



**PROCEEDINGS OF THE 24TH
INTERNATIONAL APPLIED GEOCHEMISTRY SYMPOSIUM
FREDERICTON, NEW BRUNSWICK, CANADA**



JUNE 1ST-4TH, 2009

EDITED BY

DAVID R. LENTZ, KATHLEEN G. THORNE, & KRISTY-LEE BEAL



VOLUME II



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ISBN 978-1-55131-137-1 (Volume 2)

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APPLIED GEOCHEMISTRY OF GEOLOGICAL STORAGE OF CO₂

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Composition and levels of groundwater in the CO2CRC Otway Project area, Victoria, Australia: establishing a pre-injection baseline

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ABSTRACT: Groundwater monitoring around the CO2CRC Otway Project CO₂ injection site aims to (1) establish baseline aquifer conditions prior to CO₂ injection, and (2) enable detection monitoring for CO₂ leakage, in the unlikely event any should occur in the future. The groundwater composition was monitored at 24 bores around the site for nearly 2 years before injection started. The water samples were analysed for standard bulk properties, and inorganic chemical and isotopic compositions. In addition to sampling, standing water levels were monitored continuously in 6 of the bores using barometric loggers.

The shallow groundwaters have compositions typical of carbonate aquifer-hosted waters, being fresh (EC 800-4000 µS/cm), dominated by Ca²⁺, Na⁺, HCO₃⁻ and Cl⁻, cool (T 12-23°C), and near-neutral (pH 6.6-7.5). Most of the deep groundwater samples are fresher (EC 400-1600 µS/cm), also dominated by Ca²⁺, Na⁺, HCO₃⁻ and Cl⁻, cool (T 15-21°C), but are more alkaline (pH 7.5-9.5). Time-series reveal that most parameters measured have been relatively stable over the sampling period, although some bores display changes that appear to be non-seasonal. Groundwater levels in some of the shallow bores show a seasonal variation with longer term trends evident in both aquifers.

KEYWORDS: groundwater, carbon dioxide, geosequestration, carbon capture and storage

INTRODUCTION

The CO2CRC Otway Project aims to demonstrate the feasibility of large-scale carbon capture and storage (CCS) in Australia. Up to 100,000 tonnes of supercritical CO₂-rich gas (~80% CO₂, ~20% CH₄) are being injected into a depleted gas reservoir ~2100 m below ground (Fig. 1) in south-western Victoria. This naturally occurring gas is produced from the nearby Buttress-1 well, piped to the injection site, and injected into the Naylor field (Waarre C Formation) at the CRC-1 well. Early on during the injection history, the gas was tagged with a flush of tracers (CD₄, SF₆ and Kr) (Underschultz *et al.* 2008).

An extensive world-class monitoring and verification (M&V) program (Hennig *et al.* 2008), of which the present work is but a component, was initiated before injection started to (1) document the natural state of the formation water, groundwater, soils and atmosphere, (2) monitor migration of

the CO₂ plume, and (3) detect leakage, should any occur. The groundwater monitoring project allows the natural groundwater composition and levels to be determined before any injection started [point (1) above]. In the unlikely event of CO₂ leakage into the aquifers overlying the Waarre C Formation, this work may also allow the chemical and/or isotopic detection of changes in water-mineral interactions in the aquifer systems [point (3) above].

GROUNDWATER MONITORING

As part of the M&V effort, groundwater was sampled biannually from 21 bores in the shallow, unconfined Port Campbell Limestone aquifer and from 3 bores in the deeper, confined Dilwyn Formation aquifer (Fig. 1). All these bores are within a radius of ~10 km from CRC-1 (Fig. 2). The pre-injection monitoring, which took place between June 2006 and March 2008, was limited to pre-existing water bores. These

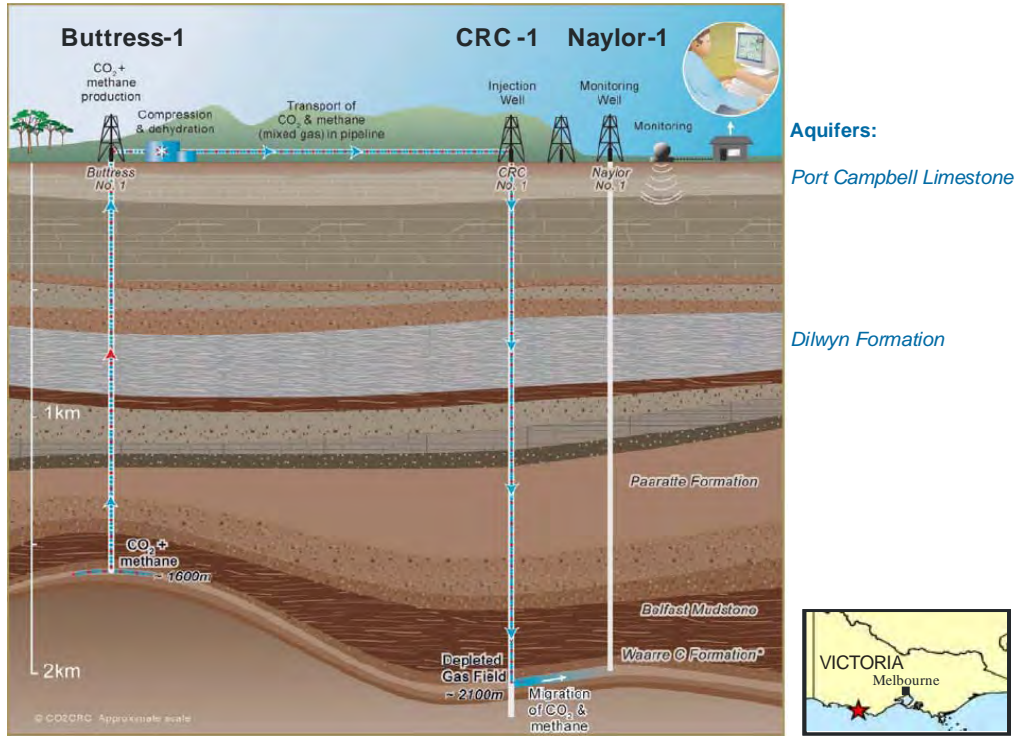


Fig. 1. CCS concept in the Otway Project (www.co2crc.com.au).

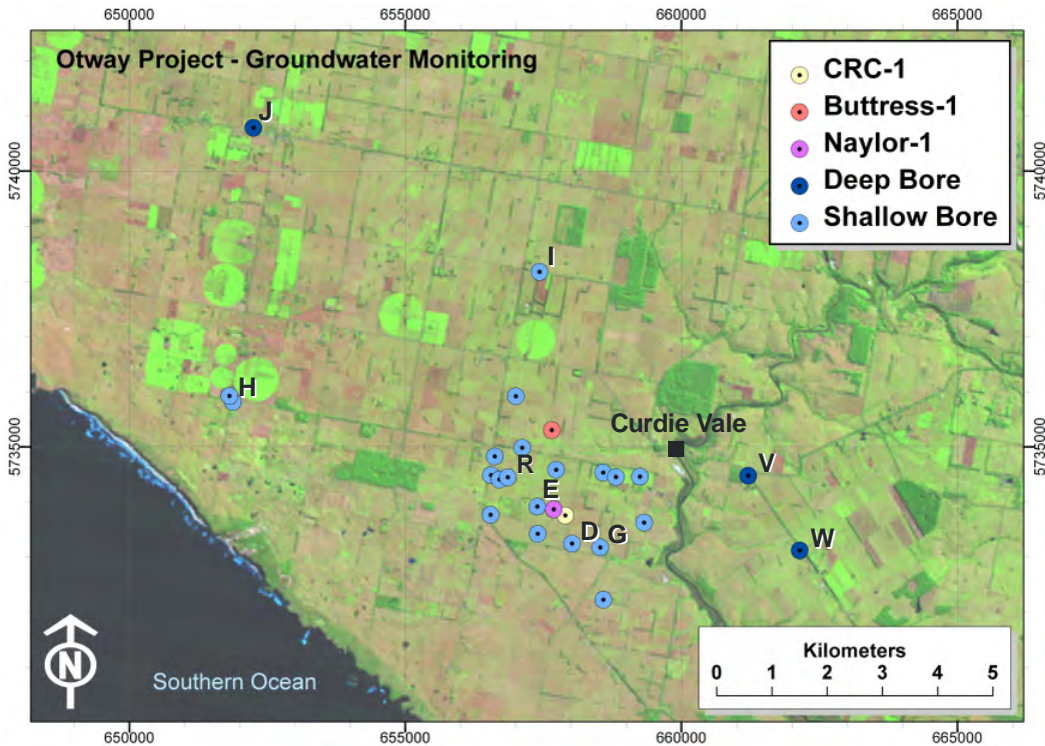


Fig. 2. Location of deep and shallow groundwater monitoring bores and CCS wells CRC-1, Buttress-1 and Naylor-1 (see Fig. 1). Bores mentioned elsewhere in this paper are labelled.

are used locally for domestic, small-scale industry (dairy farming) and environmental monitoring purposes. In addition to groundwater sampling, standing water levels (SWL) have been monitored continuously in 6 of the bores using pressure and temperature data loggers.

METHODS

The water samples were analysed for pH, electrical conductivity (EC), temperature (T), dissolved oxygen (DO), redox potential (Eh), reduced iron (Fe²⁺) and alkalinity (dissolved inorganic carbon, DIC, as HCO₃⁻) in the field. A few special water samples were collected to determine background levels of CD₄, SF₆ and Kr in the headspace gas. SWL and T were recorded hourly in 3 shallow (Sites H, I, R) and 3 deep (Sites J, V, W) open bores using automatic data loggers, which were downloaded biannually.

A suite of major, minor and trace inorganic species were analysed in the laboratory. Stable isotopes of O and H in water, of S in sulfate and of C and O in DIC were also determined.

COMPOSITIONAL TRENDS

The shallow groundwaters have compositions typical of carbonate aquifer-hosted waters, being fresh (EC 800-4000 µS/cm), dominated by Ca²⁺, Na⁺, HCO₃⁻ and Cl⁻ (Fig. 3a), cool (T 12-23°C), and near-neutral (pH 6.6-7.5). Most deep groundwater samples (Sites J, V, W) are fresher (EC 400-1600 µS/cm), also dominated by Ca²⁺, Na⁺, HCO₃⁻ and Cl⁻ (Fig. 3a), and cool (T 15-21°C), but are more alkaline (pH 7.5-9.5).

Time-series reveal that measured parameters have generally been stable over the sampling period. Some shallow bores, however, display increasing EC and T trends, and others, located mostly around the injection site, show decreasing then increasing alkalinity (Fig. 3b). Some bores located mostly further away from CRC-1 show steadily increasing alkalinity (with or without increasing Cl⁻ and Na⁺, and decreasing Ca²⁺) (Fig. 3c). Alkalinity of the deep groundwater decreased slightly over the period. Most isotope

trends are stable over the period, except perhaps for an increase in δ²H_{water} for instance at Sites D (from -34 to -25‰ VSMOW) and G (-35 to -26‰) and a decrease at Site I (-26 to -32‰).

WATER LEVELS

Data collected between January 2007 and March 2008 shows a seasonal climatic response in the shallow aquifer (Fig. 4a), which correlates well with the historic record. SWL in the Dilwyn aquifer varies little and T is essentially constant over the period (Fig. 4b); agreement with historic records, where they exist, is also good. Neither aquifer shows a response to significant perturbation such as the drilling of CRC-1 during February-March 2007.

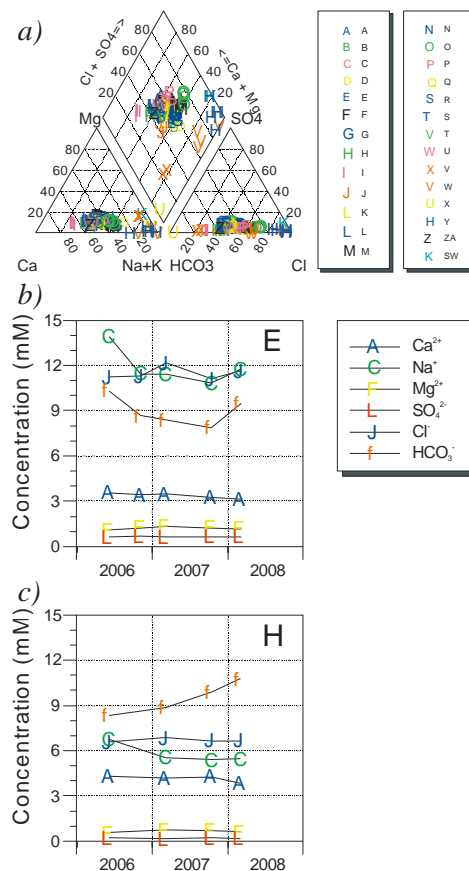


Fig. 3. Piper diagram of all water samples (symbols represent Sites; SW = seawater) (a), time-series of major elements at Site E (b), and at Site H (c).

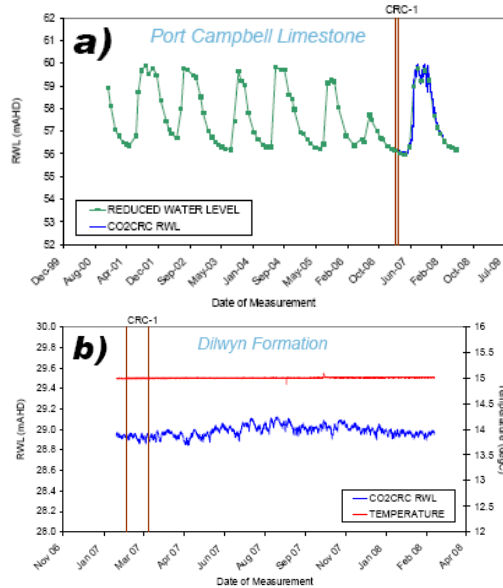


Fig. 4. Reduced water levels (RWL, in m relative to Australian Height Datum) in shallow aquifer at Site I compared to historical data (a), and in deep aquifer at Site J shown with temperature (b).

CONCLUSIONS

Monitoring of the composition and levels of the shallow and deep groundwaters in the Otway Project area has provided a pre-injection baseline revealing both seasonal and non-seasonal changes. Continued monitoring is recommended at the same frequency for at least 2 years

after the completion of CO₂ injection in order to detect any changes that it may cause. Headspace gas sampling for analysis of the chemical tracers added to the injected gas is in progress for selected bores.

ACKNOWLEDGEMENTS

Funding from the Australian Government's Cooperative Research Centres Program and CO2CRC sponsors made this work possible. We thank our colleagues within the CO2CRC for discussions and support. Chris Boreham, Rick Causebrook and Rob Langford provided internal reviews. Published with permission from the CEO of Geoscience Australia.

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Carbon mineralization in mine tailings and implications for carbon storage in ultramafic-hosted aquifers

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ABSTRACT: Atmospheric carbon dioxide is trapped within magnesium carbonate minerals during mining and processing of ultramafic-hosted ore. The extent of mineral-fluid reaction is consistent with laboratory experiments on the rates of mineral dissolution. Incorporation of new serpentine dissolution kinetic rate laws into geochemical models for carbon storage in ultramafic-hosted aquifers may therefore improve predictions of the rates of carbon mineralization in the subsurface.

KEYWORDS: carbon sequestration, tailings, serpentinite, mineral dissolution, weathering

INTRODUCTION

Recent documentation of the formation of magnesium carbonate minerals via reaction of CO₂ with ultramafic rocks and mine wastes suggests that these reactions may be very rapid under near-surface conditions. For example, Wilson *et al.* (2006, 2009) have documented the rapid uptake of atmospheric CO₂ during weathering of chrysotile mine tailings, and Keleman & Matter (2008) have documented similar rates of CO₂ uptake during weathering of the Samail ophiolite. The rates of carbon uptake in these studies are broadly consistent with experimental kinetic data for mineral dissolution and carbonation. The implications of these new rate law data for mineralization of CO₂ in serpentinite-hosted aquifers used for carbon storage is explored here.

CARBON MINERALIZATION IN MINE TAILINGS

Sulfate, halide, and carbonate minerals form in mine waste as a result of chemical weathering reactions and as a by-product of mineral processing. The formation of carbonate minerals is of particular interest for its potential in offsetting greenhouse gas emissions associated with mining. We have documented secondary carbonate mineral precipitation at the Mount Keith Nickel Mine (Western Australia) and the

Diavik Diamond Mine (Northwest Territories, Canada). Data from these active mines are compared to similar data from two closed chrysotile mines at Clinton Creek (Yukon, Canada) and Cassiar (British Columbia, Canada) as reported by Wilson *et al.* (2006, 2009).

Exposed surfaces contain secondary halide, sulfate, and carbonate mineralization. Halide and sulfate minerals are not generally present at depth, suggesting that they are dissolved upon burial. However, secondary carbonate minerals persist at depth within the tailings, but show signs of having been reworked upon burial. Differences in climate and tailings management practices have resulted in widespread mineralization and preservation of secondary carbonate minerals at Mount Keith, and limited carbonate mineralization in the tailings at Diavik, where underwater storage of tailings may have restricted mineralization.

Secondary mineralization at Mount Keith produces hydromagnesite, while mineralization at Diavik includes carbonates of Mg, Ca and Na: nesquehonite, calcite, vaterite, natrite, thermonatrite, natron, trona, gaylussite and northupite. The rate of carbon mineralization at the two mine sites was assessed using quantitative powder X-ray diffraction analysis and the Rietveld

method, as described by Wilson *et al.* (2006). Carbon uptake at Mount Keith occurs at a rate of about 50,000 tonnes CO₂ per year. The rate at Diavik is not significant. Carbon and oxygen isotope analysis of the precipitated carbonate minerals indicates that most of the bound carbonate is derived from the atmosphere. Serpentine, which is the most abundant mineral in mine tailings at Mount Keith, is implicated as the source of Mg for hydromagnesite.

SERPENTINE DISSOLUTION KINETICS FROM EXPERIMENTAL DATA AND IMPLICATIONS FOR CARBON STORAGE

The steady-state dissolution rate of chrysotile in 0.1m NaCl solutions was measured at 22°C and pH ranging from 2 to 8. Dissolution experiments were performed in a continuously stirred flow-through reactor with the input solutions pre-equilibrated with atmospheric concentrations of CO₂. Both magnesium and silicon steady-state fluxes from the chrysotile surface were regressed and the following empirical relationships were obtained:

$$F_{Mg} = -0.22 \text{ pH} - 10.02$$

$$F_{Si} = -0.19 \text{ pH} - 10.37$$

where F_{Mg} and F_{Si} are the log₁₀ Mg and Si flux in mol/m²/s from the chrysotile mineral surface, respectively (Fig. 1). Dissolution was typically non-stoichiometric. These element fluxes were used in reaction-path calculations to constrain the rate of CO₂ sequestration in two geological environments that have been proposed to mitigate anthropogenic increases of atmospheric CO₂. Results indicate that CO₂ injection into serpentinite tailings at 10°C is approximately an order of magnitude faster than CO₂ injection into a serpentinite reservoir at 60°C on a per kilogram of water basis. Aquifer injection, while slower, provides a larger sequestration capacity.

ACKNOWLEDGEMENTS

This study was supported by research

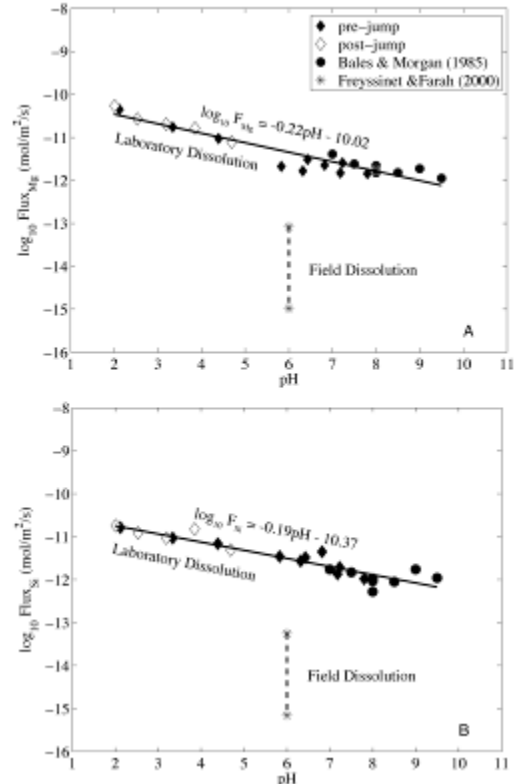


Fig. 1. Summary of chrysotile-steady state element fluxes: (A) Mg and (B) Si as a function of pH. Filled and open diamonds are steady-state fluxes determined after the onset of an experiment and after a pH-jump, respectively. Circles are Bales & Morgan (1985) element fluxes; their rates were determined in CO₂-free solutions. The solid line is the linear least square fit to all the data. The stars are the range in fluxes determined from field serpentinite weathering (Freyssinet & Farah 2000).

grants from the Natural Sciences and Engineering Research Council of Canada, BHP Billiton Limited, and Diavik Diamond Mine Incorporated.

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Comparison of CO₂-N₂-enhanced coalbed methane recovery and CO₂ storage for low- & high-rank coals, Alberta, Canada and Shanxi, China

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ABSTRACT: CO₂-ECBM Micro-Pilots have been carried out in Canada and China to assess the response of low- and high-rank coal reservoirs to CO₂ injection. The selectivity of coals for CO₂, compared to methane, can vary from 10 to 1 depending on coal rank. Although the CO₂ is more efficiently stripped by coals of low rank, permeability impairment is greater and the amount of methane recovered is less than for high-rank coals, providing other reservoir properties are similar. If a pure CO₂ source is not available, N₂-CO₂ mixtures may produce more favourable economics.

KEYWORDS: CO₂ storage, coals, sorption, swelling, methane production

INTRODUCTION

Coal gas reservoirs are dual storage reservoirs consisting of primary and secondary storage systems. The primary storage system makes up 98% or greater of the reservoir volume and contains organic matter, inorganic material, inherent water, and gas stored within very small pore spaces. Primary system gas storage is dominated by sorption phenomena because of the small size of the pores. During sorption, the molecules are within very close proximity to solid surfaces, are attracted to the solid, and are packed closer together than expected from the pressure conditions. The primary porosity system is relatively impermeable and mass transfer is dominated by diffusion (driven by gas concentration gradients). Commercially productive coal gas reservoirs contain a well-developed secondary storage system dominated by natural fractures. Without these natural fractures, commercial production would not be possible. Flow through the secondary storage system is due to pressure gradients between the fracture system and production wells. The majority of gas in a coal gas reservoir diffuses through the primary storage system, desorbs at the interface between the primary and secondary systems, and then

flows through the secondary system to wells.

ENHANCED COALBED METHANE PRODUCTION

The CO₂ storage/enhanced coalbed methane (ECBM) process works by replacing sorbed methane (CH₄) molecules in the primary storage system with sorbed CO₂ molecules (Mavor *et al.* 2002, 2004). The CH₄ molecules are displaced into the coal natural fracture system and to producing wells. The CO₂ is trapped in the primary storage system and there is little breakthrough to production wells until the majority of the well pattern is swept. A storage project terminates at breakthrough.

An alternative gas for ECBM is N₂, which has a different enhanced recovery mechanism from CO₂. N₂ is less sorptive than methane, with a sorptive capacity roughly 40% that of methane for high volatile bituminous B coal (Fig. 1). The N₂ process works by reducing the partial pressure of methane in the secondary system, increasing the rate of desorption from the primary system, and the rate of methane diffusion through the primary system. Some N₂ sorbs into the primary system but the majority remains in the secondary system. N₂ also increases the

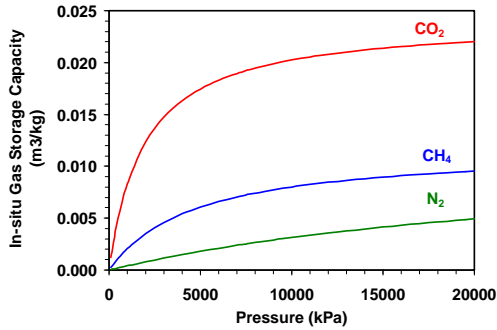


Fig. 1. CO₂ and methane sorption isotherms for the Lower Cretaceous Mannville Group high volatile bituminous B coal, Alberta.

total pressure in the natural fracture system, thereby, increasing the driving force to push gas through the fracture system to producing wells. One significant difference between N₂ and CO₂ injection is that the N₂ breaks through to the production wells and dilutes the well stream. When N₂ production becomes excessive, the production stream must be processed to reject N₂.

Figure 2 shows examples of simulation computations of ECBM recovery, which schematically illustrate the methane recovery rate for two enhanced recovery scenarios, the first due to injection of pure N₂ and the second due to injection of pure CO₂. Also illustrated is the expected recovery without injection (primary production).

N₂ injection rapidly increases the methane production rate. The timing and magnitude depends on the distance between injection and production wells, on the natural fracture porosity and permeability, and on the sorption properties. N₂ breakthrough at the production well occurs at about half the time required to reach the maximum methane production rate in this ideal case. The N₂ content of the produced gas continues to increase until it becomes excessive, i.e., 50% or greater.

The production increase due to CO₂ injection takes longer to develop. This is due to sorption of CO₂ relatively near the well with the sorbed CO₂-methane front growing elliptically out from the injection wells. After a sufficient volume of methane

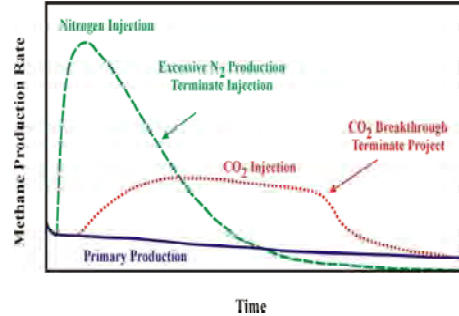


Fig. 2. Relative rates of methane production for the Mannville high volatile bituminous B coal.

has been displaced (roughly 20% of the reservoir volume), the methane productivity increases by a factor of 2 compared to primary production (Fig. 2). Eventually, CO₂ will breakthrough to the production well when sufficient CO₂ has been injected. At breakthrough, in the ideal case, 70% of the reservoir has been swept and the project is terminated.

In the absence of government incentives, the storage/ECBM process must be commercially attractive to interest investors for the large funding required for well facilities and flue gas collection systems. The source of the injected gases may be flue gas emissions from power plants (~13% CO₂, ~80% N₂, ~7% others), fertilizer plants, hydrogen plants, or the byproducts of gas treatment plants (CO₂ and mixtures of CO₂ and H₂S). Flue gas injection may enhance the process economics to the point that large-scale commercial application is possible. Compared to pure CO₂, flue gas injection requires a higher amount of compression for injecting the same amount of CO₂ downhole. One important component of the process design will be efficient compressors that minimize the volume of CO₂ created relative to the CO₂ injected. This design must also incorporate the economics of pre-treating the flue gas to increase CO₂ concentration and to reject the nitrogen from produced methane.

The optimum mix of N₂ and CO₂ in the injection gas depends on the technical and commercial requirements of the process. If CO₂ storage volume is the only consideration, the injected gas should be

100% CO₂. If rapid maximization of hydrocarbon gas recovery is the only consideration, the injected gas should be 100% N₂. The commercial and storage compromise will be between these two cases. We expect that the optimum commercial application will involve injecting variable gas composition to control storage volumes and the amount of N₂ in the produced gas stream. The range of the N₂ content in the injected gas is likely to be between 25% and 75%.

THE EFFECT OF COAL RANK

Lower rank coals, often found at shallow depths, such as the subbituminous C coal of the Fort Union Formation of the Powder River Basin, Wyoming, have a great affinity for CO₂, ten times (Mavor *et al.* 1999) that of methane. While this low-rank coal may be excellent for storage in the right reservoir setting (i.e., depth and pressure), the ECBM process will not be effective. Injection of ten volumes of CO₂ will displace only one volume of methane. As a result, the cost of injecting CO₂ cannot be significantly reduced by the sale of methane. However, in high volatile bituminous B coals, (such as those found in the Mannville Group, in Alberta, Canada, injection of two to three volumes of CO₂ will displace roughly one volume of methane (Fig. 1). The increase in the ratio of methane to CO₂ raises the chance for significant reduction in the cost of CO₂ storage. At the highest coal ranks, such as those found in the anthracitic coals of Shanxi Formation in Shanxi, China (Wong *et al.* 2007) injection of 1.2 volumes of methane will displace roughly one volume of methane (Fig. 3) resulting in production enhancements of more than five times.

CONCLUSIONS

Other reservoir properties being similar, high-rank coals are more favorable for CO₂ storage because of their methane displacement efficiency (related to lower sorption selectivity for CO₂ compared to methane and higher absolute sorption of methane with increasing rank; see Figs 1 and 3). Higher ranks of coal are also more

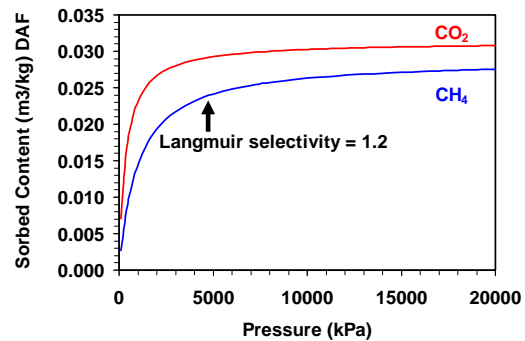


Fig. 3. CO₂ and methane sorption isotherms for the Shanxi anthracite.

favourable because the permeability is less affected by the swelling of the coal when it sorbs the CO₂ (Mavor & Gunter, 2006). Economics may demand that impure gas mixtures containing both nitrogen and CO₂ are used for enhanced recovery. However, for projects where the primary objective is storage of CO₂ in coal, pure CO₂ streams should be used.

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Geochemical modelling and formation water monitoring at the CO2CRC Otway Project, Victoria, Australia

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ABSTRACT: Formation water monitoring and geochemical modelling of the Otway Project CO₂ injection site has been carried out to determine the physical and chemical processes that take place during the injection and migration of CO₂ into a depleted gas reservoir. A U-tube downhole assembly enabled the collection of high quality samples of the gas and the aqueous phases. Integration of the fluid compositional data with numerical modelling of the system indicates the pH is buffered by CO₂-water-rock interactions both prior to and after the arrival of the CO₂. The target formation, the Waarre C sandstone, has low reactivity with respect to CO₂-driven geochemical reactions but contains sufficient calcite to buffer the pH. However, compositional changes predicted in the formation water are not observed implying that the formation waters sampled have not experienced extensive interaction with the CO₂. The interpreted compositional changes and controls appear to reflect the dynamics of a system displaying 3-phase behaviour with separate methane gas, supercritical CO₂, and aqueous phases.

KEYWORDS: formation water chemistry, carbon dioxide, geosequestration, geochemical modelling

INTRODUCTION

The Otway Project of The Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) is a demonstration site for the storage of CO₂. The site is the first extensively monitored carbon storage research study of a depleted gas reservoir. Approximately 100,000 tonnes of an 80:20 CO₂:CH₄ mixture will be injected into the Waarre C sandstone over the lifetime of phase 1 of the project. Monitoring was undertaken (1) to help determine the physical and chemical processes taking place during and after the introduction of CO₂ and (2) to validate numerical models describing the migration of the CO₂ and any geochemical interactions occurring during migration. To facilitate the monitoring and verification process during the initial injection, tracers (CD₄, SF₆, Kr) were included in the gas

injection stream to help establish breakthrough and for leakage detection.

Physical and chemical monitoring is carried out through a U-tube downhole installation (Freifeld *et al.* 2005) that allows the collection of high quality liquid and gas samples from targeted depths. The multi-level U-tube assembly is completed in the Waarre C unit approximately 300 m distant and up dip from the injector well (CRC-1). The Naylor-1 monitoring well is perforated from 2028.3 – 2032.2 m RT and 2039 – 2055 m RT. The U-tube assembly is constructed to sample from U1 at 2027 m RT (gas cap), U2 2040 m RT and U3 2045 m RT both initially below the gas-water contact.

This study describes the results of the formation water monitoring and the interpretation of the physical and geochemical processes from that data,

together with numerical simulations of the CO₂-water-rock interactions.

METHODS

On-site monitoring during sample collection includes in-line probes measuring temperature, pH, and electrical conductivity (EC). Samples were collected in high pressure vessels to limit compositional changes resulting from the exsolution of gases during collection. The high pressure vessels were transported to University of Adelaide for bench top analyses and preparation for further analytical procedures. Bench top analyses included measuring pH, Eh, T, EC, and alkalinity, and determining Fe, NO₃, PO₄ and SiO₂ using spectrophotometry. The remaining fluid was then filtered and aliquots were prepared for major, minor and trace species analyses using IC (ion chromatography), ICP-OES (optical emission spectrometry) and ICP-MS (mass spectrometry) as well as IRMS (isotope ratio mass spectrometry) for isotopes of O, H and C. Table 1 shows some of the major species chemistry for samples collected from U2.

Fluid and gas samples were also collected for hydrocarbon and non-hydrocarbon gas compositional analyses (GC), carbon isotopes of CO₂ (GCIRMS), and for tracer analyses (GC-MS).

Mineral content and composition of core plugs from the reservoir rock were determined using petrologic examination, XRF, XRD, and microprobe analyses. Geochemical modelling was carried out using SOLMINEQ.88, the Geochemist's Workbench and TOUGHREACT.

RESULTS AND DISCUSSION

Prior to injection, aqueous samples were collected from U2 and U3 in order to establish the methodology and baseline conditions. The samples were contaminated with kill fluid and the succession from the first samples shows a decrease in K and increase in most other species. Subsequent samples continued to show some contamination but it was determined that essentially baseline conditions had been achieved except for

the K. Later minor fluctuations in the K content are interpreted to indicate changes in the degree of kill fluid contamination that relate to permeability variations in the preferred interval.

The first indication of breakthrough of the CO₂ occurred in samples from all 3 U-tube samplers on 17 July, 2008 with slightly elevated CO₂ content and the presence of tracers. In mid-August, U2 became gassy and the pH dropped significantly. There was no coincident change in either the alkalinity or cation concentrations. By early September, U2 had converted entirely to gas lift. Over the same time frame, as the pH decreases, the per cent of CO₂ in the U2 samples (for gas exsolved from the water sample through decrease from formation to atmospheric pressure) increased from ~4% to >40%.

U3 samples contained high gas content in late October and reached gas lift by early January 2009. The pH followed a trend similar to that in U2 with decreases occurring with increased gas content in the sample. Alkalinity showed some increase but did not fully match the pH changes. The major cations showed changes more consistent with increased contamination than significant CO₂-water-rock interaction.

Where interactions between the (supercritical) gas and water are possible, there is rapid isotopic equilibration between the oxygen in CO₂ and H₂O. The potential to use this isotopic exchange equilibria as a measure of the extent of CO₂-water interaction, and thus as an indicator of CO₂ migration, is discussed in Kharaka *et al.* (2006). Unlike the results of Kharaka *et al.* (2006), there are no consistent changes in the oxygen isotopic composition of the fluid samples at the Otway site.

GEOCHEMICAL MODELLING

Geochemical modelling of the system at reservoir T and P were carried out to determine the relations between the CO₂, pH, and mineral phases present. SOLMINEQ.88 was used to recalculate the pH at reservoir P and T conditions.

Table 1. U2 selected data.

Date	pH	pH	Alk	K	Mg	Na	Ca	Cl
	field	lab	[mmol/l]	mg/L	mg/L	mg/L	mg/L	mg/L
11/10/2007	-	6.69	13.2	1213	92.1	5783	458	11993
31/01/2008	6.50	6.38	12.8	452	100	6331	513	12211
31/03/2008	-	6.41	10.9	295	97.6	7126	590	12525
25/05/2008	6.06	5.85	10.8	308	97.8	7207	602	12410
11/06/2008	6.23	5.91	11.0	317	97.8	7123	598	12319
26/06/2008	6.03	6.37	12.1	252	102	6809	627	12390
17/07/2008	5.85	6.17	11.5	245	98.9	6850	646	12459
31/07/2008	5.92	6.10	11.9	256	98.5	6718	642	12441
7/08/2008	6.23	6.11	11.8	261	99.1	6845	640	12350
21/08/2008	5.04	5.58	11.7	329	88.0	6734	596	12280
28/08/2008	5.14	5.34	11.3	312	90.6	6844	601	12309
4/09/2008	4.66	5.94	11.3	-	-	-	-	-

The simulated CO₂ fugacity matches the initial reservoir CO₂ content and indicates that the pH is buffered by CO₂-calcite equilibrium. Further modelling was carried out using the Geochemists Workbench React and Tact modules with the thermodynamic database modified to reflect the elevated P conditions and kinetic rate parameters consistent with the Waarre C mineralogy. The Waarre C shows low reactivity and short-term predictive modelling of the system under elevated CO₂ content changes little with time (Fig. 1).

The only significant changes anticipated are in the pH, and in the HCO₃ and Ca content if the system has calcite present, as suggested by the petrology and the SOLMINEQ.88 modelling. The field data show the decrease in pH but not the predicted increases in HCO₃ and Ca. This suggests that either there is no calcite present in the region around the Naylor-1 monitoring well or that the formation water has not had sufficient contact time with elevated CO₂ in the formation. The numerical model with calcite present predicts a pH similar to the observed pH just before gas lift (Fig. 2). Without calcite buffering the pH remains low (pH = 4.1).

It would appear that the system shows pH change and buffering but the other predicted compositional changes of the fluid are not observed. The preliminary interpretation of this data is that injection

of the CO₂ mixture has resulted in a 3 phase system, represented by the methane gas cap, the injected CO₂ mixture, and the formation water. If the CO₂ had mixed significantly with the methane gas cap changes in the total gas composition in U1 should mimic those of U2 and U3. However, this was not observed, and the CO₂ content in U1 until early November 2008. If the CO₂ had migrated in the aqueous phase there should be some evidence of CO₂-water-rock interaction and this is also not observed. As a separate phase, the supercritical CO₂:CH₄ mixture would only partially mix with the methane gas cap as the density and viscosity contrast is less than the CO₂-water difference (Oldenburg 2003). As the CO₂ migrates up dip to the Naylor-1 monitoring well the plume would increase in thickness forcing the (supercritical) gas-water contact down resulting in U2 then U3 reaching gas lift. There is little opportunity for the CO₂ to dissolve in the water except in the wellbore and at the CO₂-water interface. Thus there is no compositional change observed in the sampled water.

CONCLUSIONS

Compositional changes in the formation water sampled from the Waarre C sandstone at the Otway Project pilot site provide information on the physical and chemical processes taking place during the injection and migration of CO₂. By

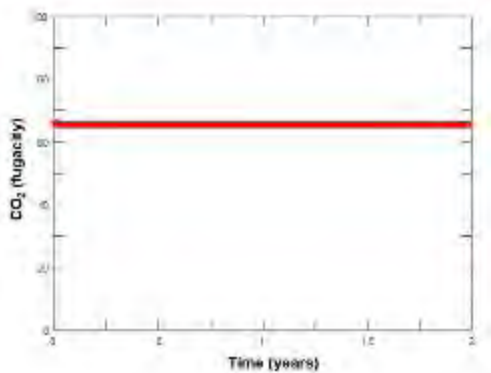


Fig. 1. Change of modelled CO₂ fugacity with time.

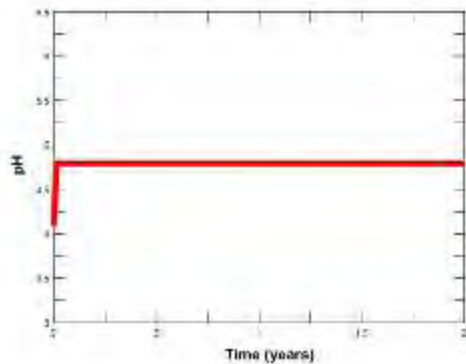


Fig. 2. Modelled pH with calcite buffering.

comparing the observed results with the chemistry predicted through numerical modelling, controls on the pH and composition are made evident. In the case of the Waarre C sandstone, the low content of mineral phases other than calcite that will react with CO₂-rich water allows several observations and interpretation to be made.

(1) pH appears to be buffered by CO₂-

calcite equilibrium both before and after the arrival of the CO₂-rich plume.

(2) The evolution of the fluid composition reflects a lack of significant contact between the aqueous phase and the CO₂ while in the pore space of the reservoir.

(3) The CO₂ migrates as an immiscible phase with respect to both the methane gas cap and the formation water.

ACKNOWLEDGEMENTS

Funding from the Cooperative Research Centres Program of the Australian Government and CO2CRC sponsors made this work possible. We thank our colleagues within the CO2CRC for discussions and support. Sample collection and analysis were greatly assisted by staff of Deakin University, Australian National University, and Monash University.

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Pembina Cardium CO₂ Monitoring Project, Alberta Canada – geochemical evaluation and modelling of the geochemical monitoring data

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ABSTRACT: A CO₂ monitoring pilot was initiated at the Penn West Energy Trust CO₂-EOR operations within the Cardium Formation of the Pembina Field. The Penn West Pembina Cardium CO₂-EOR Monitoring Research Program focused on well integrity, local and regional geology and hydrology, extensive geochemical and geophysical monitoring, and short- and long-term predictive modelling.

Changes in the composition of the produced fluids were studied within the geochemical modelling program of the Penn West Monitoring Project. These changes clearly demonstrate directional heterogeneity within the reservoir, and give a clear indication of the short-term chemical reactions controlling the produced water chemistry. Equilibrium speciation calculations demonstrated that many of the produced waters are undersaturated with respect to calcite. This is most easily explained when mixtures of waters of quite different chemical compositions are produced from a single producing well. This observation has important implications for the interpretation of produced water compositions and demonstrates that flow within the reservoir must be understood to fully interpret the chemical signatures. Finally, chemical responses associated with oil field operational procedures such as well workovers could be seen for months after the events.

KEYWORDS: *formation water chemistry, carbon dioxide, geosequestration, geochemical modelling*

INTRODUCTION

The Cardium Formation of the Pembina Field is located approximately 115 kilometres southwest of Edmonton, Alberta, Canada. The Pembina Field was discovered in 1953 and put on primary production in 1955. It was converted to a water flood starting in 1958. In March, 2005, a CO₂ monitoring pilot was initiated by Penn West Energy Trust at their CO₂-EOR operations within the field. CO₂ was injected into two wells and water into several wells around the immediate pilot area. Early in 2007, the pilot was converted to a WAG (Water Alternating Gas) EOR scheme, where on an approximately monthly basis, the injection of water and CO₂ are switched to the other well.

The Penn West Pembina-Cardium CO₂-EOR Monitoring Research program focused on establishing: (1) the state of the reservoir and wells, (2) the regional, local and site-specific geology and hydrology, (3) the movement of CO₂ in the

Cardium reservoir using seismic and monitoring of pressure, temperature, and composition of produced fluids, and (4) the short- and long-term fate of CO₂ through predictive modelling (Lakeman 2008).

The goals of the Penn West Monitoring Project were to deduce chemical processes within the reservoir, to track the path and fate of the injected CO₂ (flood performance), and to quantify the long-term CO₂ storage capacity of the reservoir. The necessary data to undertake this assessment were taken from other research in the Penn West Pembina Cardium Monitoring Research Program. This included detailed geological and reservoir studies, modelling based on history matches of the oil, gas, water production and detailed mineralogical investigations (Nightingale *et al.* 2008).

The injected and produced gases and fluids were sampled and analysed for a broad range of chemical and isotopic parameters (Shevalier *et al.* 2008). The

initial produced water chemistry was evaluated through three 'baseline' sampling trips carried out between February and April, 2005. CO₂ injection was initiated in March, 2005. From May 2005 to March 2008, monthly samples were taken, depending on operational conditions. Additionally, historical data on the Pembina Field waters were available (Melrose *et al.* 1976).

RESULTS AND DISCUSSION

The data set collected at the Penn West site is extensive, with 28 sampling trips undertaken to date. Selective data are shown in Figures 1 and 2 which show, respectively, the changes in the calculated partial pressure of carbon dioxide in equilibrium with the produced fluid, and the measured wellhead pH of the produced fluid as a function of the sampling date. These data show the response through the three baseline and the subsequent sampling trips. Some data are missing as not all the wells were operational, or producing enough water for a sample to be recovered on a given sampling trip.

The chemical effects of carbon dioxide breakthrough can be clearly seen on the right hand side of each of the figures. There is a strong directional trend reported in the reservoir, which is reflected in the geochemical signal. The producing wells which lie 'on trend' with the CO₂ injectors show a rapid chemical response in contrast to the 'off trend' wells for which the response is considerably delayed.

Figure 3 shows a schematic diagram of the CO₂-EOR site, together with the calculated calcite saturation index for each produced water sample as a function of time and for each well. This figure also shows that there is a clear difference between those wells on the fracture trend and those off-trend. For most of the on-trend wells, the calcite saturation drops shortly after the onset of CO₂ injection, becoming negative. This is contrasted by the off-trend well behavior, for which the SI remains nearly constant, and positive through most of the period represented. The rapid decrease seen in a few wells

near the end of the monitoring period is associated with the arrival of a strong signal due to injected CO₂. It is somewhat unexpected that some many of the samples were undersaturated with respect to calcite; we interpret this as indicating mixtures of waters with quite different chemical compositions are produced from these wells.

Melrose *et al.* (1976) noted that the waters produced from the Cardium reservoir under water flooding changed in composition from the initial formation water (a concentrated NaCl-dominated fluid) to a diluted Na (Cl,HCO₃) water. This evolution in water composition is associated with ion exchange reactions coupled with calcite dissolution and CO₂ stripping from the oil phase. These ion exchange reactions can control the short-term response of the produced water chemistry to any changes in the injected fluid composition. Transient responses can occasionally be seen in the composition of the produced water recovered during this study. These

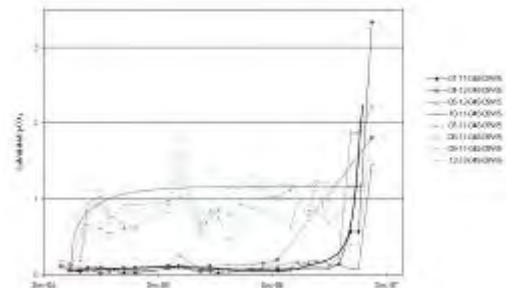


Fig. 1. Calculated partial pressure of CO₂ in equilibrium with the produced fluids.

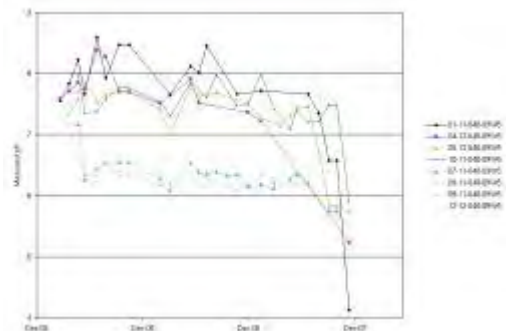


Fig. 2. Measured pH of the produced waters at the wellhead.

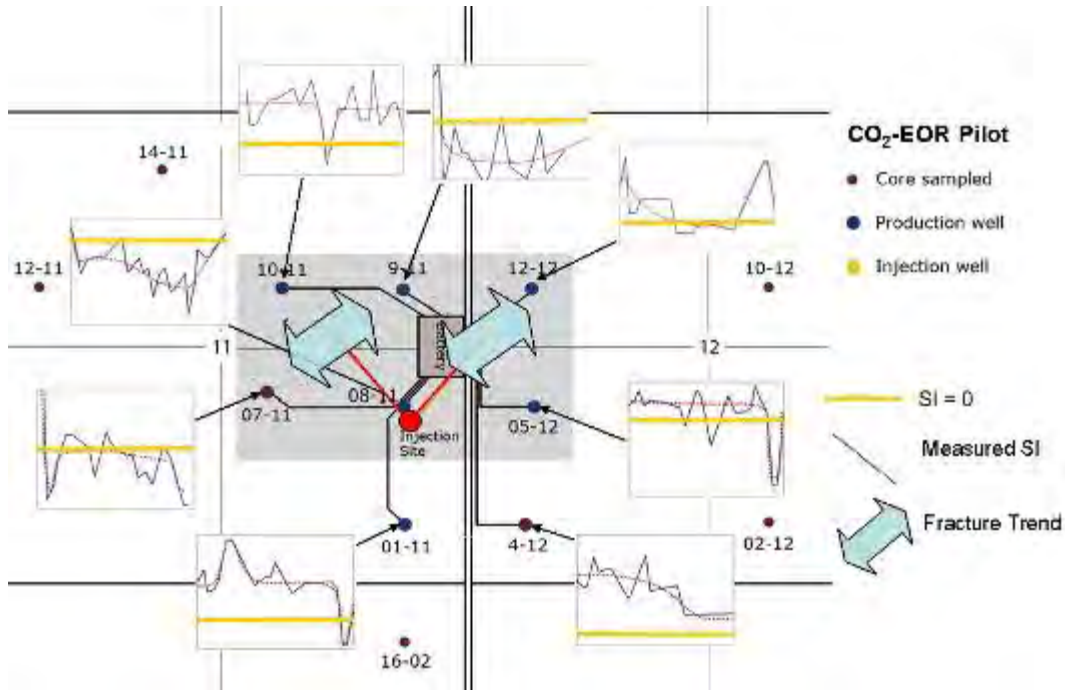


Fig.3. Schematic representation of the Penn West Cardium CO₂ EOR project together with the time evolution of the calcite saturation index. The horizontal line in each SI figure represents an SI of 0. The maximum SI on each figure is 0.8 and the minimum is -0.4, with the exception of well 08-11 with a maximum SI of 0.4 and a minimum of -1.6.

transient responses are often related to well workover events. Often, highly concentrated solutions are used as weighting fluids during well maintenance. These fluids can induce a shift in many of the equilibria which control the produced water chemistry under 'normal' operating conditions. These geochemical changes are transitory but have been observed to last for months after the operational procedures that initiated them was completed (Talman *et al.* 2009).

Filtering out the operationally induced changes from the produced fluid compositions clarified the changes induced through reactions with the injected carbon dioxide and helps establish the normal variations in fluid composition.

CONCLUSIONS

The results of this study demonstrate that geochemical analysis of CO₂-EOR operations can yield important insights into the reactions which will ultimately

determine the fate of the injected CO₂. Detailed geochemical sampling and analysis have provided the necessary data to interpret the processes occurring in the reservoir. The observed trends in the data are consistent with known geochemical process in the reservoir. The occasional large perturbations are the results of field operations, typically well workovers.

Observations of the arrival of the CO₂ acid front at different wells clearly demonstrates that there is a great deal of heterogeneity in the reservoir. Furthermore, the arrival of waters which are undersaturated with respect to calcite suggests that single producing wells are recovering waters with widely different CO₂ contents. These observations have important implications for the interpretation of produced water compositions; in complex reservoirs it must be done in conjunction with detailed reservoir flow models.

Geochemical examination of the

produced water composition has established that the primary controls on the produced water compositions are the injection fluid compositions, the formation fluid composition, and the formation mineralogy, and their interaction through mixing, dissolution, and ion exchange. Detailed historical data is critical to the interpretation of the current produced water compositions.

ACKNOWLEDGEMENTS

This work was carried out with the strategic guidance and financial support of Penn West Energy Trust, AERI (Alberta Energy Research Institute), Western Economic Diversification Canada, Natural Resources Canada, and the Alberta Government.

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Numerical assessment of CO₂ enhanced CH₄ recovery from the Mallik gas hydrate field, Beaufort-Mackenzie Basin, Canada

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ABSTRACT: The Mallik gas hydrate field represents an onshore permafrost-associated gas hydrate accumulation in the Mackenzie Delta on the coast of the Beaufort Sea, Northwest Territories, Canada. This deposit contains a high concentration of natural gas hydrate with an underlying aquifer or free-gas zone at the base of the hydrate stability field. The physical and chemical properties of CH₄ and CO₂ hydrates indicate the possibility of coincident CO₂ sequestration and CH₄ production from the Mallik gas hydrate bearing zones. This study presents a numerical assessment of CO₂ sequestration and the recovery of CH₄ from the gas hydrates at the Mallik site, Mackenzie Delta, Canada.

KEYWORDS: CH₄ hydrate; hydrate kinetics, hydrate stability, CO₂ sequestration; numerical simulation

INTRODUCTION

Gas hydrates are crystalline compounds in which smaller gas molecules (<0.9 nm) are engaged inside the lattices of hydrogen-bonded ice crystals. The gas molecules in the crystalline solids are effectively compressed, volumetrically, by a factor of 164. A comprehensive review of the physical and chemical properties of gas hydrates can be found in Sloan (1998, 2003).

The Beaufort-Mackenzie Basin hosts immense unconventional natural gas hydrate reserves that are often co-located with conventional petroleum resources. Osadetz *et al.* (2005) reported that the conventional resources are co-located with an immense gas hydrate resource estimated between 2.4×10^{12} and 87×10^{12} m³ of raw natural gas. Because the expected decline in conventional natural gas production from the Western Canada Sedimentary Basin cannot be replaced by conventional production from frontier regions alone, this immense hydrate resource offers a solution to replace the expected decline in conventional gas reserves.

Majorowicz & Osadetz (2001) reported that the Mallik gas hydrate-bearing deposit in permafrost regions tends to occur at depths of 700 m to 1400 m where the permafrost is 100 m to 900 m thick. The Mallik 2002 Gas Hydrate Production Research Well Program conducted scientifically constrained production tests of the natural gas from the Mallik gas hydrate deposit, which is situated in the Mackenzie Delta on the coast of the Beaufort Sea, Northwest Territories, Canada (Dallimore *et al.* 2005a; Satoh *et al.* 2005). Gas hydrate production tests demonstrated the potential for possible commercial production. Japan intends to establish commercial production from gas hydrates within the time frame of conventional natural gas production from the Mackenzie Delta (Yonezawa 2003).

Currently, there are three possible gas recovery processes for hydrates: (1) thermal stimulation, (2) depressurization and (3) inhibitor injection. Very limited thermal stimulation and depressurization tests were reported for the Mallik natural gas hydrate reservoirs, together with numerical simulations (Moridis *et al.* 2004,

and Kurihara *et al.* 2005). However, there is no sustainable and environmental friendly recovery technology for the Arctic gas hydrates.

The objective of this study is to evaluate the feasibility of CO₂-enhanced CH₄ recovery technology for the Beaufort-Mackenzie Basin gas hydrates. The physical and chemical properties of CH₄ and CO₂ hydrates indicate the possibility of coincident CO₂ sequestration and CH₄ production from the Mallik gas hydrate-bearing deposits.

MALLIK GAS HYDRATES

The production research well, JAPEX/JNOC/GSC Mallik 5L-38 showed three gas hydrate-bearing zones at depths from 892 to 930 m, 942 to 993 m, and 1060 to 1120 m with gas hydrate

saturations ranging from 50 to 85%, 40 to 80%, and 80 to 90%, respectively. Fig. 1 presents important geophysical log data, and estimated porosity, permeability, and hydrate saturation, and identifies three major hydrate-bearing zones. The hydrate-aquifer interface marks the bottom of the stability zone at a pressure of 12,962 kPa, temperature of 12.2°C, and pore water salinity of 45,000 ppm (45 ppt – parts per thousand) (Wright *et al.* 2005).

In the JAPEX/JNOC/GSC program, small-scale field production tests were conducted by using pressure-drawdown experiments. Data measured in response to depressurization are: pressure, temperature, gas flow, and water flow. During our study, these data were not available to us.

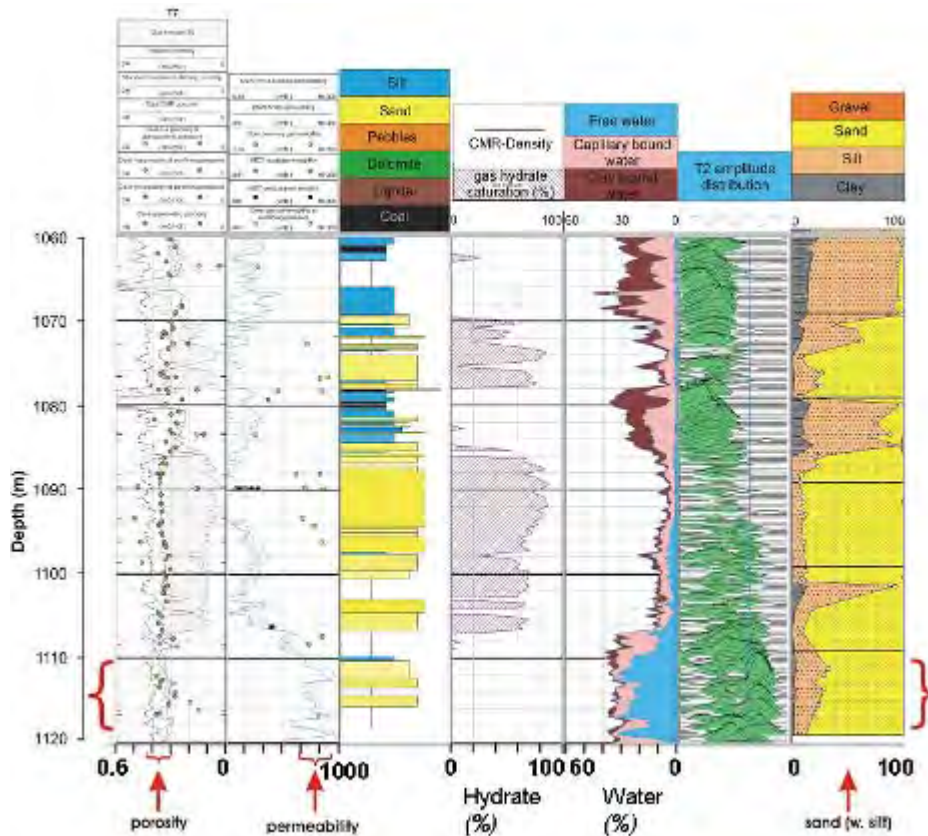


Fig. 1. Log data showing the variation of porosity, permeability, and gas hydrate saturation for the Mallik Gas Hydrate Research Program Well-5L-38 (Uddin *et al.* 2008b).

CH₄ PRODUCTION FROM THE MALLIK GAS HYDRATES

A unified gas hydrate kinetic model (developed at ARC) coupled with a thermal reservoir simulator (CMG STARS) was applied to simulate the dynamics of CH₄ production and CO₂ sequestration processes in the Mallik geological zones. The kinetic model contains two mass transfer equations: one equation transfers gas and water into hydrate, and a decomposition equation transfers hydrate into gas and water (Uddin *et al.* 2008a).

Uddin *et al.* (2008b) conducted several depressurization simulations for the Mallik 5L-38 well. Their results showed that the Mallik gas hydrate layer with its underlying aquifer could yield significant amounts of gas originating entirely from gas hydrates, the volumes of which increased with the production rate. However, large amounts of water were also produced. Sensitivity studies indicated that the methane release from the hydrate accumulations increased with the decomposition surface area, the initial hydrate stability field (P-T conditions), and the thermal conductivity of the formation. Methane production appears to be less sensitive to the specific heat of the rock and of the gas hydrate.

Fig. 2 highlights a serious practical limitation in the depressurization technology due to the drop in temperature from the heat loss during the breakdown of the hydrate (Uddin *et al.* 2008b). This leads to a new stability field at lower salinities. The stability paths in such a progressive depressurization could lead into a complex ice formation domain.

CO₂ SEQUESTRATION IN THE MALLIK GAS HYDRATES

Uddin *et al.* (2008b) presented CO₂ hydrate formation simulations for several generic reservoirs similar to Mallik 5L-38. The plots of P-T conditions (see Figs 5 to 10 in Uddin *et al.* 2008b) shows a significant increase in temperature with CO₂ hydrate formation. This leads to a new stability field at higher salinities and highlights a practical limitation in CO₂ hydrate formation (Fig. 3).

CO₂ ENHANCED CH₄ PRODUCTION

The combination of CO₂ injection and methane production over specific PT regimes allows the heat effects of CO₂ hydrate formation and methane hydrate decomposition to nullify each other resulting in a sustainable delivery process which both reduces CO₂ emissions to combat global warming and recovers methane to supplement the declining reserves of conventional natural gas (Fig. 4). This gas hydrate phase-behaviour in response to the dissociation and formation processes clearly demonstrates the potential of CO₂ enhanced CH₄ recovery from the Mallik gas hydrate deposit.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the

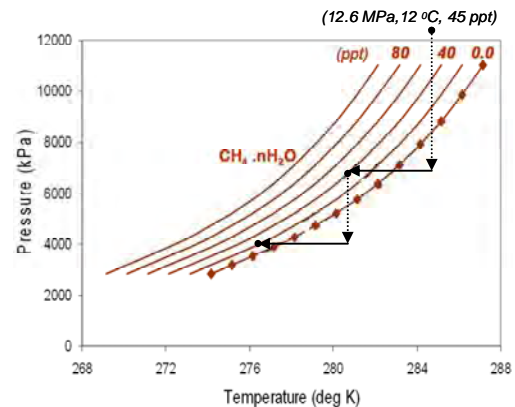


Fig. 2. CH₄ hydrate stability curves (laboratory data) showing CH₄ hydrate dissociation paths (schematic) in the depressurization method.

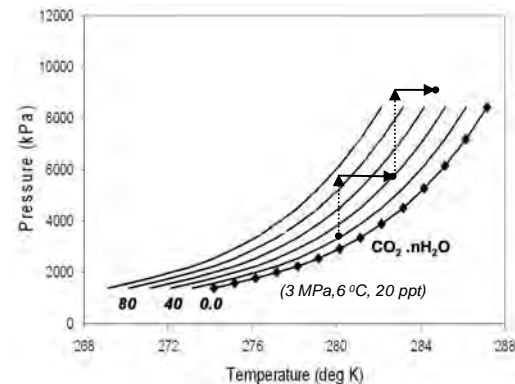


Fig. 3. CO₂ hydrates stability curves (lab data) showing CO₂ hydrate formation paths (schematic) by injection of CO₂ gas.

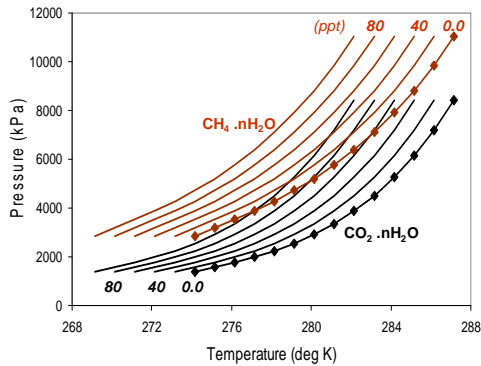


Fig. 4. CH₄ - and CO₂ hydrates stability curves showing CO₂ enhanced CH₄ hydrate dissociation zone.

support from the Alberta Research Council and the Geological Survey of Canada.

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Geochemical monitoring of chemical and isotopic compositions of CO₂ fluids and calcite precipitation during injection tests at Ogachi Hot-Dry Rock site, Japan

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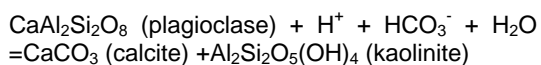
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ABSTRACT: Field experiments of CO₂ sequestration into the Ogachi hot dry rock (HDR; the temperature is 200°C) site are performed to investigate mineralization of a part of CO₂ as carbonates by interaction with rocks (Georeactor; Ca extraction from rocks and carbonate fixation). In 2007, CO₂ dissolved water (river water with dry ice) was directly injected into OGC-2 (from September 2nd to 9th) and Run #2 (from September 11th to 16th). Several tracers were also injected at the same time. Water samples are collected at the depth of ca. 800m by a sampler (500ml in volume) and monitored for their chemical and isotopic compositions. During the Run #2 experiment, river water was injected into OGC-1 at 2 days after injection of CO₂ water into OGC-2. During the field experiments, dissolution or precipitation rates of calcite were determined by using a technique of “in site analyses”. Calcite crystals covered with Au film is hold in a crystal cell and set in a crystal sonde. The crystal sonde is then put into OGC-2 and water samples at the certain depth is introduced into the sonde. After 1 hour, the sonde is recovered and the calcite crystal is observed by a newly developed phase shift interferometer to analyze the dissolution or precipitation rates of calcite from the reservoir fluids. The “in situ analyses” show that calcite precipitation was observed within 2 day after the injection. This supports the view that most of CO₂ injected might be fixed as carbonate.

KEYWORDS: georeactor, CO₂, mineralization, calcite, Ogachi

INTRODUCTION

Several research programs have been proceeded on CO₂ sequestering, where the temperatures of CO₂ reservoirs are less than 100°C and pressures are a few tens to hundreds of bars (ex. Perkins & Gunter 1996; Holloway 1996; Gale 2004). In countries such as Japan, where have many active volcanic areas, one possibility is to sequester CO₂ into hydrothermal regions. The chemical reaction rates between CO₂-saturated water and rocks are usually faster than those at room temperature. For example, the following reaction can proceed to the right side at high temperature (Gale & Shane 1905).



(1)

Carbonate-rich rock formations can be observed in most Japanese geothermal fields. In the Sumikawa field, Akita, Japan, for example, CO₂-rich ground waters are thought to have reacted with reservoir rocks according to reaction (1), to form a carbonate and kaolinite alteration assemblage. An isotopic investigation of

calcites at Sumikawa indicated that the reaction occurred at 100 to 250 °C by interaction of reservoir rocks with meteoric waters (Ueda *et al.* 2001).

THE CONCEPT OF “GEOREACTOR”

Reaction (1) moves towards the right side at higher temperature, reflecting the fact that calcite solubility decreases with increasing temperature. The calcite and kaolinite (clay)-rich rock is produced through the reaction and acts as a cap rock for the geothermal reservoir. These considerations, together with the increasing reaction rates as temperatures are elevated and the fact that precipitation of carbonate minerals fixes CO₂ suggest that CO₂ sequestration could be practicable by injection into geothermal fields (Georeactor; Fig.1).

In Japan, total rock volume in high (>150°C) and intermediate (90-150°C) temperature fields are estimated to be 2100 and 2800 km³ respectively. CO₂ storage capacity is calculated to be about 20 billion tons CO₂ (ca. 17 times Japan's total annual CO₂ emissions). The CO₂/(Ca+Mg) mole ratio of typical igneous rocks is 0.012-0.12. If

1-12% of Ca and Mg would be released, CO₂ may be fixed in carbonate minerals (Ohsumi *et al.* 2005).

In our laboratory experiments, a part of CO₂ can be precipitated as carbonate during interaction with rocks at 100 to 250°C (Ueda *et al.* 2005). To examine this phenomena in the field, CO₂ saturated water was injected into the Ogachi HDR site.

FIELD EXPERIMENTS

The Ogachi hot dry rock (HDR) field is situated at the northeast Japan and has been studied to produce geothermal electricity by Central Research Institute of the Electric Power Industry for 20 years. There are two injection/production wells (OGC-1 and -2) and an observation one (OGC-3). Two major feed zones were formed by hydro fracturing at depth of 700m and 1100m, where their temperatures are 170 and 210°C, respectively.

Field experiments of CO₂ sequestration into the Ogachi HDR have been examined for 4 years by our group (Metcalf *et al.*, 2006; Ueda *et al.* 2007). In 2007, CO₂ dissolved water (river water with dry ice) was directly injected into OGC-2 (Fig.3; Run #1 (from September 2nd to 9th) and Run #2(from September 11th to 16th)). Several tracers were also injected at the same time. Water samples are collected at the depth of ca. 800m by a sampler (500ml in volume) and monitored for their

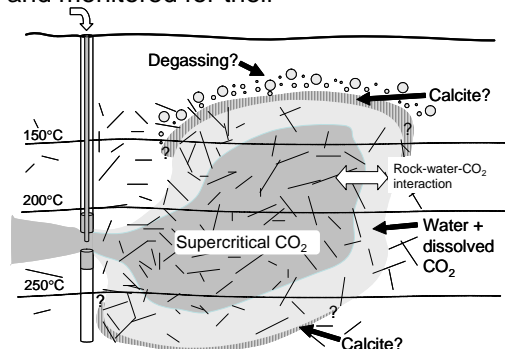


Fig. 1. Outline of CO₂ sequestration into geothermal fields.

chemical and isotopic compositions (δD , $\delta^{18}O$, $\delta^{13}C_{CO_2}$). During the Run #2 experiment, river water was injected into OGC-1 at 2 days after injection of CO₂ water into OGC-2.

During the field experiments, dissolution or precipitation rates of calcite were determined by using a technique of “in site

analyses” (Sato *et al.* 2007a). Calcite crystals covered with Ti rod or Au film is hold in a crystal cell and set in a crystal sonde. The crystal sonde is then put into OGC-2 and water samples at the certain depth is introduced into the sonde. After 1 hour, the sonde is recovered and the calcite crystal is observed by a newly developed phase shift interferometer

Injexction of CO2 and river water

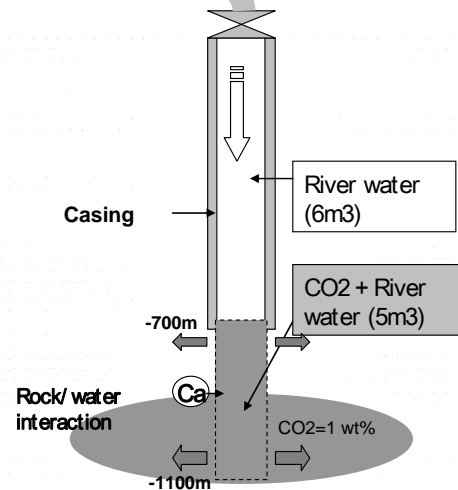


Fig. 2. . CO₂-water injection test at OGC-2 in 2007.

(Ueda *et al.* 2005; Sato *et al.* 2007b) to analyze the dissolution or precipitation rates of calcite from the reservoir fluids.

RESULTS AND DISCUSSION

During the 2007 field experiments, CO₂ concentrations of the water samples under the reservoir pressure could not be correctly monitored due to the broken of the water sampler. This means that water samples were collected around 800m depth and a part of CO₂ must be degassed during ascending to the surface from the sampler. Therefore, CO₂ concentrations of the reservoir fluids are calculated on the basis of the observed pH and charge balance of each samples (Case 1) and the tracer concentration (Case 2). The Case 2 means that CO₂ in the injected water did not react with rocks. Fig.3 shows the calculated CO₂ concentration with iodine. Iodine concentration decreases from 1000 to 200µg/L with the elapsed time. From Fig.4, the fraction of the injected CO₂ water (1 wt.% CO₂) is almost zero. This means that

the injected water was completely diluted with the reservoir fluid. The calculated CO₂ concentrations vary from 900 to 600 mg/L .

From the chemical compositions of water samples, the saturation index of calcite is calculated as follows;

$$S.I. \text{ (Saturation Index)} = \text{Log} (Q/K) \quad (2)$$

where Q and K are activity and solubility products of calcite, (Ca²⁺)(CO₃²⁻), respectively. If S.I.>0, the fluid is saturated with respect to calcite (calcite precipitation).

Fig. 4 shows the change of the S.I. during the experiments (Run2). In the case 1, the S.I. is above zero except for the sample collected just after CO₂ injection. In contrast, the S.I. is close to zero in the case 2 implying that the reservoir fluid mixed with the injected CO₂ water is almost in equilibrium with calcite. Fig. 6 also shows the observed dissolution or precipitation rates of calcites which are determined by in site analyses. From these results, the injected CO₂ water is

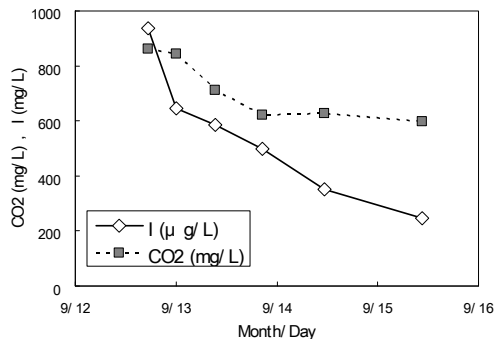


Fig. 3. Concentrations of iodine and CO₂.

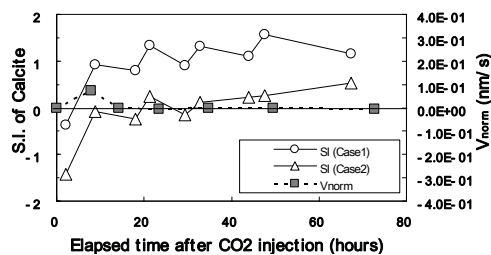


Fig. 4. Saturation index of calcite.

diluted with the reservoir fluid with 3 days and most CO₂ in them might be deposited by interaction with granitic rocks. According to the material balance, only 1μm thickness of the granitic rocks is enough to react with the CO₂ water to precipitate as carbonate

minerals. In the previous field experiments in 2002 and 2003, Ca concentration in the water samples increased from 10 to 80 mg/L with 1 day and quickly decreased to the background. These results also support

CONCLUSIONS

The injected CO₂ water is diluted with the reservoir fluid within 3 days. Most CO₂ in them might be deposited as calcite by interaction with granitic rocks. Ca concentration in the water samples increased from 10 to 80 mg/L with 1 day and quickly decreased to the background. These results also support the view that CO₂ injected is precipitated as carbonates within few days.

ACKNOWLEDGEMENTS

This research is partly supported by the grants of the Programmed Research "Development of evaluation technology for the CO₂ in the exhaust gas sequestration into geothermal fields" of RITE under the fund from METI (Ministry of Economy, Trade and Industry). We thank Odashima, Tokumaru and other members at Ogachi for their kind help during laboratory and field experiments.

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