

2020

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Stefan Iglauer
Edith Cowan University

Ahmed Zarzor Al-Yaseri
Edith Cowan University

Domenik Wolff-Boenisch

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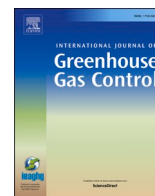


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[10.1016/j.ijggc.2020.103148](https://doi.org/10.1016/j.ijggc.2020.103148)

Iglauer, S., Al-Yaseri, A. Z., & Wolff-Boenisch, D. (2020). Basalt-CO₂-brine wettability at storage conditions in basaltic formations. *International Journal of Greenhouse Gas Control*, 102, article 103148. <https://doi.org/10.1016/j.ijggc.2020.103148>

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ARTICLE INFO

Keywords

CO₂ geo-sequestration
Basalt
Storage capacity
Wettability

ABSTRACT

CO₂ geo-storage in basaltic formations has recently been demonstrated as a viable solution to rapidly sequester and mineralize CO₂. In case CO₂ is injected into such basalt reservoirs in supercritical form, a two-phase system (reservoir brine and supercritical CO₂) is created, and it is of key importance to specify the associated CO₂-basalt wettability so that fluid distributions and CO₂ flow through the reservoir can be predicted. However, there is a serious lack of data for basalt CO₂-wettability. We therefore measured water contact angles on basalt substrates in CO₂ atmosphere. The results indicate that at shallow depth (below 500 m) basalt is strongly water-wet. With increasing depth the basalt becomes less hydrophilic, and turns intermediate-wet at a depth of 900 m. We conclude that basalt is more CO₂-wet than chemically clean minerals (quartz, calcite), especially at depths below 900 m. However, the basalt had a CO₂-wettability similar to some caprock samples and a gas-reservoir sandstone. The data presented in this paper will thus aid in the prediction and optimization of CO₂ geo-storage in basalt formations.

1. Introduction

Carbon Geo-Sequestration (CGS) in basaltic formations is termed an ‘unconventional’ storage mechanism because most CGS attention is turned towards sedimentary formations with large pore volumes and adequate seals. However, igneous lithologies, especially of ultra-mafic and mafic nature, have their merits. Firstly, peridotites and basalts and their mineralogical constituents are far more reactive than sandstones when exposed to acidic CO₂-charged brine (e.g. Wolff-Boenisch et al., 2011; Gudbrandsson et al., 2011). Secondly, peridotites consist mainly of the mafic minerals olivines and pyroxenes, whereas for basalts Ca-rich plagioclases and interstitial glass are additional major phases. For both rock types, their elemental release contains substantial amounts of divalent cations (Mg, Ca, Fe) that can effectively trap CO₂ in form of solid carbonate minerals (Oelkers et al., 2008). Hence, these rock types promise not only to take CGS to the desired end state of mineral trapping, but also to facilitate mineral trapping in a very short time frame. Indeed, successful *fast* mineralisation of CO₂ in ‘unconventional’ basalt matrices has been demonstrated recently in field studies in Iceland (Carbfix project) and Washington State (Columbia River Basalt Project), respectively (Matter et al., 2016; McGrail et al., 2016).

Furthermore, particularly basalts have been known to occur in staggering expansions and thicknesses rivalling those of sedimentary basins. Large igneous provinces for example spread over hundreds of square km (e.g. Indian Deccan Traps, Siberian Traps, Emeishan Traps) and can reach several km thickness (Ernst, 2014). These localised occurrences are supplemented by other basaltic terrains such as volcanic islands associated with hot spots (e.g. Madeira, Hawaii) and mid-ocean ridges (e.g. Iceland). MORBS (mid ocean ridge basalts) are the most voluminous volcanic rocks on Earth, constituting the top 1–2 km of the oceanic crust and covering nearly two-thirds of the Earth’s surface beneath the oceans (le Roex, 1998). So there is quite a vast playing field for finding a suitable basalt formation in terms of permeability, storage

capacity, and trapping efficiency for supercritical (sc) CO₂ injection, just as for sedimentary deposits (Goldberg et al., 2018).

One key parameter in case of direct (free) CO₂ injection into such basaltic formations is the basalt-water-CO₂ wettability, which determines the spreading and migration of the CO₂ in the basalt’s rock pore network (e.g. Donaldson and Alam, 2008; Blunt, 2017), and consequently basalt wettability also impacts on interfacial areas, mass transfer and mineralization rates (as was for instance shown for deep sandstone aquifers, Al-Khdheawi et al., 2017).

However, there is a serious lack of information on basalt-CO₂ wettability. We thus tested one basalt sample from the Hellisheidi geothermal area in Southwest Iceland (Alfredsson et al., 2013), to provide wettability data for basalt formations and thus enable associated CO₂ flow and storage predictions.

2. Experimental procedure

2.1. Basalt samples

Basalt samples from the CarbFix injection (Gislason et al., 2010; Aradottir et al., 2012; Snæbjörnsdóttir et al., 2017, 2018) site in Iceland were collected from borehole KB-01 at 535 m depth. This grey fine-grained crystalline basalt had an olivine tholeiitic composition with smectite and calcite as secondary alterations and was between 300,000 to 500,000 years old (Alfredsson et al., 2013). The basalt samples were further characterized via X-ray diffraction [XRD], scanning electron microscopy, quantitative total organic content [TOC] and surface roughness measurements. TOC was 700 ppm, and the basalt was very tight (porosity < 1%).

2.2. Experimental tests

For the CO₂-wettability experiments, cuboid basalt samples were cut

<https://doi.org/10.1016/j.ijggc.2020.103148>

Received 30 April 2020

Available online 1 October 2020

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with a high speed diamond blade (to $\sim 0.5\text{cm} \times 1\text{cm} \times 1\text{cm}$) and each sample was exposed to air plasma for 1 min to remove organic surface contaminants (Love et al., 2005; Iglauer et al., 2014). Although plasma cleaning removes the uppermost molecular organic layers of material (Alam et al., 2014), the basalt contained much more organic matter so that these naturally occurring organics were removed to only an insignificant extent.

Subsequently the advancing (θ_a) and receding (θ_r) water contact angles were measured using the tilted plate method (Lander et al., 1993) for typical storage pressures (4.48–17.23 MPa) and two temperatures (308.15 K and 333.15 K) using synthetic reservoir brine (4 wt % NaCl, 4 wt % CaCl_2 , 1 wt % MgCl_2 , and 1 wt % KCl dissolved in deionized water = 2.2 M ionic strength).

As surface roughness of a substrate can significantly influence measured contact angles (Marmur, 2006), this quantity was measured via atomic force microscopy (using a DSE 95–200 instrument). The root mean square surface roughness measured amounted to 210 nm, and thus had an insignificant influence on the CO_2 -brine-basalt contact angles (Al-Yaseri et al., 2016; Alnili et al., 2018).

The average standard deviation of the contact angle measurements was determined as $\pm 3^\circ$ based on replicate measurements.

3. Results and discussion

The brine contact angles drastically increased with pressure, Fig. 1. This is consistent with most literature published for mineral or rock surfaces (compare Broseta et al., 2012 or Arif et al., 2018; Iglauer et al., 2015a; Hobeika et al., 2017 for an overview). This effect is caused by the increase in intermolecular interactions between CO_2 and basalt with increasing pressure (as shown for quartz surfaces; e.g. Iglauer et al., 2012; Chen et al., 2015; Abramov et al., 2019). Consequently, the basalt turned intermediate-wet ($\theta > 70^\circ$) at pressures above ~ 9 MPa (this corresponds approximately to a depth of 900 m; note that the hydrostatic gradient in the subsurface is circa 10 MPa/km, Duke, 1978). Significantly more rapid CO_2 upwards movement is predicted for intermediate-wet systems (Al-Khdheawi et al., 2017), with resulting reductions in storage capacities and particularly containment security. Furthermore, the pore occupancy of CO_2 changes in an intermediate-wet rock, with significant fractions of the CO_2 now also contacting the basalt surface (precisely this depends on the exact pore morphology and capillary pressure, Blunt, 2017). This changes the basalt-acidic brine interfacial areas (note that at high partial CO_2 pressures brine is acidified considerably by the CO_2 (Peng et al., 2013)) and thus also basalt-brine reaction and mineralization rates. Moreover, a transition from strongly water-wet to weakly water-wet ($\theta > 50^\circ$) behaviour was

observed at ~ 7 MPa, which has similar but less dramatic effects as outlined above. Temperature only had a slight influence, and higher temperature led to slightly elevated contact angles.

The basalt samples showed a wettability response similar to sedimentary caprock samples of a proposed CO_2 storage site (Iglauer et al., 2015b), despite differences in mineralogical composition. This is probably due to a) the somewhat similar elemental composition of the basalt (the caprocks mainly consisted of quartz and clay, illite/chlorite; 72–82 wt% clay + quartz content); and, more importantly, b) the similar TOC content (700 ppm in the basalt versus 510–4400 ppm in the caprocks). Note that surface organic groups strongly enhance the CO_2 -rock wettability (Ali et al., 2019a, 2019b, 2020; Abramov et al., 2019). Again a similar wettability response was observed in a Warro sandstone sample (Perth Basin), despite a different mineral composition (the Warro sandstone consisted of 90 wt% quartz, 3.3 wt% kaolinite, 6.7 wt% feldspar, Alnili et al., 2018). However, TOC was similar in the Warro sample (1600 ppm). We conclude that the main driver for the wettability response in such subsurface samples is the organic content.

Based on these results it is likely that the CO_2 mineralization reaction is strongly affected by this wettability change as the CO_2 -basalt and brine-basalt interfacial areas are expected to be quite different in an intermediate-wet rock (as opposed to a strongly or weakly water-wet rock), Blunt (2017). As higher CO_2 -rock wettability dewets the rock, comparatively lower degrees of dissolution-precipitation reactions are expected in intermediate-wet rock, where brine-basalt interfacial areas would be reduced. However, if wet scCO_2 dominates the fluid-rock interactions and concomitant mineralisation (as hypothesized by Loring et al., 2011; McGrail et al., 2009; Schaefer et al., 2013; Shao et al., 2011), mineral trapping would be accelerated. As a consequence, a mineralisation rate gradient versus depth is expected.

4. Conclusions and implications

A basalt wettability shift at 9–10 MPa (~ 0.9 km depth) from weakly water-wet to intermediate-wet has been identified experimentally. It is concluded that CO_2 is significantly more wetting below 1 km depth, and flows upwards more quickly due to this wettability shift, as predicted for sandstone aquifers (Al-Khdheawi et al., 2017, 2018). Overall, this study was conducted to elucidate basalt CO_2 -wettability, and thus improve the understanding of basalt- scCO_2 -brine systems, which will aid in the optimization of CO_2 storage in basalt formations.

Declaration of Competing Interest

The authors report no conflict of interest.

Acknowledgements

The authors wish to acknowledge the Carbfix consortium, especially Sandra Snæbjörnsdóttir, for providing the basalt cores.

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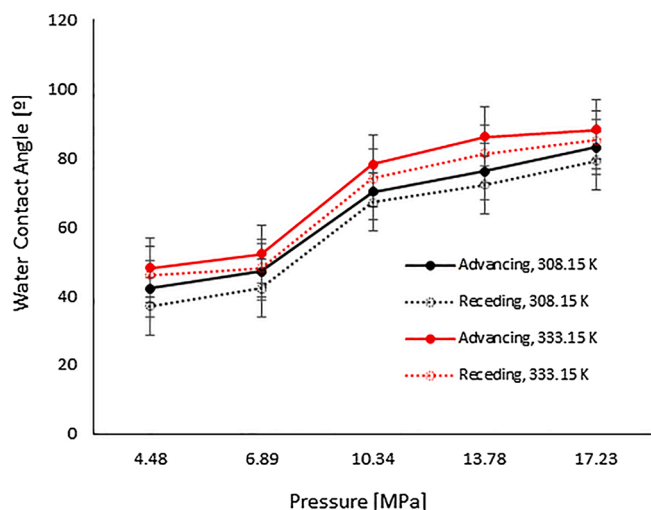


Fig. 1. Water contact angles measured on the basalt sample in CO_2 atmosphere.

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Stefan Iglauer^{a,*}, Ahmed Zarzor Al-Yaseri^a, Domenik Wolff-Boenisch^b

^a School of Engineering, Edith Cowan University, 270 Joondalup Drive, 6027 Joondalup, Australia

^b School of Earth and Planetary Sciences, Curtin University, GPO Box U1987, Perth, WA-6845, Australia

* Corresponding author.

E-mail address: s.iglauer@ecu.edu.au (S. Iglauer).