

Noble gas tracers in gas streams at Norwegian CO₂ capture plants

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ABSTRACT

Carbon capture and storage (CCS) may play a significant role in reducing greenhouse gas emissions. Noble gases are potential tracers to monitor subsurface CO₂ storage sites and verify their containment. Naturally occurring noble gases have been used successfully to refute alleged CO₂ leakage in the past.

We present results from several sampling campaigns at two Norwegian CO₂ capture facilities, the demonstration plant Technology Centre Mongstad (TCM) and the natural gas processing plant with CO₂ capture and storage on Melkøya. The gas streams in the capture plants were monitored with a combination of on-site mass spectrometry and subsequently analysed discrete samples. This allows us to define the factors controlling noble gas concentrations in captured CO₂, to monitor temporal variation of noble gas concentrations and finally evaluate the potential to use noble gases as inherent environmental tracers for labelling CO₂ in storage reservoirs.

At both sites, CO₂ is captured using amine gas treatment. Noble gas concentrations in the gas streams were observed to decrease by several orders of magnitude during the processing. Isotopic ratios are air-like for CO₂ captured after natural gas combustion at TCM and natural gas-like for CO₂ captured from natural gas processing on Melkøya. Further, we detected a solubility trend caused by the amine solvent at TCM with higher solubility for heavier noble gases.

We find that the relative concentrations of noble gases in the captured CO₂ are defined by the gas from which the CO₂ is captured and the design of the amine gas treatment process. Both factors were observed to cause temporal variation in the captured CO₂.

Using mixing and noble gas partitioning calculations we show that the significant depletion in noble gas concentrations, together with degassing of noble gas enriched formation water, means that the injected CO₂ will inherit the noble gas signature of the storage formation, even following the injection of significant CO₂ volumes. Any CO₂ leaked from the storage formation is thus likely to have a crustal noble gas signature, characteristic of the storage site, which can be targeted for monitoring.

1. Introduction

Rise of atmospheric CO₂ levels is causing significant climate change (IPCC, 2014) and nearly all countries have signed the Paris Agreement with the aim to keep global warming 'well below 2 °C' (United Nations, 2015). Carbon capture and storage (CCS) may become an important climate change mitigation technology needed to achieve the 2 °C goal (IPCC, 2014; Metz et al., 2005; van Vuuren et al., 2011; Rogelj et al.,

2018).

Large scale application of CCS requires compliance with environmental regulations and to support public acceptance sophisticated monitoring has to be in place (IEAGHG, 2015; Kheshgi et al., 2012). Even though, leakage likelihood of storage sites is estimated to be very low (Alcalde et al., 2018).

There is a manifold of geophysical (e.g. time lapse seismics) and geochemical (e.g. pH) monitoring tools available to detect CO₂ and

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verify containment in geological storage formations (IEAGHG, 2015). Commonly used set ups are, however, not necessarily sufficient to differentiate the gas origin of an observed anomaly. Evaluation of the noble gas signatures, concentrations and isotopic ratios in injected, anthropogenic CO₂ can allow differentiation from natural, geological and biologically produced, CO₂ (Holland and Gilfillan, 2012; Flude et al., 2016; Mackintosh and Ballentine, 2012; Shelton et al., 2016; Györe et al., 2015). This was demonstrated successfully at an alleged leakage case at the Weyburn-Midale CO₂ injection project (Gilfillan et al., 2017). Further, noble gases are chemically inert, hence, in contrast to CO₂ and other tracers, environmentally safe and not subject to chemical and biological processes (Holland and Gilfillan, 2012). Noble gases are widely applied as environmental tracers: inherent and naturally occurring in all terrestrial fluids (Burnard, 2013), and may therefore be a very cost-effective monitoring tracer (Roberts et al., 2017).

A baseline dataset for inherent, naturally occurring (not artificially added), noble gases in captured CO₂ from several sites was established in Flude et al., 2017. Generally, noble gas concentrations were found to decrease during the CO₂ absorption process at several capture plants. In the ICO₂P project (ICO₂P, 2020), we focus on establishing such a dataset for the CCS projects in Norway (Fig. 1). Further, we aim to contribute to the full-scale CCS project initiated by the Norwegian state and industry that combines onshore capture operations such as a cement plant with offshore storage in the North Sea (Fig. 1), aimed to be operating in 2024 (CCS Project, 2020; Norwegian Petroleum Directorate, 2016; Global CCS Institute, 2018).

From previous studies, it is not evident that noble gases in a single sample from CO₂ capture streams are representative of the overall noble gas signature, due to potential temporal variation. Therefore, we apply a novel sampling strategy in this study, monitoring gas streams on-site using a mobile mass spectrometer (Brennwald et al., 2016), combining time series of in-line sampling, with discrete gas sample analysis using a

lab-based mass spectrometer with higher analytical precision.

We observe temporal variation in the CO₂-rich fluxes and aim to determine the parameters controlling noble gas concentrations and the inherent variation. Finally, we discuss the implications of our sampling approach on monitoring CO₂ injection streams and put the identified noble gas signatures into perspective for future usage in leakage detection or in verification of storage containment.

2. Material and methods

2.1. CO₂ capture – amine gas treatment

Amine gas treatment is currently the most mature CO₂ capture technology (Rochelle, 2009; Leung et al., 2014) and is used at both study sites. In this process, CO₂ in the incoming flue gas, e.g. the exhaust from a power plant, reacts with an aqueous amine solvent in the absorber (e.g. (Rao and Rubin, 2002); Fig. 2). The CO₂-rich amine solution is transferred to the stripper where it is heated, releasing the CO₂ as gas with a concentration of up to 99% in the final gas mixture (Rao and Rubin, 2002; Dutcher et al., 2015). The heat required in the regeneration step poses an energy and cost penalty for a capture plant. The CO₂ depleted amine solvent is brought back to the absorber to close the cycle. With amine absorption a capture efficiency of 75–90% of the CO₂ in the flue gas is achieved (Rao and Rubin, 2002).

In the following, the sampling point before the absorber is referred to as ‘Input’. The sampling point after the stripper is referred to as ‘Output’ (Fig. 2).

Noble gases do not react with the aqueous amine solvent, but physically dissolve to reach equilibrium between the dissolved and the gas phase. Phase partitioning at equilibrium can be described by Henry’s law, which in its simplest form states that the dissolved concentration depends on the partial pressure of a gas species and its specific,

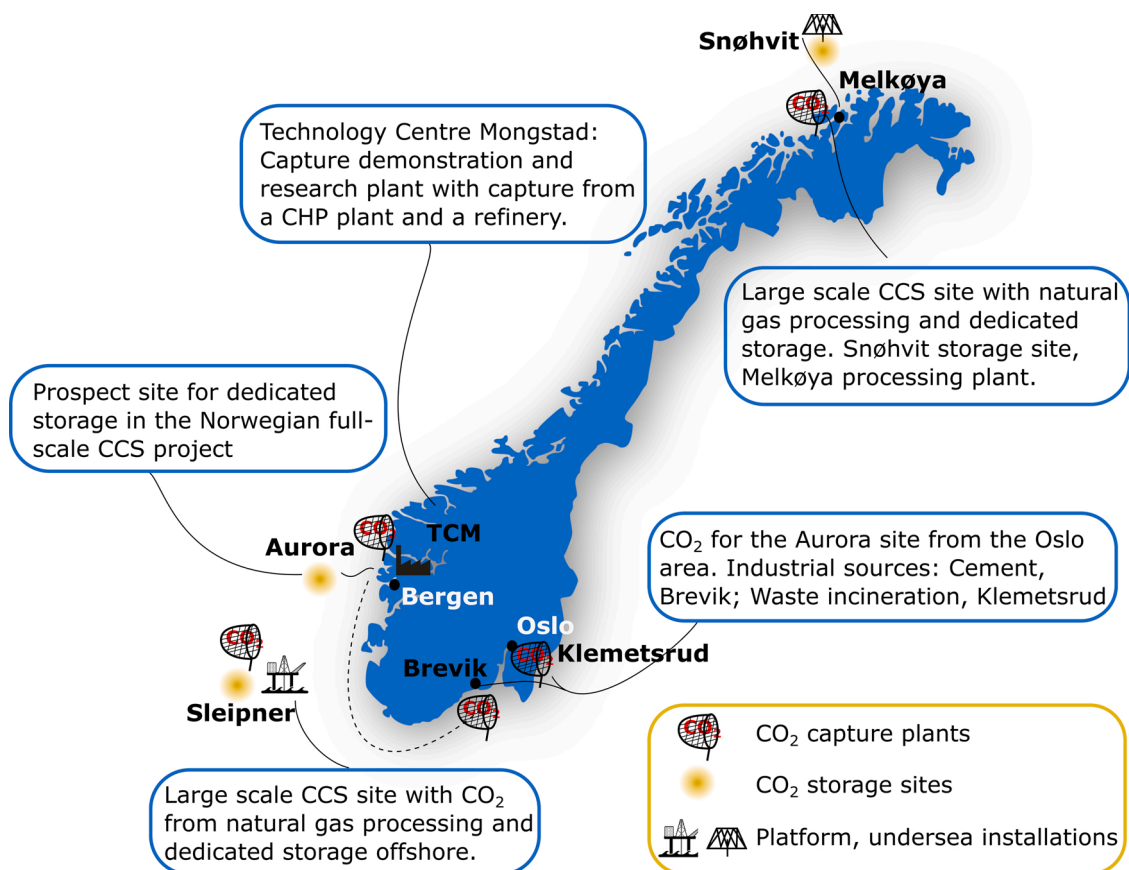


Fig. 1. CCS in Norway. For this study, sampling was conducted onshore at the Technology Centre Mongstad (TCM) and at Melkøya.

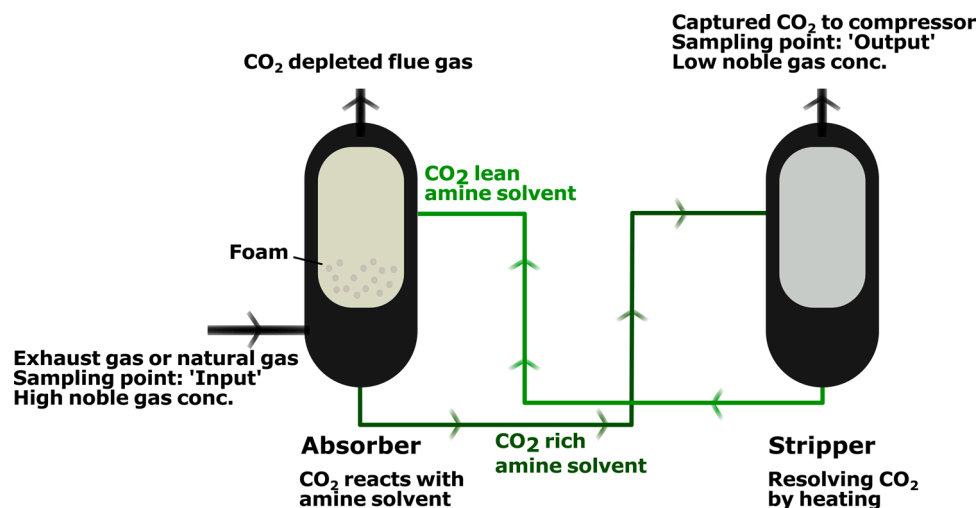


Fig. 2. Sketch of the amine capture process with the 'Input' and 'Output' sampling points labelled. CO₂ is captured by amine gas treatment in the absorber and released again in the stripper. After the process, the captured CO₂ will be compressed for transport.

temperature-dependent solubility for the respective solvent (Henry's constant).

Foam can develop in the absorber due to gas bubbles stabilizing on surfactants or contaminants in the amine solvent (Thitakamol and Veawab, 2008). Bubble-mediated physical gas exchange might then introduce additional gases into the amine solution. A foam-inhibitor chemical can be added to prevent foam formation.

2.2. Study sites

2.2.1. Melkøya

Melkøya (Equinor, 2020a), with its respective storage site Snøhvit, is after Sleipner (Equinor, 2020b) (Fig. 1), the second Norwegian commercial large-scale CCS site. It is located close to Hammerfest and was established in 2007 (Hansen et al., 2013).

The natural gas from the Snøhvit Field naturally contains 5–8% CO₂. The CO₂ is removed from the natural gas onshore at Melkøya before the gas is combusted. A solvent based on activated Methyldiethanolamine (aMDEA) is used for the amine gas treatment process. The facility runs with an approximate capture capacity of 0.7 MtCO₂/a (Hansen et al., 2013), and 6.48 Mt have been injected by the end of 2019. In comparison, annual CO₂ emissions from the Norwegian oil and gas sector are approximately 15 Mt (Statistics Norway, 2019). The natural gas is then shipped to energy markets as liquified natural gas (LNG), meanwhile the captured CO₂ is injected into the Stø Formation at >2000 m depth in the vicinity of the Snøhvit Field (Halland et al., 2013).

2.2.2. Technology Centre Mongstad

The CO₂ capture demonstration plant Technology Centre Mongstad (TCM) (TCM DA, 2020) is located north of Bergen (Fig. 1) and is one of the world's largest research facilities for non-proprietary testing of CO₂ absorption using amine gas treatment, mainly using monoethanolamine (MEA) as solvent (Faramarzi et al., 2017; Morken et al., 2017).

CO₂ is captured either from (i) the exhaust stream of a combined heat and power plant (CHP), which combusts natural gas and refinery fuel gas (RFG) from the nearby Mongstad refinery, or (ii) the residue fluid catalytic cracking (RFCC) flue gas of the Mongstad refinery processing oil and gas from the North Sea.

Combustion at the CHP plant introduces air into the gas stream and this part of the CO₂ captured at TCM is an example for a post-combustion capture plant (Leung et al., 2014). For CHP flue gas, the CO₂ content is at 3.5–4%. In the case of RFCC flue gas, the gas is not combusted before capture but air is mixed in to keep the CO₂ concentration at constant levels during capture tests (Shah et al., 2018). CO₂ concentrations are

12–15% and this flue gas source is considered equivalent to flue gas from coal power plants (Shah et al., 2018).

TCM has a total capturing capacity of 0.1 MtCO₂/a (TCM DA, 2020). During an expansion of the Norwegian CCS project, an inclusion of CO₂ captured at TCM could be a valid proposition.

2.3. Methods

2.3.1. Noble gas analysis in discrete gas samples

Discrete samples were collected in stainless steel cylinders (Swagelok, volume: 40 cm³) complementary to the continuous measurements. The cylinders were connected to the sampling lines, flushed for several minutes to avoid air contamination and closed with stainless steel needle valves.

The discrete samples were analysed at the noble gas laboratory at ETH Zurich, Switzerland (Beyerle et al., 2000). Here, noble gas analysis by static mass spectrometry reaches a typical overall error of ±1% for concentrations, ≤1% for isotopic ratios and has low detection limits due to gas purification steps (Beyerle et al., 2000).

A set of gas samples were sampled on 31.08.2018 at Melkøya. At TCM, several samples were collected accompanying the continuous measurements.

2.3.2. Continuous noble gas analysis

Noble gas partial pressures were measured continuously on-site at the Input and Output sampling points at TCM using the portable mass spectrometer 'miniRuedi' (Gasometrix GmbH, Switzerland; Fig. 3 top). Technical details of the mass spectrometer can be found in Brennwald et al. (2016). It was formerly mainly used in aquatic science but also applied for the monitoring of trial runs for radioactive waste disposal (Weber et al., 2019; Tomonaga et al., 2019).

The instrument measures ion currents on selected m/z-ratios with a Faraday detector and an electron multiplier. Partial pressures are derived from peak-height comparison with a calibration gas.

Typically, the m/z-ratios for N₂, O₂ and CO₂ were measured on the Faraday detector, ⁴⁰Ar on Faraday detector and multiplier and ⁴He, CH₄ and ⁸⁴Kr on the multiplier. With that set-up, a sampling point was measured approximately every 15 minutes and a calibration was conducted approximately every hour. From 02.10.-05.10.2018 only CO₂, CH₄, ⁴⁰Ar and ⁴He were measured to increase sampling frequency to approximately 10 min.

During the first measurement period, 11.07.-25.07.2018, air was used as calibration gas. A tailored calibration gas mixture (made on order by Praxair Inc.) was prepared for the second measurement period,

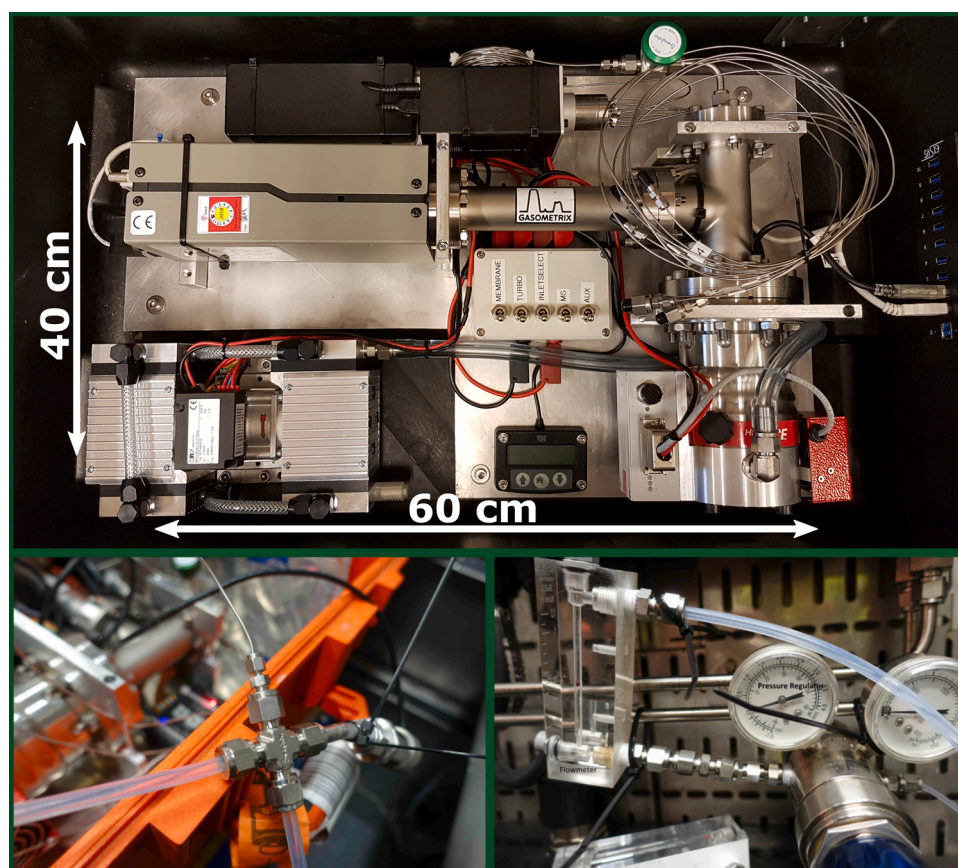


Fig. 3. Top: The portable mass spectrometer 'miniRuedi'. Bottom, left: Inlet to the mass spectrometer (cross connection): Flow-by gas stream and inlet to mass spectrometer and monitoring pressure sensor. Bottom, right: Setup before the inlet to the mass spectrometer: Flow-meter (left) and pressure regulator (right).

25.09.-05.10.2018. It consisted of 10 ppm of each noble gas (He, Ne, Ar, Kr, Xe), 1% CH₄ and 99% CO₂ to mimic the high CO₂ content of the captured CO₂. The calibration gases were filled into a Plastigas®-bag during the experiments. Basic stainless steel connections were used for the attachment to the sampling points (Fig. 3, bottom left). Pressure regulators were installed before the inlet to the mass spectrometer in order to sample the gas at the same pressure as the standard gas, i.e. atmospheric pressure (Fig. 3, bottom right).

In 2017, we conducted a feasibility study at TCM to investigate the applicability of a portable mass spectrometer on site for continuous analysis (Sundal et al., 2018). Two additional time series were subsequently collected in summer and fall 2018, specifically from 11.07.-25.07.2018 and 25.09.-05.10.2018.

3. Results

3.1. Discrete samples

The noble gas concentrations and isotopic ratios of the discrete samples (In- and Output (see Fig. 1)) both from TCM and Melkøya are shown in Table 1. Isotopic ratios are given in Table 2. The results from Melkøya provide, to our knowledge, the first dataset for noble gases of a large scale natural gas processing site.

3.2. Continuous noble gas time series

3.2.1. Helium

The first time series (11.07.-25.07.2018) recorded with the on-site mass spectrometer at TCM shows He concentrations to vary considerably at the Input ($\pm 30\%$) (Fig. 4[a]). Due to low concentrations, detection limit ≈ 0.45 ppm, it was not possible to measure the He at the

Output sampling point with on-site mass spectrometry.

The variation appears to be linked to the percentage of refinery fuel gas (RFG) added to natural gas combustion at the CHP plant (Fig. 4[b]). The RFG share was typically slightly above 50%, but shares as low as 20% were also applied. With high content of RFG, the He concentration is low and vice versa. The two time series correlate with $\rho \approx 0.8$ (Pearson correlation coefficient).

During the second monitoring period (25.09.-05.10.2018), first a CHP-derived flue gas and then only residue fluid catalytic cracking (RFCC) flue gas was analysed (see Fig. 5). The change of input gas is again observed in He concentrations which are lowered by $\approx 40\%$ (Fig. 5).

The capture plant had to be shut down for a two day period in order to change the set-up to run in high CO₂ inlet concentration mode; from $\approx 4\%$ to $\approx 12\%$. Technical changes in the plant were conducted in a second, shorter period. This caused the CO₂ stream to be interrupted and air-contaminated, which was also observed by low CO₂ partial pressures measured by the miniRuedi. Those periods are not shown in Fig. 5. Measurements of discrete samples agree with the in-line measurements and are depicted in Fig. 5.

3.2.2. Argon

In the captured CO₂ stream at TCM, only Ar was detectable with continuous measurements. Simultaneous calibration of Input and Output did not succeed since only air was available as calibration gas during this monitoring period (11.07.-25.07.2018). In air, Ar was measured on the Faraday detector and in saturation on the multiplier, meanwhile the Output had to be measured on the multiplier due to its significantly lower concentrations after absorption. Therefore, the Output values on $m/z = 40$ are depicted in the ion current, given in ampere, measured with the multiplier detector. The current has then

Table 1

Noble gas concentrations given in $\text{cm}^3_{\text{STP}}/\text{cm}^3_{\text{STP}}$, with $p_{\text{STP}}=1 \text{ atm}$ and $T_{\text{STP}}=0^\circ\text{C}$ (total concentrations, if not other stated). Atmospheric values from Sano et al. (2012). Uncertainties are one standard deviation.

#	Sample point	Source	Sample date	He	Ne	Ar	Kr	Xe	Lab Name
		Atmosphere		5.24E−06	1.82E−05	9.34E−03 ³⁶ Ar: 3.13E−05	1.14E−06	9.0E−08	
<i>Technology Centre Mongstad (TCM)</i>									
1	Input	CHP	12.07.2018	9.15E−06 ± 7.55E−08	1.88E−05 ± 9.38E−08	³⁶ Ar: 2.90E−05 ± 4.51E−08	1.17E−06 ± 5.83E−09	8.13E−08 ± 1.36E−09	TCM 2005
2	Output	CHP	12.07.2018	3.27E−09 ± 1.77E−10	4.37E−09 ± 1.96E−10	3.66E−06 ± 2.13E−08	7.32E−10 ± 1.59E−11	1.22E−10 ± 1.06E−11	TCM 2001
3	Input	CHP	25.07.2018	8.36E−06 ± 6.91E−08	1.82E−05 ± 9.14E−08	³⁶ Ar: 2.82E−05 ± 3.48E−08	1.14E−06 ± 5.02E−09	8.82E−08 ± 1.41E−09	TCM 2006
4	Input	CHP	26.09.2018	9.68E−06 ± 7.99E−08	2.05E−05 ± 1.03E−07	1.03E−02 ± 4.71E−05	1.24E−06 ± 8.28E−09	9.43E−09 ± 4.32E−10	TCM 2011
5	Input	RFCC	02.10.2018	5.57E−06 ± 4.60E−08	1.96E−05 ± 9.78E−08	9.96E−03 ± 4.56E−05	1.22E−06 ± 5.69E−09	8.93E−08 ± 1.59E−09	TCM 2013
6	Output	RFCC	02.10.2018	1.68E−09 ± 5.08E−10	4.30E−09 ± 2.67E−10	4.78E−06 ± 3.02E−08	1.00E−09 ± 2.22E−11	1.84E−10 ± 1.68E−11	TCM 2014
7	Input	RFCC	05.10.2018	5.55E−06 ± 4.58E−08	1.92E−05 ± 9.63E−08	1.65E−03 ± 1.17E−05	1.98E−07 ± 9.21E−10	1.55E−08 ± 2.66E−10	TCM 2016
<i>Melkøya: Natural gas processing</i>									
8	Untreated gas	Nat. gas	31.08.2018	1.22E−04 ± 1.01E−06	6.39E−08 ± 5.23E−09	5.66E−05 ± 3.14E−07	9.43E−09 ± 4.32E−10	2.00E−09 ± 1.89E−10	HAMM 2007
9	Input	Nat. gas	31.08.2018	1.29E−04 ± 1.06E−06	5.73E−09 ± 1.16E−09	1.75E−05 ± 8.62E−08	1.57E−09 ± 8.85E−11	5.26E−10 ± 5.86E−11	HAMM 2008
10	Output	Nat. gas	31.08.2018	2.86E−06 ± 2.36E−08	1.75E−09 ± 3.05E−10	1.01E−06 ± 1.05E−08	5.29E−11 ± 1.19E−11	3.73E−11 ± 7.52E−11	HAMM 2009
11	During compr.	Nat. gas	31.08.2018	2.64E−06 ± 2.18E−08	1.01E−08 ± 5.55E−10	3.23E−06 ± 3.69E−08	6.36E−11 ± 1.31E−11	3.96E−11 ± 2.33E−11	HAMM 2010

Table 2

Isotopic ratios for the samples as described in Table 1. Atmospheric values from (Sano et al., 2012). The $^3\text{He}/^4\text{He}$ -ratios are also reported in the Ra-notation where Ra is the $^3\text{He}/^4\text{He}$ -ratio of atmospheric air (i.e. $1.39\text{E}-06$; see e.g. Sano et al., 2012). Uncertainties are one standard deviation. Undetectable ratios with the system described in Beyerle et al. (2000) are noted with n.d., those not measured with –.

#	$^3\text{He}/^4\text{He}$	$^3\text{He}/^4\text{He}$ ([Ra])	$^{22}\text{Ne}/^{20}\text{Ne}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{86}\text{Kr}/^{84}\text{Kr}$	$^{136}\text{Xe}/^{129}\text{Xe}$	$^{136}\text{Xe}/^{134}\text{Xe}$
Atmosphere	$1.34\text{E}-06$	1.000	0.1022	296	0.303	0.335	0.849
<i>Technology Centre Mongstad (TCM)</i>							
1	$8.55\text{E}-07 \pm 5.15\text{E}-09$	0.638 ± 0.006	0.1023 ± 0.0001	–	0.306 ± 0.001	0.345 ± 0.004	0.888 ± 0.012
2	$9.35\text{E}-07 \pm 1.24\text{E}-07$	0.698 ± 0.092	0.0701 ± 0.0241	364 ± 73	0.312 ± 0.006	0.358 ± 0.015	0.922 ± 0.052
3	$9.20\text{E}-07 \pm 7.98\text{E}-09$	0.687 ± 0.006	0.1021 ± 0.0001	–	0.306 ± 0.001	0.343 ± 0.003	0.878 ± 0.005
4	$9.28\text{E}-07 \pm 5.72\text{E}-09$	0.692 ± 0.004	0.1020 ± 0.0001	320 ± 24	0.304 ± 0.001	0.326 ± 0.002	0.864 ± 0.013
5	$1.23\text{E}-06 \pm 1.27\text{E}-08$	0.919 ± 0.010	0.1020 ± 0.0001	321 ± 24	0.307 ± 0.001	0.323 ± 0.002	0.832 ± 0.007
6	$2.37\text{E}-06 \pm 2.35\text{E}-07$	1.765 ± 0.175	0.2459 ± 0.0298	371 ± 51	0.303 ± 0.006	0.318 ± 0.009	0.875 ± 0.039
7	$1.34\text{E}-06 \pm 8.80\text{E}-09$	1.002 ± 0.007	0.1020 ± 0.0001	324 ± 24	0.306 ± 0.001	0.338 ± 0.003	0.871 ± 0.009
<i>Melkøya: Natural gas processing</i>							
8	$2.45\text{E}-08 \pm 1.01\text{E}-09$	0.018 ± 0.001	0.1125 ± 0.0368	636 ± 244	0.303 ± 0.011	0.319 ± 0.009	0.719 ± 0.039
9	$2.51\text{E}-08 \pm 1.22\text{E}-09$	0.019 ± 0.001	0.3667 ± 0.0952	n.d.	0.313 ± 0.015	0.303 ± 0.016	0.712 ± 0.043
10	$2.84\text{E}-08 \pm 1.58\text{E}-09$	0.021 ± 0.001	0.1823 ± 0.0727	n.d.	0.224 ± 0.013	0.338 ± 0.020	0.834 ± 0.035
11	$2.64\text{E}-08 \pm 1.58\text{E}-09$	0.020 ± 0.001	0.0669 ± 0.0942	n.d.	0.270 ± 0.011	0.293 ± 0.019	0.786 ± 0.062

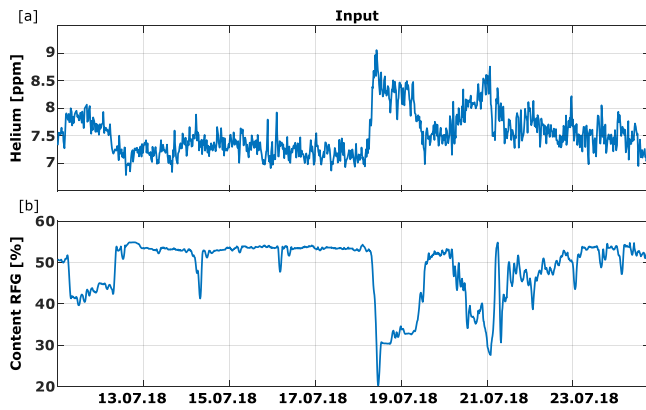


Fig. 4. [a] Time series of He concentration of the Input at TCM from 11.07.-25.07.2018 in [ppm]. Typical measurement precision: 2.5%. [b] Time series of relative content of RFG in the gas mixture combusted at the CHP plant in [%]. A strong negative correlation between the concentration and the relative share of RFG gas is observed.

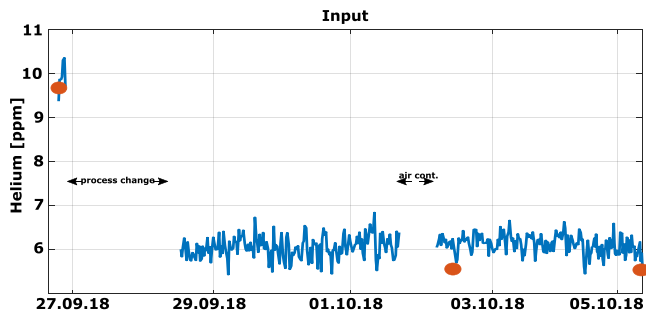


Fig. 5. Time series of He concentration of the Input at TCM from 26.09.-05.10.2018 in [ppm]. Typical measurement error: 3%. Two periods where the plant did undergo technical changes. First period is when the switch from CHP's exhaust to only RFCC gas was conducted. Orange dots are the data from the discrete samples (Table 1).

been corrected with the standard measurements on $m/z = 4$, since this mass-charge ratio is also measured on the multiplier.

Even though the values are not calibrated, the observations made are worth mentioning. During the time period, Input Ar intensities do not show significant variation (Fig. 6[a]). These Ar concentration can be used to infer the missing ^{40}Ar values in Table 1. In contrast to the Input, there

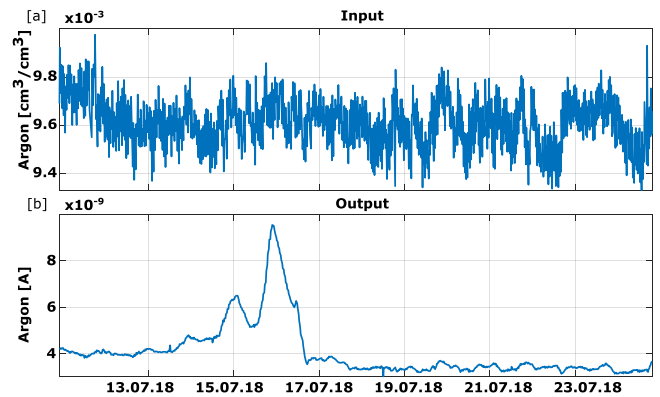


Fig. 6. Time series of Ar [a] of the Input [cm^3/cm^3] and [b] the Output on $m/z = 40$ in ampere [A] at TCM during 11.07.-25.07.2018. Typical measurement precision: 2.5%. Temporal variation in the Output seems unrelated to the Input.

is an increase in Output Ar intensities (Fig. 6[b]). The temporal variation during 15.07.2018 and 16.07.2018 in the Output gas shows no relation to the Ar concentration of the Input. Further, none of the parameters monitored in the plant such as pressure, solvent temperature or gas release temperature in the stripper correlate to the temporal variation of Ar.

4. Discussion

4.1. Effect of the flue gas

A significant control on the noble gas concentrations in the captured CO_2 is the source of the flue gas, synonymous to the Input sampling point in this study, from which CO_2 is captured. The samples from the post-combustion and RFCC (TCM) and the natural gas processing (Melkøya) plant show significantly different noble gas concentrations both at the Input (Fig. 7[a]) and at the Output sampling points (Fig. 7 [b]).

In the Input to the absorber at Melkøya, concentrations differ strongly from atmospheric values, i.e. He is enriched whereas the other noble gases are strongly depleted (Fig. 7[a]). This is common for natural gas which is enriched in radiogenic ^4He from the reservoir rock (Prinzhofer, 2013). Isotopic ratios representing the natural gas source, note the low $^3\text{He}/^4\text{He}$, are mostly conserved during gas processing and CO_2 absorption (Table 2). Captured CO_2 from Melkøya contains significantly higher He concentrations than previously observed at other

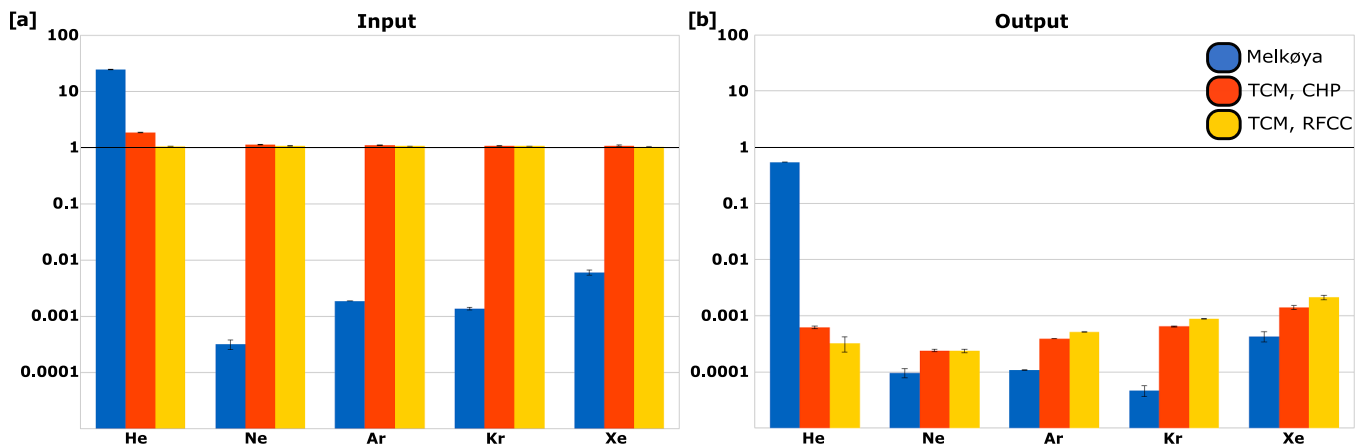


Fig. 7. Observed noble gas concentrations relative to their atmospheric concentrations showing almost atmospheric values for TCM Input samples #4 CHP and #5 RFCC and a natural gas signature for Melkøya, sample #9. After the capture process noble gas concentrations are orders of magnitude lower than in air. Output samples #2 CHP, #9 RFCC for TCM and #14 for Melkøya (Table 1). Uncertainties one standard deviation.

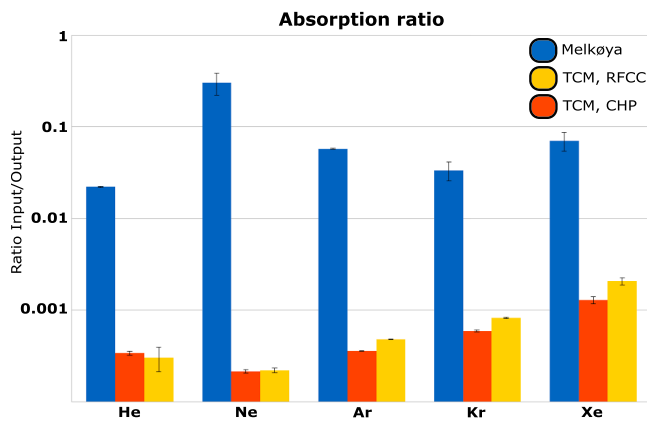


Fig. 8. Absorption ratios TCM and Melkøya. Calculated from the samples in Fig. 7. Uncertainties one standard deviation.

capture facilities (Gilfillan et al., 2017; Flude et al., 2017).

In the Input at TCM, noble gas concentrations are at or near atmospheric levels as depicted in Fig. 7[a]. This is a clear indication that combustion has introduced atmospheric noble gases, since air is used as oxygen supply for the CHP flue gas. The signature of the RFCC flue gas is derived from the air mixed in to stabilize CO₂ concentrations. He contents are high in source gas, and can still be significantly enriched relative to atmospheric equilibrium before capture, indicating the fossil origin (He enrichment) of the natural gas prior to combustion. The changing He content leads to slightly varying ³He/⁴He ratios at different dates. Flue gas from post-combustion sources, including waste incineration or bio-energy combustion, will have a signature close to air, especially when a radiogenic component from fossil fuels is not present.

Table 3

Henry's law constants ratio for water relative to Xe at 298.15 K from (Sander, 1999) and measured values from samples #5 and #6 at TCM with RFCC as source (Table 1). Uncertainties are one standard deviation.

gas species i	He	Ne	Ar	Kr	Xe
$k_{H,Xe}/k_{H,i,water}$	11.3	9.56	3.07	1.79	1
at TCM	6.8 ± 2.2	9.4 ± 1.2	4.3 ± 0.4	2.5 ± 0.3	1

4.2. Temporal variation in flue gas

The results from TCM show that the flue gas stream from which the CO₂ is captured can have temporal variation in noble gas concentrations. He concentrations at In- and Output correlate to the gas mixture that is combusted and subsequently fed to the absorber (Figs. 4 and 5).

The analysed discrete samples collected from the Output confirm that the variation in the Input shown in Fig. 5 is also present after the absorption process; i.e. Output samples #2 and #6 (Table 1) show a decrease of $50 \pm 15\%$ in the He concentrations. Concentrations for Kr (increase of $\approx 40 \pm 5\%$) and Xe of the two samples also change in the Output (increase of $\approx 50 \pm 20\%$).

4.3. Effect of the absorption process

A comparison between different absorption processes of carbon capture plants is difficult since many parameters of the process design, e.g. the absorber column and stripper internals, the liquid withdrawal configuration and the operating pressure regimes, are specific to each site. Their influences on the solubility and absorption of noble gases are briefly discussed below. A quantification of the impact of single parameters on the noble gas concentration in captured CO₂ is, however, beyond the scope of this study.

4.3.1. Absorption ratios

The data reflect that there are significant differences in the capture process at the two study sites. Absorption ratios of noble gases in the amine solvent are determined by dividing Output by Input concentrations (Fig. 8).

At Melkøya, noble gases are absorbed more efficiently, by two orders of magnitude, than at TCM, since the absorption ratio is higher. The remarkably different absorption ratios could be caused by the differences in the operating pressure, i.e. approximately 66 bar at Melkøya and 1.02 bar at TCM, and overall plant design. Further, CO₂ mass transfer was shown to be proportional with solvent temperature and circulation rates, which could also hold true for noble gases (Dey and Aroonwilas, 2009), and provide a site specific imprint on the chemical and isotopic signature.

It has been shown for N₂O that solubility is varying systematically in a suit of amine solvents in Penttilä et al., 2011. This will also hold true for noble gases in this case (MEA at TCM and aMDEA at Melkøya). Further, the addition of foam-inhibitor chemical might affect the solubility of gases in the solvent by reducing surface tension (Uhlig, 1937).

Foam development and subsequent gas entrainment is a severe

operational problem in the capture process (Thitakamol and Veawab, 2008) and may add quantitatively to the physical absorption process. Foam development was reported by the local operators to occur at Melkøya, causing introduction of CH_4 from the natural gas during foaming into the produced CO_2 without having received more detailed information. Consequently, noble gases would also be introduced increasingly in this way, explaining the observed differential absorption ratios at Melkøya.

4.3.2. Solubility trend

At TCM, the absorption ratios show a clear solubility trend towards heavier noble gases, i.e. for Xe the absorption ratio is about one order of magnitude higher than for e.g. Ne and, hence, relatively more Xe is found in the captured CO_2 stream (Fig. 8). The trend roughly follows the Henry's law constants ratios for water $k_{H,\text{Xe}}/k_{H,\text{He}}$, since the solvents are aqueous solutions, e.g. 30 wt% MEA in water, (Table 3; Henry's law constants at 298.15 K; values from Sander (1999)). For TCM, a simple form of Henry's law seems to describe the capture process reasonably well.

Henry coefficients for noble gases in water seem to be a valid approximation for the relative solubility of noble gases. However, absolute Henry's law solubility constants for noble gases vary significantly from water. Determining the absolute solubilities based on our measurements or from literature could only be a rough estimation since it is not ensured that full equilibrium is reached and because the composition of the solvent is not properly known, due to proprietary reasons. An ideal mixing rule for solubilities in such aqueous solutions has been shown to be hardly applicable for N_2O (Kierzkowska-Pawlak and Zarzycki, 2002). The ' N_2O analogy' for modelling the capture process of CO_2 lacks empirical basis to be universally applied (Monteiro and Svendsen, 2015; Kierzkowska-Pawlak and Zarzycki, 2002). Results from more systematic and controlled studies of noble gas solubilities in amine solvents could constrain Henry's law better.

4.3.3. Temporal variation in absorption process

Ar concentrations were observed to vary significantly in response to operational changes in the capture process during a feasibility study conducted at TCM in 2017 (Sundal et al., 2018). Captured CO_2 was recycled into the absorber, to simulate higher CO_2 contents in the flue gas. A decrease of the recycling ratio during the feasibility study was found to correlate with a decrease in relative Ar content.

Temporal variation at the Output, which cannot be associated with deliberate and known processes and/or source changes at the plant (e.g. during the measurement period shown in Fig. 6), is likely to be caused by slight changes in process parameters such as foam-inhibitor injection and its frequency, addition of surfactants, temperature or pressure fluctuations. It is very probable that temporal variation in noble gas composition is caused by the amine absorption process, although this could not be quantified with the current set-up and available dataset.

4.4. Implications on monitoring

4.4.1. Monitoring of noble gas signatures in captured CO_2

Our findings show that a single sample may not be representative for the noble gas signature of captured CO_2 from a given capture plant. The data suggest that injected CO_2 derived from several capture plants, such as the full-scale CCS project in Norway, may span several orders of magnitude for a single noble gases' concentration. A monitoring routine, such as presented herein, should therefore be in place before the injection, documenting the final CO_2 product where the gas streams from several plants are mixed. In the specific case of mixing captured CO_2 from a waste incineration plant and a cement plant, as proposed in the Norwegian full-scale CCS project, we expect noble gas signatures to be air-like, similar to those from other post-combustion sources (e.g. TCM), as air is used for combustion. Monitoring of the gas streams may be of minor priority at these plants.

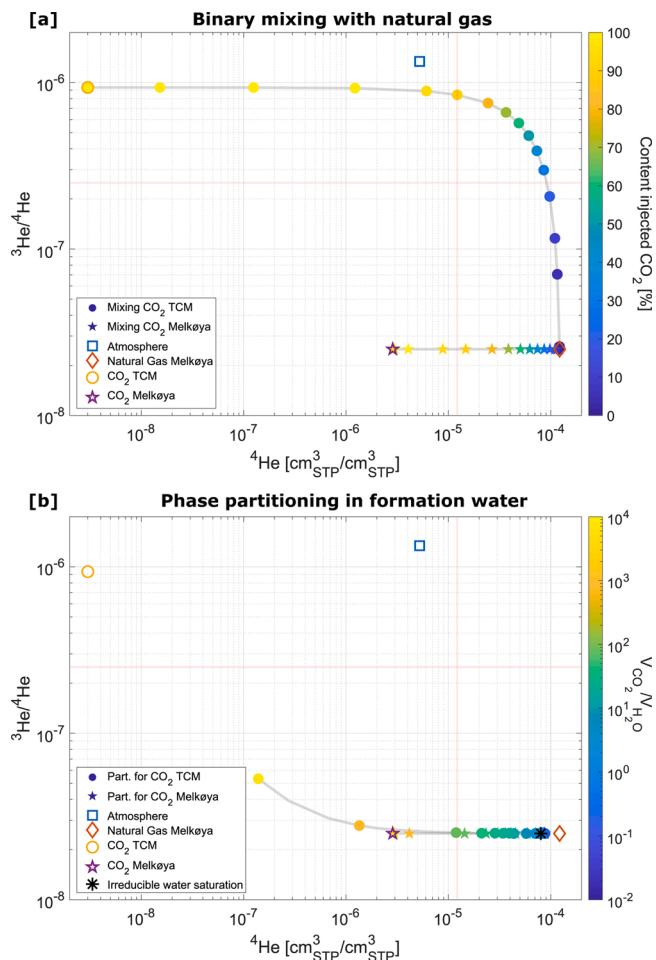


Fig. 9. [a] Mixing of ^4He and $^3\text{He}/^4\text{He}$ in captured CO_2 at Melkøya, sample #11, and TCM, sample #2 with natural gas at Melkøya, sample #8 (samples in Table 1) as function of the CO_2 content in the mixture. [b] Calculated noble gas signature for the same samples after equilibration with formation water in dependence of the $V_{\text{CO}_2}/V_{\text{H}_2\text{O}}$ -ratio. The irreducible water saturation ratio, $V_{\text{CO}_2}/V_{\text{H}_2\text{O}} \approx 1.5$, marks the value at the mean maximum observed CO_2 saturation in reservoir rocks (Burnside and Naylor, 2014). Exemplary, values are derived for depth and temperature conditions approximately found at the Snøhvit storage site: Depth of 2250 m, temperature 84.8°C . Red lines mark one order of magnitude perturbation from natural gas at Melkøya.

Baseline datasets, such as the relation of noble gas concentration to the gas mixture combusted at a CHP plant (see Fig. 4[b]), can then be used to parameterize the noble gas concentrations in the captured CO_2 once the signatures in the contributing gas streams are known. In this way, sampling frequency could be reduced and a representative estimate becomes available without extensive sampling, at low cost.

For natural gas processing plants such as at Melkøya, temporal variation may also be observed when natural gas streams from several reservoirs/wells are mixed and processed. Different geological settings (i.e. burial depths, migration paths, hydrocarbon sources) can lead to varying degrees accumulation and overall isotopic signatures. Significant variation in the He content of fossil hydrocarbon resources were e.g. observed in different wells within the Magnus Field in the North Sea (Ballentine et al., 1996). A correlation between producing wells could then be used to estimate the resulting noble gas signatures, once they are mixed with each other and have gone through the capture process.

4.4.2. Storage site monitoring

In this chapter, we discuss the implications of the observed noble gas signatures at capture plants for their applicability as monitoring tracers.

As described, noble gas concentrations in the captured, and subsequently injected, CO₂ are typically low due to the CO₂ absorption process. The absorption process can also imprint a site specific signature on the injected CO₂. While isotopic ratios of one noble gas are not significantly altered in our samples (see Table 2), absolute concentration ratios can change significantly during absorption (see Fig. 8 and Section 4.3.2). Thus, noble gas content can potentially differentiate injected gas from natural background fluids such as fossil gas (CH₄ and CO₂), biogenic CO₂, formation water or an atmospheric signature, either due to differences in isotopic ratio, elemental ratio or by absolute concentrations.

Leakage scenarios can be evaluated using binary (or ternary) mixing analysis between fluid components and the known elemental and isotopic composition of the background fluid(s). The threshold for leakage detection can be quantified and is reached at a significant perturbation from the background noble gas signature. We considered a minimum perturbation of one order of magnitude to be necessary for the discrimination of injected CO₂ and native fluids, accounting for detection or sampling uncertainties and variability in the background values. There is prior evidence that such perturbations are suitable for detection of different fluid sources, e.g. at the large scale CO₂-EOR (Enhanced Oil Recovery) site Cranfield (Györe et al., 2015). At the Kerr site, mixing analysis using He-signatures was used to exclude a major contribution of injected CO₂ in high CO₂ concentration in groundwater discharge that had an atmospheric signature (Gilfillan et al., 2017).

To evaluate the performance of the depleted noble gas signature of injected CO₂ as a fingerprint for monitoring storage sites, we must consider: (i) mixing of the CO₂ with the native gas in the reservoir and; (ii) degassing of noble gases from the formation water into the injected CO₂. In Fig. 9[a], binary mixing of He and its isotopic ratio in captured CO₂ at TCM and Melkøya with natural gas from Melkøya is shown as a function of the content of injected CO₂ in natural gas. Mixing of the CO₂ with the native gas, which is enriched in noble gases, lowers the absolute concentrations at high CO₂ content (Fig. 9[a]). For the CO₂ from TCM, the isotopic ratio could enable additional and faster discrimination (Fig. 9[a]).

Simple binary mixing calculations neglect the interactions of the injected CO₂ with background fluids during storage and/or migration due to chemical and physical processes such as: formation water degassing, gas stripping, dissolution or adsorption, which have been observed and described in several studies, e.g. (Fanale and Cannon, 1971; Flude et al., 2017; Györe et al., 2017; Ju et al., 2020). To address the impact of formation water degassing in the storage formation, we calculate noble gas signatures in the CO₂ after equilibration with formation water, at different gas-water volume ratios, $V_{\text{CO}_2}/V_{\text{H}_2\text{O}}$. The calculations follow the derivation of phase partitioning based on Henry's law for liquid-gas systems described in Ballentine et al., 2002. Additionally, experimentally derived deviations of Henry coefficients for a high density CO₂-H₂O system are applied according to Warr et al., 2015. CO₂ densities are calculated from Ouyang (2011) and water densities are taken from NIST (2020). Typical noble gas concentrations in the formation water are estimated using the concentration reported in the Melkøya natural gas (sample #8, Table 1) and partitioning coefficients were calculated at realistic reservoir conditions (i.e. in-situ temperature, pressure and salinity) in the Snøhvit storage site.

Degassing of the formation water enriches the CO₂ with noble gases even at high $V_{\text{CO}_2}/V_{\text{H}_2\text{O}}$ -ratios, as illustrated for He in Fig. 9[b]. This masks the depletion of noble gases and imprints the injected CO₂ with a crustal signature. The calculation illustrates how significantly depleted noble gas signatures may be altered during injection and migration.

Both calculations presented (Fig. 9), indicate that the initial signature and depletion in noble gas concentrations is only preserved or identifiable at extreme $V_{\text{CO}_2}/V_{\text{x}}$ -ratios. For more realistic $V_{\text{CO}_2}/V_{\text{H}_2\text{O}}$ -ratios, i.e. below the irreducible water saturation of the reservoir rock (Fig. 9[b]), the injected CO₂ will quickly inherit the noble gas signature of background reservoir fluids, making it distinct from atmospheric signature and imparting an identifiable natural fingerprint.

Seabed detection of a CO₂ leak then critically depends on effective baseline characterization of noble gas compositions in subsea gas seeps. Natural seeps are derived either from shallow biogenic gas or the breakdown of methane clathrates, and these are likely to have a composition distinct from the deep, radiogenic crust.

Aside from these model calculations, data and experience from the Melkøya site provide a practical illustration for targeted monitoring. Here, the CO₂ storage and the natural gas production reservoirs are within the same geological unit (the Stø Formation), but in different structural compartments (Halland et al., 2013). Routine measurements of noble gas content, revealing gradual depletion in the produced natural gas, could be used as a monitoring measure, if migration of injected CO₂ into the natural gas was suspected. Since it is a well characterized site, the necessary perturbation threshold may be decreased. Meanwhile, natural variation of the CO₂ content in produced gas renders the CO₂ concentration as tracer alone impractical. Here, semi-continuous measurements with the miniRuedi portable mass spectrometer could be applied to document variability in and between the various gas streams to estimate unintended, intra-formational mixing or leakage.

5. Conclusion

In this study we analysed the noble gases in the gas streams at two different Norwegian capture plants: Technology Centre Mongstad (TCM), a demonstration plant, and Melkøya, a large scale CCS site, capturing CO₂ naturally occurring in natural gas.

We observed that noble gas concentrations become depleted during the capture process. Two significant drivers affecting the noble gas concentrations in the captured CO₂ can be identified: the nature of the gas from which CO₂ is captured and the capture process itself, having site-specific properties. Concentrations of captured CO₂ span several orders of magnitude and the noble gas signature of the two plants are significantly different. Increasing the existing dataset with this study allows to infer specific noble gas concentrations for future projects.

The analytical approach developed here contributes to establishing a reliable sampling routine in capture facilities or before CO₂ injection to characterize the temporal evolution of noble gas concentrations of captured CO₂ and evaluate traceability at the storage site. The presented dataset also allows for investigation of the impact of processes such as foam development and applicability of Henry's law and forms a basis for comparison in future studies. While studies on noble gas solubilities in amine solvents in more controlled environments are necessary to quantify the single processes separately.

The recorded temporal variation does not preclude the value of noble gases as tracers since noble gas concentrations in capture streams are still significantly different, i.e. low, compared to geochemical reservoirs. Using mixing and noble gas partitioning calculations we show that the significant depletion in noble gas concentrations, together with degassing of noble gas enriched formation water, mean that the injected CO₂ will inherit the noble gas signature of the storage formation, even following the injection of significant CO₂ volumes. Any CO₂ leaked from the storage formation is thus likely to have a crustal noble gas signature, characteristic of the storage site, which can be targeted for monitoring. Seabed detection of a CO₂ leak then critically depends on effective baseline characterization of subsea gas seep noble gas compositions. Thus, more research on the change of noble gas fingerprints during migration in the subsurface and quantification of background concentrations is necessary before leakage detection using noble gases can be fully utilized. This work on noble gas signatures and temporal variation of capture streams should be an important step towards that goal.

CRedit authorship contribution statement

Ulrich W. Weber: Writing - original draft, Investigation, Methodology, Formal analysis, Software, Data curation, Visualization, Conceptualization, Writing - review & editing. **Rolf Kipfer:**

Conceptualization, Methodology, Project administration, Writing - review & editing. **Edith Horstmann**: Investigation, Writing - review & editing. **Philip Ringrose**: Conceptualization, Project administration, Writing - review & editing. **Niko Kampman**: Software, Methodology, Writing - review & editing. **Yama Tomonaga**: Investigation, Formal analysis, Writing - review & editing. **Matthias S. Brennwald**: Methodology, Resources, Writing - review & editing. **Anja Sundal**: Investigation, Methodology, Conceptualization, Supervision, Project administration, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors report that they have no known competing interests that could have influenced this work.

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