

**Carbon Dioxide Capture for Storage
in Deep Geologic Formations –
Results from the CO₂
Capture Project**

**Geologic Storage of Carbon Dioxide
with Monitoring and Verification**

Volume 2

Elsevier Internet Homepage – <http://www.elsevier.com>

Consult the Elsevier homepage for full catalogue information on all books, major reference works, journals, electronic products and services.

Elsevier Titles of Related Interest

AN END TO GLOBAL WARMING

L.O. Williams

ISBN: 0-08-044045-2, 2002

FUNDAMENTALS AND TECHNOLOGY OF COMBUSTION

F. El-Mahallawy, S. El-Din Habik

ISBN: 0-08-044106-8, 2002

GREENHOUSE GAS CONTROL TECHNOLOGIES: 6TH INTERNATIONAL CONFERENCE

John Gale, Yoichi Kaya

ISBN: 0-08-044276-5, 2003

MITIGATING CLIMATE CHANGE: FLEXIBILITY MECHANISMS

T. Jackson

ISBN: 0-08-044092-4, 2001

Related Journals:

Elsevier publishes a wide-ranging portfolio of high quality research journals, encompassing the energy policy, environmental, and renewable energy fields. A sample journal issue is available online by visiting the Elsevier web site (details at the top of this page). Leading titles include:

Energy Policy

Renewable Energy

Energy Conversion and Management

Biomass & Bioenergy

Environmental Science & Policy

Global and Planetary Change

Atmospheric Environment

Chemosphere – Global Change Science

Fuel, Combustion & Flame

Fuel Processing Technology

All journals are available online via ScienceDirect: www.sciencedirect.com

To Contact the Publisher

Elsevier welcomes enquiries concerning publishing proposals: books, journal special issues, conference proceedings, etc. All formats and media can be considered. Should you have a publishing proposal you wish to discuss, please contact, without obligation, the publisher responsible for Elsevier's Energy program:

Henri van Dorssen

Publisher

Elsevier Ltd

The Boulevard, Langford Lane

Kidlington, Oxford

OX5 1GB, UK

Phone: +44 1865 84 3682

Fax: +44 1865 84 3931

E.mail: h.dorssen@elsevier.com

General enquiries, including placing orders, should be directed to Elsevier's Regional Sales Offices – please access the Elsevier homepage for full contact details (homepage details at the top of this page).

Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO₂ Capture Project

**Geologic Storage of Carbon Dioxide
with Monitoring and Verification**

Edited by

Sally M. Benson

*Lawrence Berkeley Laboratory
Berkeley, CA, USA*

and Associate Editors

Curt Oldenburg¹, Mike Hoversten¹ and Scott Imbus²

*¹Lawrence Berkeley National Laboratory
Berkeley, CA, USA*

*²Chevron Texaco Energy Technology Company
Bellaire, TX, USA*

Volume 2



ELSEVIER

2005

Amsterdam – Boston – Heidelberg – London – New York – Oxford
Paris – San Diego – San Francisco – Singapore – Sydney – Tokyo

ELSEVIER B.V.
Radarweg 29
P.O. Box 211, 1000 AE Amsterdam
The Netherlands

ELSEVIER Inc.
525 B Street, Suite 1900
San Diego, CA 92101-4495
USA

ELSEVIER Ltd
The Boulevard, Langford Lane
Kidlington, Oxford OX5 1GB
UK

ELSEVIER Ltd
84 Theobalds Road
London WC1X 8RR
UK

© 2005 Elsevier Ltd. All rights reserved.

This work is protected under copyright by Elsevier Ltd, and the following terms and conditions apply to its use:

Photocopying

Single photocopies of single chapters may be made for personal use as allowed by national copyright laws. Permission of the Publisher and payment of a fee is required for all other photocopying, including multiple or systematic copying, copying for advertising or promotional purposes, resale, and all forms of document delivery. Special rates are available for educational institutions that wish to make photocopies for non-profit educational classroom use.

Permissions may be sought directly from Elsevier's Rights Department in Oxford, UK: phone (+44) 1865 843830, fax (+44) 1865 853333, e-mail: permissions@elsevier.com. Requests may also be completed on-line via the Elsevier homepage (<http://www.elsevier.com/locate/permissions>).

In the USA, users may clear permissions and make payments through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA; phone: (+1) (978) 7508400, fax: (+1) (978) 7504744, and in the UK through the Copyright Licensing Agency Rapid Clearance Service (CLARCS), 90 Tottenham Court Road, London W1P 0LP, UK; phone: (+44) 20 7631 5555; fax: (+44) 20 7631 5500. Other countries may have a local reprographic rights agency for payments.

Derivative Works

Tables of contents may be reproduced for internal circulation, but permission of the Publisher is required for external resale or distribution of such material. Permission of the Publisher is required for all other derivative works, including compilations and translations.

Electronic Storage or Usage

Permission of the Publisher is required to store or use electronically any material contained in this work, including any chapter or part of a chapter.

Except as outlined above, no part of this work may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the Publisher.

Address permissions requests to: Elsevier's Rights Department, at the fax and e-mail addresses noted above.

Notice

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made.

First edition 2005

Library of Congress Cataloging in Publication Data

A catalog record is available from the Library of Congress.

British Library Cataloguing in Publication Data

A catalogue record is available from the British Library.

ISBN: 0-08-044570-5 (2 volume set)

Volume 1: Chapters 8, 9, 13, 14, 16, 17, 18, 24 and 32 were written with support of the U.S. Department of Energy under Contract No. DE-FC26-01NT41145. The Government reserves for itself and others acting on its behalf a royalty-free, non-exclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform these copyrighted papers. EU co-funded work appears in chapters 19, 20, 21, 22, 23, 33, 34, 35, 36 and 37. Norwegian Research Council (Klimatek) co-funded work appears in chapters 1, 5, 7, 10, 12, 15 and 32.

Volume 2: The Storage Preface, Storage Integrity Preface, Monitoring and Verification Preface, Risk Assessment Preface and Chapters 1, 4, 6, 8, 13, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33 were written with support of the U.S. Department of Energy under Contract No. DE-FC26-01NT41145. The Government reserves for itself and others acting on its behalf a royalty-free, non-exclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform these copyrighted papers. Norwegian Research Council (Klimatek) co-funded work appears in chapters 9, 15 and 16.

© The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper).

Printed in The Netherlands.

Working together to grow
libraries in developing countries

www.elsevier.com | www.bookaid.org | www.sabre.org

ELSEVIER

BOOK AID
International

Sabre Foundation

Chapter 8

REACTIVE TRANSPORT MODELING OF CAP-ROCK INTEGRITY DURING NATURAL AND ENGINEERED CO₂ STORAGE

James W. Johnson, John J. Nitao and Joseph P. Morris

Environmental Sciences Division, Lawrence Livermore National Laboratory, Livermore, CA, USA

ABSTRACT

Long-term cap rock integrity represents the single most important constraint on the long-term isolation performance of natural and engineered CO₂ storage sites. CO₂ influx that forms natural accumulations and CO₂ injection for EOR/storage or saline-aquifer disposal both lead to geochemical alteration and geomechanical deformation of the cap rock, enhancing or degrading its seal integrity depending on the relative effectiveness of these interdependent processes. Using our reactive transport simulator (NUFT), supporting geochemical databases and software (GEMBOCHS, SUPCRT92), and distinct-element geomechanical model (LDEC), we have shown that influx-triggered mineral dissolution/precipitation reactions within typical shale cap rocks continuously reduce microfracture apertures, while pressure and effective-stress evolution first rapidly increase then slowly constrict them. For a given shale composition, the extent of geochemical integrity enhancement in the cap rock is nearly independent of key reservoir properties (permeability and lateral continuity) that distinguish EOR/sequestration and saline formation settings and of CO₂ influx parameters (rate, focality, and duration) that distinguish engineered disposal sites and natural accumulations, because these characteristics and parameter have negligible (indirect) impact on mineral dissolution/precipitation rates. In contrast, the extent of geomechanical integrity degradation is highly dependent on these reservoir properties and influx parameters because they effectively dictate magnitude of the pressure perturbation. Specifically, initial geomechanical degradation has been shown inversely proportional to reservoir permeability and lateral continuity and proportional to influx rate. Hence, while the extent of geochemical alteration is nearly independent of filling mode, that of geomechanical deformation is significantly more pronounced during engineered storage. This suggests that the currently secure cap rock of a given natural CO₂ accumulation may be incapable of providing an effective seal in the context of an engineered injection, a potential discrepancy that limits the extent to which natural CO₂ reservoirs and engineered storage sites can be considered analogous. In addition, the pressure increase associated with CO₂ accumulation in any compartmentalized system invariably results in net geomechanical aperture widening of cap-rock microfractures. This suggests that ultimate restoration of pre-influx hydrodynamic seal integrity—in both EOR/storage and natural accumulation settings—hinges on ultimate geochemical counterbalancing of this geomechanical effect. To explore this hypothesis, we have introduced a new conceptual framework that depicts such counterbalancing as a function of effective diffusion distance and reaction progress. This framework reveals that ultimate counterbalancing of geochemical and geomechanical effects is feasible, which suggests that shale cap rocks may in fact *evolve* into effective seals in both natural and engineered storage sites.

Abbreviations: CCP, CO₂ Capture Project; GEMBOCHS, Geologic and Engineering Materials: Bibliography of Chemical Species (Thermodynamic/kinetic database and software library [24,25]); LDEC, Livermore Distinct Element Code (geomechanical modeling software [32,33]); NUFT, Non-isothermal Unsaturated Flow and Transport (reactive transport software [19,20]); SUPCRT92, SUPeRCriTical (geochemical modeling software and database: [26]).

INTRODUCTION

Successful engineered CO₂ storage in geologic formations hinges on our ability to identify optimal sites and forecast their long-term security. This ability, in turn, relies upon predictive models for assessing the relative effectiveness of CO₂ migration and storage processes (isolation performance) as a function of key target-formation and cap-rock properties (screening criteria). It also relies on detailed knowledge of naturally occurring CO₂ reservoirs and clear understanding of the extent to which they represent natural analogs to engineered storage sites. In the opinion of the author, among key screening criteria, long-term cap rock integrity is the most important constraint on the long-term isolation performance of both natural and engineered CO₂ storage sites. And among predictive methodologies, the reactive transport modeling approach is uniquely well suited to quantify this fundamental constraint.

In this study, we have extended and applied our computational toolbox to address this central issue of long-term hydrodynamic seal capacity. In the development phase, we first interfaced our existing reactive transport and geomechanical modeling capabilities to facilitate assessment of stress–strain evolution along and above the reservoir/cap-rock contact during and after CO₂ influx. We then constructed a new conceptual framework for evaluating the net impact on long-term cap rock integrity of influx-triggered geochemical alteration and geomechanical deformation processes.

In the application phase, we have used our modeling capabilities to address two fundamental questions. First, what is the evolution of cap-rock integrity during engineered CO₂ storage—and does this evolution vary significantly between EOR/storage and saline aquifer settings? This work builds directly upon our earlier modeling studies, which demonstrated enhanced hydrodynamic seal capacity of shale cap rocks as a function of injection-triggered geochemical processes during saline aquifer disposal [1–4]. Here, these earlier analyses have been extended to include explicit account of the concomitant geomechanical processes, and to assess dependence of this coupled geochemical–geomechanical evolution on key reservoir properties (permeability and lateral continuity) that distinguish typical oil reservoirs and saline aquifers [5,6].

We then address a closely related key issue: is the predicted evolution of cap-rock integrity for engineered CO₂ disposal sites similar to or appreciably different from that of natural CO₂ accumulations, i.e. what is the dependence of this evolution on the rate, duration, and focality of CO₂ influx? The widely espoused natural analog concept implicitly assumes a lack of such dependence; however, this assumption—upon which strict validity of the concept hinges—may be invalid in some cases. For example, a given reservoir/cap rock system that now holds a natural CO₂ accumulation may be incapable of doing so in the context of an engineered injection owing to significant differences in the magnitude and style of CO₂ influx. Further, the currently secure cap rock of a given natural accumulation may have *evolved* into an effective hydrodynamic seal following geochemical alteration that attended some degree of CO₂ migration through it. To address these issues, we have conducted and compared reactive transport simulations of a representative generic natural CO₂ reservoir for natural and engineered “filling” modes [7,8].

Because cap-rock integrity represents the ultimate constraint on the long-term isolation performance of geologic CO₂ storage sites, our reactive transport modeling analysis is linked to a number of additional CCP-funded studies presented in this volume [9–14]. There are potential direct links to three studies: the SAMCARDS analysis of Wildenberg [9], into which our simulation results could be directly incorporated, and the natural analog and experimental studies of Stevens [10] and Borm et al. [11], respectively, with which future coordinated efforts might provide field- and laboratory-scale “proof of concept” for our modeling capabilities. In addition, the reactive transport modeling approach used here could be employed to simulate the advective and diffusive migration of imposed anomalies in noble gas isotope ratios, as measured in the field by Nimz and Hudson [12]; to generate the fluid-phase pressures, saturations, densities, and viscosities required to predict dependent geophysical properties, as discussed by Hoversten and Gasperikova [13]; and to predict the migration paths of CO₂-charged fluids within magma-hydrothermal systems, as inferred from field measurements by Evans et al. [14].

METHODOLOGY

Reactive transport modeling is a computational method for quantitatively predicting the long-term consequences of natural or engineered perturbations to the subsurface environment [15,16]. Because these predictions typically involve space, time, and system complexity scales that preclude development of direct analytical or experimental analogs, they often provide a unique forecasting tool. The necessary point of departure for predictive investigations of this kind is established by successful application of the method to simulate well-constrained laboratory experiments [17,18].

The method is based on mathematical models of the integrated thermal, hydrological, geochemical, and geomechanical processes that redistribute mass and energy in response to the disequilibrium state imposed

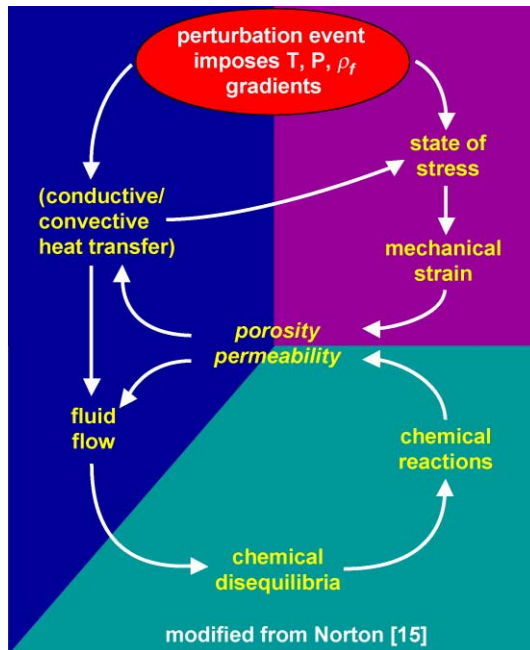


Figure 1: Schematic depiction of coupled subsurface processes that redistribute mass and energy in response to natural or engineered perturbation events. Porosity and permeability are the key variables that link hydrological, geochemical, and geomechanical sectors of the diagram.

by perturbation events such as magmatic intrusion or CO_2 influx (Figure 1). Traditionally, such models have been developed as separate entities and applied as such to address specific issues relevant to their individual scope. The fundamental advance embodied in reactive transport modeling is its explicit integration of these conceptually distinct process models. In practice, however, present-day simulators address and couple various subsets of these models, while the ultimate simulation tool—one that implements and explicitly couples all of the relevant processes—remains on the horizon.

We have developed a computational capability that integrates a state-of-the-art reactive transport simulator (NUFT), comprehensive supporting geochemical software and databases (SUPCRT92, GEMBOCHS), and a versatile distinct-element geomechanical model (LDEC). NUFT [19,20] is a software package that

simulates non-isothermal multiphase/multicomponent flow and reactive transport within a wide range of subsurface environments characterized by multiscale physical and compositional heterogeneity. NUFT uses an integrated finite-difference spatial discretization to solve the flow and reactive-transport equations, with the Newton–Raphson method to solve the resulting non-linear systems at each time step. Explicit account is taken of multiphase advection, diffusion, and dispersion; of relative permeability and capillary pressure using an extended Van Genuchten formulation [21]; and of kinetically controlled fluid–mineral reactions, using rate laws from transition state theory [22]. Moreover, explicit account is also taken of *coupling between* these transport and geochemical processes through the dependence of permeability on porosity changes due to mineral precipitation/dissolution, using a normalized Kozeny equation [23], and through the dependence of fluid-phase volumetric saturations on gas (e.g. CO₂(g)) generated or consumed by fluid–mineral reactions.

The GEMBOCHS system [24,25] integrates a comprehensive relational thermodynamic/kinetic database and dedicated software library that together facilitate generation of application-specific thermodynamic/kinetic datafiles for use with a variety of geochemical modeling codes and reactive transport simulators. The thermodynamic database covers about 3200 distinct chemical species, spanning 86 elements of the periodic table; its core component is the current version of the SUPCRT92 database [26,27], which covers about 1550 species, spanning 82 elements. Custom datafiles are generated using Jewel [24], a GUI-driven software package that extrapolates reference-state properties to elevated P – T conditions using a number of standard algorithms, the core set of which are those encoded with the SUPCRT92 software package [26]. These include global- and critical-region equations of state and a dielectric formulation for H₂O [28] that are explicitly integrated with equations of state for both aqueous solutes [29,30] and minerals/gases [31].

LDEC [32,33] is a geomechanical model that implements the distinct element method, which facilitates representation of fractured rock mass using arbitrary polyhedra, detection of new contacts between blocks resulting from relative block motion using the “Common-Plane” approach [34], exact conservation of linear and angular momentum, and simplified tracking of material properties as blocks move. Use of an explicit integration scheme allows extreme flexibility with respect to joint constitutive models, which here include effects such as cohesion, joint dilation, and friction angle. Both rigid and deformable approximations to block response are implemented. The rigid block approximation assumes that the compliance of fractured rock mass is closely approximated by lumping all compliance at the joints alone; however, this formulation also includes an optional second joint stiffness term that approximates deformation of the rock matrix.

The current method for one-way coupling between NUFT and LDEC is our integrated model’s key approximation. Specifically, the NUFT–LDEC interface facilitates mapping pressure evolution into the corresponding effective stress, fracture aperture, and permeability history; however, at present, this geomechanical-dependent evolution (LDEC) is not back-coupled into the multiphase flow and reactive transport model (NUFT). As a result, the dependence of permeability, fluid flow, and pressure (including capillary pressure) evolution on concomitant geomechanical aperture history is not represented. In the present study, the NUFT–LDEC interface is used to translate the CO₂ influx-triggered pressure perturbation within basal cap rock into the corresponding evolution of effective stress and microfracture apertures, which permits first-order assessment of influx-induced geomechanical deformation. It is important to recognize that in the context of a bi-directionally coupled multiphase flow and geomechanical model, the magnitude of this pressure perturbation would likely be diminished—through concomitant evolution (initial widening) of cap-rock microfracture apertures—relative to that predicted here. Owing to their functional dependence on such magnitude, both the extent of CO₂ migration into undeformed cap rock and that of aperture widening predicted by the present one-way coupled model should be viewed as upper-limit values; on the other hand, likely enhanced advective CO₂ migration through initially widened microfractures is not accounted for here.

In order to evaluate the net impact on long-term cap rock integrity of concomitant geochemical and geomechanical processes, we introduce a new conceptual model that depicts geochemical counterbalancing of geomechanical aperture evolution as a function of effective diffusion distance and reaction progress. This model provides a theoretical framework for assessing the extent to which cap-rock integrity will ultimately be enhanced or degraded in specific reservoir/cap-rock systems in the context of specific CO₂ influx scenarios.

RESULTS AND DISCUSSION

Predicting long-term permeability evolution within the cap-rock environment of CO₂ storage sites requires first identifying, then quantifying its functional dependence on key system parameters and dynamic processes. The most important factors influencing this evolution are conveniently subdivided into three groups: intrinsic cap-rock properties, chemical conditions at the reservoir/cap-rock interface, and the CO₂ influx-triggered pressure perturbation.

Relevant cap-rock properties include geomechanical parameters, such as fracture normal stiffness, and geochemical characteristics, such as bulk concentrations of carbonate-forming cations—principally Fe, Mg, Ca, Na, and Al. These cation concentrations represent the primary control on geochemical alteration processes, while chemical conditions at the reservoir/cap-rock interface, which are determined by reservoir compositions and CO₂ waste-stream impurities (e.g. CH₄, H₂S, SO_x, NO_x concentrations), exert a secondary control. Magnitude, duration, and focality of the injection-induced pressure perturbation—which depend on these same characteristics of CO₂ influx as well as on reservoir permeability, lateral continuity, compartment height (for laterally confined settings), depth, and thickness—represent the fundamental controls on geomechanical deformation processes.

In the context of these dependencies, long-term enhancement or degradation of cap-rock integrity hinges on the relative contributions of geochemical alteration, which tends to reduce microfracture apertures in typical shale, and geomechanical deformation, which widens them (Figure 2). As a result, long-term performance forecasting of potential CO₂ storage sites requires a predictive capability that quantifies this pivotal interplay of geochemical and geomechanical processes. Previously, we have modeled the geochemical contribution within a full system analysis of coupled hydrological and geochemical processes [1–4]. Here, we first assess the geomechanical contribution—through analysis of its dependence on hydrological processes, key reservoir properties, and CO₂ influx parameters—then evaluate the ultimate net effect of opposing geochemical and geomechanical contributions to cap-rock integrity for both natural and engineered storage scenarios.

In describing this work, we begin with a review of subsurface CO₂ migration and storage processes, which provides not only the geochemical contribution to long-term cap rock integrity, but also full-system context for the subsequent analysis, which focuses on the cap-rock environment.

Subsurface CO₂ Migration and Storage Processes

Our previous modeling studies [1–4] have been largely based on simulating CO₂ injection at Statoil's North-Sea Sleipner facility—the world's first commercial saline-aquifer storage site. Here, CO₂-rich natural gas is produced from 3500 m below the seabed. Excess CO₂ is removed by amine absorption on the platform, then stripped from the amine, and finally injected—at the rate of one million tons per year since 1996—into the Utsira formation 2500 m above the hydrocarbon reservoir [35]. The 200-m-thick Utsira is a highly permeable fluid-saturated sandstone capped by the Nordland Shale. Hydrologic and compositional properties of the Utsira are relatively well characterized [1,4,36], while those of the Nordland Shale are virtually unknown, and must be estimated [1,4].

All of our Sleipner simulations have been carried out within a common 600 × 250 m² spatial domain, which represents the near-field disposal environment, and over a single 20-year time frame, which encompasses equal-duration prograde (active-injection) and retrograde (post-injection) phases. The domain includes a 200-m-thick saline aquifer (35% porosity, 3-darcy permeability), 25-m-thick shale cap rock (5% porosity, 3-microdarcy permeability), and an overlying 25-m-thick saline aquifer. Its lateral boundaries are open to multiphase flow and mass transfer, while its top and bottom boundaries are not. During the prograde phase, pure CO₂ is injected at a rate of 10,000 ton/yr into the basal center of this domain (37 °C, 111 bar), which therefore corresponds to a 1-m-thick cross-section through the actual 100 m screen length at Sleipner.

Within the common domain, we have evaluated three distinct injection scenarios—models XSH, CSH, and DSH [1,4]. Model XSH examines CO₂ injection into a shale-capped homogeneous sandstone aquifer. Models CSH and DSH impose into XSH four thin (3-m thick) intra-aquifer shales, which are separated from the cap rock and each other by 25 m. Model CSH examines the effect of imposing laterally continuous

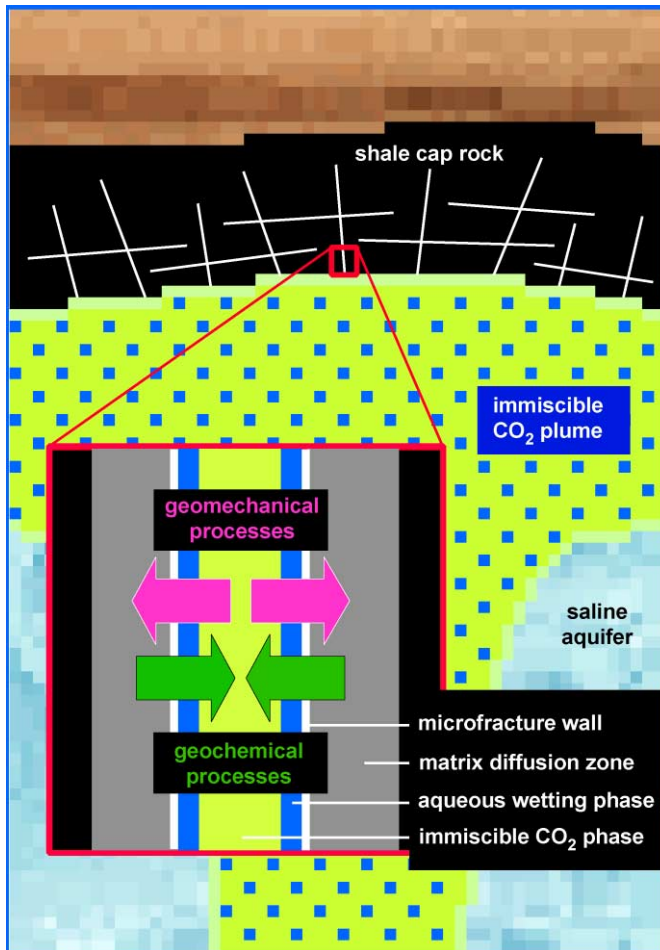


Figure 2: Schematic depiction of concomitant CO₂ influx-triggered geochemical and geomechanical processes within shale cap rock microfractures. Mineral dissolution/precipitation reactions tend to continuously reduce microfracture apertures for typical shale compositions, while pressure evolution initially widens then reduces them (net widening).

microfractured shales having assigned permeability (3 md) that equates to a continuum representation of 100 μm fractures spaced roughly 30 m apart. Model DSH examines the effect of imposing laterally discontinuous shales, which are bridged by lateral facies change to sandstone. Assigned permeability of these shales (3 μd ; same as the cap rock) reflects typical shale integrity.

Compositionally, the well-characterized saline aquifers are represented as impure quartz sand: 80% quartz, 10% K-feldspar, 5% plag-ab₈₀, 3% muscovite, and 2% phlogopite [1,4]. The virtually uncharacterized shale cap rock is estimated to contain 60% clay minerals (50% muscovite, 10% Mg-chlorite), 35% quartz, and 5% K-feldspar; this mineralogy and bulk $\text{K}_2\text{O}/(\text{FeO} + \text{MgO})$ ratio closely approximate those of typical (non-carbonaceous) shales, while permitting avoidance of more realistic illite, smectite, and montmorillonite solid solutions, for which thermodynamic and kinetic data are currently lacking [1,4]. Mg end-member

components are used to represent Fe/Mg solid solutions because *in situ* oxidation states are unknown. The saline aquifers and shale are all saturated with an aqueous phase of near-seawater composition [1,4,36].

Our Sleipner simulations suggest that the ultimate fate of CO₂ injected into saline aquifers is governed by three interdependent yet conceptually distinct processes: CO₂ migration as a buoyant immiscible fluid phase, direct chemical interaction of this rising plume with ambient saline waters, and its indirect chemical interaction with aquifer and cap-rock minerals through the aqueous wetting phase. Each process is directly linked to a corresponding trapping mechanism: immiscible plume migration to hydrodynamic trapping, plume–water interaction to solubility trapping, and plume–mineral interaction to mineral trapping.

Immiscible plume migration and hydrodynamic trapping

Intra-aquifer permeability structure controls the path of prograde immiscible CO₂ migration, thereby establishing the spatial framework of plume–aquifer interaction and the potential effectiveness of solubility

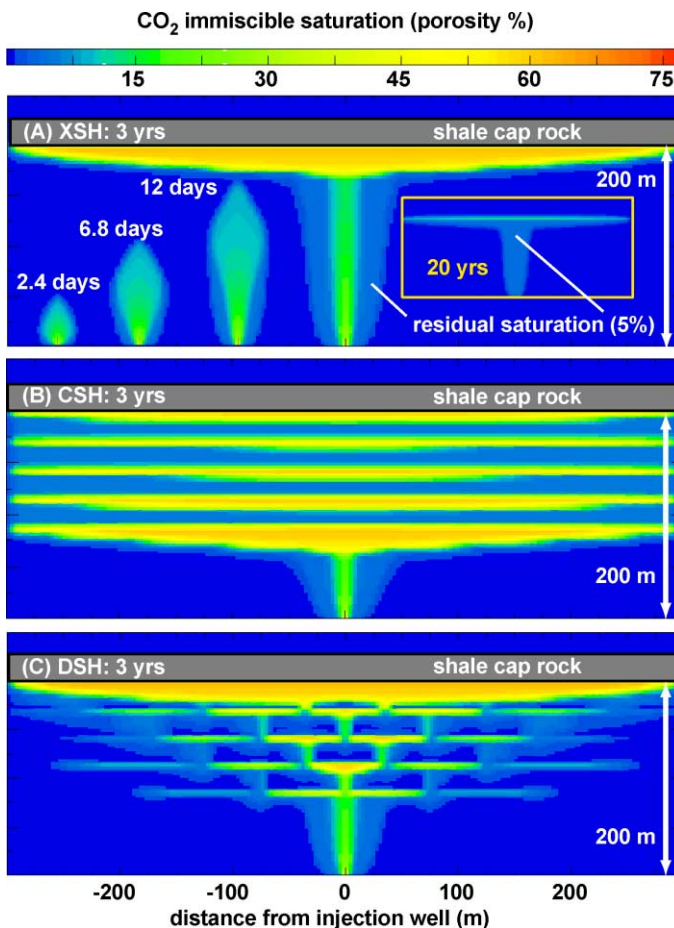


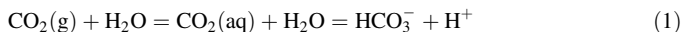
Figure 3: Immiscible plume migration and hydrodynamic trapping after 3 years in Sleipner models XSH, CSH, and DSH; interbedded thin shales not shown for CSH and DSH.

and mineral trapping. Actual efficacy of these trapping mechanisms is determined by compositional characteristics of the aquifer and cap rock. By retarding vertical and promoting lateral plume mobility, interbedded thin shales significantly expand this framework (i.e. CO₂ storage capacity), enhance this potential, and delay outward migration of the plume from the near-field environment (Figure 3). Seismic data strongly suggest that the Utsira formation combines elements of models CSH and DSH [1,3,4].

In all three models, steady-state configuration of the immiscible CO₂ plume is realized within 1 year. During the prograde phase, a residual saturation zone marks the wake of initial plume ascent to the cap rock or deepest interbedded shale (e.g. Figure 3A, left insets). During the retrograde phase, this zone encompasses virtually the entire prograde steady-state plume (e.g. Figure 3A, right inset)—effectively maintaining the prograde extent of solubility trapping and continually enhancing that of mineral trapping, as described below for model DSH. In the near-field environment of Sleipner-like settings, 80–85% by mass of injected CO₂ remains and migrates as an immiscible fluid phase ultimately subject to hydrodynamic trapping beneath the cap rock, which represents an effective seal in these models [1–4], where geomechanical processes are not accounted for.

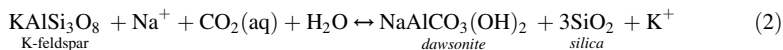
Geochemical trapping mechanisms

As the immiscible plume equilibrates with saline formation waters, intra-plume aqueous CO₂ concentrations (primarily as CO₂(aq) and HCO₃[−]) rapidly achieve their solubility limit, while pH decreases [1–4]:



For the chemical system and *P–T* conditions that characterize the Utsira formation at Sleipner, equilibrium aqueous CO₂ solubility is 1.1–1.2 m, accounting for 15–20% by mass of injected CO₂ (Figure 4A). Owing to residual saturation of immiscible CO₂, this degree of solubility trapping is virtually constant throughout the prograde and retrograde phases. The initial pH drop caused by solubility trapping—from 7.1 to 3.4—catalyzes silicate dissolution, which after 20 years has increased pH from 3.4 to 5.3. This dissolution hydrolyzes potential carbonate-forming cations (here, primarily Na, Al, and Mg) within the immiscible-plume source region, and thus represents the critical forerunner of all mineral-trapping mechanisms.

We have identified four distinct mechanisms whereby CO₂ precipitates as carbonate minerals. Intra-plume dawsonite cementation (Figure 4B) is catalyzed by high ambient Na⁺ concentration, CO₂ influx, and acid-induced K-feldspar dissolution [1–4].



The volume of co-precipitating dawsonite and silica polymorphs slightly exceeds that of dissolving K-feldspar. Hence, this kinetic dissolution/precipitation reaction effectively maintains initial CO₂ injectivity; after 20 years, porosity has decreased by a factor of less than 0.1% (Figure 5A). Pervasive dawsonite cementation will likely be characteristic of saline aquifer storage in any feldspathic sandstone. In fact, natural analogs for this process have been documented: widespread dawsonite cement in the Bowen–Gunnedah–Sydney Basin, Eastern Australia, which has been interpreted to reflect magmatic CO₂ seepage on a continental scale [37], and sporadic dawsonite cement in the clastic Springerville–St. Johns CO₂ reservoir [38].

Calcite-group carbonate rind (here, magnesite) forms along—and therefore effectively delineates—both lateral and upper plume boundaries (Figure 4C). Genetically distinct, these two processes can be described by [1–4]:



As intra-plume formation waters, progressively enriched in Mg⁺² from phlogopite dissolution, migrate

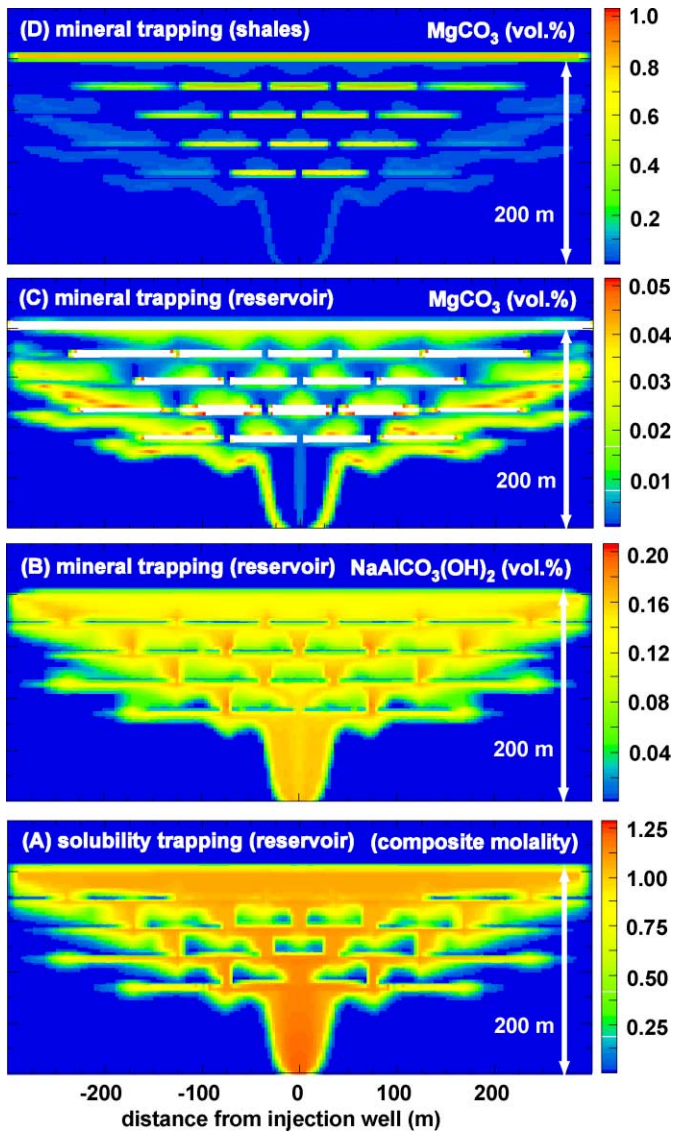


Figure 4: Geochemical trapping mechanisms after 20 years in model DSH: (A) solubility trapping (composite molality of all carbon-bearing aqueous species), (B) intra-plume dawsonite cementation, (C) plume-bounding magnesite precipitation (shales shown in white [off-scale high]), and (D) intra-shale magnesite precipitation.

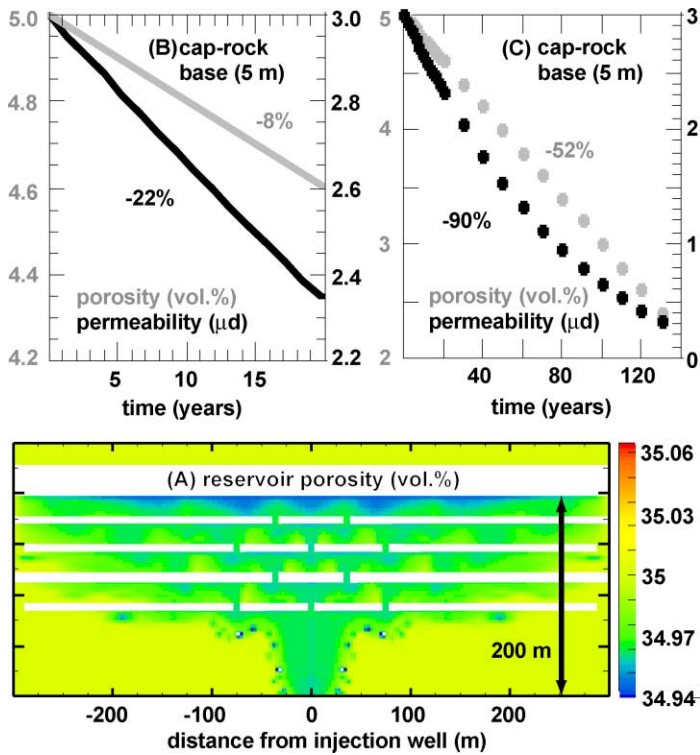
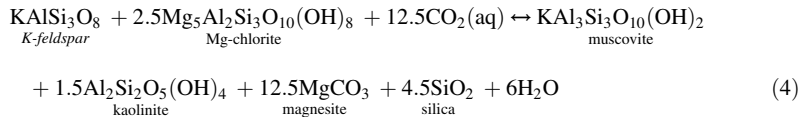


Figure 5: Porosity and permeability reduction in model DSH due to mineral trapping (A) after 20 years in the reservoir (initial porosity: 35%; shales shown in white [off-scale low]) and (B,C) after 20 and 130 years in the cap rock.

outward across lateral plume boundaries, they traverse steep gradients in $\text{CO}_2(\text{aq})$ and pH; the net effect strongly promotes magnesite precipitation. Along upper plume boundaries, $\text{CO}_2(\text{aq})$ concentration and pH are nearly constant, but aqueous Mg^{+2} concentration increases most rapidly here because formation-water saturation is minimized; this leads to magnesite cementation from the reservoir/cap-rock interface downward.

However, magnesite precipitation is most extensive from this interface *upwards* (cf. Figure 4C,D), owing to the relatively high concentration of Mg in clay-rich shales. The coupled intra-shale mineral dissolution/precipitation reaction can be expressed as [1–4]:



This kinetic reaction proceeds to the right with an increase in solid-phase volume of 18.5% (magnesite accounting for 47 vol% of the product assemblage). After 20 years, porosity and permeability of the 5-m-thick cap-rock base have been reduced by 8 and 22%, respectively, by this process (Figure 5B), which upon hypothetical completion at 130 years would reduce initial porosity by half and initial permeability by an

order of magnitude (Figure 5C), thereby significantly improving cap-rock integrity. A natural analog to reaction (4) has recently been documented in the Ladbroke Grove natural gas field, where post-accumulation CO₂ influx has converted Fe-rich chlorite to Fe-rich dolomite (ankerite), kaolinite, and silica [39].

Although composite mineral trapping accounts for less than 1% by mass of injected CO₂ in our models of the near-field disposal environment at Sleipner, it has enormous strategic significance: it maintains initial CO₂ injectivity (reaction (2)), delineates and may partially self-seal plume boundaries (reaction (3)), and—most importantly—reduces cap-rock permeability (reaction (4)), thereby enhancing hydrodynamic containment of immiscible and solubility-trapped CO₂ [1–4].

The CO₂ migration and storage processes reviewed above in the context of engineered saline-aquifer storage are equally applicable to CO₂-flood EOR operations in shale-capped water-wet oil reservoirs, which are primarily distinguished by the presence of a hydrocarbon phase and lateral confinement, and the formation of natural CO₂ reservoirs, which are fundamentally distinguished by the rate, focality, and duration of CO₂ influx. However, in all of these settings the effect of geochemical alteration to improve the seal integrity of typical (non-carbonaceous) shale cap rocks may be counterbalanced or even overwhelmed by concomitant geomechanical deformation, which initially acts in opposition. Hence, in evaluating long-term hydrodynamic sealing capacity, explicit account must be taken of both processes.

Pressure Evolution and Geomechanical Deformation

A first-order assessment of cap-rock geomechanical deformation can be obtained from evaluating the dependence of microfracture aperture evolution on the influx-triggered pressure perturbation. In a new series of NUFF/LDEC simulations, we have assessed this dependence, first as a function of reservoir permeability and lateral continuity—two key parameters that typically distinguish saline-aquifer disposal sites and oil reservoirs, and second, as a function of CO₂ influx rate—the fundamental parameter that distinguishes engineered and natural storage scenarios. Within these new models, the values adopted for other important parameters that influence geomechanical response to CO₂ injection (e.g. reservoir depth and thickness) are those used in the Sleipner simulations described above.

In the Sleipner models, we addressed coupled hydrological and geochemical processes. In the following simulations, we explicitly address only the effect of hydrological (multiphase flow) processes. However, this approximation has negligible impact for impure sandstone reservoirs (such as the Utsira formation), where reservoir porosity and permeability—and thus the injection-induced pressure perturbation—are not modified appreciably by geochemical alteration, as demonstrated above (Figure 5A).

Dependence on reservoir properties: saline aquifer versus EOR settings

In this analysis, four distinct simulations have been carried out within two spatial domains (Figure 6). Reservoir permeability and lateral continuity are varied from 3000 md and infinite in model UHP (laterally-unconfined, high permeability), which represents desirable saline-aquifer storage sites, to 300 md and 2000 m in model CLP (laterally-confined, low permeability), which represents a typical compartmentalized EOR setting. Models ULP and CHP represent cross-combinations of these values, which facilitate evaluation of specific dependence on reservoir permeability and lateral confinement. In both laterally confined models, compartment height—itsself a parameter that exerts second-order influence on the injection-induced pressure perturbation—is 150 m. In all four models, supercritical CO₂ is injected at the rate of 10,000 ton/yr during the prograde event.

Magnitude of the influx-triggered pressure perturbation within basal cap rock varies significantly with (and inversely proportional to) reservoir permeability and lateral continuity (Figures 7–10), although the general style of its evolution during prograde and retrograde phases of the influx event does not (Figure 11). For highly permeable, laterally extensive reservoirs (model UHP), this perturbation follows a characteristic three-stage evolution: (1) rapid increase to maximum pressure as the aqueous phase is displaced upwards during initial ascent of the immiscible CO₂ plume to the cap rock, (2) rapid asymptotic decrease to a near steady-state value intermediate to ambient and maximum pressures that is maintained thereafter during the prograde regime, and (3) a second rapid asymptotic decrease towards the ambient value, which is triggered by onset of the retrograde regime (Figure 7). This pressure evolution suggests that the potential for dependent geomechanical deformation events is maximized during three very brief, distinct episodes that

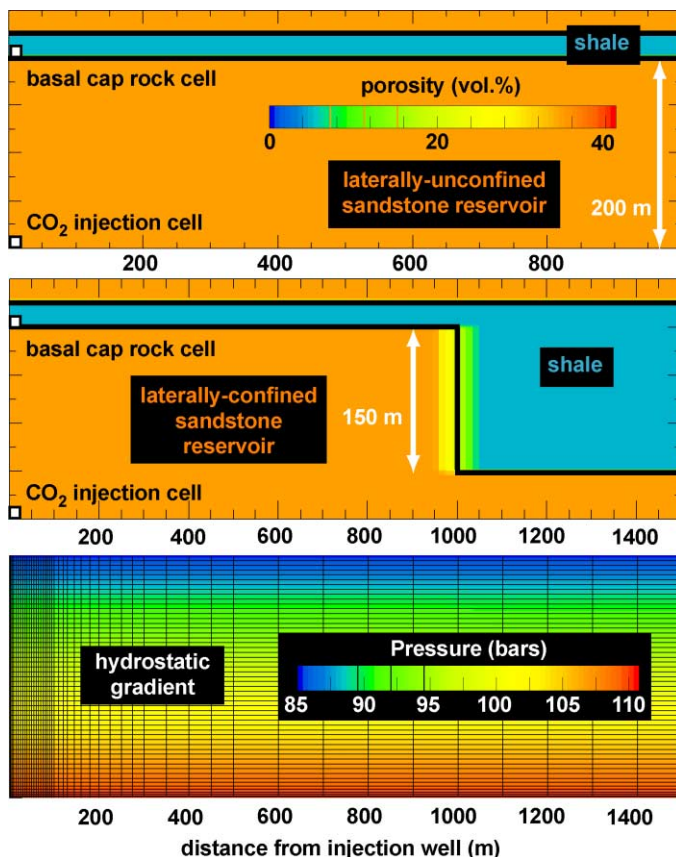


Figure 6: Schematic depiction of the laterally unconfined and laterally confined simulation domains used for models UHP/ULP and CHP/CLP, respectively. Illustrated basal cap rock and CO₂ injection cells are not drawn to scale. Actual cell granularity is overlain upon the hydrostatic gradient plot, which is identical in the two systems (shown for models CHP/CLP).

occur during the earliest stages of prograde and retrograde storage. Note that for this Sleipner-like setting, the range of injection-induced pressure variation is small—on the order of 3 bar.

Decreasing reservoir permeability from 3000 to 300 md without imposing lateral confinement (i.e. model ULP) significantly increases magnitude of the pressure perturbation—from roughly 3 to nearly 22 bar—without altering the three-stage evolution described above (cf. Figures 7 and 8). Also noteworthy from this comparison is the inverse dependence of CO₂ storage capacity on reservoir permeability, which suggests that for pure-storage scenarios the additional energy cost of exploiting less permeable reservoirs—which require higher injection pressures—may be partially offset by the benefit of increased storage and delayed migration into the far-field environment, providing cap-rock performance is not significantly compromised.

The influence of reservoir compartmentalization on the influx-triggered pressure perturbation within basal cap rock is examined in models CHP and CLP (Figures 9 and 10). Although the functional form of pressure evolution in these models is analogous to that described above for laterally unconfined reservoirs, three

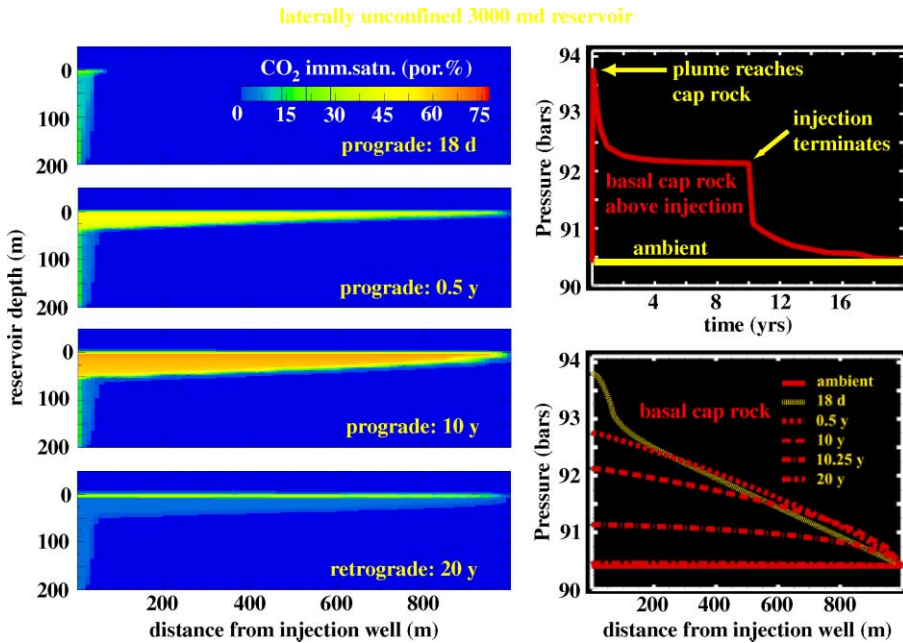


Figure 7: NUFT simulation of immiscible CO₂ migration together with associated pressure evolution within the basal cap rock directly above and as a function of distance from CO₂ injection for the laterally unconfined 3000 md reservoir.

significant variations are introduced by compartmentalization. First, the magnitude of initial pressure increase during plume ascent to the cap rock is significantly enhanced—reaching 60 bar in model CLP—owing to the restricted lateral flow (increased flow resistance) of displaced formation water. Second, a permeability-dependent fourth stage of pressure evolution—one that bridges cap-rock and spillpoint plume arrival times—is introduced that either causes a secondary pressure increase (CHP) or slows prograde decrease (CLP) of the initial pressure anomaly. Third, owing to presence of the accumulated CO₂ column, during the retrograde phase pressure decays asymptotically toward a steady-state value that exceeds hydrostatic and whose magnitude is proportional to column height. This final variation is extremely significant because it imposes a long-term pressure increase at and above the cap-rock interface, which does not occur in unconfined reservoirs.

Propagation of the injection-triggered pressure perturbation from the well to and above this interface effects CO₂ migration into undeformed cap rock in cases where its magnitude—more specifically, that of the difference between increased gas and liquid pressures—is sufficient to overcome capillary forces, i.e. capillary entry pressure is exceeded, which permits increased CO₂ saturation within the cap rock as a function of further increased capillary pressure. CO₂ migration into the 25-m-thick 3- μ d cap rock through this process is minimized in model UHP, where after 20 years CO₂ saturations of roughly 1% are obtained for a penetration distance of only 5 m, and maximized in model CLP, where CO₂ saturations of about 10% are achieved within this basal 5 m, and penetration distance actually breaches the overlying reservoir, although here CO₂ saturations of <1% are realized (Figure 12).

The injection-triggered pressure perturbation also leads to geomechanical deformation of the cap rock, through dependent changes in effective stress and microfracture apertures. Here, we adopt a simplified form

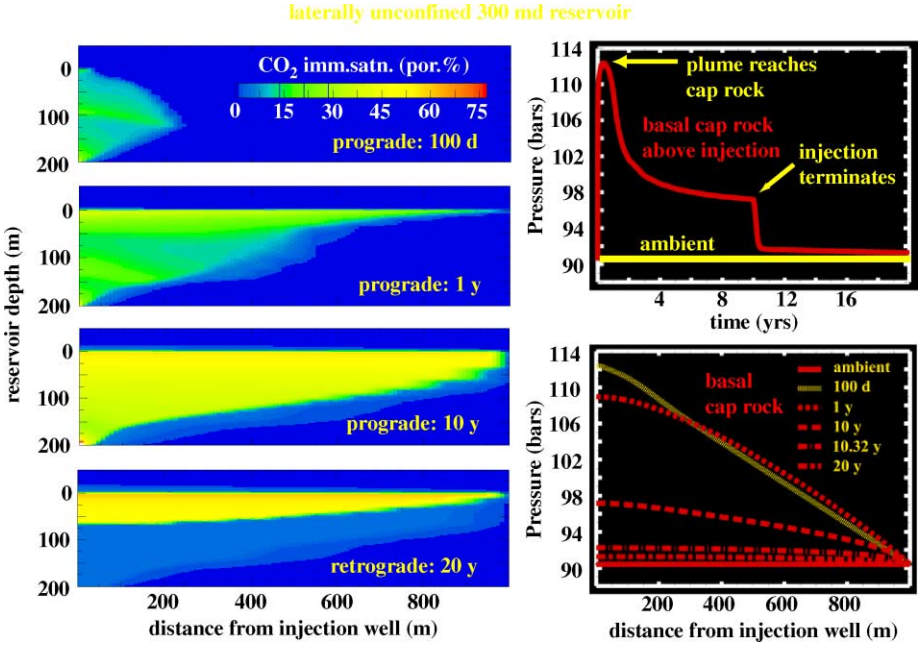


Figure 8: NUFT simulation of immiscible CO₂ migration together with associated pressure evolution within the basal cap rock directly above and as a function of distance from CO₂ injection for the laterally unconfined 300 md reservoir.

of the constitutive relationship between effective stress (σ_E), total stress (σ_T), and pressure (P_f):

$$\sigma_E = \sigma_T - P_f, \quad (5)$$

where σ_T is assumed to be constant ($\Delta\sigma_E = -\Delta P_f$). By further neglecting the non-linear aperture dependence of fracture normal stiffness (K_N), normal aperture displacement due to reduced effective normal stress (Δa_N) can be expressed as

$$\Delta a_N = (\Delta P_f / K_N). \quad (6)$$

Using Eqs. (5) and (6) together with an estimated normal stiffness for shale fractures at depth [40], we first translate the maximum injection-induced pressure perturbation within basal cap rock for each of the four models (Figure 11) into the corresponding maximum aperture normal displacement in order to gauge relative scale (Figure 13). As can be seen, the potential maximum aperture increase due to reduced effective normal stress is on the order of 100–1000 μm . Because attainment of this pressure maximum coincides with arrival of the CO₂ plume at the cap rock—after only 15–100 days in all four models—the potential for geomechanical deformation is maximized very early during the prograde phase.

Simulating long-term aperture evolution requires use of the NUFT–LDEC interface, which facilitates translation of pressure evolution within a given reservoir cap-rock system into the dependent evolution of effective stress and microfracture apertures—here cast within the simplifying context of Eqs. (5) and (6). In this application, the interface is applied to a representative sub-grid from our NUFT domains: a 60 m-by-50 m half-space that encompasses the uppermost 10 m of the lower reservoir (two NUFT grid cells), the 25 m-thick shale cap rock (five cells), and the 25-m-thick upper reservoir (five cells).

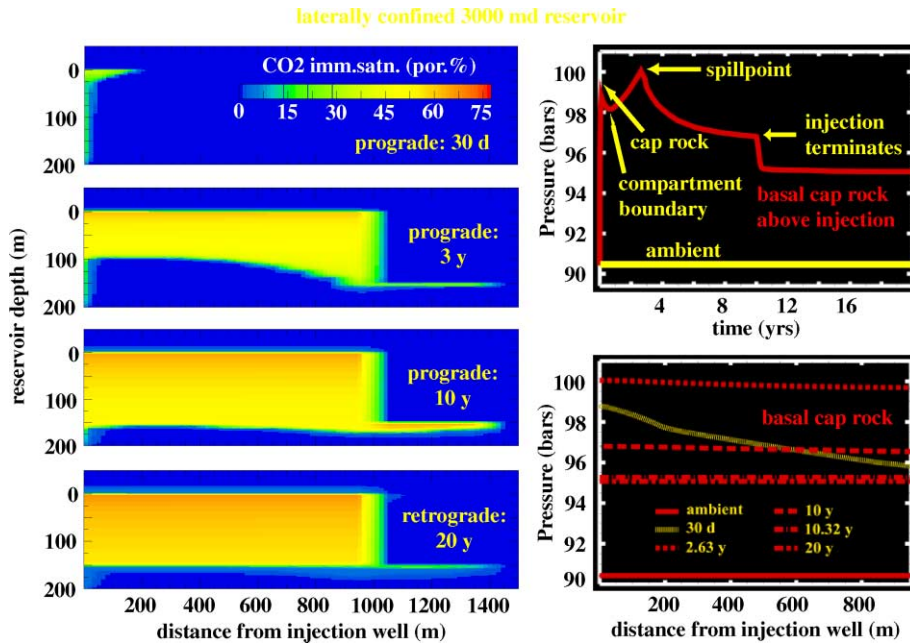


Figure 9: NUFT simulation of immiscible CO₂ migration together with associated pressure evolution within the basal cap rock directly above and as a function of distance from CO₂ injection for the laterally confined 3000 md reservoir.

The functional form of aperture evolution within basal cap rock is directly analogous to that described above for pressure, as exemplified by LDEC simulation of such evolution for model CLP (Figure 14). Here, during the prograde phase apertures rapidly increase by roughly 1000 μm during initial plume ascent, then asymptotically decrease to a steady-state value that reflects net widening of about 400 μm . During the retrograde phase, they first rapidly decrease from this prograde steady state, then continue to decrease asymptotically towards a final steady-state value that reflects ultimate net widening of roughly 100 μm per the approximate 5-bar net pressure increase associated with CO₂ accumulation. Hence, geomechanical deformation degrades cap-rock integrity only during the earliest stages of the prograde phase, after which it continuously self-mitigates this initial degradation event.

Unless counterbalanced by geochemical effects, ultimate net aperture widening through geomechanical deformation could facilitate long-term CO₂ migration into the cap rock. Moreover, although maximum prograde and ultimate net aperture increases of 1000 and 100 μm , respectively, occur just above the reservoir interface, concomitant increases of 200–900 and a few 10 s of μm , respectively, are realized *throughout* the lowest 20 m of the 25-m-thick shale cap rock (Figure 15). Such pervasiveness suggests the potential development of microfracture continuity sufficient to permit CO₂ migration into and perhaps completely through relatively thin shale cap rocks in certain influx settings.

Dependence on influx parameters: engineered versus natural storage

In this analysis, three distinct simulations have been carried out within a single spatial domain (Figure 16) that represents a confined sandstone reservoir whose compartment width (10 km), height (100 m), and width:height aspect ratio (100:1) typify those of natural CO₂ reservoirs [41]. In all three models, reservoir and shale cap rock permeability are 300 md and 3 μd , respectively. The models are distinguished primarily

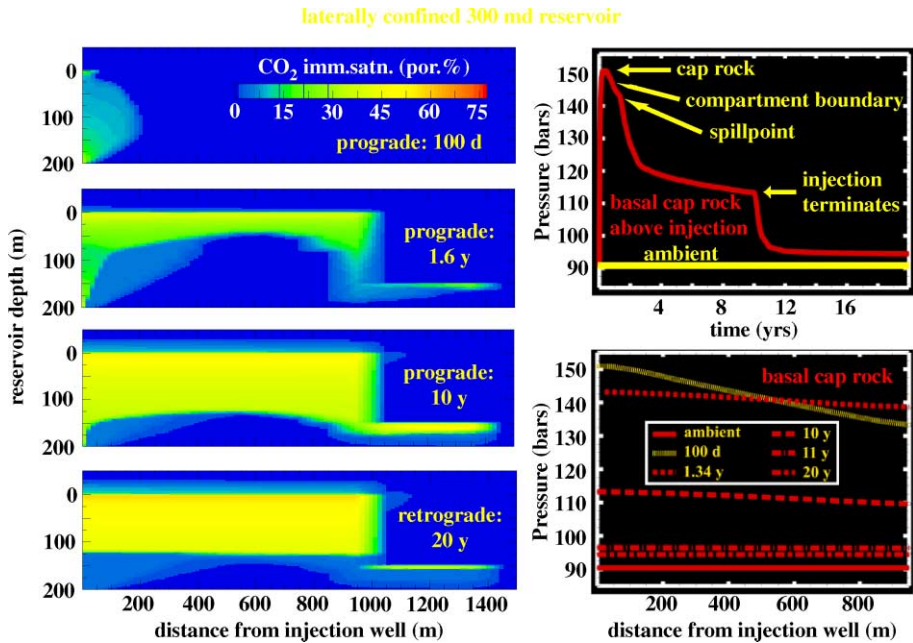


Figure 10: NUFT simulation of immiscible CO₂ migration together with associated pressure evolution within the basal cap rock directly above and as a function of distance from CO₂ injection for the laterally confined 300 md reservoir.

by prograde CO₂ influx rate, which is varied from 10^4 to 10^3 to 10^2 ton/yr, representing engineered injection, “fast” natural accumulation, and “slow” natural accumulation, respectively. The engineered injection rate is that used in all of the preceding simulations, while the two values adopted for natural accumulation rates—which are presently unknown [41]—are rough estimates. A secondary difference is duration of the prograde and retrograde events, both of which span 10 years for the engineered injection, but are extended to 40 and 20 years in both natural accumulation models.

Because the engineered-injection model adopts the same injection rate used in the preceding set of simulations, it illustrates dependence of the pressure perturbation on compartment width and aspect ratio, while providing a baseline for evaluating its dependence on influx rate per comparison with the two natural accumulation models (Figure 17). Increasing compartment width from 2 to 10 km causes pressure to increase even after the plume has reached the cap rock, owing to the increased volume of formation water that must be displaced. Hence, while pressure increases from 90 to 150 bar during initial plume ascent in both models CLP and here (cf. Figures 10 and 17), in this case pressure ultimately reaches 250 bar before declining after the plume reaches the lateral compartment boundary. Subsequent asymptotic pressure decline during the post-spillpoint prograde and retrograde phases is dampened by increased compartment width.

When influx rate is reduced by one and two orders of magnitude, migration of the plume is retarded and the pressure perturbation is reduced proportionately, while its functional form remains unchanged (Figures 18 and 19). In the “fast” natural accumulation model, the immiscible plume does not reach the lateral compartment boundary until just before termination of the 40-year prograde event, while the maximum pressure perturbation (about 22 bar) is a factor of 7–8 less than that for the engineered injection model. In the “slow” natural accumulation model, the plume has not quite advanced halfway to the compartment

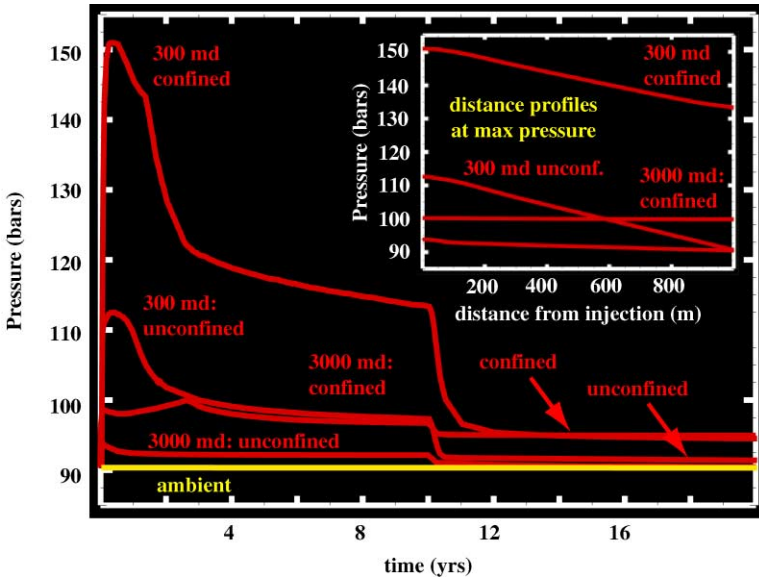


Figure 11: NUFT simulation of pressure evolution within the basal cap rock directly above CO₂ injection for models UHP, ULP, CHP, and CLP together with the distance profiles associated with attainment of pressure maxima (inset).

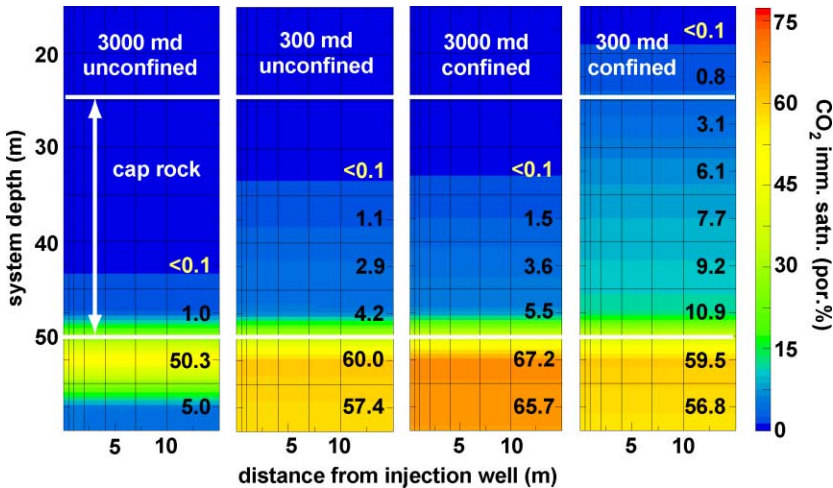


Figure 12: NUFT simulation of CO₂ migration into geomechanically undeformed cap rock as a function of the CO₂ influx-induced pressure perturbation, which in models UHP, ULP, CHP, and CLP (shown from left to right) is sufficient to overcome resistive capillary forces.

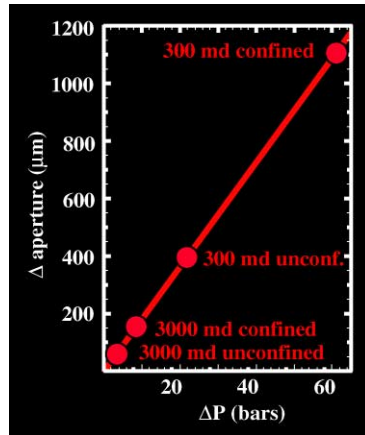


Figure 13: Maximum potential aperture increase of basal cap rock microfractures as a function of the CO₂ influx-triggered initial pressure increase and reduced effective normal stress in models UHP, ULP, CHP, and CLP.

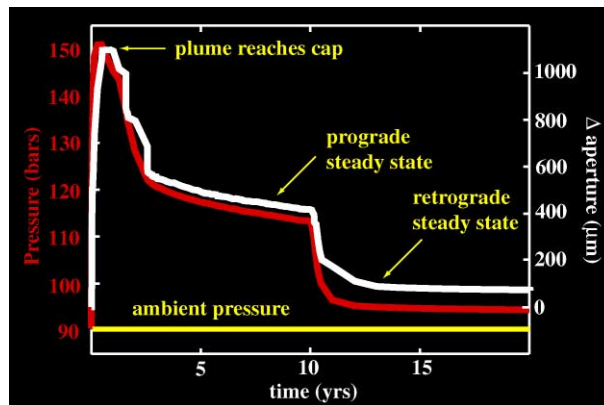


Figure 14: LDEC simulation of microfracture aperture evolution in the basal cap rock directly above the CO₂ injection well in model CLP.

boundary after 60 years (which encompasses both the prograde and retrograde events), while the maximum pressure perturbation is less than 3 bar.

The extent of CO₂ migration into undeformed shale is strongly dependent on influx rate, through dependence of the injection-triggered pressure perturbation on this rate. Such migration extends halfway through the 25-m-thick shale in the “slow” accumulation model (intra-shale saturations approaching 8%), completely through this shale and halfway through the overlying 25-m-thick reservoir in the “fast” accumulation model (upper reservoir saturations approaching 12%), and completely through this upper

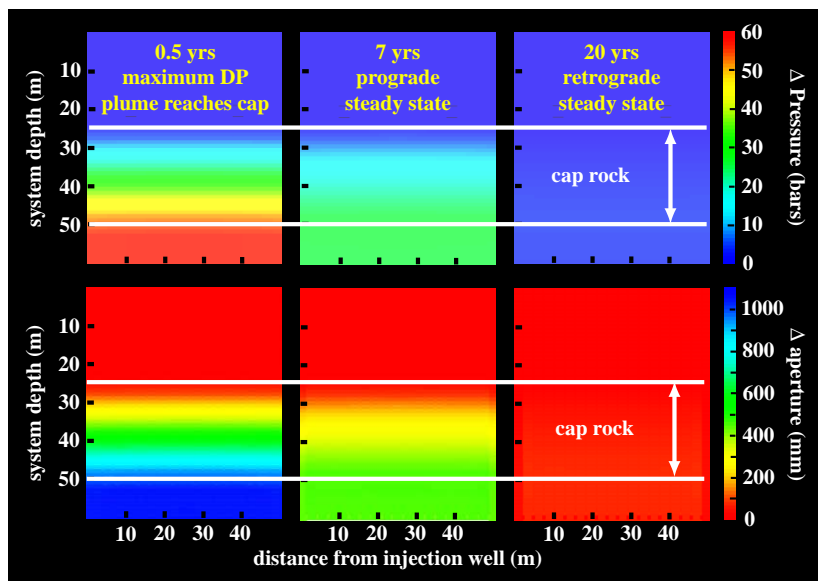


Figure 15: LDEC simulation of aperture evolution within and immediately surrounding the cap rock in model CLP.

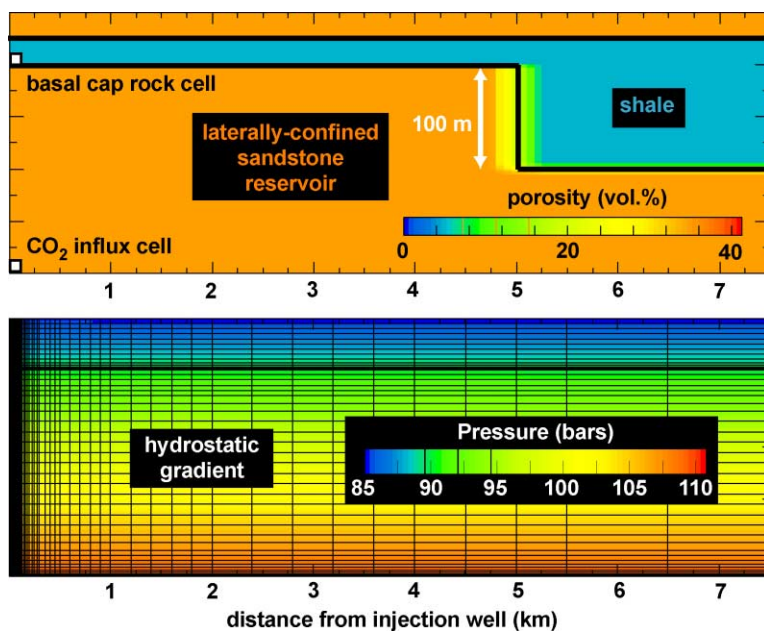


Figure 16: Schematic depiction of the laterally confined simulation domain used to represent natural CO₂ reservoirs. Illustrated basal cap rock and CO₂ influx cells are not drawn to scale. Actual cell granularity is overlain upon the hydrostatic gradient plot.

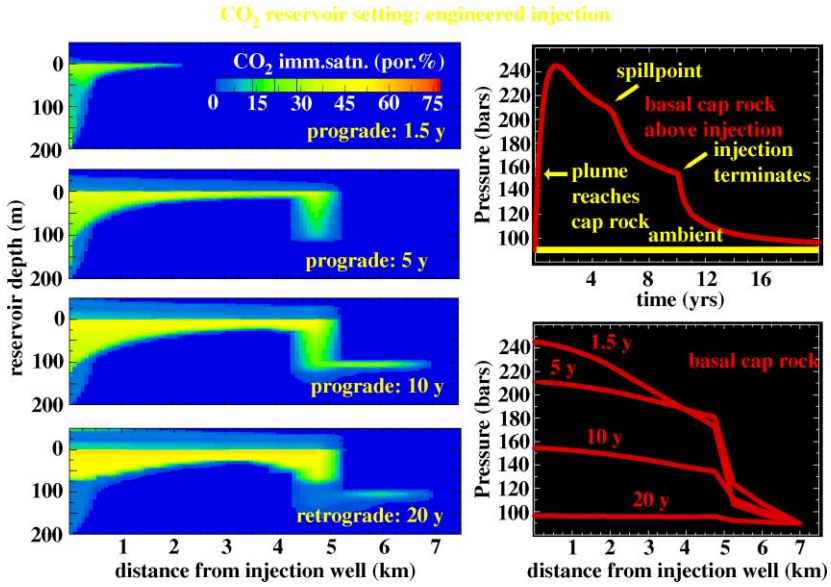


Figure 17: NUFT simulation of immiscible CO₂ migration together with associated pressure evolution within the basal cap rock directly above and as a function of distance from CO₂ injection for engineered injection.

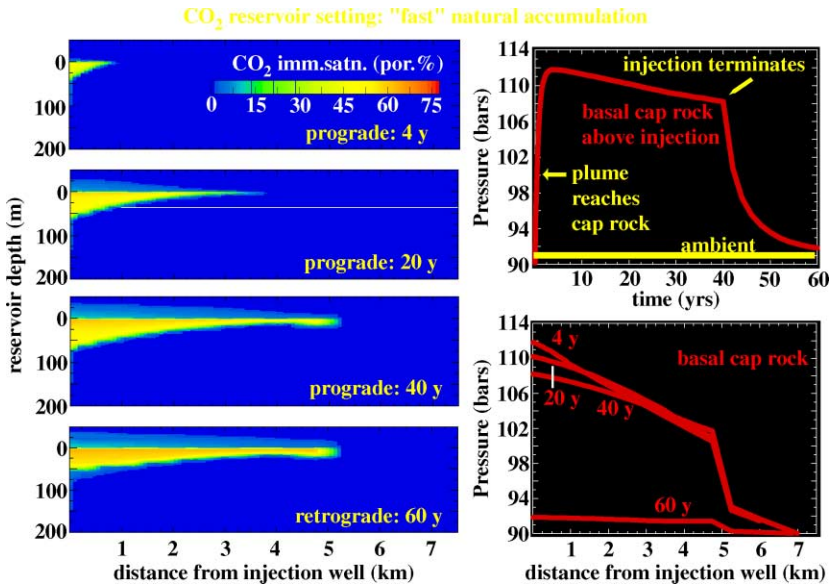


Figure 18: NUFT simulation of immiscible CO₂ migration together with associated pressure evolution within the basal cap rock directly above and as a function of distance from CO₂ influx for "fast" natural accumulation.

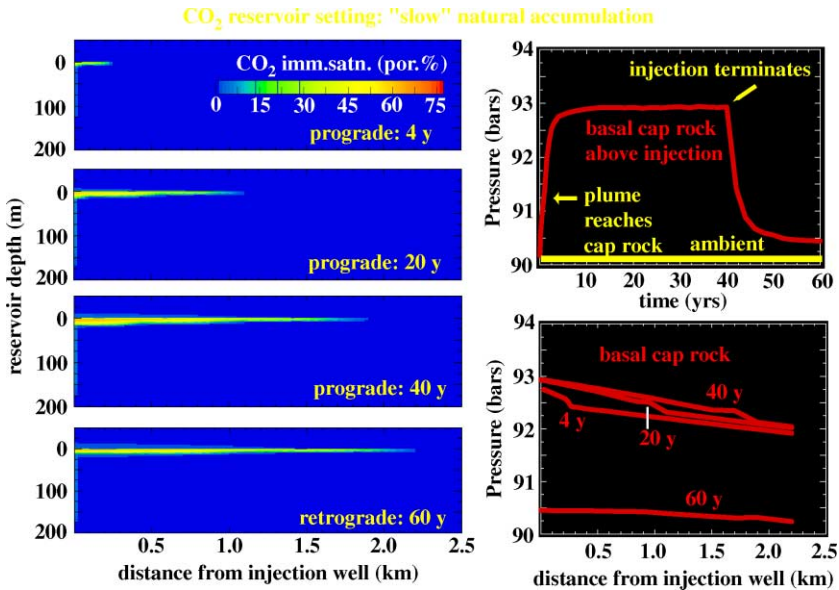


Figure 19: NUFT simulation of immiscible CO₂ migration together with associated pressure evolution within the basal cap rock directly above and as a function of distance from CO₂ influx for “slow” natural accumulation.

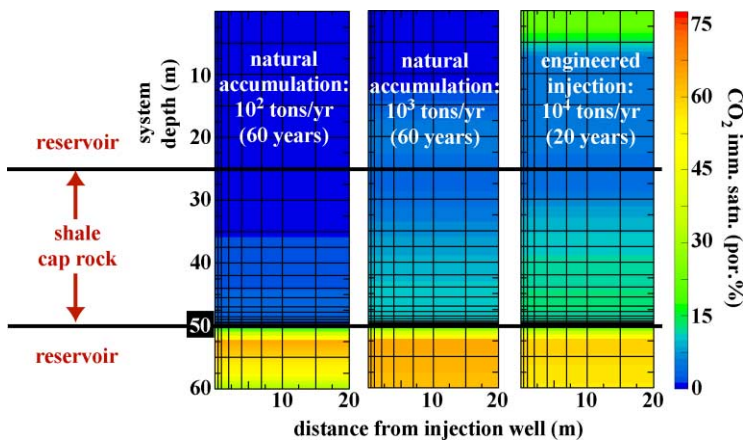


Figure 20: NUFT simulation of CO₂ migration into geomechanically undeformed cap rock as a function of the influx-triggered pressure perturbation, which in the “slow” and “fast” natural accumulation and engineered injection models (shown from left to right) is sufficient to overcome resistive capillary forces.

reservoir to form a laterally-restricted (see Figure 17) accumulation zone beneath the upper domain boundary (where saturations approach 25%) in the engineered injection model (Figure 20).

The extent of geomechanical cap-rock deformation through changes in effective stress and dependent aperture evolution is also strongly dependent on influx rate. As the maximum pressure perturbation realized within basal cap rock increases from 3 to 22 to 160 bar with a 10- to 100-fold increase in influx rate (Figures 17–19), the dependent aperture widening—evaluated in the context of Eqs. (5) and (6)—increases from approximately 50 to 350 to 2900 μm .

The three simulations described above address a fundamental question regarding natural CO_2 reservoirs: are they natural analogs to engineered CO_2 storage sites? The models suggest that geomechanical degradation of seal integrity will be characteristic of both natural and engineered CO_2 influx, but significantly more severe during the latter. This result implies that cap-rock isolation performance may vary considerably as a function of filling mode, which further suggests that the currently secure cap rock of a given natural CO_2 accumulation may be incapable of providing an effective seal in the context of an engineered injection. This potential discrepancy limits the extent to which natural CO_2 reservoirs can be considered directly analogous to engineered CO_2 storage sites.

Geochemical Counterbalancing of Geomechanical Effects

Long-term enhancement or degradation of shale cap-rock integrity ultimately hinges on the relative effectiveness of concomitant geochemical alteration and geomechanical deformation. The analyses presented above offer an opportunity to evaluate an important aspect of this geochemical/geomechanical interplay: the extent to which these initially opposing processes may ultimately counterbalance one another.

This cross-comparison requires a common reference frame, the choices for which are changes in porosity or fracture aperture, which have been used above to represent the respective contributions of geochemical and geomechanical effects. Converting aperture change into the corresponding porosity change requires an initial aperture or fracture density (neither of which are known here), while the aperture change associated with matrix expansion due to a specific mineral dissolution/precipitation reaction can be represented as a function of the dependent variables. Hence, we adopt the latter approach and translate the geochemical contribution into the aperture-change reference frame.

For a given dissolution/precipitation reaction within the matrix, the associated aperture change (Δa) depends on the initial volume fraction of the reactant assemblage (V_R/V_T), standard molal volume change of the reaction ($\Delta V_r^0 = V_p^0 - V_R^0$), effective diffusion distance (L_D , how deep into matrix blocks the reaction occurs), and reaction progress (C , the extent to which the reaction proceeds towards completion) [5]:

$$\Delta a = -2[(V_R/V_T)(\Delta V_r^0/V_R^0)L_D C] \quad (7)$$

All of these variables are typically known or can be closely estimated except for diffusion distance and reaction progress. Hence, it is both appropriate and convenient to plot Δa isopleths as a function of these latter two parameters.

We have constructed such a diagram for reaction (4) (Figure 21), where the Δa -isopleths plotted correspond to the range of geomechanical aperture widening—from initial maximum to final net values (roughly 1000 and 100 μm , respectively)—predicted for model CLP (Figure 14). Hence, they can be viewed as geochemical counterbalance isopleths for this most extreme case of the four systems modeled (CLP, CHP, ULP, and UHP), i.e. along any curve, departing to greater diffusion distances or reaction progress equates to net aperture closure (improved cap-rock integrity) as a function of combined geochemical and geomechanical effects, while departing to lesser values equates to net aperture opening (degraded integrity).

This diagram reveals that ultimate geochemical counterbalancing of initial maximum aperture widening (1000 μm) requires diffusion distances of 3–6.5 cm for reaction progress of 30–60%. Moreover, such counterbalancing of the final net widening (100 μm) requires <0.5 cm diffusion distance for the same range

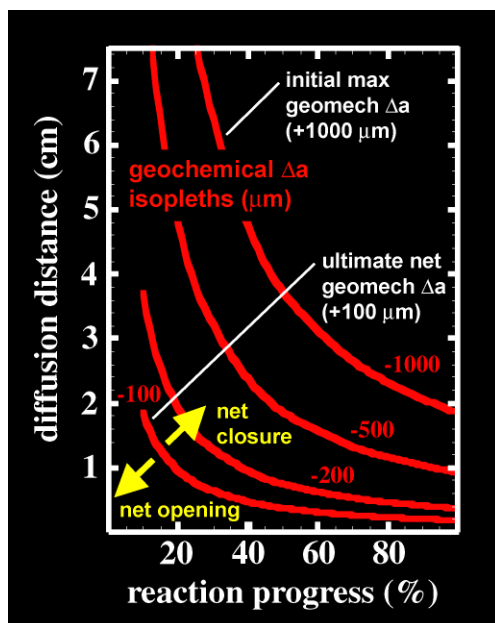


Figure 21: Conceptual framework for assessing potential long-term geochemical counterbalancing of geomechanical effects: geochemical Δa isopleths plotted as a function of diffusion distance and reaction progress for mineral dissolution/precipitation reaction (4), where $\Delta V_r^0/V_r^0$ is 0.185 and V_r/V_T is 0.1425, constructed using reaction (7) over the range of geomechanical Δa defined by initial maximum and ultimate net widening for model CLP (Figure 14).

of reaction progress; this diffusion length scale and extent of reaction progress—both of which are commonly observed in natural systems—strongly suggest that CO_2 influx-triggered geomechanical deformation may be ultimately counterbalanced by long-term geochemical alteration. This raises the distinct possibility that currently secure shale cap rocks in natural CO_2 reservoirs may have *evolved* into effective seals following some degree of CO_2 migration through them. Careful mineralogical and petrographic analyses of these shale cap rocks may shed light on this important concept.

CONCLUSIONS

Reactive transport and geomechanical models have been interfaced and a new conceptual framework developed to evaluate long-term cap rock integrity in natural and engineered CO_2 storage sites. For typical (non-carbonaceous) shale compositions, influx-triggered geochemical alteration and geomechanical deformation act in opposition to enhance and degrade hydrodynamic seal capacity through aperture narrowing and widening of cap-rock microfractures; hence, net impact of these concomitant processes hinges on their relative effectiveness. The extent of geochemical enhancement is largely independent of reservoir characteristics that distinguish saline-aquifer from EOR/storage settings and influx parameters that distinguish engineered disposal sites from natural accumulations, because such characteristics and parameters have negligible (indirect) effect on mineral dissolution/precipitation rates. In contrast, the extent of geomechanical degradation is highly dependent on these reservoir characteristics and influx parameters, because they effectively dictate magnitude of the pressure perturbation. Specifically, it has been shown inversely proportional to reservoir permeability and lateral continuity and proportional to influx rate.

As a result, while the extent of geochemical alteration is nearly independent of filling mode, that of geomechanical deformation is significantly more pronounced during engineered storage. This suggests that the currently secure cap rock of a given natural CO₂ accumulation may be incapable of providing an effective seal in the context of engineered injection, a potential discrepancy that limits the extent to which natural CO₂ reservoirs and engineered storage sites can be considered analogous. In addition, the pressure increase associated with CO₂ accumulation in any compartmentalized system invariably results in net geomechanical aperture widening of cap-rock microfractures. This suggests that ultimate restoration of pre-influx hydrodynamic sealing capacity—in both EOR/storage and natural accumulation settings—hinges on ultimate geochemical counterbalancing of this geomechanical effect, which further suggests that the well documented leaky-to-secure character of fossil CO₂ reservoirs may reflect the incomplete-to-complete nature of such restoration.

To explore these hypotheses, a new conceptual framework has been introduced that depicts ultimate geochemical counterbalancing of geomechanical aperture evolution as a function of effective diffusion distance and reaction progress. This framework reveals diffusion length scales and reaction progress extents consistent with those observed in nature, which suggests that ultimate counterbalancing of geochemical and geomechanical effects is feasible, and, therefore, that shale cap rocks may in fact *evolve* into effective seals—in both natural and engineered storage sites. Further, it provides a theoretical model for assessing the extent to which cap-rock integrity will ultimately be enhanced or degraded in specific reservoir/cap-rock systems in the context of specific engineered injection scenarios.

RECOMMENDATIONS

The present contribution can be viewed as a scoping study in which influx-triggered geochemical and geomechanical contributions to cap-rock integrity have been modeled, then merged within a new conceptual framework that facilitates assessment of their ultimate net effect for CO₂ storage sites whose compositional and influx parameters can be well characterized. As such, it provides a unique computational methodology for addressing two central issues for geologic storage—long-term prediction of isolation performance and the extent to which natural and engineered sites are analogous. A number of model development and application activities are immediately posed by this inaugural work.

In terms of important technological advances, there is a pressing need to develop a simulation capability that fully integrates reactive transport and geomechanical processes, which we have merely interfaced here. There are many ways to accomplish this, ranging from, ideally, a global-implicit approach to, perhaps more realistically in the short-term, bi-directional coupling of distinct models. Equally pressing is the need for improved kinetic descriptions of mineral dissolution and (especially) precipitation processes as well as more accurate and comprehensive databases of the associated species-specific parameters; these developments will lead to improved predictive capabilities. Also very important is the need to develop methodology for assessing the specific rates and time frames of geochemical counterbalancing that involves multiple dissolution/precipitation reactions; here, we have addressed this concept only in a time-integrated sense and for a single representative reaction.

In parallel with such development activities, several key applications could provide critical benchmarking, validation, and refinement for both the simulation capabilities and new hypotheses described above. For example, detailed reactive transport modeling of well-characterized fossil or active CO₂ reservoirs—ideally, a suite of leaky-to-secure systems for which cap-rock core is available—would provide a crucial field-scale test bed for the incomplete-to-complete geochemical counterbalancing concept. Similarly detailed modeling of carefully designed and precisely characterized batch and plug-flow reactor experiments would provide an analogous laboratory-scale test bed for this theory—as well as the ideal means of benchmarking simulation capabilities for all mineral trapping mechanisms.

Closely integrated modeling/experimental studies such as these—on both the field and laboratory scale—also provide an effective methodology for evaluating key compositional dependencies of long-term cap rock (and reservoir) integrity. Such dependencies include those associated with formation waters (e.g. salinity, specific cation/anion concentrations) and waste-stream impurities (e.g. CH₄, H₂S, SO_x, NO_x concentrations) as well as the effect of lithologic diversity, ranging from the influence of carbonate cements

on the shale-capped sandstone systems addressed here to a dramatic shift from such environments into, for example, anhydrite-capped carbonate reservoirs.

Finally, for a suite of well-characterized potential CO₂ disposal sites, reactive transport and geomechanical modeling could be used to identify and evaluate the volume change associated with key injection-triggered mineral dissolution/precipitation reactions, to assess concomitant pressure-dependent geomechanical deformation, and to determine net impact of these interdependent processes on long-term cap rock integrity (e.g. Figure 21). It would be particularly instructive and useful to carry out this modeling study for a suite of prospective sites that spans the broad range of potential reservoir/cap-rock lithologies—well beyond the single sandstone/shale combination examined here. Such an analysis would provide a unique means of quantitatively ranking long-term isolation performance as a function of important lithologic and other dependent variations.

ACKNOWLEDGEMENTS

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48. Funding support was provided by the JIP CO₂ Capture Project and the U.S. Department of Energy (Office of Fossil Energy) through a CRADA (TC-02038). It is a pleasure to thank Associate Editor Curt Oldenburg and two anonymous reviewers for their critiques of the original manuscript; each contributed a number of comments that were invaluable in preparing the revised contribution.

REFERENCES

1. J.W. Johnson, J.J. Nitao, C.I. Steefel, K.G. Knauss, Reactive transport modeling of geologic CO₂ sequestration in saline aquifers: the influence of intra-aquifer shales and the relative effectiveness of structural, solubility, and mineral trapping during prograde and retrograde sequestration, *Proc. First Natl Conf. Carbon Sequestration*, Washington, DC, May 14–17, 2001, p. 60.
2. J.W. Johnson, J.J. Nitao, C.I. Steefel, Fundamental elements of geologic CO₂ sequestration in saline aquifers, *Am. Chem. Soc., Fuel Chem. Div. Prepr.* **47** (1) (2002) 41–42.
3. J.W. Johnson, J.J. Nitao, Reactive transport modeling of geologic CO₂ sequestration at Sleipner, *Proc. Sixth Int. Conf. Greenhouse Gas Control Technologies (GHGT-6)*, Kyoto, Japan, October 1–4, 2002, vol. 1, pp. 327–332.
4. J.W. Johnson, J.J. Nitao, K.G. Knauss, Reactive transport modeling of CO₂ storage in saline aquifers to elucidate fundamental processes, trapping mechanisms, and sequestration partitioning, in: S.J. Baines, R.H. Worden (Eds.), *Geologic Storage of Carbon Dioxide*, Geological Society, London, Special Publication, **233** (2004) 107–128.
5. J.W. Johnson, J.J. Nitao, J.P. Morris, S.C. Blair, Reactive transport modeling of geohazards associated with offshore CO₂ injection for EOR and geologic sequestration, *Proc. Offshore Technology Conf.*, Houston, TX, May 5–8, 2003a, p. 9.
6. J.W. Johnson, J.J. Nitao, J.P. Morris, Reactive transport modeling of long-term cap rock integrity during CO₂ injection for EOR or saline-aquifer storage, *Second Natl Conf. Carbon Sequestration*, Alexandria, VA, May 5–8, 2003b.
7. J.W. Johnson, J.J. Nitao, J.P. Morris, S.C. Blair, CO₂ reservoirs: are they natural analogs to engineered geologic storage sites? *AAPG Annual Meeting*, Salt Lake City, UT, May 11–14, 2003c.
8. J.W. Johnson, J.J. Nitao, J.P. Morris, Reactive transport modeling of cap rock integrity during natural and engineered CO₂ sequestration, *Am. Chem. Soc. Natl Meeting*, New York, NY, September 7–11, 2003d.
9. A.F.B. Wildeborg, A.L. Leijnse, E. Kreft, M.N. Nepveu, A.N.M. Obdam, B. Orlic, E.L. Wipfler, B. van der Grift, W. van Kesteren, I. Gaus, I. Czernichowski-Lauriol, P. Torfs, R. Wójcik, Risk Assessment Methodology for CO₂ Storage—the Scenario Approach, CCP Summary, vol. 2, 2004, 1293–1316.
10. S.H. Stevens, Natural CO₂ Fields as Analogs for Geologic CO₂ Storage, CCP Summary, vol. 2, 2004, 687–697.

11. H. Schütt, M. Wigand, E. Spangenberg, Geophysical and Geochemical Effects of Supercritical CO₂ on Sandstones, CCP Summary, vol. 2, 2004, 767–786.
12. G.J. Nimz, G.B. Hudson, The Use of Noble Gas Isotopes for Monitoring Leakage of Geologically Stored CO₂, CCP Summary, vol. 2, 2004, 1113–1128.
13. G.M. Hoversten, E. Gasperikova, Non-seismic Geophysical Approaches to Monitoring, CCP Summary, vol. 2, 2004, 1071–1112.
14. Z.K. Sipton, J.P. Evans, B. Dockrill, J. Heath, A. Williams, D. Kirchner, P.T. Kolesar, Natural Leaking CO₂-Charged Systems as Analogs for Failed Geologic Sequestration Reservoirs, CCP Summary, vol. 2, 2004, 699–712.
15. D. Norton, Theory of hydrothermal systems, *Annu. Rev. Earth Planet. Sci.* **12** (1984) 155–177.
16. J.W. Johnson, J.J. Nitao, A.F.B. Tompson, C.I. Steefel, 21st-century tools for modeling reactive transport in dynamic geologic systems of economic and environmental significance, *Earth and Environmental Sciences 1998 Annual Report*, 1999, pp. 7–11, LLNL, UCRL-LR-126434-98.
17. C. Bertrand, B. Fritz, J.F. Sureau, Hydrothermal experiments and thermo-kinetic modelling of water–sandstone interactions, *Chem. Geol.* **116** (1994) 189–192.
18. J.W. Johnson, K.G. Knauss, W.E. Glassley, L.D. DeLoach, A.F.B. Tompson, Reactive transport modeling of plug-flow reactor experiments: quartz and tuff dissolution at 240°C, *J. Hydrol.* **209** (1998) 81–111.
19. J.J. Nitao, Reference Manual for the NUFT Flow and Transport Code, Version 2.0: LLNL, UCRL-MA-130651, 1998a, p. 55.
20. J.J. Nitao, User's Manual for the USNT Module of the NUFT Code, Version 2.0 (NP-Phase, NC-component, Thermal): LLNL, UCRL-MA-130653, 1998b, p. 76.
21. J.C. Parker, R.J. Lenhard, T. Kuppusamy, A parametric model for constitutive properties governing multiphase flow in porous media, *Water Resour. Res.* **23** (4) (1987) 618–624.
22. A.C. Lasaga, Kinetic Theory in the Earth Sciences, Princeton University Press, Princeton, NJ, 1998, p. 811.
23. A.E. Scheidegger, The Physics of Flow Through Porous Media, third ed., University of Toronto Press, Toronto, 1974, p. 353.
24. J.W. Johnson, S.R. Lundeen, Jewel: A Graphical–User Interface for Generating Custom GEMBOCHS Thermodynamic Datafiles for Use with Geochemical Modeling Software: LLNL-YMP Milestone Report MOL63, 1994a, p. 23.
25. J.W. Johnson, S.R. Lundeen, GEMBOCHS Thermodynamic Datafiles for Use with the EQ3/6 Software Package: LLNL-YMP Milestone Report MOL72, 1994b, p. 99.
26. J.W. Johnson, E.H. Oelkers, H.C. Helgeson, SUPCRT92: a software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bars and 0 to 1000°C, *Comp. Geosci.* **18** (7) (1992) 899–947.
27. E.L. Shock, An updated and augmented version (slop98.dat) of the original SUPCRT92 database (sprons92.dat) is available on Dr. Shock's website: <http://geopig.asu.edu>, 1998.
28. J.W. Johnson, D. Norton, Critical phenomena in hydrothermal systems: state, thermodynamic, electrostatic, and transport properties of H₂O in the critical region, *Am. J. Sci.* **291** (1991) 541–648.
29. J.C. Tanger IV, H.C. Helgeson, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: revised equations of state for the standard partial molal properties of ions and electrolytes, *Am. J. Sci.* **288** (1) (1988) 19–98.
30. E.L. Shock, E.H. Oelkers, J.W. Johnson, D.A. Sverjensky, H.C. Helgeson, Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures: effective electrostatic radii, dissociation constants, and standard partial molal properties to 1000°C and 5 kb, *J. Chem. Soc. (London) Faraday Trans.* **88** (6) (1992) 803–826.
31. H.C. Helgeson, J.M. Delany, H.W. Nesbitt, D.K. Bird, Summary and critique of the thermodynamic properties of rock-forming minerals, *Am. J. Sci.* **278-A** (1978) 229.
32. J.P. Morris, L.A. Glenn, S.C. Blair, The distinct element method—application to structures in jointed rock, *Lect. Notes Comput. Sci. Eng.* **26** (2002) 291–306.
33. J.P. Morris, M.B. Rubin, S.C. Blair, L.A. Glenn, F.E. Heuze, Simulations of underground structures subjected to dynamic loading using the distinct element method, *Eng. Comput.* **21** (2–4) (2004) 384–408.

34. P.A. Cundall, Formulation of a three-dimensional distinct element model—Part I: a scheme to detect and represent contacts in a system composed of many polyhedral blocks, *Int. J. Rock Mech. Min. Soc. Geomech. Abstr.* **25** (1988) 107–116.
35. T.A. Torp, J. Gale, Demonstrating storage of CO₂ in geological reservoirs: the Sleipner and SACS projects, *Proc. Sixth Int. Conf. Greenhouse Gas Control Technologies (GHGT-6)*, Kyoto, Japan, October 1–4, 2002.
36. U. Gregersen, P. Johannessen, J. Moller, L. Kristensen, N. Christensen, S. Holloway, A. Chadwick, G. Kirby, E. Lindeberg, P. Zweigel, SACS Phase Zero Report (provided courtesy of SACS), 1998.
37. J.C. Baker, G.P. Bai, P.J. Hamilton, S.D. Golding, J.B. Keene, Continental-scale magmatic carbon-dioxide seepage recorded by dawsonite in the Bowen–Gunnedah–Sydney Basin Eastern Australia, *J. Sed. Res.* **65** (3) (1995) 522–530.
38. J. Moore, M. Adams, R. Allis, S. Lutz, S. Rauzi, Investigations of CO₂ mobility in natural reservoirs beneath the Colorado Plateau and Southern Rocky Mountains, *Proc. Second Annu. Conf. Carbon Sequestration*, May 5–8, 2003, Alexandria, Virginia, 2003, p. 22.
39. M.N. Watson, N. Zwingmann, N.M. Lemon, The Ladbroke Grove-Katnook carbon dioxide natural laboratory: a recent CO₂ accumulation in a lithic sandstone reservoir, *Proc. Sixth Int. Conf. Greenhouse Gas Control Technologies (GHGT-6)*, Kyoto, Japan, October 1–4, 2002, vol. 1, pp. 435–440.
40. H.A. Bilgin, A.G. Pasamehmetoglu, Shear Behaviour of Shale Joints Under Heat in Direct Shear, in: N. Barton, O. Stephansson (Eds.), *Rock Joints*, 1990, pp. 179–183.
41. R. Allis, T. Chidsey, W. Gywnn, C. Morgan, S. White, M. Adams, J. Moore, Natural CO₂ reservoirs on the Colorado Plateau and Southern Rocky Mountains: candidates for CO₂ sequestration, *Proc. First Natl Conf. Carbon Sequestration*, Washington, DC, May 14–17, 2001, p. 19.

This page is intentionally left blank