Tracing injected CO2 in the Cranfield enhanced oil recovery field (MS, USA) using He, Ne and Ar isotopes

Citation for published version:

Digital Object Identifier (DOI):
10.1016/j.ijggc.2015.09.009

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published In:
International Journal of Greenhouse Gas Control

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and/or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 17. Dec. 2018
Tracing injected CO₂ in the Cranfield enhanced oil recovery field (MS, USA) using He, Ne and Ar isotopes

Domokos Györe a,*, Finlay M. Stuart a, Stuart M.V. Gilfillan b, Susan Waldron c

a Isotope Geoscience Unit, Scottish Universities Environmental Research Centre, East Kilbride G75 0QF, UK
b School of Geosciences, University of Edinburgh, Edinburgh EH9 3JW, UK
c School of Geographical and Earth Sciences, University of Glasgow, Glasgow G12 8QQ, UK

A R T I C L E   I N F O
Article history:
Received 16 April 2015
Received in revised form 7 September 2015
Accepted 14 September 2015

Keywords:
Carbon capture and storage
Geological storage
Geochemical tracing
Carbon isotope
Noble gas isotope
Mass spectrometry

A B S T R A C T
The He, Ne and Ar isotopic composition of gases collected in 2009 and 2012 from 13 production wells, injection wells and the CO₂ supply pipeline at the Cranfield CO₂-enhanced oil recovery field (MS, USA) have been measured in order to determine the extent to which they trace the fate of injected CO₂ in the reservoir. In the absence of samples of CO₂ pre-injection reservoir gas we use the Ne isotope composition of the production and injection well gases to determine the isotopic composition of the natural gas. The noble gas isotopes display binary mixing trends between the injected CO₂ and a CH₄-rich natural gas that is characterised by radiogenic He, Ne and Ar isotope ratios. ³He/⁴He and ⁴⁰Ar/³⁶Ar ratios (where ⁴⁰Ar represents the non-atmospheric ⁴⁰Ar) display coherent relationships with CO₂ concentrations that can be used to trace and quantify the injected CO₂ in an engineered site over a sustained period of injection. The presence of a small amount of air-derived Ar, from a non-atmospheric source, in many gas samples rules out using ⁴⁰Ar/³⁶Ar to track the injected CO₂. The noble gases identify the loss of a significant proportion of the CO₂ from the gas phase sampled by five production wells in 2009. Using ³He/⁴He and ⁴⁰Ar/³⁶Ar ratios to reconstruct the major gas composition, it appears that between 22% and 96% of the CO₂ has been lost in individual wells. This study demonstrates that the naturally occurring noble gases have the potential to trace the fate and quantify the sequestration of CO₂ at injection sites.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Geological storage of CO₂ is the only means to directly reduce man-made CO₂ emissions to the atmosphere from industrial point sources (Scott et al., 2013). Developing techniques for monitoring and verifying the secure storage of injected CO₂ is essential if carbon capture and storage (CCS) is to become a realistic climate mitigation option. The verification process requires an understanding of the mechanism of storage and the ability to track the fate of CO₂ in the subsurface. Numerical simulations and laboratory experiments that model fluid flow, physical-chemical processes acting on the injected CO₂ (Ennis-King and Paterson, 2007; Knauss et al., 2005; White et al., 2005; Xu et al., 2005) and trapping mechanisms within engineered fields (Arts et al., 2004; Emberley et al., 2005) have been developed. These models require validation by field measurements.

Baseline studies at CCS test sites provide constraints on the movement of injected CO₂ (Stalker et al., 2015). Injection of CO₂ into depleted hydrocarbon fields has long been used for enhanced oil recovery (EOR). Given the large volumes of CO₂ transported and injected in these sites they can serve as analogues for geological CO₂ storage (Baines and Worden, 2004; Haszeldine et al., 2005). Additional insights on the storage and movement of anthropogenic gas can be acquired by studying naturally occurring CO₂ accumulations in the shallow crust (e.g. Gilfillan et al., 2008).

Several geochemical techniques have been developed for tracking the movement and storage of CO₂ in the crust (e.g. Humez et al., 2014 and references therein). The stable carbon isotope composition of CO₂ (δ¹³C_CO₂) has been widely and successfully used to trace injected gas, and track its interaction with reservoir fluid and rocks (Assayag et al., 2009; Johnson et al., 2011; Lu et al., 2012b; Myrtille et al., 2010), as well as constrain the storage mechanism (e.g. Raistrick et al., 2006). However, the technique is less powerful if the δ¹³C of the injected and in-place reservoir CO₂ are similar (e.g. Sherwood Lollar et al., 1997; Wycherley et al., 1999), or when CO₂ is liberated from carbonate reservoir rocks during reaction with the acidified formation water generated by CO₂ dissolution (Shevalier et al., 2013). Chemical tracers such as SF₆, perfluorocarbons and CD₄ have been added to CO₂ and used in CCS analogue studies to determine the timing of breakthrough of the injected gas (Stalker et al., 2015 and references therein).

* Corresponding author.
E-mail address: d.gyore.1@research.gla.ac.uk (D. Györe).

http://dx.doi.org/10.1016/j.ijggc.2015.09.009
1750-5836/© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
The noble gases (He, Ne, Ar, Kr and Xe) are chemically inert and have several isotopes that allow them to be used to trace the physical processes that have affected crustal fluids, and to constrain gas residence time-scales. They have been used, for instance, to resolve the origin and movement of CO₂ in natural gas reservoirs (Gilfillan et al., 2009; Lafortune et al., 2009; Sathaye et al., 2014) as well as determine the long-term storage of CO₂ in natural gas fields (Ballentine et al., 2001; Gilfillan et al., 2008; Zhou et al., 2012). The addition of Kr and Xe isotopes to injected gas has been used to trace the movement of injected CO₂ in CCS trials (Lu et al., 2012a; Nimz and Hudson, 2005; Stalker et al., 2015).

The noble gases are present in trace amounts in natural CO₂ (e.g. Zhou et al., 2012). Where the isotopic composition of the noble gases in injected natural CO₂ are significantly different to those of the in-place reservoir gas they have the potential to trace the movement and mixing of the injected gas (Nimz and Hudson, 2005). Here we present the first comprehensive study to apply this technique in an EOR field that is an analogue for geologic CO₂ storage sites. We report the He, Ne and Ar isotope composition of well gases from the Cranfield EOR field, Mississippi, USA, over a period of three years after the start of CO₂ injection. The data allow us to trace the presence of injected CO₂ in the reservoir and the loss of a component of this injected CO₂.

2. The Cranfield oil and gas field

Cranfield is located in southwest Mississippi, ~20 km east of the town of Natchez (Fig. 1). The reservoir is an anticline of highly permeable fluvial sediments of the Upper Cretaceous Lower Tuscaloosa Formation. The reservoir rock is largely composed of 15–25 m thick conglomerates, and occurs at depth of ~3000 m (Hosseini et al., 2013; Lu et al., 2012b). It was discovered in 1943 and oil and gas production commenced in 1944. The field is a simple dome structure (~6.4 km diameter), with a gas cap and associated down-dip oil ring. Pressure was maintained by gas recycling until the gas cap was depleted in 1959. It was abandoned in 1966 after unsuccessful water injection tests in 1958–59. The base and cap rock of the injection zone are low permeability mudstones. A SE–NW trending normal fault bisects the reservoir (Hovorka et al., 2013).

CO₂ injection for EOR started in July 2008 by Denbury Resources Incorporated. High purity (99%) CO₂ is transported ~160 km from the Jackson Dome deposit in central Mississippi (Fig. 1). CO₂ injection started at the north part of the field (Fig. 1) and extended to the southeast over the following three years. There was a corresponding development of injection and production wells to produce the oil mobilised by the CO₂ injection. Water and gas produced with the oil are separated at the surface on site. Produced water is disposed of via a deep water injection well, while the produced gas (CO₂ and CH₄) is mixed with Jackson Dome CO₂ and re-injected (this is termed recycled gas) (Choi et al., 2013).

In April 2010 the injection rate was approximately one million metric tonnes per year. By January 2013 6.8 million metric tonnes of CO₂ had been injected, of which 4 million had been retained in the reservoir (Hosseini et al., 2013; Hovorka et al., 2013). Between July 2009 and January 2013 the proportion of recycled gas in the injected gas had increased from ~9 to ~30% (Hovorka et al., 2013).

Prior to injection the reservoir re-equilibrated to hydrostatic pressure by groundwater infiltration over the ~40 years of abandonment. Continuous CO₂ injection without water injection means that Cranfield can be considered as an analogue for injection into a saline aquifer (Hovorka et al., 2011, 2013; Lu et al., 2012b). This is significant as saline formations offer the vast majority of available global CO₂ storage capacity (Scott et al., 2013). Consequently CO₂ monitoring and flow, sequestration modelling, trapping mechanism constraining and leak detection research have been undertaken extensively in the past few years (Hosseini et al., 2013; Hovorka et al., 2013; Lu et al., 2013; Nicot et al., 2013; Zhang et al., 2013, 2014). The binary mixing of the injected CO₂ with the naturally-occurring methane-rich reservoir gas is supported by δ¹³C_CO₂ measurements of produced gases (Lu et al., 2012b).

3. Sampling and analytical methods

The samples analysed for this study were collected in December 2009 and March 2012, 19 and 45 months after the start of CO₂ injection. Only the northeast part of the field was in operation during the first sampling trip. CO₂ injection and production was extended to the southeast by March 2012 (Fig. 1). The incoming pipeline from Jackson Dome to Cranfield (termed the bulkline) was sampled in 2012. Injection wells were sampled in both years with 22 gas samples being collected from production wells: 10 in 2009 and 12 in 2012. Nine of the 2009 wells were re-sampled in 2012 whilst three of the wells sampled in 2012 were not in use in 2009. Detailed well information is shown in Table 1.

The CO₂ in the bulkline and in the injection wells were maintained at around 21 MPa and 35 °C. Production wells were operated at between 0.8 and 9.1 MPa and around 60 °C. Oil, water and gas were present in the production wells therefore gas samples were taken from the top of the pipeline in order to avoid sampling liquid. Samples were collected in 8 mm outside diameter copper tubes that were connected to a pressure regulator using flexible pipe. The tube and gauge were flushed with gas for 5 min and then clamped at the end using a purpose built steel clamp, forming a cold weld. A similar clamp at the upstream end of the copper tube was closed.
when the pressure reached 2–3 bar, again forming a cold weld and maintaining a helium tight seal.

Copper sample tubes were connected to an all-metal vacuum line maintained at ~35 °C and pumped to ultra high vacuum (p < 10^{-7} mbar) using a turbo-molecular pump. The gas from the tube was expanded into a known volume and the absolute pressure was measured using a MKS 615-A Baratron capacitance manometer. The uncertainty on the pressure measurements is typically ±0.5% (1σ). A small fraction of the gas sample was used to determine the concentration of CO₂ and CH₄ using a Pfeiffer Vacuum QMS 200 quadrupole mass spectrometer. The mass spectrometer was calibrated by series of analyses of binary mixtures of CO₂ and CH₄ over the pressure range typical of samples. In several samples a small proportion of a sample gas was trapped into ~10 cm³ glass tubes and CO₂ absorbed at ~160 °C using liquid nitrogen and iso-pentane. Hydrocarbon gases were pumped off and Δ^{13}CO₂ was determined using a VG Optima dual inlet isotope ratios mass spectrometer in dynamic mode.

The remaining gas was expanded into a VG Sciencta ST22 titanium sublimation pump that ran sequentially between ~900 °C and 15 °C. This purified gas was exposed to a SAES GP50 ZrAl alloy getter, held at 250 °C, for 20 min and subsequently expanded into a 0.5 litre reservoir. The concentration of He, Ne, and Ar were determined on the residual gas that was not trapped in the reservoir using the quadrupole mass spectrometer in order to guide subsequent isotopic analysis from the reservoir.

Typically He isotopes were measured in a ~4 cm³ aliquot of gas from noble gas reservoir. This was purified by exposure to four hot GP50 ZrAl alloy getters and the heavy noble gases (Ar, Kr, Xe) were absorbed onto liquid nitrogen-cooled charcoal prior to analysis. Neon isotopes were typically measured in a larger volume of gas than for helium. Purification followed the procedure for He isotopes, except that Ne was not trapped on charcoal at -243 °C for 20 min, helium was pumped off and the Ne released at -173 °C for 15 min prior to analysis. The gas was desorbed from the nitrogen-cooled charcoal by heating to room temperature for 15 min and the Ar isotope composition was determined.

The isotopic composition of the noble gases was measured by a MAP 215-50 mass spectrometer in static mode following established procedures (Codleian et al., 2008; Williams et al., 2005). He, Ar, Ne and Ar were measured on a Faraday detector with 10¹¹ amplification, and He, Ne, Ne on a Burle channeltron electron multiplier in pulse counting mode at 2.5 kV. The hydrogen partial pressure was minimised by a room temperature GP50 getter in the mass spectrometer source volume. During He and Ne and isotope analysis liquid nitrogen-cooled charcoal was used to minimise the heavy noble gases, hydrocarbons and CO₂ in the mass spectrometer.

The mass spectrometer sensitivity and mass fractionation was determined by repeated analysis of aliquots from reservoirs of HESJ international standard (Matsuda et al., 2002) for He, and air for Ne and Ar, during each analytical period. The reproducibility of noble gas isotope ratios and amounts presented in Table 2 are typically ±0.5% (1σ). Blanks for all isotopes were negligible.

4. Results

A sample of the bulkline gas taken in 2012 contains >99% CO₂ with a trace amount of CH₄ and noble gases. Δ^{13}CO₂ is ~2.9‰, which is similar to previous determinations (Lu et al., 2012b; Zhou et al., 2012). The noble gas isotope ratios (Table 2) are similar to those measured from the Jackson Dome CO₂ deposit (Zhou et al., 2012).

The injected gases sampled in 2009 and 2012 are significantly different from the bulkline gas. The CO₂ content is lower; 96% in 2009 and 87% in 2012, with correspondingly higher CH₄ contents. He/He (4.73–4.04), where RA is the atmospheric value of 1.39 × 10^{-6} and Ar/Ar ([Ar] ([Ar] = 2906–2763) also decrease with time (Table 2). This is qualitatively consistent with the increased proportion of (methane-rich) reservoir gas in the injected gas as a result of recycling. Ne/Ne and Ne/Ne ratios do not change with time (10.61 and 10.69, and 0.035 and 0.037 respectively) taking experimental uncertainties at the 2σ level into account.

The gases from the production wells typically show an increase in the proportion of injected gas with time. This is apparent as an increase in the proportion of CO₂ in the nine wells that were sampled in both 2009 and 2012 (e.g. from 0.9 to 81.9% CO₂ in well 28F-2). This is mirrored by increases in He/He, Ne/Ne, Ne/Ne, Ne/Ne and Ar/Ar and decreases in Ne/Ne as well as He/He, Ne/Ne and Ar concentrations (Table 2). In all the produced (and injected) bulkline gases, He/He and Ne/Ne ratios are at least five orders of magnitude higher than the atmospheric value ruling out any contamination from the atmosphere during field sampling or gas extraction from the Cu tube. Δ^{13}CO₂ measured in several gas samples (Table 2) is rather constant (~2.5 to ~3‰). When plotted against CO₂ content (Fig. 2) the data are consistent with mixing of injected gas and the in-place reservoir gas with Δ^{13}CO₂ = -10.5% determined previously (Lu et al., 2012b).

5. Discussion

5.1. Noble gas isotope systematics

Neon in natural gases is typically a mixture of three isotopically distinct sources: the crust, the mantle and the atmosphere (Ballentine and O’Nions, 1991). The Ne isotopic composition of CO₂
from the Jackson Dome field is a mixture of mantle-derived Ne with air-derived Ne that has been isotopically fractionated prior to mixing (Zhou et al. 2012). Previous measurements of Jackson Dome gas are plotted on Fig. 3, with a grey dashed line showing the mixing trend. The Ne isotope composition of gases from the injection and production wells from Cranfield define a trend between a point on the Jackson Dome mixing line that is indistinguishable from the measured bulkline gas ($^{20}$Ne/$^{22}$Ne = 10.92; $^{21}$Ne/$^{22}$Ne = 0.037), and a point along a mixing line between air and crustal (radiogenic) Ne that must represent the in-place natural gas (Fig. 3). Following Ballentine et al. (2005), a best-fit line through the data, using the least square method can be used to determine the Ne isotope composition of the natural gas end-member ($^{20}$Ne/$^{22}$Ne = 9.62 ± 0.02 and $^{21}$Ne/$^{22}$Ne = 0.0384 ± 0.001).

Figure 3. The Ne three-isotope plot of gases from the Cranfield EOR site. The data plot as a binary mixture between injected gas, which is similar to the composition of Jackson Dome CO$_2$ (Zhou et al., 2012), and reservoir gas which plots on the air-crust mixing line. The best-fit mixing line (red line) defines the composition of the reservoir gas ($^{20}$Ne/$^{22}$Ne = 9.62 ± 0.02; $^{21}$Ne/$^{22}$Ne = 0.0384 ± 0.001). The red dashed lines represent the 1σ uncertainty of the best-fit line. Black square: bulkline, triangle: injected gas, circle: produced gas, green: 2009, blue: 2012. Grey circles represent Jackson Dome CO$_2$ data from Zhou et al. (2012) and the red (natural gas) and yellow (Jackson Dome) squares represent the end-member Ne isotope compositions. MFL: mass fractionation line. All uncertainties are 1σ. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

![Figure 2](image-url)  
**Figure 2.** Plot of $\delta^{13}$C$_{\text{CO}_2}$ (%) vs. CO$_2$ concentration for production well gases from the Cranfield field. The mixing curve in inset figure is that generated by Lu et al. (2012b) for mixing of a natural gas with 4% CO$_2$ and $\delta^{13}$C = −10.5%, and bulkline composition of 99.3% CO$_2$ and $\delta^{13}$C = −2.6%. 1σ uncertainties are smaller than symbols.
The identification of this end-member allows us to determine the He and Ar isotopic composition of the in-place natural gas by plotting values against \( ^{20}\text{Ne}^{22}\text{Ne} \) (Fig. 4). These values are insensitive to natural variation in the crustal \( ^{21}\text{Ne}^{22}\text{Ne} \). For instance, if we use the highest crustal \( ^{21}\text{Ne}^{22}\text{Ne} \) (0.76) instead of 0.52 (Ballentine, 1997) the \( ^{20}\text{Ne}^{22}\text{Ne} \) of the reservoir gas is 9.68 ± 0.02. This minor shift has no significant impact on the He and Ar isotope composition of the reservoir gas (Fig. 4) and the interpretation of noble gas-CO\(_2\) data (Fig. 5).

Fig. 4A shows the \( ^{3}\text{He}^{4}\text{He} \) ratio of the injected and production well gases plotted against \( ^{20}\text{Ne}^{22}\text{Ne} \) ratios. The data, in particular the production well gases from 2012, define a trend that is...
consistent with a binary mixture of injected gas and the in-
place reservoir gas. Using the Ne isotope composition of the
end-members defined above, the best-fit mixing curve defines the
\(^1\text{He}\)/He of the natural gas of 0.05 ± 0.005\(^\text{R}_\text{N}\). This value is close to the average ratio of continental crust (−0.02\(^\text{R}_\text{N}\), after Andrews, 1985) and is lower than the lowest measured \(^1\text{He}/\text{He}\) of the pro-
duction well gases (28F-2 2009; 0.2\(^\text{R}_\text{N}\)). The hyperbolic nature of the
mixing curve indicates that the \(^1\text{He}/\text{He}\) of the natural gas end-
member is rather poorly defined. The degree of the curvature of the
mixing line is defined by \(^4\text{He}/\text{Ne}_{\text{Jackson Dome}}/\text{He}_{\text{natural gas}}\) (0.488). Combining this value with the measured \(^4\text{He}/\text{Ne}\) of the Jackson Dome gas (12,452; Zhou et al., 2012), the \(^4\text{He}/\text{Ne}_{\text{natural gas}}\) is 25,524. The lowest CO\(_2\) sample has measured
\(^4\text{He}/\text{Ne}_{\text{natural gas}}\) = 28,178 which is consistent with the calculated value.

Using a similar technique, the \(^{40}\text{Ar}/\text{Ar}_{\text{natural gas}}\) of the natural gas end-
member can be obtained (Fig. 4B). Although the Ne–Ar isotope
data is not as coherent as the He–Ne isotope data, the data is also consistent with mixing between the injected gas and reservoir gas. The best-fit line defines the natural gas \(^{40}\text{Ar}/\text{Ar}_{\text{natural gas}}\) of 836 ± 75. This is higher than the atmospheric \(^{40}\text{Ar}/\text{Ar}_{\text{natural gas}}\) (298.6; Mark et al., 2011) and is consistent with the presence of a significant concentration of crust-derived radiogenic \(^{40}\text{Ar}\) in the natural gas. The curvature of the mixing line is defined by \(^{40}\text{Ar}/\text{Ar}_{\text{Jackson Dome}}/\text{Ar}_{\text{natural gas}}\) = 0.2. Combining this value with the measured \(^{36}\text{Ar}/\text{Ar}_{\text{natural gas}}\) of the Jackson Dome gas (8.36), the \(^{36}\text{Ar}/\text{Ar}_{\text{natural gas}}\) is 41.7.

Air-derived noble gases are present to varying extents as a third component that tends to obscure the mixing trend in Ne–Ar isotope space (e.g. well 27-3, Fig. 4B). The \(^{20}\text{Ne}_{\text{natural gas}}\) close to air-saturated water values are suggesting that the atmo-
spheric noble gases likely originate from degassed formation water rather than directly from air. The low concentration of He in air (5.24 × 10^-6 cm\(^3\) (STP)/cm\(^3\)) means that air addition has no significant effect in Fig. 4A. The atmospheric \(^{40}\text{Ar}\) contribution can be removed leaving radiogenic Ar, denoted as \(^{40}\text{Ar}\) (Stuart and Turner, 1992). A plot of \(^{40}\text{Ar}/\text{He}\) vs. \(^{20}\text{Ne}/\text{Ne}\) reveals a coherent trend (Fig. 4C) that yields a \(^{40}\text{Ar}/\text{Ar}\) = 0.09 ± 0.01 for the natural gas end-member.

The He, Ne, and Ar isotope compositions of the in-place gas end-
member are radiogenic, and strongly indicative of a crustal
source with no resolvable mantle-derived volatiles. This is typi-
cal of natural gas accumulations from stable continental cratons (Prinzhofer, 2013). The \(^{40}\text{Ar}/\text{He}\) is significantly lower than pro-
duced in normal continental crust (−0.2; e.g. Torger sen et al., 1989) and likely reflects the preferential release of \(^{4}\text{He}\) from minerals in the reservoir rocks at lower temperature than \(^{40}\text{Ar}\) by diffusion and/or ejection of \(\alpha\)-particles.

5.2. Tracking the fate of injected CO\(_2\)

The coherent relationships between noble gas isotope composi-
tions in the produced gas (Figs. 3 and 4) support the hypothesi-
zed binary mixture between the injected gas and in-place gas. Con-
sequently the naturally occurring noble gases have the potential to
trace the injected CO\(_2\). A plot of the noble gas isotope ratios against the molar proportion of CO\(_2\) in the gas samples helps to elucidate the relationship (Fig. 5).

The helium isotopic composition of the production well gases is plotted against the CO\(_2\) content (Fig. 5A). Theoretical mixing curves are drawn between the 2009 and 2012 injected gases and a natural gas end-member (\(^{3}\text{He}/\text{He}\) = 0.05\(^\text{R}_\text{N}\)). The curvature of the mixing lines are calculated using the measured \(^{4}\text{He}\) concentra-
tion in the injected gas (Table 2) and the natural gas, which
is assumed to be that of the lowest CO\(_2\) sample (28F-2 2009; 3 × 10^-4 cm\(^3\) (STP)/cm\(^3\)). The 2009 and 2012 mixing lines overlap as the evolution of the injected gas mirrors the mixing of in situ and injected gases in the reservoir. With the exception of the five lowest CO\(_2\) concentration 2009 samples, the data plot within the field defined by the mixing curves and are consistent with the pre-
dicted two-component mixing. This demonstrates that He isotopes fingerprint the injected CO\(_2\) and have the potential to be used as a tracer of fugitive emissions of CO\(_2\) from CCS sites where there is significant difference between the helium isotopic composition of the injected and in-place gases.

The \(^{40}\text{Ar}/\text{Ar}_{\text{natural gas}}\) of the production well gases are plotted against CO\(_2\) content in Fig. 5B along with theoretical mixing lines between the 2009 and 2012 injected gas composition with the in-place natural gas. As in Fig. 5A, the mixing curves are defined by data from the injectors and the \(^{40}\text{Ar}/\text{Ar}_{\text{natural gas}}\) (836) determined from the Ar–Ne isotope relationship (Fig. 4B). The concentration of \(^{36}\text{Ar}\) of the reservoir gas is taken from the lowest CO\(_2\) sample (28F-2 2009; 7 × 10^-8 cm\(^3\) (STP)/cm\(^3\)). Few data plot on the mixing line, and the systematic relationship observed for \(^{3}\text{He}/\text{He}\) is not apparent. For instance, the four low CO\(_2\) samples plot above the mixing line, as observed in Fig. 5A. Gas samples from well 27-3 taken in 2009 and 2012 plot significantly below the mixing curve. This may be due to the addition of small amount of air-derived Ar that will tend to lower \(^{40}\text{Ar}/\text{Ar}_{\text{natural gas}}\) ratios but have little effect on CO\(_2\) due to its low concentration in air. In addition, four samples (two from each sampling campaign) have higher \(^{40}\text{Ar}/\text{Ar}_{\text{natural gas}}\) than the injected gases, yet below the value of Jackson Dome CO\(_2\) from the bulkline. This implies that the production wells are tapping gas that was injected earlier than that sampled at the injectors, when the Ar isotope composition of the injected gas was closer to that of Jackson Dome CO\(_2\) as the presence of atmospheric air contamination has been ruled out by the consistently high \(^{3}\text{He}/\text{He}_{\text{natural gas}}\) ratios.

The \(^{40}\text{Ar}/\text{He}\) ratio allows the effect of small contributions of air-derived Ar to be removed (e.g. Stuart and Turner, 1992). The \(^{40}\text{Ar}/\text{He}\) is plotted vs. CO\(_2\) along with theoretical mixing lines between the injected gas and a natural gas end-members in Fig. 5C. The curvature of the mixing line is defined by the concentration of \(^{4}\text{He}\) (see above). The data generally follow the mixing lines to a greater extent than Ar isotopes. As observed previously, the five low CO\(_2\) samples plot above the hypothetical mixing line.

The low CO\(_2\) concentration gases sampled in 2009 are the gen-
el exception to the systematic mixing relationships identified in CO\(_2\) vs. \(^{3}\text{He}/\text{He}\) and \(^{40}\text{Ar}/\text{He}\) (Fig. 5). In all cases, including the CO\(_2\) vs. \(^{40}\text{Ar}/\text{Ar}_{\text{natural gas}}\) plot, the data plot significantly above the mixing lines. The internal consistency of the noble gas isotope data (Fig. 4) implies that this is unlikely to be the result of the addi-
tion of another noble gas component. The simplest and most likely explanation is that it reflects the loss of CO\(_2\) from the gas phase during the early phase of CO\(_2\) injection. The proportion of CO\(_2\) that has been lost can be quantified using the measured \(^{3}\text{He}/\text{He}\) and \(^{40}\text{Ar}/\text{He}\) ratios. The distance on the ordinate between the data point and the mixing curve in Fig. 5 represents the absolute change in CO\(_2\) concentration. The proportion lost (%) is calculated by nor-
malising to the predicted CO\(_2\) content. For instance, gas from well 28F-2 2009 has 0.8% CO\(_2\) and \(^{3}\text{He}/\text{He}\) of 0.21\(^\text{R}_\text{N}\). The 2009 mixing curve for that \(^{3}\text{He}/\text{He}\) predicts 11.8% CO\(_2\), equating to a loss of 93%. The predicted CO\(_2\) concentrations and the lost proportion have been calculated using \(^{3}\text{He}/\text{He}\) and \(^{40}\text{Ar}/\text{He}\) ratios (Table 3 and Fig. 6).

The \(^{3}\text{He}/\text{He}\) data require the loss of between 28% (27-5 2009) and 93% (28F-2 2009) of the injected CO\(_2\) from the gas phase. From the \(^{40}\text{Ar}/\text{He}\) this range is 22–96%. The degree of CO\(_2\) loss from each sample calculated from the two tracers appears to be broadly consistent (Fig. 6). Uncertainties have been propagated by taking into account the uncertainty of CO\(_2\) concentration and noble gas isotopic ratios of each sample, and the mixing curve uncertainty which originates from the uncertainty of the end-member composi-
tions. It should be noted that any process that causes CO\(_2\) loss
may fractionate the $^{40}\text{Ar}^{3}/^{4}\text{He}$ ratio of the residual gas. We do not take into account here as it is likely negligible compared to the changes in CO$_2$ concentration.

Whilst the mechanism by which CO$_2$ has been sequestered (e.g. dissolution into the formation water, precipitation as carbonate, residual trapping) is not the aim of this study, the data provide a clear indication that the naturally-occurring noble gases have the potential to track the fate of injected CO$_2$ in future CCS trials. Further work will examine this topic in detail but is outside the scope of the current work.

6. Conclusions

The unique noble gas isotope composition of the Jackson Dome CO$_2$ injected in the Cranfield CO$_2$-EOR field permits evaluation of the effectiveness of using He, Ne and Ar isotopes to trace injected CO$_2$. The isotopic compositions of production well gases sampled in 2009 and 2012, 19 and 45 months after the start of CO$_2$ injection define binary mixtures between injected gas and the in-place reservoir gas. This allows the noble gas isotopic composition of the reservoir gas to be determined. $^{3}\text{He}^{4}/^{4}\text{He}$ and $^{40}\text{Ar}^{3}/^{4}\text{He}$ of produced gas samples plot on theoretical mixing lines with CO$_2$ content indicating that the noble gas isotopes track the presence of the injected CO$_2$. The five samples with the lowest proportion of CO$_2$ sampled in 2009 plot consistently above the theoretical mixing lines. This requires the loss of 22–96% of the injected CO$_2$ from the gas phase, and suggests that the noble gas isotopes have potential to quantify the storage of CO$_2$ in CCS sites. The total amount of sequestered CO$_2$ and the sequestration mechanism is currently unresolved but is the focus of ongoing work.

Acknowledgements

We thank Denbury Resources Inc. for permission to sample and providing assistance in the field and Susan Hovorka for assistance in obtaining this permission. We thank Jiemin Lu for providing useful detailed background information on the field. The work was funded by EPSRC, grant number EP/K036003/1. Thanks to Terry Donnelly and Luigia Di Nicola for invaluable help in the laboratories. We thank Chris Ballentine and an anonymous reviewer for helpful and constructive reviews which have greatly improved the manuscript.

References


