Wallula Basalt Pilot Demonstration Project: Post-Injection Results and Conclusions


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Abstract

Deep underground geologic formations are being evaluated for long-term storage of CO₂, including large continental flood basalt formations. At the GHGT-11 and GHGT-12 conferences, progress was reported on the initial phases for Wallula Basalt Pilot demonstration test (located in Eastern Washington state), where nearly 1,000 metric tons of CO₂ was injected over a 3-week period during July/August 2013. The target CO₂ injection intervals were two permeable basalt interflow reservoir zones with a combined thickness of ~20 m that occur within a layered basalt sequence between a depth of 830-890 m below ground surface. During the two-year post-injection monitoring period, downhole fluid samples were periodically collected, coupled with limited wireline borehole logging surveys that provided indirect evidence of on-going chemical geochemical reactions/alterations and CO₂ distribution. A detailed pre-closure field characterization program included downhole fluid sampling, and performance of hydrologic tests and wireline geophysical surveys. Side-wall cores also were retrieved from within the targeted injection zones. Visual observations of the core material identified small globular nodules, translucent to yellow in color, residing within vugs and small cavities, which were not evident in pre-injection side-wall cores obtained from the native basalt formation. Characterization by x-ray diffraction identified these nodular precipitates as ankerite, the identical iron and calcium rich carbonate observed to form in laboratory tests with Columbia River basalts. Isotopic characterization (δ¹³C, δ¹⁸O) conducted on the ankerite nodules indicate a distinct isotopic signature that is closely aligned with that of the injected CO₂. Final post-injection wireline geophysical logging results also indicate the presence of free-phase CO₂ at the top of the two injection interflow zones, with no vertical migration of CO₂ above the injection horizons. These findings support previous assumptions regarding storage feasibility and rapid mineralization of CO₂ injected into a suitable basalt formation.

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1. Introduction

At the GHGT-11 conference in 2009 we reported drilling of the world’s first continental flood basalt sequestration pilot borehole to a total depth of 1253 m at a paper mill site near Wallula, Washington [1]. Subsequent hydrogeologic testing identified a composite open borehole injection zone ~50 m thick containing three brecciated interflow zones separated by dense interior flows (note: a basalt interflow zone comprises the brecciated basalt flow bottom and underlying basalt flowtop). An extended-duration pumping test conducted in the Fall of 2011 resolved uncertainty over hydrologic connectivity to shallower basalts (i.e. potential for leakage) and injection zone heterogeneity, thus enabling a State permit to be issued to conduct a CO2 injection limited to a maximum 1,000 MT. The project, which was partially funded under the U.S. Department of Energy’s Big Sky Regional Carbon Partnership program, is so far the only project worldwide to have injected CO2 as a supercritical fluid into a basalt formation.

During the GHGT-12 conference, our reported progress included CO2 injection on the Wallula Basalt Pilot demonstration test [2]. Protracted hydrologic well tests performed in late 2012 prior to the CO2 injection refined delineation of the composite, heterogeneous nature of the injection reservoir, with an inner, higher permeability zone extending out ~50 meters from the pilot well, which transitions to an outer-zone having significantly lower permeability and storativity. Additionally, the chemistry of groundwater samples collected during the 20 day 2012 pumping test indicated a relatively constant and elevated fluoride concentration (7 mg/L), which supported the lack of vertical connectivity of the injection horizon with overlying basalt interflow zones that have significantly lower fluoride concentrations. Over a course of three weeks in July-August of 2013, CO2 was injected into the Columbia River basalt at a rate of ~40 MT/day for a total volume of 977 MT. Comprehensive wireline geophysical logging conducted before and after the injection provided detailed in situ reservoir conditions including an estimate of CO2 saturation reaching 90% for parts of the upper flowtop interval and a corresponding elevated formation temperature due to injection of warm CO2 relative to pre-injection reservoir temperature. Post-injection downhole fluid samples collected from reservoir depth in February 2014 revealed strongly elevated concentrations of Ca, Mg, Fe, and Mn and isotopic shifts consistent with rapid reaction of the basalt with the injected CO2. These early results signaled indirect evidence of a chemically active environment with total dissolved solids and metal cation concentrations exceeding pre-injection values by several orders of magnitude. Moreover, the findings are consistent with laboratory tests where basaltic samples reacted with scCO2 and water under similar conditions and times produced carbonate solids [3-5].

In June of 2015, prior to the Wallala Basalt Pilot well decommissioning and site closure, a final detailed characterization suite of wireline geophysical surveys was completed for assessing the presence of CO2 in the surrounding reservoir and overlying rock formations, and for assessing possible changes in the near-field, petrophysical characteristics (e.g., porosity, density) of the surrounding basalt formations. As part of the wireline survey characterization, over 50 side-wall cores (SWC) were extracted from the injection interval and subjected to an extensive geochemical, 3D imaging, and geophysical evaluation. Subsequent to wireline characterization, extended hydrologic testing was initiated for assessing potential small- to intermediate-scale permeability changes to the injection reservoir that may be attributed to the CO2 injection. The results from each of these activities are presented and discussed in the realm of utilizing a continental flood basalt formation as a repository for permanent storage of anthropogenic CO2.
2. Background

Our initial publication on the potential sequestration of CO₂ in flood basalts was focused on laboratory studies that demonstrated rapid carbonation through exposing basalt chips to water and CO₂ at reservoir conditions [3]. Since then, significant research has emerged that continues to demonstrate the feasibility of sequestering CO₂ in basalts [4-12]. In fact, the field demonstration project CarbFix has recently reported direct observation of CO₂ mineralization in an Icelandic basalt formation [13]. These findings include identification of calcite in retrieved core samples that contained an enrichment of ¹⁴C isotope injected as a tracer. However, the CarbFix test injected 175 MT of CO₂ mixed with water in the injection well such that no free phase CO₂ is present in the reservoir. Although the advantages and disadvantages of this injection technology have been discussed [14-16], it is a significantly different approach when compared to the Wallula Basalt Pilot demonstration.

A comprehensive description of pre CO₂ injection activities (drilling, hydrologic testing, and seismic surveying) along with the CO₂ injection, and post injection monitoring program are reported in McGrail et al [1, 2] and will not be repeated here. Overall, the targeted injection reservoir, depth interval of 828 and 887 m (2,716 and 2,910 feet), lies stratigraphically below the massive, regionally-extensive Umtanum Member of the Grande Ronde Basalt, whose flow-interior section possesses recognized extremely low-permeability characteristics (i.e., ~10⁻¹² to 10⁻¹³ m/sec). The identified composite injection zone characteristics provided a unique and attractive opportunity to scientifically study CO₂ migration and chemical reaction behavior of inter-connected basalt reservoir intervals below primary and secondary caprock confining zones.

3. Post-Injection Field Activities

Prior to well closure, a final extensive post-injection characterization program was performed beginning in June 2015. These final characterization activities included: downhole reservoir/borehole fluid sampling (for hydrochemical and isotopic analysis), extensive wireline logging surveys (including collection of SWC for geochemical reaction characterization), and hydrologic testing of the injection reservoir for assessing possible changes in hydraulic (permeability) and/or storage characteristics associated with the previous injection of 1,000 metric tons of CO₂ in July/August 2013.

To facilitate final characterization activities within the open borehole section, the downhole packer/pressure probe test system that was used to isolate and monitor the injection reservoir within the well at formation depth (i.e., ~826.01 m) during the active CO₂ injection and post-injection phases, was removed from the well (June 17th to 18th) (Figure 1). The packer and downhole pressure probe monitoring system performed as designed and effectively isolated the downhole injection reservoir in the well at formation depth during the two-year injection/post-injection phase of the field project. Fifty SWC samples were collected (June 20th) at selected depth intervals over the open borehole depth interval of 827.84 and 883.92 m.
3.1. Geochemical Sampling

Figure 2 shows a comparison of the average sample/depth intervals for selected major anion/cation concentrations indicating the rapid, elevated stabilization pattern exhibited during the ~2-year post-injection monitoring period (note: logarithmic concentration scale). The in-situ pre-injection formation water concentrations and Boise system water used to flush the test/well system of injected CO2 (following termination of CO2 injection in August/2013) [2] are also shown for comparison purposes. As indicated in Figure 2, the post-injection TDS, alkalinity, Ca, and Mg concentrations are ~1.5 to 3 orders-of-magnitude greater than pre-injection formation water conditions. Overall, laboratory analysis results obtained from the June 2015 downhole sampling event indicated a stabilization to a continuance of a slightly increasing trend in overall chemical concentration (TDS, EC, etc.) and major cation content over the prior February 2015 sampling event. Similar hydrochemical patterns are also evident for selected trace elements (not shown: e.g., Fe, Mn, Sr, B), which are associated with geochemical reactions of CO2 with ferromagnesian minerals within the basalts.

3.2. Wireline Geophysical Surveys

A final post-injection wireline geophysical survey characterization program was completed in June 2015 for direct comparison with the same pre-CO2 injection surveys performed in April 2009, and limited wireline logging results conducted immediately at termination of CO2 injection in August 2013. The comparative wireline logging characterization provides the means for assessing the presence of CO2 in the surrounding reservoir and overlying rock formations, and for evaluating possible changes in the near-field, petrophysical characteristics (e.g., porosity) of the surrounding basalt formations. Residual saturation and fluid temperature survey logging results during and immediately following injection indicated that the two upper-most basalt interflow zones received the majority of the injected CO2, which is consistent with permeability characterization.
results obtained previously through hydrologic testing. Time-lapsed downhole temperature surveys of the injection zone (injected CO\textsubscript{2} was \textasciitilde15 °F greater than in-situ temperature conditions) indicated that a residual thermal-decay signature (solely within the injection interflow zones) remained persistent 24-months after CO\textsubscript{2} injection termination; demonstrating its use as diagnostic tool for monitoring injected CO\textsubscript{2}. Final post-injection field wireline characterization interpretations (Figure 3) also indicate no discernable presence of CO\textsubscript{2} above the open injection zone interval, and the presence of free-phase CO\textsubscript{2} at the top of the two-upper-basalt interflow zones (as expected due to the buoyancy of CO\textsubscript{2}) that received all of the injected CO\textsubscript{2}.

3.3. Hydrological Testing

Extended hydrologic testing over 8-days was performed in June following completion of wireline characterization activities. The hydrologic testing included performance of slug/pulse tests and two injection and recovery tests. The hydrologic test characterization was initiated for assessing potential small- to intermediate-scale permeability changes to the injection reservoir that may be attributed to the injection and reaction of CO\textsubscript{2} with the surrounding basalt reservoir. Preliminary comparisons of post vs. pre-CO\textsubscript{2} injection hydrologic test response analyses indicate no discernable changes in the near to intermediate-scale interflow zone hydrologic properties. Recovery diagnostic test plots for the final post-injection tests, however, indicate the presence of a zone of increased compressibility a short distance from the well, which would be consistent with the presence of compressible free-phase CO\textsubscript{2} in the injection interflow zones. Following completion of the final post-injection hydrologic test characterization activities, the Wallula basalt pilot well was decommissioned in July 2015, pursuant to Washington State regulatory/well abandonment procedures.

4. Side-wall Core (SWC) Characterization

Side-wall core samples were geologically described and examined for the presence of carbonate minerals that potentially formed from geochemical reactions of injected CO\textsubscript{2} with minerals present in the basalt reservoir. Two distinct carbonate mineral phases were found in a limited number of SWC samples, occurring as both large (up to 1 mm) nodules within open vesicles and as thin carbonate cements coating the borehole wall face. Characterization of nodules by x-ray diffraction (XRD) revealed a mineral structure consistent with ankerite, a calcium- and iron-rich carbonate [17]. Available drill cuttings and unreacted SWCs recovered from the open bore-hole section (828 and 887 m depth interval) of the well prior to CO\textsubscript{2} injection in 2009 contained several broken carbonate mineral fragments in drill cuttings and a brecciated carbonate vein within a SWC (856.5 m) [1]. XRD analysis of the vein material recovered from the pre CO\textsubscript{2} injection SWC identified the mineral as common calcite, not ankerite. Still, differences in the carbonate mineral structure alone are not conclusive evidence of in situ carbonation.

4.1. Sidewall Core 3D Imaging

Selected SWC samples, examined by an x-ray microtomography (XMT) imaging technique, revealed a fairly extensive distribution of carbonate mineralization within several SWCs. Overall, the XMT imaging characterization effort identified nodules associated with SWCs collected from zone 2 (855.0, 856.5, 857.1 m), and zone 3 (867.2, and 874.8 m). The shallower depth, 855.0 m, contained tiny nodules, whereas SWC from 874.8 m appeared larger. SWC samples with externally visible carbonate nodules were found to have numerous nodules located within open vesicles throughout the SWC (Figure 4). Dense carbonate nodules, appearing as white

![Figure 4. XMT image of a post-injection sidewall core sample recovered from 856.5 m depth a) vertical slice, and b) horizontal slice.](image-url)
globular shapes, contrast well to the black void space of vugs and the less dense solid basalt matrix (light gray).
Also, pre-existing secondary mineral precipitates are visible in the horizontal sliced image (Figure 4b) as a dark outlining of the vesicles. In contrast, carbonate cements in the form of a white powder, were visually identified as external coatings on the borehole wall face portion of selected SWCs.

4.2. Sidewall Core Chemical Characterization

Other characterization efforts on the cores included hand removal of tiny carbonate nodules for chemical, optical, and isotopic analysis. These grains were individually mounted in epoxy and polished for scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDXS). SEM microphotographs of a cross sectional slice through a carbonate nodule (Figure 5) do not reveal an obvious zoning pattern as seen in our previous laboratory studies. However, closer examination with EDXS indicated a compositional variation that is related to nodule growth. As shown in the bottom of Figure 5, calcium concentrations dominate the nodule chemistry until about half way through the particle (spot 4). At this point and beyond, iron concentrations prevail. Overall, this analysis shows a chemically zonedankerite with a solid solution shift from a Ca-rich phase near the center (Ca$_{0.75}$Mn$_{0.13}$Fe$_{0.11}$(CO$_3$)$_2$) to an Fe-rich phase (Ca$_{0.41}$Mn$_{0.01}$Fe$_{0.57}$(CO$_3$)$_2$) near the surface of the ankerite nodule. Trace amounts of Mn were also detected in the nodule. This chemical composition variation is essentially identical to what we reported in laboratory carbonation experiments with Columbia River basalts[4].

Additional characterization of 5 different nodules by SEM-EDXS revealed a consistent chemical makeup that included variable amounts of Ca, Fe, and Mn. From these analyses, it is clear the nodules are initially Ca rich, but trend Fe rich toward the edges. Moreover, based on these analysis, evolution of pore water chemistry has clearly left a chemical signature unique to the precipitates. In contrast, chemical analysis of a subsample removed from the naturally occurring calcite vein indicated a pure Ca composition with no measurable quantities of Fe or Mn components.

4.3. NanoSIMS Isotopic Analysis

Conclusive evidence of in situ basalt carbonation resulting from the CO$_2$ injection was provided through isotopic characterization. Polished cross sections of the ankerite nodules were examined by nano secondary ion mass spectrometry (nanoSIMS) to obtain delta carbon-13 ($\delta^{13}$C) and delta oxygen-18 ($\delta^{18}$O) content (Table 1). Similar analyses were also conducted on a subsample removed the natural occurring calcite vein identified in a SWC (856.5m) retrieved during pre CO$_2$ injection characterization efforts in 2009. Details on sample preparation and the nanoSIMS technique can be found in McGrail et al [17]. Drill cuttings (pre CO$_2$ injection), post CO$_2$ injection formation water, and the CO$_2$ source were analyzed by a different method [17].

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Average Values (%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$\delta^{13}$C</td>
</tr>
<tr>
<td>Ankerite nodules</td>
<td>-37.7 ± 2.19</td>
</tr>
<tr>
<td>CO$_2$ source</td>
<td>-36.3 ± 0.09</td>
</tr>
<tr>
<td>formation water, post injection</td>
<td>-32.2 ± 0.79</td>
</tr>
<tr>
<td>natural calcite vein</td>
<td>15.8 ± 1.01</td>
</tr>
<tr>
<td>carbonate containing drill cuttings, pre-CO$_2$ injection</td>
<td>21.3 ± 6.76</td>
</tr>
</tbody>
</table>
As evident in Table 1, the ankerite nodules produced an average $\delta^{13}C$ value of $-37.7 \pm 2.19$ ‰; values were $-22.5 \pm 2.38$ ‰. Likewise, $\delta^{13}C$ values obtained post CO$_2$ injected formation waters were similar, $-32.2 \pm 0.79$ ‰. The injected CO$_2$ had a $\delta^{13}C$ value of $-36.5$‰. In contrast, those samples collected pre CO$_2$ injection contained significantly higher concentrations. The natural calcite produced a measured $\delta^{13}C$ value of $15.8 \pm 1.01$ ‰, whereas the carbonate containing drill cuttings were even more enriched ($21.3 \pm 6.76$ ‰). It is well known that isotopic composition of carbon and oxygen in a carbonate precipitating from solution is preserved [18].

5. Conclusion

The Wallula Basalt Pilot field demonstration test, which injected 977 metric tons of scCO$_2$ into two deep basalt brecciated zones in August of 2013, underwent a detailed final characterization campaign prior to decommissioning in July 2015. Residual saturation and fluid temperature survey logging results during and immediately following injection indicated that the two upper-most basalt interflow zones of the injection reservoir received the majority of the injected CO$_2$, and also indicated that no discernable presence of CO$_2$ above the open injection zone interval. The presence of free-phase CO$_2$ was indicated, however, at the top of each of the two-upper-basalt interflow zones (as expected due to the buoyancy of CO$_2$) that received all of the injected CO$_2$. Downhole groundwater samples collected throughout the 2-year post-injection monitoring duration, demonstrate an increasing complex injection zone geochemical environment with post-injection major ion concentrations (TDS, alkalinity, Ca, and Mg) approaching ~1.5 to 3 orders-of-magnitude greater than pre-injection formation-water conditions. Laboratory analysis of discrete carbonate nodules removed from post-injection side-wall cores were identified as being ankerite, and contained isotopic signatures closely aligned with isotopic composition of the CO$_2$. Consequently, the isotopic composition data coupled with groundwater chemistry data and geophysical wellbore surveys conclusively show that injected supercritical CO$_2$ was being actively converted to a stable carbonate mineral in the basalt reservoir within 24 months of emplacement. This is the first field evidence of in-situ carbonation occurring from a free phase supercritical CO$_2$ injection into a flood basalt reservoir and provides at least qualitative validation of rapid carbonation rates that were first speculated about over 12 years ago in a paper delivered at the GHGT-6 conference[19].

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References