Experimental Investigation of the Pressure of Crystallization of Ca(OH)$_2$: Implications for the Reactive Cracking Process

S. Lambart, H. M. Savage, B. G. Robinson, and P. B. Kelemen

Abstract

Mineral hydration and carbonation can produce large solid volume increases, deviatoric stress, and fracture, which in turn can maintain or enhance permeability and reactive surface area. Despite the potential importance of this process, our basic physical understanding of the conditions under which a given reaction will drive fracture (if at all) is relatively limited. Our hydration experiments on CaO under uniaxial loads of 0.1 to 27 MPa show that strain and strain rate are proportional to the square root of time and exhibit negative, power law dependence on uniaxial load, suggesting that (1) fluid transport via capillary flow is rate limiting and (2) decreasing strain rate with increasing confining pressure might be a limiting factor in reaction driven cracking at depth. However, our experiments also demonstrate that crystallization pressure due to hydration exceeds 27 MPa (consistent with a maximum crystallization pressure of 153 MPa for the same reaction, Wolterbeek et al., https://doi.org/10.1007/s11440-017-0533-5). As a result, full hydration can be achieved at crustal depths exceeding 1 km, which is relevant for engineered fracture systems.

1. Introduction

Retrograde metamorphism is an essential process of geodynamics. Hydration of igneous, oceanic crust and mantle (Craft & Lowell, 2009; Roland et al., 2010; Van Avendonk et al., 2011), followed by subduction (Carlson & Miller, 2003; Gorman et al., 2006), supplies significant volumes of water that drive arc volcanism (Schmidt & Poli, 1998; Sobolev & Chaussidon, 1996), controls the rheology of oceanic plate boundaries (Hirauchi et al., 2016), and lubricates convection by maintaining or increasing the hydrogen content of the mantle over time (McGovern & Schubert, 1989). Chemical weathering is as important as magmatism and plate tectonics in shaping the Earth’s surface (Fletcher et al., 2006; Jamtveit et al., 2009). Mineral carbonation during alteration of ultramafic and mafic rocks throughout the plate tectonic cycle is increasingly recognized as an important but poorly characterized link in the carbon cycle (Dessert et al., 2003; Kelemen & Manning, 2015). Finally, engineered methods emulating this natural process are potentially transformational technologies for extraction of oil and gas from tight reservoirs, managing the permeability of wells, facilitating or enhancing circulation of water in geothermal power generation systems, in situ solution mining, for example, for Uranium, and in situ geologic carbon capture and storage (Kelemen & Matter, 2008; Matter et al., 2016; Wolterbeek et al., 2017).

Despite the potential importance of reaction-driven cracking, fundamental uncertainties remain in methods for estimating crystallization pressures during retrograde metamorphism. Generation of stress due to crystallization has been mostly studied in environments where crystallization occurs within a porous medium whose matrix does not participate in the reaction. For instance, deterioration in building stones due to the crystallization of salt is particularly well documented with numerous experimental (e.g., Derluyn et al., 2014; Noiriel et al., 2010; Steiger, 2005) and theoretical (e.g., Coussy, 2006; Osselin et al., 2014) studies attempting to quantify the stresses involved. During mineral hydration or carbonation, however, the matrix supplies reactive components via dissolution and reprecipitation (Putnis, 2009). In either case, generation of crystallization pressure, that is, the deviatoric stress in excess of confining pressure, depends on the degree of supersaturation and the change of molar volume between the dissolving and precipitating phases (Kelemen et al., 2011; Kelemen & Hirth, 2012). However, the actual pressure generated in a rock undergoing retrograde metamorphism also depends on many other factors, including the rate of viscous deformation, formation of fractures, friction along preexisting fractures, shear heating combined with thermal diffusion, the potential for compaction, clogging of porosity, and armoring of reactive surfaces.
with product phases. As a result, there is no consensus regarding the nature of deformation due to retrograde metamorphism (e.g., Ghofrani & Plack, 1993; Kuleci et al., 2017; Ostapenko & Yaroshenko, 1975; Skarbek et al., 2018; Van Noort et al., 2017; Wolterbeek et al., 2017; Zhu et al., 2016). Moreover, it has been suggested that the upper bound of stress generated by reaction depends on the bulk pore pressure (Rahman & Grasley, 2017), the pore structure (Lee & Kurtis, 2017), and/or surface and interfacial properties between the porous solid matrix, the growing crystal, and the fluid phase (Espinosa-Marzal & Scherer, 2010; Kelemen et al., 2013; Reyne & Jamtveit, 2015; Shahidzadeh-Bonn et al., 2008; Steiger, 2005; Zheng et al., 2018; and references therein). Kelemen and Hirth (2012) developed thermodynamic and mineral physics methods to estimate crystallization pressure during hydration and carbonation of the abundant rock-forming mineral olivine. Assuming that the crystallization pressure is limited by available chemical potential energy, they suggest two possible simple formulations:

\[ P_0 = -\frac{\Delta G_r}{\Delta V_s} \]  \hspace{1cm} (1)

and

\[ P_0 \leq -\frac{\Delta G_r}{\Delta V_s} + p\frac{\Delta V_r}{\Delta V_s} \]  \hspace{1cm} (2)

where \( P_0 \) is the crystallization pressure, \( \Delta G_r \) is the Gibbs free energy of a reaction, \( \Delta V_s \) is the change in solid volume resulting from this reaction, \( \Delta V_r \) is the volume change of the stoichiometric reaction (including fluid), and \( p \) is the confining pressure. (Also, see Fletcher & Merino, 2001, Steiger, 2005, and Wolterbeek et al., 2017, for similar formulations). The inequality arises because equation (2) is derived with the assumption (implicit in prior work) that all available chemical potential energy is converted into work. Using equation (2), \( P_0 \) is on the order of 500 MPa for olivine hydration and carbonation at 200 °C. Kelemen and Hirth (2012) also developed a relationship between \( P_0 \) and the density of fractures formed by expansion during olivine hydration at ~200–300 °C, which also yields \( P_0 \) of ~300 MPa. Based on these estimates, which are higher than the differential stress required to fracture rocks (e.g., Attewell & Farmer, 1976), it may be possible for the volume change due to olivine hydration and carbonation to cause fracture formation and dilation, maintaining or increasing permeability and reactive surface area in a positive feedback mechanism. However, both the thermodynamic and physical estimates of \( P_0 \) remain highly uncertain. Moreover, this thermodynamic expression does not incorporate energy sinks such as exothermic heating, frictional heating, and/or thermal diffusion. Finally, thermodynamically calculated pressures from equation (2) provide an upper bound that commonly exceeds stresses required for rock failure, via fracture, frictional sliding on existing fractures, closing of nanofilms that allow crystal growth when disjoining pressure is exceeded, and/or viscous flow (e.g., pressure solution, as noted by Kelemen & Hirth, 2012, and references therein).

2. Materials and Methods

To explore the effect of confining pressure on volume changes during retrograde metamorphism, and ultimately provide a better estimation of the relationships between \( P_0 \), chemical potential, and confining pressure, we explored crystallization pressure in a simple system, the hydration of quicklime (CaO) to form portlandite (Ca(OH)\(_2\)) under laboratory conditions:

\[ \text{solid CaO} + \text{H}_2\text{O} = \text{solid Ca(OH)}_2. \]  \hspace{1cm} (3)

The hydration of calcium oxide is a good analog for forsterite carbonation, with faster reaction rates but similar solid volume changes (96% and 84% in stoichiometric proportions), assuming densities of 3.34 and 2.25 g/cm\(^3\) for CaO (Haynes, 2011) and portlandite (Taylor, 1997), and 3.22, 2.65, and 2.96 g/cm\(^3\) for forsterite (e.g., Kumazawa & Anderson, 1969), silica (Haynes, 2011), and magnesium carbonate (e.g., Komprobst & Plank, 2013), respectively, and \( \Delta G_r(25 \, ^\circ C) \approx -57 \) and \(-70 \, \text{kJ/mol} \) for CaO hydration and olivine carbonation, respectively (see Text S1 in the supporting information for details on calculations). Using equation (2), \( P_{\text{Ca(OH)}_2} \leq 3.5 \, \text{GPa at 25 °C and 0.1 MPa on the same order of magnitude as } P_0 \text{ estimated for olivine hydration and carbonation in the same conditions. These crystallization pressures are 2 to 3 orders of} \)
magnitude larger than the tensile strength for igneous rocks (5–30 MPa; e.g., Cai, 2010; Lumb, 1983; Schultz, 1995) and at least an order of magnitude larger than the compressive strength of igneous rocks (Attewell & Farmer, 1976).

Reagent CaCO₃ powder (99.5% purity and average size of 10 μm) was used as a starting material. The powder was decarbonated at 850 °C for 2 hr and cooled under vacuum, before being cold pressed at 6,500 psi for one half-inch-diameter samples and at 3,500 psi for 5-mm-diameter samples to form cylinders with initial porosity Φ₀, ranging from 0.38 to 0.53. Conditions were chosen to minimize the sintering effect and maximize the reactivity of the CaO powder (see Text S2 in the supporting information; Borgwardt, 1989; Shin et al., 2009). Initial porosities were calculated such as

\[ \Phi_0 = 1 - \frac{m_0}{\rho V_0} \]  

with \( m_0 \) (in grams) and \( V_0 \) (in cubic centimeters), the mass and volume of the cylinder, respectively, and \( \rho \) the density of the material. Precision of length and initial weight measurements are ±0.005 cm and ± 0.1 mg, respectively (Table 1). Once formed, these cylinders were baked again for 30 min at 850 °C—to ensure that all CaCO₃ and/or Ca(OH)₂ that might have been produced during contact with air during the cold pressing process was dehydrated to form CaO—and then cooled under vacuum for ~30 min. The samples were prepared immediately before each experiment to minimize the contact of the cylinders with air before the experiment.

Using experimental methods similar to those of Wolterbeek et al. (2017), we conducted experiments in which the cylinder of cold-pressed CaO powder was confined in hardened steel and subject to a constant uniaxial load, \( \sigma \) (between 0.1 and 27.2 MPa), while water was introduced through a 10-μm porous frit at the bottom of the sample (Figure 1). Preliminary tests performed with a 20-μm porous frit showed some extruded material inside the frit at the end of the experiment, suggesting the resulting Ca(OH)₂ grains are between 10- and 20-μm diameters. We note however that the extruded material did not significantly block flow through the frit.

The interior of the die was covered with a thin film of electrical insulating compound; this hydrophobic grease does not react with the CaO and suppresses adhesion of the material to the steel. Without lubrication, the reacted material did not expand vertically and the porosity of the cylinder dropped significantly. We recorded the displacement of the piston using either a dial indicator or a linear variable differential transformer and assumed that the effect of friction is negligible.

All but two experiments were conducted at room temperature (~22 °C). The two additional experiments were performed at ~55 °C by placing a band heater around the pressure vessel. Temperature was monitored in selected experiments with a thermocouple placed at the top of the die (Figure 1a). The temperature variation was less than ±3 °C. Once the experiments stopped, the wet cylinders were weighed and then dried (Figure 1b). We first chose to dry samples at 100 °C under vacuum, but three samples showed evidence for continuation of the reaction (deformation of the cylinder) inside the furnace. Hence, we then dried the samples at 200 °C for 1 hr. No evidence of continuation of the reaction was observed in these conditions. Table 1 summarizes the experimental conditions and results.

3. Results

We emphasize three key observations. In addition, we briefly discuss possible reasons for variability in the results of repeat experiments with the same initial conditions.

3.1. Positive Volume Change in all Experiments

A positive volume change is observed in all experiments (Figure 2a), indicating that the crystallization pressure (equation (2)) for hydration of quicklime to form portlandite (equation (3)) is higher than the maximum axial load (27.2 MPa). This is the case despite the relatively high initial porosity of the samples (Φ₀ = 0.36 to 0.52; Table 1). Final porosity is >0.05 in all samples (Table 1), and reaction was more than 80% complete in most experiments. For comparison, without expansion of the solid volume, the reaction would stop when the final porosity approaches 0 (assuming all pores are connected) at around 70% conversion of CaO to Ca(OH)₂ for samples with initial porosity of 38%.
As can be seen in Figure 2, the strain, \( \varepsilon \), exhibits a power law relationship with time,

\[ \varepsilon = k_1 \cdot t^m, \]

with \( m = 0.38 - 0.72 \). The derivative of equation (5) as a function of time is

\[ \dot{\varepsilon} = mk_1 \cdot t^{m-1}. \]

There is no systematic correlation between \( m \) and the applied load (\( \sigma \)).

Figure 2b illustrates that observed strain rates are all positive, though decreasing with time. Below, we will show that \( m \) is most likely \( \sim 0.5 \), so

\[ \dot{\varepsilon} = 0.5k_1 \frac{1}{\sqrt{t}}. \]

### Table 1
Summary of the Experimental Conditions and Results for the Hydration Experiments

<table>
<thead>
<tr>
<th>( \sigma ) (MPa)</th>
<th>( T ) (°C)</th>
<th>( r_0 ) (cm)</th>
<th>( h_0 ) (cm)</th>
<th>( V_0 ) (cm³)</th>
<th>( m_0 ) (g)</th>
<th>( \Phi_0 )</th>
<th>( t ) (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#3</td>
<td>0.11</td>
<td>22</td>
<td>0.612 (5)</td>
<td>1.830 (5)</td>
<td>2.150 (41)</td>
<td>4.5294 (1)</td>
<td>0.371 (7)</td>
</tr>
<tr>
<td>#15(^a)</td>
<td>0.11</td>
<td>22</td>
<td>0.609 (5)</td>
<td>1.690 (5)</td>
<td>1.966 (38)</td>
<td>4.0445 (1)</td>
<td>0.386 (7)</td>
</tr>
<tr>
<td>#820</td>
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<td>22</td>
<td>0.610 (5)</td>
<td>2.831 (5)</td>
<td>3.309 (60)</td>
<td>5.8124 (1)</td>
<td>0.476 (9)</td>
</tr>
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<td>0.612 (5)</td>
<td>1.830 (5)</td>
<td>2.150 (41)</td>
<td>3.9390 (1)</td>
<td>0.453 (9)</td>
</tr>
<tr>
<td>#6</td>
<td>0.4</td>
<td>22</td>
<td>0.613 (5)</td>
<td>1.379 (5)</td>
<td>1.625 (32)</td>
<td>3.4748 (1)</td>
<td>0.362 (7)</td>
</tr>
<tr>
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</tr>
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<td>2.658 (49)</td>
<td>4.5457 (1)</td>
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<td>55</td>
<td>0.610 (5)</td>
<td>1.883 (5)</td>
<td>2.201 (42)</td>
<td>4.3306 (1)</td>
<td>0.413 (8)</td>
</tr>
<tr>
<td>#B51(^c)</td>
<td>0.99</td>
<td>22</td>
<td>0.610 (5)</td>
<td>2.398 (5)</td>
<td>2.803 (52)</td>
<td>4.45 (1)</td>
<td>0.53 (1)</td>
</tr>
<tr>
<td>#B22</td>
<td>4.2</td>
<td>22</td>
<td>0.610 (5)</td>
<td>2.179 (5)</td>
<td>2.547 (48)</td>
<td>4.9075 (1)</td>
<td>0.425 (8)</td>
</tr>
<tr>
<td>#7(^d)</td>
<td>4.32</td>
<td>22</td>
<td>0.609 (5)</td>
<td>2.402 (5)</td>
<td>2.794 (52)</td>
<td>4.3729 (1)</td>
<td>0.53 (1)</td>
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<td>55</td>
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<td>1.544 (5)</td>
<td>1.808 (35)</td>
<td>3.7070 (1)</td>
<td>0.388 (8)</td>
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<td>0.610 (5)</td>
<td>1.883 (5)</td>
<td>2.201 (42)</td>
<td>4.3306 (1)</td>
<td>0.413 (8)</td>
</tr>
<tr>
<td>#17(^c)</td>
<td>27.21</td>
<td>22</td>
<td>0.240 (5)</td>
<td>1.673 (5)</td>
<td>0.303 (14)</td>
<td>0.5200 (1)</td>
<td>0.49 (2)</td>
</tr>
</tbody>
</table>

Note. All experiments reported in this table were performed with CaO powder produced after 2 hr of decarbonation of CaCO\(_3\) at 850 °C. Drying process after the experiment is either 1 hr at 100 °C under vacuum (100 v) or 1 hr at 200 °C (200). \( \sigma \) = axial load; \( T \) = temperature; \( r \) = radius; \( h \) = height; \( V \) = volume; \( m \) = weight; \( \Phi \) = porosity, subscripts 0 and fi are for initial and final, respectively; \( t \) = duration of the experiments. The limits of precision (in brackets) are given in terms of the smallest unit reported: For example, 0.612 (5) and 2.150 (41) represent 0.612 ± 0.005 and 2.150 ± 0.041, respectively.

\(^a\)The sample was lost during the extraction because it was too friable—reaction extent was approximately equal to 100%.

\(^b\)Samples lost during the drying process; % Ca(OH)\(_2\) is calculated from wet weight.

\(^c\)The calculated % Ca(OH)\(_2\) was initially higher than 100%. We corrected it to 100% and back-calculated \( m_f \).

\(^d\)See Text S1 in the supporting information for details on calculations.

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As can be seen in Figure 2, the strain, \( \varepsilon \), exhibits a power law relationship with time,

\[ \varepsilon = k_1 \cdot t^m, \]

with \( m = 0.38 - 0.72 \). The derivative of equation (5) as a function of time is

\[ \dot{\varepsilon} = mk_1 \cdot t^{m-1}. \]

There is no systematic correlation between \( m \) and the applied load (\( \sigma \)).

Figure 2b illustrates that observed strain rates are all positive, though decreasing with time. Below, we will show that \( m \) is most likely \( \sim 0.5 \), so

\[ \dot{\varepsilon} = 0.5k_1 \frac{1}{\sqrt{t}}. \]

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**Figure 1.** (a) Schematic of the experiments (not to scale). Internal diameter of the die was either 12.7 or 5 mm (run #17; Table 1). (b) Picture of the cold-pressed cylinder before and after hydration experiment with a uniaxial pressure of 0.4 MPa at 55 °C (run #18). The scale is in millimeters. LVDT = linear variable differential transformer.
3.2. Strain Rate Proportional to the Square Root of Time

Second, the evolution of strain with axial load (Figure 3) is best fit by a power law:

\[ k_1 = k_2 \sigma^{-\alpha}. \]  

Thus, one can derive a flow law

\[ \dot{\varepsilon} = \frac{0.5 k_2}{\sigma^\alpha \sqrt{t}}. \]  

By combining equations (5), (8), and (9), we obtain an alternative flow law in terms of axial load and strain rather than axial load and time:

\[ \dot{\varepsilon} = \frac{0.5 k_2^2}{\sigma^\alpha \varepsilon}. \]  

### Table 1 (continued)

<table>
<thead>
<tr>
<th>Drying (°C)</th>
<th>r_f (cm)</th>
<th>h_f (cm)</th>
<th>V_f (cm^3)</th>
<th>m_f (g)</th>
<th>% Ca(OH)_2</th>
<th>Φ_f (bulk)</th>
<th>Φ_f (Ca(OH)_2)</th>
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<tr>
<td>#3</td>
<td>100 v</td>
<td>0.612 (10)</td>
<td>6.130 (10)</td>
<td>7.28 (19)</td>
<td>5.97 (5)</td>
<td>99.0 (34)</td>
<td>0.634 (71)</td>
</tr>
<tr>
<td>#15^a</td>
<td>100 v</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>100.0</td>
<td>0.647</td>
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<tr>
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<td>4.630 (10)</td>
<td>5.41 (14)</td>
<td>7.50 (5)</td>
<td>90.2 (27)</td>
<td>0.408 (40)</td>
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<tr>
<td>#B3</td>
<td>100 v</td>
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<td>3.691 (10)</td>
<td>4.44 (12)</td>
<td>5.01 (5)</td>
<td>84.2 (40)</td>
<td>0.532 (75)</td>
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<tr>
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<td>4.59 (5)</td>
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<td>2.685 (10)</td>
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<td>88.4 (38)</td>
<td>0.236 (31)</td>
</tr>
<tr>
<td>#12^b</td>
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<td>2.750 (10)</td>
<td>3.25 (9)</td>
<td>5.97 (5)</td>
<td>&lt;74.0</td>
<td>&gt;0.308 (36)</td>
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<tr>
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<td>3.878 (10)</td>
<td>4.62 (12)</td>
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<td>3.266 (10)</td>
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<td>5.86 (5)</td>
<td>89.8 (34)</td>
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<td>3.583 (10)</td>
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<td>99.6 (36)</td>
<td>0.389 (46)</td>
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<td>5.88 (5)</td>
<td>100.0 (35)</td>
<td>0.285 (33)</td>
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<tr>
<td>#B22</td>
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<td>3.030 (10)</td>
<td>3.61 (10)</td>
<td>6.30 (5)</td>
<td>88.6 (32)</td>
<td>0.260 (30)</td>
</tr>
<tr>
<td>#7^b</td>
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<td>2.761 (10)</td>
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<td>5.56 (5)</td>
<td>&lt;82.2</td>
<td>&gt;0.306 (40)</td>
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<tr>
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<td>1.991 (10)</td>
<td>2.33 (7)</td>
<td>4.68 (5)</td>
<td>81.5 (42)</td>
<td>0.179 (28)</td>
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<td>2.723 (10)</td>
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<td>5.72 (5)</td>
<td>100.0 (36)</td>
<td>0.194 (23)</td>
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<td>200</td>
<td>0.240 (10)</td>
<td>1.800 (10)</td>
<td>0.33 (2)</td>
<td>0.69 (5)</td>
<td>100.0 (30)</td>
<td>0.054 (44)</td>
</tr>
</tbody>
</table>

![Figure 2](image-url)

**Figure 2.** Evolution of the volumetric strain, \( \varepsilon = \Delta V/V \) (a), and of the strain rate, \( \dot{\varepsilon} \) (b), as a function of time under uniaxial loads, \( \sigma \), between 0.1 and 27.2 MPa (Table S3). Experiments performed at 22 °C are represented with solid lines (recorded with LVDT) and solid symbols (recorded with dial indicator). Experiments performed at 55 °C are represented with open symbols (recorded with dial indicator). Strains are reported for displacements larger than the accuracy of the dial indicator (\( \pm 0.001" \)).
3.3. Final Porosity Correlated With Uniaxial Load

Third, the final porosity in the experimental run products varies as a function of uniaxial load (Figure 4), with smaller final porosities at higher loads.

3.4. Possible Explanation for Variation in Replicated Experiments

We did not find a systematic explanation for sample-to-sample variation in replicated experiments. The scatter may be due to a combination of the size of the initial cylinder, the initial porosity, variable lubrication between the sample cylinder and the steel die, and perhaps the amount of impurities in the starting material.

4. Discussion

4.1. Flow Law

Using Washburn’s equation (1921) for capillary rise in vertical cylindrical tubes and a capillary radius of 10 μm, we estimated that water would rise up to the top of a 4- to 6-cm cylinder in ~15–25 hr. This value is of the same order of magnitude than duration of the experiments at 0.1 MPa (Figure 2a; Table 1). In comparison, the CaO hydration reaction is fast, 2–3 min for highly reactive lime to reach full hydration (Miller, 1960).

Hence, evolution of the volumetric strain with time (equation (5)) is primarily controlled by the absorption of water in the CaO cylinder via capillary infiltration. Infiltration in a porous medium by capillarity can be described as

\[ I = S \sqrt{t} + At, \]  

where \( I \) is the liquid-front location, \( S \) is the sorptivity of the media, and \( A \) is a parameter that accounts for the contribution of gravity during vertical infiltration (Masoodi & Pillai, 2010; Philip, 1957). Because we observe that strain is approximately proportional to \( \sqrt{t} \), and that porosity is related to the axial load, our data suggest that the strain rate is related to the sorptivity (Figures 2–4). Note that the design of our experiments differs from capillarity experiments, as the base of the CaO cylinder is partly below the water level (Figure 1a). Hence, the effect of gravity will be partly counterbalanced by the effect of the pressure at the entrance of the sample. Moreover, for such small samples, the gravitational effect is usually considered to be negligible (see Text S3 in the supporting information; Selker et al., 2007; Weisbrod et al., 2002). Hence, we can rewrite equation (11) as

\[ \varepsilon = \frac{k_3 S}{h_0} \sqrt{t} + \frac{1}{\sqrt{t}} = \frac{k_3 S}{h_0} \varepsilon, \]  

in which \( h_0 \) the initial height of the cylinder. Best fit values for \( S_1 = k_3 S \) were calculated by minimizing the difference between experimental data and values predicted by equation (12).

Equation (12) explains 95% of the experimental variance and reproduces the observed strains with a standard error of estimate of 12% (see supporting information Figure S3), supporting our assumption that the volumetric strain is dominated by the sorptivity of the material.

In this analysis, \( S \) is assumed to be constant with time. Because the porosity is changing with time, and \( S \) is a function of permeability and porosity (see section 4.2), \( S \) should also be a function of time.
However, expressions including the evolution of porosity with time do not significantly change the predicted strain evolution (see Text S4 in the supporting information). Because the volumetric strain is dominated by the sorptivity of the material, we assume that equation (12) applies to our data and \( m \) in equation (5) is equal to 0.5. From equation (5)

\[
k_1 = \frac{k_3}{h_0} S
\]

and combining with equation (8)

\[
\sigma^{-m} = \frac{k_3 S}{k_2 h_0}, \quad \text{so} \quad \sigma^{m} = \frac{k_2 h_0}{k_3 S} \quad \text{and} \quad \sigma = \frac{k_4 S}{\sqrt{\sigma}}. \tag{14}
\]

Thus, the combination of our observations and theoretical expressions allows us to relate sorptivity and axial load. Note that we can differentiate equation (12), and substitute \( \frac{k_3}{h_0} S \) for \( \frac{1}{C_0} \) and \( k_2 \cdot \sigma^{-m} \) for \( \frac{k_3}{h_0} S \) to obtain equation (10).

### 4.2. Relationship Between Axial Load and Porosity

In order to test our assumptions and develop a better understanding of the relationship between axial load and porosity (Figure 4), assuming one-dimensional fluid flow following Darcy’s law, we used the following expression for \( S \) in a swelling porous media (Masoodi & Pillai, 2010):

\[
S = \sqrt{\frac{4K\gamma \cos\theta}{\Phi \eta R_c}} = \sqrt{\frac{k_5 K}{R_c}}, \tag{15}
\]

where \( K \) is permeability, \( \gamma \) is surface tension of the liquid, \( \theta \) is the contact angle, \( \eta \) is the liquid viscosity, and \( R_c \) is the capillary pore radius. Note that in equation (15), the effect of gravity is neglected. Simplified geometrical relationships between porosity, pore radius, and solid grain size (Ahern & Turcotte, 1979) yield

\[
R_c^2 = k_6 \Phi d^2, \tag{16}
\]

in which \( \Phi \) is the porosity and \( d \) is the diameter of the solid grains. Several empirical and theoretical formulas have been developed to describe the permeability of a porous media as function of the porosity, which generally have the form

\[
K = d^2 f(\Phi), \tag{17}
\]

where \( f(\phi) \) is a function of porosity (e.g., Masoodi & Pillai, 2010). Thus,

\[
S = \sqrt{\frac{k_5 K}{R_c}} = \sqrt{\frac{k_6 \Phi d^2 f(\Phi)}{k_6 \Phi^{0.5} d}} = k_7 \sqrt{\frac{f(\Phi)}{\Phi^{0.5} d}}, \tag{18}
\]

and

| Equation Used for \( f(\Phi) \) and Relationship Between \( \sigma \) and \( \Phi \) |
|-----------------|-----------------|
| \( f(\Phi) \)    | \( \sigma(\Phi) \) |
| Kozeny-Carman equation | \( \frac{\Phi^3}{(1-\Phi)^2} \) | \( k_8 \left( \frac{\Phi^{1/2}}{(1-\Phi)^{1/2}} \right)^{1/2m} \) |
| Rumpf and Gupte | 0.5 | \( k_8 \left( \Phi^{1/2} \right)^{1/2m} \) |
| Du Plessis and Masliyah | \( \Phi \left[ 1-\left(1-\Phi^{1/2}\right)^{1/2} \right] \left[ 1-\left(1-\Phi^{1/2}\right)^{1/2} \right] \left(1-\Phi^{1/2}\right)^{1/2} \) | \( k_8 \left( \Phi^{1/2} \left[ 1-\left(1-\Phi^{1/2}\right)^{1/2} \right] \left[ 1-\left(1-\Phi^{1/2}\right)^{1/2} \right] \right)^{1/2m} \)


This provides predictions of the relationship of porosity and axial load that can be compared to our observations of the final porosity in our experiments (Figure 4; Table 1). To predict porosity versus axial load using equation (19), we use three different functions for permeability as a function of $\Phi$ (Table 2): (1) the Kozeny-Carman equation (Carman, 1938, 1956; Koseny, 1956) for granular media consisting of arbitrary shaped particles, (2) Rumpf and Gupta’s equation (1971) for packed spherical particles with porosity from 0.35 to 0.7, and (3) Du Plessis and Masliyah’s model (1991) for a consolidated rock-like media with $\Phi > 0.1$.

Fixing $\alpha = 1.15$ (based on the fit to data in Figure 3), and using a grain diameter of 10 $\mu$m, we found the best fit values for $k_8$ by minimizing the sum of the squares between experimental and model values. Rumpf and Gupta’s empirical equation provides the best approximation of final porosity in the samples (Figure 4). The Kozeny-Carman equation is the most widely used relationship between porosity and permeability but has limited accuracy for the special case of sphere packing (Pan et al., 2001, and references therein). Du Plessis and Masliyah used the concept of a unit cell based on prismatic geometry (e.g., Du Plessis & Roos, 1994), whereas Rumpf and Gupta (1971) assume that grains are for packed spherical particles. Hence, our results suggest that CaO grains in our samples are better approximated by spherical particles.

### 4.3. Dependence of Strain on Axial Load

We have explored the relationship of expansion and sorptivity in the previous section to explain the power law relationship between strain and time at a given axial load (Figure 2). In this section, we discuss the negative, power law dependence between the strain and the axial stress.

In order to understand the decreasing strain at a given time with increasing uniaxial load (Figure 3; equation (12)), we first explored the role of pressure solution by performing a compaction experiment on wet portlandite with $\sigma = 4.32$ MPa (Text S5 in supporting information). If the reduction of the strain rate were due to compaction alone, we would be able to combine the power law relationship between strain and time at 0.1 MPa (Figure 2) with the compaction effect at $\sigma = 4.32$ MPa to reproduce the relationship between strain and time at 4.32 MPa. However, the compaction effect is negligible (see supporting information Figure S4; Zhang et al., 2002) and cannot be responsible for the decreasing strain at a given time with increasing uniaxial load. Instead, it is likely that our samples undergo relatively rapid compaction during the transformation from CaO to Ca(OH)$_2$.

An interesting clue is provided by considering the work rate. At a given time, the amount of work per mole, $W$ (J/mol), produced by the system on its surroundings is

$$ W = \sigma \Delta V / n, $$

with $n$ equal to the number of moles in the system. Figure 5 shows $W$ as a function of time for experiments performed at room temperature. The 3-order-of-magnitude variation in strain at a given time (Figure 2a) is greatly reduced in Figure 5. Because $\Delta V / n$ is proportional to $\varepsilon$, the work done by the system—like the strain—is approximately proportional to the square root of time and independent of the applied axial load. In turn, filling of pore space reduces the porosity (Figure 4) and permeability, reducing the rate of capillary flow to the reaction front.

Since high load experiments required longer times for complete reaction, and the work rate is approximately independent of the load, the cumulative work during complete reaction must increase with increasing load (Figure 6). (Note that the total amount of energy produced as work in these experiments, ~1 to 70 J/mol for
Figure 6. Total work, \(\bar{W}\) (J·mol\(^{-1}\)), after 80% to 100% conversion of CaO to Ca(OH)\(_2\).

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