

ON THE DISTINCTIVENESS OF NOBLE GASES IN INJECTED CO₂ FROM BACKGROUND FLUIDS

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Abstract

A comprehensive monitoring program for CO₂ storage sites is an integral part of designing CCS projects. Once a CO₂ anomaly is observed or suspected, the source of the CO₂ may be identified through evaluation of geochemical tracers. Noble gases are one of those geochemical tracers that display unique signatures for the environmental reservoirs involved in the storage site system.

The background fluids at storage prospect, such as formation water, hydrocarbons or shallow gases need to be characterized prior to injection. Typical noble gas signatures are of atmospheric, crustal/radiogenic or mantle character. Captured CO₂ can contain a large range of noble gas concentrations and ratios with typically significantly lower concentrations than the other background fluids.

Here, we collect the noble gas analysis of various environmental fluids in the storage site system relevant to the North Sea, such as hydrocarbons and shallow gases, to narrow down possible observable signatures. If samples are not available realistic values can be inferred from analogue sites/studies. Further, we show that after injection, phase partitioning, hence equilibration, of the injected CO₂ with formation water leads to adaption of a radiogenic signature from the formation water. Therefore, the initially low concentrations of the CO₂, and their associated elemental and isotopic ratios, are only preserved when remaining almost pure. These signatures can be applied to mixing calculations with the background fluids to rule out if injected CO₂ is contributing to an anomaly.

Meanwhile, noble gases are one of the environmental tracers that could be cost-effective since they are naturally inherent in the CO₂ and the storage reservoir fluids, we also model the addition of artificial noble gas tracers to increase the detectability, i.e. ability to recognize lower contributions of injected CO₂ in a background reservoir fluid. These calculations can be fed into cost calculations to estimate the economic impact of such an additional monitoring measure.

Keywords: *Monitoring and Verification, Noble gases, Tracer addition*

1. Introduction

Designing a CO₂ storage sites measurement, monitoring and verification (MMV) program is an essential part of a CCS project [1]. The Norwegian ‘Longship’ project aims to store CO₂ in the ‘Aurora’ prospect in the North Sea in the vicinity of the Troll oil and gas field. The planned, continuous MMV program does not include noble gases [2], however, with the content of ‘triggered’ environmental monitoring surveys not yet defined, this may be included there.

Noble gases are trace constituents of most environmental fluids. The concentrations of He, Ne, Ar, Kr, Xe, and their isotopic ratios constitute a signature or ‘fingerprint’ of a fluid. Due to their inertness, only physical processes influence them such that they have widespread application in deciphering physical and geochemical processes [3]. Inherent noble gas tracers were used to refute an alleged leakage from a CO₂ storage site [4].

The main groups of noble gas fingerprints are of atmospheric [5], crustal [6] and mantle character [7]. However, there are wide isotopic concentration ranges within these categories, such that characterizing the

background fluids of a storage site is key for the applicability of noble gases as tracers. Therefore, the ICO₂P project has characterized the signature of various captured CO₂ streams [8,9,10]. Noble gases showed large variation at the different sample sites and all were being depleted through the CO₂ capture process in a way that the captured CO₂ has a low noble gas content compared to other background fluids (e.g. natural gas). For background fluids at the ‘Aurora’ storage site noble gas samples have not yet been analyzed such that analogue studies e.g. describing other hydrocarbon systems in the North Sea can be used to infer the noble gas content.

One also has to consider that the CO₂ can undergo interaction with e.g. in-situ formation water or gases, subsequently altering the noble gas fingerprint. In previous work [8,9], we showed that the phase partitioning with formation water leads to the stripping of gases and inheritance of a radiogenic signature. We concluded that this provides a monitoring target in differentiating injected, “anthropogenic” CO₂ from shallow, natural CO₂ sources, e.g. biogenic or gas hydrates.

In this work, we build the foundation of noble gas signatures that may be expected for the North Sea and follow up previous calculations with mixing calculations of the injected, equilibrated CO₂ with other fluids possibly involved in anomalies.

Further, we apply the calculations to a simulated addition of noble gas tracers. This can increase the distinctiveness of the injected CO₂ relative to natural fluids. However, this comes with a cost, which can be estimated from an economic analysis including the tracer gas amounts needed and the related gas prices.

2. Baseline Concentrations

Collecting the baseline concentrations of fluids in the storage site system allows assessing differentiability of the background to injected CO₂. Tab. 1 shows a summary of the expected ranges for different environmental fluids.

Captured CO₂ has been analyzed for several capture plants in Norway [8,9,10] and other countries [11]. Noble gas concentrations are typically low and the isotopic signatures are either air-like for plants with combustion prior to capture (e.g. waste incineration) or natural gas-like (e.g. natural gas processing).

For natural gas, sample analyses for the North Sea are currently available for Sleipner Vest and the Magnus field [12,13]. The results show a typical radiogenic character, deriving from the production of ⁴He, ²¹Ne and ⁴⁰Ar through radioactive decay of the elements K, U and Th in the rocks [6]. Samples for natural, geologic CO₂ have a dominantly magmatic (mantle) signature with subsequent equilibration with radiogenic formation water. The values in Tab. 1 are from large natural CO₂ systems in the US [14,15]. Natural CO₂ in the North Sea context is typically a minor constituent of natural gas accumulations [e.g. 12] and would therefore likely have the same concentrations of associated noble gases as natural gas.

Radiogenic signatures can cover a large range since the amount of a noble gas isotope in subsurface reservoirs; natural gas, oil, natural CO₂ or in pore water, is dependent

on the exchange with other fluids from the atmosphere, crust and mantle. Further, longer time of separation from other reservoirs allows for more radiogenic accumulation. The provenance of natural gas can also have an impact i.e. stripping of noble gases during migration through formation water.

Close to the seabed gas hydrates may occur. Only elemental gas concentrations have been analyzed for gas hydrates but not the isotopic composition [16]. Those samples were collected outside the coast of Oregon, US and showed a quite specific fractionation pattern with preferential incorporation of heavier noble gases and suppression of the lighter ones (Tab. 1).

Sediment samples, i.e. the dissolved noble gases in the sediments' pore-water, are rare and for the North Sea there is no data set available. Sediment pore water concentrations are dependent on the temperature during sedimentation and if there are leakage sites, e.g. black smokers, nearby. The data from [17,18] has to be seen in the context of continental plate boundaries which may therefore not be representative for the North Sea.

Seawater, if not in the vicinity of specific fluid releases, is typically air equilibrated water at a given temperature and salinity [19]. This means atmospheric gas, including noble gases, is dissolved based on the solubility of the respective gas species at these conditions in water. In case there are seepages, ocean currents may redistribute them fast, so anomalies can be local. The atmosphere is typically well mixed and has a set noble gas signature [5].

With regards to isotopic ratios there are the three main signatures and fluids represent mixtures of these to various degrees. Typical values for the isotopes mainly affected are shown in Tab. 2.

For captured CO₂ the ratios are dependent on the source of flue gas and if combustion has taken place prior to capture, e.g. at heat and power plants. Combustion typically introduces noble gases from the air also shifting

Table 1: Observed noble gas concentrations for the different fluids in the storage site systems. Captured CO₂ from several sites [8,11]. Atmospheric values from [5]. Seawater concentrations after [19] (assuming a temperature of 7,5 °C and a salinity of 34,2 g/L). Natural gas for He, Ne and Ar compiled from the Sleipner field and Magnus oil field in the North sea from [12,13], Kr and Xe from Sleipner Field [12]. Natural CO₂ compiled from [14] and [15]. Sediment values from the South Pacific Ocean [17] and the Mediterranean ridge for helium [18]. Gas hydrates from [16].

| | He | Ne | Ar | Kr | Xe |
|------------------------------------|--------------------|-------------------|--------------------|-------------------|-------------------|
| Captured CO₂ | 2,29E-09 – 2,9E-06 | 6E-11 – 4,27E-07 | 3,7E-10 – 1,4E-04 | 3,6E-12 – 6,3E-09 | 1,1E-13 – 1,9E-09 |
| Natural CO₂ | 1E-04 – 1E-02 | 7,0E-08 – 1,8E-06 | 1,5E-05 – 2,7 E-05 | 1,0E-10 – 1,0E-08 | 5,0E-12 |
| Natural Gas | 5E-03 – 1,3E-04 | 0,8E-08 – 2,7E-08 | 1,5E-05 – 2,7E-05 | 9,5E-09 | 2,0E-09 |
| Gas Hydrates | 7,0E-10 – 9,0E-10 | 2,5E-09 – 6,2E-08 | 3,5E-05 – 5,3E-04 | 1,8E-08 – 3,0E-07 | 2,7E-09 – 9,4E-08 |
| Sediment (cm³/g) | 1,0E-04 – 1,0E-02 | 5,0E-09 – 5,0E-07 | 1,0E-05 – 1,0E-08 | 5,0E-08 – 1,5E-09 | 8,0E-09 – 1,7E-08 |
| Seawater (cm³/g) | 4,0E-08 | 5,7E-09 | 1,1E-06 | 8,5E-08 | 1,1E-08 |
| Atmosphere | 5,24E-06 | 1,82E-05 | 9,34E-03 | 1,13E-06 | 8,7E-08 |

| | ³ He/ ⁴ He (R/R _A) | ²¹ Ne/ ²² Ne | ⁴⁰ Ar/ ³⁶ Ar | ⁸⁶ Kr/ ⁸⁴ Kr | ¹³² Xe/ ¹³⁰ Xe |
|--------------------------------|--|------------------------------------|------------------------------------|------------------------------------|--------------------------------------|
| Atmospheric Signature | 1 | 0,029 | 296 | 0,303 | 6,61 |
| Crustal signature | ~0,1 | ~0,033 | ~455 | ~0,303 | ~6,61 |
| Mantle signature (MORB) | 8 | 0,06 | ~30000 | - | - |

Table 2: Isotopic ratios for the main signatures: atmospheric [5], crustal [6], hence radiogenic, and mantle [7]. If “~”- sign averaged from several samples.

ratios towards atmospheric values. At natural gas processing sites the radiogenic ratios are maintained [8].

Noble gas ratios associated with hydrocarbons are dependent on the geological setting of a reservoir and the provenance of the natural gas. In Tab. 2 isotopic ratios are shown for the North Sea [12]. However, especially the ³He/⁴He and ⁴⁰Ar/³⁶Ar ratio can be quite varying, e.g. natural gas from Snøhvit has an order of magnitude lower value for the He ratio [8].

3. CO₂ Signature after Injection

3.1 Phase Partitioning

We calculated phase partitioning with formation water that would occur after CO₂ injection and during migration in [8,9]. We showed that the depleted signature of the captured CO₂ is not maintained, but in contrast largely inherited from the formation water by gas stripping. Thereby, the CO₂ adopts a radiogenic signature.

In [8,9] we derived the assumed formation water concentrations based on assuming equilibrium of the water with natural gas of the Snøhvit Field. Since Snøhvit is located in a different geological setting compared to prospective sites in the North Sea, the noble gas accumulation is expectedly larger in the Snøhvit Field than in the North Sea. Therefore, in this work, we used the values from the Sleipner Field [12] to calculate the concentrations at the given gas-water ratios, V_g/V_w.

By calculating the ratio of the concentrations in the CO₂ relative to the concentrations at very low V_g/V_w, it becomes apparent that the formation water signature dominates up to high gas-water ratio (Fig. 1). The most relevant value for V_g/V_w is the maximum water saturation, S_{max} which is approximately at 1,5. Here, no more water can be replaced by CO₂. At the maximum water saturation, S_{max}, concentrations constitute 80-90% of that of the formation. The slight differences for the enrichment for the single gases derives from gas specific solubilities.

Only at very high V_g/V_w the concentrations of the injected CO₂ will be influential without tracer addition. However, this is likely not possible to be achieved considering maximum saturation. In a scenario where an area of a reservoir is repeatedly flushed by CO₂ significant parts of the original noble gas content could have been stripped, thereby making the signature of the injected CO₂ more influential or possible to be approached. This could for example be the case at CO₂-EOR (enhanced oil recovery).

3.1 Tracer Addition

The adopted signature of the formation water into injected CO₂ allows differentiation from fluids that do not have a radiogenic signature, i.e. shallower sources (see Tab. 1). The approach of modelling phase partitioning also allows to evaluate the active addition of a noble gas tracer to the injection stream with the goal to

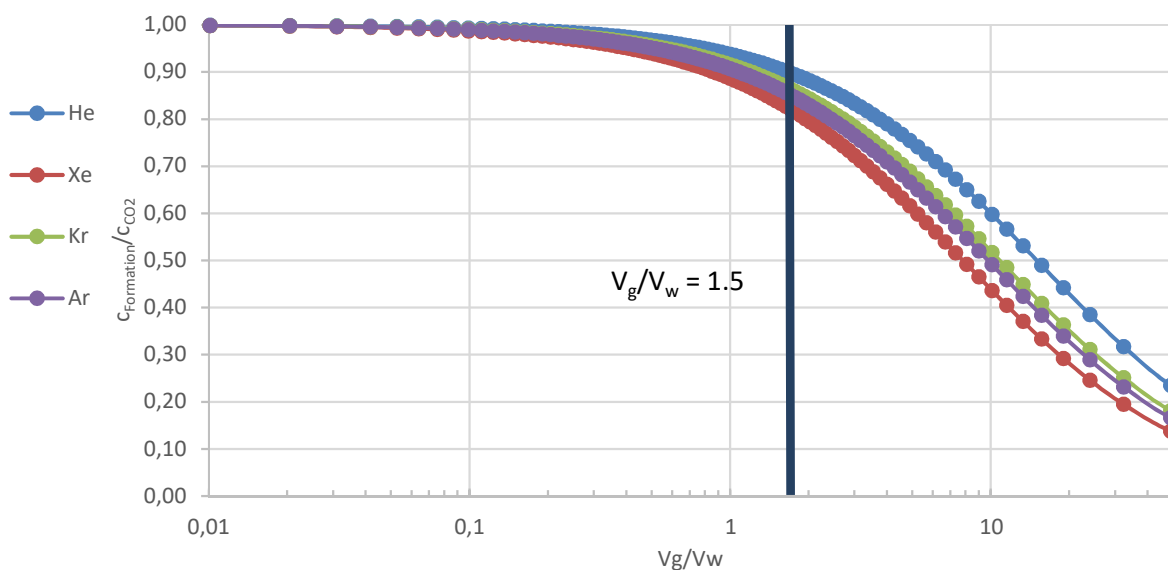
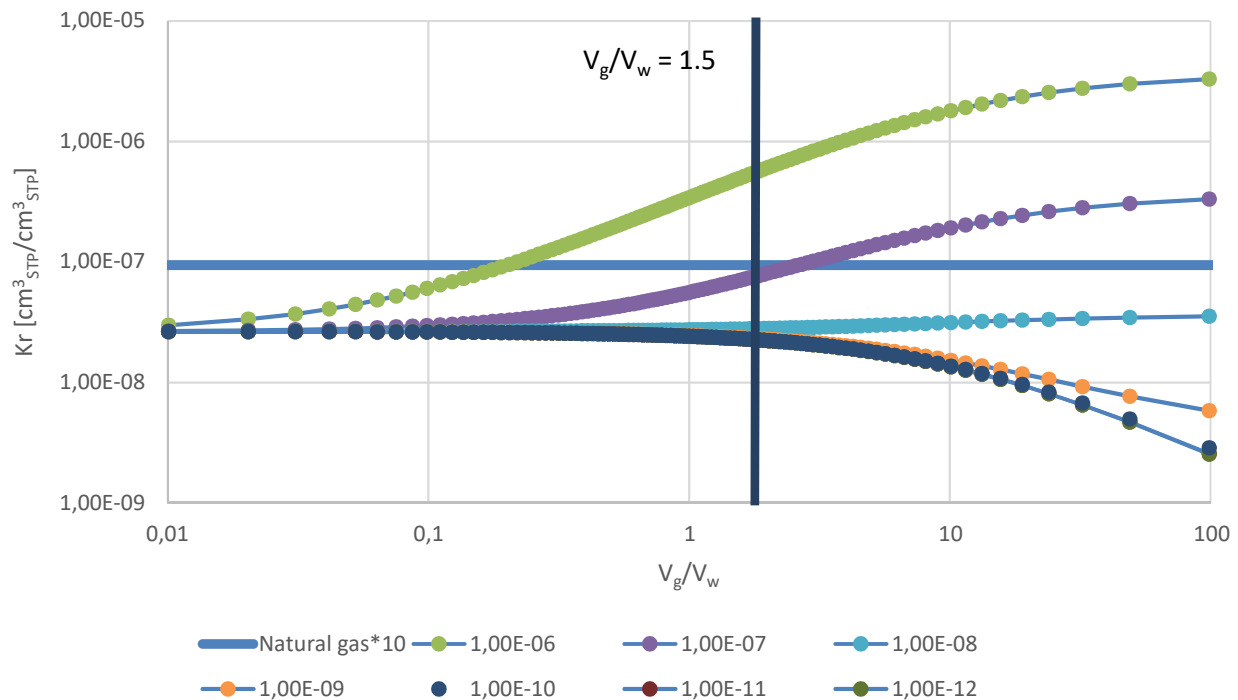


Figure 1: Phase partitioning of captured CO₂ from Klemetsrud, containing trace amounts of noble gases, with formation water with a crustal signature (equilibrated with natural gas from Sleipner. Concentration in the CO₂ relative to concentrations at a V_g/V_w of 0.0001. Modified from [9]. Up to realistic gas-water volume ratios, the formation water signature prevails.

Figure 2: Tracer concentration in injected CO₂ after equilibration for the addition of an artificial tracer; Kr in this example, in the injected CO₂ in dependence of V_g/V_{H₂O}. Lines represent values for a tracer in the given order of magnitude. Between magnitudes 5E-07 – 1E-06 cm³_{STP}/cm³_{STP} an added tracer would be one order of magnitude above natural gas concentration at S_{max} = V_g/V_w = 1.5.



maintain a significant different noble gas signature after the equilibration.

Kr and Xe are especially relevant choices for noble gas tracer addition, since they have low concentrations in background (see Tab. 1) and do not impact the main features of the radiogenic signature, in contrast e.g. to He. This could be used to differentiate the injected CO₂ from natural gas that may be in the vicinity of a storage site, as is the case at ‘Aurora’ [2].

For the addition of elemental Kr the resulting noble gas concentrations are modelled in dependence of V_g/V_w for a range of concentrations in the injected CO₂ (Fig.2). To achieve a value of one order of magnitude above the background in natural gas, to be significantly distinctive, an addition of Kr with concentrations in the injected CO₂ of 5E-07 – 1E-06 cm³_{STP}/cm³_{STP} is necessary at maximum saturation (S_{max}). At ratios lower than S_{max}, the background formation fluid signature prevails despite higher tracer concentrations. The same calculation leads to 5E-08 – 1E-07 cm³_{STP}/cm³_{STP} for Xe.

The value of one order of magnitude above a background, in this case natural gas, to reach distinctiveness is an arbitrary choice. It shall account for uncertainties in background concentrations and that a leakage may be a mixture of gases, where the CO₂ is a minor component.

The necessary amounts of a trace gas can be scaled up to a storage sites injection volume to derive the cost of such a tracer addition [20]. Including the single isotopes of the respective noble gas may reduce the amounts needed during injection. For example, ³He is significantly less abundant in the environment than ⁴He. This lower

abundance, however, typically comes with increased production cost of the respective isotope [20].

4. Mixing calculations

Having established the background concentrations (Sec. 2, Tab. 1 and 2), the concentration the captured CO₂ will likely adopt and the potential signature of a tracer addition. Mixing calculations can be performed to estimate the content of injected CO₂ in a fluid. This could for example be conducted on samples from bubbling gas on the seafloor or the production stream of a natural gas field. Once an anomaly is observed noble gas mixing calculations can be applied for leakage attribution.

The noble gas concentrations of a reservoir can vary significantly (Tab. 1). By depicting the values of some of the known signatures on a crossplot it becomes apparent that several orders of magnitude are covered (Fig. 3). Fig. 3 shows the elemental ratio of Xe/He versus Xe for the different background fluids on a double logarithmic scale. He and Xe were chosen due to the low background of Xe and the typically large difference in He between crustal and shallow signatures (Tab. 1). The addition of 1E-07 cm³_{STP}/cm³_{STP} Xe to the injected CO₂ would distinct the signature of the CO₂ after injection from the pure natural gas even further as shown in Fig. 3. Then He would still allow distinction to shallow signatures.

Three mixing calculations are performed in Fig. 3, one for mixing of injected and equilibrated CO₂ with atmosphere and mixing with gas hydrates to illustrate the content of CO₂ in a mixture being needed to change the elemental ratio. The values are derived from the binary mixture of the two end-members for a given percentage of CO₂ in the fluid mixture. Such an analysis, however,

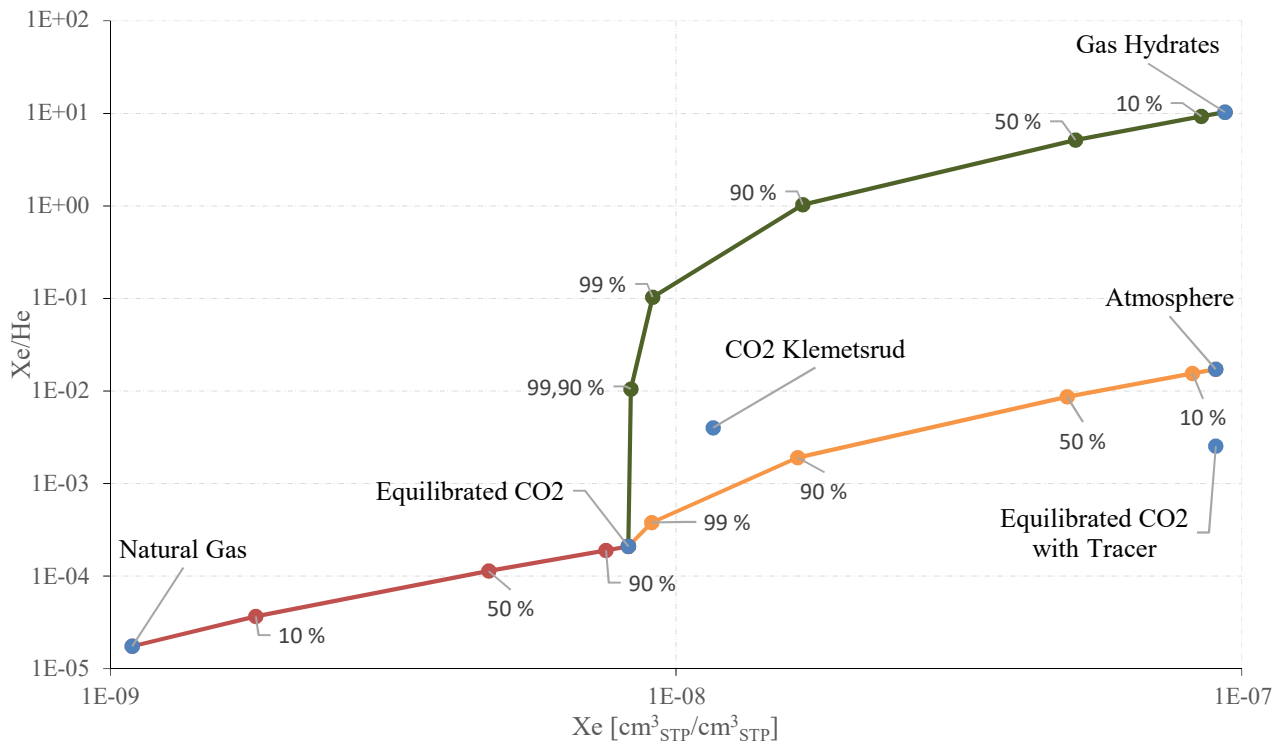


Figure 3: Xe/He vs Xe plotted with mixing lines with equilibrated CO₂ and background fluids (see Sec. 2 and Tab. 1). Mixing lines with the injected, equilibrated CO₂ and signatures of gas hydrates and the atmosphere. Also, equilibrated CO₂ with a tracer addition of 1E-07 cm³_{STP}/cm³_{STP} Xe is included. Mixing lines of injected CO₂ after equilibration with gas hydrates, atmosphere and natural gas with the content of the CO₂ in the mixture in percent.

would further have to account for analytical uncertainty and natural variation of the background fluids. At least the latter one can be addressed by performing a thorough baseline characterization of the storage site prior to injection.

5. Conclusion

The derivation of the signature of the injected CO₂ after phase partitioning with the formation water allows to evaluate differentiability of the possible signatures. Comparing the injected CO₂ to other sources depicts the identifiability and attributability of a leakage through noble gases. Here, we have shown examples how a leakage would be detectable and how the volumetric contribution of injected CO₂ can be estimated. Most notably, the difference between the adopted radiogenic signature and that of shallow fluids with atmospheric or other specific signatures, such as gas hydrates, is very pronounced. We also modelled the amounts that would be needed for tracer addition for Kr and Xe. These can be fed into cost calculations for the respective noble gases. This cost can be broken down to a price per ton and set into perspective to the cost of other monitoring measures of a storage project.

However, there are still uncertainties for some of the background fluids even though the shown inferred concentrations from analogues allow to constrain the possible observed concentrations. Thus, we aim to characterize more fluid compositions from oil and gas fields in the North Sea. Further, we aim to analyze sediment samples from the seafloor to characterize shallow signatures. The ICO₂P project will continue to focus on characterizing the area around the Aurora site,

which has been selected as the storage prospect for the ‘Longship’ project. An extended baseline database will contribute to the goal to conclude on the applicability of noble gas tracers.

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References

- [1] P. Ringrose. How to Store CO₂ Underground: Insights from early-mover CCS Projects [2020], Springer, ISBN: 978-3-030-33112-2.
- [2] Furre, A.-K., Meneguolo, R., Pinturier, L., Bakke, K. [2020] Planning deep subsurface CO₂ storage monitoring for the Norwegian full-scale CCS project. First Break, Volume 38, Issue 10, Oct 2020, p. 55 – 60. doi: 10.3997/1365-2397.fb2020074.
- [3] Burnard, P. (Ed.), The Noble Gases as Geochemical Tracers, Springer Berlin Heidelberg, 2013. doi: 10.1007/978-3-642-28836-4.
- [4] Gilfillan, S.M.V., Sherk, G.W., Poreda, R.J. and Haszeldine [2017] Using noble gas fingerprints at the Kerr Farm to assess CO₂ leakage allegations linked to the Weyburn-Midale CO₂ monitoring and storage project. Int. Jour. of Greenhouse Gas Control, 63, 215-225.
- [5] Y. Sano, B. Marty, P. Burnard, Noble gases in the atmosphere, in: The Noble Gases as Geochemical Tracers, Springer Berlin Heidelberg, 2012, pp. 17-31. doi:10.1007/978-3-642-28836-4_2

- [6] Ballentine, C. J., Burnard, P., [2002] Production, Release and Transport of Noble Gases in the Continental Crust, *Reviews in Mineralogy and Geochemistry* 47 (1): 481–538. doi: 10.2138/rmg.2002.47.12.
- [7] Moreira, M.A., Kurz, M.D., Noble gases as tracers of mantle processes and magmatic degassing, in: *The Noble Gases as Geochemical Tracers*, Springer Berlin Heidelberg, 2012, pp. 371-391. doi:10.1007/978-3-642-28836-4_12.
- [8] Weber, U.W., Kipfer, R., Ringrose, P., Horstmann, E., Kampman, N., Tomonaga, Y., Brennwald, M.S., Sundal, A. [2020] Noble Gas Tracers in Gas Streams at Norwegian CO₂ Capture Plants. *Int. Jour. of Greenhouse Gas Control*, 103205, doi: 10.1016/j.ijggc.2020.103238. Noble Gases as Monitoring Tracers in CCS: A Case Study with CO₂ from the Waste-to-Energy Plant Klemetsrud, Norway
- [9] Weber, U.W. and Kampman, N., Mikoviny, T., Thomassen, J., Sundal, A. [2021] Noble Gases as Monitoring Tracers in CCS: A Case Study with CO₂ from the Waste-to-Energy Plant Klemetsrud, Norway. *Proceedings of the 15th Greenhouse Gas Control Technologies Conference* 15-18 March 2021, doi: 10.2139/ssrn.3819288
- [10] Sundal, A., Weber, U., Brennwald, M., Ringrose, P., Flø, N. and Johnsen, K., Faramarzi, L., Aagaard, P., Kipfer, R., [2018] Monitoring Real Time, In-Line Variations of Noble Gas Concentrations During CO₂ Capture Operations by Means of a Portable Mass Spectrometer. *14th Greenhouse Gas Control Technologies Conference Melbourne (GHGT-14)*, doi: 10.2139/ssrn.3366166.
- [11] Flude, S., Györe, D., Stuart, F., Zurakowska, M., Boyce, A., Haszeldine, R., Chalaturnyk, R., Gilfillan, S. [2017] The inherent tracer fingerprint of captured CO₂. *International Journal of Greenhouse Gas Control* 65, 40-54.
- [12] P.H. Barry, M. Lawson, W.P. Meurer, O. Warr, J.C. Mabry, D.J. Byrne, C.J. Ballentine, Noble gases solubility models of hydrocarbon charge mechanism in the Sleipner Vest gas field, *Geochimica et Cosmochimica Acta*, Volume 194, 2016, Pages 291-309, ISSN 0016-7037, <https://doi.org/10.1016/j.gca.2016.08.021>.
- [13] C. Ballentine, R. O'Nions, M. Coleman, A magnus opus: Helium, neon, and argon isotopes in a north sea oilfield, *Geochimica et Cosmochimica Acta* 60 (5) (1996) 831.849. doi:10.1016/0016-7037(95)00439-4.
- [14] C. J. Ballentine, M. Schoell, D. Coleman, B. A. Cain, 300-Myr-old magmatic CO₂ in natural gas reservoirs of the west Texas Permian basin, *Nature* 409 (6818) (2001) 327-331. doi:10.1038/35053046.
- [15] S. M. Gilfillan, C. J. Ballentine, G. Holland, D. Blagburn, B. S. Lollar, S. Stevens, M. Schoell, M. Cassidy, The noble gas geochemistry of natural CO₂ gas reservoirs from the colorado plateau and rocky mountain provinces, USA, *Geochimica et Cosmochimica Acta* 72 (4) (2008) 1174-1198. doi:10.1016/j.gca.2007.10.009.
- [16] Winckler, G., Aeschbach-Hertig, W., Holocher, J., Kipfer, R., Levin, I., Poss, C., Rehder, G., Schlosser, P., and Suess, E. [2002] Noble gases and radiocarbon in natural gas hydrates, *Geophys. Res. Lett.*, 29 (10), doi:10.1029/2001GL014013, 2002.
- [17] Y. Tomonaga, M. S. Brennwald, R. Kipfer [2013] Using helium and other noble gases in ocean sediments to characterize active methane seepage off the coast of New Zealand, *Marine Geology* 344 34-40. doi: 10.1016/j.margeo.2013.07.010.
- [18] M. Nuzzo, Y. Tomonaga, M. Schmidt, V. Valadares, E. Faber, E. Pinero, A. Reitz, M. Haeckel, L. Tyroller, E. Godinho, R. Kipfer, P. G. Terrinha, C. Hensen, [2019] Formation and migration of hydrocarbons in deeply buried sediments of the gulf of cadiz convergent plate boundary - insights from the hydrocarbon and helium isotope geochemistry of mud volcano fluids, *Marine Geology* 410 56-69. doi:10.1016/j.margeo.2019.01.005.
- [19] Y. Sano, N. Takahata, Measurement of noble gas solubility in seawater using a quadrupole mass spectrometer, *Journal of Oceanography* 61 (3) (2005) 465-473. doi:10.1007/s10872-005-0055-x.
- [20] J. J. Roberts, S. M.V. Gilfillan, L. Stalker, M. Naylor [2017] Geochemical tracers for monitoring offshore CO₂ stores, *International Journal of Greenhouse Gas Control* 65, 218-234, doi: 10.1016/j.ijggc.2017.07.021