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Application of tracers to measure, monitor and verify breakthrough of sequestered CO_2 at the CO2CRC Otway Project, Victoria, Australia

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ABSTRACT

At the Cooperative Research Centre for Greenhouse Gas Technology's (CO2CRC) field site in the Otway Basin of Victoria, Australia, investigations into the storage of CO_2-rich gas in a depleted hydrocarbon gas field have been conducted in the Waarre C reservoir. The injected gas from the nearby Buttress field contained 75 mol% CO_2, 21 mol% CH_4 with the remaining balance being a mixture of wet hydrocarbons, condensate and nitrogen. Chemical tracers (sulphur hexafluoride, SF_6; krypton, Kr; perdeuterated methane, CD_4) were added on the basis of literature surveys and small volume trials at the Frio II Brine experiment in Texas. The aim of the project was to measure, monitor and verify the presence of injected CO_2 in a depleted gas field and that the arrival of tracers was a major component of demonstrating breakthrough of CO_2 at the monitoring well, Naylor-1. The paper focuses on methods developed for the injection, recovery and analysis of samples collected at the Naylor-1 well. Results of tracer analysis compare well with other data collected (including pH and density measurements) to demonstrate breakthrough.

A slip-stream injection system was designed to deliver the tracers mixed with the CO_2-rich gas into the subsurface at the CRC-1 well. The tracers were added to the gas stream 17 days after the start of injection (CO_2 injection commenced 18th March, 2008) into the depleted natural gas field at Naylor. A U-tube system was used to retrieve the samples from the Naylor-1 monitoring well. Collected gas and formation water samples were analysed in detail for gas composition, tracers, isotopes (^{13}C CO_2 mainly) and inorganic geochemistry for the broader project. The tracer results confirm that CO_2 breakthrough at the monitoring well occurred within the predicted times. However the interval between samples taken from the U-tubes was too coarse to resolve detailed differences in arrival times between the CO_2 and tracers.

Of the three tracers used, SF_6 provided the clearest evidence of breakthrough at U-tube 2. Kr, because of its abundance in air, and its potential to be present in the subsurface, was more prone to contamination and had higher background levels prior to breakthrough. CD_4 was expected to provide some more unique data based on the presence of abundant CH_4 in the reservoir interval. With hindsight, larger volumes should have been injected to facilitate comparisons with the other tracers and add value to the data set. The test of CD_4 however acted as a suitable proof of concept that CD_4 could be used in such a high background of CH_4.

Further work is ongoing to generate data for partition coefficients between supercritical CO_2, CH_4 and water under the injection conditions.

1. Introduction and history

The CO2CRC Otway Project has utilised a depleted gas reservoir to demonstrate carbon storage in the Otway Basin, Victoria, Australia. As such, it was the first depleted gas reservoir demonstration site for solely geosequestration purposes. The project site, approximately a 300 km

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drive WSW from the Victorian state capital, Melbourne, is just inland from the tourist region known as the Great Ocean Road (Fig. 1). The Otway Project utilises a former production well, Naylor-1, which has been re-completed as a monitoring well. An injection well, CRC-1, was drilled in 2007. This is connected by an ~2 km pipeline to the gas source at Buttress-1 which produces gas from the Turonian age (~90 Ma) Waarre C Formation which contains 75 mol% CO_2, 21 mol% methane and the remaining balance being a mixture of wet hydrocarbon gases, condensate and nitrogen (Boreham et al., 2011). Injection of gas commenced on the 18th March, 2008 into the sandstone of the Waarre "C" Formation at approximately 2 km depth and ceased on the 29th August, 2009 after 65,445 tonnes of gas were injected. Various methods, many adopted from the petroleum industry, were deployed to monitor the migration of the CO_2-rich plume over a distance of 300 m from the CRC-1 injector to the Naylor-1 monitoring well that sits near the top of the structure.

A key performance indicator often used to show the successful storage of carbon dioxide during pilot or demonstration projects for carbon capture and storage (CCS) is the ability to measure, monitor and verify the presence of the injected CO_2 in the reservoir. As identified by the Frio I and II Brine Pilot Tests (Hovorka et al., 2006; Sakurai et al., 2006), run by the Bureau of Economic Geology at the University of Texas, it is necessary to:

- Demonstrate to the public, government regulators and other stakeholders that CO_2 can be injected into a brine formation without adverse health, safety, or environmental effects,
- Measure subsurface distribution of injected CO_2 using diverse monitoring technologies,
- Test the validity of conceptual, hydrologic, and geochemical models.

Since CO_2 is a commonly occurring gas in the subsurface (at both deep and shallow levels), it may be difficult to unequivocally confirm that the CO_2 measured by a monitoring system is the CO_2 injected. One of the most obvious ways to circumvent this is to add chemical tracers to the injected gas that are not otherwise found in the subsurface to verify its presence and safe storage. Tracers have also played a role in assurance monitoring of the atmosphere (Etheridge et al., 2005), soil gas (Watson et al., 2006, 2009) and ground water (Hennig et al., 2008; de Caritat et al., 2009).

Aside from the observed gross enrichment in CO_2 concentration in the injection horizon, the carbon isotopic signature of injected CO_2 could be a key monitoring parameter if different from indigenous CO_2 isototopic signatures. However, CO_2 may also be isotopically similar to background readings such as CO_2 from a volcanic source with $\delta^{13}C$ −4 to −7‰ (Thrasher and Fleet, 1995) versus atmospheric CO_2 of $\delta^{13}C$ −7‰ (Hoefs, 2009). Even though some carbon dioxide may have initial isotopically distinct signatures, over time this may evolve due to known mineral reactions in the subsurface. This has been observed at the Encana Weyburn Project in Saskatchewan, Canada (Shevalier et al., 2004, 2013) and also at the Frio Brine I experiment (Kharaka et al., 2006) and has implications for longer term monitoring of $\delta^{13}C$ for CO_2 as a tracer.

The Waarre C Formation in the Naylor gas field contains about 1 mol% CO_2 with a carbon isotopic composition of $\delta^{13}C$ −11.0‰ VPDB (Boreham et al., 2011). The CO_2-rich gas from Buttress is from an igneous source with $\delta^{13}C$ −6.7% (Boreham et al., 2011). Otway Basin natural gases with low CO_2 contents (<5%) can show large carbon isotopic variations (Watson et al., 2004; Stalker et al., 2009a). In terms of assurance, as the regional variation in abundance and carbon isotopes of CO_2 is so varied, it was determined that tracers could be added to verify the presence of Buttress CO_2 in the subsurface if leakage were to occur and would contribute to the wider assurance programme.

Tracers have been used at both Frio Brine Projects (I and II) to successfully determine breakthrough times, demonstrate the presence of the injected CO_2 and provide evidence of tracer partitioning as they migrated 30 m horizontally along the injection reservoir. Tracers used

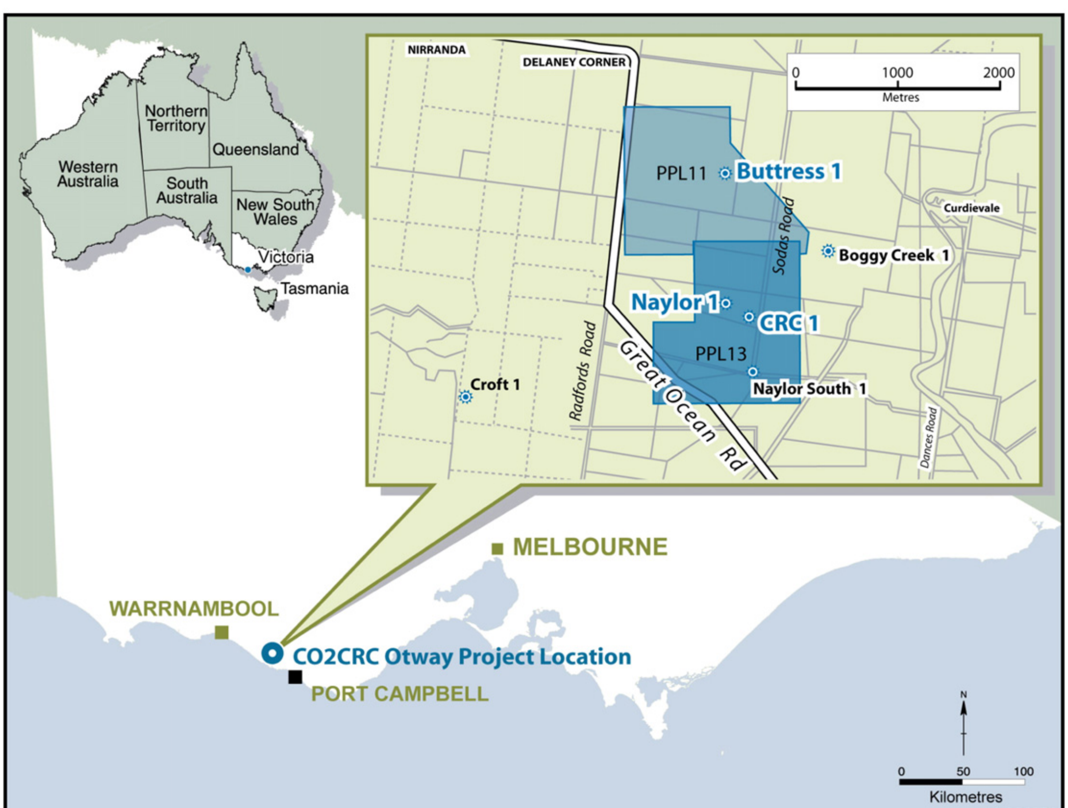

Fig. 1. Location map of site.