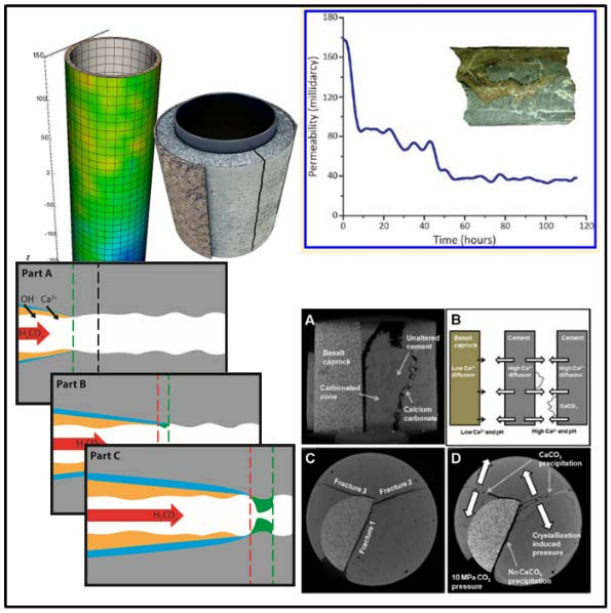
NRAP
National Risk Assessment Partnership



Well Integrity in CO_2 Storage Operations: Current Understanding and Open Questions

3 October 2016

U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

Office of Fossil Energy

NRAP-TRS-I-007-2016

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference therein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed therein do not necessarily state or reflect those of the United States Government or any agency thereof.

Cover Illustration: Quantifying the risk and behavior of well leakage requires investigating the system using a combination of laboratory experiments and numerical simulations. The resulting observations can then be used to develop reduced-order models, which are used to predict long-term leakage behavior.

Suggested Citation: Huerta; N. J.; Carey, J. W.; Carroll, S.; Dzombak, D.; Harp, D.; Li, L.; Richard, T.; Walsh, S. D. C.; Um, W.; Zhang, L. *Well Integrity in CO_2 Storage Operations: Current Understanding and Open Questions*; NRAP-TRS-I-007-2016; NRAP Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Albany, OR, 2016; p 48.

An electronic version of this report can be found at:
http://www.netl.doe.gov/research/on-site-research/publications/featured-technical-reports

https://edx.netl.doe.gov/nrap

Well Integrity in CO_2 Storage Operations: Current Understanding and Open Questions

Nicolas J. Huerta[1], J. William Carey[2], Susan Carroll[3], David Dzombak[4], Dylan Harp[2], Li Li[5], Tom Richard[5], Stuart D.C. Walsh[3], Wooyong Um[6], Liwei Zhang[1]

[1]U.S. Department of Energy, National Energy Technology Laboratory 1450 Queen Ave SW, Albany, OR 97322

[2]Los Alamos National Laboratory, Bikini Atoll Road, SM 30, Los Alamos, NM 87545

[3]Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550

[4]Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, PA 15213

[5]The Pennsylvania State University, University Park, PA 16802

[6]Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99354

NRAP-TRS-I-007-2016

Level I Technical Report Series

3 October 2016

This page intentionally left blank.

Table of Contents

EXECUTIVE SUMMARY **1**

1. INTRODUCTION **3**

2. WELL INTEGRITY FAILURE **5**

2.1 BACKGROUND ON WELL CONSTRUCTION 5
2.2 ORIGIN OF MIGRATING FLUIDS AND LEAKAGE IN WELL SYSTEMS 7
2.3 KEY PROCESSES CONTROLLING LEAK PATH EVOLUTION 10

3. REDUCED ORDER MODELS **23**

3.1 MULTI-PHASE CO_2 AND BRINE LEAKAGE WITH CONSTANT PERMEABILITY 24
3.2 CHEMICALLY INDUCED CHANGES IN PERMEABILITY 27
3.3 CHEMICALLY AND MECHANICALLY INDUCED CHANGES IN PERMEABILITY 28

4. SUMMARY **29**

4.1 LESSONS LEARNED ABOUT STATE OF KNOWLEDGE OF WELL LEAKAGE 29
4.2 RESEARCH NEEDS 29
4.3 PRACTICAL IMPLICATIONS 31

5. REFERENCES **33**

List of Figures

Figure 1: Schematic diagram illustrating the typical construction of a plugged and abandoned well. 6

Figure 2: Schematic diagram of an abandoned well showing principle leakage pathways....8

Figure 3: Schematic of interaction between H_2S/SO_2 and well cement. 13

Figure 4: Predicted self-sealing or fracture opening behavior for 225 simulations of carbonic acid injected into fractured cement (Class H) with different initial aperture size and initial fracture residence time....18

Figure 5: Image of the fracture surfaces post experiment....19

Figure 6: Hydraulic aperture as a function of time in samples of mated cement/caprock half cores with distinct flow-path geometries. 20

Figure 7: Back-scattered electron micrograph of the interface between steel (solid white material left) and Portland cement (spotted material right). 22

Figure 8: Ensemble statistics across 50 realizations for rates of (a) CO_2 and (b) brine leaking up a well in the CO_2-PENS Kimberlina simulations using the first generation well ROM....24

Figure 9: Schematic of vertical 2-D slice of second generation FEHM simulation configuration. 25

Figure 10: Flow diagram of cemented well leakage ROM development. 26

Figure 11: Schematic showing the leakage of CO_2-saturated brine (containing carbonic acid) from the leak source (D_{leak}) up to the leak top (D_{top}). 28

List of Tables

Table 1: Mass balance reactions and thermodynamics and kinetic constants for CO_2-cement alteration....11

Acronyms, Abbreviations, and Symbols

Term	Description
2-D	Two-dimensional
3-D	Three-dimensional
API	American Petroleum Institute
C_4AF	Calcium-aluminum-iron sulfates
$Ca(OH)_2$	Calcium hydroxide
CO_2	Carbon dioxide
C-A-H	Calcium aluminum hydrate
C-A-S	Calcium aluminum monosulfate
CRA	Corrosion resistant alloy
C-S-H	Calcium silicate hydrate
DOE	U.S. Department of Energy
EOR	Enhanced oil recovery
Fe^{3+}	Ferric iron
FEHM	Finite Element Heat and Mass transfer
GCS	Geologic carbon storage
H_2S	Hydrogen sulfide
IAM	Integrated assessment model
LANL	Los Alamos National Laboratory
LBNL	Lawrence Berkeley National Laboratory
LHS	Latin Hypercube Sampling
LLNL	Lawrence Livermore National Laboratory
MARS	Multivariate adaptive regression splines
mD	Millidarcy
NETL	National Energy Technology Laboratory
NRAP	National Risk Assessment Partnership
NRAP-IAM-CS	National Risk Assessment Partnership's Integrated Assessment Model for Carbon Storage
O_2	Oxygen
OPC	Ordinary Portland cement
PNNL	Pacific Northwest National Laboratory
PSUADE	Problem Solving environment for Uncertainty Analysis and Design Exploration

Acronyms, Abbreviations, Symbols (cont.)

Term	Description
RCM	Reduced complexity model
ROMs	Reduced-order models
RPM	Reduced physics model
SO_2	Sulfur dioxide
TRS	Technical Report Series
USDW	Underground source of drinking water

Acknowledgments

This work was completed as part of the National Risk Assessment Partnership (NRAP) project. Support for this project came from the U.S. Department of Energy's (DOE) Office of Fossil Energy's Crosscutting Research program. The authors wish to acknowledge Traci Rodosta (Carbon Storage Technology Manager), Kanwal Majajan (Carbon Storage Division Director), M. Kylee Rice (Project Manager), Mark Ackiewicz (Division of CCS Research - Program Manager), Susan Maley and Steve Seachman (NETL Strategic Center for Coal), and Regis Conrad (DOE Office of Fossil Energy) for programmatic guidance, direction, and support.

The authors would like to acknowledge Brian Strazisar and Preston Jordan for their help with developing an early version of the TRS; David Nakles for organizing the meeting between authors that led to a more unified effort on this report; Brian Tost for help with the reference list; and Robert Dilmore and Barbara Kutchko for their thoughtful review of the manuscript.

This page intentionally left blank.

EXECUTIVE SUMMARY

Among the various risks associated with carbon dioxide (CO_2) storage in deep geologic formations, leaky wells are an important pathway for fluid leaks and potential groundwater contamination. Injection of CO_2 will typically create a pressure perturbation in the storage reservoir that covers a larger area than the CO_2 plume itself, and any wells that penetrate that pressure footprint are potential pathways for leakage of CO_2 and/or reservoir brine (Celia et al., 2011). Historically, the mechanisms and fate of leakage through and around wells have not been extensively studied, especially from the standpoint of quantitative risk assessment. However, since the publication of the review paper by Zhang and Bachu (2011), there have been important advances, with significant contributions from researchers associated with the National Risk Assessment Partnership (NRAP). The goal of this report is to summarize recent key advances in the state of knowledge, and to detail the efforts to develop tools that can estimate leakage over the long time scales that are relevant to carbon storage (10s to 100s of years).

Leaky wells are ubiquitous in regions with a long history of oil and gas exploration, yet until recently the construction, completion, plugging, and abandonment of these wells did not anticipate the potential use of geologic reservoirs for storage of supercritical CO_2. This report explores in detail the ability of abandoned wells to retain their integrity against leakage as well as the circumstances when that integrity may be compromised, with careful examination of the coupled physical and chemical processes involved. Understanding time-dependent leakage is complicated by the coupling of fluid flow, solute transport, chemical reactions, and geomechanical stresses, which will interact over decades or longer of site operations and post-injection monitoring.

The design of a typical well incorporates several components to restrict unintended fluid migration that include cement, casing, tubing, and packers. Wells are typically constructed so that a loss of well integrity requires the breach of multiple barriers as well as leakage of fluids outside of the well. Barrier failures can originate from problems with the primary construction of the well (e.g., failure to place cement adequately or leaky connections in the casing joints) or as a result of subsequent stresses to the well system that damage these barriers.

As there are limited data on field-scale CO_2 leakage, almost all studies of the potential for well leakage have been laboratory based. Laboratory experiments show that while CO_2 and CO_2-saturated brine react with cement and casing, the rate of alteration is transport-limited and alteration of cement and casing properties is small under no flow conditions. The reactions with cement alter the physical properties of the cement, in some cases increasing permeability and in other cases decreasing permeability. The specific rate and nature of alteration depends on the cement composition, brine composition, and injected fluid composition. The presence of co-injected gases (e.g., oxygen (O_2) and sulfur dioxide (SO_2) influences the rate and the nature of cement alteration.

However, when a leak path that can conduct fluid flow is already present due to cement shrinkage, cement fracturing, gaps along interfaces (e.g., casing/cement or cement/rock), or casing failures, CO_2 injection has the potential to increase leakage risks. Laboratory experiments and numerical simulations have shown that precipitation or closure of strain-induced fractures can seal a leak pathway over time (e.g., Huerta et al., 2015; Walsh et al., 2014b). However, the large variability of material types (cement, geologic material, casing), field conditions (pressure, temperature, gradient in potential, residence time), and leaking fluid (CO_2, co-injected gases,

brine composition) makes the development of a comprehensive, process-based model of well leakage behavior challenging. Model development and application for risk assessment is an area of active research.

Although these well leakage mechanisms and their interactions with CO_2 are extremely complex, NRAP is developing reduced-order models (ROMs) that capture key coupling effects and attempt to quantitatively narrow the range of likely time-dependent leakage. ROMs can be built from reduced physics models that capture key phenomena affecting leak flux; alternatively ROMs can be developed by performing many full-physics simulations to generate look up tables that relates key system properties to leak flux. Current NRAP-developed models account for multiphase flow of CO_2 and brine, the presence of thief zones, different leak-path geometries, and different types of boundary conditions. Enhancing these ROMs to account for dynamic changes in permeability due to geochemical and geomechanical effects is an area of active research within NRAP.

NRAP's integrated experimental and modeling program has identified several issues that require further investigation. Future research plans include a combination of laboratory and numerical experiments designed to improve ROMs and provide a better quantification of well leakage.

1. INTRODUCTION

Wells are designed to facilitate the transmission of large quantities of fluid through geologic formations. In cases where existing wells from a legacy of oil and gas production, water extraction, or wastewater, steam, or gas injection may penetrate reservoirs intended for geologic carbon storage (GCS), it is critical that they are effectively plugged and sealed, and that those barriers to fluid transport remain intact over century timescales. In the context of GCS, the long-term integrity of wells is of particular concern because of the potential for carbon dioxide (CO_2) (as a free phase or dissolved in formation brine) to react with and degrade the materials used in well construction. The duration, volumes, and pressures associated with CO_2 injection (during enhanced oil recovery (EOR) or GCS) also result in geomechanical stress on well materials that can physically alter these materials or geologic material near the well. Specific mechanisms that can cause geomechanical stress alteration include volume changes due to fluid injection or withdrawal, temperature changes, and chemical alteration of fracture surfaces (Majer et al., 2012). Depending on the injection pressure, geomechanical effects include opening of pre-existing fractures, rock fracturing, weakening of the strength of materials, and density-driven stress loading (Sminchak et al., 2002). There is considerable uncertainty in predicting the integrity of existing legacy wells, as well as in assessing the costs and risks of fluid leakage because of variability in a well's age, design, construction materials, completion type, reservoir lithology, formation fluids, and reservoir management history. Well leakage and fluid migration pathways may include degraded or fractured cement, corroded casing, and borehole damage caused by drilling activities. The potential for CO_2 leakage from wells is one of the key risks identified for GCS.

Reliable and permanent storage is critical to the success of GCS programs. Leakage of CO_2 from the storage reservoir could lead to contamination of groundwater (Carroll et al., 2014), and if released to the surface would undermine the goal of decreased carbon emissions to the atmosphere. Quantitatively predicting leakage risk has therefore been a primary focus of the National Risk Assessment Partnership (NRAP) (Pawar et al., 2014). There are three primary sources of potential leakage: 1) the caprock (and any associated defect), 2) injection and monitoring wells used by the storage project, and 3) existing wells within the impact zone of the project. This report focuses on leakage risks associated with existing wells in the project area, including abandoned wells that may or may not have been properly plugged.

Assessing the leakage risks associated with wells at a specific CO_2 storage site requires both general knowledge about issues common to many sites and well types, and specific information pertaining to the characteristics of the storage site. Generic issues include knowledge regarding typical well construction methods, material properties, transport (i.e., leakage) properties, geochemical reactions, and geomechanical mechanisms. Specific information relevant to the wells impacted by a storage site include age, numbers, location, construction, completion, abandonment protocols, potential leakage paths, sizes, and impact of brine on overlying formations including groundwater aquifers. Both general and specific knowledge are important not only in risk assessment, but to support decision making related to the management of existing well fields to mitigate risk and to remediate any leaks that may occur. In the case of legacy wells whose status is unknown, there are decisions about the probability of leakage and whether to properly plug and abandon those wells that may pose a leakage risk. Knowledge related to well leakage processes and risks will also inform strategies for monitoring, mitigation, and remediation.

The tools available to address these issues include a combination of existing information on well integrity performance gathered from the literature, operators, and regulatory agencies; experimental studies of the durability of well construction materials (e.g., cement and steel casing) as a function of age and exposure to CO_2; and computational studies on the impacts of chemical and mechanical stresses to well systems.

This report summarizes current knowledge on the mechanisms by which leaks are initiated and propagate in single wells, and how single well probabilities and impacts aggregate at the scale of well fields across a CO_2 storage site. Also presented is an overview of the multiple components of the coordinated NRAP investigations of well integrity and the factors that affect well integrity. Results of laboratory, modeling, and field investigations are described. The report also describes a suite of ROMs to simulate leakage behavior within an integrated assessment model (IAM) framework.

2. WELL INTEGRITY FAILURE

Well integrity encompasses all operations necessary to construct, operate, and abandon wells safely while protecting the environment. A definition of well integrity is given by the Norwegian Technology Centre (NORSOK, 2004) handbook as the "application of technical, operational and organizational solutions to reduce risk of uncontrolled release of formation fluids throughout the life cycle of a well." This definition applies to wells impacted by CO_2 storage, whether new CO_2 injection wells or legacy wells in a reservoir being developed for CO_2 EOR or dedicated CO_2 storage. In the case of legacy oil and gas production wells, the relevant fluids and stresses associated with CO_2 injection may not have been anticipated during the design, construction, operation, and abandonment stages. Potential environmental impacts of a loss of well integrity involve the migration or leakage of fluids (e.g., CO_2 and brine) from the storage reservoir to underground sources of drinking water (USDW), to the shallow surface including soils and buildings, or to the atmosphere.

The design of a typical well involves several components that are meant to restrict fluid migration, including tubing, packers, steel casing, and cement. The casing and tubing provide mechanical support while the cement and packer create a hydrologic seal to prevent fluid from traveling through any of the well's annuli. Wells are often constructed with multiple barriers so that the failure of a single barrier does not imply that fluid migration will occur outside the well (King and King, 2013). Thus, a loss of well integrity often requires the breach of multiple barriers as well as leakage of fluids outside the well.

Barrier failures can originate from problems with the primary construction of the well (e.g., failure to place cement adequately or leaks in the joint connections in the casing or tubing) or as a result of subsequent stresses to the well that damage these barriers. In the subsequent sections, the potential for CO_2 injection and storage operations to induce chemical changes or mechanical stresses to well components that result in compromised barriers and potential leakage pathways is reviewed. After presenting background information, research is discussed on fundamental mechanisms that can damage cement, steel casing, and the interfaces between casing/cement and cement/rock.

2.1 BACKGROUND ON WELL CONSTRUCTION

Completing and abandoning a well is a complex operation, with a number of critical steps. The following description provides an overview of key aspects of the process; additional details can be found in Bourgoyne et al. (1986) and Nelson and Guillot (2006). The basic construction of wells involves drilling the wellbore (or borehole), placing steel casing, and sealing the annular space between the casing and the borehole wall with cement (Figure 1). Drilling the borehole requires circulating drilling fluid that is used to lubricate the drilling bit, carry rock cuttings to the surface, prevent damage to the borehole wall (e.g., erosion or caving of shale), and provide backpressure to subsurface formation fluids (i.e., prevent a kick and loss of well control). A concentric set of steel casing is set into a borehole of decreasing diameter and increasing length.

The specifics of casing design are highly variable but include at a minimum the conductor casing, surface casing, and production casing. The casing stabilizes the borehole from collapsing, contains the high-pressure fluids that are produced or injected at depth, and is one of the primary barriers preventing contamination of groundwater resources. Casing is generally made from low-carbon steel. The conductor casing stabilizes the soil or rock in surface layers near the well. The

surface casing extends down through the lowermost USDW and is generally required by regulation to be cemented to the surface. It is designed as the outermost barrier preventing fluids from contaminating a USDW resource. The production casing extends from the surface to the injection (or production) zone. The production casing is cemented from the bottom of the wellbore up at least through the base of the caprock overlying the production or storage reservoir, but is generally not cemented to the surface. Often, intermediate casing(s) are included to prevent formation fracturing during drilling, or to isolate potentially problematic zones. Other important components of the well include internal tubing, which is typically not cemented in place and designed to produce or inject fluids and packers that generate seals between tubing and casing or even between casing and rock.

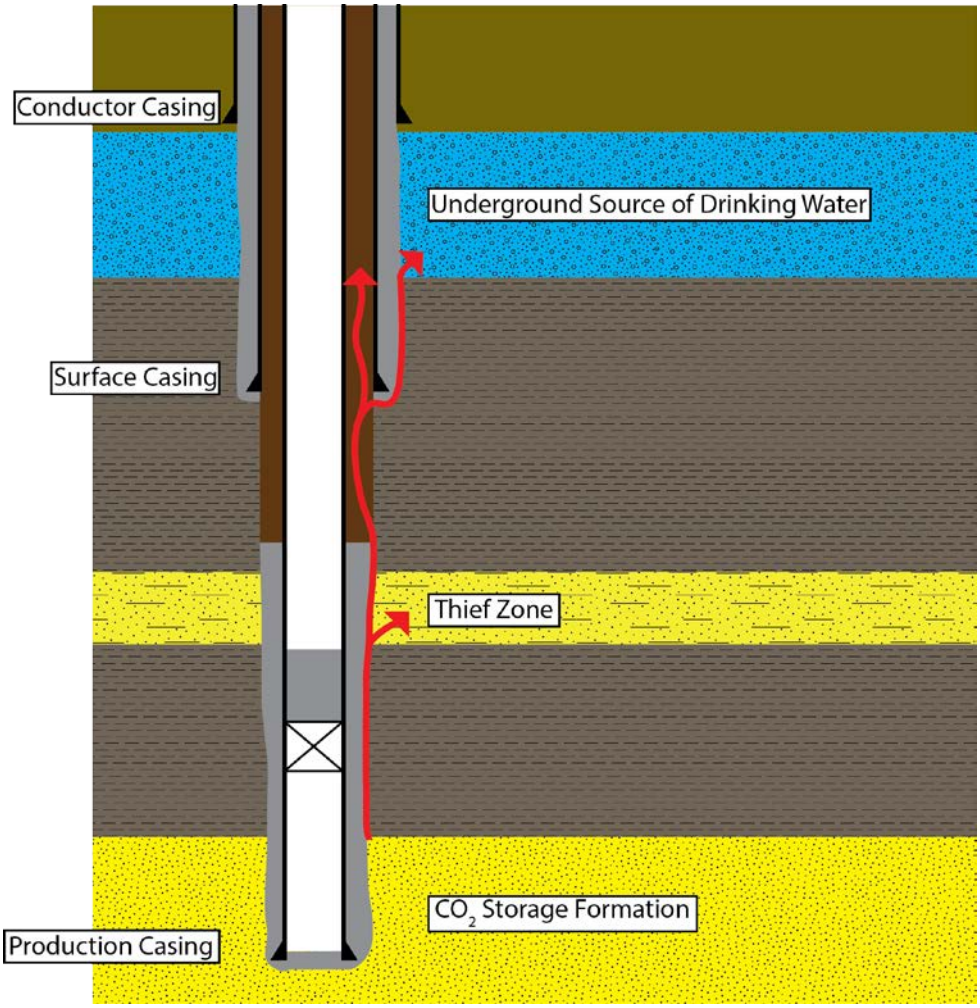


Figure 1: Schematic diagram illustrating the typical construction of a plugged and abandoned well. To construct the well, a borehole is drilled in one or more stages involving the insertion of one or more steel casings (thin black lines) and the annulus is sealed with cement (thick gray regions). To plug the well, the production tubing is removed, a packer (black box with X in it) is inserted, and cement is placed in the well on top of the packer. Potential CO_2 and brine leak paths are shown by the red arrows. Modified from Carey (2013).

Oilwell cement is an ordinary Portland cement (OPC) that may contain various additives to control setting time, density, viscosity, or durability. Hydrated or set cement consists predominantly of a calcium silicate hydrate known as C-S-H (the primary binder), calcium hydroxide ($Ca(OH)_2$), such as portlandite, and several calcium-aluminum-iron sulfates (C_4AF). Cement is highly alkaline with pH > 12.5. One of the most common additives to oilwell cement is pozzolan (chiefly fly ash), a low-cost extender that also modifies the chemistry (generally reducing portlandite), porosity, and permeability. Note that cement does not contain "aggregate" or large rock material (though it may contain fine particle silica) and thus is not concrete; when the cement contains no additives it is commonly referred to as "neat" cement.

Cement placement begins by mixing unhydrated cement with water and additives at the surface and then injecting the resulting slurry down the middle of the casing. The slurry displaces the drilling fluid and once the slurry reaches the bottom of the well it then moves up the annular space between the casing and the formation. The cement slurry is followed by spacer, completion, or drilling fluid to prevent cementing of the casing and to allow the cement to be placed over the desired interval.

When the cement sets, it forms a mechanical support for the well and a hydrologic barrier between the casing and borehole wall. This hydrologic barrier is designed to create isolation among, and between, subsurface zones and surface water. To accomplish this, cement must be bonded to both the casing and rock, and there must be 360° coverage around the casing. Cement is an integral component establishing long-term well integrity. Cement also reinforces the steel casing by supporting its weight, providing additional strength against pressure, and preventing corrosion of the steel.

Well completion involves steps necessary to produce or inject fluids into the subsurface. This includes the addition of production liners and packers, perforating the steel casing and cement in production zones, treatment of the formation to enhance permeability (e.g., hydraulic fracturing and acidizing), and installation of surface hardware. At the end of the life of the well, it is plugged and abandoned. The specific requirements have varied over time and current methods vary by region (i.e., specific methods for each State), but abandonment generally involves pulling the tubing out of the well and placing an impermeable barrier, often consisting of cement or a mechanical device, at various locations within the casing. These are generally placed at the top of the reservoir, into the caprock, and at the base of the surface casing to protect surface drinking water.

2.2 ORIGIN OF MIGRATING FLUIDS AND LEAKAGE IN WELL SYSTEMS

Modern wells are generally designed, drilled, and completed following best practices, using the best materials available, and following government regulations that were developed to address most of the common problems discussed above. As a result, modern wells have a much higher likelihood for well integrity. However, in many areas that are prime candidates for CO_2 storage there are legacy wells that were drilled when regulations were less restrictive, often using methods or materials that are now outdated (Nicot, 2009; Watson and Bachu, 2008).

Well integrity can be compromised during the construction or as a result of chemical and mechanical stresses that damage the well during subsequent operations. The likely leakage paths are illustrated in Figure 2. Key problems in poor completions include thread leaks between casing joints, accounting for as much as 90% of all tubular failures (Schwind et al., 2001) (#5 in

Figure 2); inadequate or incomplete cement placement or incomplete coverage of the cement/formation annulus, especially in non-vertical wells (#2, #9); poor cement quality (i.e., high permeability cements) (#8); development of mud or gas channels in the cement (#11); failure to adequately remove filter-cake from the borehole and other problems associated with a poor bond between casing/cement and cement/rock (#7, #12); and mechanical damage to the near wellbore environment, especially at the primary seal (#6).

Post-completion problems may be caused by thermal stresses induced by production or injection of fluids; mechanical stresses due to pressures inside tubing or within the injection/production reservoir as well as tectonic stresses; and chemical stresses due to fluids and gases within or surrounding the well attacking cement or steel (e.g., CO_2 or hydrogen sulfide (H_2S)). Potential post-completion leakage pathways include casing corrosion (Brondel et al., 1994) (#1); fractures in cement (#10); dissolution-induced cement defects (#9); formation of microannuli at the casing/cement or cement/rock interfaces (#7, #12); and chemical degradation of the cement resulting in elevated permeability (#8). If fluids migrate past the cement, then the fluid may flow more rapidly via open-hole flow within the casing (#4) or by external annulus flow (#3). If migrating fluids escape through to the external annulus, the fluids must still have access to permeable formations or the atmosphere in order to impact the environment. Although there are no statistics available that describe the relative likelihood of poor-completion versus post-completion well leakage problems, an informal assessment suggests that most problems originate due to poor completion and inadequate coverage of casing by cement.

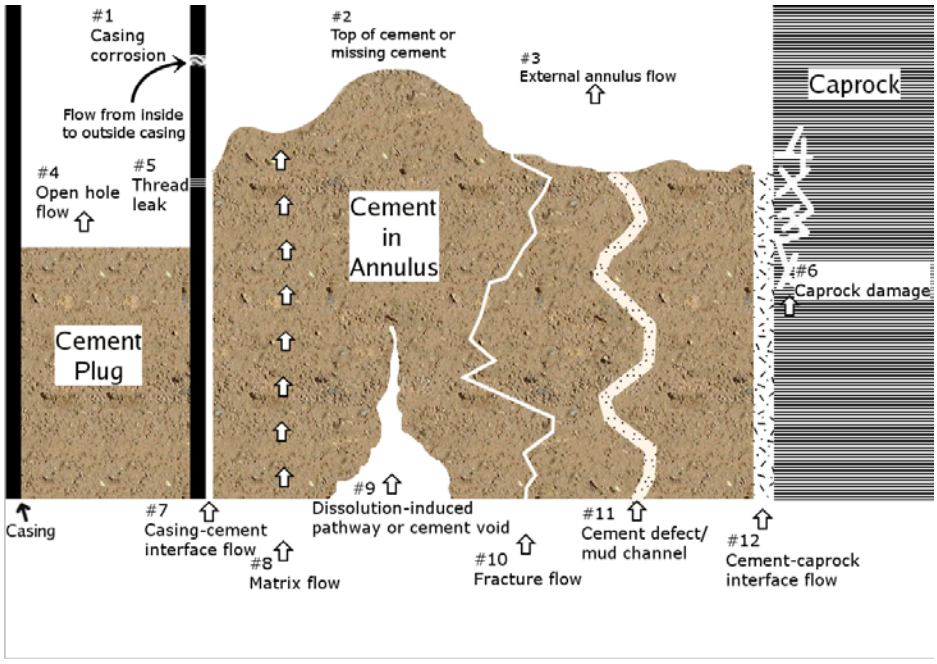


Figure 2: Schematic diagram of an abandoned well showing principle leakage pathways (not to scale; e.g., the plug may have a 10-cm diameter while the annulus will be closer to 2 cm). Note that cement plugs can have many of the same problems as cement in the annulus. These pathways may originate during well completion activities or as a result of stresses occurring during the life of the well. Modified from Viswanathan et al. (2008).

2.2.1 Cement Placement Leak Paths

Well drilling perturbs the subsurface environment, which can lead to conditions that increase the difficulty in ensuring well integrity. Ideally, the borehole should be a smooth cylinder; any washout or erosion of the borehole wall could have a detrimental effect on cementing operations. Anisotropic earth stresses can lead to boreholes with an oval cross section (Zoback, 2007). The chemical incompatibility between drilling fluid and the mineralogy of a formation can lead to shale swelling and caving into the borehole. The lithology of the formation may also be conducive to washout (e.g., vuggy carbonates or poorly lithified rock). The resulting heterogeneous borehole wall must be accounted for in calculating the volume of material needed to cement an annulus, flow rates required to displace mud by cement, and the flow velocity needed to remove any mudcake on the borehole wall. Failure to correctly account for these phenomena can lead to leakage pathways of types #11 and #12 (Figure 2).

Even with a completely cylindrical wellbore, proper displacement of drilling fluid and emplacement of cement that meets the required criteria is a challenge. To help achieve uniform flow in the annulus, the casing must be centered in the borehole. Failure to center the casing could lead to large discrepancies in local flow velocity that can affect mud displacement and cement emplacement (Duguid et al., 2014). The removal of any filter cake on the borehole is essential to ensuring a bond between the cement and formation. A drilling fluid that develops too thick a cake may be difficult to completely displace, leaving sufficient mud behind to develop mud channels in the cement (#12 Figure 2). The displacement of drilling fluid by a spacer fluid and ultimately, cement is not a trivial operation. The correct fluid composition and flow velocity must be used to ensure total removal of the drilling fluid and to prevent mixing of the cement with drilling fluid. Finally, the cement must be properly formulated to achieve successful emplacement, strength development, and compatibility with the subsurface conditions. Failure to do so could lead to cement shrinkage, gas channel development, and micro-annulus development. If a well exhibits inadequate zonal isolation, then remediation methods (e.g., a cement squeeze) may be needed to establish well integrity. The success of these techniques is not always assured and leak paths may still remain, although the risks of serious leakage should be greatly reduced.

2.2.2 Post-Completion Leak Path Development

A well that was successfully completed may still lose well integrity due to operations that impart stresses or chemical exposure to well material during production operations. High internal pressures due to acid stimulation, hydraulic fracturing, or water flooding can lead to tensile failure of the cemented annulus or microannulus debonding between the casing/cement or cement/rock interface. Likewise, injection of a fluid out of thermal equilibrium with the well will also impart stresses on the well materials and can lead to loss of well integrity. Chemical incompatibility between fluids and well material may also lead to cement degradation or casing/tubular corrosion that can induce a leak path. Leakage rates assessed from sustained casing pressure measurements are more easily detected during the injection phase when the subsurface is perturbed by pressure increases. However, leaks may be more difficult to detect after injection stops, as the pressure in storage reservoirs will be decreasing such that sustained casing pressures will also decrease.

2.3 KEY PROCESSES CONTROLLING LEAK PATH EVOLUTION

Quantifying the behavior of well leakage over time requires understanding the coupling of leak-path geometry, geochemical reactions, geomechanics, and advective/diffusive transport processes at conditions and time scales relevant to GCS. NRAP research used both laboratory experiments (static and flow-through experiments) and numerical modeling to understand the complex relationship between well materials and the reactive fluids in GCS systems. Below, the major chemical and mechanical alteration processes important to well integrity are identified.

2.3.1 Fundamental Reaction Mechanisms

2.3.1.1 Cement Alteration

Over the past decade, studies on chemical interactions of CO_2 and brine with well materials have focused on OPCs. These cements are commonly used in well completions and abandonment and are known to be reactive in GCS environments (Carey et al., 2007; Duguid et al., 2005; Huerta et al., 2013a; Kutchko et al., 2007, 2008, 2009; Mason et al., 2013; Scherer et al., 2011; Walsh et al., 2014a, 2014b). Collectively, these studies confirm that reactions between calcium-containing solid phases, especially portlandite, and CO_2-saturated brine are so fast that cement alteration is limited by the diffusion of reactants and products, which results in a series of reaction fronts that divide the cement into distinct zones (Carey et al., 2007; Kutchko et al., 2007, 2008, 2009; Mason et al., 2013; Walsh et al., 2014a; Zhang et al., 2015). The zones consist of unaltered cement, a zone depleted in portlandite, a calcium carbonate zone, and a residual amorphous silicate zone, presented in the order from inner unreacted cement to the cement-brine interface (Figure 3).

Despite the complex nature of cement, only a few chemical reactions are needed to model cement alteration for risk assessment purposes (Table 1). Aqueous complexation reactions include CO_2 dissolution into the brine and the formation of a weak acidic solution rich in dissolved carbonate species. The dissolution of CO_2 lowers the pH and induces dissolution of various calcium containing solid phases, including portlandite, C-S-H, calcium aluminum monosulfate (C-A-S), and calcium aluminum hydroxide (C-A-H). The dissolution rates for portlandite are typically faster than C-S-H by as much as four orders of magnitude (Baur et al., 2004; Galí et al., 2001; Marty et al., 2009). Faster portlandite dissolution rates are responsible for the development of the portlandite depleted zone (Carey and Lichtner, 2011; Mason et al., 2013). The calcium carbonate zone forms as dissolved calcium from the Ca-containing solid phases diffuses away from the unaltered cement and carbonic acid diffuses toward the portlandite depleted zone, leading to the precipitation of calcite or a mixture of calcite and aragonite. Residual amorphous silicate zone, located at the cement interface where the fluids are the most acidic, is a by-product of restructuring of calcium-free C-S-H phases with dissolved sodium and aluminum to form amorphous aluminosilicate (identified as mordenite in the work of Mason et al., 2013). Cement alteration can be modeled by explicitly accounting for the chemical reactions highlighted in Table 1 (Marty et al., 2009; Wolery et al., 1990; Zhang et al., 2013) or as a series of moving chemical fronts controlled by portlandite and calcium carbonate solubility (Kutchko et al., 2007; Walsh et al., 2014a). Cement alteration is initially fast and slows down at later times. The extent of alteration and the relative sizes of the layers depend on the duration, the specific reaction conditions, and the initial cement composition. The initial cement properties, in particular the ratio of the initial portlandite content to porosity, determine the evolution of cement properties. Portlandite-rich cement results in localized “sharp” reactive diffusive fronts

characterized by calcite precipitation, leading to significant porosity reduction, which eventually clogs the pore space and significantly slows further acid penetration (Brunet et al., 2013).

Table 1: Mass balance reactions and thermodynamics and kinetic constants for CO_2-cement alteration (Marty et al., 2009; Wolery et al., 1990; Zhang et al., 2013)

Precipitation and Dissolution Reactions		$logK_{eq}$ 25°C	logk ($mol/m^2/s$) 25°C	A (m^2/g)	α
Solid Phase Name	**Shorthand Name**				
Portlandite	CH	21.05	-6.20	16.50	0.18
$Ca(OH)_2 + 2H^+ \leftrightarrow Ca^{2+} + 2H_2O$					
Calcium-Silicate-Hydrate	C-S-H	19.30	-10.10	41.00	0.33
$Ca_{1.2}SiO_{3.2} \cdot 2.06H_2O + 2.4H^+ \leftrightarrow 1.2Ca^{2+} + SiO_2 + 3.26H_2O$					
Calcium-Aluminum-Monosulfate	C-A-S	73.30	Not available	10.00	Not available
$Ca_4Al_2O_6(SO_4) \cdot 12H_2O + 12H^+ \leftrightarrow 4Ca^{2+} + 2Al^{3+} + SO_4^{2-} + 18H_2O$					
Calcium Carbonate	CC	-8.11	-6.10	1.00	0.08
$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$					
Amorphous Silicon Oxide	Am-Si	-2.54	-10.00	1.00	0.00
$SiO_2 \leftrightarrow SiO_{2(aq)}$					
Mordenite	Mord	Not available	Not available	Not availab le	Not available
$Ca_{0.2895}Na_{0.361}Al_{0.94}Si_{5.06}O_{12} \cdot 3.468H_2O + 3.76H^+ \leftrightarrow 0.2895Ca^{2+} + 0.361Na^+ + 0.94Al^{3+} + 5.06SiO_{2(aq)} + 5.348H_2O$					
Calcium Aluminum Hydroxide	C-A-H	103.67	Not available	10.00	Not available
$Ca_4Al_2(OH)_{14} \cdot 6H_2O + 14H^+ \leftrightarrow 4Ca^{2+} + 2Al^{3+} + 20H_2O$					

2.3.1.2 The role of O_2, H_2S, and SO_2 impurities in the CO_2 Stream

This section outlines the modifications to the cement alteration model needed to account for the effect of O_2, H_2S, and SO_2 impurities in the injected CO_2. The reactions in Table 1 describe cement alteration in the presence of O_2 in the injected CO_2 stream. This builds on the notion that some water must be present to alter the cement, and that O_2 maintains an oxidizing environment. No additional reactions within the cement are expected because iron and sulfur are largely present in their oxidized forms of Fe^{3+} and SO_4^{2-}. However, it has been proposed that the addition of O_2 may increase the solubility and efficiency of cement mineral dissolution in a ligand-type complex behavior (Verba, 2013).

In contrast to O_2, H_2S and SO_2 impurities modify the redox potential and drive a second set of alteration reactions. Kutchko et al. (2011) observed that cement exposed to a mixture of CO_2 and H_2S underwent a sequence of oxidation–reduction and sulfidation reactions in addition to the alteration zones observed when cement is in contact with brines saturated with CO_2 only. When the brine is saturated with both H_2S and CO_2, the resulting carbonation zone contains ettringite (calcium aluminum hydroxide) and unidentified particles rich in iron and sulfur, as well as pyrite in the outer rim of the carbonation zone. The formation of ettringite is attributed to a two-step reaction (Kutchko et al., 2011). In the first step, H_2S is oxidized by Fe^{3+} in cement to form SO_4^{2-}:

$$8Fe(OH)_3 + HS^- \leftrightarrow 8Fe^{2+} + SO_4^{2-} + 5H_2O + 15OH^-$$

In the second step, SO_4^{2-} reacts with $Al(OH)_4^-$ from the dissolution of aluminum-bearing minerals to produce ettringite.

$$6Ca^{2+} + 2Al(OH)_4^- + 4OH^- + 3SO_4^{2-} + 26H_2O \leftrightarrow Ca_6[Al(OH)_6]_2 \cdot (SO_4)_2 \cdot 26H_2O$$

The formation of pyrite is attributed to a direct reaction between H_2S and Fe^{2+} from the reduction of Fe-bearing minerals in cement.

$$Fe^{2+} + HS^- \leftrightarrow FeS + H^+$$
$$FeS + H_2S \leftrightarrow FeS_2 + H_2$$

Kutchko et al. (2011) concludes that the Fe^{3+}-containing phases are the key for cement-H_2S reactions. Additionally, if O_2 were present with H_2S, the cement-H_2S reactions would be more favored as O_2 is a strong oxidant to convert H_2S into SO_4^{2-}:

$$2O_2 + H_2S \leftrightarrow SO_4^{2-} + 2H^+$$

The dominance of the sulfidation reactions may also depend on the amount of H_2S. Studies with abundant H_2S (e.g., 66 mol% in Jacquement et al. (2008)) observed iron reduction in the cement minerals to form sulfides (Jacquemet et al., 2008, 2012; Kutchko et al., 2011). In contrast, studies with much lower concentrations (1 wt% H_2S) observed the formation of minor amounts of Fe^{3+}-containing minerals like brownmillerite ($Ca_2(Al,Fe)_2O_5$, a ferrite phase). Even lower concentrations of H_2S yield cement alteration rates and products similar to those observed in the experiments with 100% CO_2.

The alteration products between well cement and a mixture of CO_2 and SO_2 are similar to those between cement and CO_2 and H_2S. Dissolved CO_2 reacts with portlandite and C-S-H to produce $CaCO_3$ precipitates such as calcite, aragonite, and vaterite, while SO_2 is oxidized by either O_2 or

Fe^{3+}containing phases to form SO_4^{2-}. Dissolved SO_4^{2-} then reacts with Ca^{2+} and various aluminum- and iron-bearing minerals to form ettringite and gypsum. Figure 3 shows how H_2S and SO_2 react with well cement.

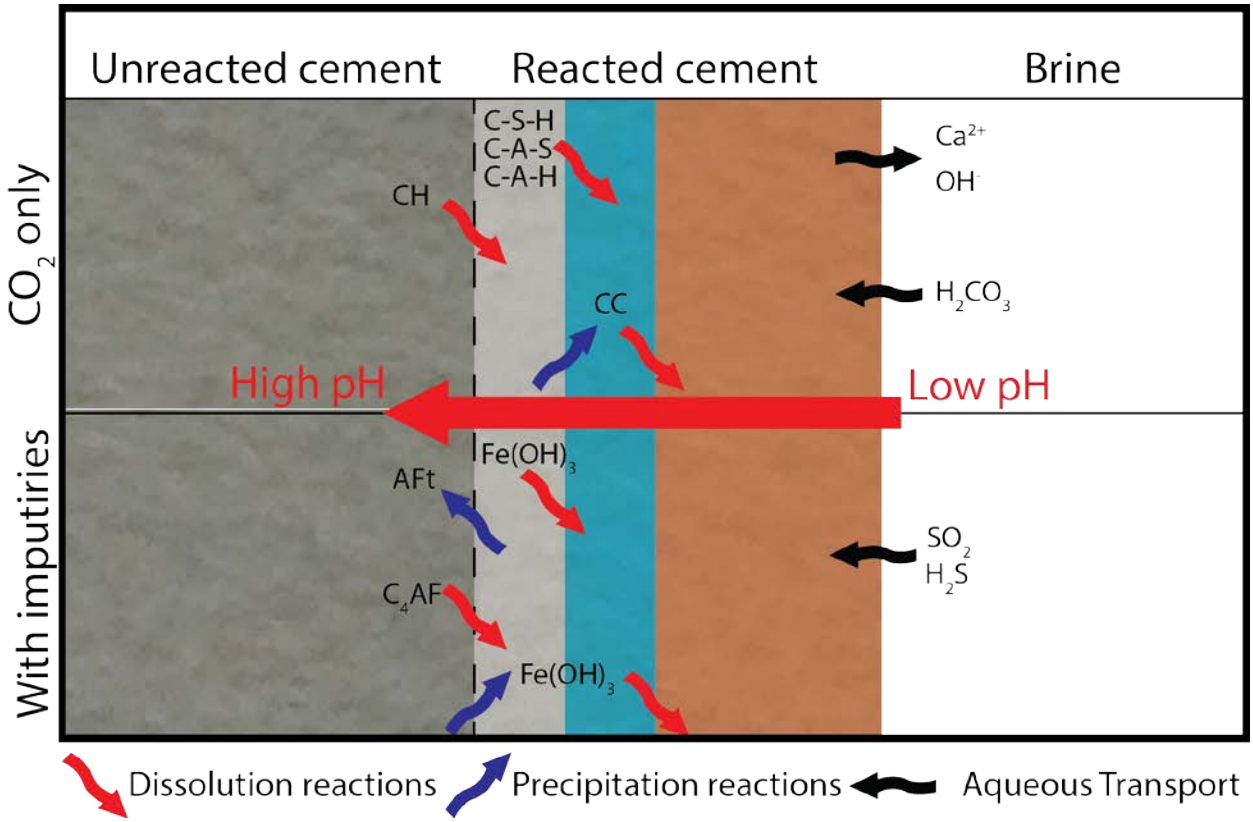


Figure 3: Schematic of interaction between H_2S/SO_2 and well cement. Modified from Kutchko et al. (2007); Kutchko et al. (2011); Mason et al. (2013); and Zhang et al. (2013).

2.3.1.3 The Role of Pozzolan Additives

Additives are commonly combined with the OPC to reduce slurry density, improve acid resistance, and reduce costs in oil and gas operations (Lyons, 1996; Neville, 2004; Sideris et al., 2006; Türkel et al., 2007). Pozzolans (typically fly ash) are one of the most common additives added in oil and gas well cement formulations and can comprise up to 75% of the cement volume (API, 2011, 1997; Kutchko et al., 2009; Lyons, 1996; Massazza, 1993; Nelson and Guillot, 2006; Neville, 2004; Sideris et al., 2006; Türkel et al., 2007). The chemical reactions for a pozzolan-amended cement are identical to those outlined in Table 1, because mixing pozzolan (amorphous aluminosilicate, crystalline and amorphous SiO_2, small amounts of lime (CaO), and hematite (Fe_2O_3)) (Papadakis, 1999; Shehata et al., 1999) with neat cement converts the portlandite and gypsum in the neat cement into C-S-H, C-A-S, and C-A-H during the hydration process (Papadakis, 1999).

Pozzolan-amended cement exhibits faster alteration than neat cement under typical CO_2 sequestration conditions with very high dissolved CO_2 concentrations. Carbonation depth was measured to be 100 times higher than neat cement after 31 days of exposure to CO_2-saturated

brine for cement with 35 vol% pozzolan and 65 vol% Class H cement (Kutchko et al., 2009, 2008). The cause of fast CO_2 penetration in pozzolan-amended cement is not clear. Research suggests that a possible explanation could be the addition of pozzolan slows the rate of hydration, leading to higher porosity in pozzolan-amended cement than the neat cement. Combined higher porosity and lower portlandite content for calcite precipitation leads to faster diffusion and a more permeability carbonate zone and, therefore a higher penetration/alteration depth for the pozzolan cement compared to neat cement (Figure 6 in Brunet et al. (2013)). Despite the extent of alteration, the altered pozzalon cements yielded good restrictive properties with permeability values that were well below the American Petroleum Institute (API) recommended maximum value of 200 μD (Kutchko et al., 2009).

2.3.1.4 Steel Corrosion

Steel casing (i.e., pipe) is the third component of the steel-cement-caprock system that determines well integrity. The steel casing must have adequate strength to contain the fluids within the well and to resist external stresses. Although casing rupture does occur, the most common problems are associated with leaking pipe connections and corrosion of steel. Well tubing comes in set lengths that must be coupled together through one of several types of connections. Leaks through these joints have been identified as the most common form of barrier failure, responsible for up to 90% of all tubular leaks according to Schwind et al. (2001).

Corrosion affects all aspects of the oil and gas industry and has a significant financial impact (Brondel et al., 1994). The steel used in most wells is low-cost, low-carbon steel that is not corrosion resistant. The near surface environment is particularly problematic, as the greater availability of oxygen can cause surface and conductor casing to rapidly deteriorate without adequate cement protection (Figure 2 #1) (Talabani et al., 2000). For steel casing, factors that can exacerbate corrosion problems include sand (introduced during hydraulic fracturing or during production of poorly lithified reservoirs, resulting in metal erosion), the presence of oxygen, hydrogen evolution (which can cause embrittlement), chloride and sulfate-rich formation waters, acids used to stimulate the formation, in situ H_2S and CO_2, and the higher temperature and pressure that occur at drilling depths (Rahman and Chilingarian, 1995; Talabani et al., 2000).

Choi et al. (2013) reviewed casing corrosion issues specifically relevant to CO_2 sequestration. CO_2 transforms the oxygen-free subsurface to a highly corrosive environment primarily because of carbonic acid (Han et al., 2011a,b; Nešić, 2007). The key half-cell reaction is:

$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^-$$

which is balanced by the dissolution of iron:

$$Fe_{(s)} + 2e^- \rightarrow Fe^{2+}$$

Corrosion can be rapid and destructive because it allows fluids to communicate between the inside and outside of the well. Uniform corrosion rates of bare metal can reach 10's of mm/year for unpassivated low-carbon steel in the presence of high-pressure CO_2 (Han et al., 2011a). Fortunately, cement carbonation appears to passivate and protect the steel surface, despite its

more acidic pH. Han et al. (2011b) reported reductions in corrosion rates by a factor of 20 due to formation of iron carbonate scale on the steel casing. These reduced corrosion rates still have the potential to impact well integrity, because CO_2 storage wells need to operate for decades and to protect against leaks for centuries. Researchers lack a good basis for predicting the impact of corrosion rates on well integrity in the presence of passivating iron carbonate scales.

In addition to these general reactions that are expected to cause relatively uniform corrosion over large areas, there will also be localized CO_2-induced corrosion rates (Kermani and Morshed, 2003). These effects can be more rapid and penetrating than uniform corrosion. Factors that exacerbate localized corrosion include stress-induced defects, incomplete passivation layers, mechanical damage to passivated surfaces, and dissolved chemical species such as acetic acid or H_2S (Kermani and Morshed, 2003).

Corrosion of low-carbon steel can be prevented through the use of corrosion inhibitors or cathodic protection among other measures. However, one of the most important methods for protecting against corrosion of external casing is an adequate coverage with cement, particularly on the surface casing and in the subsurface across formations with problematic fluids (Choi et al., 2013; Rahman and Chilingarian, 1995; Talabani et al., 2000) illustrating the importance of understanding the impact of subsurface fluids on cement alteration in CO_2 storage environments.

2.3.2 Fundamental Geomechanics

The stresses acting on a well are another important factor affecting the risk of a leakage event. These stresses will change over time, caused by mechanical stress as a consequence of injection/production or leakage, changes in subsurface temperature (potentially a byproduct of injection or leakage), or merely due to natural variations in subsurface conditions. These changes can directly affect the transmissivity of any of the previously discussed well leakage pathways through several mechanisms. Variations in the normal stress on a fracture have a non-linear effect on fracture transmissivity related to the surface roughness (Bandis et al., 1983; Barton et al., 1985), while shear motion will induce preferential flow pathways that depend on the direction and extent of the relative displacement between the two fracture surfaces (Detwiler and Morris, 2014). Likewise, multicomponent and multiphase flow along fractures are also strongly influenced by changes in stress on the well, due to the coupling between the effective stress and the aperture distribution (Walsh and Carroll, 2013), and this effect varies with the relative permeabilities of the component fluids. These complexities are enhanced by the chemical reactions that occur between cement and carbonated brine. The chemical alteration within the reaction zones changes the mechanical properties of the interface, potentially resulting in collapse of the fracture aperture (Walsh et al., 2014a,b). Due to the interplay between these different processes, the coupled effects of mechanics and flow should be incorporated into an assessment of well leakage.

Subsurface stress is concentrated around a borehole: as the well is drilled, forces previously born by the excavated rock are redistributed to the intact material surrounding the hole. While, given sufficient simplifying assumptions, analytical expressions can be found to describe the resulting stress distribution (e.g., Bradley (1979) and Peska and Zobak (1995)), in reality, the stress state around the well is more complex: a product of a dynamic layered environment consisting of the well casing, the surrounding well cement, drilling fluid filter cake (if present) and a zone of damaged rock from the drilling process, within the larger (largely undamaged) far field formation (e.g., Gray (2009) and Nygaard et al. (2014)).

After the hole is drilled and the well casing inserted, well cement is introduced in the annulus between the casing and the formation. As the cement cures, it undergoes a two stage process of hardening (conversion of the liquid cement into a solid body) and shrinkage (a reduction in volume upon curing of the solid cement) (Gray et al., 2009; Randhol, 2008; Ravi et al., 2002). Hardening has little effect on the stress state of the cement (as the cement is generally considered to remain under hydrostatic stress throughout), though it will affect cement rheology. Shrinkage, however, results in a change in the cement's stress state, which can potentially lead to plastic deformation of not only the cement, but also the casing and formation, or debonding at either the casing or formation interfaces (Ravi et al., 2002). In addition, because the casing may not be located in the center of the well, shrinkage can result in an uneven distribution of stress in the cemented annulus (Gray et al., 2009).

Pouring and setting of cement occurs in a far-from-pristine environment. In particular, the drilling fluid used to create the borehole, along with any subsurface liquids and gases, can produce fluid channels that decrease the bonding strength between the cement and the casing and the formation and may be the source of preferential flow pathways (Agbasimalo, 2012; Agbasimalo and Radonjic, 2012; Randhol, 2008). Mixing between these liquids and the well cement negatively impacts the cement's mechanical properties (El-Sayed, 1995).

Over time, a well is subjected to variations in the fluid pressure both internal to the well (during injection and production) and in the formation (again due to injection or production from either the well itself or an adjacent source, or natural fluctuations, e.g., tidal variations). In addition, the thermal changes that accompany fluid flow during injection will also change the stress state of the well. This is particularly true when supercritical CO_2 is injected into the subsurface (Nygaard et al., 2014), most notably if injection follows a cyclic pattern causing fluctuations in the thermal field and associated stresses (De Andrade et al., 2014). Cyclic stresses may encourage growth of fractures within the well cement or result in debonding between the cement and formation (De Andrade et al., 2014; Heathman and Beck, 2006; Shen and Pye, 1989). Fluctuations in stress also play a role in determining the active flow pathways due to the coupling between applied stress and fracture permeability.

2.3.3 Interplay Between Chemical, Mechanical, and Transport Processes on Well Integrity

Field observations show that in properly completed wells there is a tight physical connection between the cement and caprock (e.g., Figure 4, Crow et al., 2010). Nonetheless fluid migration, including CO_2, can occur despite visible contact and conformation at the cement/caprock interface. Crow et al. (2010) observed carbonation of cement more than 200 ft (60 m) above a natural CO_2 reservoir adjacent to shale. Carey et al. (2007) found evidence of CO_2 migration 10 ft (3 m) above a CO_2-enhanced oil recovery reservoir. The authors were able to prove that the CO_2 migrated from a zone of shale fragments between the cement and caprock. In addition to the observation of carbonated cement (Figure 2, Carey et al., 2007), unusual silica-carbonate bands were seen within the shale-fragment zone indicating mobilization and deposition of silica (Figure 6, Carey et al., 2007). The authors did not observe any evidence for CO_2 migration to a sampled location 1,000 ft (300 m) above the reservoir.

A variety of laboratory experiments, as well as numerical simulations, have been performed to characterize how flow, geochemical reactions, and mechanical alteration change permeability of fractures within the cement and at the cement/caprock and cement/reservoir rock interfaces

(Abdoulghafour et al., 2013; Cao et al., 2013; Carey et al., 2007, Crow et al., 2010; Han et al., 2011a,b; Huerta et al., 2015, 2013b; Jung and Um 2013; Jung et al., 2013; Jung et al., 2014; Luquot et al., 2013; Mason et al., 2013; Um et al., 2014; Wenning et al., 2013). Collectively, these studies have attributed the reduction of fracture permeability to swelling of the amorphous silica layer, precipitation of carbonate minerals, and concurrent chemical alteration and deformation of the cement asperities that allow fluid flow. Instances of sustained permeability have been attributed to sufficient fracture aperture and fluid flow to minimize chemical and mechanical alteration or flow through more porous reservoir rock. This section highlights the importance of these processes by weaving the results of select studies, each of which considered different of aspects permeability change.

2.3.3.1 Chemistry and Flow

This section discusses the role that fluid residence time and aperture width have for wellbore cement pathways to seal or open as a consequence of chemical reaction. Burnet et al. (2015) developed a reactive transport model calibrated against experiments (Huerta et al., 2015) that calculates change in fracture permeability as a consequence of diffusion and dispersion when CO_2-saturated water reacts with cement (Table 1). The authors conducted 225 simulations which varied aperture width from 6 to 90 μm, initial flow rates from 0.0015 to 0.130 ml/min, and fracture length from 109.6 to 328.7 mm. Each fracture was exposed to CO_2-enriched water for more than 100 days. The results suggest that the long-term permeability of the fracture depends on both the initial fluid residence time and aperture width (Figure 4). The fracture's initial residence time is defined as the ratio of the initial fracture volume by the initial flow rate. There is a clear division between the self-sealing (black dots) and fracture opening cases (grey dots). The division line represents the "critical" fracture residence time, or the tipping point for a given hydraulic aperture: $\tau_c = 9.8 \times 10^{-4} \times b^2 + 0.254 \times b$, where the fracture as a tendency to fill with calcite for residence times above the threshold and remain open when the residence times are below the threshold. A narrow transition zone is observed around the threshold, where both self-sealing or fracture opening behavior occurs and the permeability changes are sensitive to specific conditions.

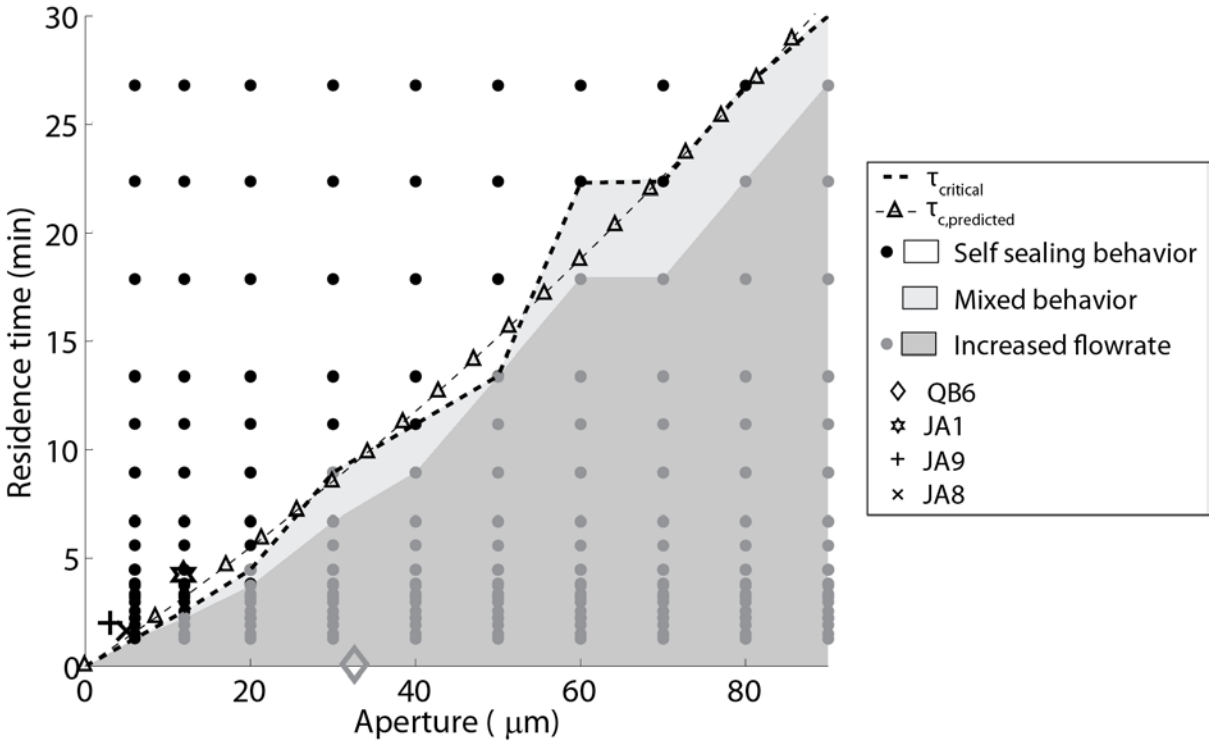


Figure 4: Predicted self-sealing or fracture opening behavior for 225 simulations of carbonic acid injected into fractured cement (Class H) with different initial aperture size and initial fracture residence time. Black dots indicate self-sealing behavior and grey dots indicate fracture opening behavior after exposure to CO_2-saturated brine for 100 days. The thick dashed line indicates the critical fracture residence time above which self-sealing occurs and below fracture opening occurs. The light grey indicates a transition zone with observation of both fracture opening and closing behavior. The thin line with triangles represents the predicted critical fracture residence time. The diamond, star, plus, and x represent the initial aperture and residence time of the experiments from Huerta et al. (2015) are also indicated (Figure 7, Brunet et al., 2016).

The simulated relationship for the critical aperture is consistent with experimental observations, which show that carbonate mineral precipitation causes fracture permeability to decrease at longer residence times. Calcite filled the fractures in cement experiments with residence times greater than the critical τ line, reduced permeability, and sealed the fractures (Figure 5). Whereas, no carbonate minerals formed and no reduction in permeability was observed for the experiment with residence times below the critical threshold (Huerta et al., 2015). Similarly, Luquot et al. (2013) observed and concluded that longer fractures (longer residence time) and smaller apertures tend to self-seal while fractures open in flow regimes with shorter path lengths and/or larger apertures.

Although the notion of critical threshold was based on data from fractured cement, it can also be used to explain the CO_2 interactions at cement/rock interfaces. For example, at a brine flow rate of 0.25 ml/min and a CO_2 flow rate of 0.08 ml/min, Newell and Carey (2013) observed self-sealing behavior in a composite cement/siltstone core. The interface suffered leaching and erosion and a carbonation front extended 5 mm into the cement. During co-injection of

supercritical CO_2, the effective brine permeability decreased from ~200 to 90 mD due to the transition to two-phase flow and then further declined to 35 mD. The permeability drop is not attributed to carbonation of cement but rather to the migration and reprecipitation of alteration products derived from cement within the defect, suggesting the potential for self-limiting flow along well defects despite flow of aggressive supercritical CO_2-brine mixtures. At much higher flow rates of 2 ml/min, Cao et al. (2013) observed a permeability increase of eight (8) times within eight (8) days during a flow experiment with a composite cement/sandstone core with a large defect void. Both the high flow rates and large void potentially contribute to the observed permeability increase. Those apertures located near the core inlet experienced more severe cement degradation, accompanied by a decrease in specific surface area, constituting evidence of a smoothing effect. The notion of a critical aperture threshold is useful metric to better define wellbore risk over time, however it does not consider role of portlandite content in the cement or mechanical deformation of the altered cement.

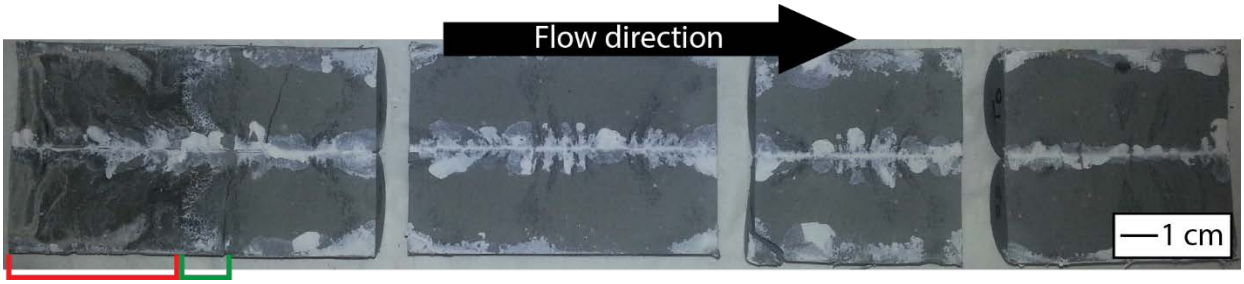


Figure 5: Image of the fracture surfaces post experiment. Flow is from left to right. Within the red area the fracture surface shows reaction of cement by the carbonic acid. In the green area is calcium carbonate precipitation. This sample showed a decrease in fluid flow over time, and sealing via precipitation in the fracture is inferred.

2.3.3.2 Chemistry, Mechanics, and Flow

Chemical alteration has the potential to change the local stress and aperture fields within the cement. Precipitation of calcium carbonate in fractures of cement/basalt samples exposed to CO_2-saturated groundwater and wet supercritical-CO_2 (Jung and Um 2013; Jung et al. 2013) caused some fractures to open as a result of crystallization-induced pressure, as well as isolating other cement fractures. Combined fracture opening and isolation consequently reduced the permeability by an order of magnitude (e.g. from 436 Darcy to 54 Darcy) (Jung et al., 2014; Um et al., 2014).

The mechanical factors affecting flow along cement interfaces are further complicated by the structural changes induced by reactions with CO_2-saturated brine. Reactions between carbonic acid and cement are often accompanied by an increase in porosity (Kutchko et al., 2007; Rimmelé et al., 2008). While this increased porosity would normally be indicative of enhanced permeability, core-flow experiments examining reaction along interfaces often report a decrease in overall sample permeability. At times, decreasing permeability can be induced by changes in the mechanical properties of the altered zones, by weakening asperities that maintain contact between cement and rock in the fracture (Walsh et al., 2013, 2014ab). Nano-indentation measurements of the reaction layers reveal that both the amorphous and depleted regions have lower elastic moduli and hardness than the unreacted cement (Kutchko et al., 2009; Walsh et al., 2014a). These findings are also consistent with the effects caused by calcium leaching from

cements exposed to uncarbonated brines (Constantinides and Ulm, 2004; Ulm et al., 2003). These results illustrate several ways that well integrity and risk of CO_2 leakage are controlled by coupled geomechanical and geochemical alterations of well materials.

The extent to which reaction-induced changes in structural properties affect transmissivity depends upon the interface geometry consistent with the notion of a critical aperture threshold that dictates change in permeability (Walsh et al., 2014b). To illustrate this, Figure 6 compares results from core-flow reaction experiments performed under confining stress representative of subsurface conditions. During the experiment, carbonated brine was introduced into a core consisting of half-cement and half-caprock samples. The interface surfaces were imprinted with two distinct geometries: a single flow channel and a grid of circular apertures. The hydraulic aperture increased over time in the channel sample, whereas a consistent decrease in aperture was observed for the gridded sample. The difference in behavior is explained by the manner in which the reaction fronts affect the contact between the sample half-cores. In the gridded sample, the reaction fronts significantly removed portlandite from the asperities maintaining the fracture, causing the asperities to deform. This deformation results in an overall decrease in the hydraulic aperture despite an increase in the cement porosity. Conversely, in the channel sample, although the reaction fronts decrease the contact area, enough unreacted cement is left at the contact to support the stress on the fracture. In this case, the permeability is increased slightly due to the increased porosity.

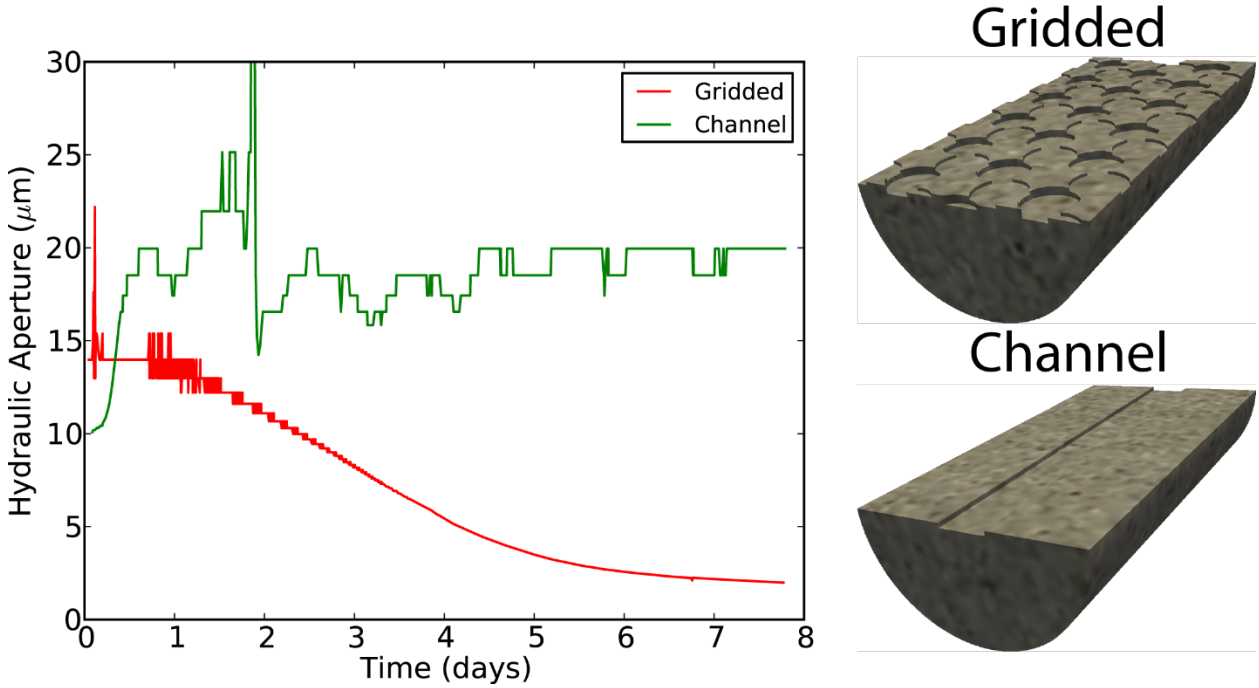


Figure 6: Hydraulic aperture as a function of time in samples of mated cement/caprock half cores with distinct flow-path geometries. Modified from Walsh et al. (2014b).

Walsh et al. (2014b) developed a coupled chemical – mechanical - transport model that ties the extent of deformation of the cement asperities to chemical alteration of the cements. Although empirical in nature, the model could be used to refine the relationship between residence time, chemical alteration, mechanical deformation, and the ability of damage pathways in the cement

to seal or open. Briefly, the model captures the response of the fracture with a set of parallel spring/frictional slider systems representing the unreacted cement and each alteration layer. Relative contributions of each layer to the effective stress and strain changes over time as the relative contact areas of the reaction zones, estimated by the depth of the alteration zones, change. The depth of the alteration zones are modeled using an idealized representation of the cement chemistry in which portlandite, calcite, and analcime equilibrium conditions are enforced as a series of discrete reaction fronts. The equilibrium conditions are coupled by diffusive transport between the fronts, which also determines the rate of front propagation.

Swelling of the amorphous silicate layer may also contribute to the reduction in fracture permeability (Abdoulghafour et al., 2013). Under these conditions, calcium carbonate precipitation does not appear to be sufficient to counteract the overall increase in porosity caused by cement dissolution. Nevertheless, despite the observed increase in porosity, the total permeability of the core decreased by two orders of magnitude over the course of the 8-day experiment.

2.3.3.3 Casing Corrosion and Flow

There has been relatively little work on the geochemical and hydrologic behavior of the casing/cement interface. The leakage pathway corresponds to #2 in Figure 2, in which flow of CO_2 and brine occurs between steel casing and cement. In the absence of a defect at this interface, the cement protects steel from corrosion due to high-pH pore fluids that create a protective iron-oxide coating. The cement/casing interface is discussed separately from the evolution of the permeability along fractures within the cement and along cement/caprock interface, because the consequences of chemical reactivity of the steal casing allow for the development of flow paths that are distinct from the aperture controlled processes discussed above.

In wells with casing made of corrosion-resistant alloy, the chief concern for this interface would be the possible dissolution of cement. However, no studies were found that have directly examined this system. Carey et al. (2010) examined the more common situation (particularly in non-CO_2-specific wells) in which there was a microannulus between low-carbon steel and cement. The author found that steel was far more reactive than cement during flow of a mixture of CO_2-brine at sequestration conditions (Figure 5). The steel showed evidence of extensive corrosion reactions that were limited to some extent by deposition of an iron carbonate. Cement, on the other hand, evidence showed only diffusion of CO_2 and carbonation of cement. The cement did not erode or noticeably dissolve. Although this study indicates that the more vulnerable component of the interface system is steel, permeability gradually increased with time, which was attributed to the accumulation of iron carbonate deposits within the interface. The long-term fate of steel under such conditions is unknown. It is possible that the iron carbonate scale may provide lasting protection; it is also possible that corrosion may eventually penetrate through the steel wall, allowing communication between the interface and the well interior.

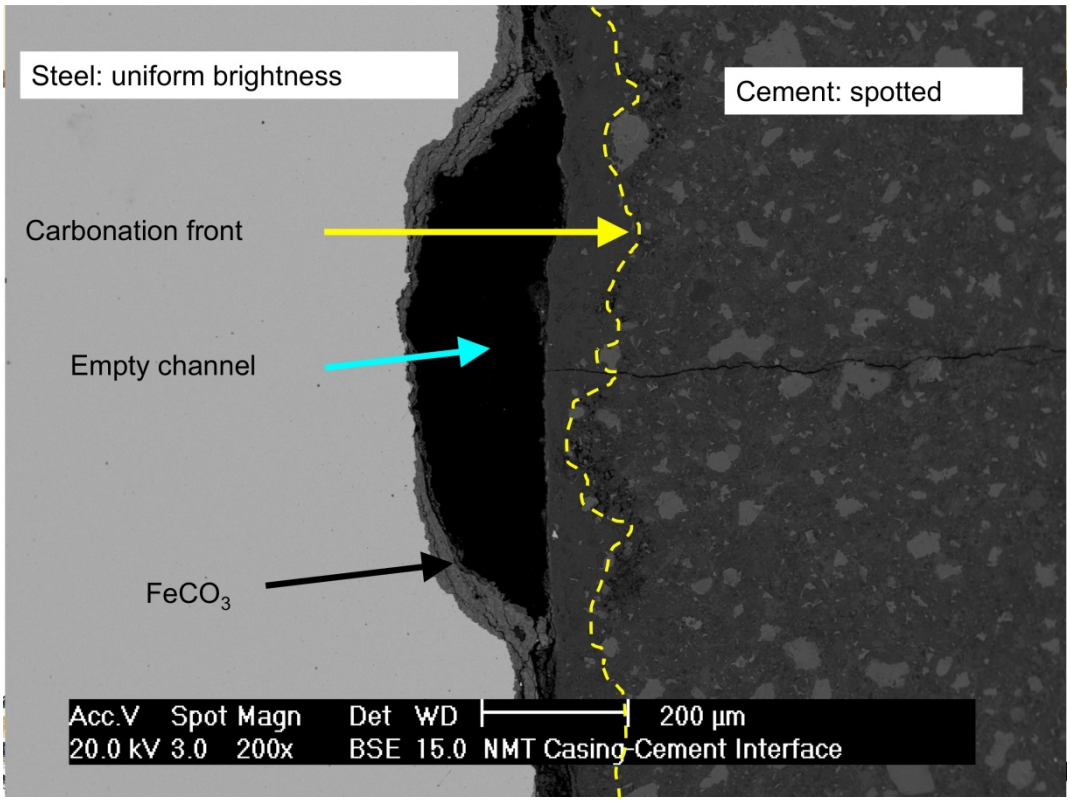


Figure 7: Back-scattered electron micrograph of the interface between steel (solid white material left) and Portland cement (spotted material right). The experiment involved flow of a mixture of supercritical CO_2-brine through notches cut into the steel. The steel corroded forming iron carbonate deposits while the cement carbonated without a significant loss of material. Modified from Carey et al. (2010).

An important research question is whether carbonated cement can protect steel from corrosion. In this scenario, CO_2-saturated brine migrates along the cement/caprock interface (#12) or through fractures in the cement (#8) and carbonates the cement that is in contact with the steel (Figure 2). In a field sample, Carey et al. (2007) found evidence of CO_2 leakage along the casing/cement interface in the form of a carbonate rind attached to the cement surface adjacent to casing. The casing was not damaged, because the well was under cathodic protection. The origin of the CO_2 creating this deposit is unknown, but may have been derived by leakage through joints in the casing. A limited number of experiments show that casing corrosion rates are less than they would in the absence of carbonated cement (Han et al., 2011a,b).

3. REDUCED ORDER MODELS

The previous sections discussed complex phenomena that individually and collectively affect wellbore integrity. Modeling the coupled processes controlling CO_2 and brine leakage in their full complexity would be computationally expensive and slow, requiring days or weeks to evaluate a single scenario. Modeling the full system would require accounting for multi-phase (supercritical, liquid, and gas phase CO_2) flow, multi-component (CO_2, brine, cement, rock, and steel) reactive transport (dissolution and precipitation), spatially and temporally heterogeneous leak path permeability, and geomechanical stresses. Full physics simulations must account for phenomena, such as the Joule-Thomson effect as CO_2 moves upwards along the well, during phase change from supercritical to gas. Three-dimensional (3-D) simulations of well leakage are necessary to capture realistic plume migration (which affects the well's inlet boundary condition) within a storage reservoir, fluid migration into intermediate zones, and leakage to aquifers. Large-scale simulations that include the reservoir, wells, intermediate zones, and aquifers often need to be performed to capture coupled effects and feedback between regions (i.e., well leakage effects reservoir CO_2 saturation and pressure).

Because of the large number of possible storage sites and the uncertainty and variability associated with the properties of the subsurface and well, large numbers of simulations are required to assess the risk of well leakage at GCS sites. These factors include the effects of heterogeneity and/or uncertainty in material properties, injection scenarios, well location and quantity, and initial and boundary conditions. Individual simulations can be constructed by sampling determined or assumed distributions for these variables and uncertainties. By running forward simulations and analyzing the resulting output distributions, it is possible to conditionally quantify predictive uncertainty. Although convergence of output distributions is problem specific, acceptable levels of uncertainty quantification can require 100s to 1,000s of simulations.

The computational expense of physics-based numerical simulations often precludes their use in rigorous, systems-level risk analysis exercises. Reduced physics models (RPMs) and ROMs, collectively called reduced complexity models (RCMs), can substantially reduce the computational expense of full-physics numerical simulations by using reduced physics (in the form of analytic or semi-analytic solutions) or response surface methodologies to produce computationally efficient models. The RPMs and ROMs are intended to capture the important details of the full physics-based simulations, but this must be confirmed by a careful evaluation process. The extent to which RCMs deviate from the full physics-based simulations must be understood and quantitatively evaluated. However, application of RCMs in combination with Monte-Carlo type stochastic simulation approaches has been shown to be an effective approach to explore the potential impact of well leakage on overall systems-level behavior.

Several highly relevant examples of reduced-physics models are the analytical solution of Nordbotten et al. (2009) for CO_2 leakage in wells, the drift-flux model for multi-phase leakage up an open well (Pan et al., 2011a, 2011b), and the model of Huerta et al. (2014) that accounts for precipitation-induced sealing of a well leaking CO_2-saturated brine. ROMs are also often generated from samples of full physics-based simulations using statistical techniques. In these cases, the model is considered a black box, and simulation inputs and outputs are analyzed statistically to produce computationally efficient mathematical relationships capturing the dependencies between simulation inputs and outputs. Such statistical techniques include response surface methodologies and regression analyses such as multivariate adaptive regression

splines (MARS) developed by Friedman (1991). The predictive capability of ROMs built in this manner can be evaluated by cross-validation, where some of the available data is removed from the build data and used to evaluate the ROM. Repeated cross-validation runs can be used to quantify the expected predictive capability of the ROM as built with all the available data. Available software packages for ROM development include Problem Solving environment for Uncertainty Analysis and Design Exploration (PSUADE) (Tong, 2005) and the Earth package available within the R statistical environment (Millborrow, 2011).

NRAP is producing ROMs for several physics-based models, with those relevant to well leakage discussed below. These ROMs can be implemented into NRAP's Integrated Assessment Model for CO_2 Storage (NRAP-IAM-CS), which was built off a previous version, CO_2-PENS (Viswanathan et al., 2008), which performs systems-level model risk analysis of CO_2 storage sites.

3.1 MULTI-PHASE CO_2 AND BRINE LEAKAGE WITH CONSTANT PERMEABILITY

NRAP developed the well leakage ROMs in three generations, with each successive generation representing an increasing level of complexity. The first-generation well leakage ROM was built using PSUADE's MARS implementation based on inputs and outputs from two-dimensional (2-D) radial steady-state simulations of leaks to the surface or shallow aquifers (Jordan et al., 2015). The numerical simulations were conducted using the Finite Element Heat and Mass transfer (FEHM) code (Zyvoloski, 2007). Jordan et al. (2015) considered well permeability, well depth, reservoir pressure, and CO_2 saturation as input. The resulting CO_2 and brine leakage ROMs were included in a system-level performance assessment using CO_2-PENS to simulate and evaluate five leaky wells at the Kimberlina, California site. Figure 8 presents uncertainty envelopes of CO_2 and brine leakage based on 50 realizations for one of the five wells.

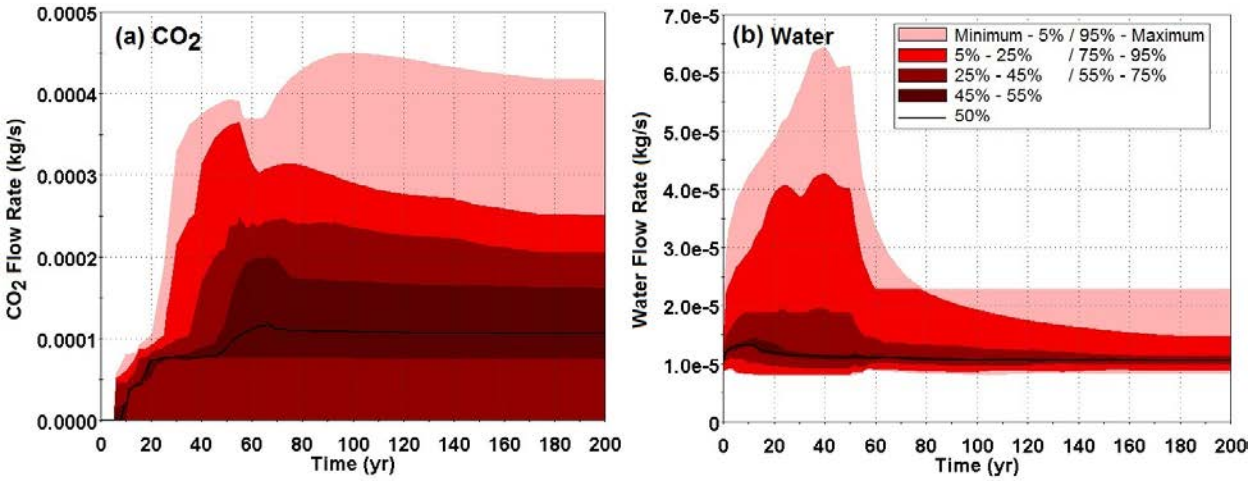


Figure 8: Ensemble statistics across 50 realizations for rates of (a) CO_2 and (b) brine leaking up a well in the CO_2-PENS Kimberlina simulations using the first generation well ROM. Envelopes represent flow rates for various proportions of realizations. Figure taken from Jordan et al. (2015).

In the second-generation of well leakage ROMs, the FEHM simulations were extended to 3-D, transient conditions. To reduce the computational expense of the 3-D simulations, caprock nodes that did not contribute to leakage calculations were removed. The resulting mesh includes the reservoir, intermediate zones, shallow aquifer, well, and caprock nodes surrounding the well to allow for heat transfer calculations. Separate reservoir and reservoir/well simulations were performed. Pressures and CO_2 saturations were collected from the reservoir simulation at the location where the well would be located. CO_2 and brine flow rates (ROM outputs) are collected from the coupled reservoir/well simulations. Figure 9 presents a schematic illustration of this second-generation simulation ROM configuration.

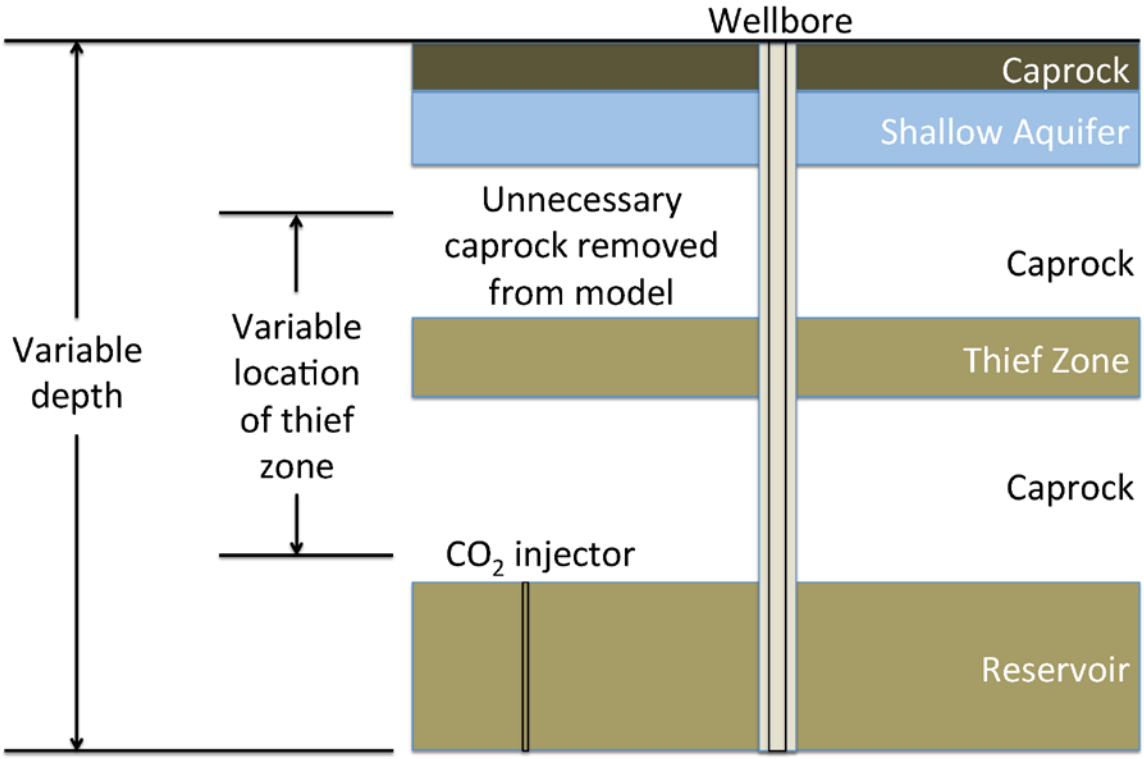


Figure 9: Schematic of vertical 2-D slice of second generation FEHM simulation configuration.

Figure 10 uses a flow diagram to illustrate the process of developing the second-generation cemented well leakage ROM. Initially, uncertainty inputs are sampled by Latin Hypercube Sampling (LHS). Depth (D) and the location of an intermediate (thief) zone within the model depth (f_{thf}) are variable and included as inputs to the ROM. These inputs are required to generate the mesh. A steady state simulation is performed on the mesh to create the initial conditions for both the reservoir and coupled reservoir/well simulations. The CO_2 injection rate (m_{inj}) is sampled by LHS, but is not included as a ROM input. Instead, variation in minj across samples results in variations in pressure (ΔP_{res}) and CO_2 saturation (S_{res}) at the well location in the reservoir simulation, which are included as inputs to the ROM. The coupled reservoir/well simulations produce ROM outputs as CO_2 and brine flow rates. In the example in Figure 10, MARS is used to generate the CO_2 and water/brine leakage ROMs of flow to the thief zone,

shallow aquifer, and atmosphere. Once the ROMs were generated, cross-validation was used to evaluate the predictive capability of the ROMs.

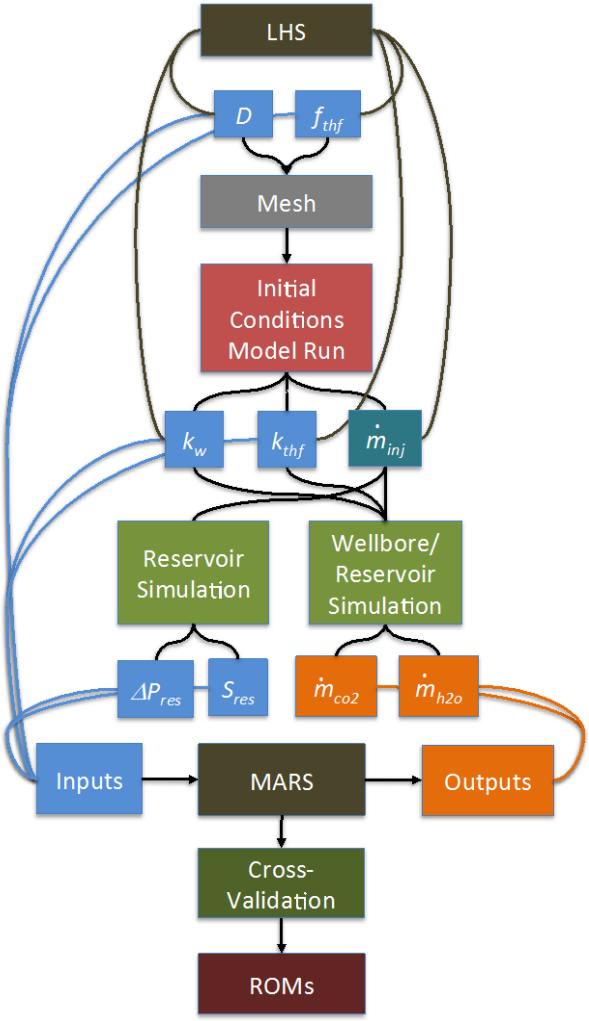


Figure 10: Flow diagram of cemented well leakage ROM development. LHS stands for Latin Hypercube Sampling and MARS stands for multivariate adaptive regression splines.

Full physics-based simulations of cemented well leakage predict non-linear responses for CO_2 and brine flow rates along the well. Capturing the transient effects of plume migration within the reservoir requires coupled reservoir/well simulations. However, inputs to well ROMs in a systems model framework (e.g., NRAP-IAM-CS) include CO_2 pressures and saturations derived from reservoir models that do not include the well, and therefore do not account for changes to storage reservoir pressures and saturations that arise from well leakage effects. This limitation is conservative in the sense that the driving force and mass of CO_2 available to leak into a well will be overestimated. This limitation could be addressed by building well leakage ROMs using CO_2 pressures and saturations in the reservoir at the location of the well from reservoir only simulations as ROM inputs and well flow rates from coupled reservoir/well simulations as ROM

outputs. In this way, the well ROM would account for leakage effects on the CO_2 pressures and saturations.

While a host of uncertainties can affect cemented well leakage at CO_2 storage sites, only a subset of those uncertainties are typically included in the well ROMs in order to focus on the major drivers of large-scale leakage phenomena. These uncertainties include well, intermediate zone, and aquifer permeabilities, location and number of intermediate zones, relative permeabilities, and location of the well with respect to the injectors. ROMs intended to capture leakage characteristics that can apply to multiple sites can include site-specific properties, such as reservoir depth, as additional inputs. ROM outputs include flow rates into and out of intermediate zones and shallow aquifers and flow rates to the atmosphere.

3.2 CHEMICALLY INDUCED CHANGES IN PERMEABILITY

The fluxes extracted from the wellbore ROM described in Section 4.1 are also influenced by chemical reactions, including both precipitation and dissolution. The development of the critical aperture threshold to define sealing of cement fractures and experimental observations (Section 3.3.2) form the basis for a simple ROM that captures the role of chemical reactions on the change in well permeability overtime (Figure 11). The ROM uses Darcy's equation for single phase flow (to match other first-generation ROMs), with a gradient in potential as the driving force. The model uses the concept of flow in series with three zones, each with distinct permeabilities. The sizes of the zones are related to the domain length and to discrete fronts defined as the brine front (first), the precipitation front (second), and the dissolution front (third). The position of the fronts are related to the total fluid volume injected, maximum extent into the core that precipitation is expected to occur, and location where dissolution is expected to dominate over precipitation on the fracture surface. Based on experimental observations, the second and third fronts are inferred to significantly lag behind the fluid front. The permeability of the first zone is the initial leak-path permeability. The permeability in the second zone (between the precipitation front and dissolution front) will evolve as fluid is injected. The permeability of the third zone represents a scenario when all precipitated material has been transported out of the domain, so that sealing via precipitation will not occur. The form of the evolving permeability for the second zone is entirely empirical and was chosen to satisfy the two observed behaviors in the experimental data (i.e. an initial lag time/volume with no change in permeability, followed by asymptotic decay). To match this behavior a logistic function was selected.

The resulting series of equations can be solved with the assumption that the fluid flux changes in time. The resulting analytic equation can then be applied to laboratory experiments or numerical simulations to tune the model's empirical parameters for different conditions. The model can also be used at the field scale to model leakage evolution in time (Figure 11).

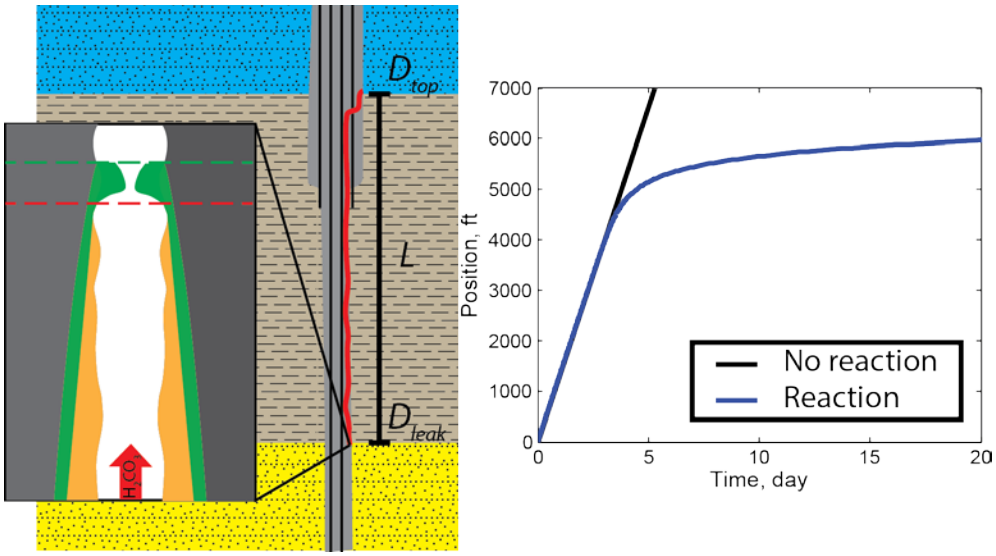


Figure 11: (left) Schematic showing the leakage of CO_2-saturated brine (containing carbonic acid) from the leak source (D_{leak}) up to the leak top (D_{top}). As the acid leaks up the fracture it reacts with cement (grey) to form a carbonated zone (green), which is followed by a zone of amorphous silica rich material (orange). Precipitation of calcite within the fracture (green) can develop in the system and lead to sealing of the leakage pathway. (right) Plot showing the position of the leaked fluid as a function of time in the well. Notice that the estimate for breakthrough of brine into the aquifer for the no reaction case (black line) is significantly faster than when precipitation reduces leak rate (blue line).

3.3 CHEMICALLY AND MECHANICALLY INDUCED CHANGES IN PERMEABILITY

Complete assessment of well integrity in CO_2 storage environments should capture the evolution of permeability because fluids and well components are reactive and will change over time. Capturing the full physics of the hydraulic response of cement interfaces in the presence of carbonated brine would require numerical models that couple the geochemical reactions to the spatial extent of cement alteration; as well as to subsequent changes to the aqueous species concentrations; and finally to the changes in the mechanical and hydraulic properties on the fracture interface. High-resolution models that are applicable to these fine scales quickly become impractical for larger-scale simulations. Explicitly resolving sub-reaction front features while representing borehole-scale flows with full numerical accuracy is impractical with current computational tools and resources. To address this challenge, NRAP has been developing ROMs that upscale the effects of small-scale reactions to the full well system, capturing the most relevant processes for reproducing the system response. This technique was employed by Walsh et al. (2014a,b) to model the growth and deformation of reaction fronts at cement/caprock interfaces, building on similar methods used in studies of calcium leaching from cements exposed to non-carbonated brines (Heukamp, 2003; Mainguy and Ulm, 2001; Ulm et al., 2003). Such meso-scale models can be developed from simulations conducted with explicit well-scale models as described in Lewis et al. (2012) and Walsh et al. (2014b).

4. SUMMARY

4.1 LESSONS LEARNED ABOUT STATE OF KNOWLEDGE OF WELL LEAKAGE

This report reviewed research outcomes that have significantly advanced understanding of the basic science, causes, and impacts associated with well leakage. This improved scientific understanding has been incorporated into a suite of analytical tools including ROMs to provide a foundation for integrated assessment modeling of well leakage risks and the potential impacts on CO_2 sequestration projects.

Through fundamental and applied investigations, NRAP has demonstrated that geochemical and geomechanical interactions between well cements and supercritical CO_2 or CO_2-saturated brine can in some circumstances promote self-sealing and closure of leak paths closure. These studies investigated different interface materials (e.g., cement-to-cement or cement-to-earth) and geometries, the role of oxygen and acids, and the impacts of driving force and residence time. This self-sealing is a function of the portlandite fraction and the porosity of the cement, as well as flow rates and residence time along the leakage path. Portlandite-rich cement increased calcite precipitation in the reaction fronts along leakage pathways, reducing porosity and sealing pores to minimize or prevent further fluid penetration. Similar phenomena were observed at the cement-rock interface under CO_2 storage conditions. These protective processes were observed under both diffusion dominated and convection dominated flow regimes, and with a range of expected pressures and fluid chemistries.

Additional NRAP research investigated corrosion of steel well piping and the interactions with cement, supercritical CO_2 or CO_2-saturated brine. While corrosion rates of un-passivated steel can be on the order of millimeters a year and lead to failure within a few years, operating conditions for CO_2 storage can lead to passivation, with the resulting iron carbonate providing some additional protection against corrosion.

These experimental observations have been implemented in a series of ROMs that simulate a range of possible leakage pathways. These include open boreholes, which represent perhaps a worst case leakage scenario, as well as cemented wells subject to coupled CO_2 and brine leakage migrating from a storage reservoir to groundwater aquifers or the surface. The self-sealing mechanisms previously described have been implemented in a special targeted ROM; these simulations were used to plot relationships between flow residence time and aperture to define regions of self-sealing, increased flow, and mixed behavior. These ROMs have been tested for various well types, configurations (including thief zones), geologies, and locations. The ROMs incorporated a range of difference scenarios of reservoir pressure, CO_2 saturation, and geochemistries in both 2-D and 3-D implementations. While questions remain regarding the best way to couple ROMs that describe different system components, such as the hand-off of CO_2 pressure, or fluid chemistries from reservoir leakage ROMs to well leakage ROMs, initial results indicate that sufficient coupling is possible to generate a reasonable set of simulations. These ROMs are now implemented in a stand-alone wellbore tool (the Well Leakage Analysis Tool), and in NRAP's Integrated Assessment Model for Carbon Storage (NRAP-IAM-CS).

4.2 RESEARCH NEEDS

By exercising the NRAP-IAM-CS to predict site-scale leakage performance, researchers have identified wells as the most likely source of leaks from geologic CO_2 storage systems that include reservoirs, aquifers, wellfields, seismic faults, and various other risk factors. Given the

importance of intact well seals to protecting groundwater and surface resources, it is essential to develop a more complete understanding of well phenomena. While considerable progress has been made advancing scientific understanding of the most critical processes and mechanisms associated with well leakage, a number of important research questions remain. These include questions of materials and transport phenomena, including cements, well casing, and their interfaces; understanding transport processes and permeability associated with multiple phases of CO_2 and brine; and the emergent properties of these processes at multiple scales ranging from micron-sized cement fractures to interfaces along hundreds of meters of well channels.

NRAP observations of experimental and numerical simulations indicate that in many circumstances well cement has the ability to seal cement fracture leaks through coupled dissolution and precipitation reactions. Preliminary evidence demonstrates that these reactions close fractures for low flux and small aperture fractures in a particular range, but under other conditions fractures can open. The potential of self-healing systems (i.e., systems able to repair a leak path with no need for outside intervention) is particularly attractive in geologic storage sites where operational success will be measured in centuries rather than years. But for operators and regulators to design and then rely on self-healing, additional experimental and modeling efforts are needed to better quantify this phenomenon and to explore how it is affected not just by flowrates and fracture geometries, but also by cement composition and other material and operational variables.

For example, there are many new and novel "CO_2-resistant cements" and alternatives whose interactions with fractures and other leakage paths have not been investigated. Given that the two major hydration products in normal cement (calcium-silicate-hydrate and calcium hydroxide) are both susceptible to alteration by CO_2 under typical geologic CO_2 sequestration conditions, novel CO_2-resistant cements that can minimize the carbonation process when exposed to CO_2 have been developed. The approach to develop CO_2-resistant cement has been to minimize the calcium-rich phases that are susceptible to carbonation (i.e., calcium-silicate-hydrate, calcium hydroxide, hydrates of calcium aluminate and calcium sulfate) (Roy and Scheetz, 2006). In CO_2-resistant cement the calcium-rich hydration products are typically replaced by some combination of alkali-rich aluminosilicate, calcium aluminate hydrates, calcium carboaluminate hydrates, and calcium aluminate phosphate (Roy and Scheetz, 2006). Although CO_2-resistant cements appear to be good candidates for new well completions or remediation under CO_2 sequestration conditions, it is not clear whether they will also provide the self-sealing capability observed with conventional well cement.

To answer this question, long term studies are needed to test the durability of CO_2-resistant cements under CO_2 sequestration conditions. There are two concerns for the long-term integrity of CO_2-resistant cements. First, in a CO_2 storage application CO_2-resistant cement will be exposed to brine with very low pH, potentially less than 3.0 if no buffering is considered (Kutchko et al., 2007). This very low pH may cause excessive dissolution of sodium and phosphate bearing minerals and thus impair cement integrity. Second, the self-sealing behavior of the leak path (achieved by carbonation) in normal cement may not occur to the same degree in CO_2-resistant cement, due to the low calcium content in CO_2-resistant cement. To investigate these concerns with CO_2-resistant cement, both static (no flow) exposure experiments and flow-through exposure experiments are needed.

There are also several important unknowns associated with material properties of low-carbon steel in contact with CO_2-saturated brine solutions. There has been limited research on corrosion

mechanisms in this environment, and no experimental assessment of localized corrosion effects. In other specialized drilling applications, conventional carbon steel pipe has been replaced by various alternatives that provide greater corrosion resistance, such as stainless steel or corrosion resistant alloy (CRA) cladding. From both economic and risk assessment perspectives, it would be helpful to know the costs, benefits and impacts on leakage phenomena that might result from use of such corrosion resistant materials in CO_2 injection wells.

Scaling up from individual materials to consider larger scale transport phenomena, there has been little research done on the effects that relative permeability and residual saturation will have on flow and stress. Investigations on the relative permeability of cement systems are particularly scarce (Monlouis-Bonnaire et al., 2004), at least in part because this research is especially difficult due to the reactive nature of both the fluid and the solid components. The additional complexities of multi-phase flow up a leakage path with multiple simultaneous geochemical reactions are quite challenging to both measure and model, but this challenge must be addressed to quantify the impacts and risks of leakage in, through and along wells.

One particularly important modeling challenge addresses coupling and decoupling the well ROMs with other components in an IAM framework. While decoupling of well leakage simulations facilitates inclusion in systems models, this comes at the cost of having to include coupled effects within decoupled models. For example, the reservoir simulations provide pressures and saturations to well ROMs, but there is no feedback on how those pressures and saturations are reduced by leakage, and the reductions in leakage impacts that would likely result. More research is needed to develop decoupled ROMs that can better capture the coupled effects of well leakage.

Finally, there is a need to connect experimental observations and model output to real world situations. There remain significant limitations with respect to availability of data on existing well construction, closure, and failure frequencies and modalities. The physical and chemical characteristics of leakage pathways in a well region are poorly constrained, with at best anecdotal observations about what a real-world leakage pathway looks like. This is true at multiple scales and for phenomena ranging from the geometry of a “typical” fracture network in fractured cement, to the fracture network in a reservoir, caprock or aquifer formation following drilling or injection induced seismicity. Understanding the characteristics of these networks, and how their physical and chemical characteristics affect transport, is essential to build predictive models that properly assess leakage risks.

4.3 PRACTICAL IMPLICATIONS

The goal of any CO_2 storage project is to inject and retain 100% of the injected CO_2 in the target reservoir. Wells at storage sites can threaten this goal, as they represent a direct connection between the CO_2 storage reservoir and risk targets such as USDW and leakage to the atmosphere. These wells penetrate protective geologic formations such as caprock, and were originally constructed to transport large volumes of fluids over long distances. While current well abandonment procedures are designed to seal these conduits, NRAP analysis of detailed well records for an oilfield developed over several decades identified a large number of legacy wells that lack appropriate cement plugs and lining, and such wells are likely to be present at many CO_2 storage sites. Even when cement plugs and seals are properly placed, experimental studies have demonstrated that geomechanical stress, geochemical corrosion, and the coupled reactions between multicomponent and multiphase fluids acting on steel-cement-rock interfaces

can introduce or extend leakage pathways during and after well operations. These fractures need to be addressed to assure adequate seals in wells near a CO_2 storage reservoir.

NRAP has demonstrated that geochemical interactions between well cements and supercritical CO_2 or CO_2-saturated brine can in some circumstances, promote self-sealing of leaking fractures and apertures. Experiments with steel/cement and cement/rock interfaces have indicated that protective mechanisms such as passivation and pore clogging can also help control leakage at these potential failure points. By simulating these and associated processes through a series of ROMs that scale from micron scale pores and interfaces to 100s of meters of well length, operators will be able to evaluate the impact these phenomena have on leakage risks. Of particular interest are the circumstances when self-sealing and other protective mechanisms are highly likely to be effective, when they are likely to fail, and the zone of uncertainty between these two extremes. Understanding the nature and extent of well leakage, whether through open boreholes, fractured plugs or seals, or at the interfaces between rock, cement and steel, will be critical to developing effective and durable strategies for safe operation of CO_2 storage sites.

5. REFERENCES

Abdoulghafour, H.; Luquot, L.; Gouze, P. Characterization of the Mechanisms Controlling the Permeability Changes of Fractured Cements Flowed Through by CO_2-Rich Brine. *Environ. Sci. Technol.* **2013,** *47*, 10332–10338. DOI:10.1021/es401317c

Agbasimalo, N. C. Experimental Study of the Effect of Drilling Fluid Contamination on the Integrity of Cement-Formation Interface (Masters), Louisiana State University, 2012.

Agbasimalo, N.; Radonjic, M. *Experimental Study of Portland Cement/Rock Interface in Relation to Wellbore Stability for Carbon Capture and Storage (CCS)*; American Rock Mechanics Association, ARMA, 2012.

API. ANSI/API 10A: Specification for Cements and Materials for Well Cementing, 2011.

API. Recommended Practice for Testing Well Cements 10B, 1997.

Bandis, S. C.; Lumsden, A. C.; Barton, N. R. Fundamentals of rock joint deformation. *Int J Rock Mech Min. Sci Geomech Abstr.* **1983,** *20*, 249–268.

Barton, N.; Bandis, S.; Bakhtar, K. Strength, deformation and conductivity coupling of rock joints. *Int J Rock Mech Min. Sci Geomech Abstr.* **1985,** *22*, 121–140.

Baur, I.; Keller, P.; Mavrocordatos, D.; Wehrli, B.; Johnson, C. A. Dissolution-precipitation behaviour of ettringite, monosulfate, and calcium silicate hydrate. *Cem. Concr. Res.* **2004,** *34*, 341–348. DOI:10.1016/j.cemconres.2003.08.016

Bourgoyne, A. T., Jr.; Chenevert, M. E.; Millheim, K. K.; Young, F. S., Jr., *Applied Drilling Engineering*. SPE Textbook Series; Society of Petroleum Engineers, 1986.

Bradley, W. B., Failure of Inclined Boreholes. *J. Energy Resour. Technol.* **1979,** *101*, 232–239. DOI:10.1115/1.3446925

Brondel, D.; Edwards, R.; Hayman, A.; Hill, A.; Mehta, S.; Semerad, T. Corrosion in the oil industry. *Oilfield Rev* **1994**.

Brunet, J.-P. L.; Li, L.; Karpyn, Z. T.; Huerta, N. J. Fracture opening or self-sealing: Critical residence time as a unifying parameter for cement–CO_2–brine interactions. *Int. J. Greenh. Gas Control* **2016,** *47*, 25–37.

Brunet, J.-P.L.; Li, L.; Karpyn, Z. T.; Kutchko, B. G.; Strazisar, B.; Bromhal, G. Dynamic Evolution of Cement Composition and Transport Properties under Conditions Relevant to Geological Carbon Sequestration. *Energy Fuels* **2013,** *27*, 4208–4220. DOI:10.1021/ef302023v

Cao, P.; Karpyn, Z. T.; Li, L. Dynamic alterations in wellbore cement integrity due to geochemical reactions in CO_2-rich environments. *Water Resour. Res.* **2013,** *49*, 4465–4475. DOI:10.1002/wrcr.20340

Carey, J. W. Geochemistry of wellbore integrity in CO_2 sequestration: Portland cement-steel-brine-CO_2 interactions. In *Geochemistry of Geologic CO_2 Sequestration, Reviews in Mineralogy and Geochemistry*; DePaolo, D. J., Cole, D., Navrotsky, A., Bourg, I., Eds.; Mineralogical Society of America: Washington, DC, 2013; pp 505–539.

Carey, J. W.; Lichtner, P. C. Computational studies of two-phase cement-CO_2-brine interaction in wellbore environment. *SPE J.* **2011,** *16*, 940–948.

Carey, J. W.; Wigand, M.; Chipera, S. J.; WoldeGabriel, G.; Pawar, R.; Lichtner, P. C.; Wehner, S. C.; Raines, M. A.; Guthrie Jr., G. D. Analysis and performance of oil well cement with 30 years of CO_2 exposure from the SACROC Unit, West Texas, USA. *Int. J. Greenh. Gas Control* **2007,** *1*, 75–85. DOI:10.1016/S1750-5836(06)00004-1

Carey, W.; Svec, R.; Grigg, R.; Zhang, J.; Crow, W. Experimental investigation of wellbore integrity and CO_2–brine flow along the casing–cement microannulus. *Int. J. Greenh. Gas Control* **2010,** *4*, 272–282. DOI:10.1016/j.ijggc.2009.09.018

Carroll, S. A.; Keating, E.; Mansoor, K.; Dai, Z.; Sun, Y.; Trainor-Guitton, W.; Brown, C.; Bacon, D. Key factors for determining groundwater impacts due to leakage from geologic carbon sequestration reservoirs. *Int. J. Greenh. Gas Control* **2014,** *29*, 153–168. DOI:10.1016/j.ijggc.2014.07.007

Celia, M. A.; Nordbotten, J. M.; Court, B.; Dobossy, M.; Bachu, S. Field-scale application of a semi-analytical model for estimation of CO_2 and brine leakage along old wells. *Int. J. Greenh. Gas Control* **2011,** *5*, 257–269. DOI:10.1016/j.ijggc.2010.10.005

Choi, Y.-S.; Young, D.; Nešić, S.; Gray, L. G. S. Wellbore integrity and corrosion of carbon steel in CO_2 geologic storage environments: A literature review. The IEAGHG Weyburn-Midale CO_2 Monitoring and Storage Project 16, Supplement 1. *Int. J. Greenh. Gas Control* **2013,** S70–S77. DOI:10.1016/j.ijggc.2012.12.028

Constantinides, G.; Ulm, F.-J. The effect of two types of C-S-H on the elasticity of cement-based materials: Results from nanoindentation and micromechanical modeling. *Cem. Concr. Res.* **2004,** *34*, 67–80. DOI:10.1016/S0008-8846(03)00230-8

Crow, W.; Carey, J. W.; Gasda, S.; Brian Williams, D.; Celia, M. Wellbore integrity analysis of a natural CO2 producer. *Int. J. Greenh. Gas Control* **2010,** *4*, 186–197. DOI:10.1016/j.ijggc.2009.10.010

De Andrade, J.; Torsaeter, M.; Todorovic, N.; Opedal, N.; Stroisz, A.; Vralstad, T. Influence of Casing Centralization on Cement Sheath Integrity During Thermal Cycling. Presented at the IADC/SPE Drilling Conference and Exhibition, Society of Petroleum Engineers, 2014.

Detwiler, R. L.; Morris, J. P. Transmissivity Anisotropy in Rough-Walled Fractures: The Combined Influence of Shear Offset and Normal Deformation. Presented at the In 48th US Rock Mechanics/Geomechanics Symposium, American Rock Mechanics Association, 2014.

Duguid, A.; Carey, J. W.; Butsch, R. Well Integrity Assessment of a 68 year old Well at a CO_2 Injection Project. 12th International Conference on Greenhouse Gas Control Technologies, GHGT-12. *Energy Procedia* **2014,** *63*, 5691–5706. DOI:10.1016/j.egypro.2014.11.602

Duguid, A.; Radonjic, M.; Scherer, G. Degradation of well cements exposed to carbonated brine. Proc. Fourth Annu. Conf. Carbon Capture Sequestration 12, 2005.

El-Sayed, A. A. H. Effect of Drilling Muds Contamination on Cement Slurry Properties. Presented at the In Fourth Saudi Engineering Conference, 1995; pp 287–295.

Friedman, J. H. Multivariate Adaptive Regression Splines. *Ann. Stat.* **1991,** *19*, 1–67. DOI:10.1214/aos/1176347963

Galí, S.; Ayora, C.; Alfonso, P.; Tauler, E.; Labrador, M. Kinetics of dolomite–portlandite reaction: Application to portland cement concrete. *Cem. Concr. Res.* **2001,** *31*, 933–939. DOI:10.1016/S0008-8846(01)00499-9

Gray, K. E.; Podnos, E.; Becker, E. Finite-Element Studies of Near-Wellbore Region During Cementing Operations: Part I. SPE-106998-PA, 2009. DOI:10.2118/106998-PA

Han, J.; Carey, J. W.; Zhang, J. Effect of debonded interfaces on corrosion of mild steel composites in supercritical CO_2-saturated brines. Presented at the NACE Annual Conference, Dallas, TX, 2011a; p 14.

Han, J.; Zhang, J.; Carey, J. W. Effect of bicarbonate on corrosion of carbon steel in CO_2 saturated brines. *Int. J. Greenh. Gas Control* **2011b,** *5*, 1680–1683. DOI:10.1016/j.ijggc.2011.08.003

Heathman, J.; Beck, F. Finite Element Analysis Couples Casing and Cement Designs for HT/HP Wells in East Texas. Society of Petroleum Engineers, 2006. DOI:10.2118/98869-MS

Heukamp, F. H. Chemomechanics of calcium leaching of cement-based materials at different scales: the role of CH-dissolution and CSH degradation on strength and durability performance of materials and structures. Massachusetts Institute of Technology, 2003.

Huerta, N. J.; Hesse, M. A.; Bryant, S. L.; Strazisar, B. R.; Lopano, C. Reactive transport of CO_2-saturated water in a cement fracture: Application to wellbore leakage during geologic CO_2 storage. *Int. J. Greenh. Gas Control* **2015**. doi:10.1016/j.ijggc.2015.02.006

Huerta, N. J.; Hesse, M. A.; Bryant, S. L.; Strazisar, B. R.; Lopano, C. L. Experimental Evidence for Self-Limiting Reactive Flow through a Fractured Cement Core: Implications for Time-Dependent Wellbore Leakage. *Environ. Sci. Technol.* **2013a,** *47*, 269–275. DOI:10.1021/es3013003

Huerta, N. J.; Hesse, M. A.; Bryant, S. L.; Strazisar, B. R.; Lopano, C. L. Experimental Evidence for Self-Limiting Reactive Flow through a Fractured Cement Core: Implications for Time-Dependent Wellbore Leakage. *Environ. Sci. Technol.* **2013b,** *47*, 269–275. DOI:10.1021/es3013003

Huerta, N. J.; Strazisar, B. R.; Bryant, S. L.; Hesse, M. A. Time-dependent Fluid Migration From a Storage Formation via Leaky Wells. Energy Procedia, 12th International Conference on Greenhouse Gas Control Technologies, GHGT-12 63, 2014; 5724–5736. DOI:10.1016/j.egypro.2014.11.605

Jacquemet, N.; Pironon, J.; Lagneau, V.; Saint-Marc, J. Armouring of well cement in H_2S–CO_2 saturated brine by calcite coating – Experiments and numerical modelling. *Appl. Geochem.* **2012,** *27*, 782–795. doi:10.1016/j.apgeochem.2011.12.004

Jacquemet, N.; Pironon, J.; Saint-Marc, J. Mineralogical Changes of a Well Cement in Various H_2S-CO_2(-Brine) Fluids at High Pressure and Temperature. *Environ. Sci. Technol.* **2008,** *42*, 282–288. DOI:10.1021/es070853s

Jordan, A. B.; Stauffer, P. H.; Harp, D.; Carey, J. W.; Pawar, R. J. A response surface model to predict CO2 and brine leakage along cemented wellbores. *Int. J. Greenh. Gas Control* **2015,** *33*, 27–39. DOI:10.1016/j.ijggc.2014.12.002

Jung, H. B.; Jansik, D.; Um, W. Imaging Wellbore Cement Degradation by Carbon Dioxide under Geologic Sequestration Conditions Using X-ray Computed Microtomography. *Environ. Sci. Technol.* **2013,** *47*, 283–289. DOI:10.1021/es3012707

Jung, H. B.; Kabilan, S.; Carson, J. P.; Kuprat, A. P.; Um, W.; Martin, P.; Dahl, M.; Kafentzis, T.; Varga, T.; Stephens, S.; Arey, B.; Carroll, K. C.; Bonneville, A.; Fernandez, C. A. Wellbore cement fracture evolution at the cement–basalt caprock interface during geologic carbon sequestration. *Appl. Geochem.* **2014,** *47*, 1–16. DOI:10.1016/j.apgeochem.2014.04.010

Jung, H. B.; Um, W. Experimental study of potential wellbore cement carbonation by various phases of carbon dioxide during geologic carbon sequestration. *Appl. Geochem.* **2013,** *35*, 161–172. DOI:10.1016/j.apgeochem.2013.04.007

Kermani, M. B.; Morshed, A. Carbon Dioxide Corrosion in Oil and Gas Production—A Compendium. *Corrosion* **2003,** *59*, 25.

King, G. E.; King, D. E. *Environmental Risk Arising From Well Construction Failure: Differences Between Barrier Failure and Well Failure, and Estimates of Failure Frequency Across Common Well Types, Locations and Well Age*; Society of Petroleum Engineers, SPE, 2013. DOI:10.2118/166142-MS

Kutchko, B. G.; Strazisar, B. R.; Dzombak, D. A.; Lowry, G. V.; Thaulow, N. Degradation of Well Cement by CO_2 under Geologic Sequestration Conditions. Environ. Sci. Technol. **2007,** *41*, 4787–4792. DOI:10.1021/es062828c

Kutchko, B. G.; Strazisar, B. R.; Hawthorne, S. B.; Lopano, C. L.; Miller, D. J.; Hakala, J. A.; Guthrie, G. D. H_2S–CO_2 reaction with hydrated Class H well cement: Acid-gas injection and CO_2 Co-sequestration. *Int. J. Greenh. Gas Control* **2011,** *5*, 880–888. DOI:10.1016/j.ijggc.2011.02.008

Kutchko, B. G.; Strazisar, B. R.; Huerta, N.; Lowry, G. V.; Dzombak, D. A.; Thaulow, N. CO_2 Reaction with Hydrated Class H Well Cement under Geologic Sequestration Conditions: Effects of Flyash Admixtures. *Environ. Sci. Technol.* **2009,** *43*, 3947–3952. DOI:10.1021/es803007e

Kutchko, B. G.; Strazisar, B. R.; Lowry, G. V.; Dzombak, D. A.; Thaulow, N. Rate of CO_2 Attack on Hydrated Class H Well Cement under Geologic Sequestration Conditions. *Environ. Sci. Technol.* **2008,** *42*, 6237–6242. DOI:10.1021/es800049r

Lewis, K.; Zyvoloski, G.; Kelkar, S.; Carey, J. W. Coupled stress and flow along interfaces in the wellbore environment in relation to CO_2 sequestration. Presented at the The 46th US Rock Mechanics Symposium, American Rock Mechanics Association, Chicago, IL, 2012.

Luquot, L.; Abdoulghafour, H.; Gouze, P. Hydro-dynamically controlled alteration of fractured Portland cements flowed by CO_2-rich brine. *Int. J. Greenh. Gas Control* **2013,** *16*, 167–179. DOI:10.1016/j.ijggc.2013.04.002

Lyons, W.C., Ed. *Standard Handbook of Petroleum and Natural Gas Engineering*, Volume 1; Gulf Publishing Company: Houston, TX, 1996.

Mainguy, M.; Ulm, F.-J. Coupled Diffusion-Dissolution Around a Fracture Channel: The Solute Congestion Phenomenon. Transp. *Porous Media* **2001,** *45*, 479–495. DOI:10.1023/A:1012096014084

Majer, E.; Nelson, J.; Robertson-Tait, A.; Savy, J.; Wong, I. Protocol for Addressing Induced Seismicity Associated with Enhanced Geothermal Systems (No. DOE/EE-0662); 2012.

Marty, N. C.; Tournassat, C.; Burnol, A.; Giffaut, E. C. Influence of reaction kinetics and mesh refinement on the numerical modeling of concrete/clay interactions. *J. Hydrol.* **2009,** *364*, 58–72.

Mason, H. E.; Frane, W. L. Du; Walsh, S. D. C.; Dai, Z.; Charnvanichborikarn, S.; Carroll, S. A. Chemical and Mechanical Properties of Wellbore Cement Altered by CO_2-Rich Brine Using a Multianalytical Approach. *Environ. Sci. Technol.* **2013,** *47*, 1745–1752. DOI:10.1021/es3039906

Massazza, F. Pozzolanic cements. *Cem. Concr. Compos., Special Issue on Composite Cements* **1993,** *15*, 185–214. DOI:10.1016/0958-9465(93)90023-3

Milborrow, S. Derived from mda:mars by T. Hastie and R. Tibshirani. *Earth: Multivariate Adaptive Regression Splines*, 2011. R package; http://www.milbo.users.sonic.net/earth/citing-earth.html

Monlouis-Bonnaire, J. P.; Verdier, J.; Perrin, B. Prediction of the relative permeability to gas flow of cement-based materials. *Cem. Concr. Res.* **2004,** *34*, 737–744. DOI:10.1016/S0008-8846(03)00071-1

Nelson, E. B., Guillot, D., Eds. Well Cementing, 2nd ed, *Developments in petroleum science*. Schlumberger, 2006.

Nešić, S. Key issues related to modelling of internal corrosion of oil and gas pipelines – A review. *Corros. Sci.* **2007,** *49*, 4308–4338. DOI:10.1016/j.corsci.2007.06.006

Neville, A. M. *Properties of Concrete*, 4th ed. John Wiley and Sons: New York, NY, 2004.

Newell, D. L.; Carey, J. W. Experimental Evaluation of Wellbore Integrity Along the Cement-rock Boundary. *Environ. Sci. Technol.* **2013,** *47*, 276–282. DOI:10.1021/es3011404

Nicot, J.-P. A survey of oil and gas wells in the Texas Gulf Coast, USA, and implications for geological sequestration of CO_2. *Environ. Geol.* **2009,** *57*, 1625–1638. DOI:10.1007/s00254-008-1444-4

Nordbotten, J. M.; Kavetski, D.; Celia, M. A.; Bachu, S. Model for CO_2 Leakage Including Multiple Geological Layers and Multiple Leaky Wells. *Environ. Sci. Technol.* **2009,** *43*, 743–749. DOI:10.1021/es801135v

NORSOK. Well integrity in drilling and well operations, Standard D-010, 2004.

Nygaard, R.; Salehi, S.; Weideman, B.; Lavoie, R. G. *Effect of Dynamic Loading on Wellbore Leakage for the Wabamun Area CO_2-Sequestration Project*; SPE-146640-PA, 2014. DOI:10.2118/146640-PA

Pan, L.; Oldenburg, C. M.; Pruess, K.; Wu, Y.-S. Transient CO_2 leakage and injection in wellbore-reservoir systems for geologic carbon sequestration. *Greenh. Gases Sci. Technol.* **2011a,** *1*, 335–350. DOI:10.1002/ghg.41

Pan, L.; Webb, S. W.; Oldenburg, C. M. Analytical solution for two-phase flow in a wellbore using the drift-flux model. *Adv. Water Resour.* **2011b,** *34*, 1656–1665. DOI:10.1016/j.advwatres.2011.08.009

Papadakis, V. G. Effect of fly ash on Portland cement systems: Part I. Low-calcium fly ash. *Cem. Concr. Res.* **1999,** *29*, 1727–1736. DOI:10.1016/S0008-8846(99)00153-2

Pawar, R.; Bromhal, G.; Carroll, S.; Chu, S.; Dilmore, R.; Gastelum, J.; Oldenburg, C.; Stauffer, P.; Zhang, Y.; Guthrie, G. Quantification of Key Long-term Risks at CO_2 Sequestration Sites: Latest Results from U.S. DOE's National Risk Assessment Partnership (NRAP) Project. Energy Procedia. 12th International Conference on Greenhouse Gas Control Technologies, GHGT-12 63, 2014; p 4816–4823. DOI:10.1016/j.egypro.2014.11.512

Peška, P.; Zoback, M. D. Compressive and tensile failure of inclined well bores and determination of in situ stress and rock strength. *J. Geophys. Res. Solid Earth* **1995,** *100*, 12791–12811. DOI:10.1029/95JB00319

Rahman, S. S.; Chilingarian, G. V. *Casing design theory and practice*; Elsevier, 1995.

Randhol, P. Assessment of sustained well integrity on the Norwegian continental shelf, 2008.

Ravi, K.; Bosma, M.; Gastebled, O. Safe and Economic Gas Wells through Cement Design for Life of the Well. Society of Petroleum Engineers, 2002. DOI:10.2118/75700-MS

Rimmelé, G.; Barlet-Gouédard, V.; Porcherie, O.; Goffé, B.; Brunet, F. Heterogeneous porosity distribution in Portland cement exposed to CO_2-rich fluids. *Cem. Concr. Res.* **2008,** *38*, 1038–1048. DOI:10.1016/j.cemconres.2008.03.022

Roy, D. M.; Scheetz, B. E. *CO_2-resistant cement*; Pennsylvania Transportation Institute, The Pennsylvania State University: University Park, PA, 2006.

Scherer, G. W.; Kutchko, B. G.; Thaulow, N.; Duguid, A.; Mook, B. Characterization of cement from a well at Teapot Dome Oil Field: Implications for geological sequestration. *Int. J. Greenh. Gas Control* **2011,** *5*, 115–124. DOI:10.1016/j.ijggc.2010.06.010

Schwind, B. E.; Payne, M. L.; Otten, G. K.; Pattillo, P. D. Development of Leak Resistance in Industry Standard OCTG Connections using Finite Element Analysis and Full Scale Testing. Offshore Technology Conference, OTC, 2001. DOI:10.4043/13050-MS

Shehata, M. H.; Thomas, M. D. A.; Bleszynski, R. F. The effects of fly ash composition on the chemistry of pore solution in hydrated cement pastes. *Cem. Concr. Res.* **1999,** *29*, 1915–1920. DOI:10.1016/S0008-8846(99)00190-8

Shen, J. C.; Pye, D. S. *Effects of CO_2 Attack on Cement in High-Temperature Applications*; Society of Petroleum Engineers, 1989. DOI:10.2118/18618-MS

Sideris, K. K.; Savva, A. E.; Papayianni, J. Sulfate resistance and carbonation of plain and blended cements. *Cem. Concr. Compos.* **2006,** *28*, 47–56. DOI:10.1016/j.cemconcomp.2005.09.001

Sminchak, J.; Gupta, N.; Bryer, C.; Bergman, P. Issues related to seismic activities induced by the injection of CO_2 in deep saline aquifers. *J. Energy Env. Res.* **2002,** *2*, 32–46.

Talabani, S.; Atlas, B.; Al-Khatiri, M. B.; Islam, M. R. An alternate approach to downhole corrosion mitigation. *J. Pet. Sci. Eng.* **2000,** *26*, 41–48. DOI:10.1016/S0920-4105(00)00019-X

Tong, C. PSUADE User's Manual, 2005.

Türkel, S.; Felekoğlu, B.; Dulluç, S. Influence of various acids on the physico-mechanical properties of pozzolanic cement mortars. *Sadhana* **2007,** *32*, 683–691. DOI:10.1007/s12046-007-0048-0

Ulm, F.-J.; Lemarchand, E.; Heukamp, F. H. Elements of chemomechanics of calcium leaching of cement-based materials at different scales. *Eng. Fract. Mech.* **2003,** *70*, 871–889. DOI:10.1016/S0013-7944(02)00155-8

Um, W.; Jung, H. B.; Suh, D. M.; Fernandez, C. A. *Geochemical and Geomechanical Effects on Wellbore Cement Fractures: Data Information for Wellbore Reduced Order Model*; PNNL-23148; Pacific Northwest National Laboratory, 2014.

Verba, C. *Potential Impacts of Formation Waters on the Integrity of Class H Cement and Reservoir Rock in Carbon [Co-] Sequestration Settings*; University of Oregon: Eugene, OR, 2013.

Viswanathan, H. S.; Pawar, R. J.; Stauffer, P. H.; Kaszuba, J. P.; Carey, J. W.; Olsen, S. C.; Keating, G. N.; Kavetski, D.; Guthrie, G. D. Development of a Hybrid Process and System Model for the Assessment of Wellbore Leakage at a Geologic CO_2 Sequestration Site. *Environ. Sci. Technol.* **2008,** *42*, 7280–7286. DOI:10.1021/es800417x

Walsh, S. D. C.; Carroll, S. Fracture-scale model of immiscible fluid flow. *Phys. Rev. E* **2013,** *87*, 013012. DOI:10.1103/PhysRevE.87.013012

Walsh, S. D. C.; Frane, W. L. D.; Mason, H. E.; Carroll, S. A. Permeability of Wellbore-Cement Fractures Following Degradation by Carbonated Brine. *Rock Mech. Rock Eng.* **2013,** *46*, 455–464. DOI:10.1007/s00603-012-0336-9

Walsh, S. D. C.; Mason, H. E.; Frane, W. L. Du; Carroll, S. A. Experimental calibration of a numerical model describing the alteration of cement/caprock interfaces by carbonated brine. *Int. J. Greenh. Gas Control* **2014a,** *22*, 176–188. DOI:10.1016/j.ijggc.2014.01.004

Walsh, S. D. C.; Mason, H. E.; Frane, W. L. Du; Carroll, S. A. Mechanical and hydraulic coupling in cement–caprock interfaces exposed to carbonated brine. *Int. J. Greenh. Gas Control* **2014b,** *25*, 109–120. DOI:10.1016/j.ijggc.2014.04.001

Watson, T.; Bachu, S. Identification of Wells With High CO_2-Leakage Potential in Mature Oil Fields Developed for CO_2-Enhanced Oil Recovery. Society of Petroleum Engineers, 2008. DOI:10.2118/112924-MS

Wenning, Q. C.; Huerta, N. J.; Hesse, M. A.; Bryant, S. L. Reactive Flow Channelization in Fractured Cement-implications for Wellbore Integrity. *Energy Procedia* **2013,** *37*, 5773–5780. DOI:10.1016/j.egypro.2013.06.500

Wolery, T. J.; Jackson, K. J.; Bourcier, W. L.; Bruton, C. J.; Viani, B. E.; Knauss, K. G.; Delany, J.M. Current Status of the EQ3/6 Software Package For Geochemical Modeling. *ACS Symp. Ser.* **1990,** *416*, 104–116.

Zhang, L.; Dzombak, D. A.; Kutchko, B. G., Wellbore cement integrity under geologic carbon sequestration conditions. In *Novel Materials for Carbon Dioxide Mitigation Technology*; Morreale, B., Shi, F., Eds.; Elsevier, 2015.

Zhang, L.; Dzombak, D. A.; Nakles, D. V.; Brunet, J.-P. L.; Li, L. Reactive Transport Modeling of Interactions between Acid Gas (CO_2 + H_2S) and Pozzolan-Amended Wellbore Cement under Geologic Carbon Sequestration Conditions. *Energy Fuels* **2013,** *27*, 6921–6937. DOI:10.1021/ef401749x

Zhang, M.; Bachu, S. Review of integrity of existing wells in relation to CO_2 geological storage: What do we know? *Int. J. Greenh. Gas Control* **2011,** *5*, 826–840. DOI:10.1016/j.ijggc.2010.11.006

Zoback, M. D. *Reservoir Geomechanics*; Cambridge University Press: Cambridge, United Kingdom, 2007.

Zyvoloski, G. A. *FEHM: A control volume finite element code for simulating subsurface multi-phase multi-fluid heat and mass transfer*; No. LA-UR-07-3359; Los Alamos National Laboratory, 2007.

NRAP is an initiative within DOE's Office of Fossil Energy and is led by the National Energy Technology Laboratory (NETL). It is a multi-national-lab effort that leverages broad technical capabilities across the DOE complex to develop an integrated science base that can be applied to risk assessment for long-term storage of carbon dioxide (CO_2). NRAP involves five DOE national laboratories: NETL, Lawrence Berkeley National Laboratory (LBNL), Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), and Pacific Northwest National Laboratory (PNNL).

Technical Leadership Team

Diana Bacon
Lead, Groundwater Protection Working Group
Pacific Northwest National Laboratory
Richmond, WA

Jens Birkholzer
LBNL Lab Lead
Lawrence Berkeley National Laboratory
Berkeley, CA

Grant Bromhal
Technical Director, NRAP
Research and Innovation Center
National Energy Technology Laboratory
Morgantown, WV

Chris Brown
PNNL Lab Lead
Pacific Northwest National Laboratory
Richmond, WA

Susan Carroll
LLNL Lab Lead
Lawrence Livermore National Laboratory
Livermore, CA

Abdullah Cihan
Lead, Reservoir Performance Working Group
Lawrence Berkeley National Laboratory
Berkeley, CA

Tom Daley
Lead, Strategic Monitoring Working Group
Lawrence Berkeley National Laboratory
Berkeley, CA

Robert Dilmore
NETL Lab Lead
Research and Innovation Center
National Energy Technology Laboratory
Pittsburgh, PA

Nik Huerta
Lead, Migration Pathways Working Group
Research and Innovation Center
National Energy Technology Laboratory
Albany, OR

Rajesh Pawar
LANL Lab Lead
Lead, Systems/Risk Modeling Working Group
Los Alamos National Laboratory
Los Alamos, NM

Tom Richard
Deputy Technical Director, NRAP
The Pennsylvania State University
State College, PA

Josh White
Lead, Induced Seismicity Working Group
Lawrence Livermore National Laboratory
Livermore, CA

Sean Plasynski
Executive Director
Technology Development and
Integration Center
National Energy Technology Laboratory
U.S. Department of Energy

Heather Quedenfeld
Associate Director
Coal Development and Integration
National Energy Technology Laboratory
U.S. Department of Energy

Traci Rodosta
Technology Manager
Strategic Planning
Science and Technology Strategic Plans
and Programs
National Energy Technology Laboratory
U.S. Department of Energy

Mark Ackiewicz
Director
Division of Carbon Capture and Storage
Office of Fossil Energy
U.S. Department of Energy

NRAP Executive Committee

Cynthia Powell
Executive Director
Research and Innovation Center
National Energy Technology Laboratory

Donald DePaolo
Associate Laboratory Director
Energy and Environmental Sciences
Lawrence Berkeley National Laboratory

Roger Aines
Chief Energy Technologist
Lawrence Livermore National
Laboratory

Melissa Fox
Program Manager
Applied Energy Programs
Los Alamos National Laboratory

George Guthrie
Chair, NRAP Executive Committee
Earth and Environmental Sciences
Los Alamos National Laboratory

Alain Bonneville
Laboratory Fellow
Pacific Northwest National Laboratory

Grant Bromhal
Technical Director, NRAP
Senior Research Fellow
Research and Innovation Center
National Energy Technology Laboratory