CO₂-EGS IN HOT DRY ROCK: PRELIMINARY RESULTS FROM CO₂-ROCK INTERACTION EXPERIMENTS

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ABSTRACT
Carbon dioxide has been identified to possess thermodynamic and transport properties that are suitable for use as "geofluid" to harness geothermal energy from hot dry rock (HDR) where water is scarce. However, limited literature is available on CO₂-rock interactions that may affect reservoir performance.

CO₂-rock interaction experiments were conducted in a flow-through titanium reactor to discover possible geochemical reactions that might affect reservoir performance of a CO₂-Engineered Geothermal System (EGS) in hot dry rock (HDR). Granite samples were collected to represent the granitic basement rock postulated to be typically present in HDR. Geothermal reservoir conditions of up to 250 °C and 20 MPa were simulated.

Preliminary results from Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), Scanning Electron Microscope (SEM), and X-ray fluorescence (XRF) analyses show that at 20 MPa and 200-250 °C reservoir conditions, there are no significant reactions/dissolutions of minerals in supercritical CO₂.

INTRODUCTION

CO₂-EGS system will develop three distinct zones (Zone 1) a central zone or “core” of single supercritical CO₂ phase; (Zone 2) a surrounding intermediate zone consisting of a two-phase water-CO₂ mixture; and (Zone 3) an outer or peripheral zone of single aqueous phase with dissolved CO₂ (Fouillac, Sanjuan, & Czernichowski-Lauriol, 2004; Ueda, et al., 2005). Numerical simulations of CO₂-H₂O-rock interaction (Zone 3) showed that diffusion of CO₂ in the periphery of CO₂-EGS may induce dissolution of primary minerals and precipitation of secondary carbonate and clay minerals. This reduces porosity which could result in a formation of low permeability barrier that may affect reservoir growth and longevity while on the other hand offer geologic storage of CO₂ as an added benefit (Xu & Pruess, 2010; Xu, Pruess, & Apps, 2008).

![Figure 1: Three phase zones that will develop in an EGS operated with CO₂. After(Xu, et al., 2008)](image-url)
CO₂-rock mineral interaction in sandstone formation experiments conducted using CO₂ revealed dissolution of ankerite/dolomite and Al-silicates could enhance porosity and permeability. However, end-member carbonates, anhydrite, and alteration of K-feldspar to form kaolinite could affect injection with the host aquifer. This has significant implications for the security and safe geological repository of CO₂.

Experiments conducted in a flexible cell hydrothermal apparatus to determine the extent of fluid-rock reactions that simulates a saline aquifer storage scenario at 200 °C and 200 bars injected with CO₂ showed geochemical reactions that extend beyond simple aqueous dissolution of CO₂ and precipitation of carbonate (Kaszuba, et al., 2003, 2005). This has significant implications for the security and safe geological repository of CO₂.

A pilot scale project located near Moomba plant in Cooper Basin is being considered for a small EGS demonstration plant utilizing CO₂ captured by the plant. One injection and one or more production wells will be drilled through sedimentary formations and up to 500 meters deep into the granitic basement. It is expected that the basement rock will be water saturated thus the initial production would be almost 100% water and the percentage of CO₂ will gradually increase as the pilot EGS is being exploited. The corrosive nature of CO₂-water mixture in the production wells would require corrosion resistant materials (Reichman, Bresnehan, Evans, & Selin, 2008).

Studies have been conducted on CO₂ sequestration by mineral carbonation in geothermal fields (Kaieda, et al., 2008; Kaieda, et al., 2009; Ueda, et al., 2005). These studies gave insights on the possible CO₂-H₂O-rock interactions at conditions where H₂O is the predominant fluid in the system. H₂O is saturated with injected CO₂ and precipitated as carbonate minerals at depth in geothermal fields.

An important step in creating EGS is reservoir stimulation which is usually done by hydraulic thermo-fracturing of re-sealed fractures in the crystalline basement rock. This procedure will inadvertently introduce water in the reservoir adding more to the in situ pore water. Injection of SC-CO₂ to the newly created EGS reservoir will create different fluid-rock interaction scenarios. During the initial stages of CO₂ injection, H₂O-CO₂-rock interaction will happen (it may be that H₂O will be dissolved in CO₂ or CO₂ will be dissolved in H₂O, depending on the relative quantities of CO₂ and H₂O). H₂O in the periphery of the reservoir will be pushed outward and might react with the surrounding rock. There will also be a region where CO₂ with minute amount of H₂O will interact with the host rocks. A simulation conducted by (Pruess & Spycher, 2010) found that in a fractured reservoir, CO₂ breakthrough at production wells would occur rapidly then subsequently a two-phase H₂O-CO₂ mixture would be produced for a few years followed by production of a single phase of SC-CO₂. However, significant dissolved water concentrations will persist in the CO₂ stream for many years.

This paper will present the preliminary results of CO₂-rock interaction experiments simulating CO₂-EGS Hot Dry Rock environment, zone 1 of Fig 1.

**METHODOLOGY**

**Fluid-Rock Interaction Apparatus**

A fluid-rock interaction apparatus was costumed built to evaluate fluid-rock interactions in EGS utilizing CO₂ as heat extracting medium. The apparatus can enable studies of unconsolidated rock samples with CO₂ and saturated brines at pressures up to 50 MPa and temperature up 400 °C. The fluid and rock are contained in a double-ended all titanium flexible cell (~160 cc) or titanium rigid reactor cell (~18 cc) both with 10 micron filter at both ends. The apparatus is composed of single non-rocking furnace with heater, pressure vessel, titanium cell assembly, digital back pressure regulator, confining pressure controller, piston accumulator with re-circulating chiller and computer hardware and software for data monitoring and acquisition (Fig 2 and 3).

![Fluid-rock interaction apparatus. Note that the high pressure pump used in the actual experiments is different from the one pictured above.](image-url)
Rock Sample Description

It is assumed that HDR geothermal reservoirs are hot granitic basement and so granite samples were collected to represent HDR geothermal reservoir. The samples were gathered and randomly collected at the surface from the granite outcrop at Monbi near the New England Highway in NSW, Australia (Fig 4).

The granite samples were cleaned, crushed and pulverized using tungsten carbide ring mill for 3 minutes. The pulverized samples were then analyzed for particle size distribution using MALVERN Instruments. The average particle size is ~ 16 μm with a range of 0.5 to 150 μm (Fig 5).

Other granite samples from drilled wells were also collected but will not be discussed in this paper. Instead, the mineral compositions will be compared with the sample gathered at the surface from Monbi.

Two drilling core samples from intersected granite from Mossgiel (Fig 6) and Nambucurra 1 (Fig 7) boreholes were collected from W B Clarke Geoscience Centre at Londonderry Core Library, Londonderry, NSW, Australia. Mossgiel samples are randomly collected from fragmented drill cores at depth of 1793-1796 m while Nambucurra 1 samples are from the drill core samples at depth of 856-857.5 ft.

The drill core samples were also pulverized using MALVERN Instruments for 3 minutes and the particle size distribution of Mossgiel and Nambucurra 1 samples are shown in Fig 8 and 9, respectively. Mossgiel has an average particle size of ~6 μm and range of up to 38 μm while Nambucurra 1 has an average of ~52 and range of up to 404 μm.
Experimental Procedure

Pulverized granite samples were used in batch experiments to determine CO$_2$-rock interaction that may affect reservoir performance of a CO$_2$-EGS. The samples were dried in 120 °C oven for more than 24 hrs. Enough pulverized samples were then packed in a rigid titanium cell reactor (about 25 g). Both ends of the titanium cell reactor have 10 µm filter which is secured by a titanium caps connected to titanium tubes (Fig 10).

After installing the titanium cell reactor at the autoclave, the whole system is then purge with CO$_2$ and the system pressure slowly increased to the designated pressure before finally set to the target temperature. At some target time interval, the "reacted" CO$_2$ was then allowed to bubble in 20 mL 2% nitric acid solution to collect cations and anions that may have dissolve in supercritical CO$_2$. While bubbling the CO$_2$, the system pressure and temperature was kept constant at designated reservoir pressure by pumping fresh CO$_2$ and operating the autoclave. Note that we used the same starting material for the specified reservoir pressure and temperature simulated in the experiment, i.e. after collecting sample at the designated time by pumping CO$_2$ into the system and bubbling the CO$_2$ in the 2% nitric acid solution, the CO$_2$ that was used to pushed the sample collected was left in the reactor and allowed to react for the next time interval.

The 2% nitric acid sample solutions were then analyzed using Varian 710/715-ES ICP-OES for elemental analyses. The untreated and treated pulverized granite samples were subjected to XRD (Spectro X’Lab 2000 Polarised ED-XRF) analyses for trace elements and major oxides, X-ray diffraction (XRD) for mineral analysis (Philips Diffractometer PW1710), and SEM (Philips XL30 SEM + Oxford ISIS EDS + Gatan Mini Cathodoluminescence Detector) analysis at the EMX Unit of the Central Scientific Services, The University of Newcastle, Australia.

PRELIMINARY RESULTS AND DISCUSSION

Sample Compositions

The approximate mineral compositions of the samples were determined using Rietveld quantitative XRD analysis and SIROQUANT™ V3 commercial software from Sietronics Pty Ltd (AMDEL, Limited). Known amount of zinc oxide (ZnO) was added as internal standard to calculate the amorphous content in the samples. Figure 11 shows the XRD trace of the three samples with ZnO and Table 1 shows the mineral compositions.

The analysis showed that the major differences between the surface sample from Monbi and borehole samples from Mossgiel and Nambucurra 1 are the presence of Amphibole (Hornblende?) and lack of Chlorite and vice versa. Monbi also has relatively low concentration of amorphous compounds compared with Mossgiel and Nambucurra 1.
Table 1: Quantitative XRD results (wt%) of the three samples from Monbi, Mossgiel and Nambucurra 1.

<table>
<thead>
<tr>
<th>Major Oxide</th>
<th>Monbi</th>
<th>Mossgiel</th>
<th>Nambucurra</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>47.25</td>
<td>40.60</td>
<td>34.45</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10.00</td>
<td>8.25</td>
<td>7.31</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.75</td>
<td>4.75</td>
<td>4.20</td>
</tr>
<tr>
<td>MgO</td>
<td>14.50</td>
<td>13.00</td>
<td>12.50</td>
</tr>
<tr>
<td>FeO</td>
<td>8.00</td>
<td>7.25</td>
<td>6.75</td>
</tr>
<tr>
<td>CaO</td>
<td>5.50</td>
<td>4.75</td>
<td>4.20</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.50</td>
<td>1.25</td>
<td>1.15</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

*Plagioclase best match of Albite.
**Alkali feldspar possible match of Microcline in Monbi, possible mixture of Microcline and Sanidine in Mossgiel and Nambucurra samples.
**Mica is most likely Muscovite.
^Amphibole possible match to Hornblende.
^Chlorite possible match with Clinohlore-ferroan.

The major oxides and trace element compositions of the three samples determined from fused bead and pressed powder XRF analysis are shown in Table 2 and 3, respectively. The three samples have similar oxides composition except that Monbi has relatively higher CaO composition, Mossgiel has relatively higher Fe₂O₃ composition, and Nambucurra 1 has the highest SiO₂ at more than 70% composition.

Table 2: Major oxides of the three samples from fused bead XRF analysis.

<table>
<thead>
<tr>
<th>Major Oxide</th>
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<th>Mossgiel</th>
<th>Nambucurra</th>
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<td>Fe₂O₃</td>
<td>5.75</td>
<td>4.75</td>
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</tr>
<tr>
<td>MgO</td>
<td>14.50</td>
<td>13.00</td>
<td>12.50</td>
</tr>
<tr>
<td>FeO</td>
<td>8.00</td>
<td>7.25</td>
<td>6.75</td>
</tr>
<tr>
<td>CaO</td>
<td>5.50</td>
<td>4.75</td>
<td>4.20</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.50</td>
<td>1.25</td>
<td>1.15</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

CO₂-Rock Interaction

The elemental compositions of the different 2% nitric acid sample solutions are shown in Fig 7 (200 °C and 20 MPa) and Fig 8 (250 °C and 20 MPa). The plots show that Si, Ca, Mg, B and Fe are the most highly to dissolve in supercritical CO₂. Although some elements like S and P dissolved at 250 °C, it is not apparent at 200 °C while it is the opposite for Na and Fe. It should be cautioned that the results are near the detection limit and/or at the lower end of the calibration standards used in the ICP-OES analysis. The highest concentration recorded is less than 5 ppm Si (~11 ppm SiO₂). For reference, the solubility of amorphous silica in pure H₂O at 25°C is ~ 116 ppm.
Preliminary studies of NaCl-H₂O-rock interactions (at 250 °C and 4-5 MPa) using drill cutting samples from Habanero 3 well in Cooper Basin, Australia showed that feldspar readily dissolved in brine solution (250 ppm NaCl) (Kuncoro, Ngothai, O'Neill, Pring, & Brugger, 2010). For comparison, the cumulative concentration of SiO₂ shown in Fig 14 is multiple times higher than the 11 ppm dissolved in supercritical CO₂ at 250 °C and 20 MPa. Other cumulative cation concentrations is shown in Fig 15 for better comparison.

Table 4 shows the comparison of major oxides compositions of untreated and treated Monbi pulverized sample at 200 °C and 20 MPa. The biggest significant change (higher than the error value) is from the composition of SiO₂ which increased in the treated specimen which may imply that other oxides must have dissolved. CaO, Fe₂O₃ and MgO compositions decreased relatively high in the samples treated at 200 °C and 20 MPa. These observations corroborated the results from ICP-OES analysis (Fig 12).

**Table 4: Major oxide compositions of untreated and treated at 200 C and 20 MPa Monbi pulverized granite samples.**

<table>
<thead>
<tr>
<th>Major Oxide</th>
<th>Unreacted Value</th>
<th>Error</th>
<th>200C 20MPa Value</th>
<th>Error</th>
<th>% diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>3.137</td>
<td>0.051</td>
<td>3.114</td>
<td>0.052</td>
<td>0.023</td>
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<tr>
<td>MgO</td>
<td>1.877</td>
<td>0.019</td>
<td>1.853</td>
<td>0.019</td>
<td>0.024</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.060</td>
<td>0.050</td>
<td>14.970</td>
<td>0.050</td>
<td>0.090</td>
</tr>
<tr>
<td>SiO₂</td>
<td>67.005</td>
<td>0.100</td>
<td>67.270</td>
<td>0.100</td>
<td>-0.265</td>
</tr>
<tr>
<td>P₂O₅</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>4.314</td>
<td>0.013</td>
<td>4.293</td>
<td>0.013</td>
<td>0.020</td>
</tr>
<tr>
<td>CaO</td>
<td>3.116</td>
<td>0.009</td>
<td>3.058</td>
<td>0.009</td>
<td>0.058</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.530</td>
<td>0.003</td>
<td>0.533</td>
<td>0.003</td>
<td>-0.003</td>
</tr>
<tr>
<td>MnO</td>
<td>0.075</td>
<td>0.000</td>
<td>0.075</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.733</td>
<td>0.015</td>
<td>3.694</td>
<td>0.015</td>
<td>0.039</td>
</tr>
<tr>
<td>Ignition Loss</td>
<td>0.69</td>
<td></td>
<td>0.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>99.79</td>
<td></td>
<td>99.79</td>
<td></td>
<td>-0.004</td>
</tr>
</tbody>
</table>

**Figure 12: Elemental compositions of 2% nitric acid sample solutions taken from 200 °C and 20 MPa fluid-rock interaction experiments.**

**Figure 13: Elemental compositions of 2% nitric acid sample solutions taken from 250 °C and 20 MPa fluid-rock interaction experiments.**

**Figure 14: Cumulative concentration of SiO₂ with time (Kuncoro, et al., 2010).**

**Figure 15: Cumulative concentration of Fe, Mg, Mn, Ca and Ba with time (Kuncoro, et al., 2010).**
CONCLUSIONS

Surface and drill core granite samples were collected and analyzed. Mineral analysis showed that the major differences between the surface (Monbi) and drill core granites collected are the presence of Amphibole (Verdun?) and absence of Chlorite and vice versa. Monbi also has significantly less amorphous substances.

Major oxide analysis using fused bead XRF showed that Monbi has higher CaO concentration compared with Mossigiel and Nambucurra samples.

CO₂-rock interaction experiments revealed that small amount of pulverized rock specimen were dissolved in supercritical CO₂. Si, Ca, Mg and Fe cations showed higher concentrations in the ICP-OES analysis compared with other elements. The calculated 11 ppm SiO₂ concentration of the 2% nitric acid sample solution used to capture dissolved minerals in supercritical CO₂ is significantly less than the ~600 ppm SiO₂ obtained from a similar other experiment involving NaCl-H₂O- rock interaction.

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