



New stable isotope results for reservoir and above zone monitoring in CCS from the Ketzin pilot site, Germany

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With rising atmospheric greenhouse gas concentrations, CCS technologies are a feasible option to diminish consequences of uncontrolled anthropogenic CO₂ emissions and related climate change. However, application of CCS technologies requires appropriate and routine monitoring tools in order to ensure a safe and effective CO₂ injection.

Stable isotope techniques have proven as a useful geochemical monitoring tool at several CCS pilot projects worldwide. They can provide important information about gas - water - rock interactions, mass balances and CO₂ migration in the reservoir and may serve as a tool to detect CO₂ leakage in the subsurface and surface.

Since the beginning of injection in 2008 at the Ketzin pilot site in Germany, more than 450 samples of fluids and gases have been analysed for their carbon and oxygen isotopic composition. Analytical advancements were achieved by modifying a conventional isotope ratio mass-spectrometer with a He dilution system. This allowed analyses of a larger number of CO₂ gas samples from the injection well and observation wells. With this, a high-resolution monitoring program was established over a time period of one year.

Results revealed that two isotopical distinct kinds of CO₂ are injected at the Ketzin pilot site. The most commonly injected CO₂ is so-called 'technical' CO₂ with an average carbon isotopic value of about -31 ‰. Sporadically, natural source CO₂ with an average $\delta^{13}\text{C}$ value of -3 ‰ was injected. The injection of natural source CO₂ generated a distinct isotope signal at the injection well that can be used as an ideal tracer. CO₂ isotope values analysed at the observation wells indicate a highly dispersive migration of the supercritical CO₂ that results in mixing of the two kinds of CO₂ within the reservoir.

Above-reservoir monitoring includes the first overlying aquifer above the cap rock. An observation well within this zone comprises an U-tube sampling device that allows frequent sampling of unaltered brine. The fluids were analysed among others for their carbon isotopic compositions of dissolved inorganic carbon (DIC). $\delta^{13}\text{C}_{\text{DIC}}$ values allowed to assess impacts of the carbonate-based drilling fluid during well development and helped to monitor successive geochemical re-equilibration processes of the brine. Based on the determined $\delta^{13}\text{C}$ baseline values of the aquifer fluid, first concepts indicate the scale of change of the $\delta^{13}\text{C}_{\text{DIC}}$ values that would be necessary to detect CO₂ leakage from the underlying storage reservoir.

Recent efforts aim at applications of new laser-based isotope sensors that allow online measurements in the field. These devices are applied for CO₂ gas tracer experiments as well as for monitoring of isotope composition of soil gases in the vicinity of the pilot site.

This new development will allow much better temporal and spatial resolution of measurements at a lower price. Therefore, stable isotope analyses can become a strong and promising tool for subsurface as well as surface monitoring at future CCS sites.