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Geochemical assessment of isolation performance during 10 years of CO₂ EOR at Weyburn

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Abstract

The Final-Phase Weyburn geochemical research program includes explicitly integrated yet conceptually distinct monitoring, modeling, and experimental components. The principal objectives are to monitor CO_2 -induced compositional evolution within the reservoir through time-lapse sampling and chemical analysis of produced fluids; to document the absence (or presence) of injected CO_2 within reservoir overburden through analogous monitoring of shallow groundwater and soil gas; to predict intrareservoir CO_2 migration paths, dynamic CO_2 mass partitioning among distinct trapping mechanisms, and reservoir/seal permeability evolution through reactive transport modeling; to assess the impact of CO_2 -brine-rock reactions on fracture flow and isolation performance through experimental studies that directly support the monitoring and modeling work; and to exploit a novel stochastic inversion technique that enables explicit integration of these diverse monitoring data and forward models to improve reservoir characterization and long-term forecasts of isolation performance.

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1. Introduction

The IEA GHG Weyburn-Midale CO_2 Monitoring and Storage Project is the world's inaugural and still premier fully integrated CO_2 EOR and sequestration project. "Inaugural" in that baseline geochemical and geophysical characterization of the site was completed prior to commencement of CO_2 injection, Weyburn remains "premier" in terms of its duration: time-lapse monitoring surveys have been carried out for 10 years; its CO_2 injection rate: at roughly 5 million tonnes per year currently, it ranks first among engineered geologic storage sites; its anthropogenic

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source and international nature: CO_2 is imported by pipeline from the Great Plains Synfuels Plant in North Dakota (USA); and the diversity and breadth of its integrated research program, which has been carried out in two parts: Phase I (2000-2004) and Final Phase (2007-2011) [1-3].

The Final-Phase research program is divided into four themes: geological integrity, wellbore integrity, storage monitoring, and risk assessment [2-3]. Within the monitoring theme, geophysical remote imaging techniques are used to track the buoyancy-driven intra-reservoir migration of CO_2 with 2-3D resolution [4-6]. These techniques delineate the spatial framework of physical and chemical trapping mechanisms as well as potential leakage sites, but cannot address chemical trapping efficacy or identify subtle degradation of seal integrity. In contrast, the geochemical sampling methods deployed are essentially limited to 1D resolution, but provide a unique means of monitoring dynamic CO_2 movement beyond the reservoir [5,7]. The geochemical research program includes explicitly integrated yet conceptually distinct monitoring, modeling, and experimental components.

2. Time-lapse geochemical monitoring

The compositional evolution that attends progressive oil-CO₂-brine-rock mass transfer during CO₂ EOR has been documented by periodic sampling and chemical/isotopic analysis of produced fluids from a suite of 50-60 wells within and near the Phase 1A area over the time frame 2000-2010 [7-10]. This unique database can be used to infer key fluid-fluid and brine-rock reactions within the overall mass transfer process [11-12], and it also represents an invaluable history-matching resource for reactive transport modeling studies. Acceptable reservoir containment requires documenting the absence (or acceptably low concentration) of injection-sourced CO₂ within overburden resources. It is particularly important to ensure that water quality within overlying potable aquifers has not been compromised, and that surface release of injected CO₂ has not occurred. To address the former concern, periodic sampling and chemical analysis of shallow groundwater from local domestic wells has been carried out from 2000-2009 [13-14]. To address the latter, periodic soil gas monitoring of a representative background site and dedicated grid system within the Weyburn field were completed during 2001-2005 [7,15], and are planned for 2010-2011.

Sampling and analysis of produced brines: During Weyburn Phase I, a baseline and 11 subsequent monitoring trips (3/year, M1-M11) were completed, and the sample suites analyzed for over 40 compositional and isotopic parameters, generating a singularly comprehensive geochemical database [7]. During Final Phase, five additional monitoring trips (M12-M16) address the same well suite sampled during M11 (September 2004), which facilitates continuity with Phase I data. To date, M12-15 (Oct 2008, May 2009, Oct 2009, May 2010) have been carried out, and completion of M16 (October 2010) will cap a 10-year record of brine compositional evolution. Although detailed interpretation of this uniquely complete and extended history is complicated by many factors (WAG schedules, poorly constrained injection-water compositions, sample mixing due to perforation lengths of vertical and horizontal wells, field development activities, routine operational procedures, etc), the most important evolutionary trends can in fact be extracted. For example, the documented evolution of pH (and, similarly, that of $\delta^{13}C_{HCO3}$.) combines two opposing components: a negative contribution from CO₂ aqueous solubility, characterized by relatively large magnitude and fast kinetics, and a positive contribution from mineral dissolution, characterized by relatively small magnitude and slow kinetics; the time-integrated net result to date is a decrease in pH from roughly 6.4-7.0 to 5.0-6.4 (and in $\delta^{13}C_{HCO3}$ from roughly -1 to -8 to -11 to -14 °/₀₀) (Figure 1A-C). In contrast, alkalinity evolution is controlled by positive contributions from both CO₂ aqueous solubility and carbonate dissolution; here, the time-integrated net result to date is an increase from roughly 300-600 to 2000-3200 mg/L (Figure 1D-F). Other CO₂-induced changes in aqueous chemistry are controlled primarily by mineral dissolution, which results in, e.g., increasing concentrations of Ca and Mg from calcite and dolomite solubility. Finally, the observed concentration evolution of non-reactive chemical components (those that do not participate appreciably in brine-rock reactions) reflects that of injection waters and the flow field, both of which also influence variations in reactive components.

<u>Sampling and analysis of produced hydrocarbons</u>: During Weyburn Phase I, the compositional evolution of produced hydrocarbons that characterizes the multiple-contact miscibility process of CO_2 EOR was documented through bi-monthly sampling and analysis of six wells located within the Phase 1A area [16]. Analytical work included the determination of minimum miscibility pressure (MMP) and PVT properties of live oil that were used to develop a Weyburn-tuned PR-EOS, which was then incorporated into the compositional reservoir simulators



Figure 1: Evolution of reservoir pH (A-C) and alkalinity (D-F) within and near the Phase 1A area (outline) primarily due to CO_2 aqueous solubility and carbonate mineral dissolution during CO_2 EOR. Baseline sampling was conducted August 2000; Monitor 11 (last Phase-I survey) was carried out September 2004; Monitor 14 (third Final-Phase survey) was completed October 2009.

adopted for modeling studies, primarily GEM and ECLIPSE [16]. During Final Phase, this sampling and analysis program has been continued to provide data continuity and enable necessary further refinement of the PR-EOS. Specifically, in April 2010 separator samples and GOR measurements were obtained from one of the original six wells, MMP and PVT properties of the reconstituted live oil and live oil-CO₂ system at reservoir conditions are being determined, and these data will be used to further tune the Phase-I PR-EOS. This refined EOS, through its incorporation into reactive transport simulators used in Final Phase modeling studies (see below), will provide improved representation of hydrocarbon compositional evolution during the overall contact miscibility process to date. Together with the degree of aqueous solubility trapping deduced from brine analyses, this re-tuned hydrocarbon EOS will permit history matching of CO_2 mass partitioning among reservoir fluid phases.

<u>Shallow groundwater monitoring</u>: Prior to Weyburn Final Phase, baseline characterization (May 2000) and ten subsequent monitoring surveys (2001-2006) of groundwater chemistry in shallow domestic wells (generally, <30m depth) within the CO₂ EOR Phase I/II areas had been completed [13]. Through the last of these sampling trips (June 2006), comparison of baseline and sequential monitoring data had not revealed any significant changes in water quality attributable to CO₂ EOR and sequestration at depth. During Final Phase, an additional monitoring survey of this well suite was carried out (July-August 2009) to document the current population of active wells; to quantify variations in water chemistry relative to baseline and 2006 data; and to recommend a frequency for future monitoring surveys [14]. Comparative analysis of data from the 2009 and all previous surveys revealed only minor changes in water quality since CO₂ injection commenced in 2000. Changes in major ion concentrations (in particular, nitrate) are observed in wells located near barns, but with respect to Saskatchewan water-quality

standards, the small percentage exceedance at Weyburn is consistent with values observed elsewhere in the province [14]. This study further concluded that for subsequent long-term monitoring of groundwater quality, surveying the well suite every 3-5 years will be sufficient; however, because the number of active private wells will likely continue to decline (from 30+ in 2006 to 24 in 2009) and monitoring may be conducted over decades, consideration should be given to constructing a network of monitoring wells strategically located throughout the Phase I/II areas.

<u>Soil gas monitoring</u>: During Weyburn Phase 1, baseline (2000) and annual monitoring (2001-2004) surveys of soil gas CO_2 flux at a representative background site and over a 360-point grid (3.6 x 4 km) within the Phase 1A area were carried out [7]. During the Phase-I/Final-Phase interim period, an additional survey was completed in October 2005 [15]. The magnitude and variation of CO_2 fluxes measured from 2001-2005 remained within the range of natural prairie soils, as confirmed by comparison with measurements at the background site. This result suggests that to date (October 2005) there had been no seepage of injected CO_2 to the biosphere. Further extension of this "clean slate" (together with that for shallow groundwater) is critical; hence, continued soil gas monitoring is planned for Final Phase, but has been delayed by contractual issues. If ultimately deployed, this monitoring effort will provide important data continuity with the previous surveys and source any anomalies that may be identified.

3. Reactive transport modelling

During Phase I, reservoir simulation efforts addressed EOR performance, CO_2 storage capacity, and CO_2 -oil-brine mass partitioning, while geochemical modeling work assessed mineral trapping [16]. Final Phase simulation efforts exploit the reactive transport modeling approach, a unique methodology that explicitly couples reservoir simulation and geochemical modeling capabilities. Building upon earlier work [16-17], advanced reactive transport simulators (GEM, NUFT) are being used to predict and evaluate observed CO_2 migration paths, EOR/isolation performance, CO_2 mass partitioning among physical/chemical sinks, and reservoir/seal permeability evolution. The goal is to minimize prediction/observation discrepancies through history matching CO_2 plume migration (from seismic monitoring), fluid recovery (from production records), evolving fluid compositions (from geochemical monitoring), and mineral trapping (as inferred from core samples and laboratory experiments). Inaugural account of constraints imposed by the latter two (geochemical) datasets will enable significant refinement of Phase-I modeling results.

The modelling work summarized here focuses on history matching produced-water concentrations of conservative and reactive chemical components [18-19]. Conservative components (e.g., Na and Cl) are not added or removed from solution to a significant degree through brine-rock reactions; hence, their concentration evolution primarily reflects that of injection waters, mixing of these waters with formation fluids, and the permeability field, which dictates fluid flow direction and magnitude. The concentration evolution of reactive components (e.g., Ca and bicarbonate) is due to these same factors plus the contribution of brine-rock mass transfer. Hence, accurate simulation of the observed compositional signals requires accurate representation of initial reservoir conditions, operational history (in particular, evolving injection-fluid compositions), and multiphase flow and geochemical processes. At Weyburn (and most CO_2 EOR projects), injection-water chemistry has not been documented during waterflood or subsequent CO_2 WAG operations; hence, both formation and injection water compositions are poorly constrained. Further, the nature of reservoir permeability is poorly understood. Phase-1 simulation work adopted the conventional single-permeability (un-fractured) reservoir model [16], but there is good evidence that the reservoir is indeed fractured; hence, a dual-permeability model is more appropriate [20]. Moreover, although it is possible to accurately model fluid production history without including the influence of fractures [16], accurate simulation of aqueous geochemical signals appears to require explicit representation of dual-permeability flow (Figure 2).

4. Supporting experimental studies

The impact of CO_2 -brine-rock interactions on reservoir mineralogy, fluid composition, porosity/permeability, and fracture flow is being assessed through laboratory reactive transport experiments, detailed analysis of selected core samples, and highly resolved characterization of fracture dynamics. Laboratory experiments are used to quantify the CO_2 -induced evolution of reservoir composition and transport properties under strictly controlled conditions. Advanced micro-beam techniques enable 3D characterization of micron-scale pore networks and pore-lining mineral compositions before and after both field and laboratory CO_2 exposure. An integrated experimental and modeling approach is used to characterize and simulate CO_2 -induced geochemical and geomechanical alteration of fractures.



Figure 2. Measured concentrations of conservative (Na, Cl) and reactive (Ca, bicarbonate [alkalinity]) chemical components in produced waters from two vertical wells (11014120, 12102130) in pattern P1612614 of the Phase 1A area (symbols in A-B); for reactive components, simulation results obtained using the single-permeability model are also plotted (curves in B). Simulated evolving age distribution of produced waters (initial formation water and four 10-year multi-well injection periods starting in 1964, 1974, 1984, and 1994) for well 11014120 for the single- and dual-permeability models (C and D, respectively). Simulated evolving source-well distribution of produced waters (initial formation water and two injection wells) for horizontal well 19101130 for the single- and dual-permeability models (E and F, respectively). The noisy evolution of measured concentrations (A-B) is inconsistent with the smooth profiles generated using the single-permeability model (C and E), but closely matched by the complex mixing relations and data scatter produced using the dual-permeability model (D and F). Modified from [18-19].

<u>CO₂-brine-rock interactions</u>: Reservoir and cap-rock samples from the Phase 1A area are being used in a series of batch and core-flood experiments designed to quantify the effect of CO₂-brine-rock mass transfer on dependent compositional and permeability evolution. Reactive transport (NUFT) simulations to obtain appropriate values for key experimental parameters (flow rates, P-T, X_{aq} , p_{CO2} , etc) have been completed. Initial core-flood simulations suggest that significant changes in porosity occur at the inlet within several hours when CO₂-rich brines react with Weyburn carbonates. In contrast, preliminary experimental results are consistent with much smaller porosity increases. This discrepancy likely reflects those between the model and experimental systems; e.g. petrophysical heterogeneity, flow rate, and mineral dissolution kinetics. Comparative synchrotron XCMT analyses of core mineralogy and pore structure before and after laboratory CO₂ exposure (at variable p_{CO2}) are being used to

document imposed dissolution/precipitation features and their impact on 3D pore geometry, porosity, and permeability. Finally, a pore-network reactive flow model is being developed using pre-exposure XCMT data and pore structure characterization procedures. Through calibration against the experimental core-flood data, this model will be used to obtain pore-scale mineral reaction rates that can be up-scaled to core- and field-scale models. The synchrotron XCMT and pore-scale modeling work is being done in collaboration with the following project.

<u>Micron-scale reservoir matrix analysis</u>: Porosity/permeability evolution caused by CO_2 -induced mineral dissolution/ precipitation exerts an important influence on isolation performance, but the slow kinetics of this process represent a significant barrier to quantifying these effects in the field over short time scales (up to several years). A comparative analysis of complementary XCMT, sXRD, and sXRF data obtained from core extracted before and after field CO_2 exposure has been used to document incipient dissolution/precipitation features and their impact on pore geometry, porosity, permeability, and pore-wall mineralogy. Synchrotron XCMT provides the micron-scale distribution of mineral phases and pore space that enables the comparison (Figure 3), but also highlights the challenge imposed by geologic heterogeneity when comparing even closely proximate pre- and post-exposure samples. Thus, comparison of the *same* sample before and after laboratory-controlled CO_2 exposure is desirable, and several unexposed core plugs that have undergone XCMT and petrophysical analysis as part of this project have been provided for use in LLNL's experimental investigations of CO_2 -induced carbonate dissolution effects (previous study). Following completion of these experiments, the now-exposed samples will be returned for post-mortem XCMT analysis, which will be compared with pre-exposure data. Finally, micro-scale finite-element meshes of the pore space and mineral grain framework have been generated from the XCMT images of pre-exposed core. 3D solutions of Navier-Stokes equations applied to these meshes are being used to quantify steady-state fluid velocities, fluxes, and permeability.



Figure 3. Micron-scale 3D distribution of minerals and pore space in the Midale reservoir (Vuggy zone) as revealed from XCMT analysis. Note good agreement of theoretical and observed LAC (Linear Attenuation Coefficient) values. Modified from [21].

Fracture characterization and alteration: Improved understanding of the manner in which coupled hydrological, geochemical, and geomechanical processes influence fracture flow is required for accurate forecasting of CO_2 EOR and isolation performance. Specifically, there is a need to develop experimentally calibrated numerical models that explicitly integrate the geochemical and geomechanical components of aperture evolution, which effectively controls that of reservoir and cap-rock integrity. Building upon recent advances [22], CO_2 -induced alteration of natural fractures within the Weyburn reservoir/seal system is being investigated using this approach. Core samples from the Midale Marly (M), Vuggy (V), and Evaporite (E) have been obtained, and their pre-experimental fracture characteristics are being quantified using optical surface profilometry and SEM/EDS. An aperture map for a specific fracture (sample E1) has been obtained by numerically mating its individually characterized surfaces, then used in initial pre-experiment reactive flow simulations to identify anticipated preferential flow paths and regions

most susceptible to reaction-induced aperture evolution. The experimental response of fracture permeability to reactive flow using CO₂-rich brine (in progress) will be used to refine mineral kinetic models and thereby improve agreement of simulation and experimental results. Following this refinement, the lab-scale computational model will be used to address greatly extended space-time dimensions. Results from this scaling investigation will be used to propose effective constitutive relationships for incorporation into field-scale reactive transport models.

5. Observation-tuned forward modeling

During Phase 1, time-lapse seismic reflection data were used to map CO₂ migration, while an extensive fluid sampling program documented the concomitant geochemical evolution triggered by oil-CO₂-brine-rock interactions. During Final Phase, these two datasets—augmented by fluid injection and production data as well as Final-Phase monitoring results—are being used to improve both reservoir characterization and dependent predictions of isolation performance. The methodology explicitly integrates reactive transport modeling, facies-based geostatistical methods, and a novel Monte Carlo Markov Chain stochastic inversion technique [23] to optimize observation/prediction agreement, which is accomplished through stepwise refinement of first the reservoir model (principally its permeability structure) and then geochemical parameters (primarily mineral kinetic data).

Algorithmic development of the seismic inversion (permeability) step has been completed by finalizing the seismic likelihood calculation and by formal constraint of all proposed reservoir realizations (perturbations on the Cenovus model) to honor initial lithologic boundaries, documented statistical trends for porosity/permeability, and known characteristics of the depositional environment. Initial test results using synthetic seismic data are promising; the stochastic inversion algorithm successfully moves toward reservoir models that are consistent with the calculated seismic response of the adopted Synthetic Truth model [4]. Significant progress has also been made on algorithmic development of the geochemical inversion (mineral kinetics) step. Most importantly, a geochemical likelihood function for kinetic-parameter inversion that accounts for aqueous concentrations of all relevant chemical components has been defined. Promising test results were obtained for a 2D problem further simplified by the use of mineral saturation indices as surrogates for mineral kinetic parameters (Figure 4).



Figure 4. Stochastic inversion of synthetic brine chemistry data (log(SI) for kaolinite and illite) to obtain optimal values of mineral reaction rate constants. The composite likelihood function, L(x), rapidly converges toward Synthetic Truth (ST) values. Monte Carlo search with multivariate linear regression provides a slightly better fit to ST, but is more computationally intensive.

6. Summary

The Final-Phase Weyburn geochemical research program includes explicitly integrated yet conceptually distinct monitoring, modeling, and experimental components. The principal objectives are to monitor CO_2 -induced compositional evolution within the reservoir; to document the absence (or presence) of injected CO_2 within reservoir overburden; to predict intra-reservoir CO_2 migration paths, dynamic CO_2 mass partitioning among distinct trapping mechanisms, and reservoir/seal permeability evolution; to assess the impact of CO_2 -brine-rock reactions and fracture flow on isolation performance; and to improve reservoir characterization and long-term forecasts of isolation performance through explicit integration of these diverse monitoring data and forward models. This contribution provides a brief review of the methodologies used and results obtained to date for each of these objectives.

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