Using oxygen isotopes to quantitatively assess residual CO₂ saturation during the CO₂CRC Otway Stage 2B Extension residual saturation test


Abstract

Residual CO₂ trapping is a key mechanism of secure CO₂ storage, and is hence an essential component of the Carbon Capture and Storage technology. Estimating the amount of CO₂ that will be residually trapped in a saline aquifer formation remains a significant challenge. Here we present oxygen isotope ratio (δ¹⁸O) measurements from a single-well experiment, the CO₂CRC Otway 2B Extension, and use them to estimate levels of residual trapping of CO₂. Following the initiation of the drive to residual saturation in the reservoir, reservoir water δ¹⁸O decreased near the well, compared to baseline conditions, over a time span of only a few days. This can be explained by isotope equilibrium exchange between residually trapped CO₂ and water. This indicates that enough oxygen sourced from CO₂ was available in the reservoir to change the oxygen isotope signature of the reservoir water after only a few hours. This provides a residual saturation estimate of 14 ± 9%. For the region further away from the well, the observed...
isotopic shift in the reservoir water can also be explained by isotopic exchange with mobile CO₂ from ahead of the region driven to residual, or continuous isotopic exchange between water and residual CO₂ during its back-production. The uncertainty surrounding the contribution of each process to alteration of δ¹⁸O in the reservoir waters complicates the interpretation of the change in terms of residual saturation in the later stages of the experiment.

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Keywords: residual saturation; oxygen isotopes; Otway; geochemical tracer; CO₂ storage

1. Introduction

Geological storage of CO₂ in rock formations, as part of Carbon Capture and Storage (CCS), is a promising means of directly lowering CO₂ emissions from fossil fuel combustion [1]. For accurately modelling the long term fate of CO₂ in a commercial-scale CCS project, it is of value to develop an efficient plan to quantitatively assess the amount of structural, residual and solubility trapping at the reservoir scale through a short-term test undertaken in the vicinity of an injection well prior to large-scale CO₂ injection. Such a test would reduce risk and uncertainty in estimating the storage capacity of a formation and would provide a commercial operator with greater reassurance of the viability of their proposed storage site. This is particularly true for residual trapping of CO₂ which can play a major role for CO₂ plume migration, immobilisation, storage security and reservoir management [2-4]. Despite the important role of residual trapping of CO₂ in commercial-scale CCS projects, there is a current lack of cost-effective and reliable methodologies to estimate the degree of residual trapping on the reservoir scale.

CO₂CRC Limited (CO₂CRC) developed and has operated the CO₂CRC Otway Facility in the Otway Basin near Nirranda South, Victoria, Australia, since 2004 [5]. The facility allows for trial injection in multiple storage types, including a saline formation that currently uses a single-well configuration. This configuration is ideal for the development of an effective reservoir characterisation test prior to commercial-scale CO₂ injection [6]. In 2011, the first single-well injection test (using the CRC-2 injection well) was undertaken at the Otway facility using 150 t of injected CO₂ to quantify reservoir-scale residual trapping of CO₂ in a saline formation in the absence of an apparent structural closure (CO₂CRC Otway Stage 2B – henceforth referred to as Otway 2B; [6]). The target reservoir for the experiment was within the Paaratte Formation, a saline formation at 1075-1472 m TVDSS (true vertical depth below mean sea level), with the target interval for the Otway 2B experiment at 1392-1399 m TVDSS. Deep saline formations are the most likely candidates for geological CO₂ storage because of their huge potential capacity and their locations close to major CO₂ sources [7]. The Paaratte Formation, while only used for research purposes, is a saline formation analogous to those proposed for commercial-scale CO₂ injection and storage. Two of the original measurements of residual CO₂ saturation were acquired using noble gas (Xe and Kr) tracer injection and recovery data [8], and pulsed neutron logging of the CRC-2 injection well [6,9]. The second part of the recent CO₂CRC Otway Stage 2B Extension project (henceforth referred to as Otway 2B Extension) was a smaller-scale repeat of these two residual saturation tests using improved methodologies.

We present oxygen (δ¹⁸O) and hydrogen isotope (δ²H) data from injected and produced water samples, and oxygen isotope data from CO₂ samples from the Otway 2B Extension. These data and their interpretation in terms of residual saturation have been recently published in Serno et al. [10]. For the first time we estimated levels of residual trapping of CO₂ based on oxygen isotope data from a single-well test. We compare our results with measures from independent techniques used to estimate residual saturation during the 2011 Otway 2B experiment.

2. CO₂CRC Otway Stage 2B Extension

The Otway 2B Extension was conducted in October-December 2014 over a time span of 80 days. The target interval
for the Otway 2B experiments is characterised by well-sorted texturally submature deltaic sandstone dominated by quartz and low clay and feldspar contents, overlain by a diagenetic carbonate seal [6,11]. The sandstone has a porosity of ~28%, an average permeability of 2.2 Darcy and a fluid salinity of 800 mg/L [6]. The target reservoir is overlain by a cemented interval and a thick non-reservoir lithofacies interval with a high sealing capacity [6]. The CRC-2 well is equipped with a U-tube geochemical sampling system [12] and a set of four pressure and temperature gauges at the top and bottom of the target interval for the Otway 2B experiments.

The aims of the Otway 2B Extension were to study differences in reservoir water quality in response to the injection of CO$_2$-saturated water with and without trace amounts of gas impurities (Phase 1), and to characterise the residual trapping levels of CO$_2$ after injection of pure CO$_2$ into the formation (Phase 2). Our study focuses on Phase 2 [10]. This phase started with the production of 75.1 t of water over two days, followed by the injection of 67 t of previously produced water for the ‘water test’ (Phase 2.1). Water production with U-tube sampling to study the tracer behaviour at reservoir conditions without CO$_2$ in the formation commenced immediately after the injection, producing 122.2 t of water over three days. This was followed by the injection of 109.8 t of pure CO$_2$ over four days (Phase 2.2). 323.7 t of previously extracted water, saturated with 17.5 t of CO$_2$, was injected to drive the reservoir to residual saturation over the following three days (Phase 2.3). The injected water that drives the reservoir to residual saturation was fully saturated with CO$_2$ to avoid dissolving the residually trapped CO$_2$. This was followed by the injection of 67.2 t of previously produced water, now saturated with 3.9 t of CO$_2$, with the production of 128.5 t of water with U-tube sampling over the next three days (Phase 2.4). The injected gas for the Otway 2B Extension was a mixture of industrial CO$_2$ captured at the Callide Oxyfuel pilot capture plant in Queensland (Callide CO$_2$) and food grade CO$_2$ (99.9 %) from the Boggy Creek well in the vicinity of the Otway site (BOC CO$_2$) [10].

3. Estimation of residual CO$_2$ saturation based on oxygen isotope values in reservoir water

Stable isotopes may be highly suitable for assessing the movement and fate of injected CO$_2$ in the formation [13,14]. There are few sources of available oxygen other than the reservoir water within reservoirs [15,16]. Any other reservoir oxygen that is available for water-rock reactions is typically in isotopic equilibrium with the reservoir fluid due to relatively fast reaction kinetics [17,18].

We report stable isotope data as delta isotope values in ‰ deviation relative to VSMOW (Vienna Standard Mean Ocean Water) according to

$$\delta_{\text{sample}} = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$  \hspace{1cm} (1)

where $R$ represents the oxygen isotope ($^{18}$O/$^{16}$O) and hydrogen isotope ($^2$H/$^1$H) ratios of samples and standards, respectively.

Concurrently increasing or decreasing final water $\delta^{18}$O ($\delta^{18}$O$_{H_2O}$) and $\delta^2$H values of reservoir water compared to baseline values can indicate admixture of different waters with variable isotopic compositions, while a change in $\delta^{18}$O$_{H_2O}$ without any change in $\delta^2$H suggests water-CO$_2$ interaction in the reservoir when mineral dissolution can be excluded [15,19,20]. In most natural environments the amount of oxygen in CO$_2$ is negligible compared to the amount of oxygen in water. Consequently, water $\delta^{18}$O remains essentially constant and $\delta^{18}$O of CO$_2$ ($\delta^{18}$O$_{CO_2}$) approaches that of the water plus the appropriate isotopic enrichment factor between the water and CO$_2$ ($\varepsilon = 10^3 \ln_{\text{CO}_2 \text{H}_2O}$), depending on the reservoir temperature [21]. At CO$_2$ injection sites, due to the large quantities of CO$_2$ injected, CO$_2$ becomes a major oxygen source, and both CO$_2$ and water will change their $\delta^{18}$O due to isotopic equilibrium exchange reactions if the injected CO$_2$ is isotopically distinct with respect to the baseline reservoir water. This has been observed in CO$_2$ injection field tests [10,15,22], laboratory experiments [20,23] and in natural settings characterised by vast amounts of free-phase CO$_2$ in contact with water [24-26].
The method used here to estimate the reservoir CO$_2$ saturation based on changes in $\delta^{18}$O of reservoir water in contact with free-phase CO$_2$ is described in detail in Johnson et al. [15]. If the majority of oxygen in the system is sourced from CO$_2$, as is the case near the injection well after Phase 2.3, $\delta^{18}$O$_{CO_2}$ will dominate the water-CO$_2$ system. The $\delta^{18}$O ratio of reservoir water will start to change from the baseline water oxygen isotope value, $\delta^{18}$O$_{H_2O}^b$, towards an end-member scenario where the water has a final water value $\delta^{18}$O$_{H_2O}^f$ lower than that of the injected CO$_2$ by the isotopic enrichment factor $\varepsilon$. In this case, the fraction of oxygen in the system sourced from CO$_2$, $X_{CO_2}^o$, can be estimated using

\[
X_{CO_2}^o = \frac{(\delta^{18}O_{H_2O}^b - \delta^{18}O_{H_2O}^f)}{(\delta^{18}O_{H_2O}^b + \varepsilon \cdot \delta^{18}O_{CO_2})}
\]

The isotopic enrichment factor $\varepsilon$ between CO$_2$ and water is reported in ‰ and determined using the equation defined by Bottinga [21]

\[
\varepsilon = -0.0206 \times \left(\frac{10^6}{T}\right) + 17.9942 \times \left(\frac{10^5}{T}\right) - 19.97
\]

where $T$ is the reservoir temperature in Kelvin. This equation is valid at atmospheric conditions as well as elevated temperatures and pressures relevant for CCS projects [20,21,27].

The water-CO$_2$ system for oxygen in a reservoir can be described quantitatively in terms of the averaged reservoir CO$_2$ saturation for the region contacted by CO$_2$ and measured with the water sample ($S_{CO_2}$) using

\[
S_{CO_2} = \frac{(B_X^{CO_2} + CX_2^{CO_2} - B)}{(A - B - AX^{CO_2} + BX^{CO_2} + CX^{CO_2})}
\]

with $A$ referring to moles of oxygen in 1 L of free-phase CO$_2$ at reservoir conditions, $B$ to moles of oxygen dissolved in 1 L water from CO$_2$ at reservoir conditions, and $C$ to moles of oxygen in 1 L water at reservoir conditions [15]. As a result of the drive to residual saturation during Phase 2.3 and the exclusion of any contribution of oxygen from dissolution of carbonate minerals to the total oxygen inventory in the target interval [10], we assume estimates of $S_{CO_2}$ based on oxygen isotopes to provide flow-weighted averages of residual CO$_2$ saturation, and we expect that $S_{CO_2}$ levels in the reservoir are variable over distance from the borehole.

4. Results

Values of $\delta^2$H in water samples remained relatively constant throughout the entire Otway 2B Extension (Fig. 1), indicating that no major evaporation or water mixing processes occurred at surface or in the reservoir [10]. For reservoir water $\delta^{18}$O, the water samples produced from the reservoir prior to CO$_2$ injection fall within the range of injected water isotope ratios. However, we observe an $\delta^{18}$O depletion in the reservoir waters produced during the three days of water production for Phase 2.4, when water samples in contact with CO$_2$ in the reservoir were sampled, compared to the injected and produced water sample ratios prior to the Phase 2.4 water production. The $\delta^{18}$O values of the samples collected from the three days of water production decreased from day 1 to day 3, with the lowest value of $-6.46 \pm 0.10$ ‰ on the last day (Fig. 1).

For the approach to estimate residual CO$_2$ saturation outlined above to be robust, it is essential to have a reliable baseline $\delta^{18}$O for the reservoir water. A total of 390.9 t of CO$_2$-saturated water was injected during Phases 2.3 (323.7 t) and 2.4 (67.2 t) prior to producing 128.5 t of water in Phase 2.4 [10]. Consequently, we expect that the water produced in Phase 2.4 was a mixture of the injection water of Phases 2.3 and 2.4. The 323.7 t of CO$_2$-saturated water injected during Phase 2.3 had an average water $\delta^{18}$O of $-6.07 \pm 0.07$ ‰ and $\delta^{18}$O$_{CO_2}$ of $+27.65 \pm 0.12$ ‰ for the co-
injected CO₂, resulting in a δ¹⁸O value for the fully CO₂-saturated water of -6.18 ± 0.07 ‰ at wellbore conditions (Fig. 1). The injected water for Phase 2.4 had an average water δ¹⁸O of -5.79 ± 0.07 ‰, and δ¹⁸O CO₂ of +29.30 ± 0.20 ‰ for the co-injected CO₂, resulting in a δ¹⁸O value for the fully CO₂-saturated water of -5.86 ± 0.07 ‰ at wellbore conditions.

The Phase 2.3 injection of CO₂-saturated water thus had a slightly different oxygen isotope signature compared to the injection water for Phase 2.4, resulting in the necessity to account for mixing of these two water masses in the reservoir to provide a reliable baseline value for the estimation of residual saturation on each of the three days of water production. We used the data on methanol co-injected with the injection water during Phase 2.4 to estimate the mixing ratio of the two water masses during the water production stage [10].

![Graph](https://via.placeholder.com/150)

**Fig. 1.** δ¹⁸O vs. δ²H in water samples from Phases 2.1, 2.3 and 2.4 [10]. Samples from injection periods were collected in Nalgene bottles from the injection line at surface and are shown as open squares. Samples from production periods were collected using the U-tube system installed in the well and are shown as filled triangles. Samples from Phase 2.1 are in blue, from Phase 2.3 in red, from the water injection for Phase 2.4 in magenta, and for the water production of Phase 2.4 in different green colours. The thick black line indicates the local meteoric water line (LMWL) for Melbourne [28].

The first 12.2 t of the 109.8 t of pure CO₂ injected and residually trapped in the reservoir were Callide CO₂ with a δ¹⁸O ratio of +26.05 ± 0.14 ‰, while the remaining 97.6 t of pure CO₂ was BOC CO₂ with an oxygen isotope signature of +29.30 ± 0.20 ‰. For the estimation of residual CO₂ saturation, we assumed perfect mixing of these two CO₂ sources in the reservoir and derived the δ¹⁸O CO₂ ratio to be used in Eq. (2) as a weighted average based on the amounts of the two injected CO₂ sources. This results in a δ¹⁸O CO₂ ratio for the residually trapped CO₂ of +28.94 ± 0.12 ‰ [10]. We consider this approach as the most reliable to assess δ¹⁸O CO₂ since we do not have an estimate for the mixing of CO₂ in the reservoir or of variable oxygen isotope signatures of CO₂ in contact with water in the reservoir.
5. Estimates of residual CO₂ saturation in the Paaratte Formation

For each U-tube sample collected for stable isotopes during the three days of water production for Phase 2.4, we used Eqs. (2)-(4) to estimate residual trapping levels. We used the thermodynamic model of Duan and Sun [29] to derive solubilities and densities of CO₂ in aqueous NaCl solutions under wellbore conditions to calculate parameters A, B and C for each individual day since temperatures and pressures varied throughout the experiment [10].

The first water production sample was collected ~7 hours after the start of water production and ~9 hours after the end of CO₂-saturated water injection. The isotopic shift compared to baseline water conditions resulted in a value for residual saturation of 14 ± 9 % for this sample. For the second sample collected on day two of the water production, Eq. (4) provides a residual CO₂ saturation based on oxygen isotopes of 28 ± 11 %, while the sample from the last day with the lowest δ^18O_H₂O value of all samples collected indicates a residual saturation in the target interval of 42 ± 16 % [10].

While our oxygen isotope data from reservoir waters show a clear shift as a result of water-CO₂ isotopic exchange in the reservoir within a few days, our estimates of residual CO₂ saturation are characterised by relatively large errors. Several factors can result in uncertainties in the oxygen isotope approach [10]. First, and most importantly, the oxygen isotopic distinction between the injected CO₂ and baseline reservoir water in consideration of the isotopic enrichment factor at wellbore conditions is relatively small during the Otway 2B Extension. While a predictable δ^18O shift to lower values in reservoir water in contact with free-phase CO₂ compared to baseline conditions was observed, the small isotopic distinction of the two main oxygen sources resulted in a small isotopic shift in the short time of the Otway 2B Extension and a large uncertainty in S_{CO₂} estimates. Second, there are uncertainties resulting from the field experiment procedure and setup due to variable reservoir conditions during the entire project and uncertainty in the mixing ratios of water masses and CO₂ sources with different isotopic signatures [10]. These uncertainties resulted in the necessity to make assumptions about mixing ratios of gases and water masses in the reservoir, and about average reservoir conditions during the different phases.

6. Implications from the comparison of independent measures of residual saturation during Otway Stage 2B

We can compare our oxygen isotope-based S_{CO₂} results to independent estimates of residual CO₂ saturation in the Otway 2B target interval based on noble gas tracers and pulsed neutron logging from the first Otway 2B experiment (Fig. 2). For the comparison of results from the two Otway 2B field experiments, we have to consider that differences in residual saturation levels between the two experiments can result from differences in the timing of events, especially during the water flood. All of three techniques we compare our results to measure a spatially varying residual saturation over different depths of investigation using different forms of averaging, and are characterised by specific uncertainties and limitations that have to be considered [10].

The stable isotope sample collected just 7 hours after the start of water production provides a near-wellbore estimate of residual trapping of CO₂, and can therefore be best compared to measures based on pulsed neutron logging which provides a residual saturation estimate for the near-wellbore reservoir (~25 cm; [9]). Saturation profiles from the first Otway 2B experiment from pulsed neutron logging showed an average residual saturation of 20 %, with an overall range of 7 to 32 % [9] (Fig. 2). While we have to consider the possibility that the water sampled just 7 hours into the water production phase may not have achieved full isotopic equilibrium with residual CO₂ in the reservoir, our estimate for this first stable isotope sample of 14 ± 9 % is similar with the saturation level reconstructed from pulsed neutron logging. The stable isotope sample from the second and third day can be best compared to the estimates based on noble gas injection and recovery, since this technique provides an average saturation for the reservoir further away from the well. Reconstructed residual CO₂ saturation levels from the multiphase flow simulations of noble gas injection and recovery ranged between 11 and 20 % for the first Otway 2B experiment [8] (Fig. 2). These estimates
fall in the range of possible $S_{CO_2}$ values based on stable isotopes from the second day (28 ± 11 %), but are lower than the results from the last day of the Phase 2.4 water production (42 ± 16 %). This trend of increasing $S_{CO_2}$ with distance from the wellbore based on oxygen isotope shifts in the reservoir water is different to the spatial residual trapping distribution in the reservoir from numerical reservoir simulations, which predict decreasing gas saturation with distance from the well, with residuals not exceeding 20 % further from the injection well [10].

![Residual CO₂ saturation (%)](image)

Fig. 2. Comparison of the residual saturation estimates from different geochemical and geophysical monitoring techniques applied during the two Otway 2B field experiments in 2011 and 2014. The bars indicate the potential range of saturation values for each method, with the black line indicating the average. Oxygen isotope-based measures for each of the three days of water production during Phase 2.4 of the Otway 2B Extension are shown in different green colours [10], the range of near-wellbore saturation values based on pulsed neutron logging during the 2011 experiment in orange [9], and the range of potential residual saturation values based on numerical simulations of noble gas injection and recovery data during the 2011 Otway 2B experiment are shown in blue [8].

Three potential mechanisms can explain the reconstructed change in oxygen isotopes in the reservoir water during the three days of water production of Phase 2.4. The observed trend can be the result of:

- A higher residual further away from the wellbore that is not reconstructed using the noble gas injection and recovery method (mechanism 1).
- Contact of the produced water from the last day of Phase 2.4 with the region of mobile CO₂ ahead of the region driven to residual (mechanism 2).
- Higher residual saturation levels reconstructed from oxygen isotopes in waters longer in contact with residually trapped CO₂ in different regions of the reservoir (mechanism 3).

The region that has been driven to residual saturation does not extend very far into the reservoir and mobile CO₂ from further out may have been pulled towards the well during production. Therefore, mechanism (2) could explain
the high $S_{CO_2}$ value reconstructed from the water sampled during the last day of Phase 2.4, but not the higher residual saturation estimate from the second day compared to the first day of water production during Phase 2.4. Mechanism (3) considers alteration of the isotopic values of reservoir water during the back-production that might complicate the interpretation of the oxygen isotope changes in terms of residual saturation in the reservoir. The oxygen isotope shift in the reservoir water away from baseline values may be simply due to the variable CO$_2$ volumes the waters were in contact with in the reservoir, with water samples characterised by a longer residence time in the supercritical CO$_2$-water system from the beginning to end of the production phase. During the back-production of Phase 2.4, the water may have continued exchanging oxygen with residual CO$_2$ with variable isotopic signatures in the different regions of the reservoir, resulting in further perturbation of $\delta^{18}O_{H_2O}$. Since residual CO$_2$ in the different regions of the reservoir may have already been in contact with other waters and had variable oxygen isotope values compared to the initially injected $\delta^{18}O_{CO_2}$ value, and since it is uncertain if there was enough time for continuous isotopic equilibrium exchange of reservoir water on its way to the well during back-production, it is difficult to resolve the potential contribution of mechanism (3) with confidence. Therefore, we cannot estimate the effect of this mechanism for the observed changes in oxygen isotopes of the reservoir water during the experiment.

Consequently, we are left with three potential mechanisms to explain the observed oxygen isotope shift in reservoir waters during the residual saturation test, and the true nature of the residual saturation distribution further away from the well remains uncertain [10]. However, mechanisms (2) and (3) are improbable to explain the observed oxygen isotope shift from baseline values for the first stable isotope sample collected shortly after the start of back-production. Therefore, this first water sample is the most reliable of the water production samples in terms of reconstructing residual trapping of CO$_2$ in the formation. Since the reconstructed residual saturation based on oxygen isotopes from this sample is similar to near-wellbore residual saturation values based on pulsed neutron logging, oxygen isotopes during the Otway 2B Extension show potential as an inherent tracer for residual saturation in a single-well experiment that should be further explored in future field and laboratory experiments.

7. Laboratory experiments to study the behavior of oxygen isotopes during a single-well field experiment

We are currently conducting laboratory experiments to constrain the exact mechanism and timing of oxygen isotopic equilibrium exchange. This experiment will help to test the validity of mechanism (3) to explain our observation of variable oxygen isotope shifts for reservoir waters produced from different regions of the Paaratte formation during the Otway 2B Extension. Mechanism (3) considers alteration of the isotopic values of reservoir water during the back-production that might complicate the interpretation of $\delta^{18}O$ changes in terms of residual saturation in a reservoir.

In the laboratory experiments, we duplicate the field setup of Phase 2 of the Otway 2B Extension, with water injection into the formation followed by back-production, using three FlexFoil PLUS sample gas bags (SKC Limited) representing different volumes of the reservoir at different distances from the well. We study if waters already in isotopic equilibrium with a CO$_2$ will continue to change due to isotopic equilibrium exchange with the same CO$_2$, but altered as a result of continuous exchange with other water masses in the reservoir. For this, we add a small amount of $^{18}$O-enriched water in each bag and add around 1 L of commercially available CO$_2$ to the first bag. Following an equilibration period of around one week, the CO$_2$ is transferred from bag one to bag two. This step is repeated, so that the CO$_2$ gas is transferred from bag one to two and then three, and again from gas bag three to two and then one. In this way, we duplicate the injection and back-production during a single-well field test. During each transfer, water and CO$_2$ gas samples are taken to better understand the change in the oxygen isotope composition of both oxygen sources during the various steps of the experiments.

8. Conclusions

Residual CO$_2$ saturation is a parameter that has been difficult to assess using previous monitoring techniques but
one which is crucial for determining the efficiency of a CO₂ storage site. Our study from the Otway 2B Extension is the first to provide evidence for a shift in oxygen isotope ratios of reservoir water due to isotopic equilibrium exchange with free-phase CO₂ in a reservoir over only a 3-day period, compared to stable baseline water values prior to CO₂ injection, which can be used to quantify residual CO₂ saturation at different distances from the wellbore.

The estimates of residual saturation based on oxygen isotopes from the different days of water production indicate an increase in residual trapping levels with distance from the wellbore. This trend is not consistent with reservoir simulations, which predict the opposite trend. We show that there are three potential mechanisms that can explain the observed oxygen isotope shift from baseline values for the water samples further away from the wellbore, resulting in considerable uncertainty about the true residual saturation distribution in the reservoir at distance from the well. However, only isotopic equilibrium exchange between water and residually trapped CO₂ can explain the isotopic shift in the water from near the wellbore. The similarity of the oxygen isotope-based result from these near-wellbore waters and independent estimates based on pulsed neutron logging indicates that monitoring of oxygen isotope ratios of reservoir water in contact with free-phase CO₂ may serve as an inexpensive inherent tracer that offers the potential to reconstruct flow-weighted averages of residual CO₂ saturation on a reservoir scale within a few days.

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References

[26] Karolyte R, Johnson G, Gilfillan SMV, Serno S. Investigating the influence of mineral dissolution and precipitation on oxygen isotope ratio ($^18$O) of CO$_2$-rich groundwater in Daylesford, South East Australia. This issue.