Subsurface characterisation and geological monitoring of the CO_2 injection operation at Weyburn, Saskatchewan, Canada

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Abstract: The IEA Weyburn Carbon Dioxide (CO_2) Monitoring and Storage Project analysed the effects of a miscible CO_2 flood into a Lower Carboniferous carbonate reservoir rock at an onshore Canadian oilfield. Anthropogenic CO_2 is being injected as part of a commercial enhanced oil recovery operation. Much of the research performed in Europe as part of an international monitoring project was aimed at analysing the long-term migration pathways of CO_2 and the effects of CO_2 on the hydrochemical and mineralogical properties of the reservoir rock. The pre-CO_2 injection hydrochemical, hydrogeological and petrographical conditions in the reservoir were investigated in order to recognise changes caused by the CO_2 flood and to assess the long-term fate of the injected CO_2. The Lower Carboniferous (Mississippian) aquifer has a salinity gradient in the Weyburn area, where flows are oriented southwest-northeast. Hydrogeological modelling indicates that dissolved CO_2 would migrate from Weyburn in an east-northeast direction at a rate of about 0.2 m/year under the influence of regional groundwater flow. The baseline gas fluxes and CO_2 concentrations in groundwater were also investigated. The gas dissolved in the reservoir waters allowed potential transport pathways to be identified. Analysis of reservoir fluids proved that dissolved CO_2 and methane (CH_4) increased significantly in the injection area between 2002 and 2003. Most of the injected CO_2 exists in a supercritical state, lesser amounts are trapped in solution and there is little apparent mineral trapping. The CO_2 has already reacted with the reservoir rock sufficiently to mask some of the strontium isotope signature caused by 40 years of water flooding. Experimental studies of CO_2-porewater-rock interactions in the Midale Marly Unit indicated slight dissolution of carbonate and silicate minerals, followed by relatively rapid saturation with respect to carbonate minerals. Carbon dioxide flooding experiments on similar samples demonstrated that porosity and gas permeability increased significantly through dissolution of calcite and dolomite. Several microseismic events were recorded over a six-month period and these are provisionally interpreted as being related to small fractures formed by injection-driven fluid migration within the reservoir, as well as other oilfield operations. Experimental studies on the overlying and underlying units show similar reaction processes, however secondary gypsum precipitation was also observed. Reaction experiments were conducted with CO_2 and borehole cements. The size and tensile strength of the cement blocks were unaffected, however their densities increased. A multidisciplinary study of the till deposits in the Weyburn area indicates that a single, heterogeneous till sheet is present. Pre- and post-injection soil gas data are consistent with a shallow biological origin for the measured CO_2 in soil gases. Isotopic ($\delta^{13}C$) data values are higher than in the injected CO_2, and confirm this interpretation. No evidence for leakage of the injected CO_2 to ground level has been detected. The long-term safety and performance of CO_2 storage was assessed by the construction of a features, events and processes (FEP) database that provides a comprehensive knowledge base for the geological storage of CO_2.

The sequestration of carbon dioxide (CO_2) by injection into the geosphere, has been proposed as an effective method of reducing anthropogenic emissions to the atmosphere without drastic changes to the energy industry. Given good reservoir integrity, underground CO_2 injection and storage is essentially permanent and has minimal impact on land usage. It is essential that the geology of each injection/storage operation should be rigorously assessed to determine that the reservoir will not return CO_2 back to the surface via faults, joints, or other migration pathways. Furthermore, during injection operations, the CO_2 storage integrity of the reservoir should be adequately monitored. Injected CO_2 is initially stored as a free phase in the host rock; subsequently it dissolves into local formation waters and initiates various geochemical reactions. Some reactions can chemically contain (i.e. 'trap') CO_2 by the formation of new carbonate minerals. By contrast, other chemical pathways can cause mineral dissolution and hence facilitate the migration of CO_2.

Several industrial operations involving CO_2 injection have been instigated, some of which are complete and others are ongoing. These fall broadly into two categories, namely storage and enhanced oil recovery (EOR). An example of an ongoing storage project is the injection of CO_2 into the Utsira Sand Formation, a Neogene siliciclastic saltwater-bearing aquifer at the Sleipner Field, in the Norwegian North Sea, east of the Shetland Islands (Chadwick *et al*. 2005). An important EOR method is the injection of CO_2, which can promote additional production. As well as being an excellent solvent for hydrocarbons, the CO_2 also reduces oil viscosity and increases its volume. The reduced viscosity and increased pressure makes the oil flow through the reservoir rock to production wells more easily. In some sophisticated CO_2-EOR operations, CO_2 is injected followed by water and this is termed a water-alternating-gas (WAG) strategy. The use of CO_2 in EOR projects is relatively common practice in North America, where the majority of these operations over the past 40 years have sourced the gas from natural underground CO_2 accumulations. Recently however, several commercial operations have used industrially-produced CO_2 for EOR

The purpose of this contribution is to summarise the work of a European research group as part of the initial phase of the IEA Weyburn CO_2 Monitoring and Storage Project (Riding *et al*. 2003; Riding & Rochelle 2005; Riding 2006). This was an investigation of the geological storage of CO_2 during a commercial EOR operation at the Weyburn oilfield. It ran from January 2001 to June 2004 and was a collaboration between workers from Europe and North America (White *et al*. 2004; Wilson & Monea 2004). The work programme of the European consortium comprised three scientific objectives:

- To consider the baseline conditions of the Weyburn oilfield prior to CO_2 injection, in particular those impacting upon geochemical, hydrochemical and hydrogeological properties of the reservoir, and their likely impact upon future reservoir performance.
- To consider the effects of injecting significant quantities of CO_2 on the above.
- To address long-term safety and performance of CO_2 storage by the use of scenario development and system analysis.

The geology of the Williston Basin and the CO_2-EOR operation at Weyburn

The Weyburn oilfield lies within the Williston Basin, a subcircular depression, covering approximately 800 000 km^2, straddling the Canadian-US border (Fig. 1). The basin began to subside in the Ordovician and underwent sporadic subsidence throughout the remainder of the Phanerozoic. The basin contains a relatively complete sedimentary rock record from the Ordovician to the Quaternary (Heck *et al*. 2000). It is a structurally simple feature, the fill being thickest at the centre, thinning towards the margins. The deepest point is believed to be near Williston, North Dakota, U.S.A. where the Precambrian surface is approximately 5 km below the surface (Fig. 1). Most of the hydrocarbons from the basin are produced from Palaeozoic rocks, although some Mesozoic units are also productive. Since the initial discovery of hydrocarbons in the basin, the Madison Group of Mississippian (Early Carboniferous) age has produced the most oil.

The Weyburn oilfield is located in southeast Saskatchewan, Canada (Fig. 1) and lies in the northeast of the Williston Basin. It was discovered in 1954 and covers approximately 180 km^2 of prairie. The oilfield is operated by EnCana Resources. Medium gravity sour crude oil (25-34 °API) is produced from the uppermost Midale Beds of the Madison Group. This is a 400–700 m thick carbonate and evaporite succession of upwards-shoaling shallow marine deposits (Mundy & Roulston 1998) (Fig. 2). The Madison Group spans the majority of the Mississippian (Early Carboniferous) part of the Williston Basin fill and includes many transgressive-regressive cycles, the top of each typically is marked by a thin, fine-grained bed.

The Midale Beds represent one of the transgressive-regressive cycles and this unit comprises a succession of upwards shoaling, shallow marine carbonate-evaporite sediments of Mississippian (Osagean) age (Fig. 2). This unit comprises the Frobisher Evaporite and the overlying Midale Carbonates. Three subdivisions of the Midale Carbonates are present, which range from deep water limestones (Midale Vuggy Unit), through an upward-shallowing succession of dolomitic mudstones (Midale Marly Unit), to supratidal evaporates (Midale Evaporite Unit).

The lowermost subdivision of the Midale Carbonates is the Midale Vuggy Unit, which has yielded most of the produced oil to date. However, the overlying Midale Marly Unit now contains the majority of the remaining oil reserves, and is the target for the miscible CO_2 flood. It has been subdivided into a lower porous and permeable zone (M3), an upper less porous zone (M1), separated by a less porous packstone (M2) by Matiisen & Shehata (1987). Porosity in this unit is on average about 17%, the pores are approximately 5 μm across and the average permeability is 17 mD (Wegelin 1984). The overlying Midale Evaporite Unit represents an emergent, supratidal environment and comprises interbedded anhydrites and dolomites. It formed in a highly restricted hypersaline sabkha setting.

EnCana Resources (formerly PanCanadian Resources) began injecting a 96% pure CO_2 stream into the principal oil reservoir, the Midale Beds, at Weyburn during September 2000. The CO_2 stream is a commercial by-product of the coal gasification process and supplied to Weyburn through a 320 km pipeline from the Great Plains Synfuels Plant in Beulah, North Dakota, U.S.A. that is operated by the Dakota Gasification Company (Fig. 3; Stelter 2001). It is anticipated that this CO_2-EOR operation will extend the life of the Weyburn oilfield by approximately 25 years with the production of an extra 130 million barrels of oil. The initial CO_2 injection rate was 5 000 tonnes per day and injection was originally in 18 patterns of nine wells, each at the west end of the oilfield. The CO_2 flood has been extended in a south-easterly direction and the aim is to flood 75 patterns in phases over the next 15 years (Fig. 4).

The minor impurities in the CO_2 comprise 2.3% C_2+ hydrocarbons, 0.9% hydrogen sulphide, 0.7% methane, 0.1% carbon monoxide, <300 ppm nitrogen, <50 ppm oxygen and <20 ppm of water. These impurities are advantageous for its use in EOR because pure (100%) CO_2 is significantly less soluble in oil than slightly impure CO_2. Hydrogen sulphide is especially effective at increasing the solubility of CO_2 in oil. The Weyburn reservoir already contains some hydrogen sulphide so the injection of this gas presents no additional problems. One disadvantage of the syngas-sourced CO_2 is the trace presence of methyl mercaptan. Mercaptans have an extremely strong odour and their presence in the CO_2 means that minor leaks can cause annoyance to people living in the vicinity. At the conclusion of this EOR operation, in 2025–2030, it is anticipated that between 15 and 20 million tonnes of anthropogenic CO_2 will have been permanently and safely stored in these Mississippian strata, which are about 1.4 km underground. Therefore, greenhouse gas emissions will have been reduced as part of a cost-effective industrial operation.

Characterisation of the reservoir

It is important to comprehensively assess the reservoir formation and its fluids prior to CO_2 injection. This serves as a baseline study from which it is possible to accurately model key reservoir changes caused by the subsequent injection of CO_2. A starting point for this was the study of core from the oil reservoir at Weyburn, which was selected for laboratory experiments and predictive modelling (Pearce & Springer 2001; Springer *et al*. 2002). In summary, cores were selected from wells within the phase 1A CO_2 flooding area (Fig. 4), and it proved possible to subdivide the cores into two units, according to the sedimentary facies (Table 1). The first are massive fine-porous and/or vuggy calcitic limestones belonging to the Midale Vuggy V2 Unit. The second are massive to fine-porous, bioturbated limestones, partly dolomitic, partly calcitic, belonging to the Midale Marly M1 to M3 units.

Another important source of baseline information was the study of reservoir fluids. Regional and local flow regimes were based on hydrogeological information reviewed by Czernichowski-Lauriol *et al*. (2001). Local, pre-CO_2 injection porewater chemistry was based on sampling during August 2000 (Emberley *et al*. 2005). This baseline information can then be used with additional data from well fluids, laboratory experiments, theoretical modelling and microseismics to predict the future behaviour and possible fate of injected CO_2 in the reservoir.

Regional groundwater in the Weyburn area

The potential long-term migration pathways and reactivity of CO_2 within the reservoir unit are largely controlled by the geochemistry and regional hydrodynamics of the aquifer system. In order to model the migration pathways and CO_2 reactivity, a detailed compilation of data on the structure, hydrology and water chemistry of the Mississippian aquifer was required. This focused on a block of 240 x 230 km, centred on Weyburn. This dataset was completed by unpublished well control data using isopach, pressure, salinity and structural data. Potentiometric surfaces, structural surfaces and total dissolved solid concentrations for the Mississippian aquifer were also used (Czernichowski-Lauriol *et al*. 2001; Le Nindre *et al*. 2002).

The formation water in the Mississippian aquifer exhibits a significantly contrasted salinity field (Fig. 5). The deeper part of the basin reaches 310 g/l, whereas in southwest Saskatchewan it is influenced by a fresh/brackish water influx (20 g/l) from the northwest. The Weyburn oilfield is therefore located on a steep salinity gradient. This may have consequences for the long-term fate of CO_2 because the water density varies from 1010 to 1210 g/l, which can significantly affect regional hydrodynamics and the migration of CO_2. The solubility of CO_2 in aquifer waters is also strongly influenced by salinity, which can affect CO_2 solubility trapping and chemical reactions with the reservoir rocks and brines.

Assessments of the salinity gradient, and the associated density contrast of the formation water, implies the revision of the regional fluid flow which had been previously assessed from the potentiometric surfaces. Considering freshwater or environmental hydraulic head gradients lead to a different overall fluid flow orientation (Audigane & Le Nindre 2004). More refined studies at the scale of the 10 km buffer zone around the injection patterns would need to consider a multilayer aquifer system. The Midale Beds reservoir unit and the underlying and overlying strata should be studied in terms of characteristics such as permeability, pressure, salinity and thickness.

A comparison between analytical and numerical methods gave a west-east trend for the regional fluid flow within the Mississippian aquifer. A numerical model was then used for determining the streamline set leaving the Weyburn oilfield area (Fig. 5). The model effectively illustrates how the salinity gradient acts as barrier for fluid flow, and how streamlines are reoriented in order to avoid the high salinity gradient present in the aquifer. Assuming pure advective transport of dissolved CO_2, this modelling shows that natural aquifer flow is capable of transporting dissolved CO_2 approximately 25 km away from the Weyburn oilfield towards the east-northeast in 100 000 years; this equates to approximately 0.2 m/year (Audigane & Le Nindre 2004).

Geochemical modelling has indicated the main *in-situ* baseline chemical characteristics of the fluids in the Mississippian reservoir at the Weyburn oilfield. It has also enabled a reliable assessment of CO_2 solubility in the Weyburn brines. In the reservoir, dissolved organic acid anions have no significant effect on alkalinity, or the pH-buffering capacity. By contrast, sulphide (HS^-) concentrations due to the sourness of the Weyburn oil may represent more than 60% of the total alkalinity. Redox disequilibrium is present in the Mississippian aquifer waters at the Weyburn oilfield. Anthropogenic contributions due to oil production and EOR has amplified this tendency. Furthermore, the Mississippian waters are largely in thermodynamic equilibrium with respect to anhydrite, barite, calcite, dolomite and a silica phase with an apparent thermodynamic stability between that of chalcedony and quartz. Dissolved aluminium concentrations could be due to equilibrium with one of several mineral phases encountered in oil-bearing sedimentary basins, i.e., illite, kaolinite, K-feldspar or montmorillonite. It has proved difficult to demonstrate possible control of HS^- concentrations by a precise mineral reaction. Thermodynamic calculations including fugacity and activity corrections for non-ideality show that no more than 1 mole of CO_2 can dissolve in 1 kg of water for typical Weyburn reservoir brines with a salinity range from 35 to 110 g/l at 50°C and 14 MPa. The steep salinity gradient in the Weyburn oilfield area will inevitably affect the solubility, migration and reactivity of the CO_2, and this should be monitored and studied in the future.

Assessment of fluid-rock interactions in the Weyburn reservoir

During and after CO_2 injection operations, the presence of supercritical CO_2 will result in chemical disequilibria and the initiation of various reactions. It is important to understand the direction, magnitude and rate of such reactions. This is both in terms of their impact upon the ability of the Midale Beds and the overlying lithological units to safely contain the injected CO_2, and in terms of the longevity of CO_2 containment.

A three-pronged approach was used to study the impact of CO_2 upon reservoir geochemistry at Weyburn:

- Monitoring changes in reservoir fluids from deep boreholes.
- Laboratory experiments to simulate *in-situ* conditions within the reservoir.
- Predictive modelling of evolving conditions within the reservoir.

The approaches above are complementary, and by combining and assimilating all their results, it is possible to obtain a coherent assessment of the geochemical evolution at the Weyburn oilfield. Some of the key findings are outlined below; for a more detailed discussion see Riding & Rochelle (2005) and references therein.

Analysis of reservoir fluids and dissolved gases. Waters from the Weyburn oilfield were sampled in order to analyse for dissolved gases, major and minor elements, strontium isotope ratios and trace metals (Table 2). The disssolved gases CO_2, carbon monoxide (CO), helium (He), hydrogen (H_2), hydrogen sulphide (H_2S), methane (CH_4), neon (Ne), nitrogen (N_2) and oxygen (O_2) were analysed by gas chromatography. The key results were:

- Dissolved CO_2 generally increased from the Monitor 5 to Monitor 10 surveys (June 2002 to March 2004). This varied from 0–30 cm^3/l (at STP) in 2002, to 1–270 cm^3/l in 2003, to 20–470 cm^3/l in 2004. The maximum values were 0.028, 0.40 and 0.80 moles/l respectively, assuming a 16.5 MPa reservoir pressure.
- The CO_2 anomaly became wider in 2003; at this time it was no longer centred on a single well, but evenly spread throughout the entire Phase 1A CO_2 injection area that was investigated.
- Dissolved CH_4 increased from the Monitor 1 to Monitor 10 surveys (March 2001 to March 2004), varying from 0–0.35 cm^3/l.
- Dissolved He and H_2 decreased in the 2003 and 2004 surveys, after an initial increase in the injection area in 2002. This is probably due to the release of trapped H_2 and He from rocks during the initial reaction with the injected CO_2.
- The range of dissolved H_2S compositions showed a similar pattern of increase between the Monitor 1 and Monitor 10 surveys (March 2001 to March 2004). It varied from 0–3.5% to 0–5%. The H_2S anomaly shifted southwards between the 2002 and 2003 surveys, and was enlarged in 2003 throughout the Phase 1A injection area.

The analytical and sampling methods used in this phase of the project were used to give a preliminary indication of major changes in dissolved gases. An uncertainty is the precise behaviour of the fluids immediately before and during sampling. As the fluids rise up the borehole and are sampled, they will degas as they drop from the reservoir pressure of 16.5 MPa pressure to atmospheric pressure. As an approximation, it was estimated that 20–30% of the total dissolved gases were exsolved during depressurisation to atmospheric conditions, although an exact value for this was not determined. Future sampling procedures could be improved by the use of high-pressure steel isokinetic sample vessels, coupled to a miniseparator.

Strontium (Sr) isotope ratios ($^{87}Sr/^{86}Sr$). Strontium isotope ratios for produced fluids from the Midale Beds vary between 0.7077 and 0.7082 (Figs. 6, 7, 8, 9, Table 3). These are consistent with published values for Mississippian fluids and carbonate minerals, which are approximately 0.7076 to 0.7082 (Figs. 6, 7, 8; Bruckschen *et al.* 1995).

The Mannville aquifer has been used as a source of water for the water-flooding of the Weyburn oilfield since 1959. It is a Cretaceous sandstone, with $^{87}Sr/^{86}Sr$ values ranging between 0.7072 and 0.7073 (Jones *et al.* 1994). A small component of the water recycled during oil production is derived from this aquifer, and this is re-injected into the Midale Beds. Strontium isotopes were first analysed for this study in 2001, approximately 40 years after the start of water flooding operations. Despite this relatively long period of time, the Sr isotope ratios of the produced waters were closer to those of the Mississippian Midale Beds reservoir. The lowest Sr isotope ratios recorded may therefore represent higher levels of mixing of the Midale Beds fluids by re-injected Mannville aquifer make-up water, i.e. the highest injection volumes. The average Sr ratios and mass balance calculations suggest that as much as 25% of the produced fluids in 2001 were derived from the Mannville aquifer, although this appears to have decreased to 15% in 2003. It is significant that there is no known natural mixing between the Mississippian and Manville aquifers, because they are separated by a large aquitard (Fig. 9).

If the leaching of the Midale Beds oil reservoir increased, for example triggered by CO_2 injection, a progressive approach toward the pre-water-flooding Sr isotope baseline values may be expected. This would act to reverse the isotopic impact of 40 years of water flooding, which has resulted in the oilfield fluids being contaminated by up to 25% Mannville aquifer fluids. This appears to be happening in the oilfield, as an apparent progressive decrease in Mannville aquifer contamination was observed from 2001 to 2003. The Sr isotope ratios between 2001 and 2003 measured on monitoring campaigns Monitor 1, Monitor 5 and Monitor 8 are illustrated in Figs. 6, 7, 8. Therefore, the progressive approach of the $^{87}Sr/^{86}Sr$ values to the Midale Beds reservoir values points to zones of carbonate dissolution as a direct result of CO_2 injection. The hypothesis of carbonate dissolution caused by CO_2 injection is supported by other chemical data, as well as $\delta^{13}C$ data, for produced bicarbonate and CO_2 (Emberley *et al.* 2005).

Laboratory experiments and associated geochemical modelling

During and after CO_2 injection operations, the presence of supercritical CO_2 will result in chemical disequilibria and the initiation of various reactions. Some of these will be important in helping the CO_2 to dissolve into formation water (i.e. the 'solubility trapping' of Bachu *et al.* 1994). Other reactions will facilitate its precipitation as carbonate phases, i.e. 'mineral trapping' as defined by Bachu *et al.* (1994). Both these trapping mechanisms will reduce the potential of buoyancy-driven fluid flow and aid the long-term containment of CO_2.

Ascertaining the direction, magnitude and rate of CO_2-water-rock reaction was achieved via an integrated study where the results from laboratory experiments were coupled with predictive geochemical modelling. The experiments utilised well-characterised borehole material from the Midale Beds that was reacted with CO_2 and synthetic reservoir formation waters under simulated *in-situ* conditions (i.e. 60°C and 160 bar pressure). Samples of both the Midale Vuggy Unit and the Midale Marly Unit were studied. The Midale Vuggy sample had a composition that is approximated as: calcite (80%), dolomite (12%), anhydrite (4%) and silica/aluminosilicate minerals

(4%). The Midale Marly sample had a composition that is approximately: dolomite (60%), calcite (15%), anhydrite (10%), quartz (5%), K-feldspar (3.8%), albite (1.9%), siderite (0.6%) and kaolinite (0.5%).

Two types of experiments were undertaken:

- *Static batch experiments*. These used initially fixed quantities of either Midale Marly Unit or Midale Evaporite Unit samples, brine and CO_2 that were allowed to react for up to 6 months. This approach facilitated the development of steady-state conditions (Rochelle *et al*. 2002; 2003*a, b*, 2004*a*).
- *Flow experiments*. These used samples of the Midale Marly Unit and continually passed fresh CO_2-rich formation water through the samples. This approach tended to maintain 'far from equilibrium' conditions, maximising the degree of rock reaction (Bateman *et al*. 2004; Olsen & Stentoft 2004).

These different approaches simulated different parts of the storage system at Weyburn. For example, conditions of relatively high fluid flow will exist close to the injection and production wells. Conversely, further from the wells, groundwater flow will be controlled by regional-scale flow regimes, which are likely to be slow or near static.

The amounts of CO_2 available for reaction were maximised by making the synthetic formation waters CO_2-saturated. This was done in part to facilitate the observation of geochemical changes, and in part because it was easier to maintain experimentally. However, it also ensured that the study considered a maximum reaction-limiting case, though it is recognised that variable degrees of CO_2 saturation will exist in the Weyburn reservoir.

Generally, there are many similarities between the results of the batch experiments reacting samples of the Midale Vuggy Unit and the Midale Marly Unit, which reflect the similar reaction processes involved. The dissolution of CO_2 acidified the brine and caused the dissolution of calcite:

$CaCO_3 + CO_2 + H_2O \Rightarrow 2HCO_3^- + Ca^{2+}$
(calcite)

This reaction could be followed in the experiments through decreases in pH and increases on bicarbonate (HCO_3^-) and calcium concentrations (Fig. 10), and was subsequently identified in scanning electron microscope (SEM) observations as dissolution features on the reacted samples. Magnesium concentrations remained relatively unchanged in the batch experiments (Fig. 11), suggesting that, at most, only limited dolomite dissolution had occurred. Other divalent metal ions that were present as trace components in the carbonates showed various degrees of reaction, though Sr showed consistent decreases indicating its probable precipitation in a secondary phase. Increases in silicon (Si) concentrations indicated that some of the silicate phases in these carbonate-dominated rocks were also dissolving. However, even after five months reaction, Si concentrations had not achieved steady-state concentrations indicating the generally slower rate of silicate phase dissolution compared to carbonate phases.

There were also significant mineralogical differences between the results of the batch experiments. The main differences were linked to increased dissolution of calcite, dissolution of anhydrite, and precipitation of gypsum in the Midale Vuggy Unit experiments, which was not observed in the Midale Marly Unit experiments.

After four weeks of reaction with CO_2, euhedral prismatic gypsum crystals up to 500 µm long formed on samples of the Midale Vuggy Unit below the water line (Fig. 12), and by 8 weeks these were 2.5 mm long. The precipitation of gypsum could be followed during the experiments through the decrease in dissolved sulphur (S).

Flowing experiments were only conducted with samples of the Midale Marly Unit, but used samples of both whole core and disaggregated material. Both showed similar results, with pronounced dissolution of minerals at the inlet end of the equipment, where the CO_2-saturated brine first encountered the rock. Unlike the static batch experiments, the flowing experiments also showed noticeable release of magnesium (Mg) to solution, suggesting that dolomite dissolution was occurring:

$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \Rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$
(dolomite)

Both types of flowing experiments showed increases in porosity after reaction, but the ones using intact core also showed increases in permeability. The flowing experiment using disaggregated material also showed an apparent increase in clay content where most dissolution occurred. This clay was not produced during the experiment, but was incorporated within the original dolomite, and was probably a result of the clay being released following carbonate mineral dissolution. Although migration of fine material was observed, no evidence of pore blocking was found, although the potential for this appears to exist within the Midale Marly Unit.

Processing of the experimental data by geochemical computer models was undertaken using PHREEQC (v. 2.8) and SCALE2000 (Azaroual *et al.* 2004a). The modelling methodologies used, including all relevant data, were fully described in Azaroual *et al.* (2004*b*). The degree of fluid-rock reaction was followed by considering the saturation index (SI) of various minerals. For example, the SI of dolomite in the Midale Marly Unit batch experiments (Fig. 13) was initially low (-4.75, i.e. well below saturation). However, this increased rapidly and in less than 200 hours it had reached +0.5 (i.e. rapid fluid-rock reaction had made the solution just saturated with respect to dolomite). This rapid attainment of saturation explains why the dissolution stopped, and Mg concentrations remained relatively unchanged (Fig. 11). Calcite also reacted rapidly, but it took about a month for it to reach saturation in the batch experiments, allowing significant concentrations of calcium to build up in solution. The presence of such high calcium concentrations, together with sulphate (SO_4^{2-}) ions present in the Weyburn brine (there are 3 to 4 g/l of SO_4^{2-} ions in the geochemical baseline fluids) helped facilitate the precipitation of gypsum. However, the overall equilibrium of calcium sulphate ($CaSO_4$) minerals is also influenced by the amount of water present:

$CaSO_4{:}2H_2O \Rightarrow CaSO_4 + 2\ H_2O$
(gypsum) (*anhydrite)*

For $CaSO_4$ minerals, if the activity of water is higher than approximately 0.8, gypsum will precipitate. This matches well with results of the relatively water-rich laboratory experiments where the water activity was 0.936, and where gypsum precipitated (Fig. 14). This mechanism could be important in the Weyburn reservoir, with anhydrite possibly favoured in areas of lower water activity (e.g. where there is higher salinity), and gypsum favoured in areas of higher water activity (e.g. where there is lower salinity).

The geochemical modelling was extended to consider potential of long-term storage of CO_2 in the Midale Beds reservoir at Weyburn, and to interpret if geochemically reactive zones exist above and below the reservoir. The effect of CO_2 injection into the Midale Marly Unit was modelled for a simulated 10 000 years under *in-situ* conditions. This modelling took into account mineral dissolution/precipitation reaction kinetics and coupled them with 1D advective/diffusive/dispersive transport processes (Azaroual *et al.* 2004*a, b*). Many long-term geochemical modelling scenarios were carried out using flow rates from 0.25 to 50 m/year. The predictions showed that 'anorthite' (as an analogue for the calcium (Ca) rich component of feldspar) would be completely exhausted from the simulated systems over scales from 400-4 000 m, depending on the flow rates, after 10 000 years of reaction. Dawsonite was predicted to precipitate over all the spatial scales considered. However, calcite was predicted to dissolve where CO_2-rich fluids first contacted the rocks, whereas anhydrite was predicted to precipitate. Albite, illite and K-feldspar were predicted to dissolve throughout the simulations, not achieving thermodynamic equilibrium, even after a simulated 10 000 years. As a consequence of these dissolution/precipitation reactions, it was predicted that the porosity throughout the modelled region would increase over 10 000 years.

Microseismic monitoring

Passive microseismic monitoring is used to map rock fracturing induced by fluid injection in EOR, by hydraulic stimulation, or by reservoir compaction phenomena linked to hydrocarbon production (Maxwell *et al.* 2003). This was undertaken at Weyburn to assess any seismic hazards caused by CO_2 injection, and to monitor the spread of injected CO_2 via fracturing and fracture reactivation induced by local overpressure within the reservoir.

The Weyburn oilfield was found to be microseismically inactive during a surface seismic survey carried out during September 2000, and during a crosswell seismic survey in 2002. In August 2003 a microseismic monitoring tool was installed in an abandoned well, number 101/06–08, located to the southeast of the Phase 1A injection area within the Phase 1B injection area (Fig. 4). Microseismic data were recorded from September 2003 to March 2004. The seismic cable comprises 8 tri-axial geophones with a resonance frequency of 20 Hz, which were cemented at 25 m intervals between 1356 m to 1181 m in the observation well. Three surface calibration shots were used to orientate the horizontal sensors and to check the system. Sixty-two microseismic events were recorded during the six-month monitoring period. The magnitude of miocroseismic events recorded ranged from -3.5 to -1, which does not exceed magnitudes associated with water flood or gas injection in similar oilfields. The average velocity model used for hypocentre determination was calculated using a representative dipole sonic log. Errors in location range from 30 m to 400 m, depending mainly on the quality of P- and S-wave onsets. Analysis of the main characteristics of the waveforms indicated that three types of events were recorded:

- Eighteen of the events were located close to the base of the nearby horizontal production well 191/11–08, approximately 150 m west of the observation well 101/06–08. These occurred during two periods when production was shut down. This microseismicity is believed to relate to pressure build-up within the formation.
- Twenty-one microseismic events were recorded close to the bottom part of injection well 121/06–08, located 51 m west of 101/06–08, corresponding

mainly to completion activities and perforation shots carried out during late November 2003.

- The remaining events were recorded prior to the start of CO_2 injection. Waveform spectra are characterised by relatively low frequencies with a peak near 20 Hz. Emergent P- and S-phases make it difficult to obtain accurate locations for these. It is suggested that these events were caused by fluid flow within or close to well 191/11–08.

These results demonstrate unequivocally that recording microseismicity in an oilfield CO_2-injection operation is technically feasible. Because the injection of CO_2 has only recently been started, no microseismicity linked directly to the spread of CO_2 within the reservoir has been unambiguously identified. Nevertheless, different types of events have been recorded and appear to be related to production or completion activities. Careful analysis of waveforms, event locations and production data will be necessary to identify events induced by CO_2 injection. With respect to seismic hazards due to injection, the microseismicity observed to date does not exceed magnitudes associated with water floods or gas injection in other monitored oilfields.

Characterisation of the reservoir overburden

This section considers the principal seals above the reservoir and till in the Weyburn area. Reservoir seals comprise the primary caprocks immediately above the reservoir and other potential stratal seals overlying the reservoir. Moreover, the Weyburn area is covered by a thick till succession which is the final barrier in the geosphere for any potential CO_2 leaking from the reservoir.

The units acting as immediate barriers to the Midale Beds reservoir units are both Mississippian anhydrites. At the base of the Midale Vuggy Unit (i.e. immediately below the reservoir rock), the Frobisher Evaporite acts as a barrier to flow. However, this anhydrite unit is not continuous, especially south of the field. At the top of the Midale Marly Unit (i.e. immediately above the reservoir rock), the Midale Evaporite is the first effective seal for parts of the Weyburn area. At the boundary between the Mississippian subcrop and the sub-Mesozoic unconformity, a thin anhydritised zone is present. This was formed by diagenetic migration of anhydrite along the unconformity surface. From cores that include the Mississippian–Triassic boundary, this zone appears to be discontinuous. These two seals were described by Rott (2003), Nickel (2004) and Nickel & Qing (2004).

The Triassic Lower Watrous Formation and the Middle Jurassic Upper Watrous Formation seal the sub-Mesozoic unconformity (Fig. 15). Although the underlying and overlying Frobisher and Midale evaporites respectively bound the Midale Beds reservoir unit, they may not be sufficient to act as an effective seal against the upward migration of CO_2 for the entire Weyburn area. The Watrous aquitard, *sensu lato*, which includes the clastic Lower Watrous Formation and the evaporitic Upper Watrous Formation, is the first main regionally extensive barrier to prevent CO_2 escape from the reservoir. Therefore, diffusion and associated reaction processes through this horizon must be considered (Fig. 16).

The remainder of the Mesozoic succession that overlies the Watrous Formation contains several thick and extensive shale units that are assumed to act as efficient barriers to vertical CO_2 migration. These are:

- The Bearpaw Formation shales (Upper Cretaceous) overlying the Belly River/Judith River aquifer (Cretaceous).
- The shales of the Colorado Group (Cretaceous) above the Viking Sandstone/Newcastle aquifer (Lower Cretaceous).
- The Joli Fou aquitard (Lower Cretaceous) of the Colorado Group (Cretaceous) overlying the Mannville Group aquifer (Lower Cretaceous).
- The Vanguard Group aquitard (Upper Jurassic) underlying the Mannville Group aquifer (Lower Cretaceous).

The Colorado Group and Bearpaw Formation shales are the principal barriers, with a thickness of several hundreds of metres each.

Sealing properties of strata above the stored CO_2

Quantification of the sealing properties of the caprocks above the Weyburn reservoir considered several sources of information. The first of these were observations of the natural system at Weyburn, either the caprocks themselves, or the chemistry of porewaters from aquifers between different caprocks. The second source of information came from transport (diffusion) modelling of scenarios similar to that shown in Figure 15. The final source of information came from geochemical interactions between CO_2-rich fluids and rock, derived from laboratory experiments and predictive modelling. However, the availability of samples and data limited what could be done on each rock type. Results are discussed below, first for the regionally extensive Watrous Formation, then the locally-extensive Midale Evaporite, and finally for other younger formations.

The Lower Watrous Formation

The Lower Watrous Formation was deposited on a subaerial shelf and is heterolithic. It is fine-grained with clasts of granite with micrite lithoclasts in a clayey-dolomitic matrix. Cements are dolomicrosparite, calcisparite and anhydrite; the anhydrite may replace the carbonate and plugs the remaining porosity. The mineralogical paragenesis was relatively constant, but mineral proportions vary rapidly laterally and vertically within a narrow range. In the potentially most porous horizons, porosity measurements indicate a maximum total porosity of about 11%, with modal pore-throat sizes of 1–10 µm. At a larger scale, a mean effective porosity of 4% and a mean permeability of 0.8 mD were assigned to the formation as a whole (Czernichowski-Lauriol *et al*. 2001).

No significant fractures were observed in the Lower Watrous Formation, although minor small (1–2 mm) offset microfractures are present in the muddier units. All the facies have carbonate and/or anhydritic cement, suggesting the Lower Watrous Formation in southeastern Saskatchewan has the potential to act as an effective seal against cross-formational fluid flow. In particular, a fine-grained unit, informally identified as the 'Upper Muddy Unit', appears to especially impermeable.

Diffusion modelling was undertaken to quantify the sealing efficiency of the Watrous Formation to CO_2. This unit was modelled as if it was a complete caprock with an estimated thickness of 8 m. For the modelling, a 10 m section was considered, which consisted of 10 cells each 1 m thick. One dimensional diffusional modelling was run for a simulated 5 000 years (Riding and Rochelle, 2005). During this period, CO_2 was present at the base of the Midale Evaporite unit at a constant fugacity corresponding to a pressure of 150 bar (Duan *et al*. 1992). Based on the calculated reactivity, diffusion modelling gave an estimate for three parameters. These are the progression of the dissolved CO_2 front in the caprock, the thickness of the lower section of the caprock affected by geochemical reactions and the potential porosity change, based on a molar volume balance calculation. In the basal metre of the caprock, some carbonate dissolution is expected to occur, leading to a significant increase in porosity. This is approximately +0.3 % over several thousands of years. Several metres higher in the caprock, some feldspar alteration to clay minerals is likely to occur; this by contrast induces a marked porosity decrease. This decrease is <0.2 % over several thousands of years. The impact of geochemical interactions that occur as a consequence of dissolved CO_2 diffusion into the base of the Watrous Formation, is therefore deemed not to be significant in terms of the overall integrity of the caprock.

Geochemical reactions of the Midale Evaporite caprock

Reactions of CO_2 with the lower part of this unit were studied because it immediately overlies stored CO_2 in the Weyburn Field. The samples were massive, locally anhydritised, dolomitic limestones (Springer *et al*. 2002). Thin sections and back-scattered electron micrograph images of the Midale Marly M1 Unit/Midale Evaporite Unit transition indicate non-porous to faintly porous dolomites, comprising crystals up to 10 mm in diameter that have been locally replaced by anhydrite nodules and/or single-crystals of anhydrite. Scattered euhedral crystals of fluorite are common. The samples of the Midale Marly M1 Unit/Midale Evaporite Unit transition exhibit a scale-dependant variation in the dolomite/anhydrite ratios from plug sample to full core sample, because the dolomite appears as randomly-scattered crystal aggregates. The crystals of euhedral fluorite and alkali feldspar form up to around 20% of the anhydrite volume. There is approximately 4% clay in the Midale Evaporite Unit.

Core analysis indicates that the Midale Marly M1 Unit/Midale Evaporite Unit transition zone is of poor quality in terms of caprock seal capacity (Table 4). The average gas permeability is 0.7 mD and the expected liquid permeability is approximately 0.1 mD at reservoir conditions. This is significantly lower than levels typically recorded from good quality caprocks of less than 1 mD. Samples having better caprock properties, presumably from a higher level in the Midale Evaporite Unit, were not analysed in this project.

A two-pronged approach was used to study the impact of CO_2 on the caprock:

- Laboratory experiments to simulate *in-situ* conditions within the caprock. These provide detailed, well-constrained quantitative information to aid modelling studies.
- Predictive modelling of evolving conditions within the Midale Evaporite Unit. This uses data from the above experiments to improve, constrain, and build confidence in geochemical models of the shorter-term evolution of the Weyburn reservoir system. These can then be extended to predict impacts of CO_2 in the longer-term, after injection operations have ceased.

Experiments. Samples of Midale Evaporite Unit core were reacted with CO_2 and synthetic reservoir formation waters under simulated *in-situ* conditions (i.e. 60°C; 160 bar) for up to six months (Rochelle *et al*. 2002; 2003*a, b, c*; 2004*a*). This approach facilitates the development of steady-state conditions; i.e. towards a point where fluid composition is stable, and where the rates of dissolution/precipitation reactions fall towards zero. The evolution of a selection of solutes was followed during the experiments. Relative to the non-reacting ‘baseline’ experiments, it was found that the impact of CO_2 was to:

- Increase the concentrations of Mg (Fig. 11), manganese (Mn), Si, HCO_3^- and possibly Al.
- Decrease the concentrations of total sulphur (S) and pH values.
- Have little impact on the concentrations of Ca (Fig. 10), Sr and barium (Ba).

Many of the solutes, most notably Mg, reached steady-state conditions within about one month, indicating relatively rapid control by dolomite dissolution. It was noted that the changes in major element chemistry are different to those found in the reservoir rock (Midale Marly Unit and Midale Vuggy Unit) experiments. This suggests that one or more different reaction mechanisms were operating between the different studies. Although aluminosilicate minerals comprise a small proportion of the rock, dissolution/precipitation reactions appeared to be happening slower than carbonate mineral reactions. Silicon concentrations appeared not to reach steady-state conditions, even after six months reaction.

Generally, there was relatively little petrographic evidence for dolomite corrosion even though significant changes in dissolved Mg concentrations were observed. However, this is not unusual given the relatively small amounts of dissolution that would have been needed to cause the observed increases in Mg concentrations. Also, it is difficult to identify small amounts of corrosion on grains that have already undergone significant pitting. Anhydrite was slightly corroded in some experiments using CO_2-rich pore water. Euhedral, elongate prismatic gypsum crystals may have formed at the expense of anhydrite. However, gypsum may also have been favoured by the release of Ca from dolomite dissolution, which with the relatively high sulphate concentration would have caused oversaturation with respect to gypsum. Crystals of gypsum were particularly well developed on the external surfaces of the core blocks in the CO_2-rich experiments, and were up to 2 mm long after 4 weeks reaction.

Modelling. The Midale Evaporite Unit experiments used the highest salinity brines in this study (c. 115 g/l). The simplified average mineralogy of the Midale Evaporite Unit used in the modelling is as follows: dolomite (60%), quartz and aluminosilicates (34%), anhydrite (5%) and calcite (1%). Chalcedony, dolomite and sulphates (anhydrite and gypsum) achieved thermodynamic equilibrium relatively rapidly (Fig. 17). Calcite shows a stationary state, as in the case of the Midale Marly Unit experiments, giving a constant value of calcite saturation index (SI approximately -0.5) for the whole of the experiment. Although this mineral is a minor component of the Midale Evaporite Unit, it still appears to show similar behaviour to that in the Midale Vuggy and Marly units (see above). Chalcedony remained at thermodynamic equilibrium for the entire experiment.

This modelling of a small-scale system was extended to the field scale through modelling of the diffusion of CO_2 into the caprock. The modelled reactivity due to the diffusion of dissolved CO_2 into the base of the Midale Evaporite Unit resulted in some carbonate dissolution in the lowermost metre of that unit. Higher in the section, alteration of feldspars dominates the reactivity. Porosity changes due to this reactivity were minor, with a predicted increase in porosity in the lower metre of approximately

0.4% after 5 000 years. Overall reactivity is of the same order as for the Watrous Formation.

Other formations

Significant salinity differences between the underlying and overlying aquifers indicate that the Watrous Formation and Vanguard Group aquitards (Triassic and Jurassic) are effective seals, at least locally (see Fig. 9 for hydrostratigraphical delineation). However, the sealing ability of these aquitards is not so well-defined throughout the Williston Basin, due to lack of data and facies complexity. Nevertheless, in peripheral areas where they are thin, and probably with enhanced permeabilities caused by local variations in lithology and fracturing, they allow discharge of the confined Mississippian aquifer.

The similarity in hydraulic heads and salinity distributions in the overlying Mannville Group and Viking aquifers is inconclusive in establishing the coherence of the intervening Joli Fou aquitard (Lower Cretaceous) (Audigane & Le Nindre 2004). However to the south, the Joli Fou aquitard is absent. The Mannville Group and Viking sandstones laterally form a single unit, the hydrogeologically continuous Dakota Sandstone.

The Cretaceous aquitard system overlying the Viking Sandstone mainly comprises thick shale successions within the Colorado and Montana groups. These include the Bearpaw, Pierre, Belle Fourche, Carlisle, and Mowry shales. This aquitard also includes closed or minor aquifers. It has a strong confining effect due to its shaly nature and to the vertically inward transient flow that acts as a sink, thereby precluding cross-formational flow (Audigane & Le Nindre 2004).

Characterisation of till in the Weyburn area

The Weyburn area is blanketed by a succession of till deposits up to c. 30 m thick (Christiansen 1992). The till belongs to the Battleford Formation of the Saskatoon Group and is of Late Pleistocene age. It forms part of a proglacial, glacial and nonglacial succession that has been subdivided largely on carbonate content (Christiansen 1992; Maathuis 2003). The tills sampled were found to vary slightly in grain size and degree of sorting and they contain laterally discontinuous sandier interlayers. However, geochemical, mineralogical, palynological and sedimentological evidence strongly indicates that the material in the Weyburn area is from a single till sheet (Pearce *et al.* 2003; Riding & Rochelle 2005). The till succession in this area is of interest because it contains locally important potable water resources. It is also the final barrier to migrating, deeply-sourced CO_2, before it reaches the regolith, biosphere and atmosphere.

Four shallow boreholes, numbered A8, A13, B23 and B46, were drilled at Weyburn. The boreholes were drilled immediately west of the oilfield at 589836.9E/5481156N, 589716.1E/5481155N, 589487E/5479941N and 588825.9E/5479939N respectively; their depths are 12.23 m, 13.73 m, 16.73 m and 22.86 m respectively (Maathuis 2003, figs. 1, 5-8; Pearce *et al.* 2003). They were located adjacent to some of the long-term near surface (1-2 m) radon (Rn) monitoring probe sites (Beaubien *et al.* 2004). These included sites where monitoring indicated significant advective gas flow as well as sites where only background diffusive flow was indicated. Knowledge of variations in Rn soil gas concentrations will provide an understanding of potential CO_2 migration in the till.

The grain sizes of the till samples are typical of those previously studied from other parts of southern Saskatchewan (Christiansen 1967). Clast numbers and types were counted at the surface during 2003. There did not appear to be any systematic difference in the rock types represented across the area of the grid. However, clast numbers vary considerably, consistent with the heterogeneity of the till. They are generally more abundant in the eastern half of the grid, but there are coherent patches of higher clast density throughout the area. There appears to be some consistency between the observed gas velocities and the grain size data, when the basal silt/clay samples are excluded. Borehole B23, with the highest velocities, has the coarsest average grain size, and hence probably the highest permeability, whereas the 'zero reference' borehole site (A8) and the lower velocity site (B46) have much finer average grain sizes and probably lower permeabilities. The data obtained so far suggest that sediment texture, and hence permeability, is an important control on Rn concentrations and gas velocities. This varies seasonally according to prevailing ground conditions and, in particular, soil moisture levels.

Characterisation of the engineered seals

The long-term integrity of engineered seals (i.e. cements) around boreholes is of crucial importance for CO_2 containment. Laboratory experiments were undertaken to assess the potential for geochemical changes resulting from the reaction of CO_2 with borehole two cements typical of those used at the Weyburn oilfield (Rochelle *et al*. 2004*b*). The cement mixtures tested are Portland cement with certain additives, and were received from BJ Services Company Canada. The higher density 'tail cement' used at the base of the well casings contains small amounts of a fluid loss additive and 2% of calcium chloride ($CaCl_2$), whereas the lower density 'fill cement' contains small amounts of a dispersant. The pressures and temperatures used within the experiments were representative of *in-situ* conditions at Weyburn. The experiments were of relatively short duration (14 days), so only limited reaction was observed. However, enough reaction took place to provide some insights into the reactions of the borehole cements with CO_2. No significant changes in the size of the cement blocks were found after this (albeit relatively short term) exposure. Although this does not preclude the possibility that carbonation shrinkage will occur, it does provide some evidence that this process might not be an important issue over shorter timescales. However, the cement blocks gained significant amounts of weight upon exposure to CO_2, with the fill cement having a greater weight increase compared to the tail cement (Table 5). However, for both fill and tail cement, greater weight gain occurred with supercritical CO_2 as compared to dissolved CO_2. Given that the blocks did not change in size, they must have increased in density. This appears to have been associated with a decrease in porosity in the outer parts of the blocks, where a carbonated layer formed. It is possible that such layers may be beneficial in that they might act to protect borehole cement against long term complete carbonation. Some simple flexture tests were carried out to assess the cement strength changes following carbonation. It was noted that the fill cement was approximately twice as strong as the tail cement, both before and after exposure to CO_2. However, no significant changes in the tensile strength of the cement monoliths were noted as a result of being exposed to CO_2.

Soil gas monitoring at Weyburn

Introduction

The monitoring of gases within the soil above a store of injected CO_2 is important to verify that gas is remaining underground. Although the absence of deep-sourced CO_2 within the soil does not prove that injected CO_2 is not migrating at depth, it does prove that it is not escaping to the surface. Being able to demonstrate that injected CO_2 is not leaking to the surface is critical for regulatory issues and public acceptability. It is important that baseline (i.e. pre CO_2 injection) data is gathered as a comparison for further monitoring campaigns.

Soil gas concentrations and flux monitoring (surface monitoring) were carried out from 2001 to 2003 in and around the Phase 1A injection area of the Weyburn oilfield (Jones *et al.* 2003; Strutt *et al.* 2003*a*, *b*; Beaubien *et al.* 2004) (Fig. 18). The objectives of this work were to:

- Establish baseline soil gas values using grid sampling and profiles, and to compare these results with future datasets.
- Evaluate natural variations in soil gas, including seasonal effects.
- Understand geochemical reactions and gas flow pathways in geological successions.
- Identify sites of higher gas flux that may be indicative of deep gas escape.
- Enable long term monitoring to evaluate possible escape of injected CO_2.
- Address possible public concerns over geological storage of CO_2.

Three principal techniques were used to address these objectives:

- Analysis of the concentrations of various gas species in the pore spaces of the shallow unsaturated soil horizon (soil gas).
- Measurement of the mass transfer rate of CO_2 across the soil-atmosphere interface (gas flux).
- Long-term monitoring of Rn flow rates, as a proxy for CO_2, using probes buried for up to a year to a depth of 2 m in the soil.

Carbon dioxide is highly soluble and can be consumed via acid-base reactions. Therefore its movement, if any has occurred, may be attenuated during the short period of the present monitoring. Furthermore, the interpretation of CO_2 data is complicated by the fact that this gas is involved in metabolic reactions, both via soil microbes and plant roots. Because of these possible sources and sinks of CO_2, a large suite of other soil gas species were analysed which might help define possible flow paths that CO_2 may follow in the future or help resolve the origin of the present CO_2 anomalies. These included less reactive gases associated with the reservoir, which could be used as tracers of deep and/or rapid flow, such as He, CH_4, and Rn, as well as gases that might be involved in shallow biological reactions such as ethylene (C_2H_4) and O_2.

Preliminary baseline soil gas data were collected in the summer and autumn of 2001, above the Phase 1A injection area of the Weyburn oilfield. At each site a hollow stainless steel probe was pounded into the soil to a depth such that atmospheric gas contamination is precluded (Hinkle 1994). This was estimated as being between 0.6 m and 0.90 m at Weyburn. *In-situ* monitoring of CH_4, CO_2, CO_2 flux, O_2, ^{222}Rn and thoron (^{220}Rn) was carried out on a 360 point grid at 200 m spacing, with points extending to the southwest of the initial injection area (Figs. 18, 19). Soil gas samples were also collected in evacuated stainless steel canisters for laboratory analysis of He, light hydrocarbons, N_2, O_2 and S species using gas chromatographs and mass spectrometers as appropriate. After a rapid appraisal of the initial grid results, data were collected in the autumn of 2001 on traverses of more closely spaced sampling points (25 m apart) that crossed anomalies seen on the grid (Profiles A to F on Fig. 20). Selected CO_2 and radon anomalies on these profiles were investigated in more detail for signs of natural pathways for deep gas escape. Continuous radon monitoring probes were installed at sites where He and Rn data, in particular, indicated the potential for deep gas migration.

The 360-point sampling grid and most of the more detailed profiles were repeated in the autumns of 2002 and 2003. The Rn monitoring probes have been in operation virtually continuously since the autumn of 2001.

Results

Significant changes were seen in CO_2 concentration and surface flux levels between each of the three datasets (Fig. 21; Beaubien *et al.* 2004). Higher values were seen during the growing season during July 2001. Lower levels were apparent in autumn 2002 and values were further reduced in autumn 2003, when conditions were cooler and the growing season almost over. These results suggest the importance of shallow biological reactions that produce CO_2 as a metabolic by-product. In contrast, the ^{222}Rn and ^{220}Rn data were found to be similar for the three years. These gases were studied primarily because they have a short half-life, for example 3.5 days for ^{222}Rn. Thus the occurrence of a significant anomaly may indicate transport of deep ^{222}Rn carried by a stream of CO_2 along a highly permeable pathway, such as a fault. The occurrence of gas anomalies, including Rn, over faults is well established (Ball *et al.* 1991; Duddridge *et al.* 1991; Klusmann, 1993; Atallah *et al.* 2001). Instead, the relatively constant distribution of ^{220}Rn and ^{222}Rn during periods when the CO_2 concentration and flux was successively reduced implies that these gases have a shallow *in-situ* origin.

The temporal variation of CH_4 was significantly different. Although there was a decrease in outlier values with each successive campaign, overall there appeared to be a slight increase over the same period. This trend may be due to the seasonal drying of the soil and subsequent increase in soil air permeability. This resulted in the greater downward diffusion of atmospheric air with its constant methane concentration of approximately 2.5 ppm. The distribution of ethane (C_2H_6) was similar to that of CH_4, although the difference from year to year with respect to outliers is more pronounced, while the distribution of the bulk of the samples is more constant. The variations in C_2H_4 and propane (C_3H_8) were markedly similar to those of CO_2 and CO_2 flux, with both the outliers and bulk of the samples decreasing significantly from year to year during each successively later season. This also implies a shallow biological origin for these gases. As the correlation between soil gas CO_2 and these two hydrocarbons is low, it is likely that they are produced via different metabolic pathways.

The spatial distributions of CO_2 and CO_2 flux showed a similar pattern and a reasonably good correlation from year to year (Fig. 21). The majority of the anomalies are in areas that have extensive ephemeral surface-water bodies. Some of these water bodies are elongate and were mapped as surface lineaments in a separate air-photo interpretation study by Mollard and Associates. Although one interpretation of these features was that they could represent the surface expression of deep faults, present data appears to indicate that the elevated values in these areas are more likely due to shallow biological reactions in the moist, organic-rich soil. There was no clear correspondence between the soil gas CO_2 anomalies and the location of the CO_2 injection wells.

The distribution of ^{220}Rn and ^{222}Rn anomalies lacked any clear elongated trends that might indicate the presence of a gas permeable fault or fracture system. Although ^{222}Rn had far fewer anomalies than CO_2, some of the high ^{222}Rn values correspond with CO_2 highs, however there are also many CO_2 anomalies that do not have a matching ^{222}Rn anomaly. The distribution of ^{220}Rn, by contrast, is different from both of these gases. Continuous profiling by gamma spectrometry has not, so far, shown any marked anomalies in uranium or thorium series radionuclides that might be linked to Rn escape through a fault or fracture system.

Carbon dioxide highs on the detailed profiles are matched by O_2 lows, whereas N_2 remains essentially constant. The same relationship is also clear in data for the grid (Fig. 22). This provides strong evidence for a biogenic origin for the CO_2 via reactions in which O_2 is consumed. If significant migration of CO_2 from depth were occurring, both O_2 and N_2 would be diluted as CO_2 levels increased, similar to areas of natural deep CO_2 escape such as Cava dei Selci in Italy (Fig. 22).

Three soil gas samples were collected in the summer of 2001 for the analysis of $\delta^{13}C$ in CO_2 in locations with elevated CO_2 concentrations, in order to better understand the origin of the gas. The isotopic values obtained were all well within the range of those to be expected from soil gas CO_2 produced by microbial or root metabolism of organic matter from local plants. However, it is difficult to draw firm conclusions from this small number of samples.

In 2003, a control or background area at Minard's Farm was sampled for the same suite of gases 10 km to the northwest of the oilfield (Fig. 19). It has similar topography, land use and soil composition to the main sampling grid. Field gamma spectrometry indicated that soil composition was comparable, at least with respect to potassium, Uranium and thorium. This site was in an area largely undisturbed by oil exploitation, allowing a general background comparison to the main grid dataset. There were 35 sample locations on a 7 x 5 point grid at the control site with 100 m spacing, plus two additional sites. The soil gas results from the control area were generally similar to those from the main grid on the oilfield. This suggests that there is no general elevation of CO_2 levels in the soil covering the injection area, and thus further supporting the lack of any escape of deep CO_2 in the main sampling area.

Together with the control site at Minard's Farm, five zones of possible CO_2 leakage were also surveyed and sampled. These are two profiles across a river lineament that may be associated with deep faulting (marked 'G' and 'H' in Fig. 19), two decommissioned oil wells (marked '2:25' and '12:18' in Fig. 19) and one site that overlies a deep salt collapse structure.

A northeast-southwest trending river lineament was identified from air photos and satellite imagery is situated immediately north of the main grid (between 'G' and 'H' in Fig. 19) and generally follows an incised river valley. Although such lineaments may reflect near surface features, there is some correspondence of their location and direction with faulting in the Midale Beds (Beaubien *et al.* 2004). This suggests they may be a surface reflection of deep fracturing and thus have the potential to act as pathways for deep gas escape. Anomalous CO_2 was associated with the valley floor and minor depressions, where there was lush vegetation and a coincident depletion of O_2. The relationship between CO_2 and other gases was variable. One CO_2 anomaly had a coincident He anomaly, but others had no related He feature. In general, CH_4 and ^{222}Rn were low when CO_2 was higher. Therefore the evidence is consistent with biogenic CO_2, but there are features, such as the coincident He/CO_2 anomaly, and rising He levels on one traverse, that merit more detailed study.

Two perpendicular profiles of 10 sites at 25 m spacing were sampled for soil gas over the mapped centre of a salt collapse feature that had been identified in the Prairie Evaporite Formation (Devonian) from seismic data. Background values of all gases were seen over the salt collapse feature except for some small He anomalies that are difficult to interpret because there are no related features for other gases.

Measuring soil gas around the two decommissioned oil wells allowed borehole integrity to be investigated. A 16-site grid was surveyed around each well. One well (12:18; Fig. 19) had been completely abandoned and the other was suspended due to failed casing. The well with failed casing (12:25; Fig. 19) had weakly anomalous CO_2 at two sites but this was unmatched for other gases. The abandoned well 12:18 had background CO_2 values. The statistical populations of CO_2 and ^{222}Rn were generally higher for the suspended well. By contrast, those for CH_4 and C_2H_6 were higher for the abandoned well, as compared to the main grid, although all individual values lay well within the range observed for the grid. There was a single He anomaly at the abandoned well site. The lack of correspondence between anomalies of different gases does not support significant leakage from depth along the well, but the results suggest more detailed follow up would be desirable.

Electronic Rn sensors with internal memory were installed between 1-2 m depths at six sites in September 2001, and data have been recorded for extended periods since. The sites were selected from the detailed soil gas profiles located across ^{222}Rn and CO_2 anomalies seen in the initial main grid data (Beaubien *et al.* 2004). Detailed CO_2, He, ^{220}Rn and ^{222}Rn measurements were made around specific anomalies and Rn probe sites chosen that reflected potential deep gas escape (He anomalies, higher ^{222}Rn) as well as ‘background’ sites for comparison. The clearest anomalies on two traverses with similar soil and crop types (mainly wheat) were chosen (Jones *et al.* 2003; Beaubien *et al.* 2004; Riding & Rochelle 2005).

Measurements of ^{222}Rn concentration, temperature and atmospheric pressure were made every hour. The datasets were merged and plotted in order to demonstrate gas transport mechanisms (e.g. diffusion and advection) and rates. The data show seasonal variations in ^{222}Rn concentrations, which were plotted against atmospheric parameters, indicating the importance of pressure, rainfall and temperature on gas migration. Moreover, CO_2 fluxes deeper in the soil were calculated and compared to surface rates. Ultimately, the probes may reveal possible modifications of the gas transfer pressure conditions constraining the gas velocity, eventually with a contribution from the reservoir. They could then detect the first precursors of any possible CO_2 escape to the surface. Data from the probes showed seasonal variations in the gas flow regime and in soil permeabilities. For example, during the winter months soil gas concentrations increased because escape to the atmosphere was hindered or prevented by the frozen soil surface, thereby allowing gas to accumulate beneath the surface. Maximum gas velocities were within the 5–15 cm/hour range. These values are typical of faults whereas, at the other end of the spectrum, background values were obtained that reflect diffusive gas transport. Since mid-2003, ^{222}Rn concentration excursions lasting for less than three hours have been observed. Typically, concentrations increased to 7 to 15 times normal values for a short time (maximum 3 hours). The increases were rapid, over 3 hours or less, and then reduced over the next 1 to 2 hours. They were not accompanied by changes in atmospheric pressure, or the occurrence of free water in the probes. These suggest transient pressure phenomena, with low fluxes and high velocities. The increases could reflect changes at reservoir level, and demonstrate the importance of continuous monitoring at sites where data suggest there is potential for migration of deep gas. Carbon dioxide fluxes at 2 m were calculated to be 10–20 times lower than those at the surface. This is consistent with declining biogenic CO_2 production with depth and suggests, that to verify that CO_2 leakage does not occur from depth, it may be better to monitor flux at 2 m where biogenic influences are muted.

Conclusions

A large background dataset has been obtained from soil gas monitoring at the Weyburn oilfield. This has revealed seasonal variations in gas concentrations and fluxes. It provides an important baseline resource against which to compare future data and evaluate any escape of injected gas at the surface. All the evidence suggests that the CO_2 in the soil gas is produced biogenically. There are no indications of any significant leakage of gas from depth, although for such a well sealed reservoir rock as Weyburn, leakage is not expected. It is, however, important to maintain the monitoring effort and to focus on development of new rapid measuring techniques, enhancement of continuous monitoring and further assessment of potential pathways for deep gas migration.

Safety and risk assessment studies

To be able to quantify the likely impacts and risks associated with the geological storage of CO_2, its likely long-term fate in the geological environment must be assessed and potential migration pathways and mechanisms need to be defined (Stenhouse 2001). This requires an understanding of complex coupled physical-chemical-mechanical processes occurring over thousands to tens of thousands of years. Relevant performance indicators in this sphere include injectivity, long-term cap-rock integrity and reservoir capacity.

Systems analysis involves the organised assembly of the features, events, and processes (FEPs) relevant to the system being studied. With regard to the geological storage of CO_2, features of the storage system could include inadequately sealed boreholes, the composition of the CO_2, or undetected geological structures. Events are usually of short duration and can be of natural or human origin, such as seismicity, or anthropogenic penetration of the reservoir. There are a large number of processes that could affect the long-term evolution of the storage system and the behaviour of CO_2, such as climate change, the variation of the physical properties of CO_2 with pressure and temperature, and chemical reactions with reservoir and cap rocks. The production of databases of FEPs has proved to be valuable in similar fields such as radioactive waste disposal.

Even for a well-characterised CO_2 storage site, there will be significant uncertainty about the future evolution of the system. Uncertainty in future states is managed by carrying out assessment calculations for stylised conceptual descriptions of possible future states, termed scenarios (Cranwell *et al.* 1982). Processes and events that determine scenarios are referred to as ‘external FEPs’ or EFEPs. It should be stressed that EFEPs are FEPs that are external to the system being considered, in terms of space or time, and that their definition depends upon the assessment context. In the context of CO_2 storage, a scenario may be defined as:

‘A hypothetical sequence of processes and events, devised to illustrate a range of possible future behaviours and states of a carbon storage system, for the purposes of making or evaluating a safety case, or for considering the long-term fate of CO_2’

In developing mathematical models for the long-term fate of CO_2, it is helpful to represent the interactions between FEPs that affect the internal evolution of the system. The two methods that have been widely used are process influence diagrams and interaction matrices (SKI 1996; Hudson 1992). This systematic approach to the examination of how the system components relate to one another can help to identify new, previously unrecognised, characteristics of the system.

The FEP database

The FEP database developed for the Weyburn project is generic; it is not specific to any particular CO_2 geological storage concept. It can cross-reference project-specific databases for individual sites, thereby maximising its utility (Savage *et al.* 2004). The FEPs included are all relevant to the long-term safety and performance of the geological storage system after CO_2 injection has ceased, and the boreholes have been sealed. However, some FEPs associated with the injection phase have been included where these can affect long-term performance and the initial status of the storage system. The FEP database can be used in two ways that can be described as ‘top down’ and ‘bottom up’. In the ‘bottom up’ approach, the database is used directly in the development of assessment models. In the ‘top down’ approach, the database is used as an audit tool to ensure that all relevant FEPs are included in the model, and to document why other FEPs are not considered. The database is available at http://www.co2captureandstorage.info/.

As previously stated, the FEP database is not Weyburn-specific. This was deliberate so that the database is potentially applicable to all CO_2 injection operations. However, because all the IEA Weyburn Carbon Dioxide (CO_2) Monitoring and Storage Project researchers had the opportunity to input to the FEP database throughout the projects duration, it is inevitable that FEPs which were deemed to be particularly relevant to the Weyburn CO_2 injection operation will be present. Because it is available online, the database can be continuously updated. This means that FEPs which emerge when the project is mature, and when injection operation is finished can be inserted.

For each FEP, there is a description and discussion of its relevance to the long-term safety and performance of the system. The database is a source of information on the geological storage of CO_2; it can be used in systemic assessments of safety and performance. For each FEP there are fields for the name, description, relevance to performance/safety issues and references/links. The categorisation as a feature (F), event (E) or process (P) is also provided. The database has a hierarchical structure with FEPs grouped into categories and classes, with an associated numbering system. Within the database, the FEPs and EFEPs are organised into a series of hierarchical groupings that include:

- The assessment basis determining ‘boundary conditions’.
- External factors containing EFEPs that describe natural or human factors outside the system domain.
- Carbon dioxide storage, specifying details of the pre- and post-closure storage concepts.
- Carbon dioxide properties, interactions and transport.

- The geosphere, concerned with the geology, hydrogeology and geochemistry of the storage system.
- Boreholes, concerned with the way that activity by humans alters the natural system.
- The near-surface environment, concerned with factors that can be important if sequestered CO_2 returns to the environment that is accessible by humans.
- Human behaviour including land/water use, buildings, diet/food processing and lifestyles.
- Impacts such as to humans, biota or the physical environment.

System-level modelling and the treatment of uncertainty

System-level modelling and uncertainty treatment contributes to the development of a safety case. This is a set of structured arguments, based on qualitative and quantitative evidence, which supports the assertion that a disposal programme will be safe. Thus, system-level modelling may contribute to the development of a safety case, but would not normally be sufficient to produce one. There are some important technical challenges for CO_2 system-level modelling. These include:

- The properties of CO_2 vary in different parts of the system; density and viscosity are complex functions of temperature and pressure.
- Unlike radionuclides in assessment models for radioactive waste disposal and contaminants in waste water leakage, CO_2 is not a ‘trace’ contaminant, so that the storage of large volumes of CO_2 at elevated pressure can directly affect the evolution of the system into which it is injected. Examples of possible CO_2-induced processes are microseismicity and subsidence due to dissolution, for example in carbonate aquifers.
- The potential impacts resulting from CO_2 transport to the accessible environment may depend critically on the location of a release, and the area where that release occurs. Impacts for a given flux to the surface may vary from insignificant to loss of life depending upon the characteristics of the release. This point is relevant to hypothetical scenarios, and does not address the probability of these releases happening.

Data and interpretations from the IEA Weyburn Carbon Dioxide (CO_2) Monitoring and Storage Project were used extensively in the evaluation of how the physical properties of CO_2 vary in carbonate reservoirs, and how large volumes of supercritical CO_2 can affect limestone/dolomite successions. Because no escapes of CO_2 have occurred at Weyburn, the project could not input to the system-level modelling of the impacts of these events.

One of the reasons for developing a model is to provide an understanding of the main features of the system that determine overall safety, and of the level of uncertainty in the calculated impacts due to uncertainties in model parameters. The use of probabilistic methods is widespread in environmental assessment (Environment Agency, 2002). Here, uncertainties in model input parameters are represented by probability density functions (PDFs), and these enable a PDF for the calculated impacts to be produced. Probabilistic techniques can be powerful in identifying the sensitivities in the model, but can lead to misleading conclusions about overall risks if not used carefully. One of the most difficult issues is future human action. For example, how likely is it that humans will drill into the CO_2 storage reservoir in future? Will they know about of the presence of CO_2 before they do this? If not, what would the consequences be? System-level models can help assess possible consequences of these actions, but cannot resolve some problems associated with making assumptions about human behaviour in the future. It is also important to evaluate low-probability/high-impact events, for example seismicity in the case of Weyburn.

Summary

- A relatively pure stream of CO_2 as an industrial by-product is being transported 320 km from its source, then successfully injected into the Weyburn oilfield as part of a successful, ongoing EOR operation without significant operational difficulties.
- The Mississippian aquifer has a salinity gradient at Weyburn; dissolved CO_2 will migrate from Weyburn at c. 0.2 m/year toward the NE under the influence of regional groundwater flow. Carbon dioxide and methane dissolved in reservoir fluids in the injection area increased significantly; the distributions of these gases allow potential transport pathways to be identified.
- Laboratory experiments and geochemical modelling have indicated that the permeability and porosity of the reservoir will not be diminished due to CO_2 injection and migration, thereby decreasing the potential reservoir volume. Furthermore, the sealing formations will not lose integrity as a consequence of CO_2 injection.
- Recording of microseismicity at Weyburn demonstrates that magnitudes of induced events are within the expected range for oilfield operations, and may be related to small fractures formed by injection-driven fluid migration. This means that CO_2 injection need not result in risks from induced seismicity.
- Surface monitoring of a variety of geochemical parameters has shown no evidence for the leakage of CO_2 from depth, nor has it demonstrated evidence for the existence of permeable pathways that might in future conduct CO_2 from the reservoir to the surface.
- Data from field investigations proved valuable in the assessment of long-term storage system performance and safety.
- The IEA Weyburn Carbon Dioxide (CO_2) Monitoring and Storage Project has successful demonstrated that the field application of a range of geoscientific characterisation and monitoring methods can improve confidence in the performance and safety of CO_2 sequestration. It is anticipated that future CO_2 sequestration operations will utilise, and build upon, the approach and template adopted here.

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FIGURE CAPTIONS

Fig. 1. The location of the Williston Basin in southern Canada and northern U.S.A.

Fig. 2. Stratigraphical correlation of the Mississippian succession in Saskatchewan, North Dakota, Montana and Manitoba; modified from Kent (1984) and Wegelin (1984).

Fig. 3. The location of the Weyburn oilfield and the route of the CO_2 pipeline (from Riding & Rochelle 2005).

Fig. 4. A map of the Weyburn oilfield (light grey) illustrating the extent of the initial CO_2 flood area (phase 1A – dark grey) in the mid-west of the oilfield, and the area of the oilfield to be subsequently flooded (the CO_2 flood rollout area – mid grey).

Fig. 5. Modelling of the natural migration pathways within the Mississippian aquifer; observed salinity distribution and simulated streamlines (modified from Audigane & Le Nindre 2004). The outline of the Weyburn oilfield is illustrated close to the western boundary. The simulated streamlines are c. 25 km long (see the scale given), and represent the transport of dissolved CO_2 toward the E-NE in c. 100 000 years. The g/l figures are contoured with high values in yellows and low values in blue.

Fig. 6. $^{87}Sr/^{86}Sr$ contour map of produced aqueous fluids within the Phase 1A CO_2 injection area at Weyburn for the monitoring campaign Monitor 1 (2001) (from Riding & Rochelle 2005). The black dots represent injection wells.

Fig. 7. $^{87}Sr/^{86}Sr$ contour map of produced aqueous fluids within the Phase 1A CO_2 injection area at Weyburn for the monitoring campaign Monitor 5 (2002) (from Riding & Rochelle 2005). The black dots represent injection wells.

Fig. 8. $^{87}Sr/^{86}Sr$ contour map of produced aqueous fluids within the Phase 1A CO_2 injection area at Weyburn for the monitoring campaign Monitor 8 (2003) (from Riding & Rochelle 2005). The black dots represent injection wells.

Fig. 9. Hydrostratigraphical delineation and nomenclature for the Williston Basin (modified from Bachu & Hichon 1996). The arrow (I) indicates that water from the Mannville Aquifer System is used for water-flooding. The symbols (?) are added to indicate the possibility of using shallower aquifers for water flooding. The arrow (II) inside the Mississippian Aquifer System is to indicate that water used for flooding is continuously being re-injected.

Fig. 10. Evolution of Ca concentrations within the static batch experiments on Midale Beds material (from Riding & Rochelle 2005).

Fig. 11. Evolution of Mg concentrations within static batch experiments using samples of Midale Beds material (from Riding & Rochelle 2005).

Fig. 12. Scanning electron photomicrographs of Midale Vuggy Unit monoliths showing the well-developed secondary growth of elongate (acicular) gypsum crystals within the aqueous phase (from Riding & Rochelle 2005). After four weeks in CO_2, the crystals grew to 500 µm long (left hand image), and after eight weeks they had grown to at least 2.5 mm long (right hand image).

Fig. 13. The saturation index (SI) of potentially reacting, i.e. dissolving and/or precipitating, minerals in BGS Midale Marly static batch experiments (from Riding & Rochelle 2005).

Fig. 14. Sulphate mineral (anhydrite and gypsum) behaviour in the Weyburn reservoir brines under CO_2 injection pressure, temperature and pCO_2 conditions. Note that the numbers in parentheses within the inset box represent the salinities of the different fluids used in the experiments (from Riding & Rochelle 2005).

Fig. 15. Stratigraphical section at the Weyburn oilfield (from Whittaker & Rostron 2001).

Fig. 16. Conceptual sketch of CO_2 diffusion in the Lower Watrous Formation (from Riding & Rochelle 2005).

Fig. 17. The saturation index (SI) of potentially dissolving and/or precipitating minerals in the BGS Midale Evaporite static batch experiments (adapted from Riding & Rochelle 2005).

Fig. 18. Soil gas measurement in the Phase 1A CO_2 injection area of the Weyburn oilfield (from Riding & Rochelle 2005).

Fig. 19. Map illustrating the locations of the various sites studied for soil gas at Weyburn (modified from Beaubien *et al.* 2004).

Fig. 20. Map of the grid area on the Weyburn oilfield illustrating sampling points, surface water, wells and air photo lineaments (modified from Beaubien *et al.* 2004).

Fig. 21. Contoured distribution of CO_2 flux and soil gas CO_2 for the three sampling campaigns (from Beaubien *et al.* 2004).

Fig. 22. Plot illustrating the relationship between CO_2, O_2 and N_2 for the grid dataset from Weyburn in July, 2001 as compared to data collected from Cava dei Selci in Italy, a dormant volcanic site which has known gas vents due to deep thermometamorphic reactions (from Beaubien *et al.* 2004).

CAPTIONS FOR TABLES

Table 1. Comparisons between Weyburn core data on gas permeability and porosity determined in this study and field average data taken from Malik & Islam (2000) (asterisked) (from Riding & Rochelle 2005).

Table 2. Details of borehole fluid monitoring surveys conducted at the Weyburn oilfield, and details of what data were collected (from Riding & Rochelle 2005).

Table 3. Statistical summary of the 2001–2003 strontium isotope ratios; the data were normalised to the Mississippian value of 0.7082 when calculating $\delta^{87}Sr$ (from Riding & Rochelle 2005).

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Table 5. Changes in weight of cement monolith samples after two weeks reaction with ‘free CO_2’ and dissolved CO_2. SMFW = Synthetic Marly Formation Water (from Riding & Rochelle 2005).

TABLES 1-5:

Lithological Unit	**BGS plugs**		**Field average***	**BGS plugs**		**Field average***	**BGS plugs**
	Gas permeability (mD)		Gas permeability (mD)	Porosity (%)		Porosity (%)	Grain density range (g/cm^{-3})
	Range	Mean		Range	Mean		
Midale Marly	0.15-33	11	10	10-35	24	26	2.69-2.85
Midale Vuggy	2.7-57	22	15	12-15	14	11	2.71-2.73

Table 1. Comparisons between Weyburn core data on gas permeability and porosity determined in this study and field average data taken from Malik & Islam (2000) (asterisked) (from Riding & Rochelle 2005).

Survey	**Dissolved gases**	**Chemical analyses (major, minor and trace elements)**	**$^{87}Sr/^{86}Sr$ ratio**
'Baseline', August 2000	NO	NO	Partially
Monitor 1, March 2001	YES	YES	YES
Monitor 2, July 2001	NO	NO	NO
Monitor 3, Sept. 2001	NO	NO	NO
Monitor 4, March 2002	NO	NO	NO
Monitor 5, June 2002	YES	YES	YES
Monitor 6, Sept. 2002	NO	NO	NO
Monitor 7, April 2003	NO	NO	YES
Monitor 8, June 2003	YES	NO	NO
Monitor 9, Sept. 2003	YES	YES	YES
Monitor 10, Mar. 2004	YES	YES	YES

Table 2. Details of borehole fluid monitoring surveys conducted at the Weyburn oilfield, and details of what data were collected (from Riding & Rochelle 2005).

$^{87}Sr/^{86}Sr$					**$\delta^{87}Sr$**			
Sampling Trip	Min.	Max.	Mean	Equivalent Manville component	Sampling Trip	Min.	Max.	Mean
Monitor 1	0.70775	0.70825	0.70798	25%	Monitor 1	-0.63	0.08	-0.31
Monitor 5	0.70800	0.70818	0.70804		Monitor 5	-0.28	-0.03	-0.23
Monitor 8	0.70797	0.70818	0.70807	15%	Monitor 8	-0.32	-0.03	-0.19

Table 3. Statistical summary of the 2001–2003 strontium isotope ratios; the data were normalised to the Mississippian value of 0.7082 when calculating δ^{87}Sr (from Riding & Rochelle 2005).

Lithology	**BGS plugs**		**BGS plugs**		**BGS plugs**
	Gas permeability (mD)		Porosity (%)		Grain density range (g/cm^{-3})
	Range	Mean	Range (%)	Mean (%)	
Midale Marly M1 unit/Midale Evaporite transition	0.03-1.8	0.7	5-15	10	2.84-2.96

Table 4. Conventional core analysis data measured for the Midale Marly M1 Unit/Midale Evaporite Unit transition zone (from Riding & Rochelle 2005).

Fill cement experiments				
Run no.	Monolith id.	Aqueous fluid	Gas	Weight change (%)
1133	A	None	CO_2	+ 11.4
	B	None	CO_2	+ 11.2
1134	C	SMFW	CO_2	+ 9.9
	D	SMFW	CO_2	+ 9.6
1139	A	SMFW	N_2	+ 1.7
	B	SMFW	N_2	+ 1.3

Tail cement experiments				
Run no.	Monolith id.	Aqueous fluid	Gas	Weight change (%)
1135	A	None	CO_2	+ 3.8
	B	None	CO_2	+ 4.2
1136	C	SMFW	CO_2	+ 0.6
	D	SMFW	CO_2	+ 0.8
1138	A	SMFW	N_2	- 0.3
	B	SMFW	N_2	- 0.4

Table 5. Changes in weight of cement monolith samples after two weeks reaction with 'free CO_2' and dissolved CO_2. SMFW = Synthetic Marly Formation Water (from Riding & Rochelle 2005).