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Effect of rock-fluid interaction and heterogeneities on the tensile, uniaxial strength and elastic behaviour of Dinantian carbonate intact rocks

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ABSTRACT

Carbonate rocks, which often serve as geo-energy reservoirs, are prone to fluid-assisted deformation, which is susceptible to fluid chemistry. Acknowledging the impact of fluids and fluid chemistry on the mechanical behaviour of rocks substantiates the safety of exploiting the geo-energy reservoirs. We saturated Dinantian carbonate samples overnight at a similar fluid mass with 4 different fluids: deionised water, calcium carbonate saturated solution, sulfuric acid, and a sodium chloride-rich geothermal brine, which cover a range of redox potentials, pH, and ionic strength. After saturation, we conducted Brazilian Disc and uniaxial compressive tests from which we obtained tensile strength, Young's modulus, Poisson's ratio and Uniaxial Compressive Strength (UCS). The tensile strength of the sample depends on both sample porosity and fluid chemistry, and tensile strength decreases with decreasing fluid ionic strength. In contrast, Young's modulus doesn't exhibit a clear dependence on pH, and instead correlates with the ionic strength of the fluids used, just as UCS. Poisson's ratio is affected by pH, redox potential and ionic strength. This correlation implies that the ionic strength induces more deformation and lowers UCS. Additionally, given the differences in the effect on Young's modulus and Poisson's ratio, the magnitude and direction of the local stress field determine if further fluid complexity affects elastic deformation and hence local stress transfer.

1. INTRODUCTION

Carbonate formations are frequently used as geo-energy reservoirs (geothermal, CO₂). Conventional geothermal plays target matrix flow-dominated reservoirs. However, the greater the reservoir depth, the lower the matrix porosity and permeability, and hence,

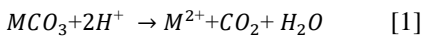
at larger depths, fractures and faults serve as fluid flow pathways. Carbonate reservoirs are actively explored for geothermal energy, particularly in Belgium (Broothaers et al. 2021), the Netherlands (Carlson et al. 2019, Heijnen et al. 2019) and Germany (Moeck et al. 2019, Schintgen et al. 2021). The Lower Carboniferous (Dinantian) formation is a (potential) geothermal reservoir both in the Netherlands and Belgium, as well as in western Germany, with matrix permeability and/or fractures and/or faults serving as geothermal fluid flow pathways. Geothermal heat is currently produced from the Dinantian formation in several projects in Belgium, among which is the geothermal project of VITO on the former Balmatt site in Mol. In contrast, in the Netherlands, the Californië geothermal wells were the first ones targeting a carbonate reservoir in the Dinantian formation. The Upper Jurassic Malm formation is a geothermal reservoir in the Molasse Basin in South Germany, producing geothermal energy from a mixed matrix and fracture permeability reservoir.

In the past decade, seismic activity has been recorded close to all the aforementioned geothermal operations. Production at the geothermal doublet of VITO in Mol has been suspended twice because of induced seismicity, in line with the traffic light system. Seismic activity here was related to the injection of fluid into the fractured Lower Carboniferous Limestone reservoir (Kinscher et al. 2023). After the suspension of the activities of the Californië geothermal wells in 2018 (Pluymakers et al., 2023, Muntendam-Bos et al 2022), due to seismic activity in this area, Vörös et al. 2022 suggested that the thermal contraction along the faults provides a possible explanation for the observed induced seismicity. In the Molasse Basin, Germany, the Malm formation has responded with seismic activity to the geothermal operations. The interpretation of the earthquakes in this region suggested that the reactivation of pre-existing faults only occurred after

significant thermal and chemical effects (Seithel et al. 2019). However, the specifics have not yet been enlightened. In all aforementioned cases of induced seismicity, the effects of fluid-rock interaction on the strength of the carbonate rocks and subsequent mechanical properties and local stresses have not been studied. Hypothetically speaking, if the fluid type induces a significant strength reduction in the matrix, this could have implications for influencing the likelihood of seismic deformation (how much, where, when) and in turn, contribute to the induced seismicity.

The exploitation of fractured and faulted carbonate geothermal reservoirs goes hand in hand with the necessity of understanding the rock strength when subject to different chemical interactions due to the introduction and circulation of fluids in the subsurface. Expanding knowledge in this domain can contribute to mitigating the risk of induced seismicity triggered by fluid-rock interactions in carbonate rocks. However, scaling the effect from nature to the laboratory and vice versa poses the challenge of transferring the chemical effects on the rock strength between the laboratory and human operation timescale contexts. Hence, we need to understand which are the mechanisms that impact rock mechanics in the presence of fluids.

From chemically simple to complex fluids, their characteristics are captured in different chemical properties, such as pH, redox potential, ionic strength, electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen, salinity, alkalinity and hardness. Dissolution of carbonate rocks is a process that is sensitive to fluid pH, salinity, and CO₂ content (Plummer et al. 1982, Sjöberg et al., 1984, Pokrovsky et al., 2005), which makes carbonate sedimentary rocks sensitive to water-assisted deformation during mechanical loading. The effect of fluid pH on carbonate rocks has been widely studied and can be described in Equation 1.



Where MCO₃ is the carbonate component (i.e. CaCO₃, MgCO₃, etc.), H⁺ is from any acid (e.g., HCl, H₂SO₄, HNO₃), M²⁺ is the resulting cation. Ionic strength is a measure of the total concentration of ions in a solution, accounting for both their concentration and their total charge, given by Equation 2.

$$I = \frac{1}{2} \sum c_i z_i^2 \quad [2]$$

Where c_i is the concentration of ion i in mol/L (M), z_i is the charge of ion i, and the sum is taken over all ions in the solution. So, ionic strength does not account only for the concentration of H⁺ but takes into consideration the total ionic presence along with their charge. Hence, ionic strength can describe the fluid characteristics in a broader spectrum, accounting for different types of ions. The redox potential (also called oxidation-reduction potential or ORP) of a fluid is a measure of its tendency to either gain or lose electrons; in other words, how oxidising or reducing it is. A positive value denotes that a fluid is oxidising, therefore accepting

electrons. The property is dependent on the presence of oxidants (O₂, Cl₂, H₂O₂, NO₃⁻), reductants (Fe²⁺, H₂, S²⁻, CH₄), pH (redox reactions are often pH-dependent), temperature, and dissolved metals (e.g., Fe, Mn). Given the diversity of the different parameters that potentially influence the mechanical behaviour, in this study, we will explore the effect of pH, ionic strength and redox potential on the tensile, uniaxial compressive strength (UCS) and elastic behaviour of the carbonate samples.

The tensile behaviour of carbonate rocks is not only relevant in a geothermal energy context, but also for fields such as the natural stone industry, subsurface geo-engineering, or more generic geo-energy exploration and exploitation. In all those cases, the operations themselves have the potential to change fluid conditions. Therefore, understanding how fluid-rock interaction affects tensile strength will improve the safety of these operations. Moreover, at larger depths, hydrofracturing is a common method to improve the connectivity of reservoirs, for which tensile strength is a key parameter. The ability to predict the stresses at which fractures are generated and how this is affected by different fluids would allow for an improved quantification of the effectiveness of hydraulic fracturing, in various forms of geo-energy applications.

Uniaxial compressive strength tests (UCS) capture the failure of laboratory samples without the presence of confining stress. Despite their simplicity, without elevated temperature or confining pressure, UCS experiments are nonetheless a great way to deliver first-order observations on the effect of different types of fluid on the uniaxial strength of rocks, as well as deriving static elastic moduli from direct measurements (Poisson's ratio, Young's modulus).

2. METHODOLOGY

2.1 Pre-experimental fluid characterisation

We utilised four different types of fluids, sulfuric acid solution (H₂SO₄) (Fluid A), a NaCl-rich geothermal brine as described by Bos and Laenen 2017 (Fluid B), de-ionised (DI) water (Fluid C), and a fully saturated solution with calcium carbonate (CaCO₃) (Fluid D). We obtained the brine from VITO, which they extracted from the production well of the geothermal site in Mol, Belgium, operating in the Dinantian formation. The deionised (DI) water and calcium carbonate saturated solution are common reference fluids, widely used in rock mechanics experiments (Kortram et al., 2023, Pluymakers et al., 2021). Table 1 contains the values for pH, redox potential, and ionic strength of these four fluids, where pH and redox potential are measured values and ionic potential is calculated based on the fluid composition, using Equation 2.

Table 1: Chemical characteristics of the fluids used for the indirect tensile and UCS experiments. Fluids from A to D exhibit increasing pH to facilitate the flow of the text.

Code	pH	Redox potential (mV)	Ionic strength (M)
A	2.3	448	$474 \cdot 10^{-5}$
B	6.7	192	3.27
C	7	240	10^{-7}
D	8.3	300	$281 \cdot 10^{-6}$

2.1 Sample characterisation and experimental setup

We used cylindrical intact Dinantian samples 30*60 mm for uniaxial compression tests and 30*15 mm disk-shaped samples for Brazilian Disc experiments and ensured the best possible reproducibility between samples by coring them from the same blocks. We measured the sample density and effective porosity using a gas expansion (Helium) pycnometer. We vacuum-saturated the samples overnight, so approximately 18 hours before the start of the experiment. The first set of experiments included Brazilian Disc experiments conducted in a 50 kN loading machine. We deformed the samples at a constant loading rate of 0.0005 $\mu\text{m/s}$. We measured the load (accuracy of 0.01 kN) and displacement by averaging the two axial Linear Variable Differential Transducers (LVDT) (accuracy of 1 μm). We logged the data at 10 Hz. The Brazilian Disc setup is shown in Figure 1.

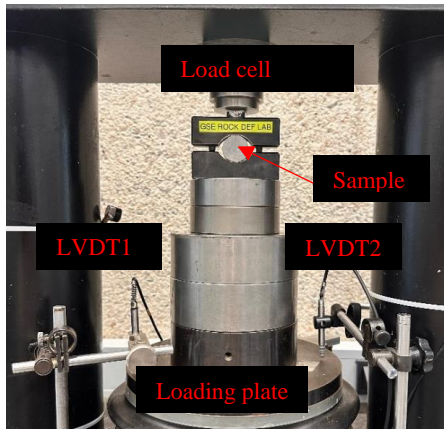


Figure 1: 50 kN apparatus with the sample configuration to conduct the indirect tensile experiments.

We performed the uniaxial compression tests (UCS) with a loading machine with a maximum capacity of 500 kN (accuracy of 0.001 kN). We deformed the samples at a constant strain rate of 0.0005 1/s. We measured the axial deformation of the rock sample using two Linear Variable Displacement Transformers (LVDTs) (accuracy of 1 μm) and radial deformation by a chain with an embedded sensor (accuracy of 1 μm). We logged the data at 1 Hz. The setup of the uniaxial compression tests is shown in Figure 2.

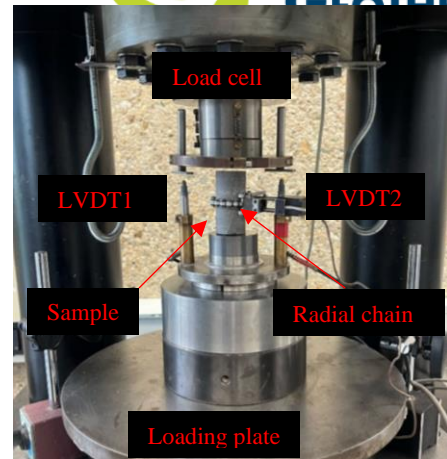


Figure 2: 500 kN apparatus with the sample configuration to conduct the UCS experiments.

2.2 Data analysis

We calculated the indirect tensile strength according to Bieniawski et al., 1978 (Equation 3), where σ_t is the tensile strength (MPa), f_1 is the first peak load force (kN), D and t are the diameter and thickness of the sample (mm).

$$\sigma_t = \frac{2f_1}{\pi Dt} \quad [3]$$

We defined the static Young's modulus, E (Equation 4) and Poisson's ratio, ν (Equation 5), at the linear stage of each uniaxial compressive strength experiment (elastic regime). $\Delta\sigma_{1(\text{elastic})}$ is the stress difference (MPa), and $\Delta\varepsilon_{1(\text{elastic})}$, and $\Delta\varepsilon_{2,3(\text{elastic})}$ (%) are the axial and radial strain differences in the elastic regime, respectively.

$$E = \frac{\Delta\sigma_{1(\text{elastic})}}{\Delta\varepsilon_{1(\text{elastic})}} \quad [4]$$

$$\nu = \frac{\Delta\varepsilon_{2,3(\text{elastic})}}{\Delta\varepsilon_{1(\text{elastic})}} \quad [5]$$

3. RESULTS & DISCUSSION

3.1 Correlation of fluid pH, redox potential and ionic strength with indirect tensile strength

Figure 3 presents the correlation of indirect tensile strength with the different fluid characteristics. There are two clusters of samples with similar porosity: one group includes samples saturated with sulfuric acid (A) and geothermal brine (B), with a porosity range of 0–3%; the other refers to samples saturated with deionized (DI) water (C) and a calcium carbonate-saturated solution (D), with a porosity range of 3–7%.

Within the same ranges of sample porosity, we observe a slight negative correlation of fluid acidity, with the tensile strength (Figure 3a). Additionally, the lower the ionic strength, the lower the tensile strength as well (Figure 3b). There is no trend with the redox potential of the fluids (Figure 3c).

These results indicate that, even though commonly used, fluid pH itself is insufficient in capturing the effect of fluids on the tensile failure of carbonate rocks. We need to further consider the total presence of ionic

compounds along with their ionic charge. Subsequently, we should investigate further the chemical properties of the used fluids and understand why and how fluid chemistry impacts tensile strength.

3.2 Correlation of fluid pH, redox potential and ionic strength with static elastic moduli and Uniaxial Compressive Strength (UCS)

The static elastic moduli (Figures 4, 5) exhibit variability per fluid type and sample porosity. Samples of 0-1% porosity have a higher Young's modulus for fluid A compared to fluid C, while Poisson's ratio is independent of fluid type. Samples with porosity of 1-2% have higher elastic moduli for Fluid C compared to fluid D. Samples with porosity of 2-3% have lower elastic moduli for fluid B than fluid D. Hence, the impact of fluids on the elastic behaviour of the tested samples is partially subject to the porosity next to the influence of the saturating fluid.

Fluid pH (Figure 4A) does not systematically impact Young's modulus, but it does decrease the Poisson's ratio (Figure 5A). Redox potential does not impact Young's modulus (Figure 4B) but solely the Poisson's ratio (Figure 5B). Both elastic moduli exhibit a decreasing trend with ionic strength (Figures 4C, 5C).

The ionic strength of the fluid reduces both Young's modulus and Poisson's ratio. Therefore the higher the ionic strength of the fluid that the carbonate rock is exposed to, the greater the magnitude of deformation and the ability to deform in all directions. We hypothesise that the number of ions along with their total charge promotes dissolution of the carbonate matrix potentially due to a reduction in activity coefficients or shifting equilibrium towards dissolution. Even though carbonate solubility is low (< 1 g/L) if the shape of grain contacts and the occurrence and shape or size of initial flaws is affected, this can change the stiffness of the matrix. This would imply that by changing the fluid composition from a low ionic strength to a high ionic strength, the material becomes more compliant, and more prone to directionally deform. Hence, this in turn suggests that it will facilitate more deformation in case of perturbing stresses in the subsurface from geo-energy operations.

These results indicate that Poisson's ratio appears to be sensitive to more chemical properties compared to Young's modulus. This implies that the directional deformation is susceptible to more chemical fluid properties than the magnitude itself of elastic deformation. However, an important limitation is that the current experimental setup only allows unconfined testing. Since confining pressure may suppress this apparent directional effect, the effect of fluid-rock interactions, in particular concerning Poisson's ratio vs Young's modulus, needs to be investigated under triaxial conditions. Additionally, to allow a priori predictions on the effect of changes in fluid composition on the mechanical behaviour of carbonates further research is required to quantitatively extend and

capture which fluid chemical properties impact the rock stiffness apart from the studied ones.

Figure 6 correlates the effect of fluid pH, redox potential and ionic strength on the UCS of tested samples. Fluid pH does not systematically impact the UCS (Figure 6A). The UCS of the samples systematically negatively correlate with increasing the redox potential of chemically simple fluids (Figure 6B) (i.e. sulfuric acid, DI water, CaCO₃ saturated solution) or with increasing the ionic strength of the fluids (Figure 6C).

As discussed above we hypothesise that fluids with high ionic strength destabilize the matrix of the carbonate rock and enhance dissolution of carbonate minerals, especially if the fluid is also acidic or contains aggressive oxidants. Therefore they lower the UCS of the carbonate rocks.

4. CONCLUSIONS

The mechanical behaviour of low porosity Dinantian carbonate rocks is subject to rock-fluid interactions. After a series of Brazilian Disc and UCS tests using four different fluids, we found the following:

- The tensile strength of laboratory samples is highly dependent on small variations of porosity (~1%). Nonetheless, increasing fluid acidity correlates with decreasing tensile strength. The ionic strength of the used fluid positively correlates with an increase in the tensile strength of carbonate samples.
- The Young's modulus correlates negatively with ionic strength. Ionic strength and redox potential both systematically impact Poisson's ratio. Poisson's ratio is sensitive to more chemical properties compared to Young's modulus.
- The uniaxial compressive strength of carbonate rocks exhibits variability, which is subject to sample porosity. When investigating a narrow porosity range, fluid acidity does not show a systematic trend with UCS. Increasing ionic strength decreases the uniaxial strength of the samples.
- All fluids have a distinctly different impact on the studied geomechanical behaviour of carbonate rocks.

These results indicate that for the Dinantian carbonate samples, the use of different solutions affects tensile strength and UCS. Furthermore, the non-matching effects of fluid acidity, redox potential and ionic strength indicate that we need to consider fluid complexity in assessing mechanical strength under realistic fluid conditions, with a broader eye than conventional methods.

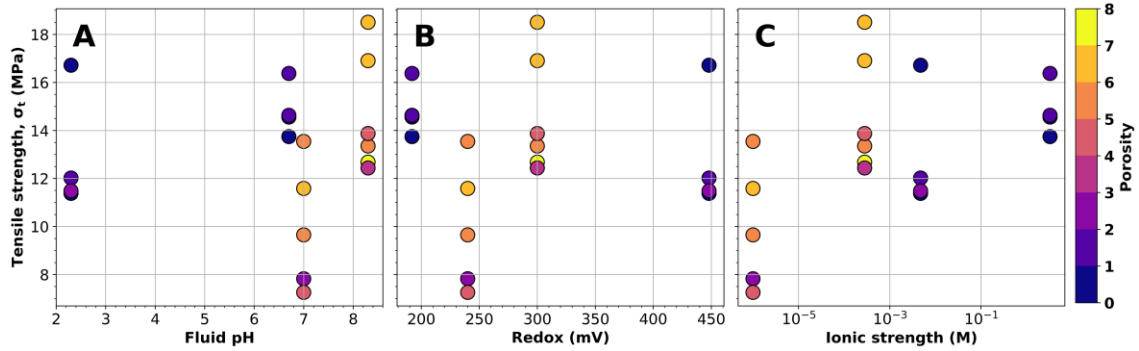


Figure 3: Correlating fluid pH, redox potential and ionic strength with indirect tensile strength for a total of 18 experiments.

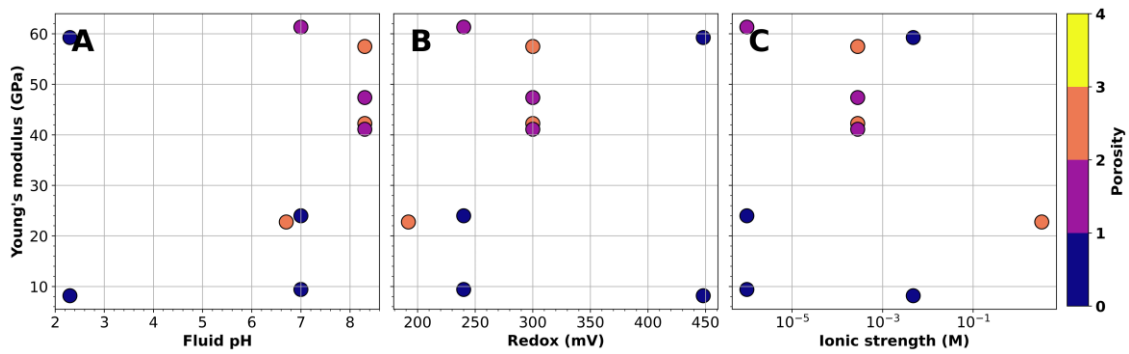


Figure 4: Correlating fluid pH, redox potential and ionic strength with the static Young's modulus for a total of 10 experiments.

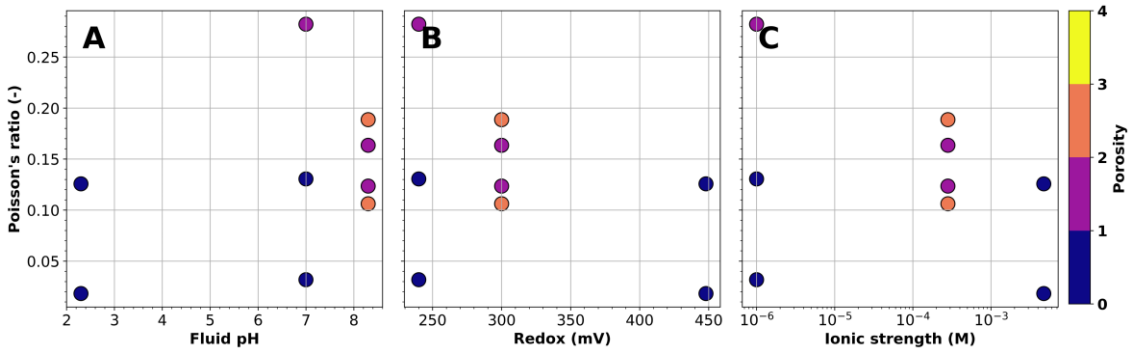


Figure 5: Correlating fluid pH, redox potential and ionic strength with the static Poisson's ratio for a total of 9 experiments.

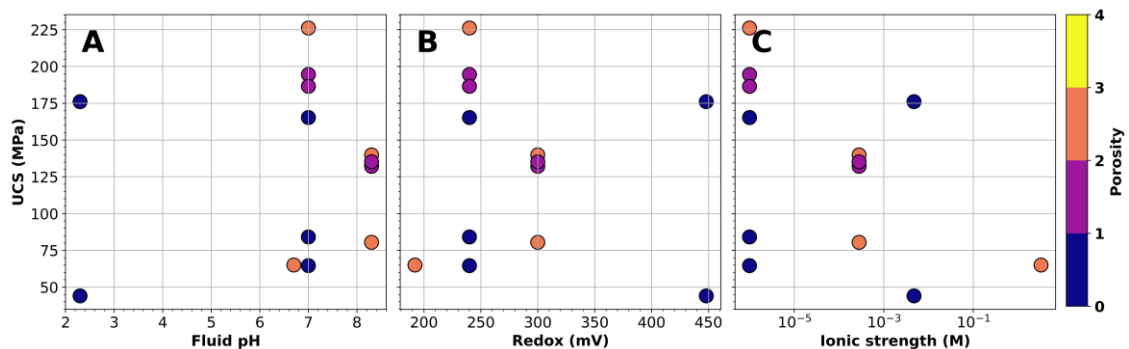


Figure 6: Correlating fluid pH, redox potential and ionic strength with UCS for a total of 13 experiments.

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