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Stepping into the same river twice: field evidence for the repeatability of a CO₂ injection test

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Abstract

A single well characterisation test was conducted at the CO2CRC Otway storage site in Victoria, Australia, in 2011 and repeated in 2014. The near-well permeability was found to have declined nearly 60% since the 2011 test, while the residual saturation inferred from a variety of techniques was lower in 2014. There was a significant change in water chemistry, suggesting an alteration of near-well reservoir properties. Possible reasons for these changes are explored, and the implications for other field tests are discussed.

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Keywords: CO₂ storage; residual saturation; field test; permeability alteration; geochemistry

1. Introduction

Almost all field tests of CO₂ injection are inherently one-off operations, and give little insight into the reproducibility of the results, yet are assumed to be representative of the reservoir unit in question. In 2011, the

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CO₂CRC Residual Saturation and Dissolution Test, conducted at the onshore Otway site in Victoria, Australia, collected field data to characterize the residual CO₂ saturation in a thin low-salinity water-saturated reservoir unit within the Paaratte Formation at 1392-1398 m depth TVDSS (total vertical depth sub-sea). The field experiment began with baseline tests to characterise the water-saturated formation, then 150 t of pure CO₂ was injected, and driven to residual by the injection of water pre-saturated with CO₂. The conceptual design was discussed in Zhang et al. [1], and an overview of the implementation is given in Paterson et al. [2,3]. The initial tests were repeated to characterise the distribution of residual CO₂ saturation in the formation. The techniques trialled and separately analysed comprised pressure and temperature measurements [4], pulsed neutron logging [5], noble gas tracers [6], reactive ester tracers [7], and a dissolution test [8]. The results provide a range of estimates of the near-well distribution of residual CO₂ saturation at different depths of investigation.

In late 2014, there was an opportunity to repeat some parts of the test in the same reservoir unit and using the same well (as part of an experiment looking at the effect of impurities in the CO₂ stream), striving to keep the test sequence similar while improving some of the operational aspects and data collection procedures. The test design again required the injection of CO₂-saturated brine at some points, and although the procedure was improved from 2011, this requirement was still challenging to achieve under field conditions. Pressure and temperature measurements, pulsed neutron logs and noble gas tracers were again used, along with analysis of oxygen isotopes, but the heating tests, the reactive tracers and the dissolution test used in 2011 were not repeated.

In the next section, the 2014 test methodology and the changes compared to the 2011 test are discussed. Then the results for the various techniques are compared between the two tests, taking account of the operational changes. The origins of the differences between the two sets of results are then discussed.

2. Method

2.1 Test sequence

The injected CO₂ used in 2014 was a mix of industrial CO₂ captured at the Callide Oxyfuel pilot capture plant in Queensland (Callide CO₂, 99.99%) and food grade CO₂ (99.99%) from the Boggy Creek well in the vicinity of the Otway site (BOC CO₂). The first part of the 2014 test involved the injection of CO₂-saturated water with impurities and tracers to study geochemical changes. Initially, 535.8 t of formation water was produced into surface tanks. Then 100.2 t of water pre-saturated with 5.2 t of CO₂ was injected back into the formation along with 2.95 kg SrCl₂·6H₂O and 2.6 kg NaBr. After 2 days of “soaking”, 10.6 t was back-produced, then a soak of 11 days and another 8.7 t of production, and a further 10 days of soak before 50.7 t of back-production. Another 100.2 t of formation water was pre-saturated with 4.52 t of CO₂ spiked with impurities (9 ppm NO₂, 67 ppm SO₂, 1100 ppm N₂, 6150 ppm O₂) and injected along with 3.1 kg LiCl and 0.8 kg Na₂Fluorescein. Back-production consisted of a soak of 2 days, 8.3 t of production, another 12 days of soak, 9.5 t of production, and then a wait of 10 days before 50.2 t of production.

For the second part of the 2014 test, designed to repeat elements of the 2011 test, additional formation water was produced into the on-site tanks. For the baseline characterization (which will be referred to as the “water test”), 67 t of water was injected at 199 t/d, with 0.66 kg of krypton and 1.0 kg of xenon added as a pulse at the start of injection. Methanol was also added to the whole injection (via mixing in the tanks) as a mass-balance tracer. The addition of methanol was a new feature of the 2014 tracer test (it was trialed in the late-stage dissolution test in 2011), designed to help clarify whether the measured tracer recovery reflected the overall recovery of injected water. Formation water was then back-produced using gas lift at an average rate of 50.4 t/d until tracer concentrations were near the detection limit (122.2 t produced). In 2011 the injected amount was larger (103 t) and no methanol was used at this stage.

The main injection consisted of 109.8 t of CO₂ at 33 t/d, followed by 323.7 t of formation water pre-saturated with 8.4 t of CO₂, in order to create a zone of residual saturation around the wellbore, but without dissolving the gas phase

(which would occur if unsaturated formation water were injected). As in the 2011 test, the injection of CO₂-saturated water required careful operational adjustments, since the mixing took place downhole. The tracer test was then repeated (which will be referred to as the “residual test”), with the difference that the 67.2 t of formation water injected was pre-saturated with 3.9 t of CO₂ via downhole mixing. The tracer pulse consisted of 0.55 kg of krypton and 1.0 kg of xenon at the start of injection. Back production of formation water continued until tracer concentrations approached the detection limit, after 128.5 t of production.

The accuracy of the flow rate measurement came under scrutiny in the 2014 tests, and there were indications that the flow gauge was affected by scaling, despite efforts to maintain it. Measurement of the tank volumes were made at each stage, and this was used to correct the overall flow rates for each part of the test, with the typical corrections being in the range $\pm 20\%$. However the lower accuracy in the flow rate determination does directly impact the estimates of permeability and the history matching of pressure response.

In most of the injections in 2014, the injection stream consisted of formation water saturated with CO₂. As detailed in [3] in regard to the 2011 test, this was done via downhole mixing. The matching of injection rates was done based on calculations for CO₂ solubility as a function of temperature and pressure, with the intention that the injection stream would be slightly under-saturated at bottom-hole conditions, and then saturated at far-field conditions in the reservoir (where the temperature is higher). As part of this design there was heating at surface of the injected water, to reduce the temperature difference at bottom-hole conditions. However intermittent failures of the heating equipment in the 2014 test meant that the injection stream was sometimes more under-saturated with respect to CO₂ at bottom-hole conditions than in the design, and this may have caused near-well dissolution of residual CO₂ at later stages of the test. Difficulties with flow rate determination discussed above might also have resulted in some deviations from the target mixing ratio for CO₂-saturated water.

2.2 Sampling protocols

Liquid phase tracers such as methanol are much easier to use, since they can be sampled from the produced water at surface. By contrast, partitioning tracers such as krypton and xenon need to be sampled at downhole conditions (since their partitioning depends on pressure and temperature), and even then the analysis protocol for the pressurized samples need careful design to avoid the complications of non-equilibrium effects. In the 2011 test, samples at downhole conditions were collected via a U-tube system into 4.7 L stainless steel cylinders. The cylinders were then partly depressurized, and gas chromatography was used to analyze the composition of the gas phase. However tracer recovery was low (around 5% for the baseline test), and this was thought to be due to nitrogen contamination from the U-tube lift gas, and from the non-equilibrium effects of depressurization [6].

For the 2014 test, the downhole U-tube sampling process was similar to the 2011 test, but two smaller samples were collected (in 142.35 mL cylinders) [9]. The first of the two samples was found to be less reliable overall (perhaps due to contamination from fluid at atmospheric pressure which was not flushed), and so only data from the second sample was used. For analysis, samples were depressurized slowly and allowed to equilibrate, and the volume of exsolved gas was measured. The mass fractions of the gases were measured by gas chromatography (GC) and mass spectrometry (MS), but the MS data was subject to systematic errors of unknown origin, so only the GC was used. For consistency with the noble gas tracer protocol, methanol concentrations were also measured from the second downhole sample (rather than at surface).

2.3 Geochemical modelling

Reaction path modelling was performed using Geochemist's Workbench 9 Pro software (GWB) and thermo.com.V8.R6+ database [10]. The modelling was employed to predict the mineral-fluid interactions during the period of > 3 years between the 2011 and 2014 tests. See Vu et al. [11] for more details.

3. Results

3.1 Pressure

The first of the baseline characterization tests in 2011 was an injection of 104 t water at a rate of 136.2 t/d, with the downhole pressure and temperature being measured by four surface-out (SRO) high-accuracy gauges. Standard pressure transient analysis was applied to the data, and inferred an average far-field permeability for the injection interval of $2.2 \pm 0.2 \times 10^{-12} \text{ m}^2$ (averaging over different stages of the test). However it is common that the exposure to drilling fluids and the use of explosive charges during perforation can change the rock properties near the well [12]. Fitting simulations directly to the pressure response gave an enhancement by a factor of 2.85 within 1 m of the wellbore [4].

The frequency of sampling the downhole gauges was increased for the 2014 test (at least once per minute), giving better quality data especially during periods of rapid pressure change. Analysis of the equivalent baseline water injection test in 2014, conducted at the rate of 199 t/d, gave a far-field permeability of $2.5 \pm 0.2 \times 10^{-12} \text{ m}^2$, again averaging over several injections, which (given the error estimates) is similar to the 2011 result. The agreement is reassuring, since the average far-field permeability in the water test is averaged over a distance of several hundred meters from the well, and there is no reason to think that parts of the reservoir this far from the well have been altered between 2011 and 2014. However the near-well permeability has changed. Direct simulation fitting gave a reduction in the near-well region by nearly 60% in the three years between tests.

3.2 Tracers

The 2014 noble gas tracer test (analysed by LaForce et al [9]) achieved much higher tracer recovery than in 2011, due to the revised protocol. In the water test the recovery was 94% for krypton and 93% for xenon (more than 20 times the recovery in the 2011 baseline test), and in the repeat residual test the recoveries were 88% and 63% respectively (about 3 times the recovery in the 2011 test). There was nearly 100% recovery of the bulk methanol tracer, confirming that the produced fluids were representative of the regions of the reservoir contacted by the injected fluids. Fig. 1 shows the production curves for the methanol during the water test and the residual test. A simple analytical theory [13,14] is fitted to this, the details of which are discussed in [9] and [15]. The radial dispersivity of the methanol in the water test is $2.4 \pm 0.9 \text{ cm}$, whereas in the residual test it is 6.2-6.7 cm. The echo dispersivity depends on the distance travelled into the reservoir, so when residual CO_2 is present the injected fluid travels further into the reservoir and is more dispersed, but the magnitude of the increase in dispersivity (at least a factor of two) indicates that the fluid flow is much more complex in the residual test, and this may account for the lower recovery of the noble gas tracers during the residual test.

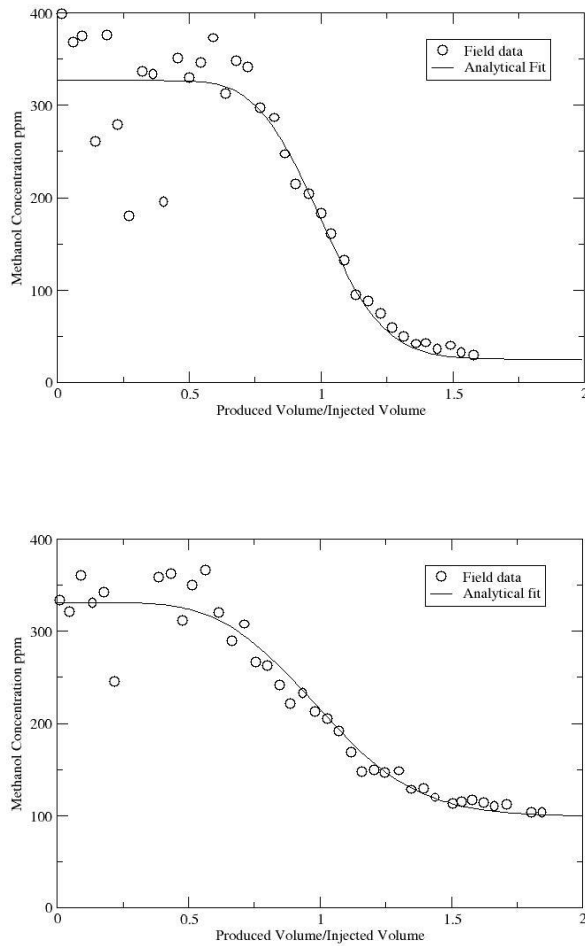


Figure 1: Methanol concentration (open circles) during back production, compared to analytical fit (solid line). The horizontal scale is the produced volume relative to the injected volume. Left: water test. Right: residual test.

The interpretation of the 2011 tracer test used air/water tracer partition coefficients [16], since these were the best available data. Interpretation of the 2014 results is complicated by the recent publication of differing sets of tracer partition coefficients for CO_2 /water at reservoir conditions [17,18]. The same approach was used as for the 2011 data [6], with dispersion coefficients for each tracer first being fitted to the water test results, and in fact the fitted values of dispersion for the 2014 data were in agreement with the 2011 results. A study was made of the sensitivity of the final estimated residual saturation to changes in tracer partitioning coefficients, thermal conditions and relative permeability curves. The greatest sensitivity was to the partitioning coefficients. With the air/water coefficients the average in-situ residual saturation was estimated at 9.3%, while with the Warr coefficients [17] it was 7.2% and with the Myers coefficients [18] it was 26.4%. The differences between the estimates using the krypton data compared to the xenon data, or estimates using different relative permeability curves, were within the error of the model. In comparison, the 2011 tracer analysis [6] using air/water partitioning coefficients estimated a residual saturation of 13-18%, distinctly higher than the 2014 result with the same partition coefficients. Note that

the residual saturation deduced from the tracer test is a flow-weighted average over the near-well region, in which residual saturation varies both vertically and laterally. Operational changes, such as the procedure for injecting CO₂-saturated water, and the timing of injection events, account for at least some of this difference in the tracer test results.

3.3 Oxygen isotopes

Changes to the distributions of oxygen isotopes due to the interaction between formation water and CO₂ have previously been used to estimate residual CO₂ saturation in field tests [19], and examined in the laboratory [20,21]. In the 2014 test, isotope ratios $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were measured for the injected and produced water (using both U-tube and surface sampling) and $\delta^{18}\text{O}$ was measured for the injected CO₂. The interpretation of the stable isotope data is described in detail in [15,22]. A change to depleted $\delta^{18}\text{O}$ has been observed for waters back-produced during the residual test, and therefore in contact with residually trapped CO₂ in the reservoir, in comparison to baseline water values prior to CO₂ injection [15].

Using the methodology explained in [19] and applied to the 2014 test [15], one can then estimate the residual saturation near the wellbore. For a sample taken after 12.1 t of back production, the estimated residual was 0.14 ± 0.09 . For a uniform vertical distribution of saturation and water production, this would correspond to a sample from about 1.57 m radially from the well. For the sample after 57.4 t of production (corresponding to 3.4 m from the well), the residual is estimated at 0.28 ± 0.11 . The third sample, after 110 t of back production (corresponding to 4.7 m from the well), gave an estimate of 0.42 ± 0.16 .

The trend of increasing estimates of residual with distance from the well does not agree with simulation, which predict residuals of no more than 0.20, with lower values further from the well, and higher ones at the top of the reservoir unit. The two later samples taken (after 57.4 t and 110 t of production) have been longer in contact with CO₂ in different parts of the reservoir as the production has drawn water in to the well, which may complicate the interpretation of the isotopic shift [15]. Thus the estimated residual from the first sample, 0.14 ± 0.09 , is probably more accurate [15]. This is also consistent with the results of the tracer test, although there is a considerable spread in both estimates.

3.4 Pulsed Neutron Logs

Fig. 2 shows the comparison of the pulsed neutron logs (PNL) taken after the main CO₂ injection in 2011 and 2014.

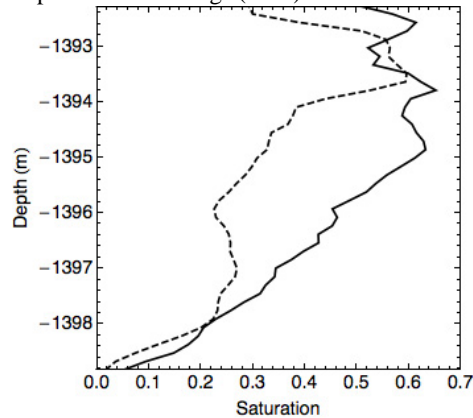


Figure 2: CO₂ saturation vs depth (in m TVDSS) from pulsed neutron logging, after main CO₂ injection but before the drive to residual. Dashed curve is 2011 result [5], solid curve is 2014 result.

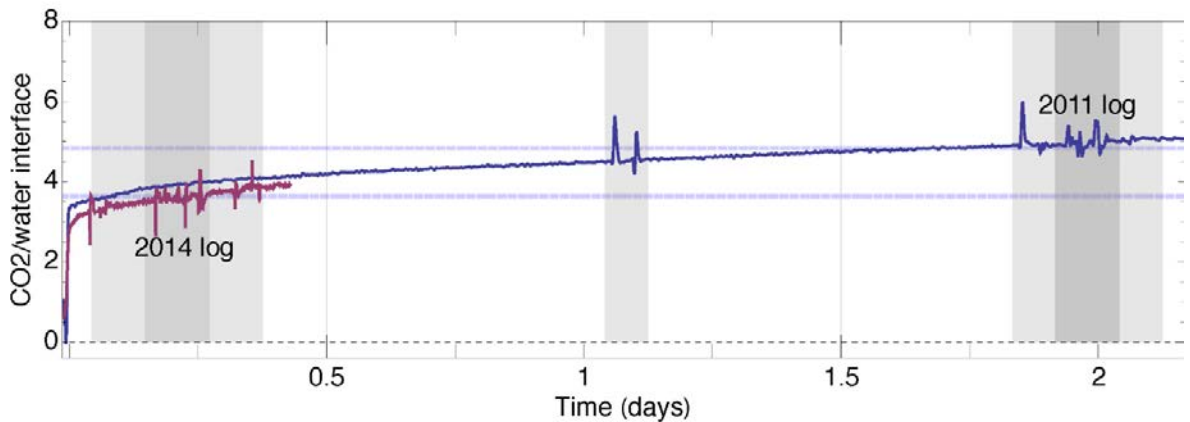


Figure 3: Distance of the CO₂/water interface above the bottom gauge following the end of CO₂ injection, determined from pressure differences between the gauges, versus time after the end of injection. Plots are for both 2011 (blue) and 2014 (red). Dashed blue line is the interface depth recorded during pulse neutron logging showing consistency with the pressure determination.

It's clear that in the 2014 test, high values of CO₂ saturation extend further down the completion interval than in 2011. One of the key causes of this difference is explained by the timing of the PNL relative to the injection in each case. Fig. 3 shows the inferred location of the CO₂-water interface in the wellbore above the lowermost gauge after injection ceases in both cases, as a function of the time after the end of injection, with the timing of the PNL runs shown. This location is deduced using the difference in pressure between the pairs of pressure gauges above and below the perforated interval [4,23]. In both tests, the movement of the interface is very similar (and the pressure response during CO₂ injection was very similar), and the key difference is that the 2011 PNL was taken almost 2 days after injection of CO₂ ceased, so that the CO₂-water interface moved higher due to buoyancy. Within the reservoir, for the 2014 test, taken about eight hours after the end of injection, this corresponds to much less upward movement of CO₂ at the time of the PNL compared to the equivalent PNL in 2011, explaining the higher saturations in the bottom section of the completion interval.

3.5 Geochemistry

The selected composition of formation water after the 2011 test and production water of the 2014 test is presented in Table 1. Note that the water composition of the formation water after the 2011 test was estimated from the production water, which was disposed of at the end of the 2011 test. The estimation took into account the precipitation of minerals due to storage conditions at the surface [24]. It can be seen from Table 1 that the composition of the formation water altered significantly between 2011 and 2014, with a significant increase in Na^+ , Ca^{2+} and Mg^{2+} concentration and a decrease in Si, Fe, SO_4^{2-} , K^+ and Cl^- concentration. The series of production water samples during the 2014 test showed a decreasing trend in the total dissolved solids (TDS), total alkalinity (TA), and concentrations of major cations such as sodium, calcium and magnesium; while an upward trend was observed in concentration of chloride. The TDS, TA, and concentrations of Na^+ , Ca^{2+} , Mg^{2+} and total Fe decreased from 2530 ppm, 2140 mg CaCO_3/L , 694.2, 146.2, 104.1 and 28.1 mg/L to 2150 ppm, 1617.5 mg CaCO_3/L , 552.0, 116.0, 104.5 and 22.4 mg/L, respectively.

Table 1. Selected composition of formation water after the 2011 test as well as the water composition of production water of the 2014 test.

Sample	Production (tonnes)	Na^+	K^+	Ca^{2+}	Mg^{2+}	Si	Fe	Cl^-	SO_4^{2-}	TDS	TA
Fm 2001	-	342.2	134.9	35.1	18.4	58.7	31.8	270.5	10.3	-	-
Prod 2014	26.2	694.2	55.1	146.2	140.1	41.7	28.1	165.9	6.3	2530.0	2140.0
Prod 2014	72.3	677.4	61.4	153.2	141.3	40.0	26.3	170.0	6.1	2530.0	2077.0
Prod 2014	111.3	653.2	63.4	148.0	135.7	40.2	26.8	172.6	6.3	2480.0	2021.5
Prod 2014	159.0	630.4	69.2	144.9	131.9	39.7	26.1	177.8	6.4	2420.0	1924.5
Prod 2014	207.7	615.1	71.9	141.3	126.5	39.8	24.6	179.9	6.2	2350.0	1850.5
Prod 2014	259.2	606.0	70.8	132.7	121.0	40.8	23.1	181.7	6.2	2270.0	1779.5
Prod 2014	318.5	589.7	69.9	129.8	117.9	41.5	23.4	183.3	6.1	2210.0	1731.0
Prod 2014	380.1	577.3	68.8	126.1	113.6	41.8	22.6	183.8	6.0	2220.0	1674.0
Prod 2014	442.7	566.2	66.9	123.1	109.0	42.4	22.5	183.0	6.1	2170.0	1621.5
Prod 2014	501.8	552.0	63.3	116.0	104.5	43.0	21.4	183.2	6.0	2150.0	1617.5

Note: Fm, Prod, TDS and TA are representing for formation water, production water, total dissolved solid (ppm) and total alkalinity (mg CaCO_3/L) respectively. All concentrations are reported in mg/L.

The upward trends in major elements, TDS and TA suggest that there was a mixing of two water bodies during the water production. The first water, close to the CRC2 well, had a higher concentration of cations, higher TDS and TA, but lower chloride concentration. In contrast, the second water body had lower concentrations of cations, TDS and TA, but a higher chloride concentration. More details of the mixing phenomenon can be found in Black et al [25].

KCl was used in the completion solution during the construction of the CRC-2 well and it is likely that this fluid contaminated the formation water. This is evidenced by the proportional increase in K^+ and Cl^- concentration during

the water production in 2011 (data not shown) and 2014 (Table 1). Thus, K^+ and Cl^- will not be employed to evaluate the change in water chemistry as well as the associated mineral-fluid interactions.

The changes in formation water chemistry, particularly the increase in concentrations of Ca^{2+} , Mg^{2+} and Na^+ , indicates that the mildly acidic water enriched in dissolved CO_2 (remaining from the 2011 test) has been reacting with the reservoir minerals, leading to the dissolution of silicates and carbonates such as albite, dolomite and calcite. Assuming the dissolution of calcite ($CaCO_3$) contributes solely to the rise in Ca^{2+} concentration, and the dissolution of dolomite ($MgCa(CO_3)_2$) and albite ($NaAlSi_3O_8$) contributes to the increase in Mg^{2+} and Na^+ concentrations, the percentages of these minerals to dissolve to obtain the Ca^{2+} , Mg^{2+} and Na^+ concentrations are 1.14, 1.33 and 1.4 wt%, respectively. This estimate is supported by the results from the reaction path modelling, which was calibrated with the 2014 field test [11, 24]. It is noted that only the surface area of calcite was adjusted (increased from $9.8 \times 10^{-5} \text{ cm}^2/\text{g}$ in Vu *et al* [11] to $1.96 \times 10^{-3} \text{ cm}^2/\text{g}$ in this study) to obtain the best match between the predicted and measured Ca^{2+} , Mg^{2+} and Na^+ concentrations. The adjustment of the surface area was justified by the assumption that in 2011 calcite existed in a larger quantity than in 2014, due to the dissolution of the mineral from 2011 to 2014. Thus the total surface area of calcite would be larger in 2011 compare to in 2014. The model predicted that 0.21, 0.85 and 0.04 wt% of calcite, dolomite and albite were dissolved, contributing to the increase in Ca^{2+} , Mg^{2+} and Na^+ concentrations, respectively (Fig. 4). The increase in Ca^{2+} and Mg^{2+} concentration is also stemmed from the predicted dissolution of dolomite and chlorite ($Mg_5Al_2Si_3O_{10}(OH)_8$, 0.11wt%) by the GWB model. Thus, there is a discrepancy between the manually estimated and predicted (by the GWB model) wt% of dissolved dolomite and calcite. Although the model predicted the dissolution of albite (0.04 wt%), it underestimated the Na^+ concentration, thus there is a difference between calculated and predicted wt% of dissolved albite. The Na^+ is also a component of drill mud that contaminated formation water in CCS projects [25], therefore, it is probable that the increase in Na^+ concentration was partly due to drill mud contamination.

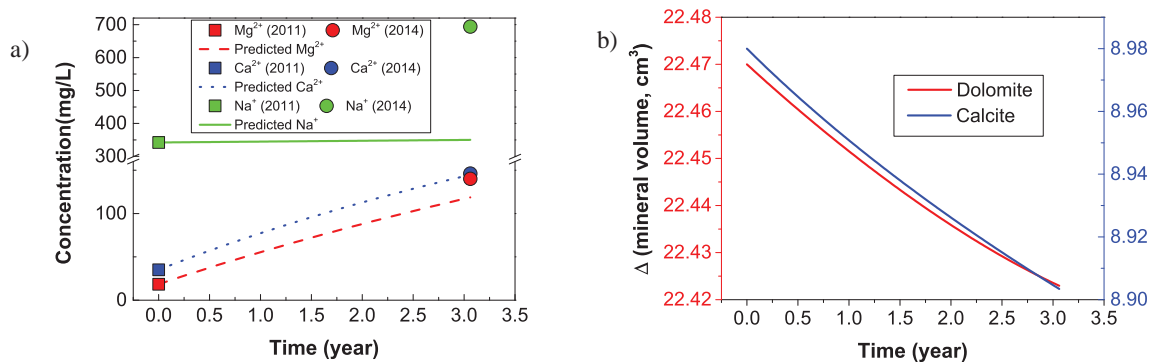


Figure 4: Changes in Ca^{2+} , Mg^{2+} and Na^+ concentrations (a) as well as mineral volumes (b, dolomite on the left and calcite on the right).

Of a total volume of all minerals of 2571.43 cm^3 that are in contact with 1000 cm^3 of fluid (with the porosity of 28% [8]), the GWB model predicted that small amounts (ranging 0.01-0.14 cm^3 , lost volumes) of calcite, dolomite, albite, siderite and chloride dissolved (Fig. 4). Coincidentally, the reaction path model also predicted insignificant precipitation of secondary minerals. Specifically, it was predicted that up to 0.08 cm^3 of kaolinite ($Al_2Si_2O_5(OH)_4$, gained volume), 0.05 cm^3 of quartz (SiO_2 , gained volume) and 0.01 cm^3 of K-feldspar ($KAlSi_3O_8$, gained volume) precipitated. The sum of gained and lost volumes of all minerals was predicted to be -0.18 cm^3 ; this loss is insignificant compared to a total volume of the minerals (2571.43 cm^3). The contribution of this decrease in total volume ($0.7 \times 10^{-2} \%$) to porosity and subsequently permeability thus would be negligible.

4. Discussion

The process of repeating a single-well field test highlights some of the sensitivities to operational and procedural details. The methodology of injecting CO₂-saturated formation water in various stages of the 2011 and 2014 tests has proved difficult to carry out consistently in the field setting. Since it was implemented via downhole mixing, intermittent changes to the fluid temperature at surface in 2014 (due to heating failures) and difficulties with calibration of flow gauges altered the extent of dissolution, and probably resulted in some dissolution of the near-well residual saturation. The use of partitioning tracers (here krypton and xenon) necessitates downhole sampling, but also raises challenges for analysis of the pressurized samples. Improvements in the methodology in 2014 achieved much better tracer recoveries than in 2011, but there were further puzzles. Disagreement in the literature over tracer partitioning coefficients has complicated the analysis procedure for this tracer test. In comparison, the use of methanol as a liquid phase tracer in 2014 was valuable for calibrating the extent of hydrodynamic dispersion, and tracking the recovery of the injected fluid. The timing of the pulsed neutron logs relative to end of injection turned out to be an important factor for interpreting the results, as the shorter time interval in 2014 meant that the CO₂ had not migrated upwards to the same extent as in 2011.

The repetition of the test also raised the question about whether the reservoir itself was the same after 3 years. Pressure transient analysis indicated that the far-field permeability is unchanged, as one would expect (once the flow rate measurements are recalibrated). However there is noticeable decrease in near-well permeability by about 60% between the two tests. The geochemical data indicate changes in water chemistry that suggest near-well precipitation of minerals is possible. However, the impact of mineral precipitation on permeability is negligible. The inflow of sand into the well caused by water production activities in the 2011 and 2014 tests, which was confirmed during a well recompletion activity in 2015, could suggest that the injection and production cycles during the test itself have altered the near-well environment by migration of fines or sand. It is also possible that the final water disposal in 2011 might have allowed the growth of biofilms that could have reduced the near-well permeability. Alongside this, the inferred residual saturation distribution is different in 2014, with the near-well values being lower than in 2011. The most likely cause of this is the slight under-saturation of the injected water, causing near-well dissolution of some of the residual CO₂, but it's also possible that the phenomenon driving the changes to near-well permeability might also have altered the in situ relative permeability curve.

The single-well residual saturation test has been shown to provide valuable information about field-scale behavior of CO₂, which reduces the uncertainty and the risk of large-scale CO₂ storage operations. The repeat of parts of the 2011 test in 2014 demonstrated improvements to the methodology, particularly for tracer analysis, but also indicated that the results of this style of test can be sensitive to finer details of the operation, such as the process for injecting water pre-saturated with CO₂, and the procedure for tracer analysis.

5. Conclusions

Parts of the 2011 CO₂CRC Residual Saturation and Dissolution Test were successfully repeated in the same well and reservoir setting in 2014, which gave an important opportunity to examine the repeatability of the measurements and to improve aspects of the operation and methodology. Issues with the low recovery of noble gas tracers in 2011 were resolved in the 2014 test, and the techniques for analysis were improved, although disagreement in the literature on tracer partition coefficients has complicated the interpretation. The use of methanol as a bulk liquid tracer was helpful in the analysis phase, allowing dispersion and mixing to be quantified. The test design requires the injection of CO₂-saturated water, and this was again found to be challenging in field operations, with slight under-saturation altering the near-well residual saturation to lower values than in 2011.

The various techniques for measuring the distribution of near-well residual saturation of CO₂ all have different ranges of investigation, and average in different ways. Analysis of the 2011 data found good consistency between these techniques [4], and similar consistency was observed in analysis of the 2014 data. The additional technique of measuring oxygen isotopes in the back-produced water to deduce saturation is promising, but the methodology needs some improvements to increase accuracy.

Well tests also have the potential to alter the near-well environment, and in this regard there were changes between the 2011 and 2014 tests, with a significant decrease in near-well permeability. The most likely reason in this case is connected with sand production and fines migration, but biofilm growth could also be contributing.

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References

- [1] Zhang Y, Freifeld B, Finsterle S, Leahy M, Ennis-King J, Paterson L, Dance T. Single-well experimental design for studying residual trapping of supercritical carbon dioxide. *Int J. Greenhouse Gas Control* 2011;5:88-98.
- [2] Paterson L, Boreham C, Bunch M, Dance T, Ennis-King J, Freifeld B, Haese R, Jenkins C, LaForce T, Raab M, Singh R, Stalker L, Zhang Y. Overview of the CO2CRC Otway Residual Saturation and Dissolution Test. *Energy Procedia* 2013; 37:6140-6148.
- [3] Paterson L, Boreham C, Bunch M, Dance T, Ennis-King J, Freifeld B, Haese R, Jenkins C, Raab M, Singh R, Stalker L. CO2CRC Otway Stage 2B residual saturation and dissolution test. In: Cook PL. editor. *Geologically Storing Carbon: Learning from the Otway Project Experience*, Melbourne: CSIRO Publishing; 2014, p. 343-380.
- [4] Ennis-King J, Paterson L, Dance T, Freifeld B, Zhang Y. Variability in field-scale residual CO₂ saturation: evidence from pressure and temperature data during the CO2CRC residual saturation and dissolution test sequence. (in preparation)
- [5] Dance T, Paterson L. Observations of carbon dioxide saturation distribution and residual trapping using core analysis and repeat pulsed-neutron logging at the CO2CRC Otway site. *Int. J. Greenhouse Gas Control* 2016; 47:210-220.
- [6] LaForce T, Freifeld B, Ennis-King J, Boreham C, Paterson L. Residual CO₂ saturation estimate using noble gas tracers in a single-well field test: The CO2CRC Otway project. *Int. J. Greenhouse Gas Control* 2014; 26:9-21.
- [7] Myers M, Stalker L, LaForce T, Pejčić B, Dyt C, Ho KB, Ennis-King J. Field measurement of residual carbon dioxide saturation using reactive ester tracers. *Chem. Geol.* 2015; 399:20-29.
- [8] Haese R, LaForce T, Boreham C, Ennis-King J, Freifeld BM, Paterson L, Schacht U. Determining residual CO₂ saturation through a dissolution test – results from the CO2CRC Otway Project. *Energy Procedia* 2013; 37:5379-5386.
- [9] LaForce T, Boreham C, Ennis-King J, Freifeld B, Serno S, Cook P, Gilfillan SMV, Johnson G, Myers M, Paterson L. Using noble gas tracers to estimate CO₂ saturation in the field: The CO2CRC Otway Repeat Residual Saturation Test. *Int. J. Greenhouse Gas Control* (submitted).
- [10] Bethke CM, Yeakel S. The Geochemist's Workbench Release 9.0, Aqueous Solutions LLC, 2012.

- [11] Vu HP, Black JR, Haese RR. The geochemical effects of O₂ and SO₂ as CO₂ impurities on fluid-rock reactions in a CO₂ storage reservoir, Int. J. Greenhouse Gas Control 2016; (submitted).
- [12] Heiland, J, Grove, B, Harvey, J, Walton, I, Martin, A. New fundamental insights into perforation-induced formation damage. In *SPE European Formation Damage Conference, Scheveningen, The Netherlands, 27–29 May 2009*, Society of Petroleum Engineers; 2009.
- [13] Gelhar LW, Collins MA. General analysis of longitudinal dispersion in nonuniform flow. *Water Resour. Res.* 1971; 7:1511-1521
- [14] Güven O, Falta RW, Molz FJ, Melville JG. Analysis and interpretation of single-well tracer tests in stratified aquifers. *Water Resour. Res.* 1985; 21:676-684.
- [15] Serno S, Johnson G, LaForce T, Ennis-King J, Haese RR, Boreham CJ, Paterson L, Freifeld BM, Cook PJ, Kirste D, Haszeldine RS, Gilfillan SMV. Using oxygen isotopes to quantitatively assess residual CO₂ saturation during the Otway 2B Extension residual saturation test. *Int. J. Greenhouse Gas Control* 2016; 52:73-83.
- [16] Fernández-Prini R, Alvarez JL, Harvey AH. Henry's constants and vapor-liquid distribution constants for gaseous solutes in H₂O and D₂O at high temperatures. *J. Phys. Ref. Data* 2003; 32:903-916.
- [17] Warr O, Rochelle CA, Masters A, Ballentine CJ. Determining noble gas partitioning within a CO₂-H₂O system at elevated temperatures and pressures. *Geochemica Cosmochim Acta* 2015; 159:112-125.
- [18] Myers M, White C, LaForce T, Heath C, Gong S, Stalker L, Pejčić B. The impact of partition coefficient data on the interpretation of chemical tracer behaviour in carbon geosequestration projects. *Chem. Geol* 2016 (submitted).
- [19] Johnson G, Mayer B, Nightingale M, Shevalier M, Hutcheon I. Using oxygen isotope ratios to quantitatively assess trapping mechanisms during CO₂ injection into geological reservoirs: The Pembina case study. *Chem. Geol.* 2011; 283:185-193.
- [20] Johnson G, Mayer B. Oxygen isotope exchange between H₂O and CO₂ at elevated CO₂ pressures: Implications for monitoring of geological CO₂ storage. *Appl. Geochem.* 2011; 26:1184-1191.
- [21] Barth JAC, Mader M, Myrtilinen A, Becker V, van Geldern R, Mayer B. Advances in stable isotope monitoring of CO₂ under elevated pressures, temperatures and salinities: Selected results from the project CO2ISO-LABEL. In: Liebscher A, Münch U, editors. *Geological Storage of CO₂ - Long Term Security Aspects*, Zürich:Springer International Publishing; 2015, pp. 59-71.
- [22] Gilfillan SMV, Serno S, Johnson G, LaForce TC, Ennis-King J, Haese RR, Boreham CJ, Paterson L, Freifeld BM, Cook PJ, Kirste D, Haszeldine RS. Using oxygen isotopes to quantitatively assess residual CO₂ saturation during the Otway 2B Extension residual saturation test. *Energy Procedia* 2016 (this volume)
- [23] Paterson, L, Ennis-King, J, Friefeld, B. Monitoring wellbore fluid displacement in the perforation interval using multiple downhole pressure and temperature gauges. In *SPE Asia Pacific Oil & Gas Conference and Exhibition, Perth, 25-27 October 2016* (paper SPE 28804). Society of Petroleum Engineers; 2016.
- [24] Vu HP, Black JR, Haese RR. Changes in formation water composition during water storage at surface and post re-injection. *Energy Procedia* 2016 (this volume).
- [25] Black JR, Haese RR, Vu HP. Aqueous phase tracers for monitoring fluid mixing in geological reservoirs: Results from two field studies, *Int. J. Greenhouse Gas Control* 2016; (submitted).