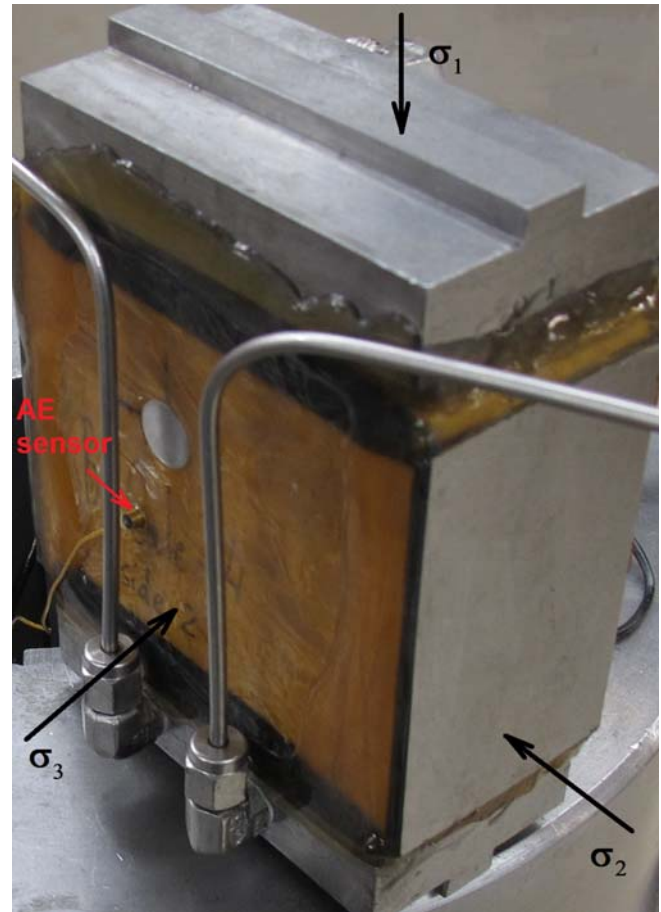


Fig. 2. Plane strain specimen covered with polyurethane with pore pressure tubes and the AE sensor on one of its sides.

Dry elastic parameters were accurately measured in uniaxial compression experiments with both strain gages and digital image correlation, DIC [14]; the axial stress – axial and lateral strain response is shown in Figure 3.

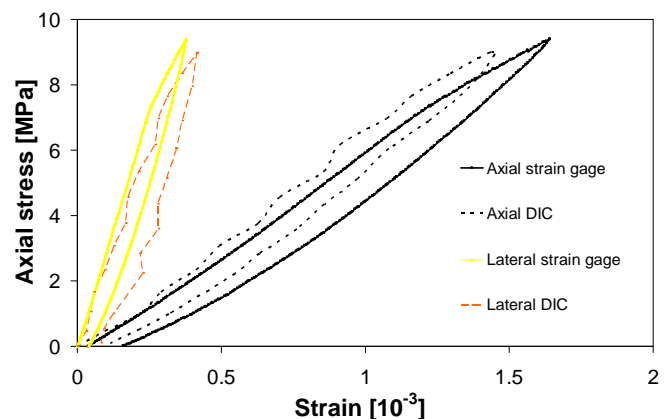


Fig. 3. Change of axial and lateral strains from DIC and strain gage data in uniaxial loading and unloading tests.

The two types of measurements provided approximately the same elastic parameters: Young's modulus $E = 7.3$ GPa and Poisson's ratio $\nu = 0.25$.

3.2. Hydrostatic compression experiments

Hydrostatic compression experiments performed on jacketed andunjacketed specimens led to the following measurements: dry bulk modulus $K = 5.1$ GPa at 5 - 7 MPa hydrostatic pressure and unjacketed bulk modulus $K_s' = 42.7$ GPa and constant throughout the loading (Figure 4). Biot coefficient was found to be $\alpha = 0.88$.

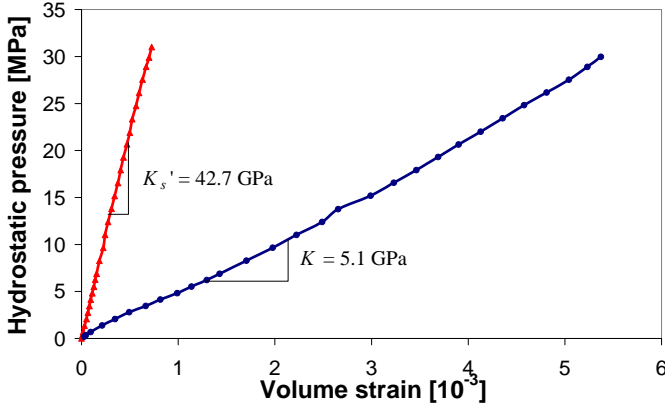


Fig. 4. Jacketed and unjacketed compression of calcarenite.

3.3. Undrained plane strain compression tests

Plane strain compression experiments were performed under undrained conditions. Calcarenite's B coefficient was calculated from the following expression [15,16]:

$$B = \frac{1}{\left(\frac{\Delta P}{\Delta p}\right)^{measured} - \frac{V_L}{V} \frac{K}{\alpha K_f}} \quad (14)$$

where the specimen volume V is approximately 383 ml and V_L is the dead volume in the pore pressure measuring system, which was determined to be 14 ml.

In equation (14), K_f can be taken equal to the bulk modulus of deaired water ($K_{water} = 2.24$ GPa) at full saturation. The same saturation technique as described in [16] was implemented: the increments of pore (or back) pressure were applied while keeping the effective mean stress approximately the same. Skempton B coefficient was measured at each increment and achievement of constant B independent of the magnitude of the back pressure would indicate full saturation. B coefficient appeared to be increasing with saturation and the maximum achieved value at 5 MPa effective mean stress was $B = 0.70$ (Figure 5).

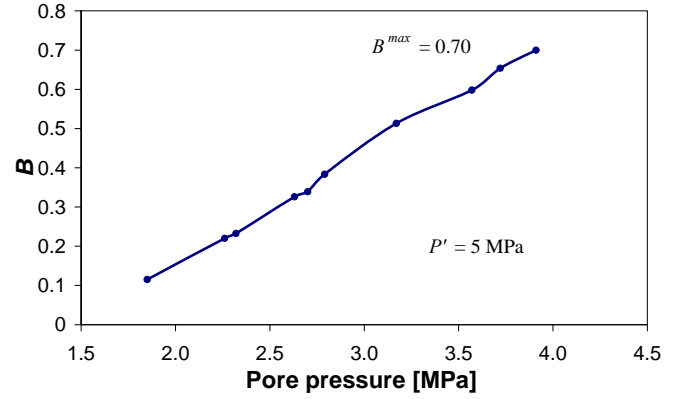


Fig. 5. Development of Skempton B coefficient of calcarenite with increasing pore pressure at constant effective mean stress.

Higher back pressures were not applied because simultaneous measurements of the undrained bulk modulus K_u indicated the values smaller than the dry bulk modulus of the rock K , which violates poroelastic inequality (8). Also, the results of experiments performed under the same conditions were not reproducible. It means that the limestone behavior was not poroelastic even at low effective mean stress ($P' = 5$ MPa) and can be related to the partial dissolution of the minerals forming the rock in pressurized water.

One of the other criteria for ensuring full saturation is that the P-wave velocity in the saturated material becomes constant with increasing back pressure keeping effective stress constant [18]. P-wave velocity in calcarenite was measured during loading of the specimen and the saturation process at constant effective mean stress $P' = 5$ MPa (Figure 6).

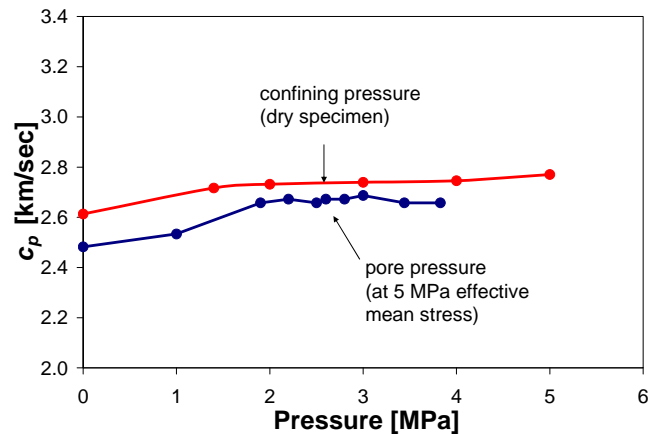


Fig. 6. P-wave velocity in calcarenite with increasing mean stress under a dry condition (red curve) and pore pressure at constant mean stress under water-saturation (blue curve).

Even though the values of c_p are approximately constant for $p > 2$ MPa, the statement of the full saturation cannot be made. This is due to the presence of two competing processes: increase of bulk fluid modulus of the rock-fluid system with increasing saturation and decrease of

solid bulk modulus due to calcite dissolution at high water pressure. The latter is observed since the beginning of water injection in the specimen (Figure 6) and is another sign of rock weakening.

Aquifers in calcite-rich formations exist because the long-term equilibrium is reached between dissolution of calcite and mineralization [9]. However, short-term chemo-mechanical effect of pressurized water on mechanical properties of calcarenite can be [19] and should be properly studied before characterizing material's response in contact with CO₂. This research is currently under way.

3.4. Specific storage

Nonetheless, not all of the poroelastic parameters were measured, specific storage can still be calculated from the available data at $p = 4$ MPa. Using equation (7), expression for S_s (13) can be written in the following form:

$$S_s = \frac{\alpha \rho^f g}{K} \left[\frac{1}{B} - \frac{4\alpha}{\frac{K}{G} + \frac{4}{3}} \right] \quad (15)$$

Calculating $G = 2.9$ GPa from uniaxial compression parameters and taking $\rho^f = 1000$ kg/m³, $S_s = 4.7 \cdot 10^{-7}$ m⁻¹ for calcarenite. This has the same order of magnitude as the specific storages measured for argillaceous rocks: $3 - 13 \cdot 10^{-7}$ m⁻¹ [20].

4. RESULTS AND DISCUSSION

Calcarenite was tested as a possible representative of calcite-rich rock that can be utilized for CO₂ storage. Drained, undrained, and unjacketed poroelastic parameters were measured in hydrostatic and plane strain compression experiments. Available sets of poroelastic data provided calculation of the material's specific storage – the parameter responsible for the fluid mass diffusion and often used in poroelastic relationships as a replacement of drained moduli, which are sometimes difficult to measure.

Inability to achieve constant values of Skempton B coefficient even at high pore pressures ($p > 4$ MPa) and decrease in P-wave velocity were related to the partial dissolution of calcite. Characterization of the dissolution effect and the experiments aimed at rock-fluid interaction characterization when supercritical CO₂ is injected are currently under consideration.

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