Quarterly Technical Report

Reactive Multiphase behavior of CO₂ in Saline Aquifers beneath the Colorado Plateau

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ABSTRACT

Field and laboratory investigations of naturally occurring CO₂-reservoirs are being conducted to determine the characteristics of potential seal and reservoir units and the extent of the interactions that occur between the host rocks and the CO₂ charged fluids. Efforts have focused on the Farnham Dome field, located in central Utah, the Springerville-St. Johns field in Arizona and New Mexico, and most recently, the Crystal Geyser-Salt Wash graben areas with their CO₂-charged geysers and springs in central Utah. At both the Springerville-St. Johns field and the central Utah CO₂ spring area, there is evidence of extensive travertine deposits that document release of CO₂ to the atmosphere. At Farnham Dome, calcite debris fields appear to be remnants of vein calcite and an earlier period of fluid leakage. The main achievements during this quarter are 1): preparation for a soil gas flux survey in October at the Crystal Geyser – Little Grand Wash fault zone, and the Salt Wash graben; 2) submission of an abstract to the upcoming Measurement, Monitoring and Verification session at the Fall AGU meeting; 3) submission of an invited abstract to the Gordon Conference on Hydrocarbon Resources; and 4) receipt of initial radiocarbon dates of travertine from the Springerville-St Johns field. Analytical results and interpretations of both the travertine deposition and the soil gas surveys are still in progress, and will be included in future quarterly reports.

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EXECUTIVE SUMMARY

During this reporting period, preparations were made for a campaign of CO₂ flux measurements along the Crystal Geyser – Little Grand Wash fault zone, and the Salt Wash graben, near Green River in central Utah. In contrast to our previous soil gas surveys at Farnham Dome, CO₂ field (Utah) and Springerville-St Johns CO₂ field (Arizona-New Mexico), where average flux values were determined from a grid of measurements at each site, measurements are planned to be made along numerous profiles at approximately right angles to the fault zones. These measurements are designed to detect CO₂ soil gas leakage which is suspected along both the Little Grand Wash fault zone and the Salt Wash graben.

The first three of seven travertine samples from the Springerville – St Johns CO₂ field that were submitted for radiocarbon dating have been analyzed. Travertine domes occur over a wide range of elevation from the banks of Little Colorado River to the hilltops over 1000 feet above the river. Two dates from near the river elevation are not more than several thousand years old, whereas the travertine at highest elevation failed to yield an age, possibly due to intense weathering. Interpretation of the age trend of travertine deposition will await the results of the remaining samples.

An enhanced numerical model of the evolution of fluid flux from the Springerville-St Johns field is being set up. This will improve the previous model presented at this year's National Carbon Sequestration Conference in Alexandria. Improvements include a better representation of the geology/permeability regime, inclusion of a 30 bar (1000 feet) head decline inferred from the travertine distribution with elevation, a CO₂ flux that better matches the observations.

An abstract was submitted to the Fall Meeting of the American Geophysical Union in a session organized by NETL (Advancements in CO₂ Geologic Sequestration Measurement, Mitigation, and Verification Technologies Applied to Field Studies II). The paper will review the results of soil gas flux surveys at the areas studied under this project. The implications of the results will be discussed. An invited abstract describing the sequestration and migration of CO₂ in the natural gas reservoir at Springerville-St. Johns was submitted for presentation at the January Gordon Conference on Hydrocarbon Resources.

EXPERIMENTAL

Not applicable.

RESULTS AND DISCUSSION

During this quarter, the focus of work was on the use of soil gas flux measurements to understand the rate and nature of the movement of CO₂ to the ground surface, improving the numerical model of the Springerville-St Johns natural CO₂ field (near the New Mexico-Arizona state line (Figure 1, 2), incorporating travertine dates into a revised model of the Springerville - St Johns field, and submitting abstracts to AGU and Gordon Conference meetings.

Soil Gas Flux Measurements

In previous quarterly reports we have discussed the results of soil gas flux surveys at Farnham Dome (central Utah) and Springerville - St Johns (Arizona-New Mexico) (Figure 1). Both these areas have natural CO₂ concentrations at depth. Although the average soil gas flux measurements ranged up to 20 g/m²/day, no areas with a clearly anomalous CO₂ flux compared to that from root zone activity were detected at these two areas. Springerville - St

Johns has significant outflows of bicarbonate-saturated water, so it is suspected that this is the main form of CO₂ flux from this field.

During this quarter, preparations were made for a third soil gas survey to be conducted during October, this time in the Crystal Geyser-Little Grand Wash fault zone, and the nearby Salt Wash graben. These fault zones are located in central Utah, 10 – 20 miles south of the town of Green River. Gas actively discharges from several springs located along these fault zones, and from the bottom of the Green River, as indicated by streams of gas bubbles, and Crystal Geyser is gas-driven, so the area is considered a good candidate for studying soil gas leakage. Results will be reported in the next Quarterly Report.

Travertine Sample Collection

As reported in the last Quarterly Report, travertine samples were collected from 8 sites around the Springerville-St Johns field and were submitted for radiocarbon dating (Table 1). The first three dates have been returned from the laboratory. Two samples near the elevation of the Little Colorado River yielded ages of 887 ± 30 and 3524 ± 30 years BP. A third sample from an elevated dome some 330 m (1000 feet) higher unfortunately failed to yield a date. The sample has been extensively weathered, and likely contaminated with young carbon.

A full interpretation of the age range of travertine deposition at Springerville-St Johns, and its implications for the rate of deposition and the outflow of CO₂ will await the results from the remaining samples submitted for dating.

Numerical Modeling

An enhanced numerical model of the evolution of fluid flux from the Springerville-St Johns field is being set up. This will improve the previous model presented at this year's National Carbon Sequestration Conference in Alexandria. Improvements include a better representation of the geology and permeability regimes, inclusion of a 33 bar (1000 feet) head decline inferred from the distribution of travertine deposits and a CO₂ flux that better matches the observations.

Paper for Fall AGU Meeting

An abstract was submitted to the Fall Meeting (2004) of the American Geophysical Union in a session organized by NETL (Advancements in CO₂ Geologic Sequestration Measurement, Mitigation, and Verification Technologies Applied to Field Studies II). The oral presentation will review the results of soil gas flux surveys at the areas studied under this project. The implications of the results will be discussed. The abstract is as follows:

Implications of Soil Gas Survey Results Over Known Carbon Dioxide Systems for Long-term Monitoring

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Soil gas surveys have been carried out over three areas with natural occurrences of carbon dioxide on the Colorado Plateau. At Farnham Dome, Utah, and Springerville-St. Johns, Arizona, carbon dioxide reservoirs occur at 600 - 800 m depth, but no anomalous soil gas

carbon dioxide flux was detected. Evidence of widespread vein calcite at the surface (Farnham Dome) and travertine deposits (Springerville-St. Johns) suggest that the fields may have leaked carbon dioxide-rich fluids in the past. At Springerville-St. Johns, there is a significant outflow of high-bicarbonate water to the surface, which may be the main mechanism that carbon dioxide is reaching the surface today. Carbon dioxide fluxes as high as 20 g m⁻² day⁻¹ in swampy ground adjacent to bicarbonate spring outflows at Springerville-St. Johns are attributed to shallow soil reactions rather than to a deep upflow. A 500 m depth, non-producing well at Springerville-St. Johns responds barometrically, sucking in air during pressure highs, and discharging a carbon dioxide-air mixture during pressure lows. Results from a third soil gas survey area of natural carbon dioxide-water discharges along fault zones in central Utah will also be presented. The unexpected results indicate that soil gas monitoring may not be easy or simple.

Paper for Gordon Conference on Hydrocarbon Resources

We have been invited to present a poster session at the Gordon Conference on Hydrocarbon Resources that will be held in Ventura, California on January 9-14. This international conference is being chaired by R. Pugmire (Univ. of Utah), Professors Norimura (Osaka Univ.) and Miura (Kyoto Univ.), P. Britt (ORNL) and R. Menendez (CSIC). The following abstract was submitted.

CO₂ sequestration and migration in a natural CO₂ field at Springerville-St. Johns, USA

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Increasing global interest in the geologic sequestration of CO₂ has raised important questions about its long-term fate. Geochemical models suggest that substantial amounts of CO₂

injected into deep reservoirs can be removed through fluid-fluid and fluid-mineral interactions, particularly those that lead to the formation of Ca, Fe and Mg carbonates. However, few studies of natural CO₂ reservoirs are currently available and autoclave experiments designed to test predictions of the geochemical models have been hampered by the slow kinetics of the mineral reactions.

In this paper, we present the results of field investigations and numerical simulations on the Springerville-St. Johns CO₂ field in eastern Arizona and western New Mexico, one of more than a dozen gas fields developed within the Colorado Plateau and Southern Rocky Mountain region. Spectacular travertine deposits covering an area of 250 km² record a long history of CO₂ migration and leakage to the atmosphere in the past. Estimates of erosion rates suggest travertine deposition spanned a period exceeding 10⁵ years. Most of the CaCO₃ deposited as travertine could have been derived from dissolution of the underlying limestones and dolomites. Although the domes are no longer active, groundwater near the field is enriched in bicarbonate and is locally acidic, suggesting a persistent flux of CO₂ from depth. Petrographic studies of core from an interval that produced dry gas document dissolution of carbonates and feldspars, and the deposition of kaolinite and dawsonite, a mineral considered to be significant in CO₂ sequestration.

Preliminary models of the hydrology and rock-fluid interactions have been conducted utilizing TOUGH2/ChemTOUGH2. An integrated finite difference model representing topography prior to erosion by the Little Colorado River, which acts as a pressure control, has been developed. Two simulations were performed. In the first, water-rock interactions were ignored and a constant flux of CO₂ was added at the base of the model beneath the CO₂

reservoir. The model, which was run for 10^5 years, predicted discharge rates close to ten times present-day rates.

Mineral reactions were simulated using ChemTOUGH. Beginning with steady-state concentrations of CO_2 in the gas and aqueous phase and assuming a 0.03 M NaCl content for the fluid, the system was simulated for a period of 800 years. Calcite and kaolinite are predicted to be in equilibrium with the reservoir fluid throughout the modeled area. Dolomite is saturated in areas of high CO_2 concentration and slightly undersaturated in other areas, whereas gypsum is everywhere undersaturated. Dawsonite is found to be undersaturated throughout most of the modeled area apart from a deep region with a high CO_2 concentration and also above a region of convective upflow. Only a small percentage of the CO_2 is naturally trapped as carbonate minerals. Most CO_2 is stored as a free gas and as dissolved carbonate species in the groundwater.

CONCLUSIONS

Results of soil gas fluxes and the dating of travertine deposits are providing new insight into the physical and chemical processes that control CO_2 migration and sequestration. These results are being incorporated into numerical models that specifically consider the mineralogical effects of CO_2 on the reservoir rocks.

The young dates (<4000 and <900 years BP) obtained so far on two samples of travertine from Springerville-St. Johns are younger than expected and suggest there is no direct relationship to volcanic activity that ended 200,000 years ago. We expect to receive the remainder of the radiocarbon dates this quarter. They will provide constraints on changes in the CO_2 pressures with time.

REFERENCES

None.

Figure 1. Location of natural CO₂ reservoirs within the Colorado Plateau and Southern Rocky Mountains region of the U.S. The two natural CO₂ fields of Farnham Dome (Utah) and Springerville-St Johns (Arizona-New Mexico), which are the mentioned in this report, are highlighted. The Crystal Geyser-Little Grand Wash fault zone and Salt Wash graben are about 50 miles south of Farnham Dome.

Figure 2. Location of the Springerville-St. Johns CO₂ field, with some CO₂ wells and the structural high highlighted. The travertine deposits that occur over a 400 km² area, and range in elevation from 5860 feet (1787 m) near the Little Colorado River, to 6970 feet (2127 m) above sea level on a plateau to the west (near well 11-21 St).

Table 1. List of the travertine samples collected for radiometric dating. The range in elevation is over 300 m, which suggests that there should have been a significant reservoir pressure difference and a significant age difference between the time of deposition at high elevation, and that at low elevation today.

Sample #	mE	mN	Height (ft)	Height (m)	Age
1	647247	3810848	5955	1816	3524 ± 30
2	646712	3808968	5880	1793	887 ± 35
3	662651	3798459	6970	2126	Not datable
4	648682	3811171	5870	1790	
5	647386	3806761	5900	1800	
6	648539	3808007	6159	1878	
7	657506	3814477	6240	1903	
8	646838	3808876	5860	1787	

note: present elevation of Salado Springs is 5840 ft

Sample

- 1 Travertine dome near Salado Spgs; sample 1 m below rim, in vent
- 2 from east side of Dome, half way from summit; near Little Colorado River
- 3 Voight's Mesa; from travertine slab 100 m from central crater, west side of summit.
- 4 upper flank of travertine slab on north-facing slope above L. Col. River
- 5 dome, 10 m in height on flood plain adjacent to L. Col River; sample from flank; dome has prominent hollow vent
- 6 dome on alluvial bench above sample 6; sample 30 cm below rim, inside crater
- 7 older vent area either side of road east of St Johns. Sample from northern side
- 8 small dome adjacent to L. Col R., was active historically (notch cut in side)