Safety and Water Challenges in CCS:

Modeling Studies to Quantify CO_2 and Brine Leakage Risk and Evaluate Promising Synergies for Active and Integrated Water Management

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Abstract

Carbon dioxide Capture and Sequestration, or CCS, is the only technology available to mitigate the high CO_2 emissions from coal-fired electricity production. Since coal is projected to continue to dominate worldwide electricity production, any global atmospheric CO_2 concentration stabilization strategy will need to include CCS. There is therefore a strong need to increase the number and scale of CCS projects by several orders of magnitude over the next two decades. Such a ramp-up in CCS projects, however, faces several potential barriers. This dissertation focuses on two such barriers: the previously identified issue of CO_2 sequestration safety, and the newly identified CCS issue of water management coupled to CCS operations. In regard to safety, this dissertation advances the capability to model CO_2 injection and migration, and the associated pressure build-up to quantify large-scale CO_2 and brine leakage risk. Limitations associated with different modeling approaches are evaluated. Regarding water issues, this dissertation improves the current CCS paradigm by considering water requirements for the overall CCS operations and identifying beneficial synergies associated with coupled carbon and water managements.

The first part of this dissertation (Chapters 2 through 4) addresses one of the outstanding unanswered CO_2 sequestration safety questions, identified by the 2005 IPCC Special Report on CCS, of how to develop reliable quantitative risk assessments of CO_2 and brine leakage. In North America, the century-long legacy of oil and gas exploration and production has left millions of old oil and gas wells. Many of these wells are co-located with otherwise good geological sequestration sites, and because the hydraulic properties of the well materials are uncertain, quantitative assessment is challenging. Chapter 2 reviews the hierarchy of vertically-integrated CO_2 injection and migration models recently developed to provide such a risk assessment. Chapter 3 presents the quantification of field-scale CO_2 and brine leakage risks through abandoned wells of an industrial CO_2 injection using a specialized sharp-interface model that is computationally very efficient. Model comparison to results from the industry-standard model ECLIPSE are presented in Chapter 4 to better understand when this vertically-integrated modeling approach is applicable and when the sharp-interface assumption is valid, focusing respectively on the time scale of brine drainage and the spatial scale of capillary effects.

The second part of this dissertation (Chapters 5 and 6) presents a paradigm shift in the way a CCS system is considered. We argue that the CCS surface facility and subsurface environment ought to be considered jointly, and that their respective implementation challenges, particularly concerning water management, should be examined collectively across all CCS operations. Retrofitting an existing power plant to capture CO_2 implies a doubling of cooling-water requirements. This additional water requirement can be technically challenging and highly publicly sensitive in water-stressed areas. At the same time, the extensive area of subsurface pressure perturbation and the CO_2 and brine leakage risks of the CO_2 sequestration operation will present regulatory and public acceptance challenges. Chapter 5 therefore provides a complete review of water, sequestration, legal, and public acceptance CCS implementation barriers and proposes a novel active and integrated CCS operation management framework to address them. Examining these barriers and challenges collectively allows us to identify multiple potentially advantageous synergies. Active management of water resources, including production and treatment of subsurface brines, can synergistically provide additional surface cooling water while reducing both the subsurface leakage risk and pressure perturbation, which will facilitate regulatory permitting and increase public acceptance. Chapter 6 quantifies the advantageous impacts of three of these identified synergies coupling simultaneous brine production to a large-scale CO_2 geological sequestration operation. Brine production can reduce the injection well pressure, which enables higher injectivity potential; can reduce the extent of the Area of Review; and can reduce the risk of CO_2 and brine leakage.

This dissertation provides novel and important contributions in advancing the fields of CO_2 sequestration safety modeling focusing on leakage risk, and in addressing CCS potential implementation barriers with a focus on water challenges. By integrating modeling progress and the broader considerations of the CCS surface and subsurface environments, presented in this dissertation, future work has the potential to provide a more complete understanding of both the CCS system and implementation barriers. The exploitation of all the identified synergies provides the best possibilities for successful large-scale implementation of CCS.

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I will start by a big “Thank you!” If you are reading this, it means this dissertation was at least partially read and will hopefully be of some use, guidance and inspiration to others. In the following pages I would like to briefly reflect upon the key moments of these last five years and thank all the people who supported and accompanied me on this rollercoaster of a journey.

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I arrived in Princeton full of personal and professional dreams. I will leave filled with stories, some happy, some less so, and wiser as to my strengths and limits. Upon arrival, I had never heard nor thought about coal (other than in 19th century French literature) and was passionately but naively convinced we could solve the climate change challenge with renewable energies alone in a matter of years… Needless to say that I have come a long way. I will try my best to keep my original optimism and not get overwhelmed by the daunting magnitude of the challenges ahead. Someone once described Princeton to me as the best spot in the world to have a 360° observation view on society challenges and environmental ones in particular. It was true! But transformational moments also took place outside of campus, from being one of two million people cheering at the inauguration of the first black president of the US, to conferences which allowed me to learn, talk, and/or teach from Western Canada to Australia through Abu Dhabi and many other places.

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Throughout the years, I was told several metaphors describing the Ph.D. process: “a marathon with a continually escaping finish line”, “a sprint running through the mud with heavy weights tied around your waist”, or my recent favorite “ if you think of a long journey as a 100 step

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Chapter 1

Introduction

1.1. The carbon challenge

1.1.1. Climate change and global warming

Climate science has shown unequivocal evidence of warming of the Earth (IPCC, 2007). Most of the observed increase in global average temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic greenhouse gas (GHG) concentrations (IPCC, 2007). Carbon dioxide (CO_2) is currently the most important GHG, based on global average radiative forcing (see Figure SPM.2 in (IPCC, 2007)), and is the sole GHG considered in this dissertation, yet attention must also be given to other non-CO_2 climate forcers. As shown in Figure 1.1 and 1.2, CO_2 emissions have risen from a pre-industrial concentration of 280 parts per million (ppm) to the current level of approximately 390 ppm. Ice cores reveal that the atmospheric CO_2 concentration over the last 650,000 years ranged between 170 ppm and 300 ppm respectively (Figure 1.2 shows the last 1000 years of this record).

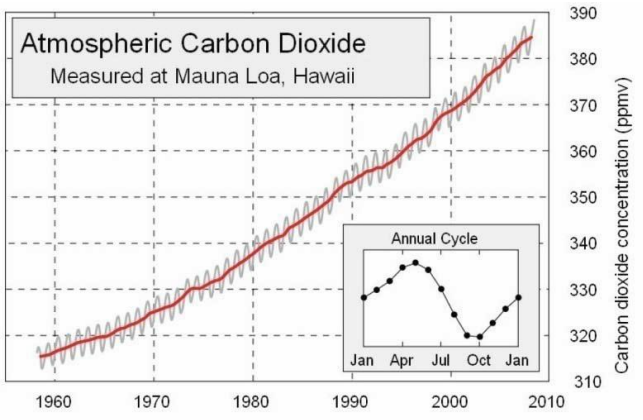
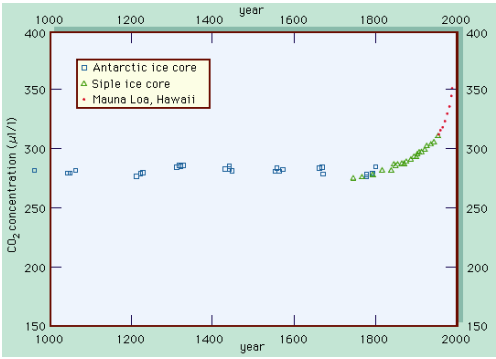


Figure 1.1: Atmospheric carbon dioxide concentration as a function of time, measured at Mauna Loa (from wikipedia.org).



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The recent increase in GHG atmospheric concentrations is expected to lead to dangerous climate change unless these concentrations are stabilized and reduced. For instance, the 2007 Fourth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) stated: “Anthropogenic warming over the last three decades has likely had a discernible influence at the global scale on observed changes in many physical and biological systems. Continued GHG emissions at or above current rates would cause further warming and induce many changes in the global climate system during the 21st century that would very likely be larger than those observed during the 20th century. For instance altered frequencies and intensities of extreme

weather, together with sea level rise, are expected to have mostly adverse effects on natural and human systems" (IPCC, 2007).

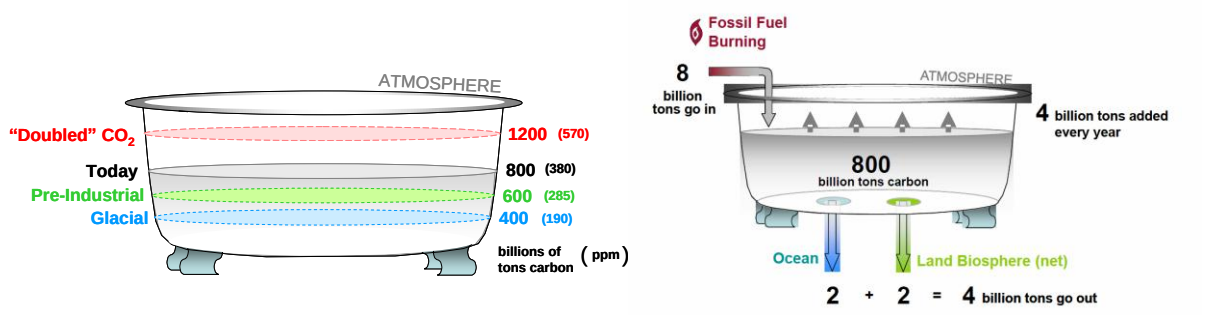

Figure 1.3: Simple conceptual model of current input, cumulative and output of carbon atmospheric concentration from CO_2 (Courtesy of Prof. Socolow).

While the climate system and science can be overwhelmingly complex, simple conceptual representations such as those shown in Figure 1.3 can be very helpful in understanding the orders of magnitude of CO_2 inputs into the atmosphere from fossil fuel burning, the uptake from the Ocean and Land systems, the increasing cumulative CO_2 mass in atmosphere (in billions of tons of carbon), and how they all relate to the global CO_2 atmospheric concentration (in parts per millions – ppm) often used in the climate policy arena.

1.1.2. Scale of the carbon problem

The scale of the challenge can be measured by society's dependence on fossil fuels. In 2006, the total annual anthropogenic emissions were estimated at approximately 8 billion metric tons (Gt) of carbon, which is about 30 Gt CO_2. Figure 1.4a shows that the largest sources of CO_2 worldwide come from electricity generation and transportation emissions representing 40% and 21% of global emissions respectively. Therefore, decarbonization of the power sector and potential electrification of the transportation sector will be a requisite in any strategy of carbon mitigation.

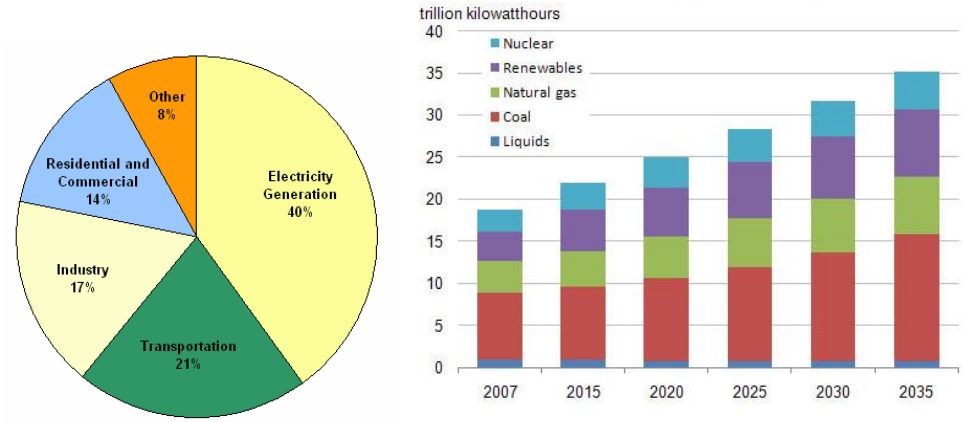

Figure 1.4: (a-left) Global carbon emissions from fossil fuel burning by sector. Data from International Energy Agency (IEA); Figure from http://www.earth-policy.org/Indicators/CO_2/2006_ CO_2sources.GIF. (b-right) World net electricity generation by fuel. Figure taken from The International Energy Outlook 2010 – Highlights available at http://www.eia.gov/oiaf/ieo/highlights.html

1.1.3. Coal challenge

The scale of the challenge posed by society's dependence on fossil fuels is particularly acute in the case of coal as shown in Table 1.1 and Figure 1.4b. Coal plays a dominant role in baseload electricity generation worldwide with coal-fired power plants supplying 41% of the global electricity demand in 2010, and in some countries, much higher percentages. This trend is highly unlikely to change over the coming decades, based on the current projection (see Figure 1.4b). Coal is a major part of the carbon problem because it is the baseload electricity fuel with the highest CO_2 intensity. The scale of coal extraction and consumption are also associated with severe negative environmental impacts (Hawkins, 2006). We note that emissions associated with natural gas, non-power sector (cement, iron&steel, refineries and biomass), and unconventional fuels, such as oil/tar sands or coal-to-liquid and gas-to-liquid transformations, must also be controlled.

South Africa	93%	Poland	92%	PR China	79%
Australia	77%	Kazakhstan	70%	India	69%
Israel	63%	Czech Rep	60%	Morocco	55%
Greece	52%	USA	49%	Germany	46%

Table 1.1: Coal in Electricity Generation adapted from [http://www.worldcoal.org/coal/uses-of-coal/coal-electricity/], Data from IEA 2010.

Global energy demand is expected to rise in the foreseeable future, and even more so as global population significantly increases. Fundamentally, the only solution to mitigate anthropogenic climate change is the cessation of fossil fuels consumption, in particular coal, and the replacement of energy production, in particular baseload electricity, by sources that are not carbon intensive. However coal is relatively cheap compared to these carbon-free energy sources, and it is also both geographically and geopolitically well-distributed. Thus widely available coal reserves will most likely continue to play a central role in the coming decades as the primary source of baseload electricity for many developed and developing nations (see Table 1.1 and Figure 1.4b). The recent international environmental conferences at Copenhagen in December 2009 and Cancun in December 2010, and the failure of the climate bill to pass in the USA during the summer 2010 do not provide encouraging signs to limit coal-based energy production.

1.1.4. Reduction of CO_2 emission: Wedges approach

In order to stabilize CO_2 emissions, drastic reductions from the business as usual scenario will be required. Pacala and Socolow offer the useful “wedges” metric (see Figure 1.5) to illustrate that there is no “silver bullet” or single technology solution to this global challenge (Pacala and Socolow, 2004; Socolow and Pacala, 2006). All options available in the portfolio (e.g. energy efficiency, energy decarbonization with renewable energy and nuclear, and enhancing natural sinks by reducing deforestation) will have to be considered and fully implemented in order to

avoid the “Stabilization Triangle” emissions shown in Figure 1.5. We refer to their seminal paper and useful website for further details.

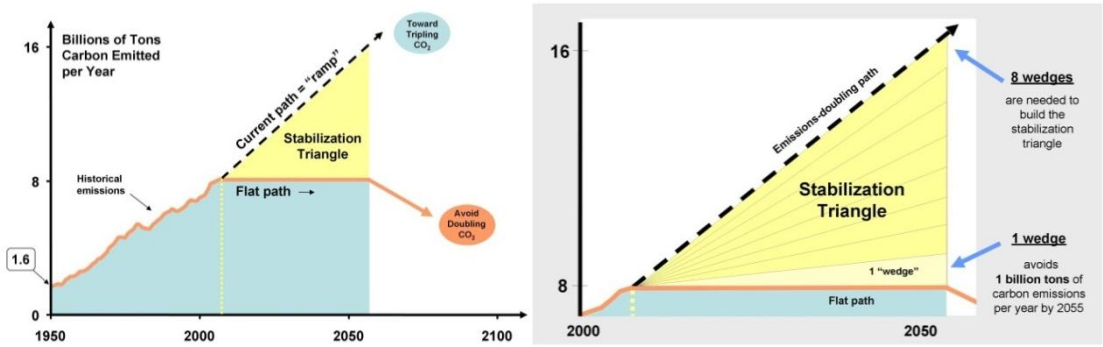

Figure 1.5 Wedge concept illustration from http://cmi.princeton.edu/wedges/

1.2. CCS introduction

1.2.1. CCS motivation

Following section 1.1.1-4, most climate change mitigation strategies to curb atmospheric CO_2 emissions must consider the continued use of coal due to existing infrastructure, lifespan, and time required to build low-carbon energy capacity at scale. Therefore a pragmatic strategy to mitigate atmospheric CO_2 emissions must integrate technologies to allow a transition period of simultaneous coal burning and CO_2 emission controls (Krey and Riahi, 2009; Calvin et al., 2009).

Emissions from large stationary sources, such as power plants, refineries and cement factories, are responsible for a significant fraction of emissions as shown in Figure 1.4. These point sources offer the possibility for very significant emission reduction through CO_2 Capture and Sequestration (CCS) technologies. CCS in deep geological saline formations is currently the most viable of these technologies (IEA 2009a,b; IPCC, 2005; MIT, 2007; Sheppard and Socolow, 2007). While CCS is not a permanent solution to the carbon problem, it offers a multi-decadal bridge solution that can allow other forms of non-carbon-based energy sources to be developed

and deployed at scale. The recent nuclear disaster in Japan in March 2011 will likely constrain any nuclear renaissance and thus put added pressure on coal baseload power generation, thereby increasing the need for CCS.

1.2.2. CO_2 capture and geological sequestration description

CCS is typically represented as a three step process: capture of CO_2 emissions at a point source, transport to a suitable target site, and sequestration of supercritical CO_2 in a deep geological formation, as shown in Figure 1.6 from the IPCC Special Report on CO_2 Capture and Sequestration (SRCCS) (IPCC 2005). This report provided the first comprehensive review of the state of the science on CCS in 2005. It was a major accomplishment that has become a key milestone and reference point for any scientist, engineer, business, regulator entering the CCS industry. As described in the SRCCS appendix section on CO_2 properties, supercritical CO_2 has the density of a fluid and the viscosity of a gas which are important to consider for the sequestration risk analysis. Ocean sequestration and CO_2 mineralization will not be considered in this dissertation and focus will be made on geological sequestration in deep saline formations as described in the next section with some discussion on Enhanced Oil Recovery (EOR).

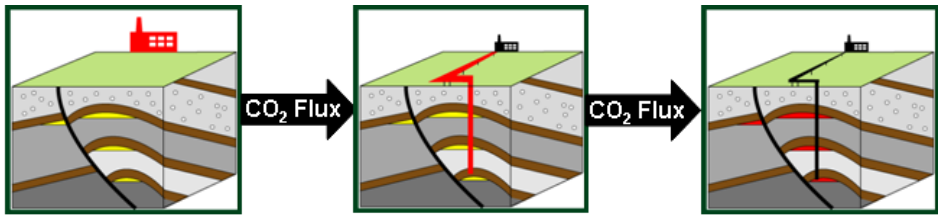

Figure 1.6: CCS main steps: CO_2 Capture at the power plan, transport and injection, and sequestration in geological media (IPCC 2005).

As shown in Figure 1.7 a–b), deep saline formations are often part of a succession of porous and permeable formations (or aquifer), typically sandstone or carbonate, overlay by an impermeable caprock (or aquitard), typically shale. It is important to keep in mind that these deep saline formations are filled with resident brine, which will be displaced by injected CO_2. As shown in Figure 1.7 c), the shale formations provide a natural seal against upward migration of CO_2.

Chapter 2 details a typical CCS operation that includes river and groundwater pumping for cooling and CO_2 injection in deep saline formations. CCS operations present a risk of CO_2 and brine leakage to shallow formations and the surface environement.

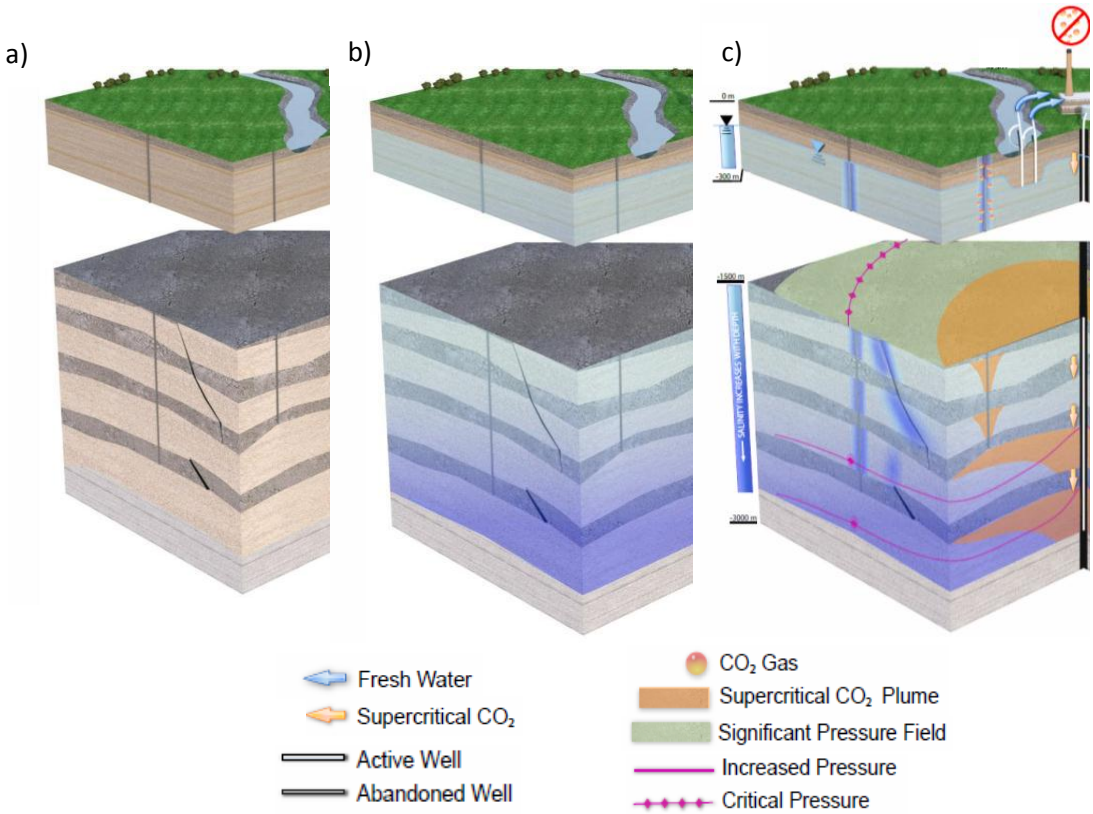

Figure 1.7: Conceptual representation of the geological aquifer- aquitard succession (a) only, (b) with the resident brine both without a CCS operation, and (c) with an CCS operation including groundwater/river pumping for cooling, CO_2 injection operation in deep saline formations, and representation of CO_2 and brine leakage risk via faults and/or wells.

1.2.3. Geological sequestration: deep saline formations & source/sink match

As shown in Figure 1.8 a and b), deep saline aquifers are ubiquitous and have been shown to hold the largest sequestration capacity (IPCC, 2005). However, because of the enormous scale of the problem, any full-scale implementation of CCS will likely require use of other geological media such as oil and gas reservoirs and coal beds (IPCC, 2005).

a)

b)

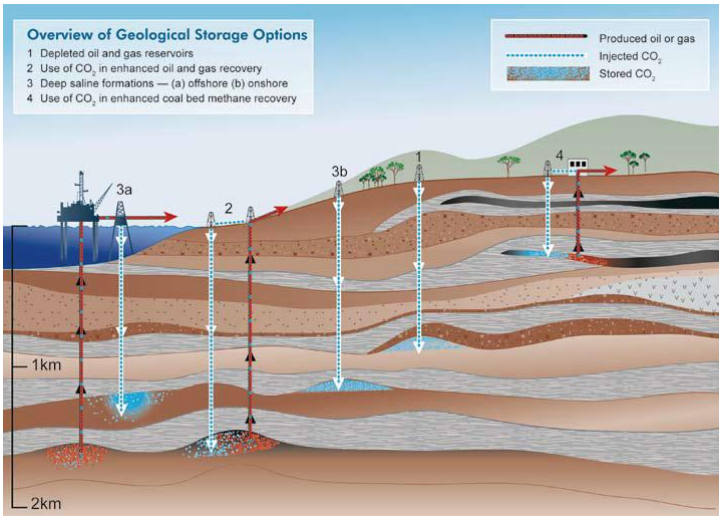

Figure 1.8. a) Prospective areas for geological storage of CO_2 on the left (Figure TS-2b from (IPCC 2005). b) on the right, different methods for storing CO_2 in deep underground geological formations. Two methods may be combined with the recovery of hydrocarbons: EOR (2) and Enhance Coal Bed Methane (4).

The consensus in the literature is that on a macro scale, the main sources of CO_2 (see Figure TS-2a in (IPCC, 2005)) match with the main sinks shown in Figure 1.8 a). Efforts implemented by the carbon sequestration atlas (described in (Litynski et al., 2009) and references therein) should be pursued and encouraged. Recent entrepreneurial development made a particular effort - in the same way attention was given to define a capture-ready power plant - to determine what

makes a site sequestration ready and the difference between a good versus excellent sequestration site (see discussion of section 5.3). Finally, experience in EOR operations, as well as with CCS demonstration projects (Michael et al. 2010, IEA) has improved our understanding of CO_2 injection and management, and will provide beneficial financial incentive for some early CCS projects.

1.2.4. CCS current implementation scale vs. a wedge of CCS

Haszeldine et al. (2009) and Michael et al. (2009) present helpful reviews of the current scale of CCS implementation via demonstration projects. Following section 1.1.4, a wedge of CCS represents a huge effort by 2055 comparable to: 3700 new Sleipner-equivalent operations of 1 $MtCO_2$/yr, about 100 times the U.S. CO_2 injection rate for EOR, or injection of CO_2 into the Earth equal to the oil produced today.

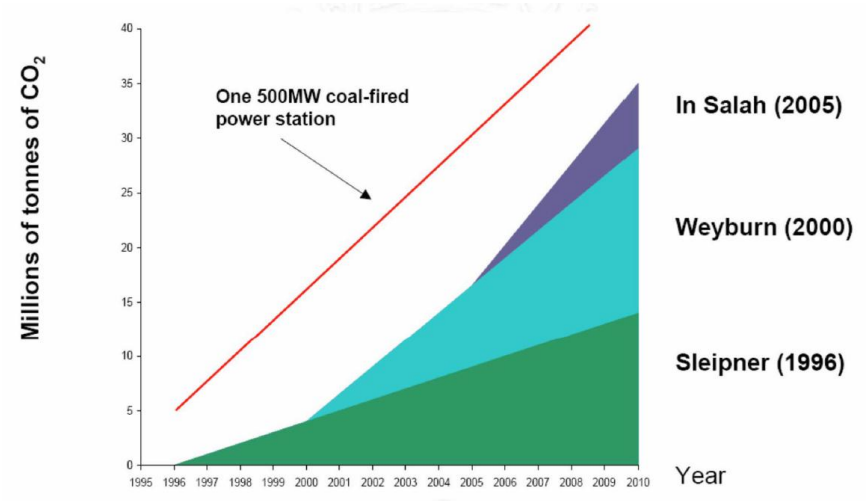

Figure 1.9: Comparison of the cumulative CO_2 emissions from a standard 500MW coal-fired power plant with the sum of the cumulative CO_2 injection from the three largest CCS demonstration projects in operation (from www.ieagreen.org.uk).

The comparison of the current cumulative emissions being sequestered to those of a single mid-size coal fired power plant, presented by Figure 1.9, shows that the three largest active CCS demonstration projects do not mitigate one plant and therefore provides a strong reminder of the magnitude of the effort ahead. Haszeldine et al. (2009) provides a review of 20

small commercial and pilot-scale projects, each with injection rates not exceeding 1 $MtCO_2$/yr, currently testing CCS technology around the world. (IEA 2009a,b) and references therein also provide useful review of CCS demonstration projects currently active, in planning, and needed in the future. As detailed in Chapter 5, the challenge ahead is to expand existing pilot CCS operations from the current cumulative demonstration projects scale of 1-10 million tons of CO_2 sequestered per year ($MtCO_2$/y), to a worldwide industrial-scale sequestration on the order of 100 $MtCO_2$/y by 2020, and 1000 $MtCO_2$/y by 2030 (see fig. 3 in (IEA 2009a), and (IEA 2009b)). The world energy outlook 2010 executive summary (IEA 2010) reaffirms the magnitude of implementation effort ahead. We note that while the focus is currently on implementing CCS in the power sector of developed nations, CCS expansion in both the non-power sector (cement and steel industries, refineries, etc.) and in developing countries will have to play a major role in the future (UNIDO, 2010).

1.2.5. Leakage challenge introduction

Among the many contributions of the IPCC SRCCS report was a widespread breaking of the "leakage taboo" threatening humans and ecosystems. In the early days of CCS discussions, it was often the case that leakage of any sort was considered unacceptable due to either the lack of experience (or experience sharing) or the lack of available and appropriate tools to physically conceptualize and ultimately quantify the problem. As described in more detail in this dissertation, it is necessary to quantify pressure build-up caused by CO_2 injection and fluid movement to mitigate the likelihood of CO_2 and/or high salinity waters (see Chapters 2, 3 and 6) migrating into Underground Sources of Drinking Water (USDW). In this system there are two main concerns: the caprock capacity to fully contain CO_2 which could be impaired by several leakage pathways; and, determining where and at what rate the CO_2 and brine flow.

(IPCC 2005) provides a detailed description of the potential environmental impacts that could result from CO_2 and/or brine leakage during sequestration of CO_2 in deep geological saline formations which fall into two broad categories: global risks which decrease climate change

mitigation, and local risks to ecosystems/animal and human health, which can be of two types: abrupt leakage through injection well failure and leakage through abandoned wells; and gradual leakage through undetected faults and fractures, or via diffuse leakage through non-fully impermeable cap rock.

1.2.6. Starting point: the 2005 IPCC SRCCS conclusions and knowledge gaps

The SRCCS identified a number of important points and knowledge gaps briefly summarized below which have motivated part of the work of our research group (subsurface.princeton.edu) focusing since the beginning of the Carbon Mitigation Initiative (cmi.princeton.edu) in 2001 on the leakage risk analysis:

Important conclusions from the SRCCS:

- *"The presence of thousands to hundreds of thousands wells* (Gasda et al., 2004) *penetrating the subsurface in mature sedimentary basins can create potential CO_2 leakage pathways that may compromise the security of a storage site* (Celia and Bachu, 2003)*."*
- *"The risk of leakage through abandoned wells is proportional to the number of wells intersected by the CO_2 plume, their depth and the abandonment method used."*
- *"Numerical simulators currently in use in the oil, gas and geothermal energy industries provide important subsets of the required modeling capabilities. They have served as convenient starting points for recent and ongoing development efforts specifically targeted at modeling the geological storage of CO_2. Simulation codes are available for multiphase flow processes, chemical reactions and geomechanical changes, but most codes account for only a subset of these processes. Capabilities for a comprehensive treatment of different processes are limited at present. This is especially true for the coupling of multiphase fluid flow, geochemical reactions and (particularly) geomechanics, which are very important for the integrity of potential geological storage sites (Rutqvist and Tsang, 200*2)."
- **Note**: Chapter 2 will describe how these physical processes are important only depending on the risk analysis question to be addressed. Several questions do not need the above processes to be included, and their coupling is very often not necessary. For instance the *"Reliable coupled hydrogeological-geochemical-geomechanical simulation models to predict long-term storage performance accurately"* knowledge gap seems inappropriate as geomechanical effects after the injection period/post pressure dissipation will be a lot less important.

- *"Demonstrating that they can model the important physical and chemical processes accurately and reliably is necessary for establishing credibility as practical engineering tools".*
- Note: this depends entirely on the time and spatial scales of interest and the exact question to be answered.
- *"Recently, an analytical model developed for predicting the evolution of a plume of CO_2 injected into a deep saline formation, as well as potential CO_2 leakage rates through abandoned wells, has shown good matching with results obtained from the industry numerical simulator ECLIPSE* (Celia et al., 2004; Nordbotten et al., 2005)*".*
- **Note**: Chapters 2 through 4 will argue that simplified tools have a very practical complementary use to traditional numerical tools and simply acknowledging the good match is an understatement of their practicality (computational efficiency), usefulness (speed and ease of interpretation), and availability (publically available and ease of use therefore not restricted to a limited number of experts).
- *"The principal difficulty is that the complex geological models on which the simulation models are based are subject to considerable uncertainties, resulting both from uncertainties in data interpretation and, in some cases, sparse data sets."*
- *"In the case of saline formation storage, history matching is generally not feasible for constraining uncertainties, due to a lack of underground data for comparison. Systematic parameter variation routines and statistical functions should be included in future coupled simulators to allow uncertainty estimates for numerical reservoir simulation results."*
- **Note**: Systematic parameter variation is essential, but probabilistic uncertainty estimation with thousands of simulations required is generally impossible with traditional numerical models particularly coupled ones unless they are drastically simplified; hence the need for accurate simplified tools.
- *"Wherever possible, it is preferable to treat uncertainty explicitly. In probabilistic risk assessments, explicit probability distributions are used for some (or all) parameters. Methods such as Monte Carlo analysis are then used to produce probability distributions for various risks."*
- *"In some cases, probabilistic risk assessment may require that the models be simplified because of limitations on available computing resources."*

Important knowledge gaps identified in the SRCCS:

- *"Risks of leakage from abandoned wells caused by material and cement degradation."*
- *"The temporal variability and spatial distribution of leaks that might arise from inadequate storage sites."*
- *"Quantification of potential leakage rates from more storage sites."*
- *"Reliable probabilistic methods for predicting leakage rates from storage sites."*

In summary, the SRCCS built on earlier research (e.g. Celia and Bachu (2003); Celia et al. (2004)) and included a balanced discussion of leakage potential and the need to confront quantitative estimates of leakage potential. Different pathways for leakage were identified, including diffuse leakage across caprock formations, leakage along fault and fracture zones, and leakage along abandoned oil and gas wells. Leakage along wells was identified as a particularly challenging problem, due in part to the high uncertainty associated with the physical state of well materials like cements and casing. Included in the conclusions and knowledge gaps presented in the SRCCS were the need to quantify leakage rates from sequestration sites and, more specifically, to develop reliable probabilistic methods to be applied to leakage analysis under high uncertainty. These kinds of analyses inevitably involve development and application of numerical models of the geological sequestration system. Recent studies like (Class et al., 2009) have shown that numerical simulation of leakage along wells is an especially challenging computational problem, even for very simple model problems involving only one injection well, one leaky well, and two aquifers separated by a caprock formation. For realistic injection sites in many parts of North America, we expect hundreds to thousands of abandoned wells to reside within the area of review for a project, and many aquifers and caprock formations to be present with the vertical stratigraphic sequence. These computational challenges have, in part, motivated the development of a new set of simulation tools and, in general, a new way of thinking about simulation tools and their applications as described in this dissertation. Note that fault, fractures, and diffuse leakage are not considered in this dissertation but are the focus of current on-going work in our research group.

An important final note is that most of the key points highlighted above were taken from technical part of Chapter 5 and almost none were clearly represented in the technical or policy maker summary. Acknowledgement of much larger uncertainty, need for improved, more practical, and widely available modeling capability -not restricted to a small community of scientists and handful of companies-, would ideally be much more present at the front of the CCS debate because of their repercussions on regulations and insurance risk analysis, operation

management, and public acceptance. In other words the SRCCS broke the leakage taboo but was not adequately clear on the insufficiency of the modeling tools. As detailed in this dissertation, five years after the SRCCS tremendous progress has been achieved theoretically (and experimentally) and in the ability to model complex case studies related to leakage risk analysis during a large-scale CO_2 injection operation. The discussion about leakage risk has now changed to be open and transparent about concerns, knowledge and limitations.

1.2.7. Previously identified CCS implementation challenges

To have a significant effect on global atmospheric carbon emissions, the scale of CCS activities must be expanded by several orders of magnitude. The required increase in CCS implementation brings several challenges that are often summarized in four major categories: (I) CO_2 capture cost; (II) sequestration safety; (III) legal and regulatory barriers; and (IV) public acceptance, the last three of which are reviewed in details in Chapter 5 of this dissertation.

1.3. Water CCS challenge introduction: a newly identified CCS implementation barrier

As detailed in Chapter 5, an energy and water nexus has clearly been identified through published literature in the United States (GAO 2009; Feeley et al. 2008; Goldstein 2008), India, South-Africa, and Brazil (McKinsey & Company 2009) and particularly in China (McKinsey & Company 2009; Sun et al. 2003; Varis and Vakkilainen 2001; Zheng et al. 2010a; Zhang 2009) where water saving methods are being considered in the coal industry (Fang 2009). Energy production and particularly coal-fired power plants already require large volumes of water for cooling processes (DOE/NETL 2007, 2008; NETL 2005). In both energy production and industry, water has become a limiting constraint nationally and internationally as shown by recent coal plant siting problems, and litigation cases in both the domestic and international arena (Sovacool 2009; Sovacool and Sovacool 2009a, 2009b).

Water was recently identified as an additional major challenge to CCS implementation due to the considerable increase in water use for power plants built or retrofitted with CCS. This is particularly significant when existing plants are retrofitted with post-combustion CO_2 capture. In this case both water withdrawal and consumption double from an identical non CO_2 capture equipped coal plant due to increased cooling need in both the regeneration process of expensive CO_2 capture chemical solvents (amines) and make-up power production (due to parasitic load), see Figure 12 and Appendix G in (DOE/NETL 2009) for details and also (DOE/NETL 2007, 2008; Ciferno et al. 2010; Zhai et al. 2011). Water scarcity will become accentuated with large-scale CCS expansion influencing and potentially constraining both CCS retrofitting of existing coal plants and siting of new construction coal generation with CCS (DOE/NETL 2008; Newmark et al. 2010) unless an active water management strategy detailed in Chapter 5 is implemented. By taking this new water challenge into account this dissertation considers a system larger than a typical single well CO_2 sequestration operation into a single formation to synergistically address: this doubling of the water requirement from the CO_2 capture retrofitting-process at the surface, and the subsurface pressure build-up following a large-scale CO_2 injection which will likely require pressure-relief-wells associated with a problematic brine disposal challenge, as investigated in Chapter 5 and 6.

1.4. Research objectives, questions, and dissertation outline

The previous sections presented an overview introduction of the carbon problem, CCS technology and its motivations, and the challenges for the required large-scale implementation of CCS. It also identified the crucial water challenge which motivated the consideration of the CCS surface and subsurface systems more globally. The two main objectives of this dissertation focus on the previously identified CO_2 sequestration safety implementation barrier, and the newly identified CCS water implementation barrier which is only starting to gain attention in the CCS community. The first objective is to advance the capability to model CO_2 injection and migration,

and the associated pressure field, to quantify the CO_2 and brine leakage risk; and to identify the limitations of the modeling approach used. The second objective is to improve the current CCS paradigm by considering both the surface and subsurface CCS systems and their implementation challenges more globally, and by integrating water management across all CCS operations.

The first part of this dissertation (Chapters 2 through 4) examines the primary risks of sequestration and required models to adequately address them, provides analysis to quantify the risk of CO_2 and brine leakage through abandoned wells, and investigates the applicability of the models and assumptions used.

The second part of this dissertation (Chapters 5 and 6) presents a paradigm shift in the way the CCS system is considered and argues that the newly identified CCS water management challenge should be carefully taken into account across all CCS operations. CCS surface facilities and the subsurface environment have to be viewed concurrently and their respective implementation challenges examined collectively. Multiple potential promising synergies, coupling brine production to CO_2 sequestration, are identified, four of which are evaluated.

In this dissertation, I address 5 research questions presented below.

What are the main modeling options to answer practical CO_2 sequestration safety questions?

In Chapter 2, I present and integrate the progress in modeling capabilities achieved since the 2005 SRCCS by our research group to answer a specific set of practical CO_2 sequestration safety questions, identified therein, facing almost all CCS operations. CO_2 sequestration safety is impaired by very numerous and complex leakage pathways with often unknown location and highly uncertain parameters. As discussed above, traditional complex numerical tools can be useful to provide physical insights of the CO_2 behavior. But they are often inappropriate to investigate risk associated with leakage, especially because the parametric uncertainty requires

probabilistic assessments with prohibitive computational cost. A range of models may be developed which become sequentially simpler as more (often restrictive) assumptions are applied to the system. Almost all sequestration safety question identified will involve large space and time scales, and models to answer these questions should be associated with those same scales. A clear accounting of these models, and their associated assumptions as well as the length and time scales, allows models to be chosen that are best suited to answer the questions being asked. This leads to a set of accurate simplified models with a broader multi-scale framework proposed that can accommodate other scales of importance and can combine different models into a so-called hybrid modeling approach. Such a multi-scale hybrid modeling approach represents a very promising direction that has evolved in the geological sequestration field since the SRCCS publication in 2005, and it provides a broad platform for on-going and future work across a wide range of modeling approaches.

What are the field-scale CO_2 and brine leakage risks of an industrial CO_2 injection in a single well and a single formation?

As discussed in section 1.2.6, CCS operations will require an environmental risk analysis to determine, among other things, the risk that injected CO_2 or displaced brine will leak from the injection formation into other parts of the subsurface or surface environments via different potential leakage pathways. In chapter 3, I complete and present the first quantification of field-scale CO_2 and brine leakage risks through abandoned wells during an industrial multi-million ton injection of supercritical CO_2. Complex leakage pathways along these wells, coupled with layered stratigraphic sequences and highly uncertain parameters, make quantitative analysis of leakage risk a major computational challenge. However, new approaches to modeling CO_2 injection, migration, and leakage allow for realistic scenarios to be simulated within a probabilistic framework. The probabilistic risk analysis focuses on the parameters uncertainty associated with these abandoned wells during the injection period, when risk of leakage is expected to be largest. This leakage risk assessment uses a novel dataset that was collected near Edmonton which includes the stratigraphy from a 50km x 50km field site and the properties of 1146 abandoned

wells located within it. The simulations involve injection, migration, and leakage over the 50-year time horizon for domains of several thousand square kilometers having multiple layers in the sedimentary succession and several thousand abandoned wells within the domain. Because I can perform each simulation in a few minutes of computer time, I can run tens of thousands of simulations and analyze the outputs in a probabilistic framework. I use these kinds of simulations to investigate the importance of residual brine saturations, the range of current options to quantify leaky well properties, and the impact of depth of injection and how it relates to leakage risk.

When are the vertically-integrated approach and the sharp-interface assumption valid in CO_2 sequestration modeling? What are the impacts of the brine drainage timescale and capillary pressure spatial scale?

In chapter 4, I investigate the applicability of vertically-integrated models and the validity of the sharp-interface assumption used in the CO_2 sequestration modeling. A family of vertically-integrated models of intermediate complexity can be derived by assuming that the strong buoyant drive in the system leads to vertical segregation of the injected CO_2 and resident brine on a time scale that is fast enough to model the system as being stratified and in vertical-equilibrium. These models range from vertically-integrated numerical models which include capillary forces via mathematical reconstruction, to numerical models assuming negligible capillary-transition-zone based on a sharp-interface assumption. The latter can simplify to semi-analytical/analytical models if we assume radial symmetry, a horizontal homogeneous formation, and a constant injection rate. This chapter investigates the limits of numerical vertical-equilibrium models and the more restricted semi-analytical vertical equilibrium sharp-interface models via comparisons with ECLIPSE simulator for various injection rates, durations, and formation characteristics.

What are the previously and newly identified CCS implementation barriers? And how can we address them?

In order to stabilize global atmospheric CO_2 concentration, CCS demonstration projects will need to increase several orders of magnitude across the globe in both number and scale over the next two decades, as discussed in section 1.2.4. This task has several potential barriers. These barriers include those that have been known for a number of years including CO_2 capture cost, absence of CO_2 transportation networks, safety of subsurface sequestration, pore-space competition, legal and regulatory frameworks, and public acceptance. In addition, water management is a new challenge that should be actively and carefully considered across all CCS operations. In Chapter 5, I complete a review of the new insights gained on these previously and newly identified challenges, since the IPCC special report on CCS. While somewhat daunting in scope, I argue that some of these challenges can be addressed more easily by recognizing the potential advantageous synergies that can be exploited when these challenges are dealt with in combination.

What are the advantageous synergies associated with simultaneous brine production and CO_2 geological sequestration? And how do we evaluate them?

In Chapter 6, I provide an initial analysis of four synergies identified in Chapter 5 related to active brine management in CCS operations. Three separate modeling studies using variations of a vertical equilibrium model are completed to investigate each of them specifically aiming to quantify the potential impacts of coupling simultaneous brine production to a large-scale CO_2 geological sequestration operation.

1.5. Contribution

1.5.1. Contribution to co-authored publication

The core chapters of this dissertation (Chapters 2 through 6) have already been published or submitted to journals for publication. The full references follow:

Chapter 2:

1 **B. Court**, M.A. Celia, J.M. Nordbotten, M. Dobossy, T.R. Elliot, K.W. Bandilla, (2011), *Modeling Options to Answer Practical Questions for CO_2 Sequestration Operations*, *available at* http://arks.princeton.edu/ark:/88435/dsp01rf55z769f.

2 J. Nogues, **B. Court**, M. Dobossy, J. Nordbotten, M. Celia, (2011), *Quantifying the Uncertainty Associated with Geological Sequestration of CO_2,* International Journal of Greenhouse Gas Control, in review.

Chapter 3:

3 M.A. Celia, J. Nordbotten, S. Bachu, M. Dobossy, and **B. Court** (2009), *Risk of Leakage versus Depth of Injection in Geological Storage*, *Energy Procedia,* vol. 1, no. 1, pp. 2573-2580.

4 M.A. Celia, J. Nordbotten, **B. Court**, M. Dobossy, and S. Bachu, (2010), *Field-scale Application of a Semi-analytical Model for Estimation of Leakage Potential Along Old Wells*, *International Journal of Greenhouse Gas Control,* vol. 5, no. 2, pp. 257-269.

Chapter 4:

5 **B. Court**, K.W. Bandilla, M.A. Celia, J.M. Nordbotten, M. Dobossy, A. Janzen, (2011), *Applicability of vertical-equilibrium and sharp-interface assumptions in carbon sequestration modeling*, International Journal of Greenhouse Gas Control, in review.

Chapter 5:

6 **B. Court**, M. Celia, J. Nordbotten, T. Elliot, (2011), *Active and integrated management of water resources throughout CO_2 capture and sequestration operations*, *Energy Procedia,* vol. 4, pp. 4221-4229

7 **B. Court**, T.R. Elliot, J.A. Dammel, T.A. Buscheck, J. Rohmer, M.A. Celia, (2011), Promising synergies to address water, sequestration, legal, and public acceptance issues associated with large-scale implementation of CO_2 sequestration, Special Issue on Carbon Capture and Storage of The Journal for Mitigation and Adaptation Strategies for Global Change, in press.

8 T.A. Buscheck, Y. Sun, Y. Hao, M. Chen, **B. Court**, M.A. Celia, and T.J. Wolery, (2011). *Geothermal energy production from actively-managed CO_2 storage in saline formations*, Proceedings for the Geothermal Resources Council 35th Annual Meeting: 23-26 October 2011, San Diego, CA, USA.

Chapter 6:

9 **B. Court,** K.W. Bandilla, M.A. Celia, T. Buscheck, A. Janzen, J.M. Nordbotten, M. Dobossy, (2011), *Initial evaluation of advantageous synergies associated with simultaneous brine production and CO_2 geological sequestration*, International Journal of Greenhouse Gas Control, in review.

10 T.A. Buscheck, Y. Sun, M. Chen, Y. Hao, T.J. Wolery, **B. Court**, M.A. Celia, S.J. Friedmann, and R.D. Aines, (2011), *Active CO_2 reservoir management for carbon capture, utilization, and storage (CCUS): producing brine to increase storage capacity, reduce cost, mitigate risk, and generate useful products*, International Journal of Greenhouse Gas Control, in review.

1.5.2. Contribution to data collection, models used, and credit to research colleagues

Throughout the dissertation, unless specified otherwise, the data used came from on an extensive data survey I conducted over the first 2.5 years of my Ph.D. in Alberta, Canada, with Stefan Bachu from Alberta Energy Resources Conservation Board and Theresa Watson from T.L. Watson & Associates Inc. The computational models I used were either the vertically-integrated sharp-interface semi-analytical model (ELSA), or the finite-capillary-transition-zone vertically-integrated numerical model (VESA) described in Chapter 2 & 3, and 4 & 6 respectively; or the Schlumberger commercial simulator ECLIPSE (Schlumberger, 2010).

I actively participated to the development of the ELSA model over the first 4 years of my Ph.D. I was very involved in the debug, test, break & repair of ELSA code, and assisted with the various versions of the analytical and semi-analytical models. The core theoretical input credit needs be given to Prof. Jan Nordbotten and Prof. Michael Celia. I wrote several versions of various modules of the code and numerous data pre-processing, data post-processing, and visualization routines. However the core computer programming must be chronologically attributed to: Dr. Dmitri Kavetski whose code version was abandoned after several years of his work and 2 years of my work because of convergence problems; Dr. Mark Dobossy whose skills were invaluably instrumental to me personally and the rest group for both ELSA and VESA codes; Dr. Sarah Gasda, Adam Janzen, and Dr. Karl Bandilla for the development and coding of the VESA code; Karl Bandilla for the Python ECLIPSE visualizer; Dr. Tom Elliot for part of the web-interface.

The possible use of ECLIPSE resulted from a 1.5 years active collaboration with Schlumberger. I defined the cooperation area and convinced both Princeton and Schlumberger's administrations and lawyers that this was a great personal development opportunity beneficial to

all parties involved. I spent a very fruitful internship at Schlumberger Paris research center during the 2009 Fall semester and also obtained a 3 years license of ECLIPSE simulator. I went to Houston to get a week-long exposure to ECLIPSE potential use and later had to teach myself how to use it. I am grateful for my various Schlumberger colleagues who shared their user-experience along the way in particular: Dr. Laure Deremble, Yves Manin, Dr. Yannick Lefevre, Ozgur Senel, Owen Brazell, Yussuf Pamucku, Bilgin Altundas, and Adrian Anton.

I would like to acknowledge the instrumental scientific input of Dr. Robert Williams, Dr. Tom Kreutz from Princeton University, and Dr. Thomas Buscheck from Lawrence Livermore National Laboratory and their colleagues throughout the second part of my dissertation addressing the newly identified CCS water challenge, and developing the active and integrated CCS operation management framework.

The modeling research effort which supports this dissertation would have not been possible without the respective contribution of every research colleague mentioned above spanning from mathematical theory, engineering expertise and scientific concepts, data collection, computer programming, model usage and application. My contribution span across all with appropriate credit to others as described above.

1.5.3. Contribution to personal interaction, conferences, and presentations

This dissertation is based on publications described above but equally important is the result of numerous interactions, conferences, and presentations. Here is a brief list of the most important ones.

2006
Courses: Princeton University.
Off-campus presentations: Institut Francais du Petrol research center.

2007
Courses: Princeton University.
Conference: Research Experience Carbon Sequestration (RECS) seminar, Bozeman, USA.

2008
Courses: Princeton University.

Conferences: 9th Greenhouse Gas Technologies (GHGT) conference, Washington DC; International Energy Agency (IEA) CCS Summer school, Vancouver, Canada.

2009

Courses: Princeton University & New York University Law School.
Conference: IEA CCS summer school, Lorne, Australia; UNFCC Copenhagen climate conference.
Off-campus presentations: Department of Mathematics, University of Bergen, Bergen Norway.

2010

Courses: Princeton University & New York University Law School.
Conferences: Department Of Energy (DOE) / Environmental Protection Agency (EPA) CCS meeting, Pittsburgh, USA; 9th Annual conference on CCS in Pittsburgh, USA; United Nations Industrial Development Organization CCS seminar, Amsterdam, Netherlands.
Off-campus presentations: Schlumberger research center, Paris, France; RECS seminar, Albuquerque, USA; Poster at GHGT10 conference, Amsterdam, Netherlands; DOE Advanced Research Projects Agency-Energy, Washington, USA; Geological Society of America meeting & EPA Regional Office, Denver, USA; Poster at American Geophysical Union annual meeting, San Francisco.

2011

Off-campus presentations: Society of Petroleum Engineering CCS workshop: *Environment, Energy Security and Opportunities for the Middle East*, Abu Dhabi, U.A.E

1.6. References

Calvin, K., Edmonds, J., Bond-Lamberty, B., Clarke, L., Kim, S.H., Kyle, P., Smith, S.J., Thomson, A. & Wise, M. 2009, "2.6: Limiting climate change to 450 ppm CO2 equivalent in the 21st century", *Energy Economics,* vol. 31, no. Supplement 2, pp. S107-S120.

Celia, M.A. & Bachu, S. 2003, "Geological Sequestration of CO2: Is Leakage Unavoidable and Acceptable?", *Proc. Sixth Intl. Greenhouse Gas Technologies Conference, Kyoto, J. Gale and Y. Kaya (eds.), Volume I, 477-482.*

Celia, M.A., Bachu, S., Gasda, S.E. & Dahle, H.K. 2004, "Quantitative Estimation of CO2 Leakage from Geological Storage: Analytical Models, Numerical Models, and Data Needs", *Proc. GHGT-7 Meeting, Vancouver.*

Celia, M.A., Nordbotten, J.M., Bachu, S., Dobossy, M. & Court, B. 2009, "Risk of Leakage versus Depth of Injection in Geological Storage", *Energy Procedia,* vol. 1, no. 1, pp. 2573-2580.

Celia, M.A., Nordbotten, J.M., Court, B., Dobossy, M. & Bachu, S. 2011, "Field-scale application of a semi-analytical model for estimation of CO2 and brine leakage along old wells", *International Journal of Greenhouse Gas Control,* vol. 5, no. 2, pp. 257-269.

Ciferno, J.P., Munson, R.K., Murphy, J.T. & Lash, B.S. March 2010, "Determining Carbon Capture and Sequestration's Water Demands", *Power Magazine.*

Class, H., Ebigbo, A., Helmig, R., Dahle, H., Nordbotten, J., Celia, M., Audigane, P., Darcis, M., Ennis-King, J., Fan, Y., Flemisch, B., Gasda, S., Jin, M., Krug, S., Labregere, D., Naderi Beni, A., Pawar, R., Sbai, A., Thomas, S., Trenty, L. & Wei, L. 2009, "A benchmark study on problems related to CO2 storage in geologic formations", *Computational Geosciences,* vol. 13, no. 4, pp. 409-434.

Court, B., Celia, M.A., Nordbotten, J.M. & Elliot, T.R. 2011, "Active and integrated management of water resources throughout CO2 capture and sequestration operations", *Energy Procedia,* vol. 4, pp. 4221-4229.

DOE/NETL 2009, "Estimating freshwater needs to meet future thermoelectric generation requirements, 2009 update".

DOE/NETL 2008, *Estimating freshwater needs to meet future thermoelectric generation requirements*, Pittsburgh, PA.

DOE/NETL 2007, *Cost and Performance Comparison Baseline for Fossil Energy Power Plants*.

Fang, C. 2009, *Study on water-saving methods and countermeasures of developing coal chemical industry in arid area.*

Feeley, T.J., Skone, T.J., Stiegel, G.J., J., McNemar, A., Nemeth, M., Schimmoller, B., Murphy, J.T. & Manfredo, L. 2008, "Water: a critical resource in the thermoelectric power industry", *Energy,* vol. 33, no. 1, pp. 1-11.

GAO 2009, *Energy-water nexus: improvements to federal water use data would increase understanding of trends in power plant water use*, United States.

Gasda, S.E., Bachu, S. & Celia, M.A. 2004, "Spatial characterization of the location of potentially leaky wells penetrating a deep saline aquifer in a mature sedimentary basin", *Environmental Geology,* vol. 46, no. 6-7, pp. 707-720.

Goldstein, N.C. 2008, "The Energy-Water Nexus and information exchange: Challenges and opportunities", *International Journal of Water,* vol. 4, no. 1-2, pp. 5-24.

Hawkins, D. 2006, "What to do about coal", *Scientific American,* vol. 295, no. 3, pp. 68-75.

IEA 2009a, "How the energy sector can deliver on a climate agreement in Copenhagen - special eraly excerpt of the world energy outlook 2009 for the Bangkok UNFCCC meeting".

IEA 2009b, "Technology Roadmaps - Carbon Capture and Storage".

IEA / CSLF 2010, "Carbon Capture and Storage: Progress and Next Steps IEA/CSLF Report to the Muskoka 2010 G8 Summit".

Krey, V. & Riahi, K. 2009, "Implications of delayed participation and technology failure for the feasibility, costs, and likelihood of staying below temperature targets—Greenhouse gas mitigation scenarios for the 21st century", *Energy Economics,* vol. 31, no. Supplement 2, pp. S94-S106.

Litynski, J., Plasynski, S., Spangler, L., Finley, R., Steadman, E., Ball, D., Nemeth, K.J., McPherson, B. & Myer, L. 2009, "U.S. Department of Energy's Regional Carbon Sequestration Partnership Program: Overview", *Energy Procedia,* vol. 1, no. 1, pp. 3959.

McKinsey & Company 2009, "Charter our water future".

Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L. & (Eds.) 2005, *IPCC Special Report on Carbon Dioxide Capture and Storage,* New York, NY: Cambridge University Press.

Michael, K., Golab, A., Shulakova, V., Ennis-King, J., Allinson, G., Sharma, S. & Aiken, T. 2010, "Geological storage of CO2 in saline aquifers-A review of the experience from existing storage operations", *International Journal of Greenhouse Gas Control,* vol. 4, no. 4, pp. 659-667.

MIT 2007, "The future of coal", *available at http://web.mit.edu/coal/.*

NETL 2005, *Power Plant Water Usage and Loss Study*.

Newmark, R.L., Friedmann, S.J. & Carroll, S.A. 2010, "Water challenges for geologic carbon capture and sequestration", *Environmental management,* vol. 45, no. 4.

Nicot, J.-. 2008, "Evaluation of large-scale CO2 storage on fresh-water sections of aquifers: An example from the Texas Gulf Coast Basin", *International Journal of Greenhouse Gas Control,* vol. 2, no. 4, pp. 582-593.

Nicot, J., Hovorka, S.D. & Choi, J. 2009, "Investigation of water displacement following large CO2 sequestration operations", *Energy Procedia,* vol. 1, no. 1, pp. 4411-4418.

Nicot, J., Oldenburg, C.M., Bryant, S.L. & Hovorka, S.D. 2009, "Pressure perturbations from geologic carbon sequestration: Area-of-review boundaries and borehole leakage driving forces", *Energy Procedia,* vol. 1, no. 1, pp. 47-54.

Nordbotten, J.M., Celia, M.A., Bachu, S. & Dahle, H.K. 2005, "Semianalytical solution for CO2 leakage through an abandoned well", *Environmental science & technology,* vol. 39, no. 2, pp. 602-611.

Pacala, S. & Socolow, R. 2004, "Stabilization wedges: Solving the climate problem for the next 50 years with current technologies", *Science,* vol. 305, no. 5686, pp. 968-972.

Schlumberger 2010, "ECLIPSE Technical Description".

Sheppard, M.C. & Socolow, R.H. 2007, "Sustaining fossil fuel use in a carbon-constrained world by rapid commercialization of carbon capture and sequestration", *AICHE Journal,* vol. 53, no. 12, pp. 3022-3028.

Socolow, R.H. & Pacala, S.W. 2006, "A plan to keep carbon in check", *Scientific American,* vol. 295, no. 3, pp. 50-57.

Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. & (eds.) 2007, "IPCC, 2007: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change", *Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.*

Sovacool, B.K. 2009, "Running on Empty: The Electricity-Water Nexus and the U.S. Electric Utility Sector", *Energy Law Journal,* vol. 30(1), pp. pp. 11-51.

Sovacool, B.K. & Sovacool, K.E. 2009a, "Identifying future electricity–water tradeoffs in the United States", *Energy Policy,* vol. 37, no. 7, pp. 2763-2773.

Sovacool, B.K. & Sovacool, K.E. 2009b, "Preventing National Electricity-Water Crisis Areas in the United States", *Columbia Journal of Environmental Law,* vol. 34(2), pp. pp.333-393.

Sun, B., Peng, R. & Chen, C. 2003, "Ecological environmental problems caused by the exploitation of mineral products and water resources in Xinjiang, China", , eds. X. Pan, W. Gao, M.H. Glantz & Y. Honda, SPIE, , July 11, 2003, pp. 780.

UNIDO - United Nations Industrial Development Organization 2010, "Carbon Capture and Storage in Industrial Applications: Technology Synthesis Report Working Paper", *available at http://www.unido.org/fileadmin/user_media/Services/Energy_and_Climate_Change/Energy_Efficiency/CCS/synthesis_final.pdf.*

Varis, O. & Vakkilainen, P. 2001, "China's 8 challenges to water resources management in the first quarter of the 21st Century", *Geomorphology,* vol. 41, no. 2-3, pp. 93-104.

Zhai, H., Rubin, E.S. & Versteeg, P.L. 2011, "Water Use at Pulverized Coal Power Plants with Postcombustion Carbon Capture and Storage", *Environmental science & technology,* vol. 45, no. 6, pp. 2479-2485.

Zhang, C. 2009, *Climate change impacts on water resources and ecological environment of inland watersheds in the Hexi region of West Gansu, China.*

Zheng, C., Liu, J., Cao, G., Kendy, E., Wang, H. & Jia, Y. 2010, "Can China Cope with Its Water Crisis??Perspectives from the North China Plain", *Ground Water,* vol. 48, no. 3, pp. 350-354.

Chapter 2

Modeling options to answer practical questions for CO_2 sequestration operations

This chapter was adapted from: B. Court, M.A. Celia, J.M. Nordbotten, M. Dobossy, T.R. Elliot, K.W. Bandilla, (2011), *Modeling Options to Answer Practical Questions for CO_2 Sequestration Operations*, available at http://arks.princeton.edu/ark:/88435/dsp01rf55z769f.

2.1. Introduction

As presented in Chapter 1, the SRCCS (IPCC, 2005) identified a number of important conclusions and knowledge gaps in CO_2 sequestration modeling. Included in these were the need to quantify leakage rates from sequestration sites and, more specifically, to develop reliable probabilistic methods to be applied to leakage analysis under (potentially high) uncertainty. Recent studies like (Class et al., 2009) have shown that numerical simulation of leakage along wells is an especially challenging computational problem, even for very simple model problems involving only one injection well, one leaky well, and two aquifers separated by a caprock formation. For realistic injection sites in many parts of North America, we expect hundreds to thousands of abandoned wells to reside within the Area of Review for a project, and many

aquifers and caprock formations to be present with the vertical stratigraphic sequence. These computational challenges have, in part, motivated the development of a new set of simulation tools and, in general, a new way of thinking about models and their application described in this Chapter based on (Court et al., 2011).

Much of the injection is expected to be deployed in widely geographically available deep saline aquifers which offer the largest volumetric potential for sequestration. As documented in the SRCCS appendix on CO_2 properties, sequestered CO_2 is supercritical (density of a liquid and viscosity of a gas), and therefore more buoyant/less dense and more mobile/less viscous than the resident brine. Hence it will naturally form a CO_2 plume with some brine trapped behind the invading front much like the illustrative Figure 2.1. The CO_2 is typically injected in a porous and permeable injection formation (or aquifer), typically sandstone, overlaid by an impermeable caprock (or aquitard), typically shale, providing a natural capillary seal against upward migration of CO_2. The porous medium is fully saturated by resident brine, which will hence be displaced by this injected CO_2. The formation pressure increase that results from injection should not exceed regulatory limits based on the caprock's fracture pressure (see (USEPA, 1994) and Chapter 5 section 5.2.2). Pressure perturbation will typically extend more rapidly and further in space than the radial outer extent of the CO_2 plume.

Modeling a CO_2 sequestration system requires standard mass conservation, fluid flow and transport equations coupled with material-dependent constitutive equations. These sets of coupled nonlinear partial differential equations (see Chapters 3,4 and 6 and references therein for details) are then resolved on a given spatial and time scale to determine magnitude and extent of the CO_2 plume and pressure perturbation. The system can span hundreds to thousands of square kilometers in area and extend vertically from the land surface to several kilometers deep. Meanwhile, the potential leakage pathways in caprock and confining units that need to be characterized are on a scale of 0.001 square meters. Flow properties along these leakage

pathways are highly uncertain and dynamic, particularly when there is potential for material degradation.

Princeton University's Subsurface Hydrology Group, Bergen University Mathematical Department, and Geological Storage Consultant Inc. have been focused and continue to work actively on geological sequestration risk. One pertinent research focus has been the issue of abandoned wells resulting from a 100-year legacy of oil and gas exploration. It was identified in the SRCCS as the biggest and most uncertain source of concern for leakage. Those wells perforate otherwise competent natural sealing caprock like described in details in Chapter 3.

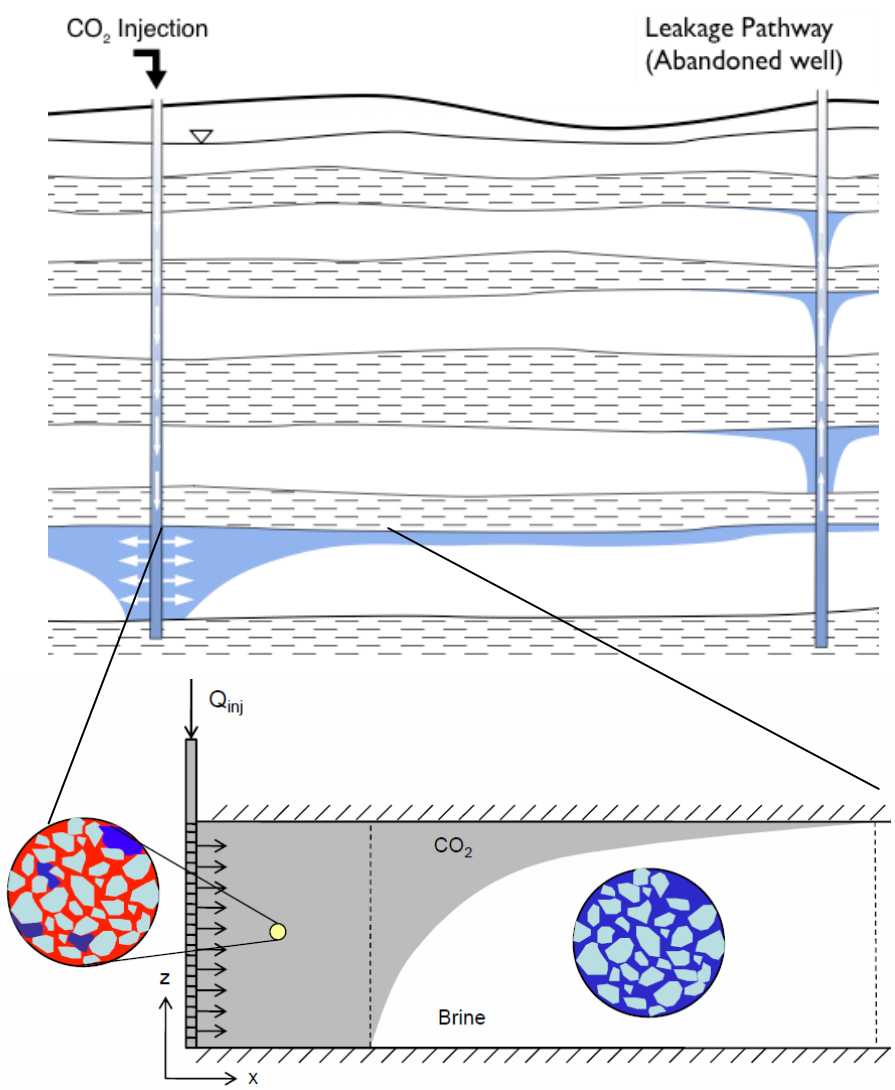

Figure 2.1: Conceptual representation of a geological CO_2 sequestration operation

This Chapter concisely presents and integrates the progress in modeling capabilities achieved since the 2005 SRCCS by our research group to answer a specific set of important practical questions to CO_2 sequestration operations. In particular, it positions my personal modeling work and the scientific contribution of this dissertation, as well as my research group's work, in the context of the CO_2 sequestration risk-modeling field and the CCS literature more broadly. The approach we have developed is based on an explicit analysis of spatial and temporal scales associated with both system features (size, shape, kinds of materials) and system processes (buoyant segregation, dissolution). Importantly, we also include in the space-time scaling analysis of the questions that the model is meant to answer. We then try to develop models that are most appropriate to answer the questions. This overall approach leads to a hierarchy of modeling options, and a broad framework for model development that is transparent in terms of the underlying assumptions and falls broadly into what is called a multi-scale modeling framework. This Chapter presents the ideas that underlie this approach, and show its utility in solving practical problems including the leakage risk analysis problem identified by the SRCCS. This work builds on the excellent review papers of Michael et al. (2009), Schnaar and Digiulio (2009) and Pruess et al. (2009), and is based broadly on some of the ideas presented in Nordbotten et al. (2009,2011), and Celia and Nordbotten (2009).

2.2. Model development for geological sequestration of CO_2

Analysis of a geological sequestration operation, including a broad safety and risk analysis, may involve different computational models that can vary in complexity and the associated computational power necessary to run them. These models of the system can have different goals but in the end should all answer the practical questions that have been posed about the problem at hand. These questions will often have associated with them a clearly defined range of spatial and temporal scales. We posit that models of the system should therefore be derived and defined on spatial and temporal scales that are consistent with those associated with the

questions to be answered. For example, if the practical questions involve issues like the maximum extent of the CO_2 plume and the associated pressure perturbation, then models must be consistent with large spatial and temporal scales. As such, use of a pore-scale model, wherein the scales of resolution are sub-millimeter in space and sub-seconds in time, is completely inappropriate. Such sub-scale models may be useful to parameterize larger-scale models, but they would not be applied to answer the practical questions. The utility of models at different scales, and their overall integration into models that answer practical questions, is important and is the focus of this section.

2.2.1. Practical questions

A set of questions that applies to most scenarios for CO_2 injection is the following:

Q1: What are the spatial extents of the CO_2 plume and the pressure perturbation as a function of time, (a) during the injection period, and (b) after injection stops?

Assuming the injection period is on the order of 50 years (a typical lifetime for a power plant), then part (a) involves decadal time scales. The associated spatial scales are likely to be on the one to ten kilometers scale. The post-injection period will be on the century to millennial time scale, and would involve tens to perhaps a hundred kilometers in the spatial scale. Therefore models must be developed to simulate the relevant processes on these length and time scales.

Q2: What fraction of the injected CO_2 and displaced brine will leak out of the injection formation? And where will the leaked fluid(s) go?

Answers to this question require knowledge, and proper model representation, of the leakage pathways as well as the important physical and chemical processes that are involved. For diffuse leakage across caprock formations, the time scales are relatively long and the spatial extent is large. However, for more concentrated leakage pathways like faults and abandoned wells, the spatial extent (in the horizontal direction) is quite small, on the order of millimeters

or centimeters, and the flow processes may be quite fast. These smaller-scale features and processes may be critical to answering this practical question, and as such they will need to be resolved and modeled. However, the size of the CO_2 plume and pressure perturbation, and the vertical extent (perhaps a kilometer or more) of the leakage pathways, also play a role. As such, leakage can be seen as a mixture of large- and small-scale features.

Q3: What is the overall long-term fate of the injected CO_2?

This question requires long time scales (century to millennial) and large spatial scales, with the explicit inclusion of trapping processes such as capillary trapping, dissolution trapping, and mineral trapping, all represented mathematically at large space and time scales.

In addition to these questions, any number of secondary questions may need to be answered. For example, chemical dissolution of caprock minerals could promote leakage of CO_2 from a sequestration reservoir (Gherardi et al., 2007), so that this small-scale geochemistry along the reservoir-caprock interface may need to be resolved. Leaked CO_2 has the potential to mobilize hazardous chemical species in shallower zones, including ground-water zones (Kharaka et al., 2006; Kharaka, 2009), and this may need to be modeled. Other geophysical and geochemical processes may also need to be included – see, for example, (Shukla et al., 2010) for a discussion of geophysical and geochemical aspects of caprock–CO_2–pore fluid interaction, stability of the caprock during and after injection of CO_2, and the impact of pre-existing fractures on seal integrity. While any given injection system may involve some subset of secondary questions (see Chapter 5 for a complete review of sequestration challenges), those identified as Q1 through Q3 above will face all CO_2 sequestration operations and therefore always need to be addressed. We take these as guiding questions in what follows.

2.2.2. Spatial and temporal scales

In Figure 2.2, we have indicated a number of the important length scales for the CO_2 sequestration problem. They range from the sub-millimeter scale (for example, fluid-fluid interfaces at the pore scale, fracture apertures – we call this the "nano" scale based on the nomenclature used in (Nordbotten and Celia, 2011)) to the intermediate scale (for example, wellbore radii or thin capillary transition zone -defined in the next paragraph- widths – the "micro" scale) to larger scales (for example, thicker capillary transition zone than the vertical thickness of a formation – the "meso" scale) to the largest scales of the problem, including the lateral extent of the CO_2 plume and the lateral extent of pressure perturbations – namely the "macro" scale. As noted above, most practical questions involve the macro-scale, including questions about the size of the plume, the size of the Area of Review (defined as the area in which operators must procure property rights, and monitor and remediate potential leakage pathways, and the risk of CO_2 and brine leakage, discussed and defined in details in Chapter 5). Leakage may also involve the micro or even nano scales depending on the nature of the leakage pathways. Because each of the practical questions posed above involves the macro scale either fully or partially we highlight it with a box in Figure 2.2 and we focus on it as the scale at which we should write our governing equations. Within these equation sets, important smaller-scale features will have to be represented in some way.

While there are many comments that can be made about these scale estimates, we will focus on only two of the spatial scales: the thickness of a capillary transition zone and the thickness of the formation. The Capillary Transition Zone (CTZ) is defined as the region over which fluid phase saturations change from their maximum to their minimum values. That is, it is the "transition zone" for fluid saturations under buoyant segregation. This CTZ is investigated and illustrated in Chapter 4. Formation thickness is self-explanatory, and plays an important role in our proposed simplified (multi-scale) models.

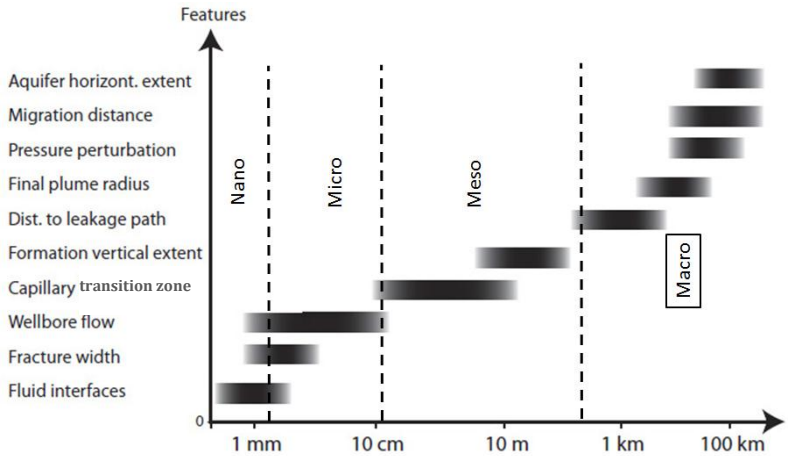

Figure 2.2: Spatial scales (adapted from (Nordbotten and Celia, 2011))

Temporal scales are somewhat more challenging to estimate, in part because they are not as easily observable as some of the spatial scales. As with the spatial scales, we group the temporal scales into different categories, beginning with the smallest scale, which we again call the "nano" scale. Processes at this time scale include the dynamics of fluid-fluid interfaces and the partitioning of components among phases at the pore scale, both of which are assumed to occur very fast (and therefore the processes can be assumed to be at equilibrium for models written at larger time scales). The "micro" temporal scale includes wellbore flows (leakage) and the faster end of density segregation. Density segregation is an important consideration and refers to the vertical segregation of CO_2 and brine due to their density differences. This "buoyant segregation" is often required for simplified models to apply, so its time scale is quite important.

The next temporal scale is the "meso" scale, which includes density segregation as well as capillary segregation (which is the time for the capillary transition zone to develop fully). The remaining two time scales, the "macro" and the "mega", include additional processes such as convective mixing (the unstable, gravity-driven miscible mixing of dissolved CO_2 in the bulk brine) and long-time mineral reactions involving precipitation of some of the injected carbon. These scales, which correspond to the multi-year to multi-decade to multi-century scales, are again where many of the practical questions are asked, and they are highlighted with boxes around the

labels in Figure 2.3 to indicate that we usually need to write governing equations at these scales. Detailed discussion of the different time scales can be found in (Nordbotten and Celia, 2011).

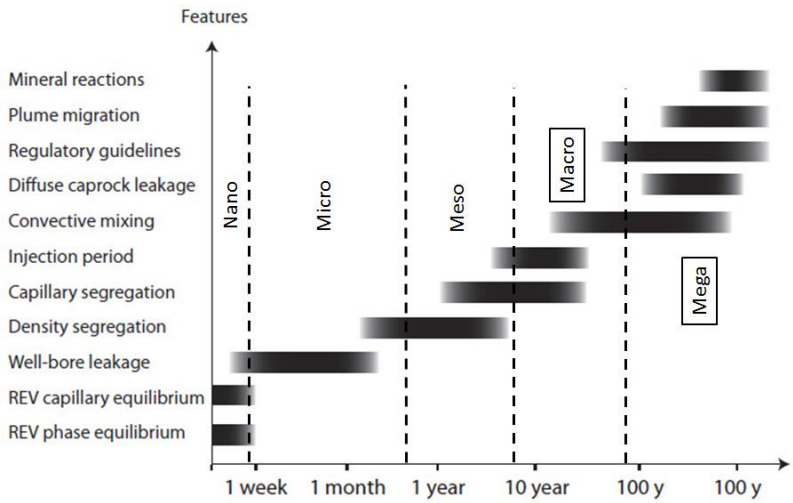

Figure 2.3: Temporal Scales (from (Nordbotten and Celia, 2011))

2.2.3. Modeling philosophies

While a wide range of modeling philosophies can, and often are, followed, there are two specific concepts that seem to be fairly prevalent in CO_2 sequestration modeling literature. In some ways, these represent end-members of the spectrum for modeling possibilities. The first says that as many processes as possible should be represented, in as much detail as possible. Spatial and temporal resolution should be as fine (small) as possible, so that material heterogeneities and other non-uniformities should be represented across many scales, beginning with the smallest possible. Usually the limit on what is "possible" is computing resources, since inclusion of all processes at fine scales of resolution requires use of all available computing resources. Of course, these kinds of high-end models are also limited by data scarcity, but that is often overcome by assumptions about small-scale heterogeneities and associated synthetic data fields.

The second idea is to use a model that is as simple as possible. Such an approach allows for very simple and fast calculations, even to the point of using pencil and paper or a simple spreadsheet. These models, if analyzed in terms of assumptions and limitations, are

found to be very highly restrictive in their assumptions. However, they can provide insights into the system behavior and provide a basis for order-of-magnitude estimates of system responses.

For most practical problems, neither of these approaches is optimal. The first is often so complicated, and requires so much data that is often not readily available, that the end result is an impressive calculation in terms of applied computer science but with results that have very limited practical value in terms of understanding the overall system behavior. Often, the best use of these kinds of highly complex, coupled models is to understand very specific aspects of the system, with the results obtained used to represent the process being studied in some simpler way at larger space or time scales. Similarly, the extreme simplicity of the very simple models provides results that are often so limited in their (restrictive) assumptions that they are also of limited value. They are at best used in the context of broad screening calculations and initial assessments. These observations motivate us to consider the broad middle ground between these two extremes, and to construct a sequence, or hierarchy, of models that become progressively more (or less) complex as assumptions are either added or removed.

2.2.4. Assumptions

The key elements of the second approach followed was to identify the physical processes -and associated relevant spatial and time scale- necessary to address the question posed and ignore, upscale or represent via sub-scale corrections as described in section 2.4, all the remaining ones; and subsequently develop models that are as simple as possible while still capturing/representing the essential physics. Various dominant features of the system are essential in this development of simplified models. The key assumptions, as modified from (Celia and Nordbotten, 2009), to the system used in this dissertation are:

(1) Vertical Equilibrium: It assumes that the dominant flow component is horizontal, that vertical flow components within a given formation can be neglected, and hence both fluids are assumed to be in vertical equilibrium or at hydrostatic.

(2) Dominant spatial features are large-scale layering and concentrated leakage pathways: This allows us to assume a strong spatial scales separation so that the aquifers are treated horizontally and coupled vertically via the vertical wells.

(3) Locally, fluid properties and isotherm systems are constant within a given formation (but can be changed from one formation to another) when both temperature and pressure are not close to the critical point and associated possible phase changes. Thus energy balance equations can be ignored.

(4) Macroscopic Sharp-interface: When local capillary pressure is insignificant, no capillary transition zone will develop leading to both a strong separation between CO_2 and the resident brine, and a clear override of the CO_2 to the top of the formation. See section 2.3.3 and Chapter 4 for more details on this capillary transition zone.

(5) The formations are horizontal and homogeneous: The governing equations can be simplified to analytical solutions (see section 2.3.4) thanks to this strong assumption which is reasonable for a number of practical cases. (Gasda et al., 2008) concluded that during the injection phase of an operation, midcontinent sedimentary formations in North American maybe reasonable approximated by ignoring the slope. In addition assumption of homogeneity is reasonable as the size of the plume increases because its length scale becomes large relative to the heterogeneities within the formation.

(6) Localized leakage pathways parameters uncertainty is a dominant characteristic of the system: Small scale abandoned wells/fractures/faults characterization uncertainty is often much larger than the uncertainty associated with large scale formation parameters (permeability and porosity). We hence assume uncertainty associated with leakage features to be the focus of probabilistic analysis with the concomitant assumptions that formation parameter uncertainty is negligible small in comparison.

Several different combinations of these assumptions can greatly simplify the mathematical description of the system described in section 2.3. An important note is that these assumptions are not hierarchical and are to be considered as independent. Vertical integration does not make sense if the fluids and the flow in the formation are not at Vertical equilibrium. But the Vertical equilibrium assumption does not necessarily imply vertically-integrated governing equations.
For instance, Vertical equilibrium assumption allows a faster vertically averaged pressure solver. But this pressure solution is then used to solve fluid movement and fluid saturation in 3D (hence not vertically-integrated to 2D). In this case there is no flow in the vertical component but fluid movement and saturation can be modeled in full 3D heterogeneous media and pressure solution can then be reconstructed in 3D.

Despite the fact that they are commonly applied together, another example that simplifications associated with vertical equilibrium and vertical integration are in principle independent is the non-equilibrium pressure distribution used to derive the vertically-integrated upconing models developed in (Nordbotten and Celia, 2006b) to model the micro-scale physics close to the leakage pathways. Conversely, a hydrostatic pressure distribution may be considered for simplicity when making estimates of vertical fluxes of a mobile CO_2 phase. Note that using assumptions where they are required and/or appropriate in a modular fashion corresponds well to the object oriented embedded philosophy of C++ our software/framework is based upon.

A final note is that in this work we ignore the drying CO_2 front inside the CO_2 plume, shown in figure 2.4, but will refer to (Nordbotten and Celia, 2006c) for more details.

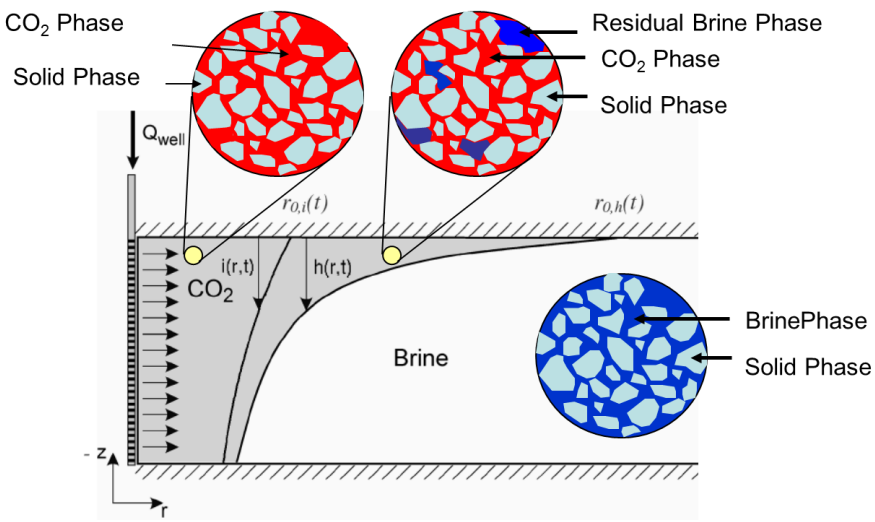

Figure 2.4: Conceptual representation of the CO_2 drying front in the plume

2.3. Modeling options and model hierarchies

2.3.1. Fully coupled 3D numerical models

Many modeling studies are based on the philosophy that a model is always better if it includes as many processes as possible, and resolves space and time as finely as possible. This leads to models that include all processes that could be important, including multi-phase flow, multi-component transport with complex phase partitioning, coupled geomechanical and geochemical reactions, and energy transport with nonisothermal effects. The models include coupling among all of the processes and parameters. The resulting equations are then solved on the most highly-resolved numerical grid that can be computed, usually on massively parallel supercomputers. The general equations will involve mass balances for each component in the system, with appropriate expressions for relative permeability and capillary pressure, multi-phase multi-component diffusion and dispersion, full equations of state, complex flash calculations to determine component partitioning and the resulting phase compositions, energy transport with associated parameters, geomechanical equations with associated parameters, and the usually extensive list of geochemical reaction equations. A complete writing of the equations would take at least one full page and probably more. The fine resolution of space and time also implies a

requirement that all parameters (and there are many) need to be defined over finely resolved spatial domains.

While this approach provides a fairly complete model for the system, it is fraught with complications, including parameter identification for a very large number of parameters (this includes nonlinear functions which need to be parameterized for each material type), a representation of small-scale material heterogeneities and the associated material properties, proper model couplings, nonlinearities throughout the system including some that can be extreme, and severe computational limitations. These models seem generally inappropriate to answer the practical questions, Q1-Q3, posed previously.

2.3.2. Simplified 3D numerical models

There are many ways to simplify the full set of coupled equations described in the previous section. These simplifications almost always include a significant amount of de-coupling of the equations. For example, the flow equations may be de-coupled from the equations for geomechanics by assuming the deformations do not change flow properties significantly. With that assumption, there is only a one-way coupling, so that the geomechanical response may be ignored while solving the flow equations. This simplification often leads the modeler to ignore geomechanics, since it does not have a significant impact on the flow, and the practical questions all revolve around the flow system. Similarly, the geochemical responses may be deemed to take so long that they are insignificant over the time scales of interest for the analysis, and therefore they can be eliminated. Or, like the geomechanics, they may result in changes to flow properties like permeability that are so small that they can be ignored. In these cases, geochemical reactions may be deemed unimportant and therefore not included in the model. Similarly, if the CO_2 is injected into a formation at temperatures close to the temperature of the formation, and no significant changes in temperature are anticipated, then the energy equations may be eliminated. In addition, component partitioning may be described by a simple (equilibrium) partitioning rule (like Henry's Law) rather than a full flash calculation, and miscible displacement of dissolved CO_2

may also be ignored (which is appropriate for time scales small relative to the time scale associated with the onset of the convective mixing process). In these ways, the governing equations may be simplified to, for example, bulk mass balance equations for the two fluids in the system (brine and CO_2) coupled with the multi-phase version of Darcy's Law, an equation for capillary pressure, and a restriction that the phase saturations sum to one. The equation set is then greatly simplified. Of course, some of the couplings can be eliminated while others remain which provides a broad range of possible models.

These simplified 3D models are in fairly wide use and include the codes TOUGH2 (Pruess, 2004), a standard code in the petroleum industry called ECLIPSE (Schlumberger, 2010), and a number of other similar codes that reside at different national laboratories in the US (For example, STOMP from PNNL (White, Oostrom, 1997), NUFT from LLNL (Nitao, 1998)). Examples of partial couplings include the work of (Pruess, 2005) looking at nonisothermal systems and the impact on leakage rates; the work of (Johnson et al., 2005) on coupling geochemical reactions with multi-phase, multi-component flows, and the work of (Rutqvist et al., 2010) on coupling flow and geomechanics. These and other related examples provide ample evidence for the need for these kinds of models for at least some subset of CO_2 injection problems.

Note that these equations still apply over the three-dimensional domain, and are derived based on small spatial scales (due to assumptions like capillary equilibrium and equilibrium phase partitioning). The fine spatial scale of resolution makes these equations challenging to solve when thousands of probabilistic simulations over large-scale highly-refined grid are necessary. But governing equations resulting from the application of simplifying assumptions listed earlier in section 2.2.4 are much more manageable than the fully coupled system.

2.3.3. Vertically-integrated (2D) numerical models with multiple sharp-interfaces

Vertically-integrated equations are motivated, in part, by the much larger lateral size of a formation, compared to its thickness, which motivates models that do not resolve vertical flows but instead concentrate on the much more expansive horizontal dimensions. The resulting equations are derived by integration of the full three-dimensional equations over the direction perpendicular to the top and bottom boundaries of the formation of interest. This direction is often closely aligned with the vertical direction, and for this discussion we will simply assume that it is the vertical direction. While this kind of integration can be performed under any condition, it leads to useful (and simplified) governing equations when the system has developed some identifiable structure in the vertical direction. Often this involves vertical structure to the velocity field, which then translates, via Darcy's law, to a structure for the pressure field. The most common (and simplest) of these structures is an equilibrium condition such that no flow occurs in the vertical direction. This leads to a hydro-static kind of pressure distribution (assuming non-zero vertical permeability). For horizontal formations, this is usually referred to as a condition of "vertical equilibrium" for the pressure distribution. For sloping formations, we refer to it as the “Dupuit assumption”. With this as an assumption for the pressure field, the equations can be simplified significantly. Note that the pressure in each fluid will vary linearly in the vertical direction, with the slope of each line being proportional to the fluid density multiplied by the gravitational constant. Given that the slope is known, we only need to determine the pressure at a single point in the vertical, from which all other pressures can be determined. This kind of pressure distribution, for both the CO_2 and the brine, is shown schematically in Figure 2.5.

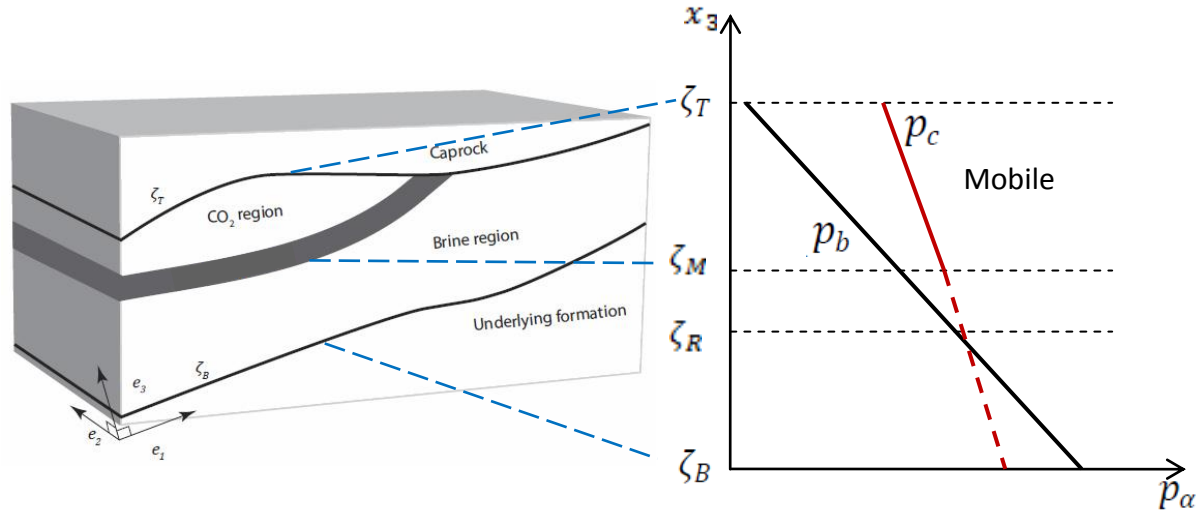

Figure 2.5: Vertical pressure distributions across the formation (adapted from (Celia and Nordbotten, 2011)).

The condition for vertical equilibrium in a CO_2-brine system is that density segregation has taken place. This puts a restriction on the time scale of our model, as discussed earlier and further illustrated in Chapter 4. As shown in Figure 2.3, this is usually a good assumption for models at the macro and mega time scales. If the equations are integrated over the thickness of the formation, then the length scale of the resulting equations will necessarily be larger than the formation thickness, which is consistent with the macro spatial scale. Therefore, vertically-integrated models are usually macro-scale models in both space and time. Given that the macro scale is where our practical questions also reside, this becomes an attractive model to answer practical questions.

We note that vertically-integrated models lead to the widely-used set of sharp-interface models when the thickness of the capillary transition zone is negligibly small (see Chapter 4 for investigation of the applicability of vertical-equilibrium and sharp-interface assumptions). In such cases, simplifications arise because the associated local capillary pressure function, as shown earlier in Figure 2.5, now has a negligibly thick transition zone, so the function becomes a step function (the thickness of the capillary transition zone in Figure 2.5 goes to zero). Two versions of sharp-interface models are shown in Figure 2.6. The left panel is a simple case of CO_2 and

brine with a negligible transition zone. The right panel involves additional regions so that the mobile CO_2 region (bounded below by ζ_M), a region with CO_2 at residual saturation (bounded below by ζ_R – see Figure 2.6), and a region containing dissolved CO_2 that is subjected to convective mixing (bounded below by ζ_C) are all included in the model. See (Nordbotten and Celia, 2011) or (Gasda et al., 2009; Gasda et al., 2011) for details of these kinds of models, which can predict, in a very efficient computational algorithm, both the short-term (injection period) and long-term (post-injection) period of the CO_2 and the displaced brine, including estimates of amounts of mass trapped by both capillary and dissolution trapping. These models, while simplified, still apply to systems with general heterogeneities in all three spatial dimensions, and with irregular topography for the top and bottom boundaries.

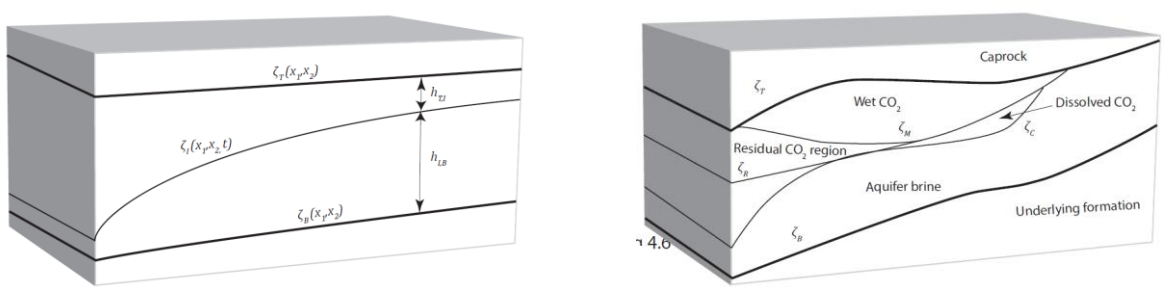

Figure 2.6: Single (a-left) and multiple (b-right) sharp-interface models (from Celia and Nordbotten (2011)).

2.3.4. Simplified Vertically-integrated Analytical and Semi-Analytical Models

The sharp-interface model corresponding to the left panel of Figure 2.6 can be further simplified with the assumption that the entire formation is homogeneous (in both the vertical and horizontal directions), and the top and bottom boundaries are horizontal. With constant fluid properties, and a single vertical injection well delivering CO_2 at a constant rate to the formation (denoted by Q_c), the equations can be greatly simplified through the use of a similarity transformation. The solution for this simple injection problem exhibits radial symmetry, so that the solution depends only on the radial distance from the injection well (r) and time (t). With the definition of the dimensionless group $\chi \equiv \frac{\pi\Phi(1-s_b^{res})}{Q_c}\frac{r^2}{t}$, where Φ is porosity and s_b^{res} is the residual saturation

(fraction of void space occupied by brine) within the CO_2 plume, the equations that depend on radial distance and time can be transformed into a set of Ordinary Differential Equations (ODE) that depends only on the one independent variable, χ. As such, the complicated set of coupled partial differential equations is reduced to a simpler set of ordinary differential equations. When another dimensionless group, given by the ratio of buoyancy forces to viscous forces (see Nordbotten and Celia, 2006a, 2011), is sufficiently small, the equations for simple injection simplify further so that a very simple analytical solution can be written for both the CO_2 thickness and the pressure field. The solution for the CO_2 thickness has the following form,

$$S_c(\chi) = \begin{cases} 0 & \text{if} \quad \chi \geq \lambda \\ \dfrac{1 - s_b^{res}}{\lambda - 1}\left(\sqrt{\lambda/\chi} - 1\right) & \text{if} \quad \lambda^{-1} < \chi < \lambda \\ 1 - s_b^{res} & \text{if} \quad 0 < \chi \leq \lambda^{-1} \end{cases} \tag{1}$$

where S_c represents the thickness of the CO_2 plume, and $\lambda = \frac{k_{rc}/\mu_c}{k_{rb}/\mu_b}$ is the mobility ratio, with μ_c and μ_b denoting viscosity of the $CO_2$and brine, respectively, k_{rc} being the relative permeability for the CO_2 when brine is at residual saturation, and k_{rb} being the relative permeability for the brine in the brine-filled region. Usually $k_{rb} = 1$. Note that, among other things, this equation implies that the CO_2 plume expands in the radial direction in proportion to the square root of time. See (Nordbotten and Celia, 2006a), (Nordbotten and Celia, 2011) and (Celia et al., 2011) for more details about these solutions.

In addition, the shape of the plume has an important dependence on the mobility ratio. Note the potentially important role played by the relative permeability of the CO_2 in the CO_2 region of the plume. This can be a fairly small number (that is, much less than 1), depending on the saturation of brine that is left behind (residual brine saturation). This factor can counter the strong viscosity ratio, and can "flatten" the invading front much more toward a piston-like displacement than the profile with a strong buoyancy override (see Chapter 4 and Nordbotten and Celia (2006a)). Similar closed-form expressions may be derived for the pressure field (see Chapter 3),

from which estimates of important characteristics like Area of Review can be calculated. Note that these general kinds of sharp-interface models have received increased attention recently, especially in the context of modeling CO_2 injection and migration – see (Juanes et al., 2010; Mathias et al., 2009; Dentz and Tartakovsky, 2009a, 2009b; Hesse et al., 2007, 2008).

One limitation of the sharp-interface models described above is the inability to resolve the capillary transition zone. However, the assumption of a sharp-interface can be relaxed so that the vertical integration of the saturations and relative permeabilities reflect the impact of vertically changing saturations. A fully developed capillary transition zone is an example of why gradually changing saturations are of interest in vertically-integrated models. Comparisons of a vertically-integrated model including a capillary transition zone with the commercial simulator ECLIPSE show good agreement for a homogeneous and horizontal formation (see Chapter 4 for more details). The lower computational cost of the vertically averaged model now allows for a study on the impact of choice of saturation – capillary pressure – relative permeability relationship.

2.4. Hybrid models and practical applications

The different simplifications and level of complexity can be collected and placed into an overall hybrid multi-scale modeling framework where detailed numerical models are applied for the processes and specific time and spatial scales where they are needed, and simpler models are used in other regions or as built-in subscale correction to augment the coarse numerical models accuracy while keeping down the number of grid cells by avoiding any grid refinement. Here we present 3 such model types.

The first uses the sharp-interface formulation of Section 2.3.3, following the extended model of Figure 2.6b, applied to the Johansen formation under the North Sea. It models both the injection and post-injection periods, and tracks the mobile and trapped phases of CO_2. Those

results are used to quantify the hypothetical “Sequestration security” figure from the SRCCS – see Figure 2.7 below. The equations are solved numerically in both space and time.

The second model type uses numerical solutions in both space and time, like the model in the first example, with sub-scale analytical corrections around both injection and leaky wells, but also includes diffuse leakage of brine through the confining (caprock) layers. This kind of leakage can have important effects on the development of the pressure field. The model is applied to a hypothetical reservoir set, although it has been applied to both the Alberta Basin and the Illinois Basin (Janzen, 2010).

The third model type is used to model both a single formation injection of CO_2, and a multiple formation one with leakage of both CO_2 and brine along more than a thousand existing wells at a field location in the Alberta Basin. This later model uses a hybrid formation based on a group of models following the simplified sharp-interface models of Section 2.3.4. Different analytical and semi-analytical solutions are used in combination to solve for the CO_2 and brine leakage profiles along all leaky wells, across a stratigraphic sequence involving more than 10 reservoirs in the vertical stack.

2.4.1. Models for both leakage and post-injection

Vertically-integrated numerical models with multiple sharp-interfaces plus sub-scale analytical corrections allow quantification of leakage through local scale features, like wells, while modeling accurately post-injection behavior of the CO_2 plume. In these macro-scale, vertically-averaged numerical models coarse grid blocks are used to avoid high computational demands. When injection wells, leaky wells, or faults are present in a grid block analytical solutions are used locally -within that given grid block- to represent the local behavior of these features. This avoids the need for fine grid resolutions in the x and y directions while still representing the local features accurately. This is a hybrid numerical-analytical model that applies different solutions at different length scales.

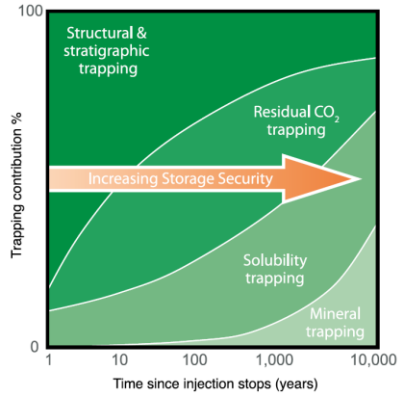

Figure 2.7: Sequestration security depends on a combination of physical and geochemical trapping. Over time, the physical process of residual CO_2 trapping and geochemical processes of solubility trapping and mineral trapping increase. (Figure 5.9 from SRCCS (IPCC, 2005)).

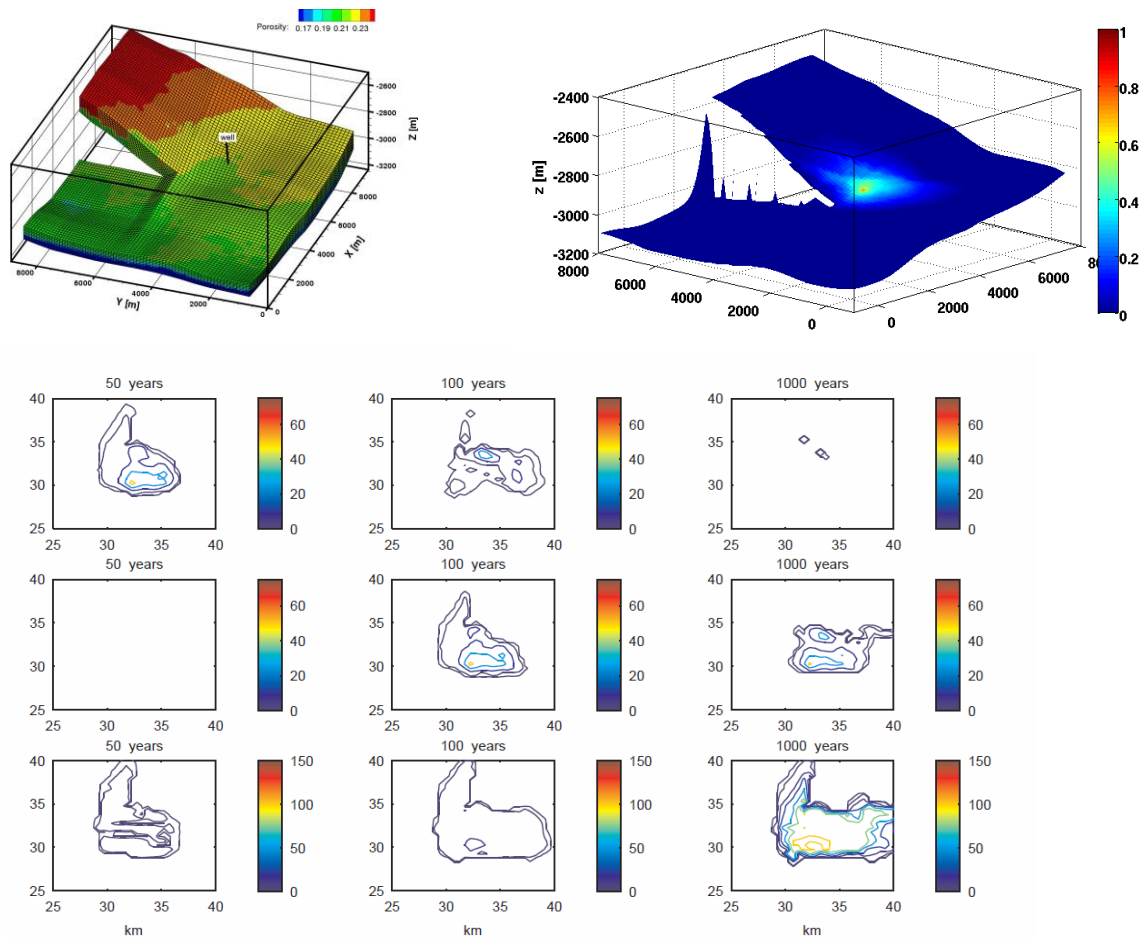

Figure 2.8: Post-injection CO_2 migration and trapping modeling results (six panels) of a multiple sharp-interfaces model applied to the Johansen formation (shown in the upper two figures). Shown is the thickness in meters of the mobile CO_2 in the top panels, of the residual CO_2 in the middle panels, and of the dissolved CO_2 in the bottom panels over 1,000 yrs. (zoom of Figure 5 from (Gasda et al., 2010) and (Gasda et al., 2011)).

An example application of this kind of model has been presented by Gasda et al. (2009). Injection of CO_2 into a spatially heterogeneous formation deep under the North Sea was modeled as part of a code comparison exercise. Results from the model compared wells, see Class et al. (2009), to other codes which solved simplified 3D models from section 2.3.2. The domain involves a deep formation that is split by a large fault zone, with thickness of the sloping formation, permeability, and porosity all varying in space. This calculation showed that fairly complex geometries as well as spatial heterogeneities can be accommodated readily in this model.

The results in Figure 2.8 show how much of the injected CO_2 is present in the mobile phase, the dissolved phase, and as a capillary-trapped phase. Note that this serves as a quantification of the famous Figure 2.7 in the SRCCS, which is a hypothetical figure showing how sequestration security evolves as a function of time since injection has ceased. Figure 2.8 quantifies this concept, and shows for this case that virtually all of the CO_2 is in a trapped state within about 1000 years.

Gasda et al. (2009) also applied to another problem in Class et al. (2009) with expression for analytical solutions for upconing interface location (Nordbotten and Celia, 2006b) and flow rates in the leaky wells, in addition to pressure correction within a grid cell containing a leaky well to relate the cell-average pressure to the local pressure at the leaky well. Results for the test problem, which involved one injection well and one leaky well, matched very well with other solutions solved by simplified 3D models on refined grids taking much more computational effort to compute.

2.4.2. Models with diffuse leakage

The vertically-integrated numerical model with a single sharp-interface (Figure 2.6a) was used in the recent work of Janzen (2010). The model included sub-scale analytical corrections in grid cells that include an injection well hence eliminating the need for any grid refinement. Similarly,

the upconing solution of Nordbotten and Celia (2006b) are used for local correction to grid cells that include leaky wells –this follows the earlier work of Gasda et al. (2009) and Gasda (2008). Janzen (2010) showed that, with these local analytical corrections, kilometer-scale grid sizes can be used while still capturing the local effects of wells with the cells. This includes development and use a modified "Peaceman-type" correction for pressure within the cells that contain wells. This provides significant computational benefits, because the vertical integration is now complemented by a hybrid numerical-analytical multi-scale algorithm in the horizontal directions. Grid blocks have discretization lengths on the macro scale while the micro- and meso-scale effects of local well behaviour are capture by local analytical solutions around the injection well, the leaky wells and ultimately the faults. An example of results of the pressure of the entire system including diffuse brine leakage is show in Figure 2.9.

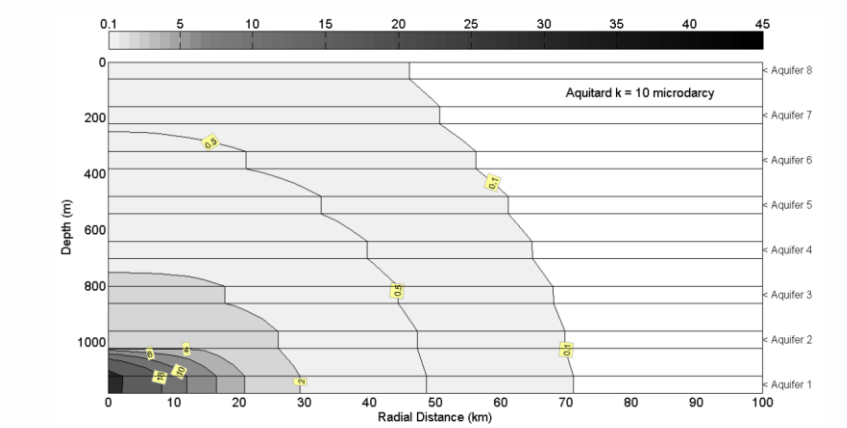

Figure 2.9: Pressure build up contour for system including diffuse brine leakage across caprock formations (taken from (Janzen, 2010).

2.4.3. Large-scale models with leakage along multiple wells

Semi-analytical models based on different analytical solutions using simplified sharp-interface models have been constructed to model multiple formations (10+) and multiple wells (1000+) within a realistic domain. The models represent the entire vertical succession and simulate injection, migration, and leakage across caprock formations into other formations. Here the semi-analytical model uses simple single sharp-interface solutions within each of the formations, and focuses on abandoned wells as leakage pathways across the different formations in the domain.

This model allows quantitative estimation of both CO_2 and brine leakage along the entire vertical succession of permeable and impermeable formations via thousands of abandoned wells, and is sufficiently fast in terms of computation that many thousands of simulations can be run to investigate the impacts of uncertainties in the parameter space. This is a very computationally challenging problem that can only be solved with this class of simplified model.

This modeling approach uses analytical and semi-analytical models described in section 2.3.4. Flow across caprock formations is restricted to flow along wells which is represented by the standard two phase form of Darcy's equation. The solution includes the upconing solutions of Nordbotten and Celia (2006b) with details available in Nordbotten et al. (2005, 2009). The overall algorithm was restricted to hydrostatic initial conditions for pressure with no initial saturation of CO_2 in the domain. Constant pressure conditions were applied along the outer boundary of the domain, which can be either finite of infinite in areal extent. The algorithm required to solve this kind of leakage problem use supplementary assumptions including radial symmetry of all plumes, with no major overlap of CO_2 plumes, superposition of pressure fields, and linearization of all non-linear parameters within a simple time-stepping algorithm. The time stepping is necessary because the nonlinearities in the problem are important and cannot be accommodated in any other way. The need for time-stepping, with the associated updating of the nonlinear terms each time step, is the reason these solutions are referred to as semi-analytical.

The semi-analytical model provides a flexible and very efficient computational framework to study many aspects of the system response to CO_2 injection while accommodating very large numbers of potentially leaky wells (many thousands) and many alternating layers of aquifers and caprock formations. The following sections show some of the results that can be obtained.

- **Multiple formation, multiple wells: choice of injection formation, injection rates, and impacts impacts of $S_{b,res}/k_{rel,C}$**

Many potential injection sites in North America are likely to have tens to hundreds, and possibly thousands, of existing oil and gas wells within the radius of influence (or Area of Review) of a CO_2 injection operation, and this modeling framework allows these systems to be analyzed quantitatively. Thanks to the speed of this semi-analytical model, a user can explore on a standard single-processor personal computer many aspects of the system in a stochastic, or probabilistic, framework.

In Chapter 3 based on (Celia et al., 2011), a realistic example field site is used to simulate injection of CO_2 and possible leakage of CO_2 and brine along old oil and gas wells. The site, around the Lake Wabamun area in Alberta, Canada, involves more than a thousand wells in a domain that was 50 km by 50 km. Each permeable layer in the stratigraphic sequence is assigned parameter values including porosity, permeability, thickness, residual brine saturation (S_B^{res}), and CO_2 relative permeability evaluated at the residual brine saturation ($k_{rel,C}$), based on actual field and laboratory data. Fixed (average) values of porosity and permeability are assigned to each formation, based on measured values, and several different values of residual saturation and relative permeability are considered. The results indicate the system response involves a complex interplay among formation properties, fluid properties, and properties of the leaky wells. An important limitation on injection rates in formations like those around Lake Wabamun is the maximum pressure at the injection well, which in turn depends critically on residual saturation of the displaced brine and the associated relative permeability to the CO_2 in the region containing residual brine. Use of measured values of residual brine saturations and associated CO_2 relative permeability can reduce injection rates by up to 70%. While the measured values were from a single core plug experiment, and questions about upscaling and the appropriate large-scale effective relative permeability remain to be answered, these results indicate quite clearly that careful design of injection well location and orientation will be very important in the overall system design. The work reported in Chapter 3 does not address well design and well placement;

however, well design is certainly a topic that can be studied with the computational modeling approach presented therein.

For all of the injection scenarios considered, the CO_2 plume is significantly smaller than the areal extent of the pressure perturbation. This has implications for well design, where close spacing may be preferred to maximize CO_2 coverage within the domain but is limited due to pressure interference from adjacent wells. It also has important implications for leakage behavior. Because the pressure perturbation tends to spread much farther than the CO_2 plume, brine leakage is observed along many more leaky wells as compared to wells with CO_2 leakage. The signature of brine leakage in these layered sedimentary successions tends to differ from the CO_2 leakage due to the significant buoyant drive that contributes to upward movement of CO_2 in leaky wells but is absent from the brine leakage. Brine will leak both upward and downward, while CO_2 leaks primarily upward. CO_2 also tends to migrate upward over much longer distances, being driven strongly by buoyancy, than does the leaking brine, which is driven only by the pressure increase. Therefore, more CO_2 migrates into shallow subsurface zones as compared to brine leakage, although both tend to exhibit patterns of leakage into intervening permeable layers while flowing along leaky wells.

The lack of data for hydraulic properties of abandoned wells requires a stochastic approach for leakage analysis, where the dominant uncertainty is in the properties of leaky wells. Chapter 3 uses several different methods to characterize the randomness of the effective permeability of the well materials and surrounding damage zone in the rock. When no information is available to constrain the parameters, then a purely random method is used with a given probability distribution used to assign well properties randomly. When qualitative information about the wells is available, a systematic evaluation of those data, like that used by Watson and Bachu (2008, 2009), may be used to constrain the randomness. In those cases, the well properties have a mixed deterministic-stochastic nature through constraints on the probability distributions used to define the effective well permeabilities. Spatial correlation structure

assigned along a given well also plays an important role in the amount and nature of the resulting leakage. Additional spatial correlation among neighboring wells may also be assigned, although not explored to date. These and other stochastic approaches fit naturally into the computational model developed.

- **Impact of abandoned wells parameter uncertainty on leakage**

Another investigation using this semi-analytical model is achieved where two sets of scenarios are used to explore the impact that material conditions of different well segments have on the total amount of leakage. They illustrate a methodology that quantifies the amount of CO_2 leakage one can expect as a function of the dominant parameters describing the probability density function for effective permeability of leaky wells. The first scenario explores the impact the permeability of different well regions (shallow and deep regions as defined in Watson and Bachu (2008)) had on the total amount of leakage. The second set of simulations looks at the interplay between wells with degraded cement and the fraction of wells that had intact cement. The methodology presented addresses broad issues such as the design of sequestration operations, safety compliance expectations, amount of information needed for permitting procedures, site specific regulations, and issuance of carbon credits.

In the first case the results show that shallow permeability is as important as deep permeability, largely due to the fact that wells ending in deeper formations than the injection formation would be characterized by “shallow” permeability in the zones of CO_2 injections. Moreover, in the first scenario presented in Nogues et al. (2011) it is proposed based on studies done by Watson and Bachu (2008) that most of the well is comprised by what is categorized as “shallow region”. Therefore, it is natural that leakage across a well would be dominated by the characteristics of this region. This finding is interesting because the shallow region of a well would most likely receive less attention when abandoning or constructing the well since it is the deeper region of the well where most of the production or injection occurs. Policymakers could

address this issue by making sure future well abandonments provide good sealing throughout the entire depth of the well.

In the second scenario the results show that the permeability of the degraded wells tends to more strongly control the total leakage than the fraction of degraded wells. This highlights the need for a comprehensive measurement program focused on reentering abandoned wells, to determine effective well permeabilities.

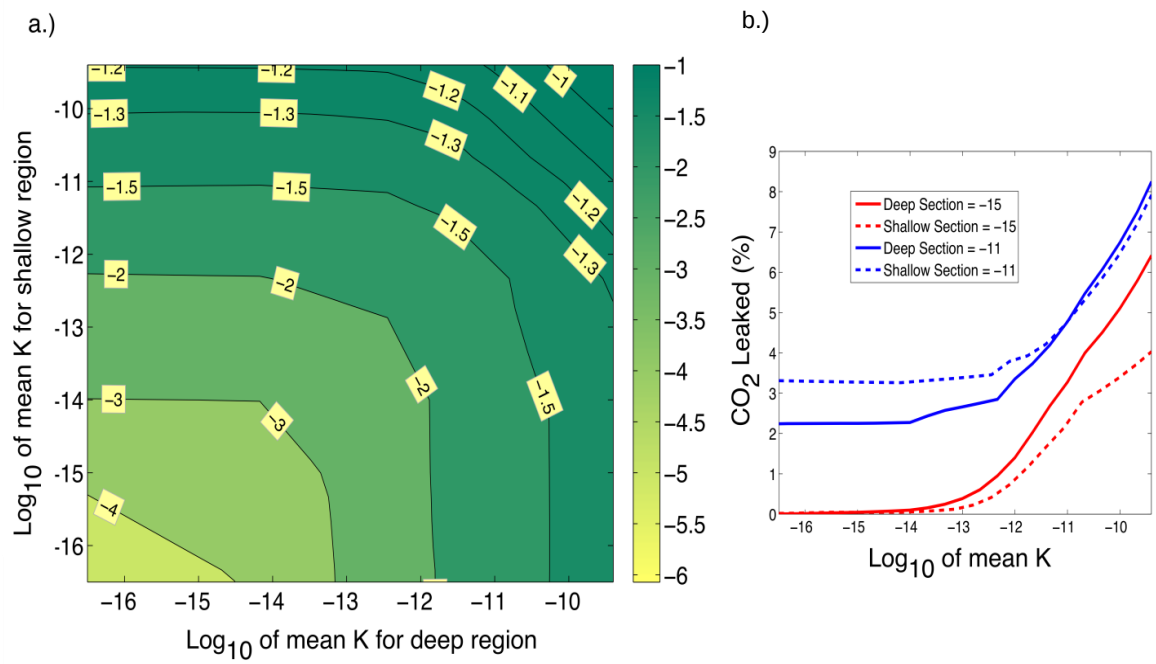

Figure 2.10: a.) Parameter space of CO2 leakage: the color scale is a log base 10 of the ratio of the amount of CO_2 leaked to CO_2 injected after 50 years of injection as a function of mean permeability of well sections. The abscissa represents the mean permeability of the deep region of a well, while the ordinate represents the mean permeability of the deep region of the well. The leakage values represent the maximum amount of CO_2 leaked with a 95% confidence. b.) Transects showing the percent of CO_2 leaked across a range of mean permeability values while maintaining one of the well section's mean permeability constant. (Taken from Nogues et al. (2011))

These kinds of results may be used to relate leakage target values to specific well field parameters, thereby providing a basis for well integrity assessment. For instance, for the specific case considered herein, and for the strong assumptions used to generate the distributions of well

permeabilities (see Nogues et al. (2011), the leakage of CO_2 is not expected to exceed 1% if the mean permeability of leaky wells does not exceed 1 Darcy, as shown in Figure 2.10. It can also be concluded that for the given injection rates and formation parameters, and the constriction on the permeability probability density functions (i.e. unit variance) one can expect at most a total leakage of CO_2 around 12%. These results have direct implications for policy makers and operators. Policy makers on one hand should be aware when writing regulations that there is a direct correlation between a certain amount CO_2 leakage and a maximum value of well permeability. This is an indication that regulation for CCS should be adaptive and flexible enough to capture the specific details of each operation. Operators on the other hand should be able to prove in some logical manner that the well permeabilities are below an established threshold or that the design of the operation will prevent the passing of a leakage threshold.

Though more detailed analysis could be done in the future (i.e. impact of well remediation, considering correlations among wells, changing formation parameters, injection rates, number of injection wells etc.), Chapter 3 and Nogues et al. (2011) provide two useful examples of frameworks using this semi-analytical model allowing to determine probabilistically - via tens of thousands of simulations - risk profiles involving statistically significant total CO_2 and brine leakage amounts, given an uncertainty in the well permeability parameters. These modeling frameworks and the methodology could be considered when designing CCS regulations and CCS operation standards.

While the semi-analytical model is able to provide many insights into the overall system behavior, it is clearly limited in its scope by the restrictive assumptions on which it is based. Recent work in Princeton University's Subsurface Hydrology Group, Bergen University Mathematical Department, and Geological Storage Consultant Inc., continues to move toward hybrid models that can provide numerical solutions in regions where the restrictive assumptions are not applicable, while continuing to use analytical and semi-analytical solutions in regions where they are appropriate. They are also working with other groups to try to develop the

beginnings of a database for appropriate hydraulic properties for old – and potentially leaky – oil and gas wells. We believe these additions in both model capabilities and in data collection will allow for reductions in uncertainties and associated increases in confidence as large-scale field sites are studied for possible injection of captured CO_2.

- **Site selection using the CO_2 plume and the pressure analytical solution**

Deardorff (2009), Deardorff and McCray (2011), and Bandilla et al. (2011) provide a specific application example of the simplified analytical solutions described in section 2.3.4, CO_2 plume outer radius equation in this case, which incorporated into screening methodologies offer key advantages for early-phase project siting, particularly where little or no geologic data is available. They described how these can be rapidly applied at little or no cost, and can thus enable more costly site characterization methods to be effectively and efficiently utilized. Their approach allows a user to evaluate the most likely radius of a CO_2 plume given available subsurface data and injection rate, as well as the likely range and sources of uncertainty in the model result. This information enables a preliminarily determination of whether the total volume of CO_2 can likely be stored in a particular saline aquifer, and enables the evaluation of known or assumed risk associated with CO_2 plume (and critical pressure in the case of Bandilla et al. (2011) discussed in Chapter 5) intersection with leakage pathways (e.g., oil-gas wells, fractures, faults, or mineral resources). Quantification of the result uncertainty as a function of combined input-parameter uncertainty can be utilized for decision-making purposes or to narrow the focus of further subsurface investigation to reduce the uncertainty and risk associated with a decision.

Model sensitivity analysis and Monte Carlo simulation were applied within a geospatial framework in (Deardorff, 2009; Deardorff, McCray 2011) for example to enable the risk-based evaluation of CCS potential based on two types of risk: 1) the leakage risk associated with CO_2 plume size and intersections with existing oil-gas well infrastructure and 2) the project development risk associated with uncertain geologic characteristics. The model was applied to 16 candidate saline aquifers near the site of a proposed coal-fired power plant in the Denver-

Julesburg Basin of Colorado, to preliminarily qualify CCS potential based on expected plume size and the number of expected oil-gas well intersections, and to narrow the focus of further subsurface investigation. Simulations were implemented in Microsoft Excel, enabling the rapid computation of up to 32,000 injection simulations with random number generation of uncertain input parameters from expected ranges or known data distributions. For the cases evaluated, the model (ignoring the economic component) was most sensitive to the hydrostatic pressure of the injection formation, followed by temperature, thickness, porosity, injection rate, time of injection, and relative permeability of CO_2 of roughly equal sensitivity and showing formation fluid salinity to be of least importance to the model output. Six formations at the site were determined to offer high potential as CCS targets and five formations were screened out as viable CCS targets based on the chosen screening criteria. Five known formations with no characterization data screened favorably based on expected ranges of uncertainty and were designated as having moderate CCS potential based on project development risks posed by geologic uncertainty.

The methodology applied in these studies could be helpful to both regulators and the private sector to rapidly assess multiple targets for relative CCS potential, and enable a risk-based decision on which targets should be selected for additional data collection or numerical modeling, especially in cases where little or no geologic data is available.

2.5. Summary of the modeling progress since SRCCS: 2011 state of play

The range of models described in this Chapter and conceptually summarized in Figure 2.11, along with the associated hybrid and multi-scale approaches, can be used as a framework for general model development to specifically address questions Q1-3 presented in section 2.2.1 but also a broader range of practical questions for CO_2 injection operations.

2.5.1. Summary of the various vertically-integrated models

Figure 2.11 is a simple attempt to visually conceptualize the differences between the main approaches described in section 2.3.

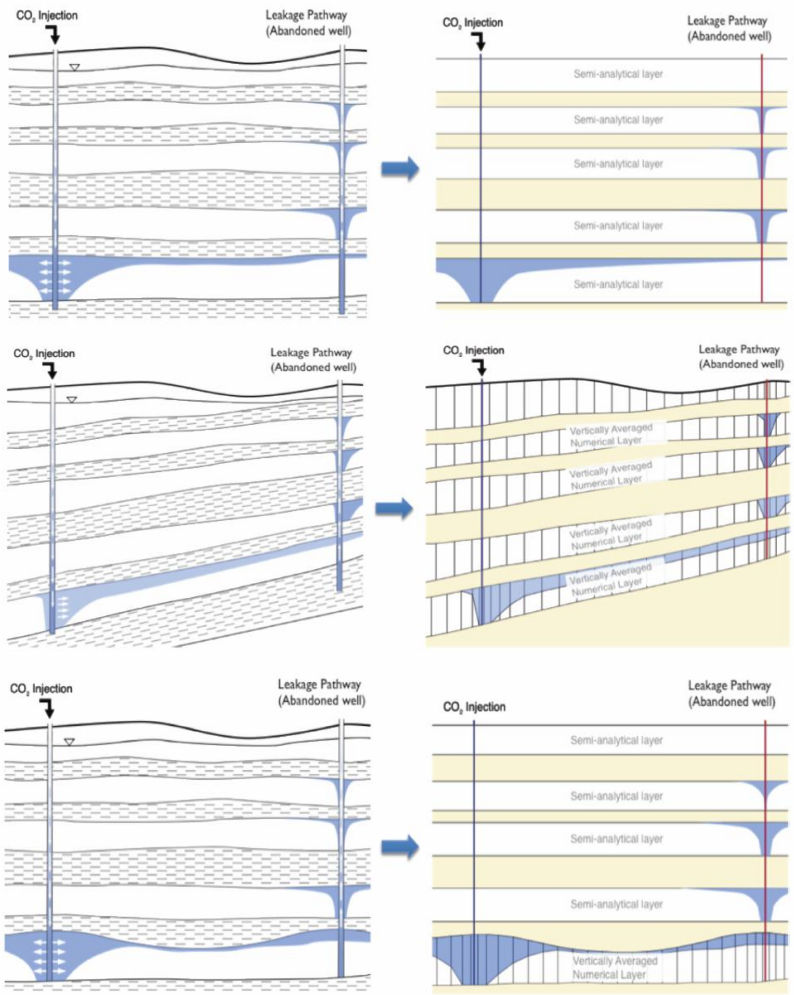

Figure 2.11: Conceptual schematics of vertically-integrated (top) semi-analytical model, (middle) numerical model, (bottom) hybrid model mixing the two. (from (Dobossy et al., 2011))

An over-arching goal is the development of a very flexible hybrid-modeling environment where combinations of all of the modeling types outlined in Section 2.3.3 and 2.3.4 could be deployed within a single simulation project. In regions of high concentrated leak rates, for example along poorly sealed abandoned wells, complex nonisothermal effects may need to be coupled with the multi-phase flow along the wellbore. In the multi-scale context, this would be a

very involved calculation, but it is made manageable by only performing the calculation along the (one-dimensional) wellbore.

These leakage scenarios can be embedded within an overall semi-analytical framework for most parts of the domain, while the remainder would be simulated by a more complex numerical model that may or may not involve the vertical equilibrium assumption, depending on the appropriate length and time scale analyses. Finally, the models used in different regions of the domain may also change with time, again based on time-scale analysis for an ongoing injection operation. The challenge to design the appropriate hybrid computational schemes while make the underlying algorithms transparent to the user, but still allowing some amount of user control to guide the simulation, is a significant challenge but one worth pursuing as the CCS industry develops and matures.

2.5.2. Commercial software development by Geological Storage Consultant Inc.

With evolving legislation in both the United States and Europe (see Chapter 5), a need is emerging for practical assessment of leakage risk. As described above in order to accurately predict leakage of brine and CO_2 from the injection layer, the geological information for the injection site and the location and makeup of the man-made leakage pathways previously alluded to must be taken into account. Unfortunately, both the geology and abandoned well metadata are typically high in uncertainty, which must be accounted for. With such a high number of random variables, the current state of the art is running many realizations of a system, using a Monte Carlo approach. This requires that the underlying solution algorithms be accurate, and efficient. As described in section 2.3.2 many researchers in both academia and industry have turned to robust numerical analysis packages used in the oil industry. However, due to the large range of scales important to this problem such modeling techniques become computationally expensive for all but the most basic analysis. The computational model described above, developed at Princeton University, and currently being commercialized by Geological Storage Consultants, has been shown to be efficient with sufficient accuracy to allow for comprehensive financial risk

assessment of CO_2 injection projects (see Figure 2.12). (Dobossy et al., 2011) present how the model allows for mixing solution methods- using computationally expensive algorithms for formations of greater importance (e.g.- the injection formation) and more efficient, simplified algorithms in other areas of the domain. This ability to arbitrarily mix solution methods offers significant flexibility in the design and execution of models. These models have very promising applications in both the CCS regulatory permitting and insurance sectors.

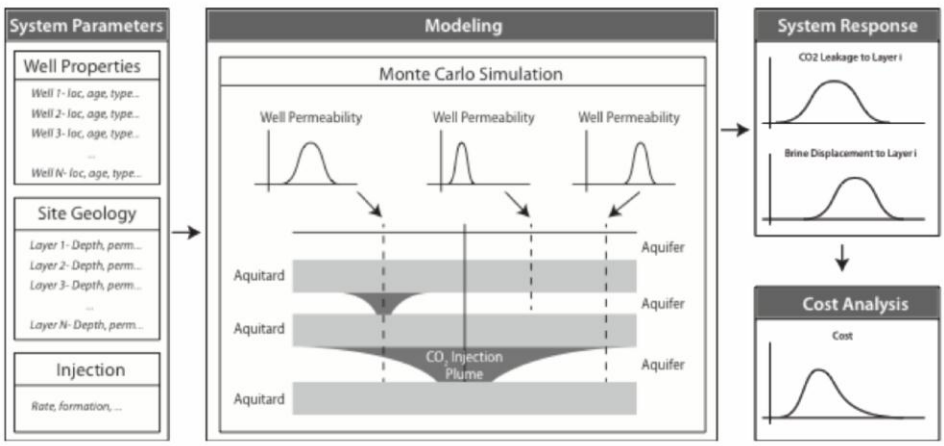

Figure 2.12: Risk assessment of leakage through abandoned wells utilizing Monte Carol simulation (from (Dobossy et al., 2011))

2.5.3. Publically available web-interface

Finally, while more involved and coupled hybrid models are being pursued, it is also extremely worthwhile to make some of the very simple solutions described above available for general use. This is also complementary to Pruess et al. (2009) remark “CCS regulations (in formative stage) must be based on a rational, process-based understanding of CO_2 behavior in the subsurface. Mathematical models are a chief source of such understanding, informing regulators about what is practical and feasible; At the same time, it is evolving regulations that will influence/determine the needs and objectives that must be met by mathematical models.” (Pruess et al., 2009)

For example, the solution given in section 2.3.4 can form the basis for a set of simple models that can describe the CO_2 plume, the associated pressure field, and some simple forms

of leakage along, for example, abandoned wells. Such a set of simple solutions now exists as part of a web interface – see subsurface.princeton.edu/CO2interface/ and Figure 2.13. We believe that this tool and others like it that are certain to be developed by various research groups around the world (see for example (MIT, 2011) and (Stanford, 2011)), can provide very useful tools for policy makers and the general public. Of course, the assumptions that underlie the solutions, and thereby restrict their usage, need to be emphasized whenever possible. But the availability of such tools seems to be a goal that is worth pursuing.

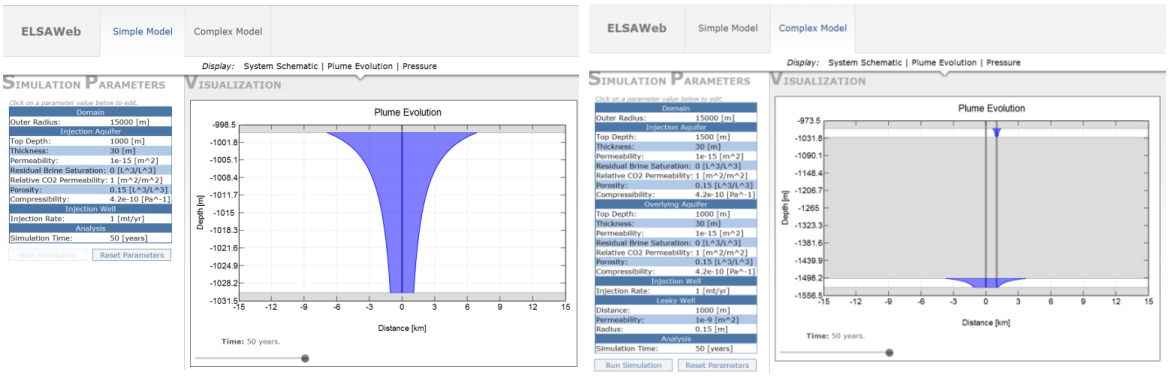

Figure 2.13: Simple solutions from the web interface [subsurface.princeton.edu/CO2interface/]

2.6. Conclusion

The range of models described in this Chapter, based on (Court et al., 2011), along with the associated hybrid and multi-scale approaches, can be used as a framework for general model development to address a wide range of practical questions for CO_2 injection operations. A number of enhancements would lead to a robust and very useful modeling toolkit. Among the many possibilities for additions and improvement, we mention just a few that are ongoing in their development. These include more general implementations of models that use vertical equilibrium of pressure as the sole assumption. These models would include heterogeneity of material properties in all three dimensions, fully developed (nonzero) capillary transition zone thicknesses, irregular and sloping geometries, and other complications. In hybrid models that

include leaky wells, the local analytical corrections would need to be modified to accommodate the more complex local environments within a single grid cell in a simulator, and other local corrections would need to be developed, but the general outline remains as presented herein.

Overall, these and other modeling approaches, following in the broad hybrid and hierarchical framework outlined herein, provide a valuable foundation on which quantitative analyses of CO_2 sequestration projects can be analyzed and evaluated. Through a comprehensive analysis of the important space and time scales associated with the injection operation, models can be developed that are motivated by the questions that need to be answered. Development of a hierarchy of modeling approaches allows all of the relevant assumptions (and associated limitations) to be presented in a transparent way. Furthermore, the scaling arguments investigated further in Chapter 4 show when certain models may be appropriate while others may not be. Overall, site- and situation-specific hierarchical models are developed by defining the question to be answered, which then guides the choice of relevant physical processes, temporal and spatial dynamics, and mathematical description within the modeling tools. This hierarchy covers an entire spectrum of modeling options: from simplified and CPU-efficient analytical and semi-analytical models, used in Chapter 3, for multiple formations (10+) and multiple wells (1000+) capable of large-scale probabilistic investigations of a system's parameters; to vertically-integrated numerical models solving injection (used in Chapter 4 and 6) and post-injection CO_2 migration, incorporating heterogeneity and complex topography, without the CPU-cost of traditional numerical models. Combining these different modeling approaches into a broad hybrid-model approach represents some of the most significant progress in the field since the 2005 SRCCS with very promising on-going and future work.

2.7. References

Bandilla Karl W., Kraemer Stephen R. & Birkholzer, J. 2011, "Using the concept of critical pressure to define the Area of Review for CO2 injection", International Journal of Greenhouse Gas Control. in review.

Celia, M.A. & Nordbotten, J.M. 2011, "How simple can we make models for CO2 injection, migration and leakage?", Energy Procedia, vol. 4, pp. 3857-3864.

Celia, M.A. & Nordbotten, J.M. 2009, "Practical Modeling Approaches for Geological Storage of Carbon Dioxide", Ground Water, vol. 47, no. 5, pp. 627-638.

Celia, M.A., Nordbotten, J.M., Court, B., Dobossy, M. & Bachu, S. 2011, "Field-scale application of a semi-analytical model for estimation of CO2 and brine leakage along abandoned wells", International Journal of Greenhouse Gas Control, vol. 5, no. 2, pp. 257-269.

Class, H., Ebigbo, A., Helmig, R., Dahle, H., Nordbotten, J., Celia, M., Audigane, P., Darcis, M., Ennis-King, J., Fan, Y., Flemisch, B., Gasda, S., Jin, M., Krug, S., Labregere, D., Naderi Beni, A., Pawar, R., Sbai, A., Thomas, S., Trenty, L. & Wei, L. 2009, "A benchmark study on problems related to CO2 storage in geologic formations", Computational Geosciences, vol. 13, no. 4, pp. 409-434.

Court, B., Celia, M.A., Nordbotten, J.M., Dobossy, M., Elliot, T.R., Bandilla, K.W., 2011, "Modeling Options to Answer Practical Questions for CO2 Sequestration Operations", available at http://arks.princeton.edu/ark:/88435/dsp01rf55z769f.

Deardorff, J. 2009, "The geologic carbon sequestration potential of the Denver-Julesburg Basin of Colorado: applied methodologies for basin scale and site specific assessment of CO2 sequestration potential.", M.S. Thesis, Environmental Science and Engineering Division, Colorado School of Mines, Golden CO.

Deardorff, J. & McCray, J.E. 2011 "A risk-based analytical method for assessing CO2 sequestration potential", submitted to Ground Water.

Dentz, M. & Tartakovsky, D.M. 2009a, "Abrupt-Interface Solution for Carbon Dioxide Injection into Porous Media", Transport in Porous Media, vol. 79, no. 1, pp. 15-27.

Dentz, M. & Tartakovsky, D.M. 2009b, "Response to "Comments on Abrupt-Interface Solution for Carbon Dioxide Injection into Porous Media by Dentz and Tartakovsky (2008) by Lu et al. Transport in Porous Media, 79(1), pp 39-41. doi: 10.1007/s11242-009-9363-8.", Retrieved from: http://escholarship.org/uc/item/2h02b5tq.

Dobossy, M.E., Celia, M.A. & Nordbotten, J.M. 2011, "An efficient software framework for performing industrial risk assessment of leakage for geological storage of CO2", Energy Procedia, vol. 4, pp. 4207-4214.

Gasda, S., Nordbotten, J. & Celia, M. 2009, Vertical equilibrium with sub-scale analytical methods for geological CO_2 sequestration, Springer Netherlands.

Gasda, S.E., Celia, M.A. & Nordbotten, J.M. 2008, "Upslope plume migration and implications for geological CO_2 sequestration in deep, saline aquifers", The IES Journal Part A: Civil & Structural Engineering, vol. 1, no. 1, pp. 2.

Gasda, S.E., Nordbotten, J.M. & Celia, M.A. 2010, "THE IMPACT OF LOCAL-SCALE PROCESSES ON LARGE-SCALE CO2 MIGRATION AND IMMOBILIZATION", XVIII International Conference on Water Resources CMWR 2010 J. Carrera (Ed) CIMNE, Barcelona, available at http://congress.cimne.upc.es/cmwr2010/Proceedings/docs/a176.pdf.

Gasda, S.E. 2008, "Numerical Models for Evaluating CO2 Storage in Deep Saline Aquifers: Leaky Wells and Large-scale Geological Features", Ph.D Thesis available at http://arks.princeton.edu/ark:/88435/dsp01j098zb09n.

Gasda, S.E., Nordbotten, J.M. & Celia, M.A. 2011, "The impact of local-scale processes on large-scale CO2 migration and immobilization", Energy Procedia, vol. 4, pp. 3896-3903.

Gherardi, F., Xu, T. & Pruess, K. 2007, "Numerical modeling of self-limiting and self-enhancing caprock alteration induced by CO2 storage in a depleted gas reservoir", Chemical Geology, vol. 244, no. 1-2, pp. 103-129.

Hesse, M.A., Orr, F.M., Jr. & Tchelepi, H.A. 2008, "Gravity currents with residual trapping", Journal of Fluid Mechanics, vol. 611, pp. 35-60.

Hesse, M.A., Tchelepi, H.A., Cantwell, B.J. & Orr, F.M., Jr. 2007, "Gravity currents in horizontal porous layers: transition from early to late self-similarity", Journal of Fluid Mechanics, vol. 577, pp. 363-383.

Janzen, A. 2010, "Development and Application of a Multi-scale, Multi-layer Numerical Model for CO2 Injection", Master Thesis available at http://arks.princeton.edu/ark:/88435/dsp01np193917f.

Johnson, J.W., Nitao, J.J. & Morris, J.P. 2005, "Reactive transport modeling of cap rock integrity during natural and engineered CO2 storage, Carbon Dioxide Capture for Storage in Deep Geologic

Formations", Results from the CO2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson, (ed.), Elsevier, London, pp. 787–814.

Juanes, R., MacMinn, C. & Szulczewski, M. 2010, The Footprint of the CO_2 Plume during Carbon Dioxide Storage in Saline Aquifers: Storage Efficiency for Capillary Trapping at the Basin Scale, Springer Netherlands.

Kharaka, Y.K. 2009, "Reactive transport modeling to study changes in water chemistry induced by CO2 injection at the Frio-I brine pilot", Chemical Geology, , no. LBNL-3056E.

Kharaka, Y.K., Cole, D.R., Hovorka, S.D., Gunter, W.D., Knauss, K.G. & Freifeld, B.M. 2006, "Gas-water-rock interactions in Frio Formation following CO2 injection: Implications for the storage of greenhouse gases in sedimentary basins", Geology, vol. 34, no. 7, pp. 577-580.

Mathias, S.A., Hardisty, P.E., Trudell, M.R. & Zimmerman, R.W. 2009, "Approximate Solutions for Pressure Buildup During CO2 Injection in Brine Aquifers", Transport in Porous Media, vol. 79, no. 2, pp. 265-284.

Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L. & (Eds.) 2005, IPCC Special Report on Carbon Dioxide Capture and Storage, New York, NY: Cambridge University Press.

Michael, K., Arnot, M., Cook, P., Ennis-King, J., Funnell, R., Kaldi, J., Kirste, D. & Paterson, L. 2009, "CO2 storage in saline aquifers I—Current state of scientific knowledge", Energy Procedia, vol. 1, no. 1, pp. 3197-3204.

MIT 2011, "Carbon Capture and Sequestration Technologies at MIT, CO2 thermophysical property calculator,", http://sequestration.mit.edu/tools/index.html..

Nitao, J.J. 1998, "Reference manual for the NUFT flow and transport code, version 3.0", Lawrence Livermore National Laboratory, UCRL-MA-130651-REV-1.

Nogues, J.P., Court, B., Dobossy, M., Nordbotten, J.M. & Celia, M.A. 2011, "Quantifying CO2 Leakage in a Geological Sequestration Operation under Parameter Uncertainty", International Journal of Greenhouse Gas Control, in review.

Nordbotten, J.M. & Celia, M.A. 2011, "Geological Storage of CO2: Modeling Approaches for Large-Scale Simulation", with John Wiley and Sons, Inc., in press.

Nordbotten, J.M. & Celia, M.A. 2006a, "Similarity solutions for fluid injection into confined aquifers", Journal of Fluid Mechanics, vol. 561, pp. 307-327.

Nordbotten, J.M. & Celia, M.A. 2006b, "An improved analytical solution for interface upconing around a well", Water Resources Research, vol. 42, no. 8, pp. W08433.

Nordbotten, J.M. & Celia, M.A. 2006c, "Analysis of Plume Extent using Analytical Solutions for CO2 Storage", From Proceedings of 2006 CMWR Conference available at http://arks.princeton.edu/ark:/88435/dsp01z603qx41q.

Nordbotten, J.M., Celia, M.A. & Bachu, S. 2005, "Injection and storage of CO2 in deep saline aquifers: Analytical solution for CO2 plume evolution during injection", Transport in Porous Media, vol. 58, no. 3, pp. 339-360.

Nordbotten, J.M., Kavetski, D., Celia, M.A. & Bachu, S. 2009, "Model for CO2 Leakage Including Multiple Geological Layers and Multiple Leaky Wells", Environmental science & technology, vol. 43, no. 3, pp. 743-749.

Pruess, K. 2004, "The TOUGH Codes—A Family of Simulation Tools for Multiphase Flow and Transport Processes in Permeable Media", Vadose Zone J., vol. 3, pp. 738-746.

Pruess, K., Birkholzer, J.T. & Zhou, Q. 2009, "Mathematical models as tools for probing long-term safety of CO2 storage", LBNL Paper LBNL-1587E. Retrieved from: http://www.escholarship.org/uc/item/04w053xn.

Pruess, K. 2005, "Numerical studies of fluid leakage from a geologic disposal reservoir for CO2 show self-limiting feedback between fluid flow and heat transfer", Geophysical Research Letters, vol. 32, no. 14, pp. L14404.

Rutqvist, J., Vasco, D.W. & Myer, L. 2010, "Coupled reservoir-geomechanical analysis of CO2 injection and ground deformations at In Salah, Algeria", International Journal of Greenhouse Gas Control, vol. 4, no. 2, pp. 225-230.

Schlumberger 2010, "ECLIPSE Technical Description".

Schnaar, G. & Digiulio, D.C. 2009, "Computational Modeling of the Geologic Sequestration of Carbon Dioxide", Vadose Zone Journal, vol. 8, no. 2, pp. 389-403.

Shukla, R., Ranjith, P., Haque, A. & Choi, X. 2010, "A review of studies on CO2 sequestration and caprock integrity", Fuel, vol. 89, no. 10, pp. 2651-2664.

Stanford 2011, "Relative permeability explorer", http://pangea.stanford.edu/research/bensonlab/relperm/index.html.

USEPA (U.S. Environmental Protection Agency) 1994, "Determination of Maximum Injection Pressure for Class I Wells, United States Environmental Protection Agency Region 5—Underground Injection Control Section Regional Guidance #7", EPA, Washington, DC, USA; available at http://www.epa.gov/r5water/uic/r5guid/r5_07.htm.

Watson, T.L. & Bachu, S. 2009, "Evaluation of the Potential for Gas and CO2 Leakage Along Wellbores", Spe Drilling & Completion, vol. 24, no. 1, pp. 115-126.

Watson, T.L. & Bachu, S. 2008, "Identification of wells with high CO_2-leakage potential in mature oil fields developed for CO_2-enhanced oil recovery", Paper SPE 112924. SPE Improved Oil Recovery Symposium, Tulsa, OK, U.S.A., 19–23 April.

White, M.D. & Oostrom, M. 1997, "STOMP, Subsurface Transport Over Multiple Phases", Pacific Northwest National Laboratory Report PNNL-11218, Richland, WA, October 1997.

Chapter 3

Field-scale application of a semi-analytical model for estimation of CO_2 and brine leakage along old wells

This chapter was adapted from: M.A. Celia, J. Nordbotten, B. Court, M. Dobossy, and S. Bachu, (2010), *Field-scale Application of a Semi-analytical Model for Estimation of Leakage Potential Along Old Wells*, *International Journal of Greenhouse Gas Control,* vol. 5, no. 2, pp. 257-269.

3.1. Introduction

When considering geological sequestration of CO_2, the main environmental concern is leakage of the injected CO_2, as well as possible leakage or large-scale displacement of the resident brine. One potentially important leakage pathway is associated with the century-long legacy of oil and gas exploration and production, which has resulted in many millions of wells having been drilled around the world through otherwise excellent caprock formations. Because a successful CO_2 sequestration operation requires a competent caprock formation overlying the injection formation, these oil and gas wells may compromise the efficacy of sequestration operations by providing

preferential flow pathways through the caprock. This is especially true in North America, where millions of oil and gas wells have been drilled since the late 1800's – see Figure 3.1.

Gasda et al. (2004) analyzed the spatial density of wells that perforate a particular formation in the Alberta Basin in Canada. Their results indicated that tens to hundreds of wells might be contacted by a typical CO_2 plume. If the area of concern is expanded to include regions of possible brine migration and leakage, the number of wells of concern increases further. For a large-scale injection operation that continues over several decades, the domain that needs to be analyzed may be on the order of thousands of square kilometers. Within that domain, the vertical structure, particularly the major layers of permeable (aquifer) and essentially impermeable (caprock or aquitard) formations, must be taken into account (see, for example, Nordbotten et al. (2004)). Within this three-dimensional domain, many hundreds of wells may exist, each with a different depth of penetration, and with properties that have large uncertainty. The uncertainty of the key parameters associated with well leakage, coupled with the underlying complexity associated with the physics and mathematics of two-phase flow (CO_2 and brine), make this a computationally challenging problem. Among others, Schnaar and Diguilio (2009) provide a useful review summarizing different modeling approaches and Michael et al (2009a,b) provide a good overview of current state of scientific knowledge on CO_2 sequestration in saline aquifers and experience from existing sequestration operations.

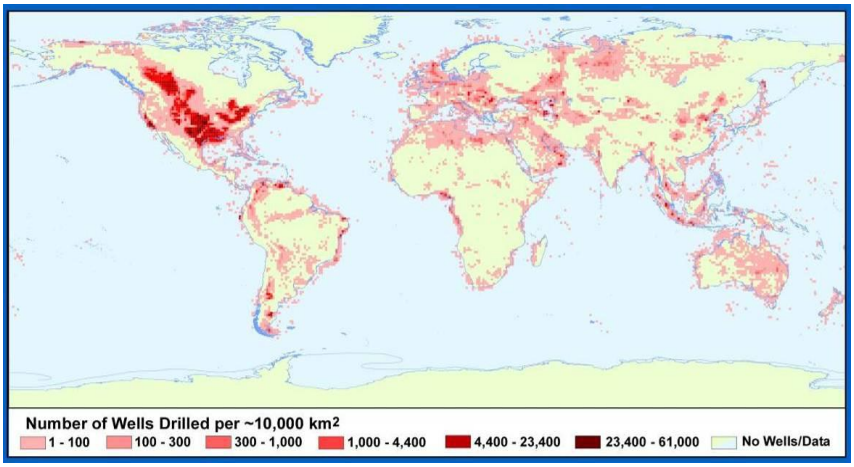

Figure 3.1: Worldwide density of wells (from IPCC, 2005).

To overcome computational limitations of existing multi-phase simulators, a new set of computational models has been developed that can solve problems involving large spatial domains with many vertical layers and many existing wells. The basic components of the model can be found in Nordbotten et al. (2004, 2005a,b, 2009), Nordbotten and Celia (2006a,b), and Celia and Nordbotten (2009, 2011). Simple example applications of different parts of the model can be found in those papers as well as in Nordbotten et al. (2005a), Celia et al. (2006), Kavetski et al. (2006), and Bachu and Celia (2009). The model takes advantage of specific assumptions, consistent with the physics and chemistry of the system, to simplify the equations such that analytical and semi-analytical solutions can be obtained (see Celia and Nordbotten, 2009, 2011; Nordbotten and Celia, 2011).

In the present work we demonstrate the application of this overall modeling approach for a specific field site in Alberta, Canada. The location corresponds to an area where four large power plants currently operate, emitting collectively about 30 million tonnes (Mt) of CO_2 per year (Michael et al., 2008). We use detailed stratigraphic descriptions and actual locations and depths of 1,146 wells over a study area of 2500 km^2. We use the model to demonstrate the most important characteristics of the problem, including the vertical structure in the stratigraphic sequence, the nature of possible leakage in such systems, the importance of injection location within the vertical sequence and the sensitivity of maximum injectivity on residual brine saturations. Model results show how leakage risk can change as a function of depth of injection due to a number of competing factors. The results also illustrate the potentially limiting nature of injectivity in deep sedimentary basins like the Alberta Basin, where the existence of large capacity does not guarantee that a site is appropriate, because the rate at which the overall capacity can be accessed must be considered. As such, injectivity can be more important than capacity. Our model calculates both CO_2 and brine migration and leakage throughout the duration of the active period of CO_2 injection.

This chapter based on (Celia et al., 2011) is organized as follows. We begin with an overview of the model used in the analysis. Next we describe the field site, including the different permeable formations and their properties, the location and depth of all known oil and gas wells in the area, and the choice of domain and associated boundary conditions. Next we present the simulations we have run, and focus our results on the issues of (1) critical well properties, (2) the trade-off between depth of injection and risk of leakage, (3) the important role of injectivity limitations, and (4) comparison between CO_2 and brine leakage characteristics. We conclude with comments about modeling options and the kinds of analysis tools that are needed to further refine the calculations presented herein.

3.2. Computational model

The computational model used in this work is based on a set of analytical and semi-analytical solutions for CO_2 injection (Nordbotten and Celia, 2006a), leakage along segments of wells (Nordbotten et al., 2009), and upconing in the vicinity of leaky wells (Nordbotten and Celia, 2006b). These individual components are integrated into an overall solution algorithm that can accommodate arbitrary numbers of sedimentary layers (aquifers and aquitards) and arbitrary numbers of potentially leaky wells. The combined algorithm is described in Nordbotten et al. (2009) and Celia and Nordbotten (2009). These algorithms and calculations complement the related recent work of Grimstad and Lindeberg (2009), Pawar et al. (2009), and Stauffer et al. (2009), among others, who have studied different aspects of CO_2 injection and leakage. These analytical and semi-analytical models are part of an on-going group effort to build a hierarchy of practical models to answer specific practical questions about geological CO_2 sequestration safety as described in Chapter 2.

3.2.1. CO_2 plume evolution

The fundamental building block of the model is a solution for a single injection well in a horizontal, confined, homogeneous deep saline aquifer. The model uses the assumption of strong buoyant segregation, driven by the large density difference between the CO_2 and brine, coupled with the complementary assumption that once the fluids are separated by buoyancy, they attain vertical equilibrium in their pressure distributions. Those equilibrium pressure profiles coupled with the local capillary pressure function to give a vertical profile of the fluid saturations. If the capillary transition zone associated with the local capillary pressure is small relative to the thickness of the formation, then the transition zone can be approximated by a sharp interface, thereby providing a simpler vertical representation of the saturation profile. For the present model, we assume vertical equilibrium coupled with a sharp interface. Using these assumptions, coupled with the assumption of homogeneity of material properties within a given formation and horizontal top and bottom boundaries for the formation, Nordbotten and Celia (2006a) derived a similarity solution for the system shown in Figure 3.2.

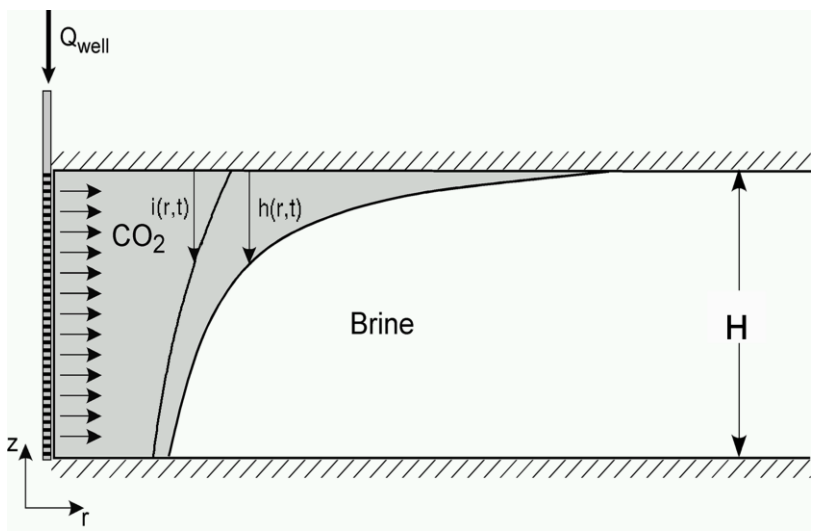

Figure 3.2: Schematic of CO2 plume of thickness $h(r, t)$. Also shown is the drying front, with dry CO_2 having thickness $i(r, t)$. From Nordbotten and Celia (2006a).

The solution involves an interface separating the leading edge of the CO_2 and the resident brine, with the thickness of the CO_2 plume denoted by $h(r,t)$, where r is radial distance

from the injection well and *t* is time since start of injection. Behind this front is a region of CO_2 and brine, where the brine is assumed to be at residual saturation. If dry CO_2 is injected into the formation, the water in the residual brine saturation will eventually evaporate and disappear, leading to the formation of a drying front, behind which only dry CO_2 exists in the pore space. The drying front is denoted by *i(r,t)* in Figure 3.2. The solutions of Nordbotten and Celia (2006a) solve the system for the location of the two fronts, *h(r,t)* and *i(r,t)*, as well as the pressure in the formation, taken as the pressure along the bottom, $p_{bot}(r,t)$. Knowledge of p_{bot} and *h(r,t)*, coupled with the assumption of vertical equilibrium, allows the pressure to be determined at all points in the domain. The resulting set of nonlinear, coupled partial differential equations can be rewritten in terms of a similarity variable, χ, such that the three unknowns are a function of only χ, and the partial differential equations reduce to a set of ordinary differential equations. The variable χ is defined by

$$\chi = \frac{2\pi H \varphi \left(1 - S_B^{res}\right) r^2}{Q_{well}\, t} \tag{3.1}$$

where *H* is the thickness of the aquifer, *φ* is the porosity of the injection formation, S_B^{res} is the residual saturation of the brine, and Q_{well} is the volumetric injection rate of CO_2. Note that χ is dimensionless, and is proportional to $\frac{r^2}{t}$. Note also that the boundary condition applied at the well is a constant flux given by Q_{well}. The resulting ordinary differential equations only need to be solved once, resulting in the solutions *h(χ)*, *i(χ)*, and $p_{bot}(\chi)$. Then, for any values of space (*r*) and time (*t*), a value of χ is determined and the solutions for the interface locations and pressure can be solved immediately. In the following, we will not consider the drying front, and will only concentrate on the invading CO_2 front *h(r,t)* and the pressure field $p_{bot}(r,t)$.

While these ordinary differential equations are useful in that they provide relatively simple solutions for both the pressure field and the CO_2 plume, the solutions simplify further depending on the dimensionless grouping Γ, given by

$$\Gamma = \frac{2\pi(\rho_B - \rho_C) g k H^2}{\mu_B Q_{well}} \tag{3.2}$$

where ρ_B and ρ_C denote density for brine (B) and CO_2 (C), respectively, g is the gravitational acceleration, k is permeability of the formation, and μ_B is the viscosity of the brine. This dimensionless group, defined elsewhere as the gravitational number (see, e.g., Kopp et al., 2009) represents the ratio of buoyancy forces to viscosity forces acting on the buoyant CO_2 and plays an important role in CO_2 sequestration capacity (Kopp et al., 2009). When values of Γ are small (for this work we use the cutoff value Γ<0.1), the solutions for the CO_2 plume and the pressure field simplify further. In this simplified case, the expression for the CO_2 plume may be written as

$$h'(\chi) = \frac{h(\chi)}{H} = \frac{1}{\lambda - 1}\left(\sqrt{\frac{2\lambda}{\chi}} - 1\right) \tag{3.3}$$

In this equation, the plume thickness is zero whenever the expression on the right side of Equation (3.3) is negative, and is equal to H whenever the right side of the equation exceeds unity. The associated pressure field may be expressed as follows,

$$\Delta p'(\chi) - F(h') = \begin{cases} 0, & \chi \geq \Psi \\ -\frac{1}{2\Gamma}\ln\left(\frac{\chi}{\Psi}\right) + \Delta p'(\Psi), & \Psi > \chi > 2\lambda \\ \frac{1}{\Gamma} - \frac{\sqrt{\chi}}{\Gamma\sqrt{2\lambda}} + \Delta p'(2\lambda), & 2\lambda > \chi > 2/\lambda \\ -\frac{1}{2\lambda\Gamma}\ln\left(\frac{\chi\lambda}{2}\right) + \Delta p'(2/\lambda), & 2/\lambda > \chi \end{cases} \tag{3.4}$$

In these equations, λ is the mobility ratio, $\lambda = \lambda_C/\lambda_B$, which is the ratio of the phase mobilities $\lambda_C = k_{rel,C}/\mu_C$ and $\lambda_B = k_{rel,B}/\mu_B$, where $k_{rel,C}$ is the relative permeability of the rock to the CO_2 phase and $k_{rel,B}$ is the relative permeability to brine. In regions where $h>0$, $k_{rel,C}$ is evaluated with the brine phase at residual saturation, which means the relative permeability will be less than one whenever the brine residual saturation is greater than zero. Because we focus only on injection scenarios in this work, the brine saturation is always equal to one ahead of the CO_2 front (that is, ahead (or below) the interface $h(r,t)$), and therefore the value of $k_{rel,B}$ is always equal to one. In Equation (3.4), p' is a dimensionless pressure, $\Delta p'$ denotes the change in pressure relative to the initial value, Ψ is the location of the outer boundary at which the pressure has not changed

relative to the initial pressure, which is taken as being hydrostatic everywhere, and F is an offset term associated with the vertical pressure distribution. The three variables introduced above have the following definitions (see Nordbotten and Celia (2006a, 2011) and Nordbotten et al. (2009) for more details):

$$\Delta p' = \frac{p - p_0}{(\rho_B - \rho_C) g H} \tag{3.5a}$$

$$\Psi = \frac{4.5 \pi H \varphi k \left(1 - S_B^{res}\right)}{\mu_B c_{eff} Q_{well}} \tag{3.5b}$$

$$F(h') = -\frac{\lambda}{\lambda - 1}\left[h'(\chi) + \frac{\ln\left[(\lambda - 1) h' + 1\right]}{\lambda - 1} \right] \tag{3.5c}$$

where p_0 is the initial pressure, and c_{eff} is the effective compressibility coefficient for the fluid and the solid matrix. We take the compressibility to be fixed and equal to the compressibility of brine, since most of the computational domain is filled with brine. We also repeat the comment that the definition of Ψ is based on the logarithmic approximation to the exponential integral, and more specific treatment of pressure thresholds associated with the area of review estimation can be used in place of this specific expression for Ψ.

As stated previously, we ignore the drying front and the associated dry CO_2 region. Recent work (Pruess, 2009; Pruess and Muller 2009) suggests that salt precipitation in the dry region may be significant – our use of residual brine saturation throughout the entire CO_2 region may be seen as using residual brine saturation to represent the fractional pore space occupied by either brine or precipitated salt. The solution in Equations (3.4) and (3.5) also ignores any diffuse leakage across the caprock formations. While contributing little to vertical mass transport, such diffuse leakage could have significant impact on the pressure fields, affecting Equations (3.4) and (3.5) including the location of the outer boundary of the pressure perturbation, which is given by Equation (3.5b). The recent work of Mathias et al. (2009a), Dentz and Tartakovsky (2009), Szulczewski and Juanes (2009), and Hesse et al. (2007, 2008) uses similar mathematical methods to study the CO_2 injection and migration problem, although none of these authors deals with leakage for the kinds of problems we consider herein. The recent work of Birkholzer et al.,

(2009), Zhou et al., (2008), Mathias et al., (2009b), and the older work of Hunt (1985), examines pressure propagation due to injection and the impacts of diffuse leakage.

These analytical solutions form one of the basic building blocks for the overall analysis of CO_2 plume and pressure evolution with leakage along wells in multi-layer, multi-well problems. They also form simple and powerful stand-alone tools to analyze the basic behavior of a plume of CO_2 and the associated pressure field in an aquifer into which CO_2 is injected, without adding the complications of wells and leakage (see section 2.4.3). Equation (3.3) provides a simple estimate for the plume size and shape, and can easily give estimates for the location of the outer edge of a plume: set Equation (3.3) to zero and find $\chi = 2\lambda$, which represents the outer edge of the plume, called $r_{\text{outerPlume}}$, located at

$$r_{\text{outerPlume}} = \sqrt{\frac{\mu_B Q_{well} t}{\mu_C \pi \left(1 - S_B^{res}\right) \phi H}} \tag{3.6a}$$

Note that the outer edge of the CO_2 plume grows with the square root of time. Similarly, Equation (3.5b) provides information about the maximum spatial extent of the pressure perturbation and is obtained by imposing the following maximum pressure perturbation outer radius in the brine region.

$$r_{\text{outerPressure}} = \sqrt{\frac{2.25\text{k}t}{\mu_{\text{b}} c_{eff}}} \tag{3.6b}$$

This follows from Nordbotten et al. (2004). Both of these equations are very useful for simple screening calculations, although we note that Equation (3.6b) does not include the effects of diffuse leakage through the caprock.

3.2.2. Leakage along wells

Leakage along wells is treated as Darcy flow, using the two-phase extension of Darcy's Law. While we recognize the complicated flow paths that can be associated with leakage along wellbores, especially at small spatial scales, we focus our modeling on mathematical descriptions across relatively large distances along a well. In addition, we assume that in the majority of

cases leakage will take place outside the well casing, along the complex zone that involves cement and residual drilling fluids in the annular space, as well as possible damaged rock zones caused by the drilling process (leakage that takes place through the well tubing is akin to a well blow out and needs to be dealt with differently). We lump all of these materials, and the complex flow paths through them, into a bulk 'effective' permeability coefficient that represents the ability of fluid to flow along a well. The permeability is meant to apply, in bulk, over a length along the well that corresponds to the thickness of a caprock formation. With reference to the schematic of flow and leakage given in Figure 3.3, each potential leaky well will be characterized by an effective permeability assigned to each segment of the well that crosses an individual caprock formation. That is, if a well crosses some number, say N_c, of caprock formations, then it will be characterized by N_c different permeability values. How these values relate to one another, and perhaps to values in other wells, is discussed later in the chapter.

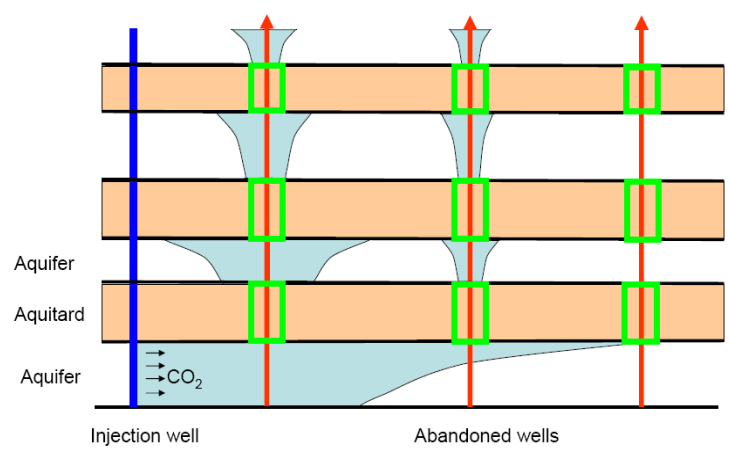

Figure 3.3: Schematic of flow and leakage in a multilayer system. Well permeabilities are assigned to each segment of each well, as indicated by the boxes. Modified from Kavetski et al. (2006).

With this idea in mind, the one-dimensional multi-phase version of Darcy's Law may be written to represent flow along a leaky well as follows,

$$q_\alpha = -\frac{kk_{rel,\alpha}}{\mu_\alpha}\left(\frac{\partial p_\alpha}{\partial z} + \rho_\alpha g\right) \tag{3.7}$$

In this equation, q_α is the volumetric flux of phase α (α =B,C) along the well (volume of phase α per area per time), assumed positive upward, and $k_{rel,\alpha}$ is the relative permeability (dimensionless), taken to be a function of phase saturation, S_α, along the well. In this work, we have taken relative permeability to be a linear function of saturation along the well segment. We reiterate that the permeability, k, is interpreted as the effective permeability over the length of the caprock. Given that the length scale is set by the caprock thickness, we may write a discrete version of the Darcy equation with respect to the caprock segment as follows,

$$q_{\alpha,i} = -\frac{k_i k_{rel,\alpha,i}}{\mu_\alpha}\left[\frac{p_{\alpha,i+} - p_{\alpha,i-}}{\ell_i} + \rho_\alpha g\right] \tag{3.8}$$

where subscript i denotes the ith caprock in the vertical sequence, and i+ and i- denote values at the top and bottom of the caprock formation, respectively. We also assume this leakage flux occurs over an effective flow area A_{well}, such that $q_\alpha A_{well}$ gives the total volumetric flow rate along the well.

3.2.3. Interface upconing

The third important part of the simulation package we have developed is a solution that describes so-called upconing of the CO_2-brine interface around a leaky well. The idea is that when a well is leaking, the flow of fluid along the well represents a net loss of mass in the formation from which the leakage is occurring (for example, the injection formation). This causes a local decrease in pressure around the well, which induces the CO_2-brine interface to move upward, reducing the thickness of the CO_2 plume in the vicinity of the leaky well. If the thickness goes to zero locally at the well, then both brine and CO_2 can flow along the well. If the thickness of the plume remains greater than zero, then only CO_2 will flow along the well. And if the CO_2 plume has not yet reached the well, then only brine can leak along the well.

Our approach is to use an improved analytical solution to the interface upcoming problem, as derived in Nordbotten and Celia (2006b). The solution uses existing interface thickness, pressure, and leakage conditions to determine the thickness of the CO_2 plume at a

leaky well. If the thickness goes to zero, then an additional calculation is performed to determine the fraction of flow along the well that comes from each of the two fluids, CO_2 and brine. This is then used in the remainder of the calculations for the overall pressure and CO_2 fields.

3.2.4. Overall computational algorithm

The three major computational components, described in Sections 3.2.1, 3.2.2, and 3.2.3, form the core of our model. Details about how these are put together, the way discrete time-stepping is imposed, and other considerations are described in associated references by the authors (e.g., Nordbotten et al., 2009). We note that, contrary to traditional numerical models for these kinds of problems, our model has no spatial grid but rather uses analytical solutions in space that are associated with the physical features of the problem, specifically the wells and the permeable layers. However, because of the nonlinearity of the underlying equations, discrete time steps are required. Because of the discretization in time, we refer to the overall solution process as a semi-analytical algorithm.

The overall algorithm proceeds as follows. For any given time step, we begin by solving for pressures at each well segment in each permeable formation. This is based on superposition of solutions associated with individual wells, with coupling across formations due to the Darcy flows along leaky wells. The result of this step is a set of algebraic equations with the number of unknowns equal to the product of the number of wells times the number of permeable layers. Solution of this set of algebraic equations gives discrete pressure values evaluated at each well in each permeable layer. With the assumption of vertical equilibrium within each permeable formation, and the analytical solutions for pressure variations moving radially away from any well, the pressure field becomes known at all points in space.

Next the calculated pressures are used to update fluid flows, with the update augmented by upconing calculations around all leaky wells to determine the impact of leakage on the location of the CO_2-brine interface locally. Finally, all CO_2 plumes are updated to properly redistribute

mass according to the pressure and flow fields. Once all pressures, flow rates, and CO_2 plume shapes are updated, the time step is advanced and the procedure is repeated for the next time step. We have found this algorithm to be robust and efficient, and to provide reliable computations of the critical variables in the problem. Herein we apply the model to a specific field location to show how the model can be applied to estimate potential leakage in complex, realistic domains.

3.3. Site description

We have identified a field location where a large-scale CCS activity might reasonably take place in the future. The location is southwest of Edmonton, Alberta, Canada, where four large coal-fired power plants currently emit about 30 million tonnes of CO_2 per year (Mt CO_2/yr) (Michael et al., 2009c). Furthermore, one of the plant operators intends to implement at a new generation unit a commercial scale demonstration CCS project. The project, designed to capture approximately 1 Mt CO_2/year, has received significant financial support from the Alberta provincial government and from the Canadian federal government and is expected to be operational by 2015. The location of our study area is shown in Figure 3.4. Data have been collected for site characterization in the area outlined in the figure, with the area being 50 km × 50 km. Within that area, 1,146 existing oil and gas wells have been identified. The locations of these wells are shown in Figure 3.4. These wells have variable characteristics, including depth of penetration and age. We have also identified the general stratigraphic sequence in the area (shown in Figure 3.4), which consists of alternating permeable and impermeable layers, with the permeable layers corresponding to sandstones in the higher layers and carbonates in the lower layers. The impermeable caprock formations are shales. The characteristics of the permeable layers, including number of wells, are summarized in Table 3.1. Additional information can also be found in Michael et al., (2009c) and on the Alberta Geological Survey (AGS) website http://www.ags.gov.ab.ca/

The average slope of the different formations across the area was determined by examination of well logs associated with the different wells, and the associated estimation of vertical locations of the different formations. In general, the slopes are less than 1%. When considered in the context of the analysis presented by Gasda et al. (2008), we conclude that the buoyant movement of the CO_2 injection plume due to caprock slope will be insignificant during the entire period of injection. As such, the assumption of horizontal formations may be seen as reasonable.

The permeable layers have associated with them a number of small-scale (core-plug) measurements of permeability. These have been aggregated into formation averages (see Michael et al., 2009c) as shown in Table 3.1. We use these estimates directly in our simulations. All caprock formations are assumed to be impermeable, except for possible flows along the existing wells. We have assigned an effective compressibility for the system of c_{eff}= 4.6.10^{-10} m^2/N. We take the domain size to be 50 km × 50 km, although we have assigned lateral fixed-pressure boundary conditions along boundaries that are typically taken to be much larger than the 50×50 domain of interest (see later discussion about r_{outer}), with the values along these outer boundaries held constant at the initial values, which are taken to be hydrostatic conditions within all formations. The boundary condition at the injection well is a fixed flux equal to Q_{well}. Initially all formations are saturated with brine at hydrostatic pressure. The bottom of the deepest permeable formation – Basal Sandstone – is taken as the bottom boundary, with a no-flow condition imposed. The top-most layer is taken as a 30m thick, 20 milliDarcy permeable aquifer just above a very thick aquitard located between the depths of 30m and 728.8m. A no-flow condition is also imposed at the top of this top-most aquifer. We report accumulations of mass in the upper-most permeable formation as an indication of the amount of mass that would continue to move upward toward the land surface. Note that we do not include any phase change for the CO_2 as it moves upward via leakage along wells, since CO_2 is in supercritical phase in all aquifers listed in Table 3.4 except for the Belly River aquifer.

Each of the 1,146 existing oil and gas wells within the domain is assigned a finite depth, based on well logs and records. Depending on its depth, any given well will perforate a sequence of caprock formations, and eventually end in a specific formation. We have collectively grouped all of the wells based on the deepest formation penetrated. Table 3.1 shows this information. We see, for example, that about 900 wells perforate the caprock of the Viking Formation, 719 perforate the caprock of the Nordegg/Banff Formation, and then there is a large drop, to 39 wells, penetrating the Nisku Formation (the large drop in the number of wells is due to the fact that the upper units are oil and gas producing, while the lower ones are not). As must be the case, the number of wells perforating the caprock formation above any given permeable formation decreases as one proceeds deeper into the vertical succession.

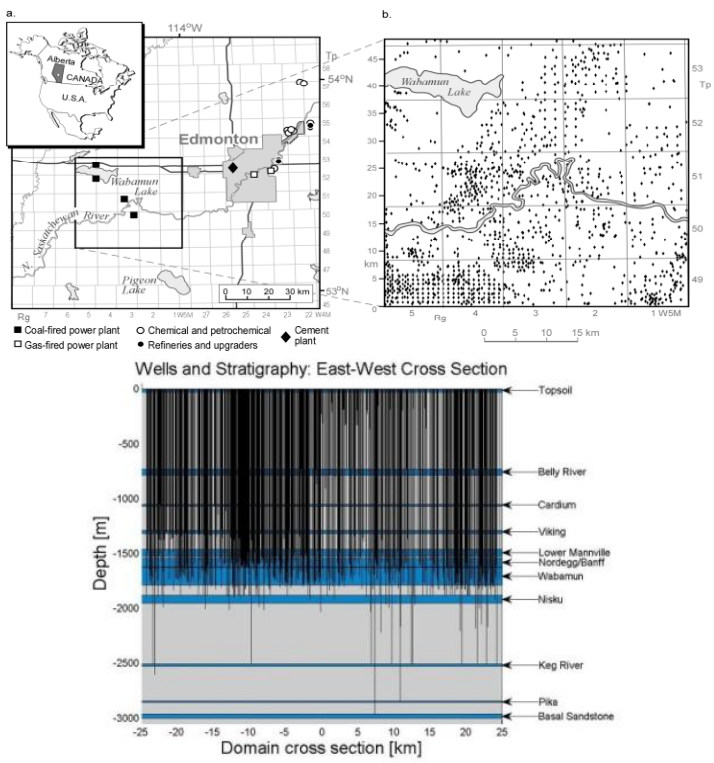

Figure 3.4: Wabamun Lake area study site in Alberta, Canada with both a top view and vertical section of all wells in the domain.

Aquifer Name*	Top depth [m]	Thickness [m]*	Intrinsic permeability [milliDarcy]*	Porosity*	Wells ending in layer
Belly River	728.8	56	86	0.15	1146
Cardium	1051.8	15	7	0.19	1131
Viking	1287.8	30	53	0.11	878
Mannville	1461.8	65	7	0.14	874
Nordegg/Banff	1537.8	80	4	0.10	719
Wabamun	1628.8	160	4	0.12	136
Nisku	1881.8	72	170	0.12	39
Keg River	2506.8	22	3.5	0.12	11
Pika	2844.8	14	16	0.12	2
Basal Sandstone	2964.8	38	23	0.12	1

Table 3.1: Characteristics of permeable layers in the study area. Shaded rows correspond to formations into which injection is simulated. Data in columns marked with * are from Michael et al., (2009c).

3.4. Computational algorithm and parameter choices

Our computational approach is based on assignment of all formation properties deterministically, using the values listed in Table 3.1. Because of the overridingly large uncertainty associated with properties assigned to leaky wells, we take the effective well permeabilities to be the dominant uncertainty and treat that parameter stochastically. Each well is divided into segments, with a segment defined as the section of well that crosses one caprock formation. Effective permeability values are assigned randomly to each well segment based on specified probability distributions. Because very few measurements of effective permeability along well segments have been reported in the literature (see the recent work of Crow et al. (2010) for one example), we are motivated to use the recent analyses of well characteristics by Watson and Bachu (2008, 2009). Watson and Bachu developed a scoring system meant to represent the likelihood that a well will leak based on "soft" information about various well characteristics such as well type, depth, time of drilling, completion and abandonment, and regulatory requirements at these times, rather than actual permeability measurements (which are not available). They developed two metrics: a Deep Leakage Potential associated with the well segments in the deeper caprock formations overlying the deepest formation reached by a given well, and a Shallow Leakage Potential associated with well segments across all shallower caprock layers. Both metrics are based on a set of attributes for each well in Alberta inclusive of the study area. For example the Deep Leakage Potential is based on: number of perforations, treatment of producing intervals, and abandonment type. We have developed a simple algorithm to map the scores identified by Watson and Bachu (2008, 2009) into a probability distribution for values of effective permeability. We do this with a direct map of score into the mean of a lognormal probability distribution with unit variance. A given score is then translated into an effective permeability by a random choice from this probability distribution. Relevant information associated with the mapping of scores into permeabilities is provided in Table 3.2. This method to estimate effective permeabilities along well segments provides an alternative to our earlier approach, in which we had assumed *a priori* probability distributions for effective well permeability (see, for example, Celia et al. (2006) or

Kavetski et al. (2006)). Those distributions were bi-modal lognormal distributions with one mode corresponding to intact cement and the other corresponding to degraded cement regions. For the current application, we have used both the scoring approach and the bi-modal distribution, although we focus on the scoring system for most of the results.

When assigning effective permeability values to segments of a particular well, we have allowed for two different choices of spatial correlations. The first assumes that all segments along a given well have permeability values that are independent and uncorrelated. As such, the permeability value for each segment is chosen independently. The second assumes that the quality of materials in a given well is uniform along the entire well, which means that the effective permeability values are completely correlated. In this case, one value of effective permeability is chosen from the probability distribution, and that value is assigned to all segments of a given well. Note that the results shown herein will compare two scenarios of simulations where permeability values assigned along a given well were either fully correlated or fully uncorrelated. For all cases, we assume no horizontal correlation so that the values assigned to one well are independent of values assigned to any neighboring wells.

Deep Leakage Potential*	Score range*	Well effective permeability mean [mD]
Low	< 2	0.01 to 0.02
Medium	2 to 6	0.02 to 0.5
High	6 to 10	0.5 to 8
Extreme	> 10	8 to 10,000

Table 3.2: Mapping of well score to mean effective well permeability (data in columns marked with * from Watson and Bachu (2008)).

For a given probability distribution and correlation structure, one thousand simulations were run, each using a different set of randomly generated effective permeability values. The outputs that we analyze include CO_2 and brine leakage after 50 years of injection, and the calculated pressure perturbation in the system. All simulations use one vertical injection well,

placed at the center of the domain, with injection taking place in only one formation for any given simulation. Injection rates are determined based on the maximum allowable injection, constrained by the pressure at the injection well not exceeding 90% of the estimated fracture pressure as per regulatory requirements in Alberta.

3.5. Results

We use a number of injection scenarios to demonstrate several general results. These include (1) the importance of residual brine saturation on injection rate limitations; (2) the impact of depth of injection on risk of leakage; (3) the characteristics of brine leakage and its relationship to CO_2 leakage; and (4) the critical role played by choices for the assignment of leaky well parameters. We consider injection into three of the permeable formations listed in Table 3.1: the Nordegg/Banff Formation, the Nisku Formation, and the Basal Sandstone Formation. These cover a characteristic range of formation behaviors, including limits on injectivity and the number of wells penetrating the respective caprock formations.

3.5.1. Residual brine saturation and limits on injection rates

We inject CO_2 into each of the formations based on the maximum allowable injection pressure. According to injection regulations in Alberta, the maximum bottom hole pressure should not exceed 90% of the fracture pressure of the injection formation. We use a fracture pressure gradient of 20 kPa/m, as used in Michael et al. (2009c), and consider three different values of residual brine saturation (S_B^{res}) and the associated CO_2 relative permeability ($k_{rel,C}$) within the given injection formation. Case 1 assumes S_B^{res} is equal to zero and hence $k_{rel,C}$ is equal to 1. Case 2 assumes that all permeable formations have the same properties as those of the Basal Sandstone: S_B^{res} and the associated relative permeability evaluated at this value of saturation is $k_{rel,C} = 0.55$ (taken from Figure 3g in Bennion and Bachu, 2008). In Case 3, each formation is

assigned the specific measured values for S_B^{res} and $k_{rel,C}$ when available from the measurements reported in Bennion and Bachu (2008), otherwise the formation is assigned the values from the Basal Sandstone formation. For all simulations, values of density and viscosity were set to 479kg/m^3 and 0.0395 mPa·s for CO_2 and 1045kg/m^3 and 0.2535 mPa·s for brine (following from Tables I and II in Nordbotten and Celia 2005a). As stated previously, we do not include a drying front in the analysis, so its impact on injectivity through time is not considered.

Results for maximum injection rates for these three cases are shown in Table 3.3. Note that the different choices for relative permeability evaluated at residual saturation have a substantial effect on the maximum injection rate. As shown in the table, the maximum allowable injectivity in the Nordegg Formation is reduced by about 27 % between Cases 1 and 2. In the Nisku Formation it is reduced by about 30 % between Cases 1 and 2 and 52 % between Cases 2 and 3. In the Basal Sandstone Formation the injection rate is reduced by 32 % between Cases 1 and 2. Note that these reductions are significant relative to the total emissions that need to be sequestered (30 Mt/yr). While the Nisku formation can take about 17 Mt/yr when there is no reduction to the relative permeability, when the estimated value of relative permeability at residual saturation for Case 3 is used, that injection rate is reduced to about 6 Mt/yr. The Nisku has, by far, the largest injectivity of all the formations. So this reduction in injectivity means that the domain goes from one that can accept a large majority of the annual emissions to one that can accept well below 50% of those emissions, under an assumption of a single vertical injection well. Hence residual brine saturation, and the associated reduction in CO_2 relative permeability, is a critical parameter in CO_2 injection scenarios.

Aquifers' injection rates [Mt CO_2/yr]	Case 1: S_B^{res} =0 $k_{rel,C}$ =1	Case 2: S_B^{res} =0.3 $k_{rel,C}$ =0.55*	Case 3: Measured S_B^{res} and $k_{rel,C}$ *
Nordegg/Banff	0.35	0.25	0.25
Nisku	17.44	12.30	5.93
Basal Sandstone	2.30	1.58	1.58

Table 3.3: Maximum injection rates in each aquifer for different brine residual saturation scenarios (data in columns marked with * from Bennion and Bachu 2008).

These reductions in injectivity also have a significant impact on the resulting CO_2 plume size and hence on the associated number of wells contacted by the CO_2. The relevant numbers are shown in Table 3.4. For example, even though the Nordegg Formation has more than an order of magnitude more wells penetrating its caprock, the low injectivity of the formation leads to a maximum injection rate that is almost two orders of magnitude lower than that for the Nisku Formation. This leads to a much smaller CO_2 plume, which in turn contacts very few wells in the Nordegg Formation.

	Number of wells reaching this layer	Number of wells contacted by the CO_2 plume			Number of wells contacted by the pressure perturbation
		S_B^{res} =0; $k_{rel,C}$ =1	S_B^{res} =0.3; $k_{rel,C}$ =0.55*	Measured S_B^{res} and $k_{rel,C}$ *	
Nordegg/Banff	719	4	1	1	140
Nisku	39	21	17	2	39
Basal	1	1	0	0	1

Table 3.4: Number of wells contacted by CO_2 plume and pressure perturbation (data in columns marked with * from Bennion and Bachu 2008).

While the size of the CO_2 plume is strongly influenced by the residual brine saturation through the reduced CO_2 permeability, the spatial extent of the pressure perturbation is not affected significantly. This is because the pressure calculation uses a fixed value of reservoir permeability and compressibility for the system, independent of the location of the CO_2 plume, as described in Section 3.2.1 (Equations (3.4), (3.5), and (3.6)). The important characteristic of the

pressure perturbation is that it tends to extend much further than the CO_2 plume, and therefore the zone of elevated pressure contacts many more wells that the CO_2 plume. This can be seen in Table 3.4. To avoid non-physical interactions with the outer boundary of the domain, we set the outer boundary (with a fixed pressure condition) at a radius of 130 km from the injection well. We note that for injection into the Nisku Formation, the maximum extent of the pressure perturbation reaches 72 km after 50 years of injection. In the Nordegg Formation the extent of the pressure perturbation is 11 km, and in the Basal Sandstone Formation it is about 26 km after 50 years of injection. As noted earlier, these are affected most strongly by the limited injection rates in the different formations.

3.5.2. Depth of injection and its impact on risk of leakage

Because the number of wells penetrating the caprock associated with a given injection formation generally decreases as a function of increasing depth, the initial assumption is that risk of leakage should decrease continuously as a function of depth. That is true, assuming the CO_2 plume size and the pressure field are the same for all formations. However, as seen in the previous set of results, the size of a single CO_2 plume is constrained by the maximum pressure at the injection well which in turn constrains the injection rate. Therefore if we consider a single injection well, a formation with more wells penetrating its caprock may or may not have a higher risk of leakage. We observe this in the following results, which we take to be based on only one injection well. In general, the overall leakage risk clearly depends on many factors, with the number of wells being only one of those factors.

To examine the effect of depth of injection on leakage of CO_2 and brine, we consider injection into both the Nodergg and the Nisku formations, and examine the overall leakage that develops in the system. We do this by running one thousand simulations for injection into each of the two formations identified above, with a given set of stochastic parameters (which are the effective permeabilities of the well segments) to define the system, and we examine the resulting histogram of leakage amounts for both CO_2 and brine. In Figures 3.5 and 3.6 we plot the total

amounts of CO_2 and brine that leak from the injection formation, assuming a single injection well that injects at the maximum permissible rate and using the data from the middle column of Tables 3.3 and 3.4 (that is, residual saturation of brine of 30% and relative permeability to CO_2 being 0.55). We represent the total amount of CO_2 that leaks out of the injection formation by the fraction of the total injected mass – this is shown on the horizontal axis in Figure 3.5. We do this for injection into both the Nordegg and Nisku formations. We see that the limited injectivity, and associated small number of leaky wells contacted by the CO_2 plume, especially in the Nordegg Formation, give leakage amounts for injection into the Nordegg Formation that are about an order of magnitude lower than those for injection into the Nisku Formation, despite the much larger number of wells overall in the Nordegg formation. We also observe that, for the permeabilities based on the well scores of Watson and Bachu (2008, 2009) (see Table 3.2), for all cases the amounts for CO_2 leaked does not exceed 1% and for almost all cases it does not exceed 0.1%, for both formations. When we examine similar results for the brine leakage, we see that the larger number of wells impacted by the pressure perturbation leads to the largest brine leakage cases occurring for injection into the Nordegg Formation, followed by the Nisku Formation. The brine leakage results, presented as a fraction of the volume of injected CO_2, can be seen in Figure 3.6 for the scenarios of injection into the Nordegg and Nisku formations.

While the issue of leakage risk versus depth of injection is obviously related to the number of wells that penetrate the caprock of a given formation, the injectivity of a single vertical well also plays a central role. As these calculations imply, the design of injection wells will play an important part because injection well locations and numbers will dictate what part of the domain is contacted by the CO_2 plume and pressure buildup. These decisions, in turn, depend on the injectivity of the formation, which depends on the permeability, thickness, depth, initial pressure, and residual brine saturation and the associated CO_2 relative permeability. We have chosen to use only one injection well for the purpose of consistency across the different simulations, but this clearly brings the size of the CO_2 plume into consideration and with it many other factors in addition to simply the number of wells penetrating a given formation.

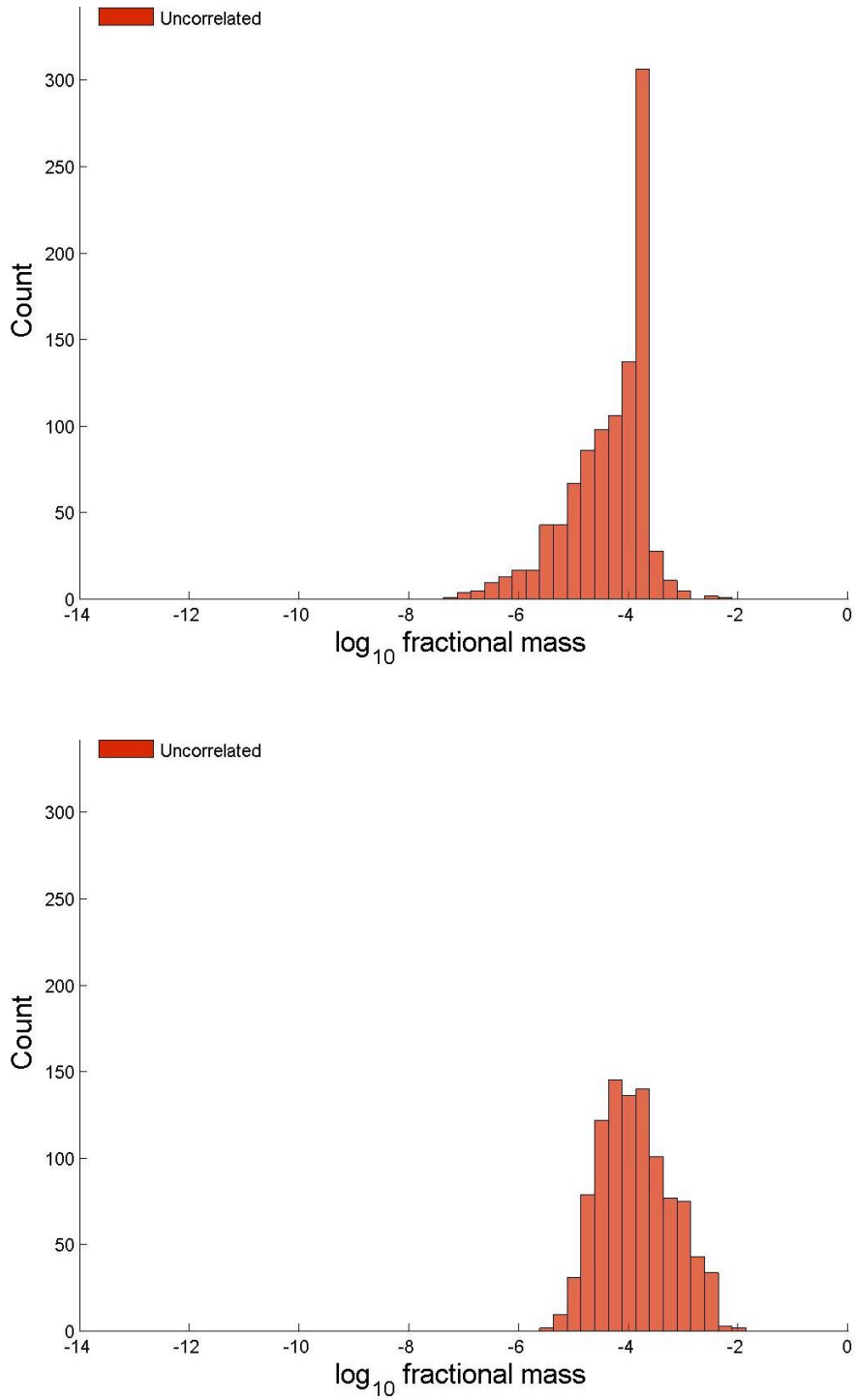

Figure 3.5: Total CO_2 fractional mass leakage (Total mass leaked out of the injection formation / Total mass injected) for Nordegg (top) and Nisku (bottom) with the scoring system used for well permeabilities. Permeability values are uncorrelated. Residual saturations and relative permeabilities correspond to Case 2 (S_B^{res} =0.3; $k_{rel,C}$ =0.55).

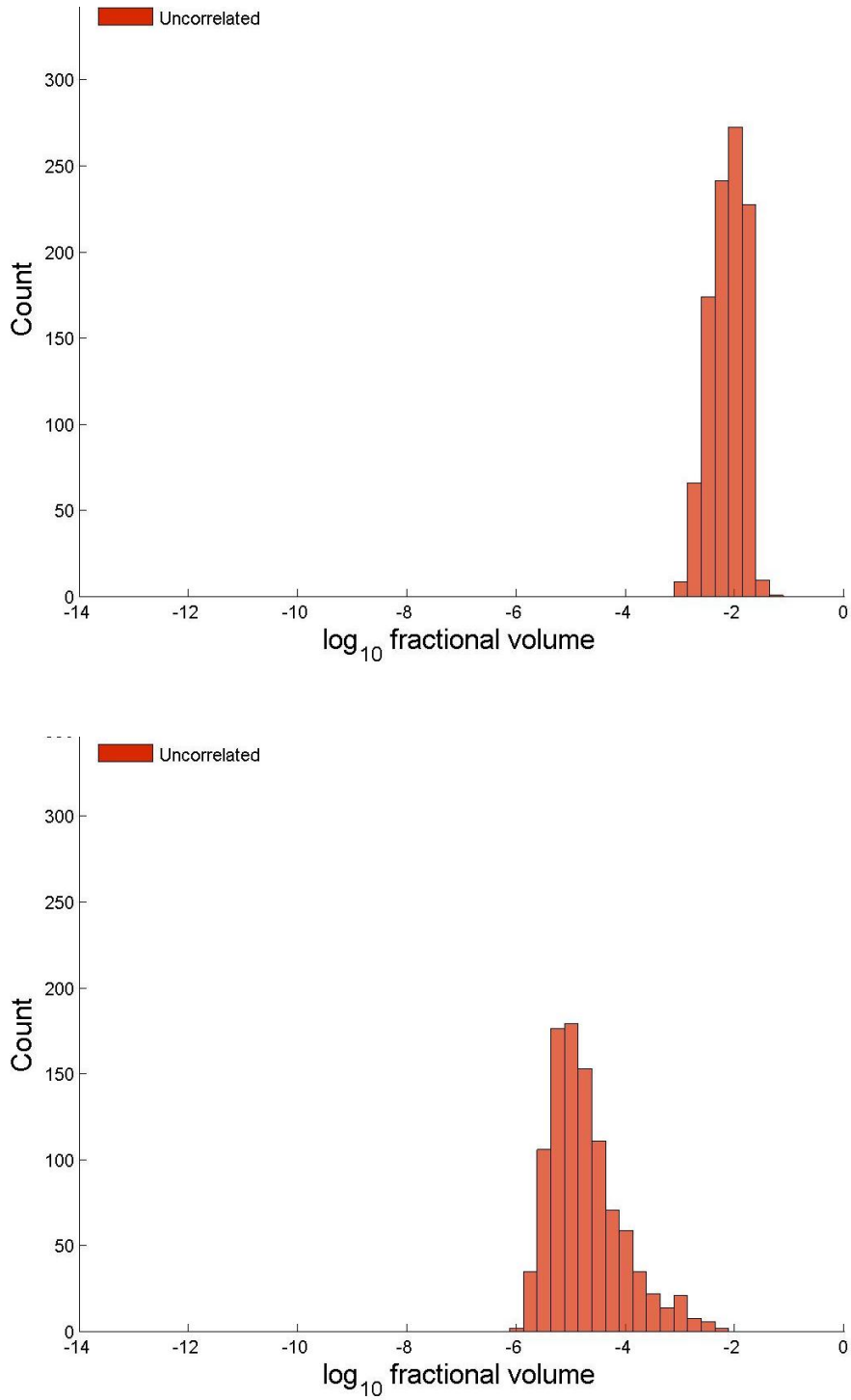

Figure 3.6: Total brine fractional volume leakage (Total brine volume leaked out of the injection formation / Total CO_2 volume injected) for Nordegg (top) and Nisku (bottom) with the scoring system used for well permeabilities. Permeability values are uncorrelated. Residual saturations and relative permeabilities correspond to Case 2 (S_B^{res} =0.3; $k_{rel,C}$ =0.55).

3.5.3. Characteristics of CO_2 leakage and of brine leakage

As we have already observed, the larger spatial footprint associated with the pressure perturbation, as compared to the footprint of the CO_2 plume, tends to drive brine leakage through many more wells than those wells contacts by the injected CO_2. This means that brine leakage tends to occur over a much larger sample of the wells penetrating a formation, and therefore the brine leakage tends to reflect the number of wells in the formation, even for a single injection well. While this can be a general expectation, it is instructive to examine the leakage patterns of CO_2 and brine in somewhat more detail to observe characteristic spatial patterns in the vertical direction. For example, while Figures 3.5 and 3.6 show the total amount of CO_2 and brine that leaves the injection formation, Figures 3.7 and 3.8 show the amounts of CO_2 and brine that leak into the top-most formation in the domain. We see that most of the CO_2 that leaks does not reach the shallow subsurface zones, and even less of the brine reaches the shallow zones. This highlights the potentially important role played by intermediate permeable formations between the injection formation and the shallow subsurface (often referred to as secondary barriers to leakage; see Nordbotten et al., 2004; Oldenburg, 2008). More of the CO_2 makes it to the shallow zones because of the buoyant drive that combines with the pressure drive associated with injection. The brine is driven only by the imposed pressure gradients, and lacks the additional buoyant drive. Therefore there is a weaker vertically upward drive, and this is reflected in the last two figures. The two dominant characteristics of the brine versus CO_2 leakage are the presence (or absence) of buoyant flow components, and the much larger spatial footprint of the pressure perturbation as compared to the CO_2 plume. These should be taken into account when making any analysis of leakage potential and associated suitability of a given site or formation.

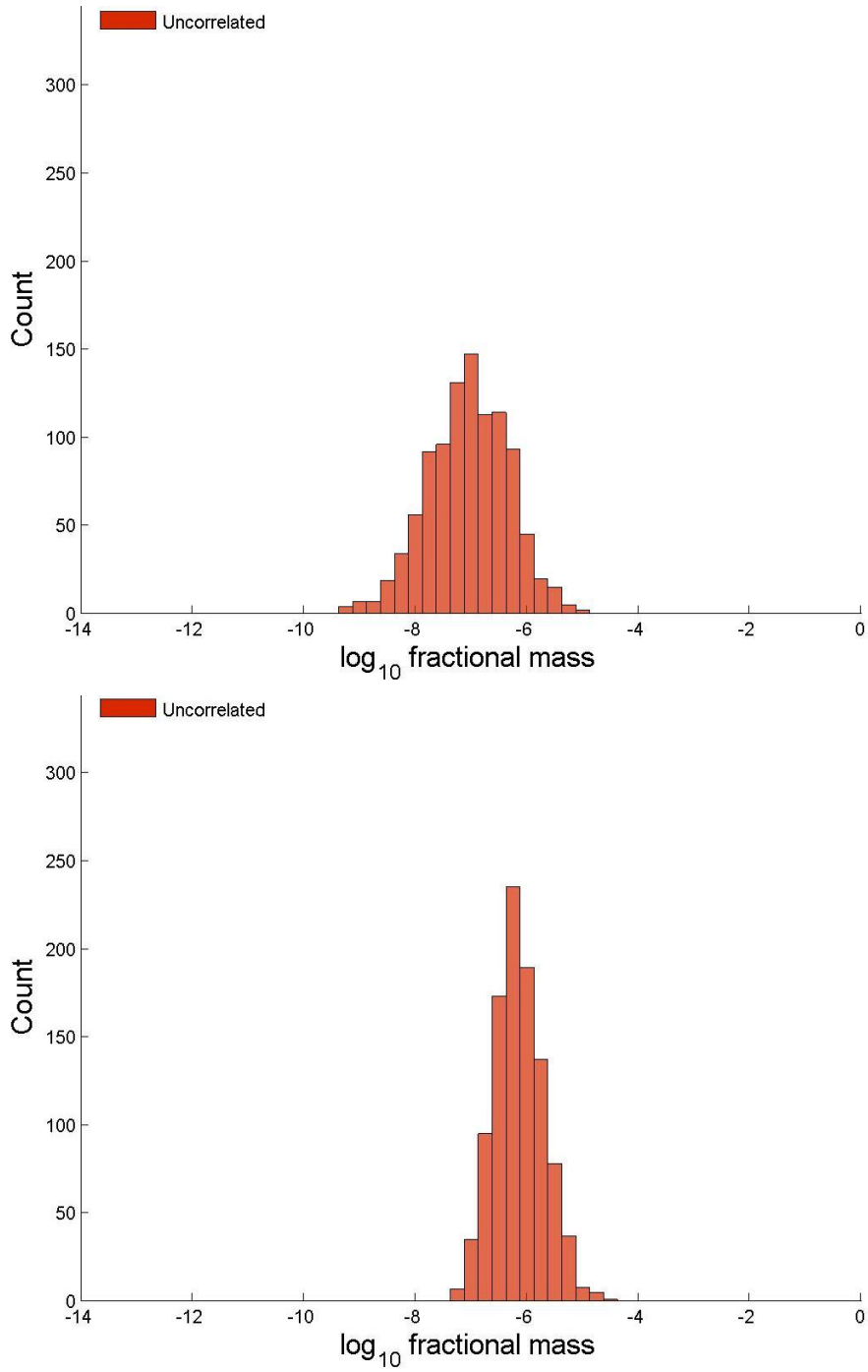

Figure 3.7: Shallow zone CO_2 fractional mass leakage (Total mass leaked into the shallow zone / Total mass injected in the injection formation) for Nordegg (top) and Nisku (bottom) with the scoring system used for well permeabilities. Permeability values are uncorrelated. Residual saturations and relative permeabilities correspond to Case 2 (S_B^{res} =0.3; $k_{rel,C}$ =0.55).

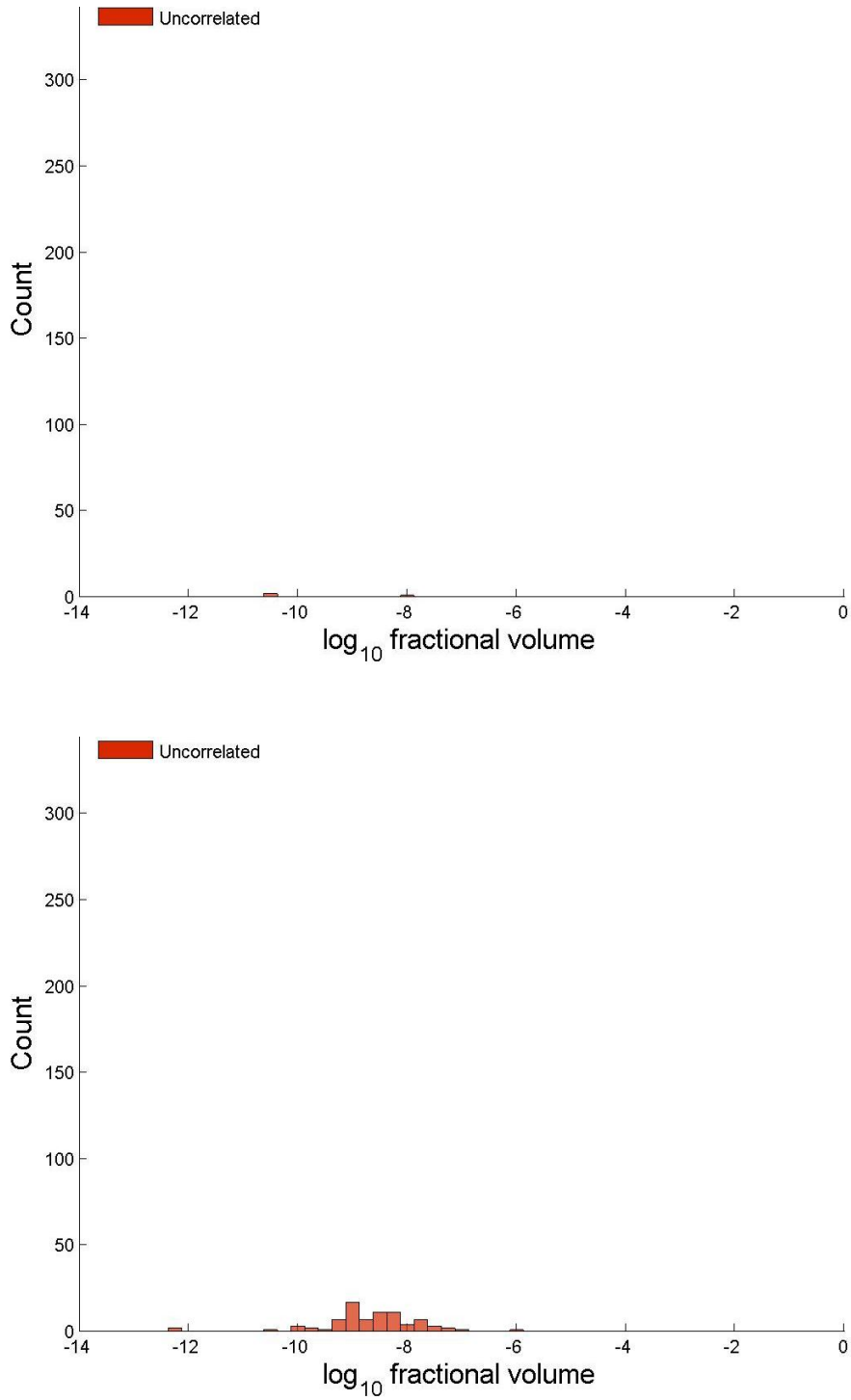

Figure 3.8: Shallow zone brine fractional volume leakage (Total brine volume leaked into the shallow zone / Total CO_2 volume injected in the injection formation) for Nordegg (top) and Nisku (bottom) with the scoring system used for well permeabilities. Permeability values are uncorrelated. Residual saturations and relative permeabilities correspond to Case 2 (S_B^{res}=0.3; $k_{rel,C}$=0.55).

3.5.4. Dependence on stochastic parameters

Clearly, all of the results generated using our model of leakage depend on the assignment of leakage properties for the existing wells, which means the assignment of the values of effective permeability along each well segment. When using the scoring system of Watson and Bachu (2008, 2009), the mapping between well scores and effective permeabilities is the crucial step. Our approach for the current work is summarized in Table 3.2. Until we develop a set of data points with which to populate this kind of transformation (see, for example, Crow et al., 2010), these mappings will remain hypothetical, constrained only by expert opinion and simple estimates associated with micro-annular flows. In lieu of a scoring system, we have used a bi-modal lognormal distribution to describe the effective permeabilities, with one mode corresponding to 'good cement' and a second mode corresponding to 'bad cement'. We characterize this bi-modal distribution by the mean values of the two modes, as done, for example, in Celia et al. (2006) and Kavetski et al. (2006). Celia et al. (2009) compared simulations using these two different approaches for assignment of well permeabilities. Among other things, their results showed that the distribution of well permeability values affects the shapes of the resulting leakage histograms. In general, the overall magnitudes of leakage are strongly controlled by the actual values assigned in the mappings as well as the means for the bi-modal distribution. These are the critical parameters and our overall lack of knowledge about these parameters argues strongly for the need for a comprehensive, systematic experimental program to identify these values.

In addition to the actual distributions used, another important consideration is the degree of correlation along a given well and among adjacent wells. For example, along a given well, each well segment might be assigned values of permeability that are independent of all other values assigned to other sections along that well. This means there would be no correlation among those values. Conversely, one might argue that a bad cement job means that all values along a given well should have similar values of permeability. If a well is assigned the same permeability values to all segments along its vertical extent, then those values will be perfectly correlated. Any degree of correlation between these two limits is possible. To examine the

impact of correlation, we have conducted numerical experiments for the case of fully uncorrelated permeability values and fully correlated values. For each case, we have assigned values to the wells as described previously, but now either all segments along the well are assigned the same value, or each segment is generated independently (note that all previous results have assumed an uncorrelated data structure for the well permeabilities).

Figure 3.9 shows results for the bi-modal distribution, using fully correlated and fully uncorrelated values for well permeabilities where the two mean values for the bi-modal distribution were set to 0.1 milliDarcy and 1 Darcy, respectively, and 50% of the wells, chosen randomly, were assumed to have 'good cement' with the remaining 50% having 'bad cement'. Each mode was assigned a unit variance in log space. We again use the Nordegg and Nisku formations with the residual brine saturation of 30% and CO_2 relative permeability of 0.55. We see that the correlation structure has a major effect on the resulting CO_2 leakage amounts. The correlated structure allows much more CO_2 to leak toward the surface, in these cases increasing the fraction of CO_2 leaked by 4 to 5 orders of magnitude. Similar results are seen for permeabilities based on the scoring system, although for the parameters in Table 3.2 the differences are only one to two orders of magnitude. The corresponding results are shown in Figure 3.10.

These results are consistent with our understanding of the system. In the one-dimensional flow system corresponding to a leaky well, the effective permeability is controlled by the segment with the lowest permeability. Thus, when permeabilities are fully uncorrelated, the only way to have a large permeability along the entire length of a well is for all of the segments to have high values. When each value is chosen independently from a given probability distribution, the probability of all values being large is relatively low. Hence the probability of a large leakage value is also low, resulting in the much lower estimates for leakage to shallow zones in systems where the well permeabilities are uncorrelated. Conversely, when all of the values are correlated, once a large permeability is assigned, it persists along the entire well, leading to substantially

larger leakage rates into shallow zones of the subsurface. This is clearly seen in the results, and points to another important set of data that must be determined to properly characterize well leakage.

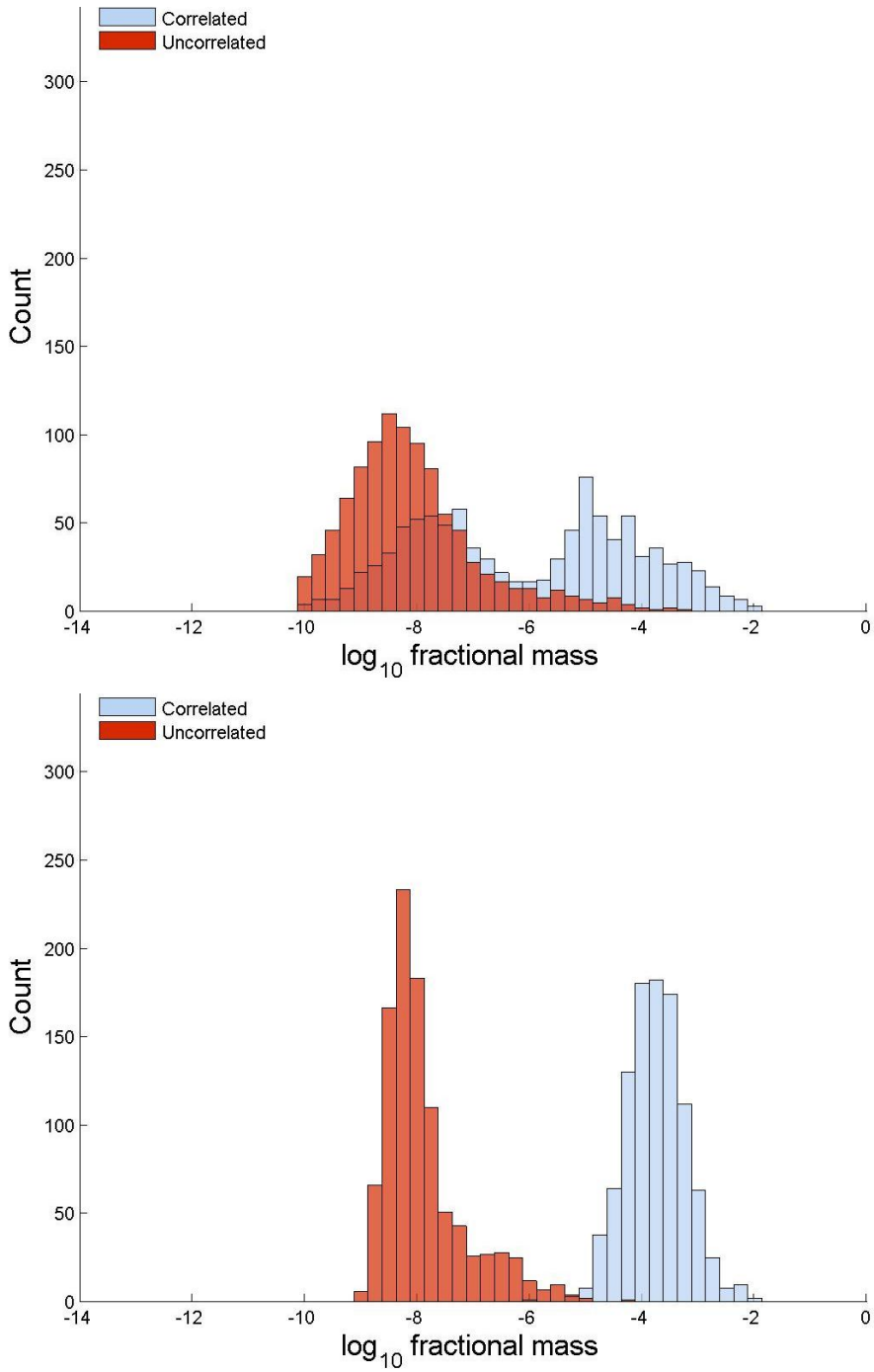

Figure 3.9: Shallow zone CO_2 fractional mass leakage for Nordegg (top) and Nisku (bottom) for Case 2 comparing the bimodal 50% weight distribution fully correlated (blue) and uncorrelated (red).

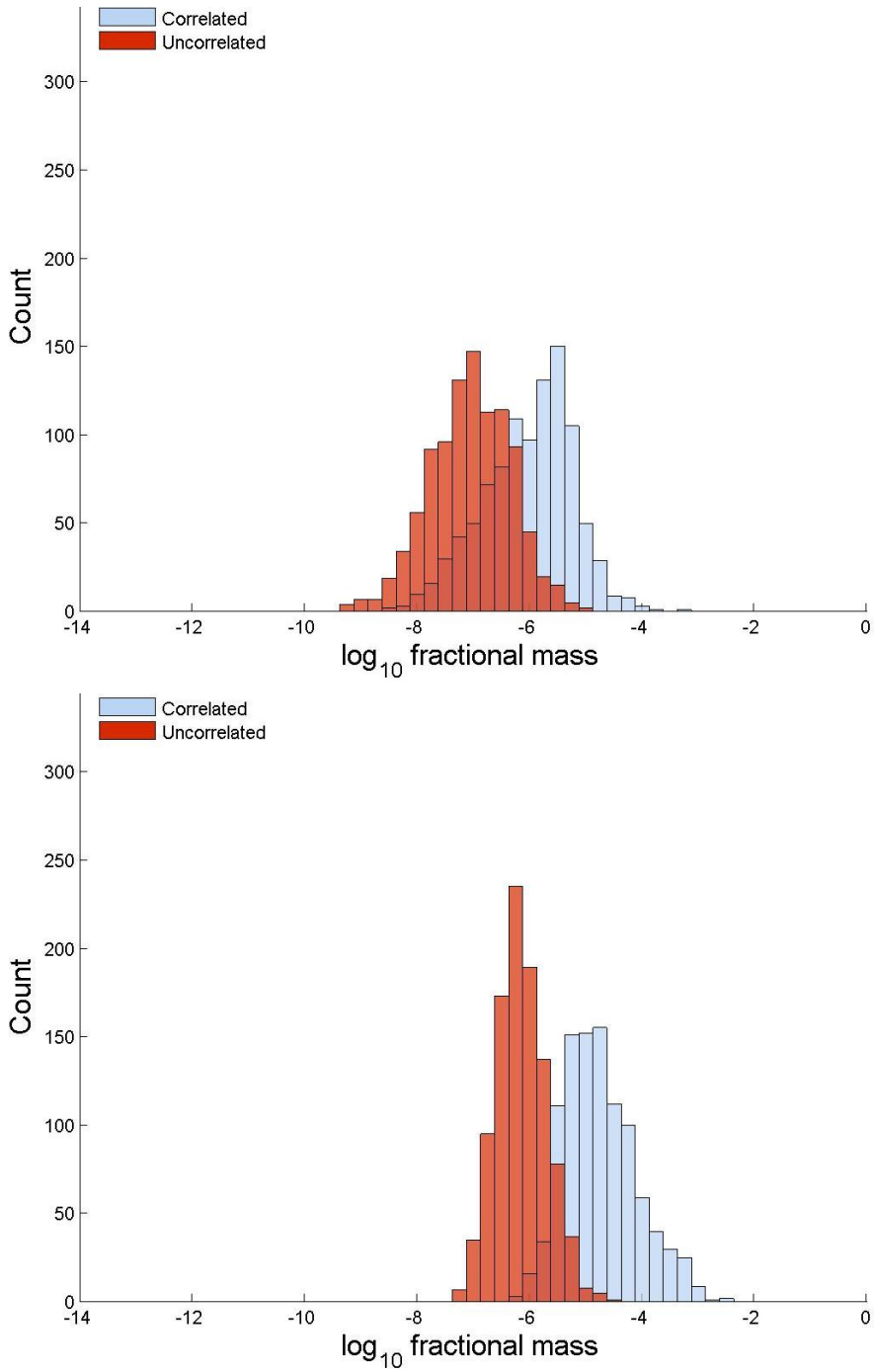

Figure 3.10: Shallow zone CO_2 fractional mass leakage for Nordegg (top) and Nisku (bottom) for Case 2 comparing the scoring system distribution fully correlated (blue) and uncorrelated (red).

The fact that leakage results using the bi-modal distribution show much larger impact of correlation, as compared to the scoring system, is also consistent with the characteristics of the two different approaches. While the bi-modal approach is fully random, such that each permeability value is chosen from the entire span of the bi-modal distribution, the scoring system has constrained randomness through the assignment of the score. Once a well is given a score, it is then immediately given a corresponding mean permeability value, and then the probability distribution from which the permeability value is assigned is a lognormal distribution that has the assigned mean and a unit variance. This gives a significantly diminished range of values from which permeability values are assigned. This is consistent with the idea that some amount of 'soft' information is being used to constrain the randomness of the problem, and therefore should result in replacement of some of the randomness with a deterministic component. That is exactly what we see in the computational results.

Finally, we point out that after 50 years of injection, in all cases presented herein as well as a range of other cases we have run, leakage of CO_2 into the shallowest formation almost never exceeds one percent of the mass of injected CO_2, and is usually less than 0.1 percent. A few scenarios involving large fractions of leaky wells and injection into the Nordegg and Nisku formations can result in leakage slightly larger than one percent, while for injection into the Basal Sandstone Formation, leakage is estimated to be always less than 0.01% of the injected mass after 50 years of injection. We stress that our results obviously depend on the permeability values assigned to leaky wells, as well as our injection strategy, but over the permeability distributions we have considered leakage appears to range from modest to insignificant. With our simple injection strategy –a single vertical injection well in the center of the domain – injectivity limitations become significant and could be more important than leakage considerations. More complex injection scenarios, involving multiple wells and including horizontal wells, will be considered in future work and are expected to increase the injectivity associated with these formations, with a concomitant increase in estimated leakage due to increased numbers of potentially leaky wells contacted by the plumes. The Nisku Formation, with its much higher

injectivity, should be considered as the best formation for injecting captured CO_2. The Basal Sandstone Formation is the next-best choice, although its injectivity is significantly lower than that of the Nisku Formation. Finally, despite the relatively small number of potentially leaky wells contacted by the CO_2 in the Nordegg Formation, thereby leading to relatively little leakage, this formation is not very useful because its injectivity is much too low.

3.6. Conclusion

The semi-analytical model for CO_2 and brine migration and leakage provides a flexible and very efficient computational framework to study many aspects of the system response to CO_2 injection into deep saline aquifers. This particular model can accommodate very large numbers of potentially leaky wells (many thousands) and many alternating layers of aquifers and caprock formations. Many potential injection sites in North America are likely to have tens to hundreds, and possibly more, of existing or abandoned oil and gas wells within the radius of influence of a CO_2 injection operation, and this modeling framework allows these systems to be analyzed quantitatively. Because the semi-analytical modeling framework can simulate the movement and leakage of CO_2 and brine over a typical injection period of 50 years using only a few minutes of computing time on a standard single-processor personal computer, we can explore many aspects of the system in a stochastic, or probabilistic, framework.

We have used a specific site in Alberta, Canada, in the Wabamun Lake area, to explore some of the characteristics of the system response to realistic injection scenarios. Each permeable layer in the stratigraphic sequence was assigned parameter values including porosity, permeability, thickness, residual brine saturation, and CO_2 relative permeability evaluated at the residual brine saturation, based on actual field and laboratory data. Fixed (average) values of porosity and permeability were assigned to each formation, based on measured values, and several different values of residual saturation and relative permeability were considered. As the

results in Section 3.5 indicate, the system response involves a complex interplay among formation properties, fluid properties, and properties of the leaky wells. An important limitation on injection rates in formations like those around Lake Wabamun is the maximum pressure at the injection well, which in turn depends critically on residual saturation of the displaced brine and the associated relative permeability to the CO_2 in the region containing residual brine. Use of measured values of residual brine saturations and associated CO_2 relative permeability can reduce injection rates by up to 70%. While the measured values were from a single core plug experiment, and questions about upscaling and the appropriate large-scale effective relative permeability remain to be answered, these results indicate quite clearly that careful design of injection well location and orientation will be very important in the overall system design. While we do not address well design and well placement herein, it is a topic that can be studied with the computational modeling approach presented herein.

For all of the injection scenarios considered in this Chapter based on (Celia et al 2011), the CO_2 plume was significantly smaller than the areal extent of the pressure perturbation. This has implication for well design, where close spacing may be preferred to maximize CO_2 coverage within the domain but is limited due to pressure interference from adjacent wells. It also has important implications for leakage behavior. Because the pressure perturbation tends to spread much farther than the CO_2 plume, brine leakage is observed along many more leaky wells as compared to wells with CO_2 leakage. The signature of brine leakage in these layered sedimentary successions tends to differ from the CO_2 leakage due to the significant buoyant drive that contributes to upward movement of CO_2 in leaky wells but is absent from the brine leakage. Brine will leak both upward and downward, while CO_2 leaks primarily upward. Carbon dioxide also tends to migrate upward over much longer distances, being driven strongly by buoyancy, than does the leaking brine, which is driven only by the pressure increase. Therefore, more CO_2 migrates into shallow subsurface zones as compared to brine leakage, although both tend to exhibit patterns of leakage into intervening permeable layers while flowing along leaky wells, as illustrated in Figure 3.3.

The lack of data for hydraulic properties of old wells requires a stochastic approach for leakage analysis, where the dominant uncertainty is in the properties of leaky wells. We have used several different methods to characterize the randomness of the effective permeability of the well materials and surrounding damage zone in the rock. When no information is available to constrain the parameters, then a purely random method is used with a given probability distribution used to assign well properties randomly. When qualitative information about the wells is available, a systematic evaluation of those data, like that used by Watson and Bachu (2008, 2009), may be used to constrain the randomness. In those cases, the well properties have a mixed deterministic-stochastic nature through constraints on the probability distributions used to define the effective well permeabilities. These and other stochastic approaches fit naturally into the computational model we have developed.

Independent of the specific probability distributions used to define the well properties, another critical choice in the parameter description involves spatial correlation. Along a given well, a single effective permeability may be assigned to the entire length of the well, or each well segment along the vertical direction may be assigned a different value of well permeability. The first case, involving only a single value for a given well, may be seen as using values for each segment that are completely correlated and therefore identical. In the second case, if all segments along a given well are assigned permeability values that are independent of one another, then the values may be seen as being completely uncorrelated. The correlation structure assigned along a given well plays an important role in the amount and nature of the resulting leakage. Additional spatial correlation among neighboring wells may also be assigned, although we have not explored this kind of correlation to date.

While the semi-analytical model is able to provide many insights into the overall system behavior, it is clearly limited in its scope by the restrictive assumptions on which it is based. Our research group's current work as described in Chapter 2 is moving toward hybrid models that can

provide numerical solutions in regions where the restrictive assumptions are not applicable, while continuing to use analytical solutions in regions where they are appropriate. Chapter 4 identifies improvement for vertically-integrated models to provide accurate results when the fluids are no yet fully segregated. We are also working with other groups to try to develop the beginnings of a data base for appropriate hydraulic properties for old – and potentially leaky – oil and gas wells. We believe these additions in both model capabilities and in data collection will allow for reductions in uncertainties and associated increases in confidence as large-scale field sites are studied for possible injection of captured CO_2.

3.7. References

Alberta Geological Survey website http://www.ags.gov.ab.ca/

Bachu, S., Celia, M.A., 2009. Assessing the potential for CO_2 leakage, particularly through wells, from geological storage sites. The Science of CO_2 Storage (McPherson, B.J., Sundquist, E., eds.), Geophysical Monograph Series GM148, American Geophysical Union, Washington, D.C., USA.

Bennion, D. B., Bachu, S., 2008. Drainage and imbibition relative permeability relationships for supercritical CO_2/brine and H_2S/brine systems in intergranular sandstone, carbonate, shale and anhydrite rocks. SPE Reservoir Eval. and Eng., 11 (3), 487-496, DOI: 19.2118/99326PA.

Birkholzer, J.T., Zhou, Q., Tsang, C-F., 2009. Large-scale impact of CO_2 storage in deep saline aquifers: a sensitivity study on the pressure response in stratified systems. Int. J. Greenhouse Gas Control, 3 (2), 181-194.

Celia, M.A., Bachu, S., Nordbotten, J.M., Kavetski, D., Gasda, S.E., 2006. A risk assessment modeling tool to quantify leakage potential through wells in mature sedimentary basins. Proc. 8th Int. Conf. Greenhouse Gas Control Technologies, (Gale, J., Rokke, N., Zweigel, P., Svenson, H., eds.), Trondheim, Norway, June 19-22, 2006, CD ROM, Elsevier

Celia, M.A., Nordbotten, J.M., 2009. Practical modeling approaches for geological storage of carbon dioxide. Ground Water, 47 (5), 627-638.

Celia, M.A., Nordbotten, J.M., Bachu, S., Dobossy, M., Court, B., 2009. Risk of leakage versus depth of injection in geological storage. Proc. 9th Int. Conf. Greenhouse Gas Control Technologies, Washington, D.C., November 16-20, 2008. Elsevier, Energy Procedia, 1 (1), 2573-2580.

Celia, M.A., Nordbotten, J.M., Court, B., Dobossy, M. & Bachu, S. 2011, "Field-scale application of a semi-analytical model for estimation of CO2 and brine leakage along old wells", *International Journal of Greenhouse Gas Control,* vol. 5, no. 2, pp. 257-269.

Celia, M.A. & Nordbotten, J.M. 2009, "Practical Modeling Approaches for Geological Storage of Carbon Dioxide", *Ground Water,* vol. 47, no. 5, pp. 627-638.

Crow, W., Carey, J.W., Gasda, S., Williams, B., Celia, M.A., 2010. Wellbore integrity analysis of a natural CO_2 producer, Int. J. Greenhouse Gas Control, 4, 186-197.

Dentz, M, Tartakovsky, D.M., 2009. Abrupt-interface solution for carbon dioxide injection into porous media. Transport in Porous Media, 79, (1), 15-27.

Gasda, S.E., Bachu, S., Celia, M.A., 2004. Spatial characterization of the location of potentially leaky wells penetrating a deep saline aquifer in a mature sedimentary basin. Env. Geol. 46 (6-7), 707-720. DOI 10.1007/s00254-004-1073-5.

Gasda, S.E., Nordbotten, J.M., Celia, M.A., 2008. Upslope plume migration and implications for geological CO2 sequestration in deep saline aquifers. The IES Journal Part A: Civil and Struct. Eng., 1 (1), 2–16.

Grimstad, A-A., Georgescu, S., Lindeberg, E., Vuillaume, J-F.,. 2009. Modelling and simulation of mechanisms for leakage of CO_2 from geological storage. Energy Procedia, 1 (1), 2511-2518.

Hesse, M. A., Tchelepi, H. A., Cantwell, B. J., Orr Jr., F. M., 2007. Gravity currents in horizontal porous layers: Transition from early to late self-similarity. J. Fluid Mech., 577, 363-383.

Hesse, M. A., Orr Jr., F. M., Tchelepi, H. A., 2008. Gravity currents with residual trapping. J. Fluid Mech., 611, 35-60.

Hunt, B. 1985. Flow to a well in a multiaquifer system. Water Resour. Res., 21 (11), 1637-1641.

Intergovernmental Panel on Climate Change (IPCC). 2005. Special Report on Carbon Dioxide Capture and Storage, (Metz, B., Davidson, O., de Coninck, H., Loos, M., Mayer, L., eds.). Cambridge University Press, Cambridge, UK, and New York, NY, USA..

Kavetski, D., Nordbotten, J.M., Celia, M.A.,. 2006. Analysis of potential CO_2 leakage through abandoned wells using a semi-analytical model. Proc. XVI International Conference on Computational Methods in Water Resources, (Binning, P.J., Engesgaard, P., Dahle, H., Pinder, G., Gray, W., eds.). Copenhagen, Denmark, June 2006. http://proceedings.cmwr-xvi.org (accessed May 19, 2009).

Kopp, A., Class, H., Helmig, R., 2009. Investigations on CO_2 storage capacity in saline aquifers. Part 1. Dimensional analysis of flow processes and reservoir characteristics. Int. J. Greenhouse Gas Control, 3 (3), 263-276.

Mathias, S.A., Hardisty, P.E., Trudell. M.R., Zimmerman, R.W. 2009a. Approximate solutions for pressure buildup during CO_2 injection in brine aquifers. Transport Porous Media, 79, (2), 265-84.

Mathias, S.A., Hardisty, P.E., Trudell. M.R., Zimmerman, R.W., 2009b. Screening and selection of sites for CO_2 sequestration based on pressure buildup. Int. J. Greenhouse Gas Control, 3 (5), 577-585..

Michael, K., Arnot, M., Cook, P., Ennis-King, J., Funnell, R., Kaldi, J., Kirste, D., Paterson, L., 2009a. CO_2 storage in saline aquifers I - Current state of scientific knowledge. Energy Procedia, 1 (1), 3197-3204.

Michael, K., Allinson, G., Golab, A., Sharma, S., Shulakova, V., 2009b. CO_2 storage in saline aquifers II–Experience from existing storage operations. Energy Procedia, 1 (1) 1973-1980.

Michael, K., Stefan Bachu, B.E. Buschkuehle, K. Haug and S. Talman, 2009c. Comprehensive Characterization of a Potential Site for CO2 Geological Storage in Central Alberta, Canada. Carbon Dioxide Sequestration in Geological Media – State of the Art, (Grobe, M., Pashin, J., Dodge, R., eds.), AAPG Studies in Geology 59, 227-240.

Nordbotten, J.M., Celia, M.A., Bachu, S., 2004.. Analytical solutions for leakage rates through abandoned wells. Water Resour. Res. 40, (4), W04204.

Nordbotten, J.M., Celia, M.A., Bachu, S., 2005a. Injection and storage of CO_2 in deep saline aquifers: Analytical solution for CO2 plume evolution during injection. Transport Porous Media, 58, (3), 339-360.

Nordbotten, J.M., Celia, M.A., Bachu, S., Dahle, H.K.,2005b. Semianalytical solution for CO_2 leakage through an abandoned well. Env. Sci. Technol. 39(2), 602-611.

Nordbotten, Jan M., and Michael A. Celia. 2006a. Similarity solutions for fluid injection into confined aquifers. J. Fluid Mech., 561, 307-327.

Nordbotten, J.M., Celia, M.A., 2006b. An improved analytical solution for interface upconing around a well. Water Resour. Res., 42, (8), W08433.

Nordbotten, J.M., Kavetski, D., Celia, M.A., Bachu, S., 2009. Model for CO2 leakage including multiple geological layers and multiple leaky wells. Env. Sci. Technol. 43 (3), 743-749.

Nordbotten, J.M. & Celia, M.A. 2011, "Geological Storage of CO2: Modeling Approaches for Large-Scale Simulation", in preparation for John Wiley and Sons, Inc.,

Oldenburg, C.M., 2008. Screening and ranking framework for geologic CO_2 storage site selection on the basis of health, safety, and environmental risk. Env. Geol. 54 (8), 1687-1694.

Pawar, R. J., Watson, T.L., Gable, C.W., 2009. Numerical simulation of CO_2 leakage through abandoned wells: Model for an abandoned site with observed gas migration in Alberta, Canada. Energy Procedia 1 (1), 3625-3632.

Pruess, K., 2009. Formation dry-out from CO2 injection into saline aquifers: 2. analytical model for salt precipitation. Water Resour. Res. 45, W03403.

Pruess, K., Muller, N., 2009. Formation dry-out from CO_2 injection into saline aquifers: 1. effects of solids precipitation and their mitigation. Water Resour. Res. 45, W03402.

Schnaar, G., Digiulio, D.C., 2009. Computational modeling of the geologic sequestration of carbon dioxide. Vadose Zone J., 8 (2), 389-403.

Stauffer, P. H., Viswanathan, H.S., Pawar, R.J., Guthrie, G.D., 2009. A system model for geologic sequestration of carbon dioxide. Env. Sci. Techn., 43 (3), 565-570.

Szulczewski, M., Juanes, R., 2009. A simple but rigorous model for calculating CO_2 storage capacity in deep saline aquifers at the basin scale. Energy Procedia, 1 (1), 3307-3314.

Watson, T.L., Bachu, S., 2008. Identification of wells with high CO_2-leakage potential in mature oil fields developed for CO_2-enhanced oil recovery. Paper SPE 11294, SPE Improved Oil Recovery Symposium, Tulsa, OK, USA, 19-23-April 2008.

Watson, T.L., Bachu, S., 2009. Evaluation of the potential for gas and CO_2 leakage along wellbores. SPE Drilling & Completion, 24 (1), 115-126. March 2009.

Xu, T., Apps, J.A., Pruess, K., Yamamoto, H., 2007. Numerical modeling of injection and mineral trapping of CO_2 with H_2S and SO_2 in a sandstone formation. Chem. Geol., 242 (3-4), 319-46.

Zhou, Q., Birkholzer, J.T., Tsang, C-F., Rutqvist, J., 2008. A method for quick assessment of CO2 storage capacity in closed and semi-closed saline formations. Int. J. Greenhouse Gas Control, 2 (4), 626-639.

Chapter 4

Applicability of vertical-equilibrium and sharp-interface assumptions in carbon sequestration modeling

This chapter was adapted from: B. Court, K.W. Bandilla, M.A. Celia, J.M. Nordbotten, M. Dobossy, A. Janzen, (2011), *Applicability of vertical-equilibrium and sharp-interface assumptions in carbon sequestration modeling*, International Journal of Greenhouse Gas Control, in review.

4.1. Introduction

When analyzing the viability of a proposed sequestration site, mathematical models are typically used to determine available sequestration volumes, sequestration safety (i.e., leakage risk), and migration of the injected CO_2 and displaced resident brine. These models range in complexity from simple pore volume calculations (Bachu et al, 2007; Kopp et al., 2009; Szulczewski and Juanes 2009) to three-dimensional (3D) multi-component, multi-phase reservoir simulators such as ECLIPSE (Schlumberger, 2010), NUFT (Nitao, 1998), TOUGH2 (Pruess, 2004), and STOMP (White and Oostrom, 1997). Several useful review papers and benchmark code comparison

have been completed by (Michael et al., 2009; Pruess et al., 2009; Schnaar and Digiulio, 2009), and by (Class et al., 2009; Ebigbo et al., 2007; Nilsen et al., 2011; Pruess et al., 2002, 2004; Pruess and Nordbotten, 2011) respectively. Figure 4.1 presents a conceptual model of the system considered showing a section of a single supercritical CO_2 plume in a deep saline injection aquifer bounded by impermeable aquitards above and below.

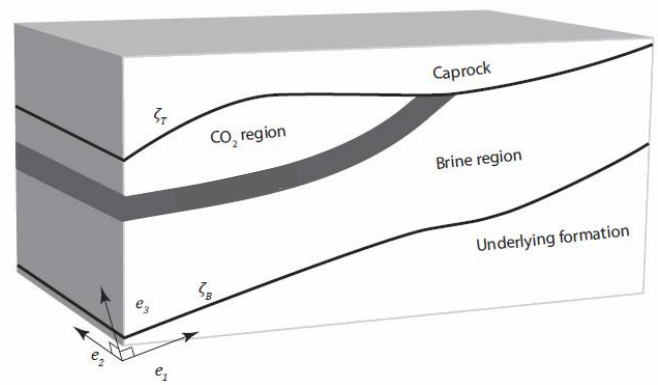

Figure 4.1: Conceptual model domain where the grey zone denotes the Capillary Transition Zone (adapted from Celia and Nordbotten (2011)).

A family of models of intermediate complexity can be derived by assuming that the strong buoyant drive in the system leads to vertical segregation of the injected CO_2 and resident brine on a time scale that is fast compared to the time scale of the simulation (Celia and Nordbotten, 2011; Nordbotten and Celia, 2011). This leads to a system where each fluid has a pressure distribution that is essentially hydrostatic, which is often referred to as vertical equilibrium (VE). While the applicability of the vertical-equilibrium assumption has been analyzed based on spatial scales (see, for example, Lake, 1989 or Yortsos, 1995), herein we consider the problem in terms of temporal scales. When the local-scale capillary pressure forces are negligible, the stratified fluids may be assumed to be separated by a macroscopic sharp-interface with constant fluid saturations on either side. These vertical-equilibrium, sharp-interface models have been used widely in the petroleum industry and, more recently, to analyze CO_2 injection and migration problems (Coats, 1971; Huppert and Woods, 1995; Woods and Mason, 2000; Nordbotten and

Celia, 2006, 2011; Hesse et al., 2007, 2008; Juanes et al., 2010; Celia and Nordbotten, 2009, 2011; Celia et al. 2011).

In a recent publication, Lu et al. (2009) compared fully resolved numerical simulations to simple analytical solutions based on the vertical-equilibrium and sharp-interface assumptions. The examples were based on injection of supercritical CO_2 from a single vertical well into a hypothetical formation that was considered to be homogeneous, isotropic, and horizontal with no leakage along the top or bottom boundaries, which leads to a radially symmetric solution. Lu et al. concluded that the vertical-equilibrium sharp-interface analytical approaches of this simple radial solution presented by (Dentz and Tartakovsky, 2009a, 2009b; Nordbotten et al., 2005) were unable to accurately predict the CO_2 front position. As such, they concluded that these simplified models were not appropriate to model CO_2 injection. In this paper, we look more closely at the conditions under which vertical-equilibrium models are appropriate, and the conditions under which sharp-interface models are appropriate, noting that the two conditions are largely independent. We show that for many cases vertical-equilibrium models are reasonable, whether or not the sharp-interface assumption applies. We also explain the results from the work of Lu et al. in light of this broader analysis.

The objective of this Chapter, based on (Court et al., 2011c), is to study the conditions under which both vertical-equilibrium and sharp-interface models are appropriate to model CO_2 injection and migration. We first examine different time scales to understand when vertical-equilibrium of phase pressures can reasonably be assumed. We then investigate the spatial scale associated with the capillary pressure – saturation function to understand when sharp-interface models are appropriate and when models including capillary forces (with no sharp-interface) are necessary. To put this into context, we consider a number of publications from the CO_2 sequestration literature that have reported both capillary pressure-saturation (P_c-S) and relative permeability-saturation (k_{rel}-S) relationships, whether using them in simulations or measuring them experimentally. From these papers, we extract several P_c-S functions

representative of the range found, and use them to study a generic injection scenario of an industrial-scale CO_2 capture and sequestration (CCS) operation. We also use the parameters and associated k_{rel}-S and P_c-S functions applied by Lu et al. (2009). Direct comparisons are made between results from the commercial simulator ECLIPSE and results from models based on vertical-equilibrium, both with and without the sharp-interface assumption. Our overall purpose is to identify the limits of vertically-integrated numerical models and of the sharp-interface assumption, thereby providing some practical guidance for the level of mathematical model complexity required to model CO_2 injection and migration.

The Chapter proceeds as follows. In the next section, we outline the two vertical-equilibrium models used in this study: a numerical model without the sharp-interface assumption, and an analytical model with the sharp-interface assumption. In Section 4.3, we present a review of the different k_{rel}-S and P_c-S functions that have been reported in the CCS literature. We include an analysis of the capillary pressure functions that provides a length-scale estimate of the "capillary transition zone", which guides the analysis of the sharp-interface assumption. We then use selected functions from this range of injection formation characteristics (P_c and k_{rel}) to explore, in Section 4.4, how the system behaves. We begin by presenting a time evolution of the plume in a generic injection scenario modeled with ECLIPSE. This provides an illustration of time-scaling arguments associated with the establishment of vertical-equilibrium. We then combine this with the spatial-scale analysis associated with capillary pressure, and consider other kinds of problems including that used by Lu et al. (2009). We end the chapter with a set of conclusions.

4.2. Model description

Injection of supercritical CO_2 into the subsurface involves the flow of both the injected fluid and the resident brine. The movement of CO_2 and brine, assumed to be immiscible, may be modeled using standard two-phase porous media flow equations, assuming CO_2 is the non-wetting phase (n) and brine is the wetting phase (w). The governing equations are based on the multi-phase version of Darcy's Law and the mass balance equation for each phase. The multi-phase extension of Darcy's law relates the volumetric flux of each phase to the respective phase pressure:

$$u_\alpha = -\frac{k k_{r\alpha}}{\mu_\alpha}(\nabla p_\alpha + \rho_\alpha g \nabla z) = -\lambda_\alpha k(\nabla p_\alpha + \rho_\alpha g \nabla z), \qquad \alpha = n, w \quad (4.1)$$

where u_α is the volumetric flux [LT^{-1}] of phase α, k is the intrinsic permeability [L^2] of the formation, $k_{r\alpha}$ is the relative permeability [-] of phase α, μ_α is the viscosity [$M(LT)^{-1}$] of phase α, p_α is the pressure [$ML^{-1}T^{-2}$] of phase α, ρ_α is the density [ML^{-3}] of phase α, g is gravitational acceleration [LT^{-2}], and z is the vertical coordinate [L] (positive upward). The phase mobility λ_α is defined by:

$$\lambda_\alpha = \frac{k_{r\alpha}}{\mu_\alpha}. \quad (4.2)$$

The mass balance equation for each phase is given by:

$$\frac{\partial(\rho_\alpha \phi s_\alpha)}{\partial t} + \nabla \cdot \rho_\alpha u_\alpha = \rho_\alpha q_\alpha \ , \qquad \alpha = n, w \quad (4.3)$$

where ϕ is the formation porosity [L^3L^{-3}], s_α is the phase saturation [-], t is time [T], and q_α is the source/sink term [T^{-1}] of phase α. By inserting equation (4.1) into (4.3) one obtains a system of two equations with seven unknowns: $\rho_n, \rho_w, \phi, p_n, p_w, s_n, s_w$. The system of equations is closed by requiring that the pore space is completely filled by the two fluids (so that the additional equation $s_n + s_w = 1$ is included), by imposing compressibility relationships relating the fluid densities and the porosity to the fluid pressures (while assuming negligible thermal effects), and by relating the two phase pressures to the saturation via the capillary pressure p_c [$ML^{-1}T^{-2}$], with $p_c \equiv p_n - p_w = p_c(s_\alpha)$. We also assume that the relative permeability is a function of saturation, $k_{r\alpha} = k_{r\alpha}(s_\alpha)$, and that viscosities are known.

We consider injection of supercritical CO_2 into a single formation bounded above and below by impermeable layers. Initially, the entire domain is at hydrostatic pressure and the pore space is fully saturated with brine. The focus of this study is on the injection period therefore only primary drainage is considered, which means that CO_2 residual saturation ($S_{CO2,res}$) is not relevant. Note, however, that residual brine saturation is present and can play an important role in the results.

The system described thus far can be solved using three-dimensional numerical simulators such as ECLIPSE. However, modeling CO_2 injection at the basin scale is computationally intensive due to the need for local grid refinement around injection wells and around local features including faults/fractures and existing wells. In North America, the number of existing wells in an expected area of review for an injection operation can be very large (IPCC 2005), making three-dimensional grid refinement computationally prohibitive. This is especially true when Monte Carlo analysis is required, which can involve tens of thousands of full simulations. This motivated the development of different kinds of vertical-equilibrium models.

- Vertically-integrated numerical model

Under appropriate conditions, the three-dimensional governing equations may be simplified by assuming vertical flows to be negligible, which enables reduction of dimensionality via vertical integration. As noted earlier, vertical flow can be neglected once density-driven segregation of the fluids has occurred. This implies that the time scale of simulation must be longer than the segregation time scale. Thus the vertical-equilibrium assumption may not be valid at early time when fluids have not segregated, or close to the leading edge of the plume, where CO_2 may displace brine vertically. Negligible vertical flow can be interpreted as a vertical pressure distribution that is close to hydrostatic, and thus the phase pressures are assumed to be in vertical-equilibrium. We refer to (Class et al., 2009; Celia and Nordbotten, 2011; Gasda et al., 2009; Lake, 1989; Nilsen et al., 2011; Nordbotten and Celia, 2006, 2011; Pruess and Nordbotten,

2011; Yortos, 1995) for details on vertically-integrated models and their applications, and to Norbotten and Dahle (2011) for a recent detailed discussion of this segregation time scale. We note that (Lake, 1989; Yortos, 1995) assume vertical-equilibrium with respect to a length scale argument, when the vertical-equilibrium assumption made by Nordbotten and Celia is based on a time scale argument. The requirement used by Lake's argument that the effective reservoir length-to-thickness ratio R_L be large, "may be regarded as a ratio of a characteristic time for fluid to cross the reservoir in the x direction to that in the z direction" (Lake, 1989). Nordbotten and Celia's argument requiring that the segregation time scale (i.e. the z characteristic time in Lake) be small is therefore equivalent to "R_L (being) large, (leading to) saturation or pressure fluctuations in the z direction decay much faster than those in the x direction".

Assuming vertical-equilibrium and no flow across the top and bottom boundaries the mass balance equation can be integrated over the thickness of the formation H leading to:

$$\frac{\partial}{\partial t}(\Phi S_\alpha) + \nabla \cdot U_\alpha = Q_\alpha \tag{4.4}$$

where Φ is the depth-averaged porosity [-], S_α is the depth-averaged saturation [-], U_α is the depth-averaged flux [LT^{-1}], and Q_α is the depth-averaged source/sink term [T^{-1}]. The depth-averaged parameters are found by vertically averaging the fine scale parameters:

$$\Phi(x,y) = \frac{1}{H}\int_0^H \phi dz \tag{4.5}$$

$$S_\alpha(x,y,t) = \frac{1}{\Phi H}\int_0^H \phi s_\alpha dz \tag{4.6}$$

$$\mathrm{Q}_\alpha = \frac{1}{H}\int_0^H q_\alpha dz \tag{4.7}$$

The depth-averaged flux U_α is found by vertical integration of Darcy's law:

$$U_\alpha(x,y,t) = -\Lambda_\alpha K(\nabla P_\alpha + \rho_\alpha g \nabla z) \tag{4.8}$$

where P_α is the pressure [$ML^{-1}T^{-2}$] of phase α at the bottom of the formation, K is the depth-averaged permeability [L^2], $\Lambda_\alpha = \frac{K_{r_\alpha}}{\mu_\alpha}$ is the depth-averaged mobility [$ML(T)^{-1}$], and K_{r_α} is the depth-averaged relative permeability [-].

When the local-scale capillary pressure forces are important, a significant Capillary Transition Zone (Lake, 1989) will develop in the vertical direction where fluid saturation will gradually vary from full brine saturation with no CO_2 outside of the plume, to a combination of high CO_2 saturation and low brine saturation inside the plume (see conceptual representation in Figure 1). We note that the thickness of the Capillary Transition Zone (CTZ) grows proportionally to the range of capillary pressures (ΔP_c), imposed by the P_c-S curve, between full and residual brine saturations (or some other threshold, as discussed in Section 3) as conceptually represented in Figure 2 and in (Lake, 1989).

- Reconstruction of the vertical saturation profile when capillary forces are significant

In this vertically-integrated numerical model the governing equations are solved by using an Implicit Pressure Explicit Saturation (IMPES) approach, where the phase pressures and saturations are computed sequentially for each time step. As the phase pressures are related by the capillary pressure function and the sum of the two depth-averaged saturations is 1, only one depth-averaged phase pressure and one depth-averaged saturation need to be modeled. However, the vertical saturation distributions for both phases need to be reconstructed from the depth-averaged saturation, because the depth-averaged phase mobilities depend on the relative permeability distributions which typically are a non-linear function of brine saturation. The reconstructed saturation profile is then used in combination with the k_{rel}-S relationship to find the relative permeability profile, which is then integrated in the vertical direction to find the depth-integrated mobility. This mathematical reconstruction of the vertical saturation profile is conceptually described in Figure 4.2. We refer to the vertically-integrated model including this reconstruction as having a finite Capillary Transition Zone (CTZ), and therefore refer to the model as a finite-CTZ model.

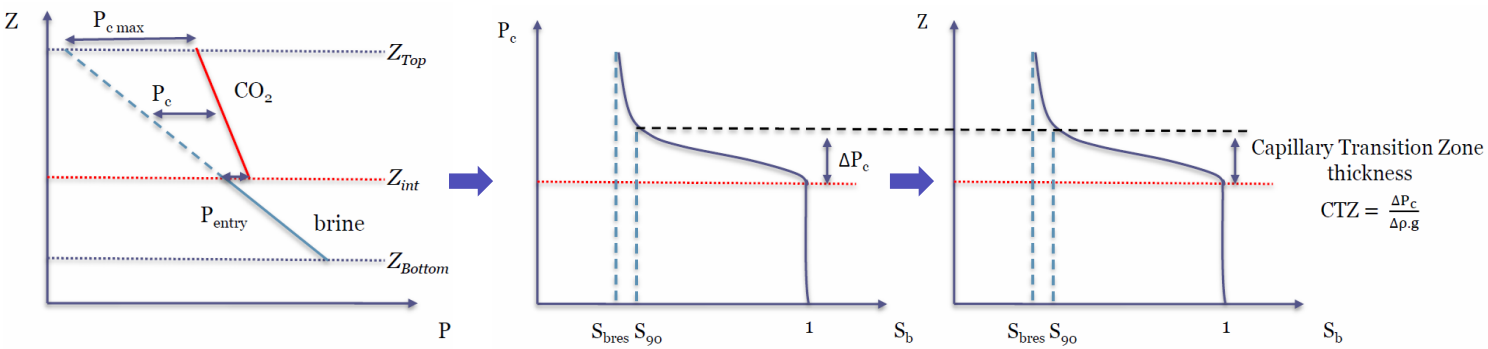

Figure 4.2: Conceptual (a) pressure, (b) capillary pressure, and (c) saturation vertical profiles.

- Sharp-interface assumption neglecting capillary forces in vertically-integrated numerical model

When the CTZ is small, the stratified fluids may be assumed to be separated by a macroscopic sharp interface. In the sharp-interface case, the pores above the interface are filled with brine and CO_2, with brine at residual saturation ($s_{b,res}$) and with CO_2 filling the remainder of the pore space. Because we only consider the injection period (drainage process), the pores below the interface are fully saturated with brine. The thickness of the CO_2 plume h [L] thus gives a complete description of the vertical saturation distribution, with $S_{CO2} = \frac{h}{H} - s_{b,res}$ and $S_b = \frac{H-h}{H} + s_{b,res}\frac{h}{H}$. Note that lower-case *s* is the local saturation while upper-case *S* is the depth-averaged saturation. The depth averaged relative permeabilities are also directly described by the plume thickness, with $K_{rel_CO2} = \frac{h}{H}k_{rel_CO2,max}$ and $K_{rel_b} = \frac{H-h}{H}$, where $k_{r_CO2,max}$ is the relative permeability of CO_2 at its saturation endpoint (that is, when brine is at its local residual saturation, $s_{b,res}$).

- Analytical sharp-interface model

If we assume radial symmetry, along with the assumptions of a horizontal, homogeneous formation and a constant rate of injection, the sharp-interface model becomes a partial differential equation that has a self-similar solution (see Nordbotten and Celia (2006) for details) which depends only on the dimensionless group χ, as defined below. When viscous forces dominate gravity forces, the solution is particularly simple and takes the following analytical form,

$$\mathrm{h} = \begin{cases} \mathrm{H} & for \quad \chi \leq 2/\lambda \\ \frac{\mathrm{H}}{\lambda-1}\left(\sqrt{\frac{2\lambda}{\chi}} - 1\right) & for \quad \frac{2}{\lambda} < \chi < 2\lambda \\ 0 & for \quad \chi \geq 2\lambda \end{cases} \tag{4.9}$$

where

$$\chi = \frac{2\pi H\phi\left(1-s_{b,res}\right)}{Q}\frac{r^2}{t}$$

where r is the radial distance from the injection well, t is the time since injection started, $s_{b,res}$ is the brine residual saturation, and Q is the constant volumetric injection rate (Note when viscous

forces do not dominate gravity forces, the solution to the governing equation does not have the above simple analytical form and has to be solved numerically, see Nordbotten and Celia (2006, 2011) for details).

4.3. Literature review

Capillary pressure and relative permeability functions can have a significant impact on the CO_2 plume shape and outer extent. Coupled with intrinsic (absolute) permeability, they also have important impacts on pressure build-up during injection. To investigate the impacts of parameter choices, specifically relative permeability and capillary pressure, we reviewed the range of P_c-S and k_{rel}-S relationships reported in the CCS literature. We found that P_c-S and k_{rel} -S relationships reported are typically based on Brooks-Corey (Brooks and Corey, 1966), Van Genuchten (Van Genuchten, 1980), and Corey (Corey, 1954) models (see (Olafuyi, 2088) for helpful review), as well as direct fits of experimental data, or purely mathematical theoretical relationships (linear, cubic, etc.). We observed a wide range in values of $s_{b,res}$ and associated endpoint k_{rel_c}, and in entry pressure and pore size distribution indices used in P_c-S relationships. From this review (summarized in Tables 4.1 and 4.2), we extracted several capillary pressure functions representative of the range found and use them in our numerical simulation in Section 4.

References	k_{rel} formula	Parameters	$S_{b,res}$	Endpoint k_{relc}	Form. H [m]	Fig
(Dentz and Tartakovsky, 2009) (Nordbotten and Celia, 2006)	<u>Linear</u>: $k_{rc} = S_c$; $k_{rw} = S_w$;	- -	0	1	- -	7,11
(Lu et al., 2009)	Linear <u>VGM:</u> $k_{rw} = \sqrt{S_w}[1-(1-S_w^{\frac{1}{m}})^m]^2$ $k_{rc} = \sqrt{1-S_w}[1-S_w^{\frac{1}{m}}]^{2m}$ <u>Experimental:</u> $k_{rw} = \sqrt{S_*}[1-(1-S_*^{\frac{1}{m}})^m]^2$ $k_{rc} = \sqrt{1-S_w}[1-S_w^{\frac{1}{m}}]^{7m}$ <u>Cubic</u>: $k_{rc} = S_c^3$; $k_{rw} = S_w^3$	- m=0.75 m=0.75 -	0	1	62	7,11 8,9 8,9 8,9
(Gasda et al., 2010) (Class et al., 2009)	Linear	-	0.2	1	90-140	7,11
(Dahle et al., 2009)	$k_{rc} = 0.4(1-S_e^2)(1-S_e)^2$ $k_{rw} = S_e^4$		0.2	0.4	50	-
(Ebigbo et al., 2007)	$k_{rc} = (1-S_e)^2\left(1-S_e^{\frac{2+\lambda}{\lambda}}\right)$ $k_{rw} = S_e^{\frac{2+3\lambda}{\lambda}}$	λ =2	0.2	1	30	7,12,13
(Birkholzer et al., 2009) (Zhou, 2008) (Zhou, 2010) ***	VG***: $k_{rc} = \sqrt{1-S_*}[1-S_*^{\frac{1}{m}}]^{2m}$ <u>VG</u>: $k_{rw} = \sqrt{S_*}[1-(1-S_*^{\frac{1}{m}})^m]^2$	m=0.46	0.3	1	60 ~250 300-700	6,7,12,13
(Bennion and Bachu 2008)	Fit of experimental data - Nisku 1 Fit of experimental data - Basal	-	0.3 0.3	0.2 0.55	72 23	7 7
(Pruess et al., 2002) (Pruess and Muller, 2009)	$k_{rc} = (1-S_e^2)(1-S_e)^2$ VG k_{rw}	-	0.3	1	100 100 & 10	-
(Alkan et al., 2010) case 1 case 2	$k_{rc} = (1-S_e)(1-S_e)^2$ $k_{rw} = S_e^4$	-	0.2 0.3	1	100	-
(Doughty, 2007) (Doughty et al., 2008) (Doughty, 2010)	$k_{rc} = (1-S_e^2)(1-S_e)^2$ VG k_{rw}	-	0.3 0.0-0.45 0.2	1	100 5.5-8 160	-
(Benson et al., 2009)* small berea (Krause, 2009)* medium berea	Fit of experimental data	-	0 0	1 0.65	-	-

(Izgec et al., 2006)	$k_{rc} = (1 - S_e)^2 \left(1 - S_e^{\frac{2+\lambda}{\lambda}}\right)$ $k_{rw} = S_e^4$	λ =0.4	0.13	1	70	-
(Plug and Bruining, 2007)	$k_{rc} = (1 - S_*)^2 \left(1 - S_*^{\frac{2+\lambda}{\lambda}}\right)$ $k_{rw} = S_*^{\frac{2+3\lambda}{\lambda}}$	λ = 3.56 7.32 5.87	0.01 0.075 0.03	1	-	-
(Olafuyi, 2008) Berea Bentheim Mt. Gambier	Theoretical review + Fit of experimental data		 0.46-0.48 0.49-0.51 0.58	 0.41 0.31 0.34	-	-
(Bergmo et al., in press) **						

where $S_e = \frac{(S_w - S_{b,res})}{(1 - S_{b,res} - S_{CO2,res})}$; $S_{b,res} \leq S_w \leq 1 - S_{CO2,res}$ $S_* = \frac{(S_w - S_{b,res})}{(1 - S_{b,res})}$;

* & ** see associated (Krause et al., 2011) and (Bergmo, 2011) and *** modified k_{rc} from (Fischer, 1997; Olafuyi, 2008)

Table 4.1: Review of relative permeability - saturation (k_{rel}-S) relationships from the geological sequestration modeling literature. $s_{b,res}$ is the brine residual saturation and k_{relc} the associated endpoint of the CO_2 k_{rel} curve. Form. H is the thickness of the injection formation when reported (N/A for experimental studies). The last column indicates which relationships were used in Section 4.4 simulations, and the corresponding result's figure number.

References	P_c formula	Parameters		$S_{b,res}$	CTZ [m]	Form. H [m]	Fig
(Dentz and Tartakovsky, 2009) *(Nordbotten and Celia, 2006)* Many others	Assumed negligible	-	-	0	0	-	6-9
(Lu et al., 2009)	Linear: $P_c = P_d(1 - S_w)$	P_d = 1	-	0	31.6	62	11
(Gasda et al., 2010) (Dahle et al., 2009) (Delshad, 2010)	$P_c = P_d\, S_*^{-1/2}$	 P_d= 0.2	-	 0.2	 13.4	90-140 50 50	- - -
(Ebigbo et al., 2007) (Class et al., 2009)	Brooks-Corey: $P_c = P_d S_*^{-1/\lambda}$;	P_d= 0.1	λ = 2	0.2	11.12	30 90-140	12,13 -
(Birkholzer et al., 2009) (Zhou, 2008) (Zhou, 2010)	VG: $P_c = P_d\left(S_*^{-\frac{1}{m}} - 1\right)^{1-m}$	P_d= 0.2 P_d=0.19607 P_d= 0.04 P_d= 0.21 P_d= 0.4 P_d= 0.79	m = 0.46 m = 0.46 m = 0.41	 0.3	104.54 102.4 38.5 202.4 385.5 761.4	60 ~250 300-700	- 12,13 - - 12 -
(Bennion, 2006)	Experimental Nisku 1 Experimental Basal	-	-	0.3 0.3	309.3 7.5	72 23	- -
(Pruess et al., 2002) (Pruess and Muller, 2009)	VG	P_d= 0.1961	m=0.45	0.3	105.9	100 100 & 10	- -
(Alkan et al., 2010) case 1 case 2	VG: $P_c = P_d\left(S_*^{-\frac{1}{m}} - 1\right)^{1-m}$	P_d= 0.1 P_d= 1	m=0.4 m=0.25	0.2 0.3	110.9 23.5k	100	-
(Doughty, 2007) (Doughty et al., 2008) (Doughty, 2010)	$P_c = P_d\left(\frac{(S_w-0.03)^{-\frac{1.7}{1-1.7}}}{(1-0.03)} - 1\right)^{1/1.7}$ Above / VG	P_d= 0.133 P_d= 0.065 P_d= 0.188	- - -/m=0.416	0.3 0-0.15-0.45 0.2	19.9 20.76 44.8/167	100 5.5-8 160	-
(Benson et al., 2009)* small berea (Krause, 2009)* medium berea	Experimental	(See paper)		0 0	122.8 147.9	-	-
(Izgec et al., 2006)	Brooks-Corey	P_d= 1.1	λ =0.4	0.13	1703.21	70	-
(Plug and Bruining, 2007)	Experimental	(See paper)		~0	<1	-	-
(Olafuyi, 2008) Berea Bentheim Mt. Gambier	Brooks-Corey / VG fit of Experimental	P_d= 0.06 0.048 0.048	λ /m = 1.1/0.45 1.7/0.65 1.0/0.45	 0.15 0.10 0.10	 17/35 6.5/5.7 17/28	- - -	-
(Bergmo et al., in press) **	Johansen Utsira no P_c data	-	-	-	~1	-	-

** see associated (Bergmo, 2011)

Table 4.2: Review of capillary pressure - saturation (P_c - S) relationships from the geological sequestration modeling literature. $s_{b,res}$ is the brine residual saturation. CTZ stands for the Capillary Transition Zone thickness, which is equal to $\Delta P_c/(\Delta\rho g)$ and is calculated using $s_{10\%}$ (at 10% of the range between $s_{b,res}$ and s_b =1) with constant ρ_c= 710 kg/m^3 ρ_w= 1000 kg/m^3; Form. H is the thickness of the injection formation when reported (N/A for experimental studies); P_d is the entry pressure x 10^5 [Pa]; λ, m are the reported pore size distribution indices. The last column indicates which relationships were used in Section 4.4 simulations, and the corresponding result's figure number.

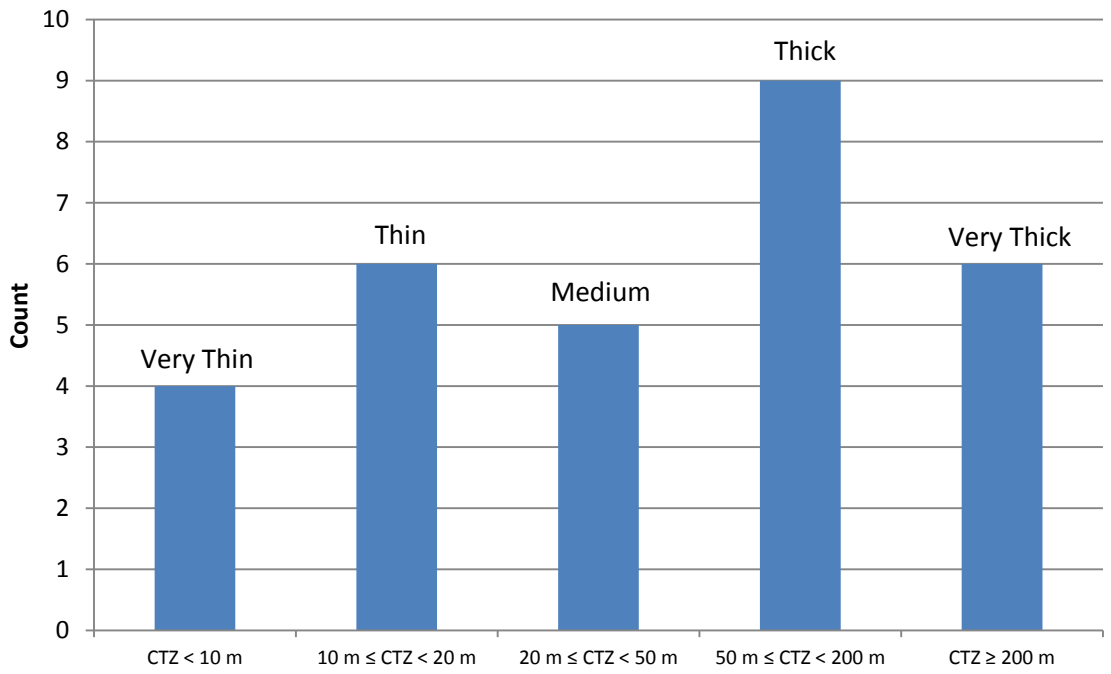

Figure 4.3: CTZ thicknesses reported in Table 4.2 grouped into five typical aquifer thickness categories.

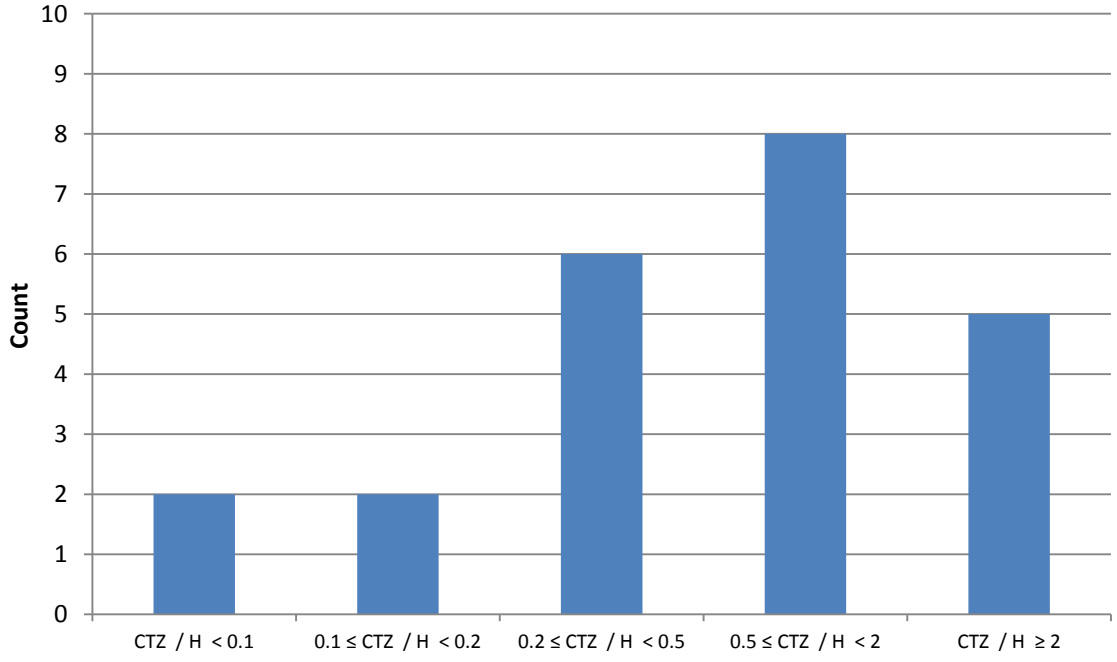

Figure 4.4: Normalized CTZ values range (CTZ / injection formation thickness reported from Table 4.2).

We used the reported Pc-S relationships to establish the associated CTZ thicknesses. Among other things, this metric provides an indication of when the sharp-interface assumption is reasonable. Because of the unbounded (asymptotic) character of many P_c–S relationships, we decided to use the value of P_c at a specified saturation threshold to determine the CTZ. In particular, we define the CTZ as covering the capillary pressure range from initial entry (s_b=1) to the P_c value when s_b differs from the final brine residual saturation by 10% which we denote by $s_{10\%}$ (I.e., $s_{10\%} = s_{b,res}+0.1(1-s_{b,res})$). To compare these in a consistent manner across the P_c-S curves of different formations (see Table 4.2), we used a constant $\Delta\rho$ based on ρ_c= 710 kg/m^3 for CO_2 and ρ_w= 1000 kg/m^3 for brine.

Figure 4.3 groups the calculated CTZ into bins of thickness ranges, for which we assign descriptors like “thin” and “thick” based on comparisons to typical injection formation thicknesses .

In Figure 4.4 we take the formation thickness reported in the specific publications and calculate the normalized thickness of the CTZ to the formation. This relative measure provides an indication of whether or not capillary forces are important, and thus whether or not the sharp-interface assumption is reasonable as discussed in Section 4. . We note that the difference in count between Figure 4.3 and Figure 4.4 is because 7 experimental capillary thicknesses did not have an associated formation thickness. When a range of formation thicknesses or two different calculated CTZ thicknesses were reported, the average value was used for Figure 4.4.

These results show a remarkably wide range of P_c-S functions and associated CTZ thicknesses. This gives caution to the assumption that the impact of capillary forces can be neglected. For the very large values of the CTZ, one may also question the physical reasonableness of the functions used. Independent of the specific lengths involved, these results indicate that the spatial scales associated with the CTZ must be considered when deciding on appropriate models, just as the time scale for vertical-equilibrium must be considered. We explicitly evaluate these in the next section.

4.4. Results

In this section we use numerical experiments to explore conditions under which vertically-integrated models are applicable. We also consider the impacts of finite CTZ values. First, numerical simulations using ECLIPSE are used to investigate the time scales for vertical-equilibrium (VE) to develop. This is followed by a comparison of 3D model results to results using the vertically-integrated sharp-interface model for several different k_{rel}-S relationships. Finally, we explore cases where capillary forces cannot be neglected (i.e. sharp-interface assumption is not valid), by comparing the results from a 3D model and a finite-CTZ vertically-integrated numerical model with reconstruction of the vertical saturation profile. The commercial simulator ECLIPSE (Schlumberger, 2010) is used for 3D model simulations. The vertically-integrated research codes VESA (Gasda, 2008; Gasda et al., 2009; Janzen, 2010) and ELSA (Nordbotten et al., 2009; Celia et al., 2011; Dobossy et al., 2011) are used for finite-CTZ numerical and sharp-interface analytical model simulations, respectively.

The computational experiments are based on a constant CO_2 volumetric injection across the entire thickness of a horizontal, isotropic and homogeneous aquifer. This allows the ECLIPSE runs to use a radial grid to minimize the number of cells, while VESA runs were done on a full cartesian grid and the ELSA analytical model does not require a grid. The ECLIPSE CO2SOL module was used to model immiscible fluids and the brine phase was taken as water to exclude the impact of salt on our results. Supercritical CO_2 is injected at 0.939 Mt/yr and 0.1 Mt/yr to represent industrial scale and pilot scale injection scenarios. Two intrinsic permeabilities (10 mD and 100 mD) are used to show the impact of intrinsic permeability on the CO_2 plume evolution. The values of the aquifer parameters as well as grid discretization can be found in Table 4.3.

	Generic injection scenario	Lu et al. (2009) problem set up
Top depth	2000m	2000m
Thickness	50m	62m
Intrinsic permeability	100mD	10mD
Porosity	0.15	0.15
Injection rate	1Mt/y for 50 years	0.1Mt/y for 10 years
Grid discretization	Horizontal: 5m in r to 6km, gradually increasing to 1km block until 60km Vertical: 1m in z	Horizontal: 2m in r to 1024m Vertical: 2m in z
Outer boundary condition	Fixed hydrostatic pressure	Fixed hydrostatic pressure

Table 4.3: Numerical simulation parameters

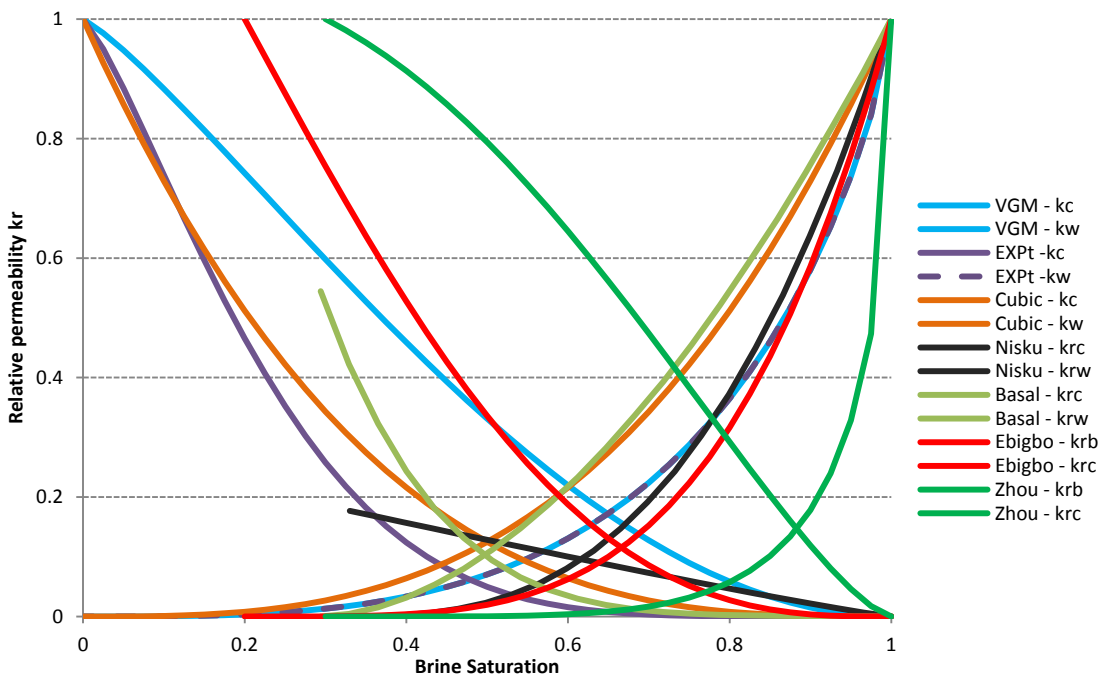

Figure 4.5: Relative permeability - saturation curves used in numerical simulations; only primary drainage is considered.

4.4.1. Time evolution of the CO_2 plume without capillary forces

The ECLIPSE model is used to simulate an injection of 0.939 $MtCO_2$/yr in an aquifer with an intrinsic permeability of 100 mD. Capillary forces are neglected. The k_{rel}-S relationship from Zhou et al. (see Table 4.1 for details) is used here. The time evolution of CO_2 saturation profiles (Figure 4.6) starts with a plume approaching a radial piston displacement at the very early stages (1 year and before), which then evolves into a more curved-shaped plume spreading further in

space. As described by Norbotten and Celia (2006), the vertical plume in homogeneous aquifers where capillary forces can be neglected is dictated by the ratio of the mobilities of the two fluids, $r_\lambda = \frac{\lambda_n}{\lambda_w}$. A small mobility ratio leads to a piston-shaped plume, while larger ratios lead to a CO_2 plume spreading further in space with a relatively thin layer at the top of the injection formation, see Nordbotten and Celia (2006) for more details. At early times the average CO_2 saturation within the plume is relatively low, thus leading to low relative permeability for CO_2 (see k_{rel}-S curve plot in Figure 4.5). This lower relative permeability compensates for the large viscosity difference, thereby leading to a lower mobility ratio and an associated piston-shape plume (note that, for drainage, the brine relative permeability used in the mobility ratio is the permeability ahead of the front, which is always equal to one). As the average CO_2 saturation increases over time, the CO_2 relative permeability increases, leading to a larger mobility ratio. Therefore, the CO_2 plume spreads further in space and forms as expected a relatively thin layer at the top of the formation after 50 years of injection.

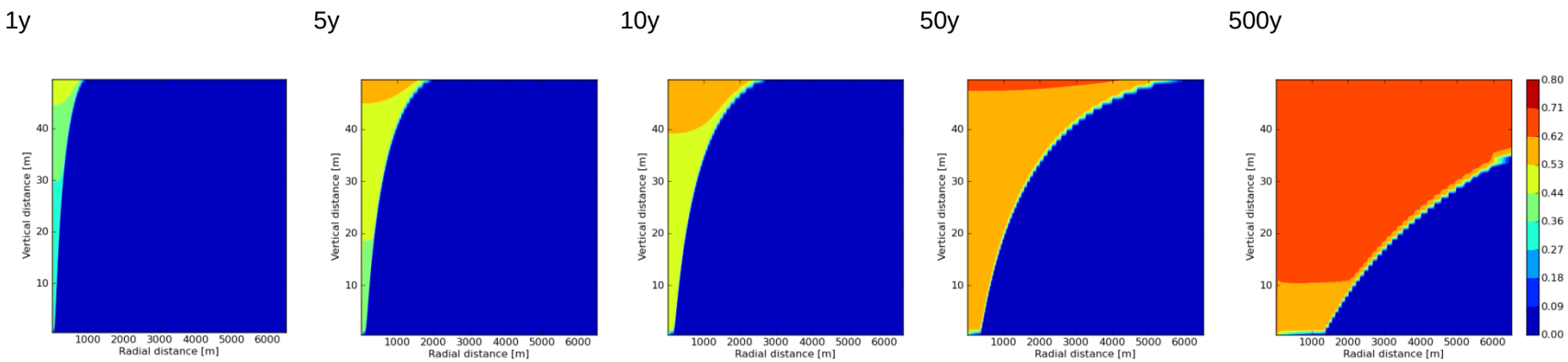

Figure 4.6: ECLIPSE time evolution of CO_2 saturation profiles using the k_{rel}-S from Zhou et al. (see Table 4.1) with no Pc.

The time evolution of the plume profiles shows that the saturation behind the front does not drop to the brine residual saturation immediately ($s_{b,res}$ = 0.3) because the brine needs time to drain vertically out of the CO_2-rich region behind the front. The simplest analysis, based on gravity drainage of brine in a background of vertically equilibrated CO_2, gives the following time estimate:

$$T_{b_dr} \sim \frac{H\, \emptyset\, \mu_b}{k_{rel,b,local}\, k_Z\, \Delta\rho\, g} \tag{4.10}$$

Note that, as the brine saturation behind the front decreases asymptotically to residual, the local relative permeability of the brine ($k_{rel,b,local}$) also decreases rapidly. The vertical brine drainage slows over time because the flow resistance increases as the relative permeability decreases, while the driving force (i.e. gravity) remains constant. Fifty years, a typical lifetime of a coal-fired power plant, is a realistic estimate for the life of a CO_2 injection operation. However, the time at which all the brine in the plume behind the front has drained may be very long as illustrated in Figure 4.6 by brine saturations higher than residual within the plume, even after 500 years of injection. Of course, this is strongly related to the parameters assigned to the formation, as we will see in subsequent results in this section. We also note that an initial analysis shows that drainage time is heavily dominated by the local brine relative permeability which decreases rapidly as brine gets close to residual (see Figure 4.5). A more detailed investigation of the vertical drainage process is beyond the scope of this dissertation, and will be addressed in a future publication.

We also note that, independent of the saturation values behind the front, for the case that does not include capillary pressure, the invading front is always sharp. This demonstrates that when capillary pressure is neglected, the CTZ will be zero, so that a sharp-interface approximation is appropriate.

4.4.2. Brine drainage time scale determines applicability of vertical-equilibrium

In this section, several relative permeability functions from the literature review completed in Section 4.3 are applied to the generic injection scenario from Section 4.4.1. Problem setup

conditions and relative permeability from Lu et al. (2009), neglecting capillary pressure, are also examined (see Table 4.3). We model industrial scale (0.939 $MtCO_2$/yr) and pilot scale (0.1 Mt CO_2/yr) injection scenarios to examine the impact of both intrinsic permeability (10 mD and 100 mD) and relative permeability on the CO_2 plume evolution. Because we ignore capillary pressure and model a radially symmetric, homogeneous, and isotropic CO_2 plume, ELSA (vertically-integrated analytical sharp-interface model) can be appropriately compared to ECLIPSE in order to determine when vertically-integrated models are applicable (i.e. the sharp-interface numerical model would give the same results).

We first apply three theoretical (Linear, Ebigbo et al. (2007), Zhou et al. (2010)), and two experimental (Nisku and Basal from Bennion and Bachu (2008)) sets of relative permeability curves (see Figure 4.5 and Table 4.1) to the generic injection scenario with the higher injection rate and higher intrinsic permeability. The resulting CO_2 plumes after 50 years are presented in Figure 4.7.

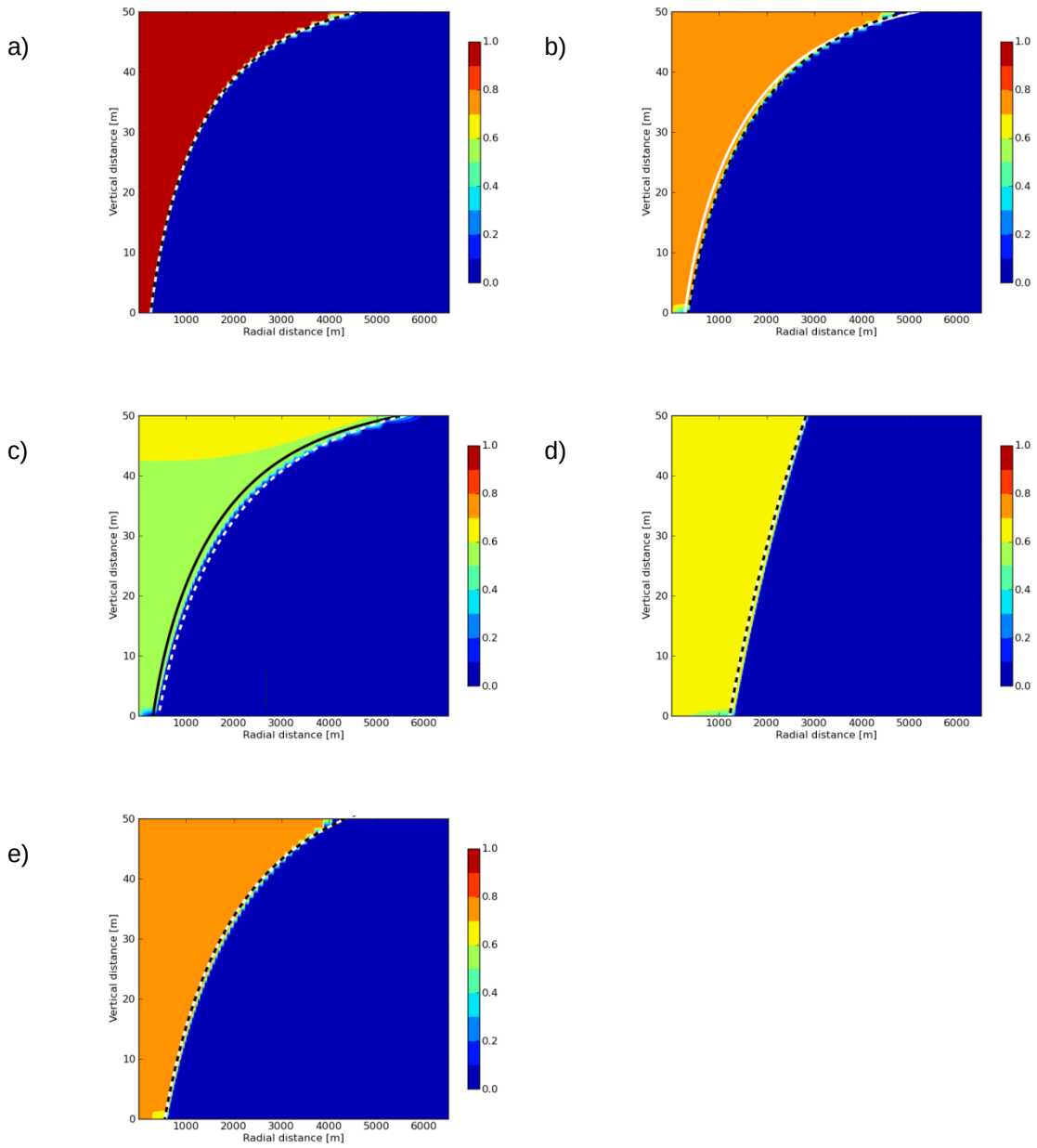

Figure 4.7: Comparison of ECLIPSE (color coded contours) CO_2 saturation profiles after 50 years of 0.939 Mt/yr injection in a 100 mD intrinsic permeability aquifer with analytical sharp-interface lines for (a) linear, (b) Ebigbo, (c) Zhou, (d) Nisku, and (e) Basal k_{rel}-S curves with no Pc. The colors of the solid and dotted lines are modified for maximum visibility; these lines are collinear on a, d, and e. Solid and dotted lines are based on $S_{b,res}$ & associated endpoint k_{rel_CO2} and time-dependent representative S_b and associated $k_{rel_CO2,}$ respectively.

We note that the three theoretical curves have different $s_{b,res}$ (0, 0.2, 0.3) but all have an endpoint CO_2 relative permeability (k_{rel_CO2}) equal to one. The experimental curves both have non-zero $s_{b,res}$ (0.33, 0.54) and endpoint k_{rel_CO2} much lower than one (0.18, 0.54). Several important observations can be drawn from the results in Figure 4.7. First, the Nisku (d) case confirms the observation from Section 4.1 and (Nordbotten and Celia, 2006) that low endpoint k_{rel_CO2} values give low mobility ratios for a given set of viscosity values, leading to more piston-like CO_2 plume shapes (that is, the invasion interface is close to vertical). Comparing all 5 cases, we observe that brine has not yet fully drained to $s_{b,res}$ only in the Zhou (c) case. This is because the Zhou k_{rel_brine} curve is the steepest, so it very quickly reaches low values (see Figure 4.5) and slows down the drainage process as described in Section 4.1 and shown by equation (4.10). The linear relative permeability (a) case has the fastest drainage and is the only case that reaches a CO_2 saturation of 1 because it assumes $S_{b,res} = 0$. We note that the Zhou case CO_2 plume profile in Figure 4.7 is wider and the outer extent reaches farther into the formation than in the linear case because of the additional volume of the residual brine combined with the high endpoint k_{rel_CO2} values from k_{rel_CO2} curve (see Figure 4.5). In summary, the k_{rel_CO2} curve has a large impact on the CO_2 profile shape, and the k_{rel_brine} curve has a large impact on the time scale of the brine drainage and hence whether the CO_2 and brine segregate.

Figure 4.7 a,b,d, and e) show that for most relationships the ELSA analytical model results based on theoretical $s_{b,res}$ and endpoint k_{rel_CO2} closely match ECLIPSE results because there is close to complete brine drainage behind the front. However, in the Zhou case (Figure 4.7c) the brine saturation is not completely drained after 50 years. We observe a representative brine saturation at 50 years of about 0.425 from the range of values in the ECLIPSE plume, greater than the theoretical residual value of $s_{b,res} = 0.3$. Therefore, using this theoretical $s_{b,res}$ and its associated endpoint k_{rel_CO2} of 1 as the analytical model inputs leads to ELSA results that slightly underestimate the plume volume width (see the solid line in Figure 4.7c). When the time-dependent $s_{b,res}$ and mobility ratio, based on associated time-dependent endpoint k_{rel_CO2}, are incorporated the analytical model results (see the dotted line in Figure 4.7c) match 3D model

results very well. We note that because the time-dependent representative ECLIPSE plume k_{rel_CO2} of 0.83 (determined from the range of values observed) is close to 1, the mobility ratio is not that different and the analytical shape and outer extent based on theoretical values (solid line) are still quite close to the ECLIPSE results.

Overall, the analytical results match ECLIPSE results well for cases where brine has reached, or is close to reaching, residual saturation (Figure 4.7); however, they do not match well for cases where the fluids are far from being segregated. As presented in (Nordbotten and Celia, 2006; Celia and Nordbotten, 2009), fluid segregation is a key assumption that must be respected when using these vertically-integrated models. This can be seen clearly in the scenario posed by Lu et al. (2009), who used the lower permeability value (10 mD) and the lower injection rate (0.1 Mt/yr) and performed simulations for only 10 years. The first row of Figure 4.8 presents ECLIPSE results that qualitatively replicate Figures 3b-3d from Lu et al. (2009) with minor discrepancies caused by slight differences in the ECLIPSE fluid properties calculation. The simulation results are based on use of the Van Genuchten-Mualem (VGM) [see (Mualem, 1976; Van Genuchten, 1980)], Experimental, and Cubic relative permeability curves plotted in Figure 4.5. The solid white lines in Figure 4.8a-8c clearly show that use of vertically-integrated analytical models with zero $s_{b,res}$ and associated endpoint k_{rel_CO2} of 1 to represent a time scale when the fluids have not segregated, as done per Lu et al. (2009), is inappropriate. The reason is that after 10 years of 0.1 $MtCO_2$/y injection in a 10 mD aquifer, the representative ECLIPSE brine saturations (0.45, 0.4, 0.33) and k_{rel_CO2} (0.4, 0.12, 0.3) from the range of values observed behind the plume are far from 0 and 1, respectively. We note that the larger this difference in $S_{b,res}$ and k_{rel_CO2} is, the worse the analytical overlay in plume volume and CO_2 profile shape and outer extent is. This should be expected from the theory of the solutions. We also note that while the results do not match, the ECLIPSE results again show a sharp interface, consistent with the fact that capillary pressure effects are ignored in the simulations.

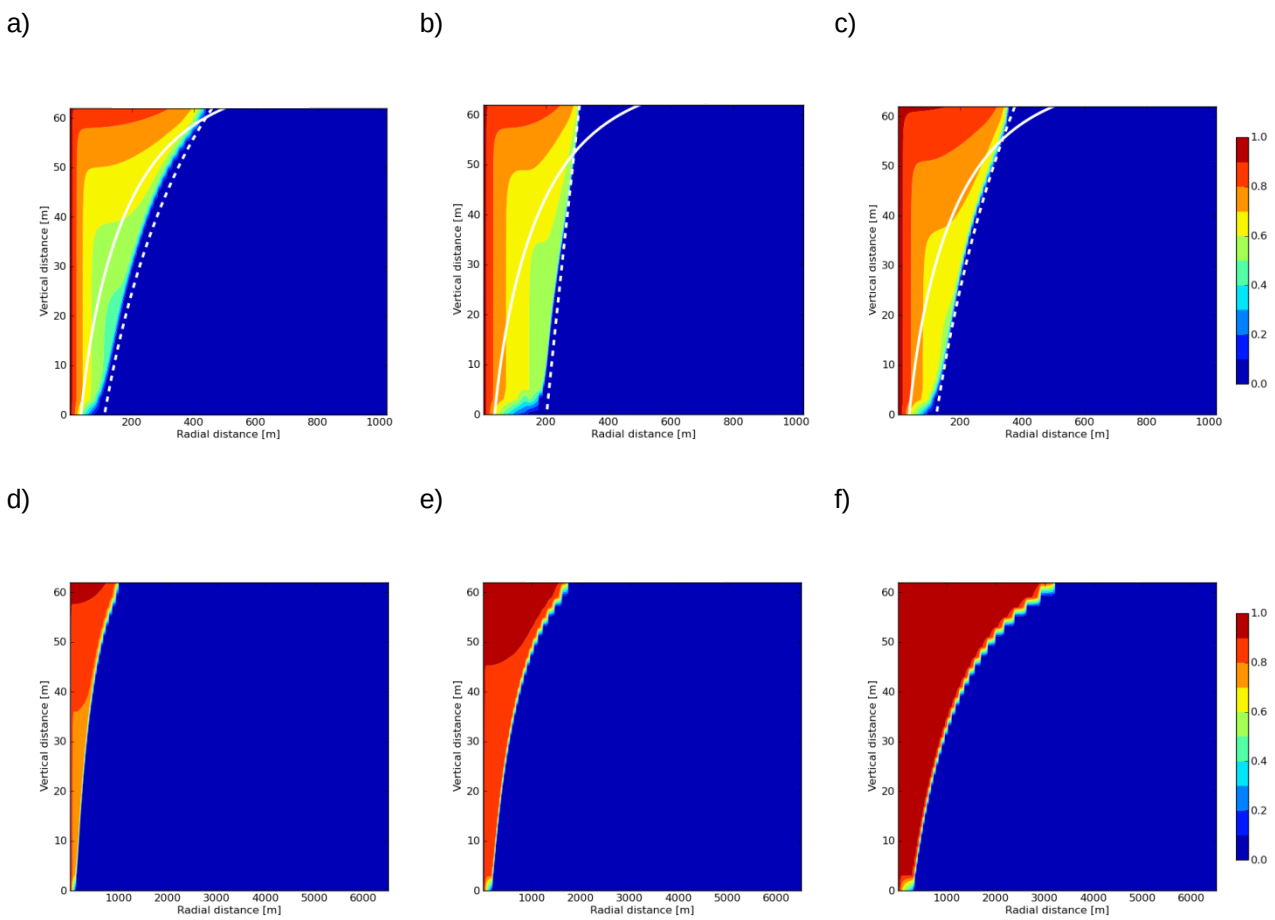

Figure 4.8: Row 1 shows comparison of ECLIPSE (color coded contours) CO_2 saturation profiles after 10 years of 0.1 Mt/yr injection in a 10 mD intrinsic permeability aquifer with the analytical sharp-interface lines for (a) VGM, (b) Experimental, and (c) Cubic k_{rel}-S curves with no P_c (from Lu et al. (2009)). Solid and dotted lines are based on $S_{b,res}$ & associated endpoint k_{rel_CO2} and time-dependent representative S_b and associated $k_{rel_CO2,}$ respectively.
Row 2 extends part (a) to (d) 50, (e) 150, and (f) 500 years of injection.

The importance of vertical brine drainage dynamics is confirmed by the analytical simulations based on the transient fraction of brine segregated after 50 years. Taking these time-dependent brine saturation (0.45, 0.4, 0.33) and k_{rel_CO2} (0.4, 0.12, 0.3) values as ELSA inputs provides remarkably close matches as shown by the dotted lines in Figures 4.8a, b, and c). These results demonstrate that sharp-interface analytical models can provide helpful and accurate answers even when the fluids have not yet fully segregated if brine drainage dynamics are somehow included within the model. This finding considerably increases the potential scope

of application of these analytical models, which until now have been restricted by their segregation time scale assumption. The strategy to obtain these time-dependent brine saturation and k_{rel_CO2} values using simplified dynamic reconstruction models will be the focus of a future publication.

The difference between the ECLIPSE and analytical results does not originate from the choice of relative permeability curves. Figures 4.9a, b, and c apply the same 3 curves from Figures 4.8a, b, and c) to the generic injection scenario (0.939 $MtCO_2$/yr; 100mD; 50 years) from Section 4.1. After 50 years, the top row of Figure 4.9 clearly shows close matches in CO_2 profile shape and plume outer extent between ECLISPE and ELSA. Running both the low injection Lu et al. (2009) problem setup (Figure 4.8 d, e, and f) and the high injection generic scenario (Figures 4.9d, e, and f) in a 10mD intrinsic permeability aquifer for 500 years confirms that the time scale of drainage is the key determinant on whether vertically-integrated models are valid or not. Only one time series (VGM) is presented in the bottom row of Figures 4.8 and Figures 4.9 because the Experimental and Cubic k_{rel}-S cases show the same behavior. Fluid segregation time scale, which is dominated by permeability-driven brine drainage, dictates the applicability of vertically-integrated models.

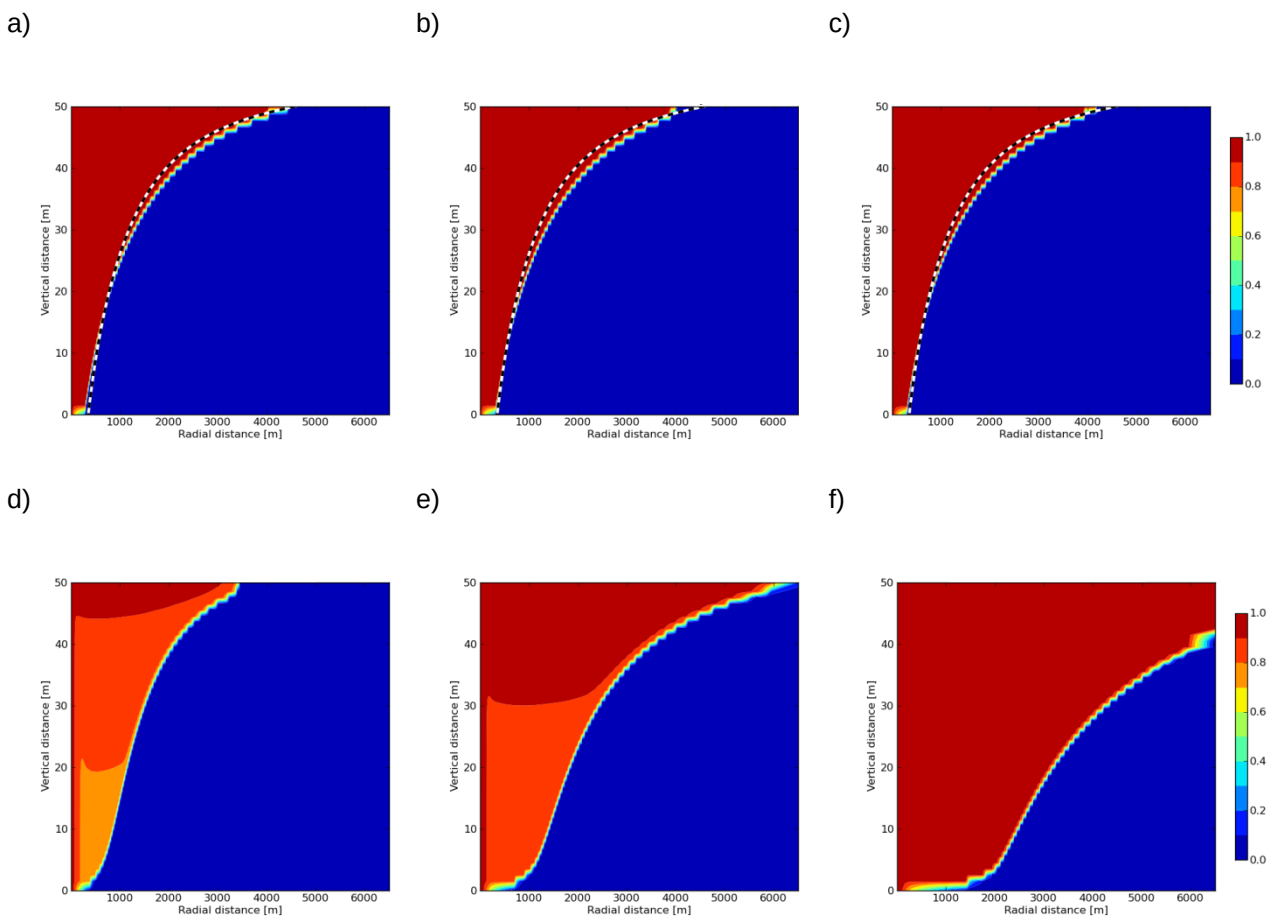

Figure 4.9: Row 1 shows the comparison of ECLIPSE (color coded contours) CO_2 saturation profiles after 50 years of 0.939 Mt/yr injection in a 100 mD aquifer with the analytical sharp-interface lines for (a) VGM, (b) Experimental, and (c) Cubic k_{rel}-S curves with no P_c (from Lu et al. (2009)). Solid and dotted lines are based on $S_{b,res}$ & associated endpoint k_{rel_CO2} and time-dependent representative S_b and associated $k_{rel_CO2,}$ respectively.
Row 2 shows ECLIPSE saturation profiles for (d) 50, (e) 150, and (f) 500 years of 0.939 Mt/yr injection in a 10 mD aquifer with the VGM k_{rel}-S curve .

In conclusion, our results show that the applicability of vertically-integrated models is determined by the time scale of vertical brine drainage. We demonstrated that sharp-interface analytical models are useful and accurate when applied within the appropriate time scale associated with their fundamental fluid segregation assumption. Finally, our results indicate that these analytical models have a promising potential to provide accurate modeling results even

when fluids have not fully segregated. In such cases, vertical brine drainage dynamics must be included; how to do this is the emphasis of on-going research by the authors.

4.4.3. Inclusion of capillary pressure effects

The wide range of capillary transition zones found in the literature review in Section 3 suggests that capillary pressure effects may need to be considered in many simulations. The impact of different P_c-S curves on the CO_2 plume and the implications for modeling strategies is the focus of this section. We explore cases where capillary forces cannot be neglected (i.e. where the sharp-interface assumption is not valid) by comparing the results from ECLIPSE and the VESA finite-CTZ vertically-integrated numerical model with reconstruction of the vertical saturation profile. Four P_c-S relationships are used (See Figures 4.10): Ebigbo, Linear (thin CTZ ~10 & 30 m), Zhou (thick CTZ ~100m; P_d = 0.19607e5 [Pa] in Table 4.2), and Zhou 04 (very thick CTZ ~400m; P_d = 0.4e5 [Pa] in Table 4.2).

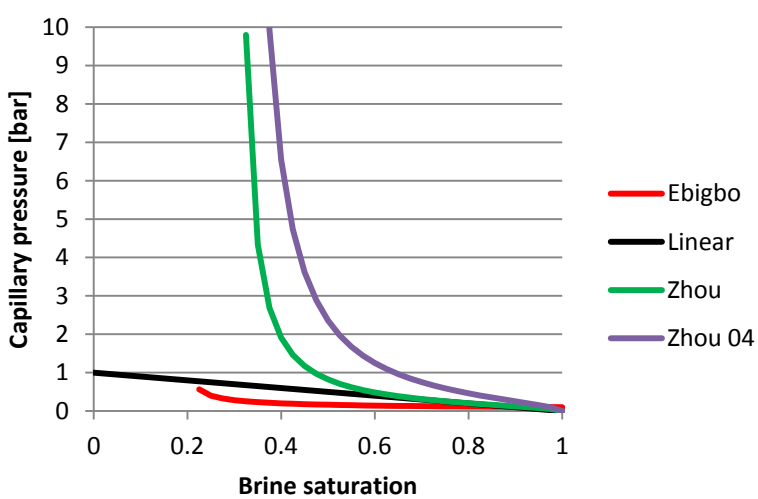

Figure 4.10: Four P_c-S curves used: Ebigbo, Linear, Zhou (P_d = 0.19607e5 [Pa]), and Zhou 04 (P_d = 0.4e5 [Pa]). See Table 4.2 for more details and Table 4.1 for associated k_{rel}-S relationship.

When the local-scale capillary pressure forces are important, a significant CTZ will develop in which fluid saturation varies gradually from full brine saturation with no CO_2 outside of

the plume to a combination of high CO_2 saturation and low brine saturation inside the plume. Capillary forces counteract the buoyant segregation, holding brine within the CO_2 plume, and a "drainage equilibrium" is reached where no more drainage occurs, although brine above residual saturation and CO_2 coexist in the capillary transition zone. The thickness of, and the saturation distribution inside, this capillary transition zone are determined by the P_c-S curve, as illustrated by the ECLIPSE results in Figure 4.11, which replicate Figure 4 from the Lu et al. (2009) using the linear P_c-S curve. We note the linearly distributed CTZ that develops across a roughly 30 m thickness at a radius of 200 m away from the injection well, clearly showing both the impact of the shape of the P_c curve and the size of the CTZ (31.6 m) reported in Table 4.2. We also note that this is very well represented in the vertical-equilibrium model VESA (not shown here), with results that are essentially identical.

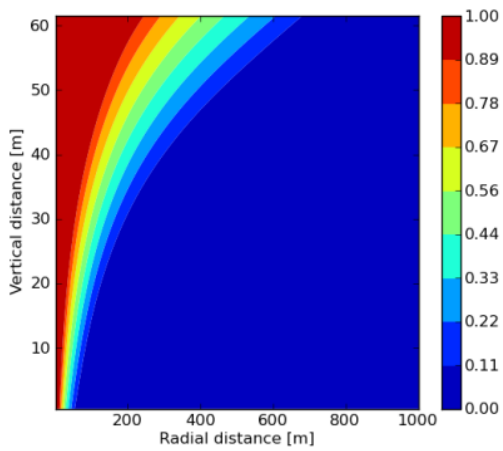

Figure 4.11: CO_2 saturation profiles after 10 years of 0.1 Mt/yr injection in a 10 mD intrinsic permeability aquifer using ECLIPSE model with linear k_{rel}-S and P_c-S curves (Figures 4.10) reproducing Figure 4 from Lu et al.

In Figures 4.12a-12c, the use of the 3 different non-linear P_c-S curves (Figures 4.10) as ECLIPSE inputs demonstrates the impact of different CTZ sizes (thin, thick, and very thick) on the CO_2 plume in the generic injection scenario (larger permeability and injection rate). Larger CTZs result in the plume spanning a smaller brine saturation range, across a given vertical cross-section, in the high part of the saturation spectrum due to capillary forces. This variable

saturation profile will influence the relative permeability profile, and hence the plume shape and outer extent of the CO_2 plume (see Equation (4.9)). The latter will have important implications for monitoring, pressure build-up control, and potential remediation or plume steering strategies involving brine production wells, as discussed in Chapter 5 based on (Court et al., 2011a) and investigated by Chapter 6 based on (Court et al., 2011b). This change in saturation distribution within the plume also impacts the definition of the two-phase flow region, which may mean prolonged contact of acidified brine with the overlying caprock (Ellis et al., 2011) and wellbore cements (Matteo and Scherer, 2011), possibly leading to enhanced degradation along these potential leakage pathways. Anticipating the order of magnitude of the injection formation P_c-S curve's spatial impact on the CO_2 plume before model simulations was one of the motivations for classifying the CTZ in Section 4.3. Among other things, it provides direct measures for when the sharp interface assumption will be reasonable. (Note the fit of the sharp-interface model shown in Figure 4.12a, which is the only result with a "thin" CTZ and therefore compares well to ECLIPSE results).

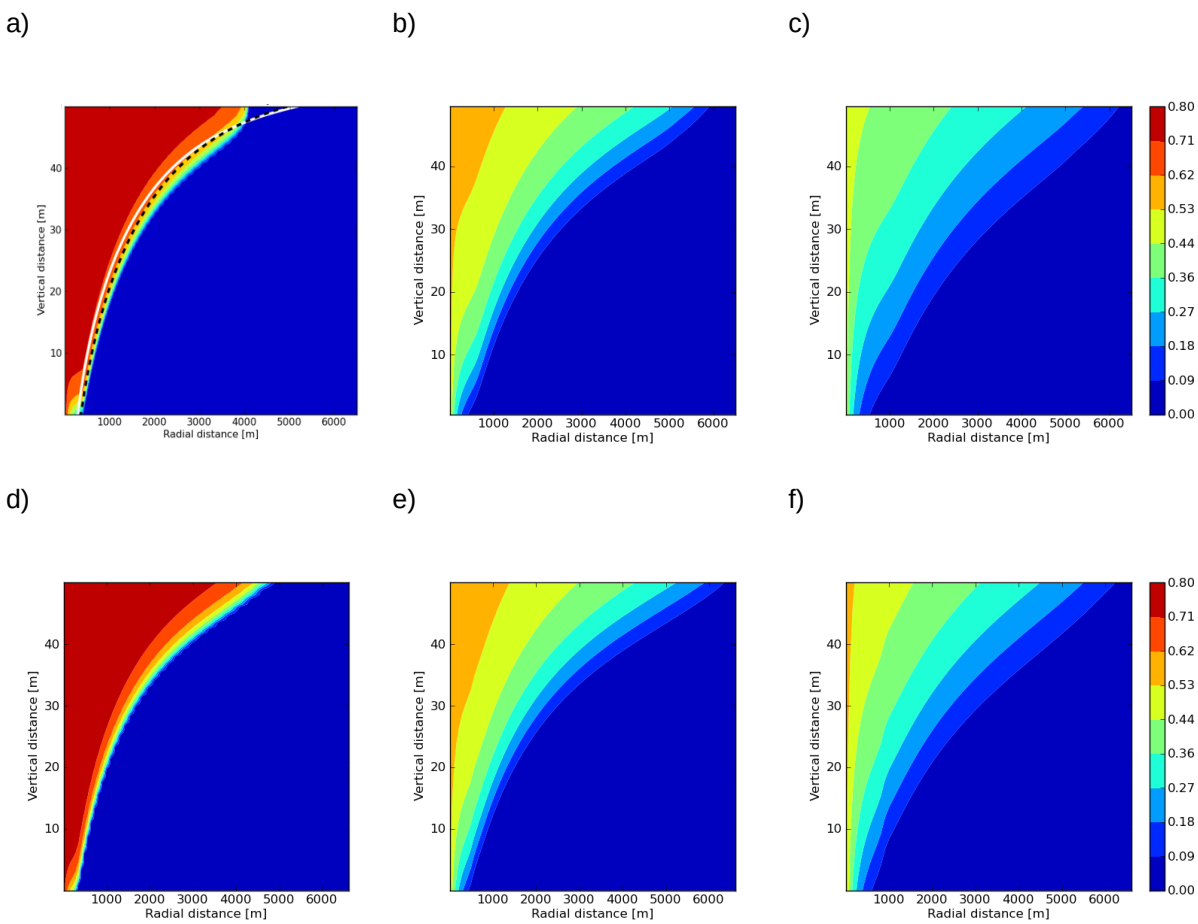

Figure 4.12: Comparison of CO_2 saturation profiles after 50 years of 0.939 Mt/yr injection in a 100 mD intrinsic permeability aquifer comparing (row 1) ECLIPSE to (row 2) VESA runs with (column 1) Ebigbo, (column 2) Zhou, and (column 3) Zhou04 k_{rel}-S and P_c-S curves (Figure 4.10). Plot (a) has the analytical sharp-interface line superimposed.

Figure 4.12 also shows that the finite-CTZ vertically-integrated numerical model provides a close match with ECLIPSE results when injecting 0.939 $MtCO_2$/y into a 100mD aquifer for 50 years, regardless of the P_c-S or k_{rel}-S curves used. As described previously, capillary forces will keep the saturation of brine behind the front at a higher value than the residual saturation, in cases where the CTZ is significant. This leads to the “drainage equilibrium” profile, where no more brine drainage will occur, being reached faster because of the higher relative permeability (this has been confirmed by time series not presented here). However, like any vertical-equilibrium model, there is still a finite time scale for the assumption to be valid. Figure 4.13 illustrates that when this “drainage equilibrium” has not been reached, because the low intrinsic

permeability (10 mD) increases the drainage time, finite-CTZ vertically-integrated model results do not closely match ECLISPE results for the same P_c-S curves after 50 years. These results are again consistent with the sharp-interface results in the previous sections. Inclusion of vertical brine drainage dynamics in this model is also the focus of current work.

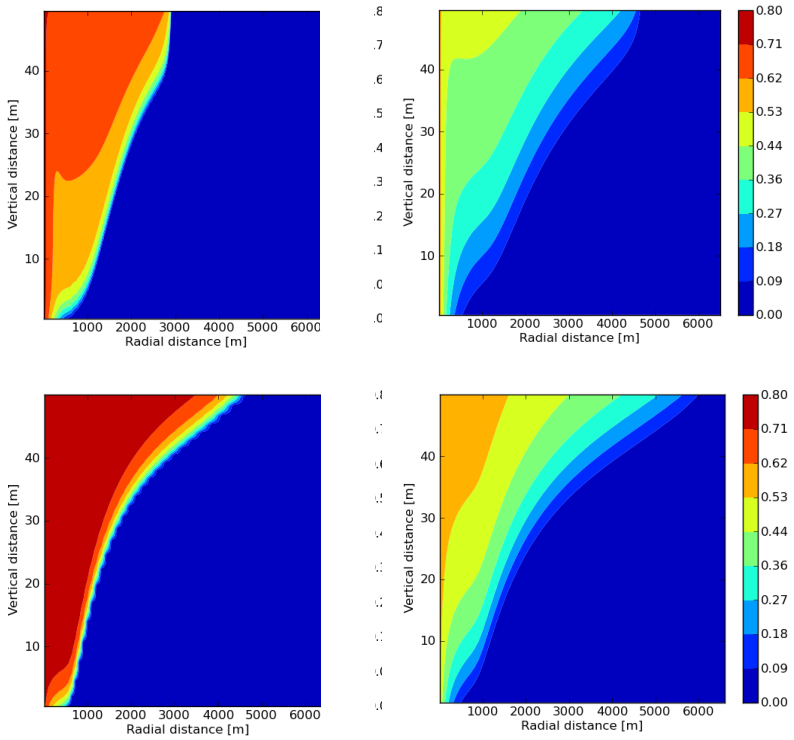

Figure 4.13: Comparison of CO_2 saturation profiles after 50 years of 0.939 Mt/yr injection in a 10 mD intrinsic permeability aquifer comparing ECLIPSE (row 1) to VESA (row 2) runs with (column 1) Ebigbo and (column 2) Zhou k_{rel}-S and P_c-S curves (Figure 4.10).

4.5. Conclusion

CO_2 sequestration safety evaluation will involve mathematical models of various complexity levels to answer different practical questions. While full 3D numerical models are useful to answer many of these questions, simpler models can often provide similar information at a fraction of the computational cost, and with data requirements that are more comparable with the data sparsity often seen for injection operations into deep saline aquifers. One family of simpler models is

based on the assumption of vertical-equilibrium, with the associated vertical integration of the governing equations. This reduces the number of active spatial dimensions from three to two, thereby reducing the computational costs associated with the simulations. When coupled with additional assumptions, including the assumption of a sharp interface separating the CO_2 and brine, these vertical-equilibrium models can lead to simpler model equations that are amenable to analytical solutions.

In order to place this work into the context of other modeling studies for CO_2 injection, we present a compilation of the P_c-S and k_{rel}-S relationships that have been reported in the literature involving CO_2-brine systems. We defined a Capillary Transition Zone (CTZ) where the brine saturation ranges from full saturation to 10% above the residual brine saturation. Considering the P_c-S relationships from the literature, we found a wide range of values for the thickness of the transition zone, ranging from a few meters to many hundreds of meters. Direct comparison of these CTZ thickness to the thickness of the injection formation provides a simple guideline for the applicability of sharp-interface models.

In this Chapter based on (Court et al., 2011c), we investigated the conditions under which vertical-equilibrium models can be applied, and the associated conditions under which the sharp-interface assumption is valid. The vertical-equilibrium assumption is applicable once vertical fluid movement due to buoyancy has ceased. Choice of vertically-integrated models is therefore driven by time scales, specifically the time scale for the fluid to segregate by buoyancy and its relationship to the overall time scale of the simulation. Numerical experiments from 3D simulation using ECLIPSE showed that when the segregation time scale is small relative to the simulation time, vertically-integrated models can be a good choice to simulate CO_2 injection problem. We also noted, although we did not discuss it in detail, that the relative permeability function for the brine has important impacts on the drainage time. As the brine saturation within the CO_2-rich plume decreases asymptotically to its residual value, the relative brine permeability decreases rapidly, leading to a significant slowing down in vertical drainage. The vertical intrinsic

permeability of the injection formation was shown to be an important factor in determining the segregation time scale at which this drainage equilibrium is reached. The behavior of the CO_2 relative permeability curve in the range of low brine saturation also has an important impact through the mobility ratio, which impacts the shape and outer extent of the invading CO_2 plume. Numerical experiments using 3D models also showed that capillary forces counteract the segregation, holding brine within the CO_2 plume, and that a drainage equilibrium is reached where no more drainage occurs, although brine above residual saturation and CO_2 coexist in the capillary transition zone. Transition zones that are thick compared to the formation thickness lead to shorter segregation/drainage equilibrium time scales, because less brine needs to be drained vertically and the relative permeability for brine is higher due to the higher saturation. Comparison of vertical-equilibrium models with 3D models identified that brine drainage dynamics inclusion was a promising improvement for both analytical and finite-CTZ models to provide accurate results in cases when the fluids are not yet fully segregated, increasing their range of applicability.

The sharp-interface assumption is based on spatial scales associated with capillary pressure and the CTZ. Given the applicability of the vertical-equilibrium assumption, the sharp-interface assumption can be reasonably applied when capillary forces are negligible. Our literature review and modeling results indicate that capillary forces can be ignored when the CTZ is small relative to the thickness of the formation. We note that the sharp-interface assumption requires vertical-equilibrium, but the converse is not true in that vertical-equilibrium does not require a sharp interface to exist. However, when capillary forces are important (i.e., CTZ is large relative to the thickness of the formation), capillary pressure needs to be included in the simulation, and the sharp-interface assumption is not valid. Comparison of results from full three-dimensional simulations including capillary pressure using ECLIPSE and the finite-capillary-transition-zone vertically-integrated numerical model with saturation reconstruction show close match as long as the segregation/drainage equilibrium time scales are respected.

We believe that the simple metrics involving time scale for buoyant segregation and spatial scale for the CTZ provide valuable information about the way the system will behave and, more importantly, about the levels of simplification that can be used in modeling. Vertical-equilibrium models provide an important tool that can significantly simplify calculations while properly representing the flow physics, as long as the appropriate time scales are respected. Sharp-interface models can provide further simplifications in cases where capillary effects are not important. These simple guidelines can help navigate the plethora of modeling options and provide a sound basis for model choice.

4.6. References

Alkan, H., Cinar, Y. & Ülker, E. 2010, "Impact of Capillary Pressure, Salinity and In situ Conditions on CO_2 Injection into Saline Aquifers", *Transport in Porous Media,* vol. 84, no. 3, pp. 799-819.

Bachu, S., Bonijoly, D., Bradshaw, J., Burruss, R., Holloway, S., Christensen, N.P. & Mathiassen, O.M. 2007, "CO2 storage capacity estimation: Methodology and gaps", *International Journal of Greenhouse Gas Control,* vol. 1, no. 4, pp. 430-443.

Bennion, B. 2006, "The impact of interfacial tension and pore-size distribution/capillary pressure character on CO2 relative permeability at reservoir conditions in CO2-brine systems", *Proceedings - SPE Symposium on Improved Oil Recovery,* vol. 1, pp. 142-151.

Bennion, D.B. & Bachu, S. 2008, "Drainage and imbibition relative permeability relationships for supercritical CO2/brine and H2S/brine systems in intergranular sandstone, carbonate, shale, and anhydrite rocks", *Spe Reservoir Evaluation & Engineering,* vol. 11, no. 3, pp. 487-496.

Benson, S.M., Esposito, A., Li, B., Krause, M.H., Krevor, S., Kuo, C.W. & Zou, L. 2009, "Residual Trapping of Carbon Dioxide - Investigations in Geologic Carbon Sequestration: Multiphase Flow of CO2 and Brine, Leak Remediation, and Monitoring", *GCEP Annual Report, Department of Energy Resources Engineering, Stanford University available at http://gcep.stanford.edu/pdfs/zEVLdhAVLgi--xWiiZyjiA/2.5.2_Benson_Web_Public_2010.pdf.*

Bergmo, P.E.S. 2011, *Communication on (Bergmo et al. in press)*.

Bergmo, P.E.S., Grimstad, A. & Lindeberg, E. "Simultaneous CO2 injection and water production to optimise aquifer storage capacity", *International Journal of Greenhouse Gas Control,* vol. In Press, Corrected Proof.

Birkholzer, J.T., Zhou, Q. & Tsang, C. 2009, "Large-scale impact of CO2 storage in deep saline aquifers: A sensitivity study on pressure response in stratified systems", *International Journal of Greenhouse Gas Control,* vol. 3, no. 2, pp. 181-194.

Brooks, R.H. & Corey, A.T. 1966, "Properties of porous media affecting fluid flow", *Journal of Irrig. Grain. Div.,* vol. 6, pp. 71-78.

Celia, M.A. & Nordbotten, J.M. 2011, "How simple can we make models for CO2 injection, migration and leakage?", *Energy Procedia,* vol. 4, pp. 3857-3864.

Celia, M.A. & Nordbotten, J.M. 2009, "Practical Modeling Approaches for Geological Storage of Carbon Dioxide", *Ground Water,* vol. 47, no. 5, pp. 627-638.

Celia, M.A., Nordbotten, J.M., Court, B., Dobossy, M. & Bachu, S. 2011, "Field-scale application of a semi-analytical model for estimation of CO2 and brine leakage along old wells", *International Journal of Greenhouse Gas Control,* vol. 5, no. 2, pp. 257-269.

Class, H., Ebigbo, A., Helmig, R., Dahle, H., Nordbotten, J., Celia, M., Audigane, P., Darcis, M., Ennis-King, J., Fan, Y., Flemisch, B., Gasda, S., Jin, M., Krug, S., Labregere, D., Naderi Beni, A., Pawar, R., Sbai, A., Thomas, S., Trenty, L. & Wei, L. 2009, "A benchmark study on problems related to CO2 storage in geologic formations", *Computational Geosciences,* vol. 13, no. 4, pp. 409-434.

Coats, K.H., Dempsey, J.R. & Henderson, J.H. 1971, "The Use of Vertical-equilibrium in Two-Dimensional Simulation of Three-Dimensional Reservoir Performance.", *SPE Journal,* vol. 11 (1), pp. 63-71.

Corey, A.T. 1954, "The interrelation between gas and oil relative permeabilities", *Producers Monthly,* vol. Nov., pp. 38-41.

Court, B., Bandilla, K.W., Celia, M.A., Buscheck, T.A., Nordbotten, J.M., Dobossy, M.E. & Janzen, A. 2011a, "Initial evaluation of advantageous synergies associated with simultaneous brine production and CO2 geological sequestration", *International Journal of Greenhouse Gas Control, submitted.*

Court, B., Dammel, J.A., Elliot, T.R., Rohmer, J., Buscheck, T.A. & Celia, M.A. 2011b, " Promising synergies to address water, sequestration, legal, and public acceptance issues associated with large-scale implementation of CO2 sequestration", *Special Issue on Carbon Capture and Storage of The Journal for Mitigation and Adaptation Strategies for Global Change, in review.*

Court, B., Bandilla, K.W., Celia, M.A., Janzen, A., Dobossy, M.E., & Nordbotten, J.M. 2011c, "*Applicability of vertical-equilibrium and sharp-interface assumptions in carbon sequestration modeling"*, International Journal of Greenhouse Gas Control, submitted.

Dahle, H.K., Eigestad, G.T., Nordbotten, J.M. & Pruess, K. 2009, "A model-oriented benchmark problem for CO2 storage", *available at http://arks.princeton.edu/ark:/88435/dsp01pn89d657g.*

Delshad, M. 2010, *A Critical Assessment of CO2 Injection Strategies in Saline Aquifers*.

Dentz, M. & Tartakovsky, D.M. 2009a, "Abrupt-Interface Solution for Carbon Dioxide Injection into Porous Media", *Transport in Porous Media,* vol. 79, no. 1, pp. 15-27.

Dentz, M. & Tartakovsky, D.M. 2009b, "Response to “Comments on Abrupt-Interface Solution for Carbon Dioxide Injection into Porous Media by Dentz and Tartakovsky (2008) by Lu et al. *Transport in Porous Media*, 79(1), pp 39-41. doi: 10.1007/s11242-009-9363-8.", *Retrieved from: http://escholarship.org/uc/item/2h02b5tq.*

Dobossy, M.E., Celia, M.A. & Nordbotten, J.M. 2011, "An efficient software framework for performing industrial risk assessment of leakage for geological storage of CO2", *Energy Procedia,* vol. 4, pp. 4207-4214.

Doughty, C. 2010, *Investigation of CO_2 Plume Behavior for a Large-Scale Pilot Test of Geologic Carbon Storage in a Saline Formation*, Springer Netherlands.

Doughty, C. 2007, "Modeling geologic storage of carbon dioxide: Comparison of non-hysteretic and hysteretic characteristic curves", *Energy Conversion and Management,* vol. 48, no. 6, pp. 1768-1781.

Doughty, C., Freifeld, B. & Trautz, R. 2008, "Site characterization for CO_2 geologic storage and vice versa: the Frio brine pilot, Texas, USA as a case study", *Environmental Geology,* vol. 54, no. 8, pp. 1635-1656.

Ebigbo, A., Class, H. & Helmig, R. 2007, "CO_2 leakage through an abandoned well: problem-oriented benchmarks", *Computational Geosciences,* vol. 11, no. 2, pp. 103-115.

Ellis, B.R., Peters, C.A., Fitts, J.P., Bromhal, G.S., McIntyre, D.L., Warzinski, R.P. & Rosenbaum, E.J. 2011, "Deterioration of a fractured carbonate caprock exposed to CO2-brine flow", *Greenhouse Gases: Science and Technology. in review.*

Fischer, U. 1997, "Modeling nonwetting-phase relative permeability accounting for a discontinuous nonwetting phase", *Soil Science Society of America Journal,* vol. 61, no. 5, pp. 1348-1354.

Gasda, S., Nordbotten, J. & Celia, M. 2009, *Vertical-equilibrium with sub-scale analytical methods for geological CO_2 sequestration*, Springer Netherlands.

Gasda, S.E., Nordbotten, J.M. & Celia, M.A. 2010, "The Impact of Local-Scale Processes on Large-Scale CO_2 Migration and Immobilization", *International Conference on Greenhouse Gas Technologies (GHGT 10), Elsevier/Energy Procedia.*

Gasda, S.E. 2008, "Numerical Models for Evaluating CO2 Storage in Deep Saline Aquifers: Leaky Wells and Large-scale Geological Features", *Ph.D Thesis available at http://arks.princeton.edu/ark:/88435/dsp01j098zb09n.*

Hesse, M.A., Orr, F.M., Jr. & Tchelepi, H.A. 2008, "Gravity currents with residual trapping", *Journal of Fluid Mechanics,* vol. 611, pp. 35-60.

Hesse, M.A., Tchelepi, H.A., Cantwell, B.J. & Orr, F.M., Jr. 2007, "Gravity currents in horizontal porous layers: transition from early to late self-similarity", *Journal of Fluid Mechanics,* vol. 577, pp. 363-383.

Huppert, H.E. & Woods, A.W. 1995, "Gravity driven flows in porous layers", *J. Fluid Mech.,* vol. 292, pp. 55-69.

Izgec, O., Demiral, B., Bertin, H. & Akin, S. 2006, "Experimental and Numerical Investigation of Carbon Sequestration in Saline Aquifers", *Paper SPE 100809, SPE ATCE 2006, San Antonio, TX.*

Janzen, A. 2010, "Development and Application of a Multi-scale, Multi-layer Numerical Model for CO2 Injection", *Master Thesis available at http://arks.princeton.edu/ark:/88435/dsp01np193917f.*

Juanes, R., MacMinn, C. & Szulczewski, M. 2010, *The Footprint of the CO_2 Plume during Carbon Dioxide Storage in Saline Aquifers: Storage Efficiency for Capillary Trapping at the Basin Scale*, Springer Netherlands.

Kopp, A., Class, H. & Helmig, R. 2009, "Investigations on CO2 storage capacity in saline aquifers: Part 1. Dimensional analysis of flow processes and reservoir characteristics", *International Journal of Greenhouse Gas Control,* vol. 3, no. 3, pp. 263-276.

Krause, M.H. 2009, "MODELLING SUB-CORE SCALE PERMEABILITY IN SANDSTONE FOR USE IN STUDYING MULTIPHASE FLOW OF CO2 AND BRINE IN CORE FLOODING EXPERIMENTS", *Master thesis available at pangea.stanford.edu/ERE/pdf/pereports/MS/Krause09.pdf.*

Krause, M., Perrin, J. & Benson, S. 2011, "Recent Progress in Predicting Permeability Distributions for History Matching Core Flooding Experiments", *Energy Procedia,* vol. 4, pp. 4354-4361.

Lake, L. 1989, *Enhanced Oil Recovery,* Prentice Hall.

Lu, C., Lee, S., Han, W., McPherson, B. & Lichtner, P. 2009, "Comments on “Abrupt-Interface Solution for Carbon dioxide Injection into Porous Media” by M. Dentz and D. Tartakovsky", *Transport in Porous Media,* vol. 79, no. 1, pp. 29-37.

Matteo, E.N. & Scherer, G.W. 2011, "Experimental Study of the Diffusion-Controlled Acid Degradation Kinetics of Class H Portland Cement", *International Journal of Greenhouse Gas Control, in review.*

Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L. & (Eds.) 2005, *IPCC Special Report on Carbon Dioxide Capture and Storage,* New York, NY: Cambridge University Press.

Michael, K., Arnot, M., Cook, P., Ennis-King, J., Funnell, R., Kaldi, J., Kirste, D. & Paterson, L. 2009, "CO2 storage in saline aquifers I—Current state of scientific knowledge", *Energy Procedia,* vol. 1, no. 1, pp. 3197-3204.

Mualem, Y. 1976, "A new model for predicting the hydraulic conductivity of unsaturated porous media", *Water Resour.Res.,* vol. 12 (3), pp. 513-522.

Nilsen, H., Herrera, P.A., Ashraf, M., Ligaarden, I., Iding, M., Hermanrud, C., Lie, K., Nordbotten, J.M., Dahle, H.K. & Keilegavlen, E. 2011, "Field-case simulation of CO2 -plume migration using vertical-equilibrium models", *Energy Procedia,* vol. 4, pp. 3801-3808.

Nitao, J.J. 1998, "Reference manual for the NUFT flow and transport code, version 3.0", *Lawrence Livermore National Laboratory, UCRL-MA-130651-REV-1.*

Nordbotten, J.M. & Celia, M.A. 2011, "Geological Storage of CO2: Modeling Approaches for Large-Scale Simulation", *with John Wiley and Sons, Inc., in press.*

Nordbotten, J.M., Celia, M.A. & Bachu, S. 2005, "Injection and storage of CO2 in deep saline aquifers: Analytical solution for CO2 plume evolution during injection", *Transport in Porous Media,* vol. 58, no. 3, pp. 339-360.

Nordbotten, J.M. & Dahle, H.K. 2011, "Impact of the capillary fringe in vertically integrated models for CO2 storage", *Water Resources Research,* vol. 47, no. 2, pp. W02537.

Nordbotten, J.M. & Celia, M.A. 2006, "Similarity solutions for fluid injection into confined aquifers", *Journal of Fluid Mechanics,* vol. 561, pp. 307-327.

Nordbotten, J.M., Kavetski, D., Celia, M.A. & Bachu, S. 2009, "Model for CO2 Leakage Including Multiple Geological Layers and Multiple Leaky Wells", *Environmental science & technology,* vol. 43, no. 3, pp. 743-749.

Olafuyi, O.A. 2008, "Capillary pressure and relative permeability of small cores", *Proceedings - SPE Symposium on Improved Oil Recovery.*

Plug, W.-. & Bruining, J. 2007, "Capillary pressure for the sand–CO2–water system under various pressure conditions. Application to CO2 sequestration", *Advances in Water Resources,* vol. 30, no. 11, pp. 2339-2353.

Pruess, K. 2004, "The TOUGH Codes—A Family of Simulation Tools for Multiphase Flow and Transport Processes in Permeable Media", *Vadose Zone J.,* vol. 3, pp. 738-746.

Pruess, K., Birkholzer, J.T. & Zhou, Q. 2009, "Mathematical models as tools for probing long-term safety of CO2 storage", *LBNL Paper LBNL-1587E. Retrieved from: http://www.escholarship.org/uc/item/04w053xn.*

Pruess, K., Garcia, J., Kovscek, T., Oldenburg, C., Rutqvist, J., Steefel, C. & Xu, T. 2002, *Intercomparison of Numerical Simulation Codes for Geologic Disposal of CO2*, United States.

Pruess, K. & Nordbotten, J.M. 2011, "Numerical simulation studies of the long-term evolution of a CO2 plume in a saline aquifer with a sloping caprock", *submitted to Transport in Porous Media.*

Pruess, K., García, J., Kovscek, T., Oldenburg, C., Rutqvist, J., Steefel, C. & Xu, T. 2004, "Code intercomparison builds confidence in numerical simulation models for geologic disposal of CO2", *Energy,* vol. 29, no. 9-10, pp. 1431-1444.

Pruess, K. & Muller, N. 2009, "Formation dry-out from CO2 injection into saline aquifers: 1. Effects of solids precipitation and their mitigation", *Water Resources Research,* vol. 45, pp. W03402.

Schlumberger 2010, "ECLIPSE Technical Description".

Schnaar, G. & Digiulio, D.C. 2009, "Computational Modeling of the Geologic Sequestration of Carbon Dioxide", *Vadose Zone Journal,* vol. 8, no. 2, pp. 389-403.

Stanford 2011, "Relative permeability explorer", *http://pangea.stanford.edu/research/bensonlab/relperm/index.html.*

Szulczewski, M. & Juanes, R. 2009, "A simple but rigorous model for calculating CO2 storage capacity in deep saline aquifers at the basin scale", *Energy Procedia,* vol. 1, no. 1, pp. 3307-3314.

Van Genuchten, M.T. 1980, "A closed form equation for predicting the hydraulic conductivity of unsaturated soils", *Soil Science Soc. Am. Journal,* vol. 44, pp. 892-898.

White, M.D. & Oostrom, M. 1997, "STOMP, Subsurface Transport Over Multiple Phases", *Pacific Northwest National Laboratory Report PNNL-11218, Richland, WA, October 1997.*

Woods, A.W. & Mason, R. 2000, "The dynamics of two-layer gravity-driven flows in permeable rock", *Journal of Fluid Mechanics,* vol. 421, pp. 83.

Yortos, Y.C. 1995, "A theoretical analysis of vertical flow equilibrirum", *Transport in Porous Media,* vol. 18, pp. 107-129.

Zhou, Q., Birkholzer, J.T., Tsang, C. & Rutqvist, J. 2008, "A method for quick assessment of CO2 storage capacity in closed and semi-closed saline formations", *International Journal of Greenhouse Gas Control,* vol. 2, no. 4, pp. 626-639.

Zhou, Q. 2010, "Modeling basin- and plume-scale processes of CO2 storage for full-scale deployment", *Ground Water,* vol. 48, no. 4, pp. 494-514.

Chapter 5

Promising synergies to address water, sequestration, legal, and public acceptance issues associated with large-scale implementation of CO_2 sequestration"

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5.1. Introduction

Despite efforts to move toward non-fossil-fuel energy sources, the general consensus is that widely available and inexpensive coal reserves will continue to play a central role in electricity production. Therefore, climate change mitigation strategies to curb atmospheric CO_2 emissions

must consider the continued use of coal due to existing infrastructure lifespan and the time requirement for building capacity of low-carbon energy generation. Therefore a pragmatic strategy to curb atmospheric CO_2 emissions must integrate CCS to allow a transition period of simultaneous coal burning and CO_2 emission controls (Krey and Riahi 2009; Calvin et al. 2009). Experience in CCS demonstration projects (Michael et al. 2010; IEA/CSLF 2010), as well as in Enhanced Oil Recovery (EOR) operations has improved our understanding of CO_2 injection and management. To have a significant effect on global atmospheric carbon emissions, the scale of CCS activities must be expanded by several orders of magnitude which would bring several challenges: CO_2 capture cost; absence of CO_2 transport network; sequestration safety; legal and regulatory barriers; and public acceptance.

In this Chapter based on (Court et al. 2011a) we first present a review of the new insights gained on one newly and several previously identified challenges to the necessary large-scale implementation of CCS since the Intergovernmental Panel on Climate Change Special Report on CCS (SRCCS) (IPCC 2005). We then explore potential solutions/paradigm shifts that have or could be implemented to address these potential barriers. The newly identified challenge is the required water management across all CCS operations, which arises from the additional cooling water requirement of the CO_2 capture retrofitting process. Previously identified barriers that will be reviewed include CO_2, brine, pressure and pore-space competition challenges; legal and regulatory barriers; and public acceptance and technical communication.

The goal of this Chapter is to present a comprehensive overview of these potential barriers in the context of the required large-scale CCS implementation. An organization of these challenges into a single framework is presented in Section 5.2. This enables us to identify promising synergies which span across different operations, fields, and types of expertise. Potential synergistic solutions are then presented in Section 5.3. We believe the identified synergies provide a roadmap for further investigations and will expand and enhance the ways in which large-scale CCS development is envisioned.

5.2. Implementation barriers

5.2.1. Water, sequestration, and pore space competition challenges

We believe that water management constitutes a key new challenge for CCS operations. This joins already-identified challenges that include reservoir management (CO_2, pressure and brine) and pore-space competition already identified in the SRCCS. We propose that water management should include both freshwater resources and brine management. CCS retrofitted coal-fired power plants require about twice the cooling water as the original plant. This could put a significant strain on freshwater resources, especially in water-limited areas. However, a broader view of reservoir management leads to the possibility of brine production from the injection reservoir, which can provide water while also allowing for significant reductions in pressure build-up in the injection reservoir. Such a strategy avoids additional stresses on local water resources, provides large-scale pressure management of the injection formation that could increase CO_2 injectivity, reduce the pressure perturbation areal extent, and decrease CO_2 and brine leakage risk into Underground Sources of Drinking Water; and in regions with scarce water supplies and sufficiently low salinity brine formations, brine production, coupled with desalination, may constitute a viable source of either freshwater or, "greywater" suitable for irrigation or other industrial processes. These benefits could prevent water availability, already a sensitive public issue, from becoming a new barrier to CCS implementation. This coupling of CO_2 injection, brine production and treatment described in Section 5.3.2 would be specific to each CCS operation's local, surface and geological characteristics, and clearly dependent on the distance between the sequestration and capture sites. Establishment of pipeline infrastructure could be considered as studied in the literature (see among others (Seevam 2007, 2009; Johnson and Ogden 2011; Kuby et al. *in press*)). Both on-going research efforts would complement the current CO_2 source and sink matching effort implemented by the carbon sequestration atlas (described in (Litynski et al. 2009) and references therein).

At present the interactions among freshwater extraction, CO_2 injection, pressure, and brine management are being considered too narrowly, particularly in the case of freshwater where it is only just starting to gain attention in the CCS literature, debates and conferences. Active management of CCS operations through an integrated approach should address all of the following challenges simultaneously by considering their interactions as described in Section 5.3.2.

The water, sequestration, and pore space competition challenges have been explored separately but have not been viewed in a broader, integrated context. Figure 5.1 is a conceptual graphic, adapted from (Court et al. 2011b) comparing the operational impacts for the same CCS-retrofitted coal-fired power plant under two scenarios: a "passive" CO_2 injection operation on the left side versus multiple active and integrated CCS operations on the right. For instance, in a passive supercritical CO_2 injection operation (Buscheck et al. 2010), migration of CO_2 and displaced brine occurs unrestrained. Whereas in an active CO_2 reservoir management, CO_2 and brine migration are actively controlled via brine production and residual-brine reinjection wells, as described in Section 5.3.2.1. In practice a large-scale CO_2 sequestration project would not likely be permitted without a pressure control system and a clear remediation strategy plan. In this sense the "passive" injection case representation may appear as somewhat unrealistic but, to the authors knowledge, the majority of the current or planned CCS operations in industry –except for the Gorgon project in Australia (Flett 2008)-, and CCS scientific studies in the literature (Michael et al. 2010) are lacking an "active" management component. Finally this "passive" case is helpful in order to explore concepts and provide a reference point for the somewhat idealized representation of active and integrated CCS operations.

Figure 5.1 identifies **Challenges** posed by passive injection with red numbers (identified in the text as X^C and on the figure as X, where X is the number), **Synergies** associated with integrated management by blue numbers (X^S and X).

5.2.1.1. Increased water demand from CO_2 capture

An energy and water nexus has clearly been identified through published literature in the United States (GAO 2009; Feeley et al. 2008; Goldstein 2008), India, South-Africa, and Brazil (McKinsey & Company 2009) and particularly in China (McKinsey & Company 2009; Sun et al. 2003; Varis and Vakkilainen 2001; Zheng et al. 2010a; Zhang 2009) where water saving methods are being considered in the coal industry (Fang 2009). Energy production and particularly coal-fired power plants already require large volumes of water for cooling processes (DOE/NETL 2007, 2008; NETL 2005). In both energy production and industry, water has become a limiting constraint nationally and internationally as shown by recent coal plant siting problems, and litigation cases in both the domestic and international arena (Sovacool 2009; Sovacool and Sovacool 2009a, 2009b).

(**1**[c]) Water is an additional major challenge to CCS implementation due to the considerable increase in water use for power plants built or retrofitted with CCS. This is particularly significant when existing plants are retrofitted with post-combustion CO_2 capture. In this case both water withdrawal and consumption double from an identical non CO_2 capture equipped coal plant due to increased cooling need in both the regeneration process of expensive CO_2 capture chemical solvents (amines) and make-up power production (due to parasitic load), see Figure 12 and Appendix G in (DOE/NETL 2009) for details and also (DOE/NETL 2007, 2008; Ciferno et al. 2010; Zhai et al. 2011). Water scarcity will become accentuated with large-scale CCS expansion influencing and potentially constraining both CCS retrofitting of existing coal plants and siting of new construction coal generation with CCS (DOE/NETL 2008; Newmark et al. 2010) unless an active water management strategy is implemented.

5.2.1.2. Sequestration challenges

- CO_2 injection, migration, and leakage challenges

A number of issues related to CO_2 injection, migration, and potential leakage were identified in the SRCCS and are reviewed in this section. These include geochemical reactions within the formation, at the caprock-formation interface, and along potential concentrated leakage pathways. These can alter injectivity within the formation as well as alter (perhaps enhancing) leakage pathways. Geomechanical stresses associated with the injection (including thermal stresses when cooler CO_2 is injected into warmer formations) can have the potential to create new fractures or reactivate old fractures. And any leakage of either CO_2 (or resident brine – see next section) can have impacts on freshwater aquifers, the unsaturated soil zone, and the atmosphere. Each of these processes is identified in Figure 5.1, and described as follows,

(2[C]) Geochemical reactions between CO_2-acidified-brine and injection formation minerals might reduce injectivity by decreasing the intrinsic permeability and porosity of the injection aquifer (Kaszuba et al. 2005; Xu et al. 2003). Ongoing work is also investigating permeability alteration due to mineral dissolution in fractures (Detwiler 2010). (3[C]) Both supercritical CO_2 and/or CO_2-rich-brine are potentially corrosive to the sealing cement, if present, in the well segments perforating the overlaying aquitards. The resulting loss of integrity increases upward leakage risk, which is a key component of permitting and regulation such as the United States Class VI well discussed in section 5.2.2. Chemical dissolution of caprock minerals outside of the well could also lead to potential leakage of CO_2 from the sequestration reservoir (Gherardi et al. 2007). Shukla et al. (2010) provides a useful review of: geophysical and geochemical aspects of caprock–CO_2–pore fluid interaction; stability of the caprock during and after injection of CO_2; probability of fault reactivation; and, influence of pre-existing fractures on seal integrity. Major research gaps were also identified by Shukla et al. (2010), who call for further study on: caprock integrity under the combined effects of high pressure and high temperature; changes in pressure and stress field caused by CO_2 injection (also recently investigated by Preisig and Prevost (2011)); and, the interaction of supercritical CO_2 with the brine in the reservoir formations. The

spatial and temporal scales of the impact of each of these geochemical and geomechanical processes need to be clearly identified, communicated, and put in context.

(4[C]) CO_2 leakage can be driven by buoyancy plus the injection formation pressure build-up via: natural faults, induced fractures, and active and/or abandoned wells. Leakage to shallower geological formations is a concern for Underground Source of Drinking Water (USDW) contamination. CO_2 injection and migration modeling capabilities have been enhanced considerably (Michael et al. 2009; Schnaar Digiulio 2009; Pruess et al. 2009). Celia and Nordbotten take a particular focus on the practical questions, the relevant time and spatial scales of CO_2 sequestration challenges, and have developed a hierarchy of models to address them (Celia and Nordbotten 2010; Nordbotten and Celia *in press*). While Celia et al. (2011), and references therein, are focused on leakage through abandoned wells it is pertinent to note their ongoing efforts to model fault and fractures which complement existing work by groups such as (Gherardi et al. 2007; Iding and Ringrose 2010; Rutqvist et al. 2010; Woods and Norris 2010; Andreani et al. 2008).

(5[C]) Leaked CO_2 potentially alters shallow aquifer water / groundwater chemistry due to its reaction with aquifer minerals, decreases local pH, and increases metal mobility and concentrations (Smyth et al. 2009) as demonstrated by various studies, either based on numerical investigations (Apps et al. 2010; Lu et al. 2010; Kharaka et al. 2006) or at field site/natural analog (Kharaka 2009; Keating et al. 2010). (6[C]) Furthermore, brine leakage potentially increases USDW salinity.

(7[C]) Finally, the leaked CO_2 may eventually reach the shallow subsurface vadose zone, leading to high soil CO_2 concentrations. This could pose health and environment risks in the near surface environment or at the ground surface where CO_2 can accumulate in basements of buildings as detailed in the SRCCS (IPCC 2005). Assessing such risks is likely to be a key component of regulatory approval process and public acceptance (Stenhouse et al. 2004, 2005).

However quantitative safety assessments are unlikely to be the only means of building confidence in CCS projects (METI 2007). Inclusion of risk management strategies in CCS projects as imposed by the 2009 European Directive (European Parliament 2009) and the 2007 OSPAR guidelines (OSPAR 2007) will certainly participate to install confidence in all stakeholders. Whereas safety assessment tackles the « what if » issues, risk management strategies tackle the question of « what can be done » in case of « abnormal behavior » of the sequestration complex. In practice, this implies the combination of appropriate monitoring and remediation plans.

(8[C]) CO_2 plume tracking, monitoring, and accounting present a unique set of challenges. In particular, (Chadwick 2009) outlined the challenges (recalled by the IEA GHG Monitoring network e.g., (Dixon et al. 2009)) of: selecting tool combinations which can provide a cost-effective and technically robust site monitoring system; and designing techniques not only to monitor the fate of CO_2 and pressure at depth, but also to verify that the physical processes at depth are acting as predicted which raise the issue of signal resolution. High-quality baseline data improves reliability and resolution of all early-detection measurements and will be essential for indentifying small leakage rates. Zeidouni et al. explored the possibility of detecting leakage through pressure-monitoring wells located in formations overlying the injection formation (Zeidouni et al. 2010; Zeidouni and Pooladi-Darvish 2010). Their results can ultimately lead to practical design strategies for monitoring schemes, including quantitative estimation of increased probability of leak detection per added observation well.

(9[C]) The second risk management component, namely remediation plans, aims at demonstrating that any undesired consequences can be mitigated or effectively corrected. It will be vital to develop appropriate procedures and strategies to manage the outer extent of the CO_2 plume, and be able to remediate if CO_2 unexpectedly appears in an undesired zone such as a neighbouring production field or a densely populated area as advocated by the European directive on geological sequestration of CO_2 (European Parliament 2009). The (IEA-GHG 2007)

review has identified potential remediation measures, which draw from experience in the oil and gas industry (particularly natural gas storage), which include intervention strategies to correct / repair wellbore systems, and from the field of pollution engineering. Considering the unsaturated zone, Zhang et al. 2004 showed that CO_2 at ambient conditions presents several similarities with Volatile Organic Compounds (VOC) indicating that passive remediation or active extraction techniques such as "Soil Vapour Extraction" are applicable. Esposito and Benson (2010) have investigated phreatic freshwater aquifers contamination remediation. However, challenges reside in accounting for the unique characteristics of CO_2 geological sequestration, namely: time scales (from decades, centuries, to millennia); potential large spatial scale impact; depth of the possible source of "pollution" (sequestration reservoir are located at depth >800m); and uncertainties inherent to potential leakage pathways. Recent remediation strategies have been proposed, and are described in Section 5.3.2.2, although future research is needed to explore the effectiveness of such strategies, applicability, time, and cost of managing such large volumes of fluid.

- Pressures and brine leakage challenges

(**10**[C]) In the United States CCS operators are required by law (U.S. Environmental Protection Agency 1994) to limit injection formation pressure to the overlying aquitard fracture pressure to avoid initiating or re-activating a hydraulic leakage pathway (Iding and Ringrose 2010; Rutqvist et al. 2010; Rutqvist et al. 2007). This sealing unit fracture pressure constraint will limit injectivity and hence sequestration capacity and should be included in regional capacity estimates. (**11**[C]) Pressure is the primary driving mechanism for brine leakage via: natural faults; man-made active and/or abandoned wells (Celia et al. 2010); up-dip of the injection formation; and, by diffuse leakage through aquitards (Janzen 2010). Pressure build-up challenges are particularly important in closed/semi-closed aquifers. (**12**[C]) The outer extent of the injection pressure perturbation typically extends well beyond the CO_2 plume outer radius. The Area of Review (AoR) is defined in the recently finalized U.S. Environmental Protection Agency (EPA) rule, which will be discussed in Section 5.2.2, as "the region surrounding the geologic sequestration project where USDWs may be endangered by the injection activity. The AoR is delineated using

computational modeling that accounts for the physical and chemical properties of all phases of the injected CO2 stream and displaced fluids and is based on available site characterization, monitoring, and operational data as set forth in § 146.84. The Agency is developing guidance on AoR and corrective action to support AoR delineation (*i.e.,* including regions of the CO2 plume and pressure front)." (Federal Register 2010). The AoR is therefore expected to be based on the largest spatial extent out of the CO_2 plume or a pressure front endangering USDW, such as the "critical pressure" (defined as the pressure increase necessary to lift resident brine from the injection formation to the USDW) discussed in (Bandilla et al. *in review*) and (Nicot et al. 2009; Birkholzer and Zhou 2009; Birkholzer et al. *in press*).

(**13**[C]) In order to obtain injection permits operators will have to demonstrate that they can accurately define, control, and minimize the AoR. Reservoir-model analyses imply that pressure management has the potential to reduce the AoR by two orders of magnitude (Buscheck et al. 2010). Furthermore, the uncertainty in geological parameters is a critical component of CO_2 geological sequestration risk modeling, as discussed in Section 5.2.1.4, where the first order effect is proportional to the AoR. Therefore, active pressure management has the potential to greatly reduce cumulative uncertainty, particularly when coupled to characterization and reservoir analysis. To the authors' knowledge, there is currently no publically available research of active AoR management and corrective measures by operators to achieve this despite the requirement in existing regulatory documents (see Article 9, paragraph 6 and Article 16 of (European Parliament 2009)).

Studies considering the consequences of large-scale CO_2 injection at the basin scale contribute to understanding reservoir response to sequestration (Birkholzer and Zhou 2009; Lindeberg 2009; Person et al. 2010; Birkholzer et al. 2009; Yamamoto et al. 2009). By extending these models to include pro-active pressure control strategies recommended by (Court et al. 2011b; Buscheck et al. 2010) -which very few studies have implemented other than recent work

by (Bergmo et al. *in press*)- valuable insight into implementation strategies and operational planning can be gained.

The potential for induced seismicity resulting from pressure build-up industrial scale CO_2 injection needs to be carefully taken into consideration (Person et al. 2010). Although distinct from CCS, deep geothermal activities examined in (Majer et al. 2007), particularly the Basel case, provide a reminder of potential induced seismicity by deep underground activities involving fluid injection/extraction. It is important that cross-disciplinary knowledge (e.g. (Huenges and Kuhn 2010; Haszeldine 2010)) from the geothermal energy field be utilized in CCS operations.

- Challenges of single well CCS operations

Review of deep geological drilling safety procedures and investigation of remediation options should shift CCS operational planning away from a single $MtCO_2$/y injection well. A majority of CCS scientific and demonstration project only include a single (injection) well. Only having one access point to the porous medium presents several important technical and public acceptance challenges. First if something goes wrong it will take several weeks or months to drill another well which has proven to be problematic. As detailed in Section 5.2.1.4, the large uncertainty in the geological medium parameters, lack of underground data, and need for characterization and history matching all point toward the weakness of a single access point via a unique injection well,

Additional drilling of secondary wells and extended operations will carry a cost not typically included in current sequestration cost estimates. For perspective, order of magnitude examples for individual well drilling and completion costs range from about $0.2 M for some onshore sites to $15 M at Sleipner and $25 M at Snohvit both of which are offshore horizontal wells (IPCC 2005).

In this context, the authors would like to stress, it may be desirable to anticipate the need and evaluate the advantages of pre-establishing dynamic multiple wells i*n situ* strategies. Section 5.3.2.2 details these synergistic advantages including monitoring, pressure control, leakage risk reduction, and enhanced remediation capabilities. Not including these from the start of the operation planning could incur later operational, financial, public acceptance, and legal penalties. We acknowledge they are difficult to anticipate and give monetary values to, yet we believe they should be incorporated in the future operation planning cost benefit analysis required to fully evaluate these options.

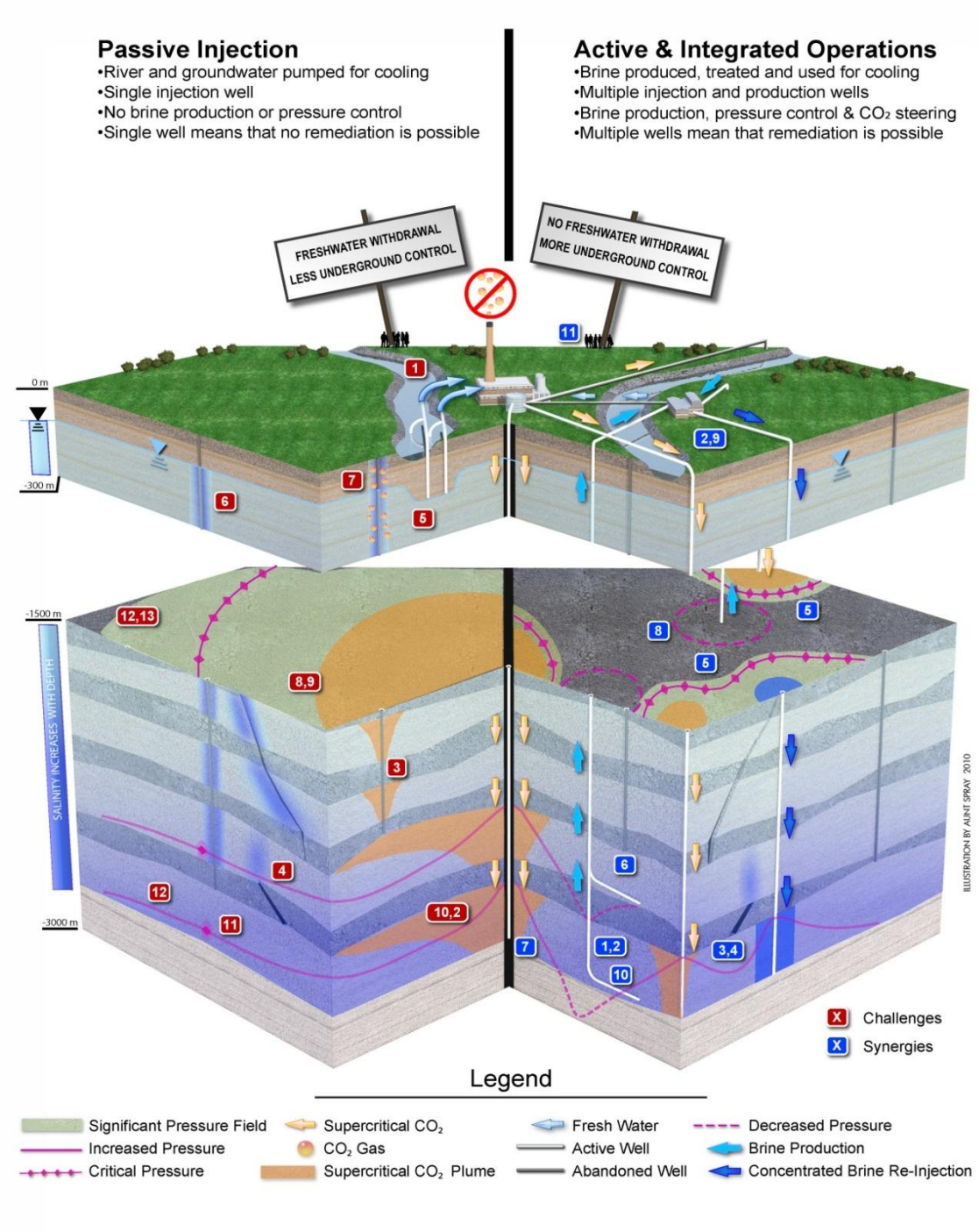


Figure 5.1: (a)(left) Current CCS operation paradigm challenges (X^C in Section 5.2.1.1-3) with power plant cooling water drawn from surface or groundwater, a single CO_2 injection well, and no pressure control/remediation strategy via other wells. (b)(right) Synergistic advantages (X^S in Section 5.3.2.2) of multiple active and integrated CCS operations including: multiple CO_2 injection wells, multiple brine production/re-injection wells -conceivably used for remediation-, a produced brine treatment plant, and treated-brine use for power plant cooling leaving the river and groundwater withdrawal-free. This figure is adapted from (Court et al. 2011b).

5.2.1.3. Competition for pore space

In addition to challenges 5.2.1.1-2, it is important to note long-term competition for pore space that could restrict the required CCS expansion. The SRCCS briefly mentions minimizing damage to other property rights, such as mineral resources and water rights, but does not cover pore space competition in details. A report to congress by (U.S. Department of Interior 2009) indicated that CCS "may potentially conflict with other [...] uses including existing and future [...] oil and gas fields, [...] and drinking water sources [...] These impacts need to be addressed". Current literature on competition for pore space is summarized as follows:

- Future groundwater demand

In the United States the Underground Injection Control (UIC) program protects any aquifer under the 10,000mg/l salinity threshold as USDW. The preliminary analysis of (Davidson et al. 2009) concludes that competition concerns for CCS versus future demand for deep saline groundwater exceeding 10,000mg/l for public supply, agriculture, or industry "are likely to be warranted in limited select regions across the United States, particularly in areas that are already facing water scarcity". However, CCS capture operation will compete also for use of surface water/subsurface treated water, which was not included in the preliminary analysis presented by (Davidson et al. 2009).

- Natural gas storage

Demand for natural gas storage is increasing drastically (McLeod and Kelly 2007; Hoffler and Kubler 2007; Amirault 2005; Le Fevre 2005). Even though temporal dynamics, namely the permanent containment for CO_2 versus yearly to seasonal natural gas storage, are drastically different, natural gas storage is often referred to as a useful experience or technological analogue that CCS can build (Lewicki et al. 2007). However, CCS versus natural gas storage competition for pore space is rarely mentioned, at best simply acknowledged, and has not yet been quantified (U.S. Department of Interior 2009; McLeod and Kelly 2007; Klass and Wilson 2010; Damen et al. 2009; Vedder 2008; UK Department for Business Enteprise & Regulatory Reform 2007; Kelly

2009). Kelly and McLeod present several gas fields as good candidates for CO_2 sequestration, but caution that irreversible CO_2 sequestration removes a site for any other use whereas a cyclical gas storage reservoir may be used for CO_2 sequestration in the future (Kelly 2009; McLeod and Kelly 2007).

- Liquid waste disposal

Tsang et al. (2008) provide a comparative review of hydrologic challenges between CCS and liquid waste disposal (municipal sewage effluent and industrial wastes). Pressure perturbation from liquid waste injection is localized to the sequestration site due to the smaller injection volume, however competition with CCS should be considered due to the potential overlapping injection depth range of 1500 to 2500 m that is typical for liquid waste disposal. The authors are not aware of any investigation of pore space competition between CCS and disposal of liquid waste.

- Shale gas

The recent shale gas boom in the US and around the world brings a potential competition to CCS. As shown in Figure 5.2, they are mutually exclusive because a shale gas operation would stimulate the shale formation by destructive hydraulic fracturing, thereby rendering the shale unsuitable as an intact protective caprock, preventing upwards leakage of CO_2 out of the injection formation, for a CCS operation. The authors are not aware of available literature on this competition, but given the acceleration of shale-gas production this may be significant.

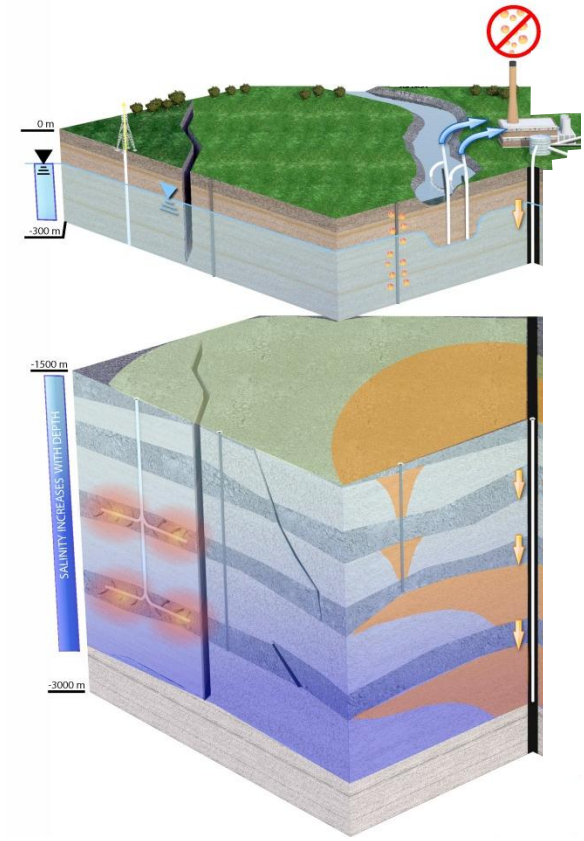


Figure 5.2: Conceptual representation of CCS incompatibility with Shale gas exploration hydraulic fracturing. This figure is adapted from (Court et al. 2011b).

- Other CO_2 sequestration projects

The required scale-up of CCS capacity described in the Introduction, will inevitably result in multiple CO_2 sequestration operations being developed in the same geologic basin which, if not properly integrated, may operationally constrain each-other. Determination of the respective pressure buildup contributions, CO_2 and brine leakage, and responsibilities/liabilities will be difficult unless active reservoir management practices and synergies identified in Section 5.3 can be incorporated from the earliest stages of implementation. CO_2 sequestration projects may compete for the same pore-space, or could interfere with each other, in ways similar to early oil and gas exploration and reservoir management. Early CCS projects may favor, for cost-saving purpose, injecting in the shallowest saline formation (still below 800m) if multiple are available. Operationally, later deep sequestration projects may encounter challenges when crossing

through earlier shallow projects for exploration and injection. In particular, liability and ownership issues, as well as technical challenges will arise if a suitable order of implementation is not developed. Conflict between early shallow projects and later and deeper ones could jeopardize current capacity estimates (Grahame 2001), and also applies to other pore-space competitions described above.

5.2.1.4. Managing geological parameter uncertainty

One of the most challenging aspects of geological CO_2 sequestration is the uncertainty associated with the characterization, representation and modeling of the geological medium that will have to be managed over a wide range of spatial and temporal scale (Celia and Nordbotten 2010; Nordbotten and Celia *in press*) .

When considering geological CO_2 sequestration risk modeling, parameters have to be assigned to the set of equations used to mathematically represent the system. They must describe both the large-scale formation properties and the small-scale heterogeneous leakage pathways, all of which are fundamentally uncertain. If one decides to simplify this uncertainty range and only consider leakage pathways (fractures, faults, up dipping formations, diffuse leakage, and wells) they collectively represent an enormous source of uncertainty with regard to their location, number, and conditions, even without considering the numerous dynamic effects during and after injection. Further narrowing the focus by considering only abandoned wells, the lack of reliable data on their integrity level (for example degraded versus intact cement) makes quantitative description highly unreliable. Parameters are often rough-estimates from soft data such as (Watson and Bachu 2008, 2009); however, very few direct measurements, such as (Carey et al. 2007) exist, even though computational studies like (Celia et al. 2010) require such data. Ongoing modeling and experimental efforts to address this well-bore data uncertainty, such as (Huet et al. 2010; Bachu and Bennion 2009; Carey and Lichtner 2009; Crow et al. 2010; Duguid and Scherer 2010; William et al. 2010; Matteo et al. 2010; Matteo and Scherer *in prep*) and industrial examples (Duguid et al. 2010; Loizzo 2009; Deremble et al. 2010; Le Guen et al.

2010; Loizzo et al. 2010), are very challenging but extremely valuable and necessary due to a lack of alternative or cost-effective tools (e.g., geophysical tools, such as seismic surveys, are typically cost prohibitive) to address the challenges posed by the ubiquitous abandoned wells. Geological parameters uncertainty in CO_2 sequestration is a central issue that has to be strategically addressed in the way one defines the requirements of a CCS Ready project (Global CCS Institute 2010), estimate the cost of reducing this uncertainty, and finally builds computer models to address sequestration safety concerns such as leakage risk.

To address this uncertainty in geological parameters (Melzer and Davis 2010) indicated that a continual characterization scheme for updating heterogeneous reservoir parameters should occur with CO_2 EOR operations. Characterization, history matching, and model calibration will be important components of addressing the large uncertainty in a CO_2 injection operation. Characterization efforts will be directly proportional the size of the reservoir and the AoR that an operator will have to demonstrate control over. However, the SRCCS stated *"In the case of saline formation storage, history matching is generally not feasible for constraining uncertainties, due to a lack of underground data for comparison."* (IPCC 2005). Monitoring the CO_2 plume with geophysical and geochemical methods can provide constraints for simulations. Other monitoring methods are now proving successful, at least in some case, such as employing satellite monitoring of the ground surface (Davis T.L. 2010).

Active pressure management, as discussed in Section 5.3.2.2, has the potential of greatly reducing the operational uncertainty, along with the characterization and reservoir analysis of the smaller AoR. Costs saving incurred by this reduction of uncertainty should be factored into the comparison to any large-scale implementation strategy without such active pressure management. Coupling CO_2 injection with brine production in saline formation could provide equivalent history matching data than obtained from production / injection wells pairs during EOR.

5.2.2. Legal and regulatory development and remaining barriers

Since the 2005 SRCCS, scholars, governments, and industry members have continued to theorize what form CCS liability and regulatory regimes might take. The future of pore space ownership and long term liability regimes for CCS may be better understood, but thus far, it is more a patchwork than a comprehensive solution

5.2.2.1. Recent action on CCS

Across the world, countries who tie the technology of CCS with the potential emissions reductions from their emission portfolios have been the first to develop and implement legal and regulatory regimes (International Energy Agency 2010). A complicating factor arises in determining who has authority to regulate CCS; in some cases it is at the federal level, in others at the state, and in others, a combination. International initiatives such as the Asia-Pacific Partnership on Clean Development and Climate, the IEA GHG program, and the Carbon Sequestration Leadership Forum are investigating and demonstrating technologies (van Alphen et al. 2010).

The first piece of legislation directed solely at CCS was introduced in 2007 when the European Union proposed a Directive that would establish a regulatory framework (Kerr et al. 2009). *Directive 2009/31/EC* was adopted in 2009 and covers all carbon dioxide sequestration in geologic formations in the EU (European Parliament 2009). It focuses on setting criteria for site selection and requires a finding of “no significant risk” before a project is permitted. Additionally, it sets guidelines for the post-closure transfer of responsibility to member states as well as financial mechanisms related to post-closure risk.

In Australia, the Commonwealth’s 2008 amendment to the *Offshore Petroleum and Greenhouse Gas Storage Act of 2006* addresses the sequestration of carbon dioxide, has been supplemented in 2010 by a series of regulations (International Energy Agency 2010). Three of Australia’s states (Victoria, Queensland, South Australia) have CCS legislation in place while two

other states (New South Wales, Western Australia) are developing legislation (International Energy Agency 2010).

In North America, the United States Congress has not approved climate change legislation, although several programs have been dedicated to CCS research in the past decade, with significant progress in the past five years. The U.S. Department of Energy has formed partnerships under the Clean Coal Power Initiative, FutureGen, and the Carbon Sequestration Program with various institutional and industry participants to study and develop different technologies (van Alphen et al. 2010). Regulatory action on CCS has taken place on the federal and state level in the United States. The federal Underground Injection Control (UIC) program of the U.S. EPA governs the injection of fluids underground. Its goal is to protect USDW, where the agency or a delegated state agency issues permits to operators. The EPA developed a new class of wells, Class VI, which governs the injection of CO_2 for the purpose of geologic sequestration, which became effective January 10th 2011 (Federal Register 2010). The permitting rules are more protective and generally more demanding than the rules for other types of UIC wells (Pollak and Wilson 2009). The EPA is employing an adaptive rulemaking approach to regulation with, for example, performance-based AoR criteria with frequent re-evaluation. Further, the rule requires site characterization analyses to include information typically required under the UIC framework, with additional measures specifically tailored to the injection and sequestration of CO_2. Regarding well construction, the Class VI rules require operators to meet specifications regarding the surface and long-string casing mirroring current Class I hazardous waste wells with additional tailoring for CO_2 injection and some flexibility for operators. The rule leaves well stimulation decisions, such as hydraulic fracturing, up to the discretion of the Director, with the express condition that well stimulation techniques in no way affect USDWs. Finally, monitoring for mechanical integrity (MI) of the well is accomplished by both internal and external monitoring and testing. Internal well MI is monitored continuously as a first-indicator of corrosion or other integrity problems while external MI testing is required at least annually during the injection phase of the project. Some commentators, while viewing the rulemaking as a positive

initial step towards regulating geologic sequestration, note some gaps in the rule (Flynn and Summer 2009; Gerard and Wilson 2009; Klass and Wilson 2010; Pollak and Wilson 2009). The regulatory scope is limited to the protection of USDW because the regulations are promulgated out of the authority given by the Safe Drinking Water Act; thus, other CCS-related considerations, such as capture and transport, property right, liability, and GHG accounting, are not addressed (Federal Register 2010). Individual states, however, have addressed some of these issues through more comprehensive statutory frameworks for CCS, with Pollak and Wilson (2009) providing a detailed overview of this early state and federal action.

In addition the authors wish to acknowledge the useful work by (Bachu 2008; Mace et al. 2007; Sharma et al. 2007) who present different regulatory challenges in Canada, Europe and Australia respectively.

5.2.2.2. Liability and regulatory regimes

The SRCCS noted “sparse” literature on liability for sequestration; five years later, scholars have taken significant steps towards filling gaps in knowledge. One accepted notion of environmental regulation, still worth noting has been striking a balance between private and public interests incentivizing investors to develop the technology while ensuring the public will be adequately protected in the event of leakage or other unexpected event (CCSReg Project 2009; Klass and Wilson 2008). One area of progress has been identifying the types of financial assurance mechanisms best-suited to handling both the short- and long-term obligations of operators. Trust funds and environmental bonds appear to be frontrunners in this debate, but there is still much uncertainty regarding specific implementation and cost (Environmental Financial Advisory Board 2010; Flynn and Summer 2009; Gerard and Wilson 2009; Trabucchi and Patton 2008).

After noting that neither public nor private, nor a combination of traditional risk management structures would be appropriate for regulating CCS, some scholars call for the creation of a new “federal government corporation” which oversees a national trust of a

specialized suite of financial assurance mechanisms tailored to the unique risks of CCS (Trabucchi and Patton 2008). These mechanisms must be designed to incentivize development while limiting the problem of moral hazard from parties too well-insulated from liability (Trabucchi and Patton 2008). Others also address the applicability of traditional financial assurance mechanisms like environmental bonds (Gerard and Wilson 2009). Gerard and Wilson propose a three-tiered approach to structuring financial assurance and the release of liability (Gerard and Wilson 2009). Flynn (2009) calls for congressional action to establish a trust fund, paid into by operators during the operational phase, to cover potential costs incurred after release of the operator's liability. Finally, the duration of post-closure liability has been discussed and ranges from as little as 10 years (Wyoming working group recommendation) to 50 years (EPA UIC rule) (Carbon Sequestration Working Group 2009; Federal Register 2010). The EU's Directive Article 18: Transfer of responsibility, noted that the responsibility from the operator to the regulating authority can be transferred after a minimum period no "shorter than 20 years" has elapsed provided that "all available evidence indicates that the stored CO_2 will be completely and permanently contained" (European Parliament 2009).

5.2.2.3. Pore space ownership

One of the most important differences among countries and jurisdictions is who owns the pore space. In the United States, for example, private ownership is common, in other countries, such as Canada and Australia, the government owns the pore space (International Energy Agency 2007). Considering the scale, both spatially and temporally, of CCS, this difference in ownership conceptions could have a significant impact on how regulation proceeds. Even in a jurisdiction where the state owns the subsurface, permits to use the space are issued by the government for hydrocarbon production, or other uses, which could result in future conflict with CO_2 sequestration. Australia uses an "impacts test" to assess (and protect) potential influence on existing hydrocarbon permit holders by greenhouse gas title holders (Kerr et al. 2009). A balance should be struck to protect both types of users – hydrocarbon and GHG sequestration – from adverse interference from other operators (International Energy Agency 2007).

In the U.S., states have begun to address pore space ownership in the context of CCS, either laying groundwork for future legislation or including pore space provisions within larger CCS legislation (Klass and Wilson 2010). For example, Montana, Wyoming, and North Dakota have explicitly defined pore space ownership as vesting in the surface owner, though the severability of that interest differs between states (Klass and Wilson 2010). Because of the potential conflicts between mineral interest-holders, some advocate that a saline aquifer sequestration and recovery-based framework be established, in which government would declare geologic formations, like saline aquifers, to be a public interest for the goal of addressing climate change (Fish and Wood 2008). This may encourage saline aquifer sites to be favored over the more conflict-prone hydrocarbon reservoirs. Further, it would not be an unprecedented action: in the U.S., airspace for air travel and other modern conveniences was long-ago declared a "public good" in order to avoid the possibility of liability for commercial airlines as they travel above private property. Additionally, underground natural gas storage has been deemed a public good in order to allow for the establishment of sufficient storage space across property lines. Like the examples of airspace and natural gas storage, injection operators would then require only a permit to inject CO_2, as opposed to potentially litigious dealings with private pore space owners (Fish and Wood 2008).

5.2.2.4. Shale Gas: A Case Study

Drilling for shale gas by using horizontal drilling and hydraulic fracturing has been practiced for more than a half-century. Recently, a combination of technological advances and economic conditions have contributed to a boom in the practice, especially in parts of the Eastern U.S. where the Marcellus Shale play stretches some 95,000 sq. miles and is the largest such formation in the country and the epicenter of this boom. In one government estimate, shale gas is expected to make the largest contribution to U.S. natural gas growth in the coming decades, doubling its contribution to the supply by 2035, to ~35% (U.S. EIA 2010). Our understanding of EPA's hydraulic fracturing position is that it acknowledges it is important for US energy, however

some evidence suggest it may be contaminating groundwater, and thus it is conducting a study to determine if it is. [see http://water.epa.gov/type/groundwater/uic/class2/hydraulicfracturing/index.cfm]

The development of this resource will have implications for the future of geologic sequestration, especially in places where the two activities directly compete for pore space as shown in Figure 5.2. Further, because of an exemption from federal regulation though the UIC program, state regulation of fracturing and the handling of subsurface disputes in that context could provide critical lessons for state and federal agencies attempting to address CCS (Dammel 2010).

5.2.3. Societal acceptance and communication

The issue of public acceptance, or the lay-person response, was briefly covered for geological CO_2 sequestration in the SRCCS, wherein three public acceptance conditions for implementation were identified. In this section we will review advancement on the public acceptance conditions necessary for implementation of CCS that were identified in the SRCCS; examine societal acceptance, defined as the lay and stakeholder [government, industry and environmental NGO's] response (van Alphen et al. 2007), of CCS since the SRCCS; and, further investigate some of the communication challenges that CCS is facing.

5.2.3.1. Public acceptance conditions

The SRCCS previously identified three public acceptance conditions for CCS implementation which have been explored in recent media and literature under the topics of: anthropogenic climate change (ACC) as a real and serious problem (Seitter 2009; Stoker and Dahe 2009; International Panel Review 2010); identifying a need for large reductions in CO_2 emissions to mitigate global climate change (United States Global Change Research Program 2009); and, improving communication of CCS as a viable and effective option to address the previous two topics (Ashworth et al. 2010; de Best-Waldhober et al. 2009; de Coninck 2010).

- Anthropogenic climate change as a real and serious problem

The topic of ACC as a real and serious problem faced a period of difficulty in late 2009, referred to as the "Climategate" involving the University of East Anglia's Climatic Research Unit, which ultimately saw a decrease in societal acceptance (Leiserowitz et al. 2010). The late 2009 episode also decreased perceived public trust in the scientific community regarding ACC, which will have ramifications for future evidenced-based arguments toward CCS, even when presented in an appropriately neutral manner as per (de Coninck 2010).

Stakeholder organizations, as significant components of societal acceptance, have demonstrated an increasing awareness and acceptance of the scientific basis for anthropogenic sources contributing to gaseous radiative forcing. An example of which is the revised content of annual governmental reporting, from the minimalist "Climate Variability and Change" section of a U.S. Global Research Program 2006 report (United States Global Change Research Program 2006) to an enhanced and more comprehensive report that included a "Human Contributions and Responses" section in the 2010 report that had an emission reporting component (United States Global Change Research Program 2010). The improved recognition of human influence on the environment, specifically in stakeholder communication, has demonstrated that anthropogenic climate change is gaining public acceptance as a real and serious problem.

- Need for large reductions in CO_2 emissions

The need to decrease atmospheric CO_2 emissions is evidenced by communication from stakeholder organizations whose perspective, as previously indicated, has a large influence on public acceptance. The recent classification and subsequent legal challenges of CO_2 as a substance hazardous to human health by the U.S. EPA (U.S. Environmental Protection Agency 2009) has polarized societal acceptance between industrial and environmental NGO stakeholder groups. Stakeholder groups that gain from current unregulated atmospheric emission standards, obviously, lobby against the need for reductions and incite a fear response in the lay public

through exemplifying punitive economic outcomes, such as shutdown of certain industries (Kharecha and Hansen 2008). Arguably there is evidence indicating that public health, economics and environmental decline would benefit from regulation of carbon emissions, wherein it would be necessary to demonstrate and plan for uncertainty and associated risk in CO_2 sequestration (Lackner and Brennan 2009). The need for large reductions in CO_2 emissions has also been recognized by enhanced research on CCS deployment potential, even by foreign interests, most notably in China (Zheng et al. 2010b). Finally, in addition to the public identifying a need for large reductions in CO_2 emissions, motivators provided by stakeholders, such as governmental emission policy or industrial growth with restricted emissions, will be needed to initiate CCS projects (Selighsohn et al. 2010; Wilson et al. *in press;* Davis SJ 2010).

- Communicating CCS as a viable and effective option

The viability and efficacy of CCS is poorly understood by the general public and stakeholders, which has resulted in a low societal acceptance of CCS as an option to address anthropogenic climate change. In order to communicate CCS viability, regulatory and legal issues aside (de Coninck et al. 2006), the hydrogeologic environment must be considered and vetted through the best available mechanism. However, for any vetting mechanism, the initial parameter assumptions of a hydrogeologic scenario can pre-determine the results to evidence a supportive or detractive outcome to the proposed CCS system. We therefore believe it is vital to examine how base assumptions in recent scientific developments and published work influence communication and acceptance of CCS as a viable option to address anthropogenic climate change.

5.2.3.2. Societal acceptance challenges

Societal acceptance has largely been neutral to CCS and is highly responsive to stakeholder perspectives (van Alphen et al. 2007). As the SRCCS first identified, there has been a continued cynical skepticism in the efficacy of CCS for greenhouse gas control as a necessary concurrent effort to planned energy efficiency and demand-reduction strategies (van Alphen et al. 2007).

The skepticism has, in some cases, turned to direct Not In My BackYard (NIMBY)-style opposition to CCS projects due to a fundamental operator/government miscomprehension of: the 'playing field', comprised of the people, reasoning, knowledge, comprehension and experience of those involved; the local value proposition, which is a function of local benefit, impact and risk, and national benefit; and, the societal acceptance strategy (Kuijper 2011). The consequence of such opposition will clearly impact siting of CO_2 capture facilities and sequestration wells, particularly for areas with litigious private pore space ownership as described in Section 5.2.2.

The lack of public insight into atmospheric carbon accumulation, carbon mitigation strategies, and sequestration methods currently employed at small scale and in industry indicate that there is ineffectual, or a lack of, communication on these related topics (Ashworth et al. 2010; Sharp 2008; de Best-Waldhober et al. 2009). Furthermore, the magnitude of carbon emissions and actions necessary to reduce them in order to meet international emission targets is poorly communicated to lay-people through stakeholders, resulting in very low awareness of the relational greenhouse issues, CCS technology and actionable opportunities (de Best-Waldhober et al. 2009).

5.2.3.3. Communication challenges

Efforts toward improving communication for CCS as an effective method for mitigating atmospheric carbon accumulation have improved societal acceptance of CCS in recent years (Davis SJ 2010; Pacala and Socolow 2004; Guggenheim 2006). However, a persistent issue about communicating the efficacy of CCS is a perceived biased presentation of research models by investigators (de Coninck 2010), wherein base assumptions are selected to be untenable or unrealistic to produce a particular result. De Coninck (2010) warns that CCS advocacy by academics could result in the public losing its trust in them as independent experts.

Models of geological CO_2 sequestration scenarios have been examined in works such as (Nicot 2008), (Zhou et al. 2008), (Yamamoto et al. 2009) as well as (Ehlig-Economides and

Economides 2010), which have arrived at both supportive and detractive verdicts on CCS efficacy. Ultimately, the reality of a CCS project, as with any engineered approach, will be found in-between restrictive (Zhou et al. 2008) or (Ehlig-Economides and Economides 2010) and ideal (Dooley and Davidson 2010) perspectives. Unfortunately, it has proven to be beyond the capacity of the media, or other authors of mass-communication for the lay-person, to examine the influence of hydrogeologic parameters, scientific engineering model complexity, and assumptions regarding geological CO_2 sequestration. Rather, the typical scenario sees the key results published in direct social media without explanation, often to the direct detraction of anthropogenic climate change and mitigation initiatives (Singleton et al. 2009). The use of proactive information opportunities and material to better communicate the technology and risk associated with CCS has proven to be effective (Oltra et al. 2010).

5.3. Paradigm shifts through promising synergistic solutions

In this section, we propose a framework for a possible paradigm shift that can address many of the challenges identified in Section 5.2.

Despite the fact we do not comprehensively review the CO_2 capture cost challenge category we would like to point out several worthy new development since SRCCS in this area. Real progress was achieved in the CO_2 capture cost category by several groups such as (Al-Juaied and Whitmore 2009; Chen and Rubin 2009; D'Alessandro 2010; Davison 2007; Pennline 2008; Rubin et al. 2007; Yang 2008, DNV 2010) on the intrinsic CO2 capture energy penalty/parasitic load, power plant performance reliability, and high operating costs challenges. The creation in the United States of Advanced Research Projects Agency – Energy will be one of the key elements to kick start capital intensive investments to bring down capture cost by accelerating promising ideas from the basic research stage towards large-scale demonstrations and ultimately, commercialization. The effort and findings of Larson et al. (2010), Kreutz (2010),

Liu et al. (2010), Williams et al. (2010) to analyze the carbon mitigation benefits of co-processing biomass in coal and/or gas CCS energy systems should be furthered and implemented at scale. We also note that (Eccles et al. 2009; McCoy 2008; McCoy and Rubin 2009) provide an excellent review of sequestration cost and (McCoy 2008; McCoy and Rubin 2008) of transport cost which will not be discussed in further details in this dissertation.

5.3.1. Addressing water and sequestration challenges require both an integrated operation management and a synergistic paradigm shift

We will first describe how integrated management of the CCS operations can address both the newly identified cooling water requirement from the capture retrofitting process and the CO_2, brine, and pressure challenges. Then we will identify several additional advantageous synergies if this active and integrated management is implemented.

5.3.1.1. Integrated management to address the new water challenge

As described in Section 5.2.1, there are at the same time a cooling water supply challenge at the surface for the capture process, and a clear sequestration challenge of pressure build-up in the subsurface particularly in closed/semi-closed aquifers. Production of water out of the injection reservoir to release the pressure, and use of the water at the surface for cooling purposes represent an attractive synergy. Ideally the CCS operation, as represented in Figure 5.1, could function in a closed loop, not adding any additional stress on local surface water resources, although the entire process may be restricted by the need for surface treatment of the produced brine. However in regions with scarce water supply where this resource is a very sensitive public issue, such technical integration even at an additional cost could bring numerous benefits to the projects as described in Section 5.3.2.2 and 5.3.3.

The United States Interagency Task Force on CCS reported in August 2010 on both the CO_2 capture increased water need, and “Pressure management schemes, such as brine extraction […] to mitigate some of the basin-scale factors associated with wide scale deployment”

even though synergies between the two were not established (Interagency Task Force on Carbon Capture and Storage 2010). A similar note comes from the CCS Ready brief (Global CCS Institute 2010) by the Global CCS Institute about “any additional water requirements”, however it is lacking the integration with brine production described below.

Recent studies have identified the freshwater challenge described in Section 5.2, pointing toward a similar brine production concept (Ciferno et al. 2010; Newmark et al. 2010; Interagency Task Force on Carbon Capture and Storage 2010; Wolery et al. 2009; Aines et al. 2009; Surdam et al. 2009; Kobos et al. 2008a; Kobos et al. 2008b; Veil et al. 2010; Friedmann 2009; Buscheck et al. 2010; Veil et al. 2011; Harto and Veil 2011). A serious effort has begun to identify suitable formations deeper than 800 meters with low salinity brines (Veil et al. 2011; Harto and Veil 2011; Aines et al. 2010) and quantify the feasibility and cost of treating the produced brine and using it for cooling. First order economics indicate the positive potential of such concepts using current seawater desalination technologies (Reverse Osmosis) for brines with salinity equal of below 85,000mg/l TDS which are found to be abundant in the United States. Predicted desalination costs for brines having salinities equal to seawater are about half the cost of conventional seawater desalination assuming the energy can be obtained from excess pressure at the well head. We refer to (Wolery et al. 2009; Aines and Bourcier 2009; Bourcier et al. *in review*) for details on cost and technical limits. It must be noted that some brines could be of high salinity and include undesirable trace metals and therefore not be suitable to be treated and used, in which case it should be fully re-injected or not be produced to avoid the problematic large volume disposal. Note that these activities are complemented by several studies that include or consider brine production wells solely to avoid pressure build-up, see (Flett 2008; Lindeberg 2009; Le Guénan and Rohmer *in press*; Nicot 2008) and the recent (Bergmo et al. *in press*).

The brine treatment plant will generate an output of residual saltier brine which needs to be disposed of safely – this is discussed in Section 5.3.2.2. But brine desalination for freshwater production is just one of several brine utilization options. Produced brine can be used directly for

cooling purposes, such as in saltwater or brackish-water cooling towers (California Energy Commission 2010). Compared to desalination, this option requires less-costly brine treatment, such as softening by ion exchange or nanofiltration, and/or the addition of corrosion inhibitors (Duke 2007). Because of the inherent evaporative losses, zero liquid discharge (ZLD) approaches for cooling towers (Duke 2007) can be useful by reducing (or even eliminating) the volume of residual brine requiring reinjection or disposal. Untreated brine can also be injected as make-up water for pressure support in oil and gas reservoirs, enhanced geothermal systems (Harto and Veil 2011), and conventional geothermal reservoirs (Bourcier et al. 2007).

Air/Dry cooling systems, which would suppress the additional cooling water need, exist and are compared with water consuming ones in (Zhai and Rubin 2010; Zhai et al. 2011). Zai et al. conclude that replacing wet towers with air-cooled condensers for dry cooling would reduce plant water use by about 80% (without CCS) to about 40% (with CCS) but could approximately triple cooling system capital cost.

In summary, addressing the presented water and pressure management challenges requires an integrated approach -which represents a significant shift from the current CCS paradigm- including, but not limited to, the active production, treatment, use for cooling, and partial re-injection of brine as conceptually represented in Figure 5.1. This technical integration of CO_2 injection, brine production and treatment will be specific to each CCS operation and dependent on the distance between the sequestration and capture sites. It is also important to note that this global strategy will have to be carefully adapted to each country, region, and CCS project depending on respective water availability, public sensitivity, cost and available technical knowledge.

5.3.1.2. Additional synergistic advantages of active and integrated operations

When considering active management to handle freshwater, CO_2, brine and pressure CCS challenges, several additional synergies to the ones described in the last section are worth taking

into account. They are identified below and related to the different options shown schematically in Figure 5.1.

(1^{S} synergy 1 in Figure 5.1 b) The increased cooling water volume required annually for a standard 1GW coal-fired power plant CCS retrofitted is on the same order of magnitude, roughly 10 millions m^3 (Mm^3), as the emitted CO_2 volume to be sequestered. Brine production could therefore free up this equivalent pore volume for CO_2 sequestration which could minimize the displacement of the equivalent brine volume out. For context this amount of water would supply 1/3 of the annual drinking water delivered to Copenhagen (at 32.6 Mm^3 in 2005) (Rygaard et al. 2009). The 235 Mm^3 annual withdrawals from municipal water supply wells from deep aquifers beneath the city of Chicago are of the same order of magnitude as the volume of CO_2 generated across the Illinois basin by dozens of coal-fired power plants (Person et al. 2010). Other examples of fluid volume handled in different industries are presented in (Nicot 2008).

(2^{S}) Several synergies were identified at the treatment plant. First, if brine pumping and treatment were considered, both could potentially take advantage of the local pressure increase resulting from the CO_2 injection by reducing the pressure difference that needs to be applied along the producing well and across the desalination membrane respectively (Wolery et al. 2009; Aines et al. 2009; Bourcier et al. *in review*).

Produced brine will carry a significant heat, depending on the site-specific geological temperature gradient and the pumping depth, which may be viewed as conflicting with its use as a coolant. However, the heat content of the produced brine can be used to advantage in several ways. One obvious way is to capture the heat and use it, for example in a district heating system. Such a system could provide a significant benefit to the local community, thereby improving the CCS operation's societal acceptance. Alternatively, if the temperatures are sufficiently high, an electricity generating geothermal unit taking advantage of this heat could cover part of the treatment plant energy penalty. More broadly, integration of CCS with geothermal energy recovery is currently being investigated by the authors. Geothermal energy production can be

limited by pressure depletion, whereas pressure buildup is the limiting consideration for CCS sequestration capacity and risk mitigation. These two complementary systems can be integrated synergistically, with CO_2 injection providing pressure support to maintain the productivity of geothermal wells, while the production of geothermal brine, through desalination technologies such as reverse osmosis provides pressure relief and improved injectivity for CO_2-injection wells (Buscheck 2010). An integrated geothermal–CCS reservoir system, actively managed to yield a volumetric balance between injected and produced fluids, mitigates the environmental and economic risks of reservoir overpressure or underpressure (e.g., induced seismicity or insufficient well productivity). An economic study of pressure relief from brine production and reverse osmosis treatment showed substantial cost benefits (Neal et al. 2010). In cases where CCS already includes a brine-production infrastructure in their designs, the capital and operating costs of the well system would not be considered part of geothermal heat recovery costs, which would lower the levelized cost of electricity and financial risks of an integrated geothermal–CCS system. Even without extraction of heat energy from the produced water, heat will need to be carefully integrated in the treatment process management with both potential advantages (e.g. higher temperature could favors higher flux through reverse osmosis membranes, or could be used for high salinity brine thermal distillation) and disadvantages (e.g. reverse osmosis membranes' internal support structure deforms more readily at higher temperature than 40-50°C reducing their operating lifetime) which need to be further researched (Aines and Wolery 2010).

(3[S]) Multiple injection/production wells strategies could also be used for monitoring, remediation, and pressure control. Monitoring potential for CO_2 and brine leakage through a system relying on monitoring wells in the overlying aquifer was recently studied by Chabora and Benson (2009) and Zeidouni et al. (2010). Potential remediation capabilities through multiple wells in the injection formation near the CO_2 plume were recently numerically investigated by Réveillère and Rohmer (2010) and Esposito and Benson (2010). When CO_2 has been detected in an undesirable neighboring field, the CO_2 plume would then need to be either "steered" away, and/or pumped and vented (Akervoll et al. 2009). Finally, pressure control via production wells

located further afield was numerically explored both in a risk preventive approach (Lindeberg 2009) an in a risk corrective approach (Le Guénan and Rohmer *in press*).

(4[S]) Brine treatment plant output (a saltier residual brine) needs to be appropriately disposed of. While use of an evaporation pond, or pumping into a river or the sea represent significant environmental risks, re-injection of the more concentrated brine could be advantageous in several ways. Injecting it: in the former CO_2 injection well could help immobilize and dissolve the CO_2 injected (Manceau et al. 2010); or, in an additional well located optimally could reinforce a steering effort of the CO_2 plume in a "push-pull" injector/producer wells pair strategy. Finally, re-injecting residual or untreated brine in an overlying aquifer could create a beneficial hydraulic barrier through over-pressuring, thereby reducing leakage via fracture or wells and diffuse leakage across the caprock (Réveillère and Rohmer *in press*). Reinjection of the residual brine into the original CO_2 sequestration formation or into an oil, gas, or geothermal reservoir will not necessitate additional geological characterization, while re-injection into a new formation will incur additional cost which needs to be considered.

If brine is pumped out of the injection formation, it could result in several advantageous impacts (5[S]-10[S]) represented in Figure 5.1 and summarized here. Brine production will (5[S]) significantly reduce the outer extents of both the pressure perturbation and critical pressure (AoR); and (6[S]) decrease the local pressure which will concomitantly lead to a decrease of CO_2 and brine leakage pressure drive and hence in the leakage risk. (7[S]) Remembering the fracture pressure constraint at the injection well, increased injection capacity could be realized by reducing local formation pressure. (8[S]) Smaller and more controlled pressure and CO_2 footprints would allow multiple CCS operations in a single basin to co-exist without constraining each other. This is because active reservoir management will allow for much easier determination of the respective pressure build-up contributions, and CO_2 and brine leakage responsibilities/liabilities of different CCS operation deployed in the same geologic basin. This would result in projects less prone to permitting, accounting, and legal/insurance disputes. (9[S]) As described in the last

section active water management may provide a new source of water for cooling purposes or other uses. This local benefit could significantly improve the societal acceptance of CCS projects in the future. (**10^{S}**) A brine producing well could actively provide history matching data while active, then if reached by CO_2, could be turned into an in situ monitoring well and potentially later on into a CO_2 injection well.

Lastly, (**11^{S}**) proactive and integrated management and containment control -as opposed to passive CO_2 injection management with no in situ monitoring, control, and pressure release of the system- will inspire confidence to the public. Moreover, because CO_2 breakthrough in the geothermal or brine treatment plant is operationally prohibitive, operators will have a vested financial interest to prevent any occurring. This presents an additional argument towards convincing the public that this active and integrated operations management provides more underground control than a passive injection.

5.3.1.3. Active and integrated management research questions

This integrated proactive management of freshwater, CO_2, brine and pressure is a newly proposed process and will lead to a number of important **Questions,** presented by black numbers (**X^{Q}** and X), that need to be addressed including the following: (**1^{Q}** Question 1 in Figure 5.3) Does the additional water demand for the worldwide projected CCS expansion match with projected available water supply? This is particularly relevant for the largely coal dependent nations (see (World Coal Institute 2010) and Table 1.1 in Chapter 1) already suffering from restrained water in local regions; (**2^{Q}**) What is the most environmentally friendly and cost-effective technical configuration to treat, use produced brine in power plant cooling, and dispose of the treatment plant's saltier output?; (**3^{Q}**) If CO_2 reaches the brine producing well it not only defeats the enterprise's purpose but would it also prevent the treatment system from functioning?; (**4^{Q}**) CO_2 might have changed water and brine chemistry to the point that it affects the technical feasibility or economic viability of a chosen brine treatment process. What technical solution could address this plausible scenario?; (**5^{Q}**) Do relevant legal and regulatory processes exist to

address this CCS additional water and brine disposal requirement? Will the cross-border/cross-state water dilemma (Sovacool 2009; Sovacool, Sovacool 2009a,b; Klass and Wilson 2010) get worse or could a legal framework tackle it?; (**6**^{Q}) How will the pore space ownership procedure and appropriation process be affected by this novel deep brine commodity previously considered valueless?; (**7**^{Q}) Who will publish detailed integrated case studies that, (a) incorporate CO_2 capture and power plant cooling processes using produced brine, and CO_2 injection operations coupled with brine production, and (b) carefully quantify cooling water and energy cost (like (Kvamsdal et al. 2010)), sequestration safety, and public acceptance?; (**8**^{Q}) How would the necessary local power plant water strategy evolve if the cooling water now comes from the CO_2 sink geographic location?; (**9**^{Q}) Does the industry have the CO_2 remediation capabilities and has it agreed with regulatory authorities on emergency procedures to pump and vent the CO_2 out of danger zone in case of a natural or human health hazard threat?

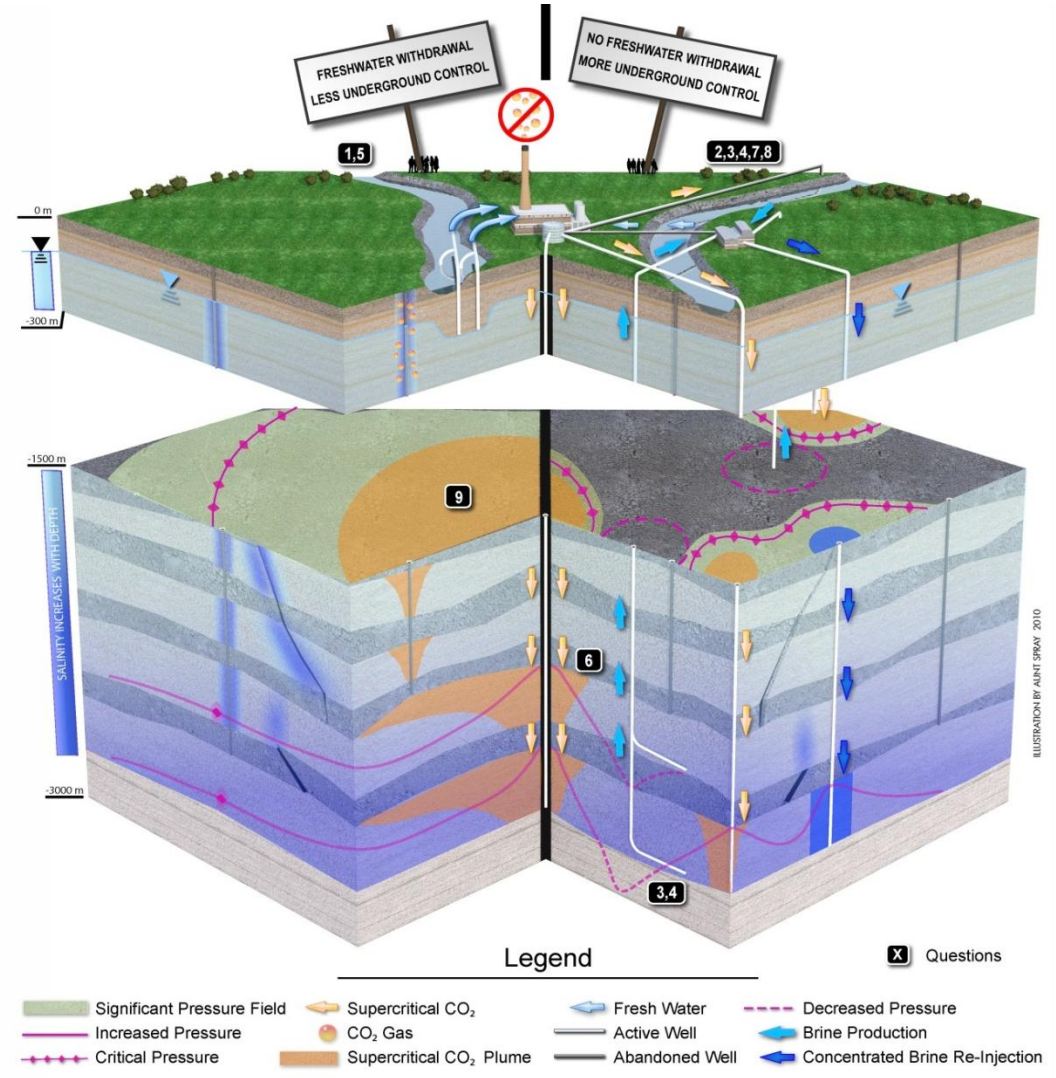


Figure 5.3: Same as Figure 5.1 showing the research questions described in section 5.3.2.3.

5.3.2. Shifting the risk paradigm for societal acceptance

In order to fulfill the public and societal acceptance challenges outlined in Section 5.2.3, the motivators of public and stakeholder behavior need to addressed. This section will examine societal decision-making as based on risk perception, and how better communication can facilitate an improved societal acceptance of CCS.

5.3.2.1. Definition of risk perspectives

The polarized influences on societal acceptance presented in Section 5.2.3 can be associated with stakeholders' risk perspectives, where societal decision-making can be attributed to one, the

other, or a mixture of both perspectives. The global environmental movement currently operates under social constructive risk (risk based on interpolated consequence of current trends), wherein it is argued that extrapolation of quantifiable and modeled systems should be used for decision-making. It is a practice that encounters passive opposition from industry and economic groups who rely on a realist risk (risk based on observed likelihood of occurrence) to dictate behavior (Frikckel et al. 2010). However, societal acceptance of CCS operates on a mixture of both social constructive risk and realist risk, which is termed psychometric risk (Singleton et al. 2009). For example, episodes of long term environmental degradation, such as: atmospheric ozone layer depletion by use and release of CFC's and other chlorinated hydrocarbons; or the anoxic lakes at mid to high latitudes caused by low latitude sulphur dioxide emission and global circulation, cause a shift toward social constructive risk for a short period of time that is correlated to stakeholder attention to the issue, after which psychometric risk dominated by realist risk was the primary motivator (Frikckel et al. 2010).

The 2005 SRCCS explored potential environmental impacts of CCS leakage, from which the impact-risk can be categorized into two broad groups: global and local. Global impact-risks, such as increased atmospheric radiative forcing, evoke social constructive risk due to the longer-term impact occurrence as well as an indirect cause-effect relationship and therefore have low-level influence on societal acceptance (Herzog 2010). However, societal acceptance would be heavily motivated by risk of local impacts from leakage, that can be sub-categorized into gradual and abrupt events, which incur both social constructive and realist risk (Singleton et al. 2009). A gradual local leakage event, such as long-term flow through faults that could contaminate underground potable water sources, is a psychometric risk that could have a moderate influence on societal acceptance (Wallquist et al. 2010). Although, gradual events are ongoing processes, presenting opportunity for remediation (Herzog 2010) improves societal acceptance by reducing the realist risk component of psychometric risk. An abrupt leakage event incurs a sense of dread and unknown which raises overall psychometric risk and particularly realist risk, which is similar to the risk response related to sulfur-gas extraction wellheads, and therefore is a motivator for

NIMBY opposition and low societal acceptance. With little or no remediation options and little individual preparedness response available to abrupt leakage events, societal acceptance is heavily weighted by the resulting increased psychometric risk.

Finally it is important to put local health, safety and environment risks of geological sequestration in context; moreover, it is of primary importance that a CCS project seeks local approval through technical and non-technical information availability and relation to better-known and safe industries, such as natural gas storage, EOR and deep underground disposal of acid gas, to minimize psychometric risk (Oltra et al. 2010).

5.3.2.2. Improved communication for societal acceptance

Reporting on CCS, and subsequent interpretation by non-experts, face issues of clarity and parameterization that has decreased societal acceptance of scientific results. One approach to reassure societal acceptance of numerical model validity has been comparison of results from multiple simulation methods when operating under identical assumptions and parameters (Pruess et al. 2004; Ebigbo et al. 2007; Class et al. 2009). However, the issue of reservoir data (i.e. parameterization) uncertainty has not been incorporated into full numerical solutions, whereas Monte-Carlo simulations can provide a probabilistic results range (Celia et al. 2010), which can be communicated in a comprehensible manner to stakeholders and the lay public. Herein we will propose communication methods that operate with societal acceptance risk paradigms to ensure clear delivery of projected CCS outcomes and uncertainty surrounding the projections.

A pragmatic communication method to improve societal acceptance of CCS would be to alleviate psychometric and social constructive risk through familiarization with currently ongoing subsurface disposal and expansion of CCS conceptual understanding (Wallquist et al. 2010). By increasing the general public's exposure to ongoing CCS operations, and therefore associating CCS with a well-developed safe operation practice, the psychometric risk would decrease due to an increased awareness of the low probability for abrupt local event occurrence (Singleton et al.

2009; Oltra et al. 2010; Wallquist et al. 2010).

Furthermore, a decoupling of CCS implementation from the perceived 'business as usual' operation of carbon emitters, which incurs strong social constructive risk aversion, will improve societal acceptance (Schackley et al. 2005; Oltra et al. 2010). With the current perception of CCS dominated by psychometric risk from: leakage events (Singleton et al. 2010); unfamiliarity (Oltra et al. 2010); necessity and efficacy of CCS as an unsustainable personal socioeconomic cost (Wallquist et al. 2010), it is unlikely that distancing CCS from business as usual or other stigmatized industries will result in a significantly improved societal acceptance unless other conjunctive communication efforts are taken. Beneficial utilization of produced waters, reduction in coal plant water requirement, and district heating should be communicated, as a conjunctive effort, to demonstrate opportunities associated with full scale CCS deployment.

If CCS is perceived as decoupled from continued 'business as usual' high carbon-emission operations, communicating the concept of 'infrastructure inertia' would result in the desired psychometric risk reduction. Infrastructure inertia is defined as the occurrence where infrastructure (energy, industrial, etc.) have committed atmospheric carbon emissions, due to a lack of low-carbon infrastructure alternatives, which outstrip the capacity to retrofit or capture emissions from these facilities at an acceptable level (Davis et al. 2010). An infrastructure inertia concept, while admittedly requiring acceptance of anthropogenic climate change as a real and serious issue, would effectively identify CCS as an essential measure while there is concurrent development of alternatives to carbon-intense process (Davis et al. 2010). To build on the concept of infrastructure inertia, emphasis should be placed on a public engagement method of carbon and water efficiency. Much akin to energy or process efficiency, which has widespread societal acceptance, a carbon and water efficiency concept would see personal carbon and water minimization strategies and could subsequently permit development of a personal carbon tax, which is reportedly more acceptable than a general carbon tax (Bristow et al. 2010), or support technological low carbon and water -intensity production methods (Oltra et al. 2010).

Furthermore, since an established water efficiency concept is widespread in many arid environments, if CCS produced water is desalinated and utilized the CCS option would be an enticing synergistic opportunity.

With regard to recent NIMBY social opposition that has resulted in planned CCS projects to be postponed pending review or cancelled outright (Kuijper 2011); the effective communication of active water management in CCS operations could result in improved local societal acceptance through mitigation of psychometric risk and provision of direct social benefit. The water produced from active management in CCS not only reduces psychometric risk through minimizing pressure buildup and therefore realist risk of an abrupt leakage event, but also reduces social constructive risk due to a variety of positive industrial synergies indicated in section 5.3.3. These opportunistic advantages of active management scenarios can, and should, be offered to host communities to reduce public NIMBY opposition and improve local societal acceptance of CCS operations.

In summary, the issue of CCS societal acceptance must be approached by: using a cohesive presentation of scientific evidence and linkages between anthropogenic climate change and atmospheric carbon emissions; shifting the psychometric risk dominance from realist risk to social constructive risk as supported by evidence of climate change (Singleton et al. 2009; Gee and Stirling 2003); and, offering synergistic benefits to local stakeholders and communities to reduce social constructive risk and improve psychometric risk.

5.3.3. CCS sequestration site ready: promising development through landowner engagement

We have observed a very interesting recent development as entrepreneurs have begun to develop sequestration sites within the current legal context. Until recently the general consensus was that:

-The difference between public/state ownership of the pore space vs private in the US (see section 5.2.2), would mostly be detrimental to the expansion and rapid large scale CCS implementation in the US. The reason was perceived to be the difficulty to include multiple

stakeholders in the US case vs the state in the other case could simply decide where CCS would be implemented.

-There has been various estimation of CCS sequestration capacity and location in the US and other countries (Litynski et al. 2009) but to our knowledge there has been no clear distinction and database/organization of these sites on a precise value scale (average, good, very good, excellent). Whereas there are multiple studies in the literature and an active discussion about what "CCS Capture ready" would mean for a power plant [see http://www.captureready.com], the obvious question becomes: What is a sequestration ready site?

-Liability and hence insurance of any sequestration site is perceived to be a major barrier

In this context we were very impressed to learn that entrepreneurs have entered the sequestration arena and have transformed this list of potential barriers into a sound and logical argument for commercially-practicable implementation of CCS in the U.S. Among other things, these entrepreneurs are:

-Taking advantage of private pore ownership rights to ensure community support for sequestration projects. It is becoming increasingly clear that CCS projects will not occur absent of strong community support. For example, the recent failure of the Barendrecht project in the Netherlands was based on public opposition, as described in (Kuijper 2011). The best way to achieve this support is to work directly with landowners overlying the sequestration site to explain the risks and benefits of CCS and to compensate them for sequestering CO_2 beneath their land. The costs of compensating landowners are small relative to the overall costs of CCS projects, and are a very wise investment in the long-term viability of the project. Any attempt to use condemnation proceedings or other forms of government seizure are likely to add to the public opposition to a sequestration project, and thus introduce added commercial uncertainty. As with all aspects of the energy sector, private enterprise working within an established system of private property rights is, in these entrepreneurs' experience, the only way to achieve long-term viability in the CCS industry.

-Identifying the best geologic sequestration sites. While general sequestration capacity estimates are useful, the ultimate question is whether a site may be permitted and operated in a viable matter. Complete confinement – that is, total geologic confinement of CO_2 in the vertical and horizontal directions – makes commercial-scale CO_2 sequestration feasible, and that anything short of great geology for early-stage CCS projects will stop the industry before it gets started. Only those sites with great geologic characteristics will be able to satisfy the permitting and operating (including insurance) requirements within the U.S. legal context. Absent of complete confinement, the fate of the CO_2 plume is a lot more unpredictable and thus undermines the certainty needed for early commercial implementation of CCS.

-Managing sequestration risk through site selection, utilizing commercial insurance and not assuming future government liability during operation phase. While perceived sequestration risks may be high, these risks can be greatly minimized through appropriate site selection. By limiting CO_2 injection to only those sites that exhibit complete confinement, sequestration risks can be managed downward as the CO_2 plume distribution pathways can be predicted with sufficient certainty to be effectively managed through existing commercial insurance policies. Furthermore, managing sequestration risks through the commercial sector obviates the need for the government to assume liability during the operations phase, and thereby eliminates another obstacle – public backlash concerning perceived risks (e.g. “it must be really dangerous if the government must assume liability”) as well as the impression of private gain at the public expense – to widespread implementation of the CCS industry. Such opposition has been the primary obstacle to government-led initiatives to create nuclear waste disposal sites (e.g., Yucca Mountain), and it is very likely that such opposition would arise if the government were to take the lead role (e.g., condemnation, public liability, etc.) in the CCS industry. Liability transfer mechanisms during the post-closure phase of sequestration sites – that is, once the CO_2 plume has stabilized after cessation of injection, and capillary trapping, geochemical reaction, dissolution all add to sequestration security with time see Figure 2.7 in Chapter 2– is less likely to engender public opposition as the public assumption of risk is much lower and more distant in the future.

By taking these proactive and practical steps, these entrepreneurs are helping to define a clear path toward widespread deployment of CCS in the U.S. We are encouraged to see these on-the-ground developments. Further policy initiatives (e.g., permitting requirements to ensure complete confinement of the CO_2 plume within the sequestration site, additional clarity around private pore space ownership, etc.) to ensure the CCS industry moves down the path outlined by these 'first-mover' entrepreneurs (rating of the site classification and change in the debate on liability) could help the much needed acceleration of the CCS implementation in order to meet the 2020 100MtCO2/y and 2030 1000MtCO2/y goals.

5.4. Conclusion

Addressing the challenge posed by the dominant coal-share of baseload-electricity production will be vital in order to stabilize CO_2 atmospheric concentration for climate change mitigation. This will require a global increase of CO_2 capture and sequestration (CCS) implementation by several orders of magnitude in the next two decades. This task has several potential barriers that were previously identified in the 2005 IPCC special report on CCS (SRCCS). Water management across all CCS operations was recently identified as a new important one to address.

This Chapter based on (Court et al. 2011a) presents a comprehensive review of the development, since the SRCCS, on the following CCS large-scale implementation challenges: water, sequestration, and pore-space competition; legal and regulatory; and, societal acceptance and technical communication. Management of both surface and deep subsurface water resources was found to be critical and must be considered through every CCS operations. CO_2, brine, and pressure challenges assessment clearly calls for active measures to reduce the impacts of a CCS operation, the uncertainty in geological parameters, and address regulatory and societal acceptance challenges. The review of pore-space competitions with other

subsurface activities, like the growing shale gas production, identified a need for further research. The analysis of recent legal and regulatory development concluded that a comprehensive solution for pore space ownership and long term liability regimes for CCS is not yet in place. Finally, the current state of societal acceptance and technical communication of CCS was investigated.

While large in scale and scope, presenting all of these challenges in the same framework enabled the identification of several promising synergies which warrant further investigation. They span across different operations, fields, and types of expertise, and therefore can only be exploited when those challenges are dealt with in combination. One of the more striking synergies allowing to address both surface and subsurface challenges is the active management of water resources. The additional cooling requirement of the CO_2 capture retrofitting process can be supplied via the production of brine from deep subsurface formations that can concomitantly reduce leakage risk and the Area of Review. Operational expense of the likely required brine treatment at the surface could be reduced by potential coupling with geothermal energy. Disposal of produced brine could be addressed via re-injection that has several identified synergistic advantages leading to improved reservoir management. Finally these proactive measures can provide public reassurance and improved risk management, while also facilitating the permitting process.

The water, sequestration, legal, and societal acceptance challenges should all be investigated individually but also examined collectively so that the promising synergies identified herein can be exploited to provide the best possibilities for successful large-scale implementation of CCS.

5.5. References

Aines, R. & Bourcier, W. 2009, Decarb/Desal: Separation of Carbon Dioxide from Flue Gas with Simultaneous Fresh Water Production, United States.

Aines, R.D. & Wolery, T.J. 2010, from Lawrence Livermore National Laboratory, Personal Communication.

Aines, R.D., Wolery, T.J., Bourcier, W.L., Wolfe, T. & Haussman, C. 2010, "Fresh Water Generation from Aquifer-Pressured Carbon Storage: Feasibility of Treating Saline Formation Waters", Proceedings of the GHGT-10 conf., Amsterdam, .

Aines, R.D., Wolery, T.J., Hao, Y. & Bourcier, W.L. 2009, Fresh Water Generation from Aquifer-Pressured Carbon Storage: Interim Progress Report2009, United States.

Akervoll, I., Lindeberg, E. & Lackner, A. 2009, "Feasibility of Reproduction of Stored CO2 from the Utsira Formation at the Sleipner Gas Field", Energy Procedia, vol. 1, no. 1, pp. 2557-2564.

Al-Juaied, M. & Whitmore, A. 2009, Realistic Costs of Carbon Capture. Discussion Paper 2009-08, United States.

Amirault, P.M. 2005, "Industry leader's discuss future gas storage trends", Pipeline and Gas Journal, vol. 232, no. 6, pp. 26-37.

Anderson, O.L. 2009, "Geologic CO2 Sequetration: Who Owns the Pore Space?", Wyoming Law Review, vol. 9, no. 1, pp. 97.

Andreani, M., Gouze, P., Luquot, L. & Jouanna, P. 2008, "Changes in seal capacity of fractured claystone caprocks induced by dissolved and gaseous CO2 seepage", Geophysical Research Letters, vol. 35, no. 14, pp. L14404.

Apps, J., Zheng, L., Zhang, Y., Xu, T. & Birkholzer, J. 2010, Evaluation of Potential Changes in Groundwater Quality in Response to CO_2 Leakage from Deep Geologic Storage, Springer Netherlands.

Ashworth, P., Boughen, N., Mayhew, M. & Millar, F. 2010, "From research to action: Now we have to move on CCS communication", International Journal of Greenhouse Gas Control [Int.J.Greenhouse Gas Control]., vol. 4, no. 2, pp. 426-433.

Bachu, S. 2008, "Legal and regulatory challenges in the implementation of CO2 geological storage: An Alberta and Canadian perspective", International Journal of Greenhouse Gas Control, vol. 2, no. 2, pp. 259-273.

Bachu, S. & Bennion, D.B. 2009, "Experimental assessment of brine and/or CO2 leakage through well cements at reservoir conditions", International Journal of Greenhouse Gas Control, vol. 3, no. 4, pp. 494-501.

Bandilla Karl W., Kraemer Stephen R. & Birkholzer, J. in review, "Using the concept of critical pressure to define the Area of Review for CO2 injection", International Journal of Greenhouse Gas Control, .

Bergmo, P.E.S., Grimstad, A. & Lindeberg, E. "Simultaneous CO2 injection and water production to optimise aquifer storage capacity", International Journal of Greenhouse Gas Control, vol. In Press, Corrected Proof.

Birkholzer, J.T., Nicot, J.P., Oldenburg, C.M., Zhou, Q., Kraemer, S. & Bandilla, K. "Brine flow up a well caused by pressure perturbation from geologic carbon sequestration: Static and dynamic evaluations", International Journal of Greenhouse Gas Control, vol. In Press, Corrected Proof.

Birkholzer, J.T. & Zhou, Q. 2009, "Basin-scale hydrogeologic impacts of CO2 storage: Capacity and regulatory implications", International Journal of Greenhouse Gas Control, vol. 3, no. 6, pp. 745-756.

Birkholzer, J.T., Zhou, Q. & Tsang, C. 2009, "Large-scale impact of CO2 storage in deep saline aquifers: A sensitivity study on pressure response in stratified systems", International Journal of Greenhouse Gas Control, vol. 3, no. 2, pp. 181-194.

Bourcier, W., Burton, E., & Newmark, R. 2007, "New materials and separations science for sustainable water", presented at First Western Forum on Energy and Water Sustainability, University of California, Santa Barbara, March 22-23, 2007., .

Bourcier, W.L., Wolery, T.J., Wolfe, T., Haussman, C., Buscheck, T.A. & Aines R.D. in review, "A Preliminary Cost and Engineering Estimate for Desalinating Produced Formation Water

Associated With Carbon Dioxide Capture and Storage", International Journal of Greenhouse Gas Control, .

Bristow, A.L., Wardman, M., Zanni, A.M. & Chintakayala, P.K. 2010, "Public acceptability of personal carbon trading and carbon tax", Ecological Economics, vol. 69, no. 9, pp. 1824-1837.

Buscheck Thomas A., Hao Yue, Sun Yunwei, Aines Roger D., Wolery Thomas J., Bourcier William & Friedmann, S.J. 2010, "Combining Brine Extraction, Desalination, and Residual-Brine Reinjection with CO2 Storage in Saline Formations: Implications for Pressure Management, Capacity, and Risk Mitigation", presented at the Ninth Annual Conference on Carbon Capture & Sequestration, .

Buscheck, T.A., Sun, Y., Hao, Y., Wolery, T.J., Bourcier, W.L., Tompson, A.F.B., Jones, E.D., Friedmann, S.J. & Aines R.D. 2010, "Combining brine extraction, desalination, and residual-brine reinjection with CO2 storage in saline formations: Implications for pressure management, capacity, and risk mitigation", Proceedings of the GHGT-10 conf., Amsterdam, .

California Energy Commission 2010, "Performance, cost, and environmental effects of saltwater cooling towers, PIER Final Project Report", prepared for California Energy Commission, CEC-500-2008-043 available at http://www.energy.ca.gov/2008publications/CEC-500-2008-043/CEC-500-2008-043.PDF, .

Calvin, K., Edmonds, J., Bond-Lamberty, B., Clarke, L., Kim, S.H., Kyle, P., Smith, S.J., Thomson, A. & Wise, M. 2009, "2.6: Limiting climate change to 450 ppm CO2 equivalent in the 21st century", Energy Economics, vol. 31, no. Supplement 2, pp. S107-S120.

Carbon Sequestration Working Group 2009, Report and Recommendations of the Carbon Sequestration Working Group to the Joint Minerals, Business and Economic Development Committee and Joint Judicial Committee of the Wyoming State Legislature, Wyoming Department of Environmental Quality.

Carey, J.W. & Lichtner, P.C. 2009, "Computational studies of two-phase cement-CO2-brine interaction in wellbore environments", SPE International Conference on CO2 Capture, Storage, and Utilization, 2-4 November 2009, San Diego, California, USA, .

Carey, J.W., Wigand, M., Chipera, S.J., WoldeGabriel, G., Pawar, R., Lichtner, P.C., Wehner, S.C., Raines, M.A. & Guthrie, J.,George D. 2007, "Analysis and performance of oil well cement with 30 years of CO2 exposure from the SACROC Unit, West Texas, USA", International Journal of Greenhouse Gas Control, vol. 1, no. 1, pp. 75-85.

CCSReg Project 2009, Policy Brief: Governing Access to and Use of Pore Space for Deep Geologic Sequestration, Carnegie Mellon University, Pittsburgh, PA.

Celia, M.A. & Nordbotten, J.M. 2010, "How simple can we make models for CO2 injection, migration and leakage?", Proceedings of the GHGT-10 conf., Amsterdam, .

Celia, M.A., Nordbotten, J.M., Bachu, S., Dobossy, M. & Court, B. 2009, "Risk of Leakage versus Depth of Injection in Geological Storage", Energy Procedia, vol. 1, no. 1, pp. 2573-2580.

Celia, M.A., Nordbotten, J.M., Court, B., Dobossy, M. & Bachu, S. 2011, "Field-scale application of a semi-analytical model for estimation of CO2 and brine leakage along old wells", International Journal of Greenhouse Gas Control, vol. 5, no. 2, pp. 257-269.

Chabora, E.R. & Benson, S.M. 2009, "Brine Displacement and Leakage Detection Using Pressure Measurements in Aquifers Overlying CO2 Storage Reservoirs", Energy Procedia, vol. 1, no. 1, pp. 2405-2412.

Chadwick, A. 2009, "Monitoring Challenges for CO2 storage", Geophysical Research Abstracts, Vol. 11, EGU2009-14104, 2009. EGU General Assembly, .

Chen, C. & Rubin, E.S. 2009, "CO2 control technology effects on IGCC plant performance and cost", Energy Policy, vol. 37, no. 3, pp. 915-924.

Ciferno, J.P., Munson, R.K., Murphy, J.T. & Lash, B.S. March 2010, "Determining Carbon Capture and Sequestration's Water Demands", Power Magazine, .

Class, H., Ebigbo, A., Helmig, R., Dahle, H., Nordbotten, J., Celia, M., Audigane, P., Darcis, M., Ennis-King, J., Fan, Y., Flemisch, B., Gasda, S., Jin, M., Krug, S., Labregere, D., Naderi Beni, A., Pawar, R., Sbai, A., Thomas, S., Trenty, L. & Wei, L. 2009, "A benchmark study on problems related to CO_2 storage in geologic formations", Computational Geosciences, vol. 13, no. 4, pp. 409-434.

Court, B., Dammel, J.A., Elliot, T.R., Rohmer, J., Buscheck, T.A. & Celia, M.A. 2011a, " Promising synergies to address water, sequestration, legal, and public acceptance issues associated with large-scale implementation of CO2 sequestration", Special Issue on Carbon Capture and Storage of The Journal for Mitigation and Adaptation Strategies for Global Change, in review, .

Court, B., Celia, M.A., Nordbotten, J.M. & Elliot, T.R. 2011b, "Active and integrated management of water resources throughout CO2 capture and sequestration operations", Energy Procedia, vol. 4, pp. 4221-4229.

Crow, W., Carey, J.W., Gasda, S.E., Williams, D.B. & Celia, M.A. 2010, "Wellbore integrity analysis of a natural CO2 producer", International journal of greenhouse gas control, vol. 4, no. 2, pp. 186-197.

D'Alessandro, D. 2010, "Carbon dioxide capture: Prospects for new materials", Angewandte Chemie (International ed.in English), vol. 49, no. 35, pp. 6058-6082.

Damen, K., Faaij, A. & Turkenburg, W. 2009, "Pathways towards large-scale implementation of CO2 capture and storage: A case study for the Netherlands", International Journal of Greenhouse Gas Control, vol. 3, no. 2, pp. 217-236.

Dammel, J.A. 2010, "Note, Subsurface 2.0: How Hydraulic Fracturing is Setting the Stage for Geologic Storage of Carbon Dioxide.", In preparation for submission to the Minesota Journal of Law, Science, and Technology., .

Davidson, C.L., Dooley, J.J. & Dahowski, R.T. 2009, "Assessing the impacts of future demand for saline groundwater on commercial deployment of CCS in the United States", Greenhouse Gas Control Technologies 9, Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), 16–20 November 2008, Washington DC, USA, vol. 1, no. 1, pp. 1949-1956.

Davis SJ,Caldeira K, Matthews,H.D. 2010, "Future CO2 Emissions and Climate Change from Existing Energy Infrastructure", Science, vol. 329, no. 5997, pp. 1330-1333.

Davis SJ, C.,K. 2010, "Consumption-based accounting of CO2 emissions", Proceedings of the National Academy of Sciences of the United States of America, vol. 107, no. 12, pp. 5687-5692.

Davis, T.L. 2010, Personal communication with Professor Thomas Davis (RCP Director at the Colorado school of mine).

Davison, J. 2007, "Performance and costs of power plants with capture and storage of CO2", Energy, vol. 32, no. 7, pp. 1163-1176.

de Best-Waldhober, M., Daamen, D. & Faaij, A. 2009, "Informed and uninformed public opinions on CO2 capture and storage technologies in the Netherlands", International Journal of Greenhouse Gas Control, vol. 3, no. 3, pp. 322-332.

de Coninck, H. 2010, "Advocacy for carbon capture and storage could arouse distrust", Nature, vol. 463, no. 7279, pp. 293-293.

de Coninck, H., Anderson, J., Curnow, P., Flach, T., Flagstad, O., Groenenberg, H., Norton, C., Reiner, D. & Shackley, S. 2006, "Acceptability of CO2 capture and storage – a review of legal, regulatory, economic and societal aspects of CO2 capture and storage", Energy Research Centre of the Netherlands, .

Deremble, L., Loizzo, M., Huet, B., Lecampion, B. & Quesada, D. 2010, "Stability of a leakage pathway in a cemented annulus", Proceedings of the GHGT-10 conf., Amsterdam, .

Detwiler, R.L. 2010, "Permeability alteration due to mineral dissolution in partially saturated fractures", J.Geophys.Res., vol. 115, pp. B09210.

Dixon, T., Matsuoka, T. & Dodds, K. June 2009, "Conclusions: Key Learning for other networks and summing-up including topics for next meeting: 5th Meeting of the Monitoring Network", .

DNV 2010, ""Qualification procedures for CO2 capture technology" (Recommended Practice DNV-RP-J201, April 2010).", .

DOE/NETL 2009, "Estimating freshwater needs to meet future thermoelectric generation requirements, 2009 update",

DOE/NETL 2008, Estimating freshwater needs to meet future thermoelectric generation requirements, Pittsburgh, PA.

DOE/NETL 2007, Cost and Performance Comparison Baseline for Fossil Energy Power Plants.

Dooley, J.J. & Davidson, C.L. 2010, A Brief Technical Critique of Ehlig- Economides and Economides 2010: "Sequestering Carbon Dioxide in a Closed Underground Volume", United States Department of Energy.

Duguid, A., Butsch, R., Loizzo, M. & Stamp, V. 2010, "Collection of baseline wellbore cement data in multiple wells in the same field", Proceedings of the GHGT-10 conf., Amsterdam, .

Duguid, A. & Scherer, G.W. 2010, "Degradation of oilwell cement due to exposure to carbonated brine", International journal of greenhouse gas control, vol. 4, no. 3, pp. 546-560.

Duke, D. 2007, "ZLD: New silica based inhibitor chemistry permits cost effective water conservation for HVAC and industrial cooling towers", IWC Report 07-11, Proceedings for the 69th Annual International Water Conference, October 26-29, 2008, San Antonio, Texas.available at http://www.water-cti.com/pdf/IWC_07-11_Report.pdf, .

Ebigbo, A., Class, H. & Helmig, R. 2007, "CO_2 leakage through an abandoned well: problem-oriented benchmarks", Computational Geosciences, vol. 11, no. 2, pp. 103-115.

Eccles, J.K., Pratson, L., Newell, R.G. & Jackson, R.B. 2009, "Physical and Economic Potential of Geological CO2 Storage in Saline Aquifers", Environmental science & technology, vol. 43, no. 6, pp. 1962-1969.

Ehlig-Economides C, E.,M.J. 2010, "Sequestering carbon dioxide in a closed underground volume", JOURNAL OF PETROLEUM SCIENCE AND ENGINEERING, vol. 70, no. 1-2, pp. 118-125.

El-Naas, M.H., Al-Marzouqi, A.H. & Chaalal, O. 2010, "A combined approach for the management of desalination reject brine and capture of CO2", Desalination, vol. 251, no. 1-3, pp. 70-74.

Environmental Financial Advisory Board 2010, Financial Assurance for Underground Carbon Sequestration Facilities, Environmental Protection Agency.

Esposito, A. & Benson, S.M. 2010, "Remediation of Possible Leakage from Geologic CO2 Storage Reservoirs into Groundwater Aquifers", Proceedings of the GHGT-10 conf., Amsterdam, .

European Parliament 2009, Directive 2009/31/EC of the European Parliament and of the Council of 23 april 2009 on the geological storage, available at http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:140:0114:0135:EN:PDF.

Fang, C. 2009, Study on water-saving methods and countermeasures of developing coal chemical industry in arid area,

Federal Register 2010, "Federal Requirements Under the Underground Injection Control (UIC) Program for Carbon Dioxide (Finalized and Published rule)", (75 FR 77230 (2010)) available at http://www.federalregister.gov/articles/2010/12/10/2010-29954/federal-requirements-under-the-underground-injection-control-uic-program-for-carbon-dioxide-co2#h-34, .

Federal Register 2008, Federal Requirements Under the Underground Injection Control Program for Carbon Dioxide Geologic Sequestration Wells (Proposed Rule).

Feeley, T.J., Skone, T.J., Stiegel, G.J., J., McNemar, A., Nemeth, M., Schimmoller, B., Murphy, J.T. & Manfredo, L. 2008, "Water: a critical resource in the thermoelectric power industry", Energy, vol. 33, no. 1, pp. 1-11.

Fischedick, M. 2010, "Shaping the energy future - new technologies in the context of climate change", International Conference: Geothermal Energy and CO2 Storage: Synergy or Competition? 10-11 February 2010Posdam, Germany.

Fish, J.R. & Wood, T.R. 2008, "Geologic Carbon Sequestration: Property Rights and Regulation", Proceedings of the Rocky Mountain Mineral Law Fifty-Fourth Annual Institute.

Flett, M. 2008, Gorgon project: Subsurface evaluation of carbon dioxide dsposal under Barrow Island, .

Flynn, D.&.S.M.M. Summer 2009, "Carbon Sequestration: A Liability Pathway to Commercial Viability", Natural Resources and Environment, vol. 24, pp. 37.

Frickel. Scott., Gibbon. Sahra., Howard. Jeff., Kempner. Joanna., Ottinger. Gwen. & Hess. David. 2010, Undone Science: Charting Social Movement and Civil Society Challenges to Research Agenda Setting, Sage, Thousand Oaks, CA, ETATS-UNIS.

Friedmann, S.J. 2009, Emerging technical challenges of 5-million-ton/yr injections, .

GAO 2009, Energy-water nexus: improvements to federal water use data would increase understanding of trends in power plant water use, United States.

Gee, D. & Stirling, A. 2003, "Late Lessons from Early Warnings: Improving Science and Governance Under Uncertainty and Ignorance." in Precaution, Environmental Science, and Preventive Public Policy, ed. J.A. Tickner, Island Press, Washington, D.C., pp. 195.

Gerard, D. & Wilson, E.J. 2009, "Environmental Bonds and the Challenge of Long-Term Carbon Sequestration", Journal of Environmental Management, vol. 90, pp. 1097-1105; 1097.

Gherardi, F., Xu, T. & Pruess, K. 2007, "Numerical modeling of self-limiting and self-enhancing caprock alteration induced by CO2 storage in a depleted gas reservoir", Chemical Geology, vol. 244, no. 1-2, pp. 103-129.

Global CCS Institute 2010, "CCS Ready – Issues brief 2010 no. 1", available at http://www.globalccsinstitute.com/downloads/general/2010/GCCSI_Issues_Paper_10.01_CCS_Ready.pdf, .

Goldstein, N.C. 2008, "The Energy-Water Nexus and information exchange: Challenges and opportunities", International Journal of Water, vol. 4, no. 1-2, pp. 5-24.

Grahame, S. 2011, "ETI Storage Project", presented at SPE Applied Technology Workshop: Carbon Capture, Utilisation and Storage (CCUS): Environment, Energy Security and Opportunities for the Middle East" 7 – 9 March 2011 Abu Dhabi, U.A.E., .

Guggenheim, D. 2006, An Inconvenient Truth: The Planetary Emergence of Global Warming and What We Can Do About It., Rodale, New York.

Harto, C.B. & Veil, J.A. 2011 Mar 11, "Management of water extracted from carbon sequestration projects", Argonne National Laboratory Technical Report OSTI ID: 1009368 available at http://www.osti.gov/bridge/product.biblio.jsp?osti_id=1009368, .

Haszeldine, S. 2010, "Geology of carbon dioxide storage compared to enhanced geothermal systems", GFZ Potsdam 10 11 Feb 2010., .

Herzog, H.J. "Scaling up carbon dioxide capture and storage: From megatons to gigatons", Energy Economics, vol. In Press, Corrected Proof.

Hoffler, F. & Kubler, M. 2007, "Demand for storage of natural gas in northwestern Europe: Trends 2005-30", Energy Policy, vol. 35, no. 10, pp. 5206-5219.

Huenges, E. & Kuhn, M. 2010, "Geothermal energy provision and/or CO2 storage using deep saline aquifers – lessons learnt from operational in situ laboratories", GFZ Potsdam 10 11 Feb 2010., .

Huet, B.M., Prevost, J.H. & Scherer, G.W. 2010, "Quantitative reactive transport modeling of Portland cement in CO2-saturated water", International Journal of Greenhouse Gas Control, vol. 4, no. 3, pp. 561-574.

Iding, M. & Ringrose, P. 2010, "Evaluating the impact of fractures on the performance of the In Salah CO2 storage site", International Journal of Greenhouse Gas Control, vol. 4, no. 2, pp. 242-248.

IEA 2010, "World Energy Outlook 2010 Executive Summaries", available at http://www.worldenergyoutlook.org/, .

IEA 2009a, "How the energy sector can deliver on a climate agreement in Copenhagen - special eraly excerpt of the world energy outlook 2009 for the Bangkok UNFCCC meeting", .

IEA 2009b, "Technology Roadmaps - Carbon Capture and Storage", .

IEA / CSLF 2010, "Carbon Capture and Storage: Progress and Next Steps IEA/CSLF Report to the Muskoka 2010 G8 Summit", .

IEA-GHG 2007, "Remediation of Leakage from CO_2 Storage Reservoirs", IEA Greenhouse Gas R&D Programme, 2007/11, September 2007, .

Interagency Task Force on Carbon Capture and Storage August 12 2010 Report.

International Energy Agency 2010, Carbon Capture and Storage: Legal and Regulatory Review, 1st edn, , Paris, France.

International Energy Agency 2007, Legal Aspects of Storing CO2: Update and Recommendations.

International Panel Review 2010, "Report of the International Panel set up by the University of East Anglia to examine the research of the Climatic Research Unit", East Anglica University, [Online], .

IPCC 2005, IPCC Special Report on Carbon Dioxide Capture and Storage, Cambridge University Press.

Janzen, A. 2010, "Development and Application of a Multi-scale, Multi-layer Numerical Model for CO2 Injection", Master Thesis available at http://arks.princeton.edu/ark:/88435/dsp01np193917f, .

Johnson, N. & Ogden, J. 2011, "Detailed spatial modeling of carbon capture and storage (CCS) infrastructure deployment in the southwestern United States", Energy Procedia, vol. 4, pp. 2693-2699.

Kaszuba, J.P., Janecky, D.R. & Snow, M.G. 2005, "Experimental evaluation of mixed fluid reactions between supercritical carbon dioxide and NaCl brine: Relevance to the integrity of a geologic carbon repository", Chemical Geology, vol. 217, no. 3-4, pp. 277-293.

Keating, E., Fessenden, J., Kanjorski, N., Koning, D. & Pawar, R. 2010, The impact of CO_2 on shallow groundwater chemistry: observations at a natural analog site and implications for carbon sequestration, Springer Berlin / Heidelberg.

Kelly, R.T. "The Competition for UK Pore Space: Natural Gas Storage versus CCS", presented at IQPC CCS&Transport Summit, London 2009, .

Kerr, T., Havercroft, I. & Dixon, T. 2009a, "Legal and Regulatory Developments Associated with Carbon Dioxide Capture and Storage: A Global Update", GHGT-9.

Kerr, T., Havercroft, I. & Dixon, T. 2009b, "Legal and Regulatory Developments Associated with Carbon Dioxide Capture and Storage: A Global Update", GHGT-9.

Kharaka, Y.K. 2009, "Reactive transport modeling to study changes in water chemistry induced by CO2 injection at the Frio-I brine pilot", Chemical Geology, , no. LBNL-3056E.

Kharaka, Y.K., Cole, D.R., Hovorka, S.D., Gunter, W.D., Knauss, K.G. & Freifeld, B.M. 2006, "Gas-water-rock interactions in Frio Formation following CO2 injection: Implications for the storage of greenhouse gases in sedimentary basins", Geology, vol. 34, no. 7, pp. 577-580.

Kharecha, P.A. & Hansen, J.E. 2008, "Implications of "peak oil" for atmospheric CO2 and climate", Global Biogeochemical Cycles, vol. 22, no. 3, pp. GB3012.

Klass, A. & Wilson, E. 2010a, "Climate change, carbon sequestration, and property rights", University of Illinois law review, , no. 2, pp. 363-428.

Klass, A.B. & Wilson, E.J. 2010b, "Climate Change, Carbon Sequestration, and Property Rights", U. Ill. Law rev., vol. 2010, no. 2, pp. 363.

Klass, A.B. & Wilson, E.J. 2008, "Climate Change and Carbon Sequestration: Assessing a Liability Regime for Long-term Storage of Carbon Dioxide", Emory L.J., vol. 58, no. 1, pp. 103.

Kobos, P., Aragon, M.J., Krumhansl, J., Borns, D., Hightower, M. & McNemar, A. 2008a, Study of the Use of Saline Aquifers for Combined Thermoelectric Power Plant Water Needs and Carbon Sequestration at a Regional-Scale: Phase I Report.

Kobos, P., Cappelle, M., Krumhansl, J., Dewers, T., Borns, D., Brady, P. & McNemar, A. 2008b, "Using Saline Aquifers for Combined Power Plant Water Needs and Carbon Sequestration", .

Kreutz, T.G. 2010, "Prospects for producing low carbon transportation fuels from captured CO2 in a climate constrained world", Proceedings of the GHGT-10 conf., Amsterdam, .

Krey, V. & Riahi, K. 2009, "Implications of delayed participation and technology failure for the feasibility, costs, and likelihood of staying below temperature targets—Greenhouse gas mitigation scenarios for the 21st century", Energy Economics, vol. 31, no. Supplement 2, pp. S94-S106.

Kuby, M., Bielicki, J. & Middleton, R. "Optimal Spatial Deployment of Carbon Dioxide Capture and Storage Given a Price on Carbon Dioxide", International Regional Science Review Special Issue for ISOLDE XI (Forthcoming) available at http://belfercenter.ksg.harvard.edu/publication/19211/optimal_spatial_deployment_of_carbon_dioxide_capture_and_storage_given_a_price_on_carbon_dioxide.html, .

Kuijper, M.I. 2011, "Public acceptance challenges for onshore CO2 storage in Barendrecht", Energy Procedia, vol. 4, pp. 6226-6233.

Kvamsdal, H.M., Hetland, J., Haugen, G., Svendsen, H.F., Major, F., Kårstad, V. & Tjellander, G. 2010, "Maintaining a neutral water balance in a 450 MWe NGCC-CCS power system with post-combustion carbon dioxide capture aimed at offshore operation", International Journal of Greenhouse Gas Control, vol. 4, no. 4, pp. 613-622.

Lackner, K. & Brennan, S. 2009, Envisioning carbon capture and storage: expanded possibilities due to air capture, leakage insurance, and C-14 monitoring, Springer Netherlands.

Larson, E.D., Fiorese, G., Liu, G., Williams, R.H., Kreutz, T.G. & Consonni, S. 2010, "Co-production of decarbonized synfuels and electricity from coal + biomass with CO2 capture and storage: an Illinois case study", Energy & Environmental Science, vol. 3, no. 1, pp. 28-42.

Le Fevre, C. 2005, "Outlook for gas storage in Europe", Petroleum Review, vol. 59, no. 703, pp. 15-16+45.

Le Guen, Y., Huot, M., Loizzo, M. & Poupard, O. 2010, "Well Integrity Risk Assessment of Ketzin Injection Well (ktzi-201) over a Prolonged Sequestration Period", Proceedings of the GHGT-10 conf., Amsterdam, .

Le Guénan, T. & Rohmer, J. "Corrective measures based on pressure control strategies for CO2 geological storage in deep aquifers", International Journal of Greenhouse Gas Control, vol. In Press, Corrected Proof.

Leiserowitz, A., Maibach, E.W., Roser-Renouf, C., Smith, N. & Dawson, E. July 2, 2010, Climategate, Public Opinion, and the Loss of Trust.

Lewicki, J., Birkholzer, J. & Tsang, C. 2007, "Natural and industrial analogues for leakage of CO_2 from storage reservoirs: identification of features, events, and processes and lessons learned", Environmental Geology, vol. 52, no. 3, pp. 457-467.

Lindeberg, E. 2009, "Determination of the CO2 storage capacity of the Utsira formation", Energy Procedia, vol. 1, no. 1, pp. 2777-2784.

Litynski, J., Plasynski, S., Spangler, L., Finley, R., Steadman, E., Ball, D., Nemeth, K.J., McPherson, B. & Myer, L. 2009, "U.S. Department of Energy's Regional Carbon Sequestration Partnership Program: Overview", Energy Procedia, vol. 1, no. 1, pp. 3959.

Liu, G., Williams, R.H., Larson, E.D. & Kreutz, T.G. 2010, "Design/economics of low-carbon power generation from natural gas and biomass with synthetic fuels co-production", Proceedings of the GHGT-10 conf., Amsterdam, .

Loizzo, M. 2009, "CO2 storage wells Challenges and solutions", 3rd International Symposium on Capture and Geological Storage of CO2 Paris available at http://www.colloqueco2.com/presentations2009/Session3/Matteo_Loizzo.pdf, .

Loizzo, M., Lombardi, S., Deremble, L., Lecampion, B., Quesada, D., Huet, B., Khalfallah, I., Annunziatellis, A. & Picard, G. 2010, "Monitoring CO2 migration in an injection well: evidence from MovECBM", Proceedings of the GHGT-10 conf., Amsterdam, .

Lu, J., Partin, J., Hovorka, S. & Wong, C. 2010, Potential risks to freshwater resources as a result of leakage from CO_2 geological storage: a batch-reaction experiment, Springer Berlin / Heidelberg.

Mace, M.J., Hendriks, C. & Coenraads, R. 2007, "Regulatory challenges to the implementation of carbon capture and geological storage within the European Union under EU and international law", International Journal of Greenhouse Gas Control, vol. 1, no. 2, pp. 253-260.

Majer, E.L., Baria, R., Stark, M., Oates, S., Bommer, J., Smith, B. & Asanuma, H. 2007, "Induced seismicity associated with Enhanced Geothermal Systems", Geothermics, vol. 36, no. 3, pp. 185-222.

Manceau, J.C., Réveillère, A. & Rohmer, J. 2010, "Forcing gaseous CO2 trapping as a corrective technique in the case of abnormal behavior of a deep saline aquifer storage", Proceedings of the GHGT-10 conf., Amsterdam, .

Matteo, E.N. & Scherer, G.W. "Boundary Condition Effects on the Acid Degradation Kinetics of Class H Portland Cement", In preparation, .

Matteo, E.N., Scherer, G.W., Huet, B. & Pel, L. 2010, "Understanding Boundary Condition Effects on the Corrosion Kinetics of Class H Well Cement", Proceedings of the GHGT-10 conf., Amsterdam, .

McCoy, S.T. 2008, "The Economics of CO2 Transport by Pipeline and Storage in Saline Aquifers and Oil Reservoirs, in Engineering & Public Policy. Ph.D. Thesis", Carnegie Mellon University http://repository.cmu.edu/epp/1/, .

McCoy, S.T. & Rubin, E.S. 2009, "Variability and uncertainty in the cost of saline formation storage", Energy Procedia, vol. 1, no. 1, pp. 4151-4158.

McKinsey & Company 2009, "Charter our water future", .

McLeod, N.J. & Kelly, R.T. 2007, "Identifying and filling western europe's natural-gas storage needs for the next decade", vol. 4, pp. 2504-2522.

Melzer, L.S. & Davis, T.L. 2010, "A pragmatic look at carbon capture and storage: from global issues to the technical details", First Break Special Topic January 2010 - Issue 1 - Volume 28, .

METI (Ministry of Economy Trade and Industryof Japan) 2007, Building Confidence in Geological Storage of Carbon Dioxide.

Michael, K., Arnot, M., Cook, P., Ennis-King, J., Funnell, R., Kaldi, J., Kirste, D. & Paterson, L. 2009, "CO2 storage in saline aquifers I—Current state of scientific knowledge", Energy Procedia, vol. 1, no. 1, pp. 3197-3204.

Michael, K., Golab, A., Shulakova, V., Ennis-King, J., Allinson, G., Sharma, S. & Aiken, T. 2010, "Geological storage of CO2 in saline aquifers-A review of the experience from existing storage operations", International Journal of Greenhouse Gas Control, vol. 4, no. 4, pp. 659-667.

Neal, P.R., Cinar, Y. & Allinson, W.G. 2010, "The economics of pressure-relief with CO2 injection", Proceedings of the GHGT-10 conf., Amsterdam, .

NETL 2005, Power Plant Water Usage and Loss Study.

Newmark, R.L., Friedmann, S.J. & Carroll, S.A. 2010, "Water challenges for geologic carbon capture and sequestration", Environmental management, vol. 45, no. 4.

Nicot, J. 2008, "Evaluation of large-scale CO2 storage on fresh-water sections of aquifers: An example from the Texas Gulf Coast Basin", International Journal of Greenhouse Gas Control, vol. 2, no. 4, pp. 582-593.

Nicot, J., Oldenburg, C.M., Bryant, S.L. & Hovorka, S.D. 2009, "Pressure perturbations from geologic carbon sequestration: Area-of-review boundaries and borehole leakage driving forces", Energy Procedia, vol. 1, no. 1, pp. 47-54.

Nordbotten, J.M. & Celia, M.A. in press, "Geological Storage of CO2: Modeling Approaches for Large-Scale Simulation", with John Wiley and Sons, Inc., .

Oltra, C., Sala, R., Sola, R., Di Masso, M. & Rowe, G. 2010, "Lay perceptions of carbon capture and storage technology", International Journal of Greenhouse Gas Control, vol. 4, no. 4, pp. 698-706.

OSPAR (OSlo - PARis) convention for the protection of the marine environment of the North-East Atlantic 2007, "OSPAR Guidelines for Risk Assessment and Management of Storage of CO2 Streams in Geological Formations. Reference: 2007/12", .

Pacala, S. & S. 2004, "Stabilization wedges: Solving the climate problem for the next 50 years with current technologies", Science, vol. 305, no. 5686, pp. 968-972.

Pennline, H. 2008, "Progress in carbon dioxide capture and separation research for gasification-based power generation point sources", Fuel Processing Technology, vol. 89, no. 9, pp. 897-907.

Person, M., Banerjee, A., Rupp, J., Medina, C., Lichtner, P., Gable, C., Pawar, R., Celia, M., McIntosh, J. & Bense, V. 2010, "Assessment of basin-scale hydrologic impacts of CO2 sequestration, Illinois basin", International Journal of Greenhouse Gas Control, vol. 4, no. 5, pp. 840-854.

Pollak, M. & Wilson, E. 2009, "Regulating geologic sequestration in the united states: early rules take divergent approaches", Environmental science & technology, vol. 43, no. 9, pp. 3035-3041.

Preisig, M. & Prevost, J.H. 2011, "Coupled multi-phase thermo-poromechanical effects. Case study: CO2 injection at In Salah, Algeria", International journal of greenhouse gas control, .

Pruess, K., Birkholzer, J.T. & Zhou, Q. 2009, "Mathematical models as tools for probing long-term safety of CO2 storage", LBNL Paper LBNL-1587E. Retrieved from: http://www.escholarship.org/uc/item/04w053xn, .

Pruess, K., García, J., Kovscek, T., Oldenburg, C., Rutqvist, J., Steefel, C. & Xu, T. 2004, "Code intercomparison builds confidence in numerical simulation models for geologic disposal of CO2", Energy, vol. 29, no. 9-10, pp. 1431-1444.

Purkus, A. & Barth, V. "Geothermal power production in future electricity markets--A scenario analysis for Germany", Energy Policy, vol. In Press, Corrected Proof, pp. 357.

Réveillère, A. & Rohmer, J. 2010, "Managing the risk of CO2 leakage from deep saline aquifer reservoirs through the creation of a hydraulic barrier", to be submitted to the GHGT10 conference in Amsterdam, .

Rubin, E.S., Chen, C. & Rao, A.B. 2007, "Cost and performance of fossil fuel power plants with CO2 capture and storage", Energy Policy, vol. 35, no. 9, pp. 4444-4454.

Rutqvist, J., Birkholzer, J., Cappa, F. & Tsang, C.-. 2007, "Estimating maximum sustainable injection pressure during geological sequestration of CO2 using coupled fluid flow and geomechanical fault-slip analysis", Energy Conversion and Management, vol. 48, no. 6, pp. 1798-1807.

Rutqvist, J., Vasco, D.W. & Myer, L. 2010, "Coupled reservoir-geomechanical analysis of CO2 injection and ground deformations at In Salah, Algeria", International Journal of Greenhouse Gas Control, vol. 4, no. 2, pp. 225-230.

Rygaard, M., Arvin, E. & Binning, P.J. 2009, "The valuation of water quality: Effects of mixing different drinking water qualities", Water research, vol. 43, no. 5, pp. 1207-1218.

Schnaar, G. & Digiulio, D.C. 2009, "Computational Modeling of the Geologic Sequestration of Carbon Dioxide", Vadose Zone Journal, vol. 8, no. 2, pp. 389-403.

Seevam, P. 2009, "Transporting the next generation of C02 for carbon capture and storage: The impact of impurities on supercritical C02 pipelines", Proceedings of the Biennial International Pipeline Conference, IPC, vol. 1, pp. 39.

Seevam, P. 2007, "Carbon dioxide pipelines for sequestration in the UK: An engineering gap analysis", Global Pipeline Monthly, vol. 3, no. 6.

Seitter, K.L. 2009, "Impact of CRU Hacking on the AMS Statement on Climate Change", American Meteorological Society, [Online], .

Seligsohn, D., Liu, Y., Forbes, S., Dongjie, Z. & West, L. 2010, "CCS in China: Toward an Environmental, Health, and Safety Regulatory Framework", World Resources Institute available at http://pdf.wri.org/ccs_in_china.pdf, .

Shackley, S., McLachlan, C. & Gough, C. 2005, "The public perception of carbon dioxide capture and storage in the UK: results from focus groups and a survey", vol. 4, pp. 377-398(22).

Sharma, S., Cook, P., Robinson, S. & Anderson, C. 2007, "Regulatory challenges and managing public perception in planning a geological storage pilot project in Australia", International Journal of Greenhouse Gas Control, vol. 1, no. 2, pp. 247-252.

Sharp, J. 2008, "Carbon Capture and Storage: The Views of the Canadian Public", Pembina Institute, [Online], . Available from: http://pubs.pembina.org/reports/ccs-discuss-public-views.pdf.

Shukla, R., Ranjith, P., Haque, A. & Choi, X. 2010, "A review of studies on CO2 sequestration and caprock integrity", Fuel, vol. 89, no. 10, pp. 2651-2664.

Singleton, G., Herzog, H. & Ansolabehere, S. 2009, "Public risk perspectives on the geologic storage of carbon dioxide", International Journal of Greenhouse Gas Control, vol. 3, no. 1, pp. 100-107.

Smyth, R.C., Hovorka, S.D., Lu, J., Romanak, K.D., Partin, J.W., Wong, C. & Yang, C. 2009, "Assessing risk to fresh water resources from long term CO2 injection–laboratory and field studies", Energy Procedia, vol. 1, no. 1, pp. 1957-1964.

Sovacool, B.K. 2009, "Running on Empty: The Electricity-Water Nexus and the U.S. Electric Utility Sector", Energy Law Journal, vol. 30(1), pp. pp. 11-51.

Sovacool, B.K. & Sovacool, K.E. 2009a, "Identifying future electricity–water tradeoffs in the United States", Energy Policy, vol. 37, no. 7, pp. 2763-2773.

Sovacool, B.K. & Sovacool, K.E. 2009b, "Preventing National Electricity-Water Crisis Areas in the United States", Columbia Journal of Environmental Law, vol. 34(2), pp. pp.333-393.

Stenhouse, M.J., Wilson, M., Herzog, H., Cassidy, B., Kozak, M. & Zhou, W. 2005, "Regulatory issues associated with deep geological CO2 storage", Seventh International Conference on Greenhouse Gas Control Technologies, 7-11 June 2010Vancouver, Canada.

Stenhouse, M.J., Wilson, M., Herzog, H., Cassidy, B., Kozak, M. & Zhou, W. 2004, Regulatory issues associated with the long-term storage of CO2.

Stephens, J.C. & Jiusto, S. 2010, "Assessing innovation in emerging energy technologies: Socio-technical dynamics of carbon capture and storage (CCS) and enhanced geothermal systems (EGS) in the USA", Energy Policy, vol. 38, no. 4, pp. 2020-2031.

Stoker, T. & Dahe, Q. 2009, "Statement by Working Group I of the Intergovernmental Panel on Climate Change on stolen emails from the Climatic Research Unit at the University of East Anglia, United Kingdom", IPCC WGI – The Physical Science Basis, [Online], .

Sun, B., Peng, R. & Chen, C. 2003, "Ecological environmental problems caused by the exploitation of mineral products and water resources in Xinjiang, China", , eds. X. Pan, W. Gao, M.H. Glantz & Y. Honda, SPIE, , July 11, 2003, pp. 780.

Surdam, R.C., Jiao, Z., Stauffer, P. & & Miller, T. 2009, An integrated strategy for carbon management combining geological CO2sequestration, displaced fluid production, and water treatment: Wyoming State Geological Survey Challenges in Geologic Resource Development.

Trabucchi, C. & Patton, L. 2008, "Storing Carbon: Options for Liability Risk Management, Financial Responsibility", Daily Environment, vol. 170.

Tsang, C., Birkholzer, J. & Rutqvist, J. 2008, "A comparative review of hydrologic issues involved in geologic storage of CO_2 and injection disposal of liquid waste", Environmental Geology, vol. 54, no. 8, pp. 1723-1737.

U.S. Department of Interior 2009, Report to Congress:Framework for Geological Carbon Sequestration on Public Land.

U.S. EIA 2010, Annual Energy Outlook 2010 with Projections to 2035, U.S. Energy Information Administration.

UK Department for Business Enteprise & Regulatory Reform 2007, "Offshore natural gas storage and liquefied natural gas import facilities: a consultation", available at http://webarchive.nationalarchives.gov.uk/+/http://www.dti.gov.uk/consultations/page35612.html, .

UNIDO - United Nations Industrial Development Organization 2010, "Carbon Capture and Storage in Industrial Applications: Technology Synthesis Report Working Paper", available at http://www.unido.org/fileadmin/user_media/Services/Energy_and_Climate_Change/Energy_Efficiency/CCS/synthesis_final.pdf, .

United States Global Change Research Program 2010, Annual Report to Congress.

United States Global Change Research Program 2009, Scientific Assessment of Global Climate Change Impacts in the U.S.

United States Global Change Research Program 2006, Annual Report to Congress.

USEPA (U.S. Environmental Protection Agency) 2009, " Proposed Endangerment and Cause or Contribute Findings for Greehouse Gases Under Section 202(a) of the Clean Air Act, published at 74 FR 1886.", .

USEPA (U.S. Environmental Protection Agency) 1994, "Determination of Maximum Injection Pressure for Class I Wells, United States Environmental Protection Agency Region 5—Underground Injection Control Section Regional Guidance #7", EPA, Washington, DC, USA; available at http://www.epa.gov/r5water/uic/r5guid/r5_07.htm, .

van Alphen, K., van Voorst tot Voorst, Q, Hekkert, M,P, & Smits, R,E,H,M, 2007, "Societal acceptance of carbon capture and storage technologies", Energy Policy, vol. 35, no. 8, pp. 4368-4380.

van Alphen, K., Noothout, P.M., Hekkert, M.P. & Turkenburg, W.C. 2010, "Evaluating the Development of Carbon Capture and Storage Technologies in the United States", Renewable and Sustainable Energy Reviews, vol. 14, no. 2010, pp. 971-986.

Varis, O. & Vakkilainen, P. 2001, "China's 8 challenges to water resources management in the first quarter of the 21st Century", Geomorphology, vol. 41, no. 2-3, pp. 93-104.

Vedder, H. 2008, "An Assessment of Carbon Capture and Storage Under EC Competition Law", SSRN eLibrary, .

Veil, J.A., Harto, C.B. & McNemar, A. 2011, "Management of Water Extracted From Carbon Sequestration Projects: Parallels to Produced Water Management", SPE 140994 - SPE Americas E&P Health, Safety, Security, and Environmental Conference, 21-23 March 2011, Houston, Texas, USA, .

Veil, J.A., McNemar, A. & Harto, c. 2010, "Management of Water Extracted in Conjunction with Carbon Sequestration Programs", presented at the Ninth Annual Conference on Carbon Capture & Sequestration, .

Wallquist, L., Visschers, V.H.M. & Siegrist, M. 2010, "Impact of Knowledge and Misconceptions on Benefit and Risk Perception of CCS", Environmental science & technology, vol. 44, no. 17, pp. 6557-6562.

Watson, T.L. & Bachu, S. 2009, "Evaluation of the Potential for Gas and CO2 Leakage Along Wellbores", Spe Drilling & Completion, vol. 24, no. 1, pp. 115-126.

Watson, T.L. & Bachu, S. 2008, "Identification of wells with high CO_2-leakage potential in mature oil fields developed for CO_2-enhanced oil recovery", Paper SPE 112924. SPE Improved Oil Recovery Symposium, Tulsa, OK, U.S.A., 19–23 April., .

William, J., Svec, R., Grigg, R., Zhang, J. & Crow, W. 2010, "Experimental investigation of wellbore integrity and CO2-brine flow along the casing-cement microannulus", International journal of greenhouse gas control, vol. 4, no. 2, pp. 272-282.

Williams, R.H., Liu, G., Kreutz, T.G. & Larson, E.D. 2010, "Alternatives for Decarbonizing Existing USA Coal Power Plant Sites", Proceedings of the GHGT-10 conf., Amsterdam, .

Wilson, E., Zhang, D. & Zheng, L. "The socio-political context for deploying CCS in China and the U.S", Global Environmental Change, vol. In Press, Corrected Proof.

Wolery, T.J., Aines, R.D., Hao, Y., Bourcier, W., Wolfe, T. & Haussman, C. 2009, Fresh Water Generation from Aquifer-Pressured Carbon Storage: Annual Report FY09, United States.

Woods, A.W. & Norris, S. 2010, "On the role of caprock and fracture zones in dispersing gas plumes in the subsurface", Water Resources Research, vol. 46, no. 8, pp. W08522.

World Coal Institute . Available: http://www.worldcoal.org/coal/uses-of-coal/coal-electricity/ [2010, 08/02].

Xu, T., Apps, J.A. & Pruess, K. 2003, "Reactive geochemical transport simulation to study mineral trapping for CO (sub 2) disposal in deep arenaceous formations", Journal of Geophysical Research, vol. 108.

Yamamoto, H., Zhang, K., Karasaki. K., Marui, A., Uehara. Hitoshi. & Nishikawa, N. 2009a, "Numerical investigation concerning the impact of CO2 geologic storage on regional groundwater flow", International Journal of Greenhouse Gas Control, vol. 3, no. 5, pp. 586-599.

Yamamoto, H., Zhang, K., Karasaki, K., Marui, A., Uehara, H. & Nishikawa, N. 2009b, "Numerical investigation concerning the impact of CO2 geologic storage on regional groundwater flow", International Journal of Greenhouse Gas Control, vol. 3, no. 5, pp. 586-599.

Yang, H. 2008, "Progress in carbon dioxide separation and capture: A review", Huanjing Kexue Xuebao (Yingwenban), vol. 20, no. 1, pp. 14-27.

Zeidouni, M., Pooladi-Darvish, M. & Keith, D.W. 2010, "Leakage Detection and Characterization through Pressure Monitoring", Proceedings of the GHGT-10 conf., Amsterdam, .

Zeidouni, M. & Pooladi-Darvish, M. 2010, "Characterization of Leakage through Cap-Rock with Application to CO2 Storage in Aquifers - Single Injector and Single Monitoring Well", Canadian Unconventional Resources and International Petroleum Conference, 19-21 October 2010Alberta, Canada.

Zhai, H. & Rubin, E.S. 2010, "Performance and cost of wet and dry cooling systems for pulverized coal power plants with and without carbon capture and storage", Energy Policy, vol. 38, no. 10, pp. 5653-5660.

Zhai, H., Rubin, E.S. & Versteeg, P.L. 2011, "Water Use at Pulverized Coal Power Plants with Postcombustion Carbon Capture and Storage", Environmental science & technology, vol. 45, no. 6, pp. 2479-2485.

Zhang, C. 2009, Climate change impacts on water resources and ecological environment of inland watersheds in the Hexi region of West Gansu, China, .

Zhang, Y., Oldenburg, C. & Benson, S.M. 2004, "Vadose zone remediation of carbon dioxide leakage from geologic carbon dioxide sequestration sites", Vadose Zone Journal, vol. 3, no. 3, pp. 858.

Zheng, C., Liu, J., Cao, G., Kendy, E., Wang, H. & Jia, Y. 2010a, "Can China Cope with Its Water Crisis??Perspectives from the North China Plain", Ground Water, vol. 48, no. 3, pp. 350-354.

Zheng, Z., Larson, E.D., Li, Z., Liu, G. & Williams, R.H. 2010b, "Near-term mega-scale CO2 capture and storage demonstration opportunities in China", Energy environmental science, vol. 3, no. 9, pp. 1153-1169.

Zhou, Q., Birkholzer, J.T., Tsang, C. & Rutqvist, J. 2008, "A method for quick assessment of CO2 storage capacity in closed and semi-closed saline formations", International Journal of Greenhouse Gas Control, vol. 2, no. 4, pp. 626-639.

Chapter 6

Initial evaluation of advantageous synergies associated with simultaneous brine production and CO_2 geological sequestration

This chapter was adapted from: B. Court, K.W. Bandilla, M.A. Celia, T. Buscheck, A. Janzen, J.M. Nordbotten, M. Dobossy, (2011), *Initial evaluation of advantageous synergies associated with simultaneous brine production and CO_2 geological sequestration*, International Journal of Greenhouse Gas Control, in review.

6.1. Introduction

In this Chapter based on (Court et al., 2011d), we provide an initial quantitative analysis of four specific synergies, identified in Chapter 5, related to active brine management in CCS operations. The first three represent separate operational benefits resulting from an active pressure management of the injection formation, accomplished by combining brine production (extraction) with CO_2 injection. The fourth focuses on the possibility of explicit "plume steering" by combinations of injection and production wells.

The reduction of pressure build-up at a CO_2 injection well due to brine production operations is the first beneficial outcome investigated. Regulations in the United States limit injection rates to keep the resulting injection formation pressure below the overlying aquitard fracture pressure to avoid initiating or re-activating hydraulic leakage pathways (U.S. EPA, 1994). Injection well pressures typically cannot exceed some specified fraction - 80 to 90 % - of the estimated fracture pressure of the aquitard. Active control of this pressure build-up can allow higher injection rates and therefore a more efficient CO_2 injection operation. We examine this effect through a series of simulations.

The second beneficial outcome involves reduction in the Area of Review (AoR), which is the area an operator needs to identify as being impacted by the injection operation. The AoR is defined in the recently finalized U.S. Environmental Protection Agency (EPA) rule as “the region surrounding the geologic sequestration project where [Underground Sources of Drinking Water] USDWs may be endangered by the injection activity. The AoR is delineated using computational modeling that accounts for the physical and chemical properties of all phases of the injected CO_2 stream and displaced fluids and is based on available site characterization, monitoring, and operational data as set forth in § 146.84. The Agency is developing guidance on AoR and corrective action to support AoR delineation (*i.e.,* including regions of the CO_2 plume and pressure front)" (Federal Register, 2010). The AoR is expected to be based on the concept of “critical pressure”, defined as the pressure increase necessary to lift resident brine from the injection formation to the USDW, as discussed in Bandilla et al. (2011), Birkholzer and Zhou (2009), Nicot et al. (2009), and Birkholzer et al. (2011). Active pressure control through brine production can greatly reduce the AoR, thereby providing important benefits to both the operator and regulators, while simultaneously improving public confidence in the operation.

The third operational benefit comes from the reduction in CO_2 and brine leakage potential through abandoned wells when brine production is coupled to large-scale CO_2 injection. In fields involving large numbers of existing oil and gas wells, leakage can be a significant issue. By greatly reducing the size of the AoR and the injection formation pressure build-up, we can concomitantly reduce both the area over which leakage can take place (and therefore the number

of wells contacted) and its main physical drive. This benefit can have important consequences for risk reduction and risk management.

Finally, the fourth investigated synergy involves the idea of “plume steering”, wherein brine production is used to affect the flow direction of the CO_2 plume by modifying the pressure field. Effective plume steering could have important implications when considering possible remediation strategies.

While these four topics are the focus of this study, there are other important synergies that are being addressed elsewhere. Perhaps most important among those is the possible beneficial uses of the produced brine at the surface, including extraction of geothermal heat from the brine and possible desalination of brines with moderate salinity, especially in water-stressed regions of the world. For more details about these issues, see Buscheck (2010), Buscheck et al. (2011a, 2011c), Court et al. (2011b), and references therein.

In the studies we present, three variations of a vertical equilibrium model were used to simulate supercritical CO_2 injection into deep saline formations. The first is a sharp-interface model for which an analytical solution is available. The second is a semi-analytical model that includes many geological layers and many leaky wells. The third is a general numerical model that solves the vertically-integrated two-phase flow equations. Additional comments about each model are given in the respective sections. For more detailed descriptions of the models, see Nordbotten et al. (2005); Nordbotten and Celia (2006, 2011); Celia and Nordbotten (2009, 2011), and references therein.

The Chapter is structured as follows. In Section 6.2, we present results showing brine production impacts on pressure build-up, including impacts on injection-well pressure, as well as impacts on the AoR. As explained in that section, we use a simple, radially symmetric model with an analytical solution for these simulations. In Section 6.3, we use a semi-analytical model that includes multiple leaky wells and multiple geological layers to quantify reductions in leakage

potential associated with brine production. Finally, in Section 6.4, we use a more general numerical model to examine the impact of a single ring of four brine production wells on the movement of the CO_2 plume and on the resulting pressure field. We end the chapter with a discussion of potential advantageous uses of brine disposal management and of different CO_2 management strategies to include or avoid breakthrough, and a set of conclusions.

6.2. Pressure management: injection well pressure build-up and Area of Review (AoR)

In this section we examine the impact that brine production could have on pressure management in a CCS operation. This pro-active pressure-relief strategy would have several advantages, including control of pressure build-up at the injection well and reduction in the size of the AoR. While this is not a new concept - the oil and gas industry has been managing pressure build-ups (and pressure losses) in reservoirs for decades - brine production has not been part of the recent CCS paradigm as pointed out by Court et al. (2011b), (2011c) and Buscheck et al. (2011a). The two main objectives of this section are to quantify the reduction in injection well pressure and the reduction in the AoR.

6.2.1. Model choice: vertically-integrated sharp-interface analytical model

We investigate the impact of the pressure control distance, which depends on the spacing between the injection and production wells, on the injection well pressure decrease and the AoR reduction using the vertically-integrated sharp-interface analytical model presented in Nordbotten et al. (2005), Nordbotten and Celia (2006), and Celia et al. (2011). This model is based on the assumption of a horizontal, homogeneous, and isotropic formation with impermeable boundaries at the top and bottom, constant fluid properties, buoyant segregation of the less-dense CO_2 and the more-dense brine, vertical equilibrium of the pressures in both fluids, and negligible local capillary pressure such that a macroscopic sharp interface separates the two fluids. While the model is simple, it is useful as a screening tool. Of course, industrial projects will require detailed

site characterization, and may need analysis supported by full numerical models such as ECLIPSE (Schlumberger, 2010), NUFT (Nitao, 1998), TOUGH2 (Pruess, 2004), and STOMP (White and Oostrom, 1997), depending on the practical question being addressed.

A simple calculation to assess the impact of brine production on the pressure can be defined by assuming a fixed-pressure boundary condition at a specified radial distance from the injection well. Buscheck et al. (2011a) show that a radial model is a good approximation for modeling the pressure buildup around an injection well by comparing it to 3D simulations of five-spot or double-ring nine-spot well patterns. As a brine production well is activated, a cone of pressure decrease will develop around the well. When it is coupled with a CO_2 injection well, with which one finds an associated cone of pressure build-up, a point in space between the two wells will be at a fixed pressure that does not change with time. As such, the use of a fixed hydrostatic pressure boundary condition in the analytical solution can be viewed as representative of the impact of a ring of brine production wells despite the fact these production wells are not explicitly modeled.

With this radial model, many scenarios can be considered easily, allowing us to perform an initial screening of the concept. The simple model also provides the additional benefit that it enables much broader audiences to comprehend this concept with simple and easily accessible tools such as the web-interface subsurface.princeton.edu/CO2interface/. This could significantly improve public acceptance of CCS. It also allows us to determine whether brine production impact on the pressure profile is significant before undertaking complementary (and often necessary) full numerical modeling of a particular site.

6.2.2. Case study 1

The case study is a hypothetical 50-year injection with a fixed rate of 10Mt/y of supercritical CO_2 into a 62-m thick horizontal, homogeneous, and isotropic aquifer. This injection rate was chosen so that the injection well pressure never exceeds 90 % of the fracture pressure using a 20 kPa/m gradient from Michael et al. (2009). The injection formation has a permeability of 50 milliDarcy

(mD), a porosity of 0.15, and a top depth of 2000 m as summarized in Table 6.1. We use a residual brine saturation of 0.2 and an end-point CO_2 relative permeability (k_{rel}) of 1. As mentioned earlier, capillary pressure (P_c) effects are ignored except for the possible effect of the end-point relative permeability. Note also that the critical pressure is defined as the minimum pressure required to drive brine of a given density into an overlying freshwater zone (Nicot et al., 2009; Bandilla et al., 2011).

Injection rate	10 $MtCO_2$/y
Thickness	62 m
Permeability	50 mD
Porosity	0.15
Top depth	2000 m
CO_2 density**	888.6 kg/m^3 (warm basin Temp. gradient 25 C/km)
CO_2 viscosity**	7.59e-5 Pa.s
Brine density**	1045 kg/m^3
Brine viscosity**	2.535e-4 Pa.s
Fracture pressure	P_{frac} ~ 26.38 MPa
Critical pressure#	$P_{critical}$ ~ 1.1 MPa
Compressibility	4.2e-10 Pa^{-1}

Table 6.1: Parameters used in Case study 1. Data in rows marked by ** are based on (Fenghour et al., 1998; McPherson et al., 2008; Abramson, 2009), and by # are based on (Bandilla et al., 2011).

6.2.3. Result: brine production allows injection well pressure decrease and higher injectivity potential

In Figure 6.1 we plot the time evolution of the injection-well pressure for 10 different simulations where the radial distance of the fixed-pressure outer boundary condition was varied from 1 to 20 km. Not surprisingly, the closer the fixed pressure boundary condition is to the injection well, the larger is the injection-well pressure reduction.

The CO_2 plume with no brine production reaches about 9 km after 50 years. If we define “breakthrough” (referred to as BT, with time of occurrence indicated in Figure 6.1) as the arrival of the CO_2 plume at the location of the fixed pressure outer boundary condition we see that for boundary distances less than 10 km, breakthrough of the CO_2 occurs. Of course, these “close”

configurations of the production wells also provide the largest reduction of pressure at the injection well. The observed trade-off between having an impact but avoiding breakthrough suggests that production well strategies with either a horizontal well that has producing sections changing dynamically outwards as the plume progresses or multiple rings (inverted 5 spots) of vertical production wells could be considered (see Buscheck et al. (2011a) for the latter). However, even when the fixed pressure ring is at 10 km, the reduction in pressure over 50 years can be significant.

As soon as any significant pressure change approaches the fixed pressure boundary, the injection well pressure decreases as shown in Figure 6.1. At early time there is essentially no brine flow at the outer boundary because compressibility (assumed to be equal to water compressibility: 4.2e-10 [Pa^{-1}]) within the domain is dominant. But at later times significant brine flow occurs through the boundary, enhanced by the fixed pressure boundary (which is induced by the production wells). While this occurs, the less viscous CO_2 is replacing the more viscous brine in the domain, which means the overall resistance to flow in the domain decreases. This explains why, for a fixed injection rate, after an initial increase the pressure at the injection well decreases with time.

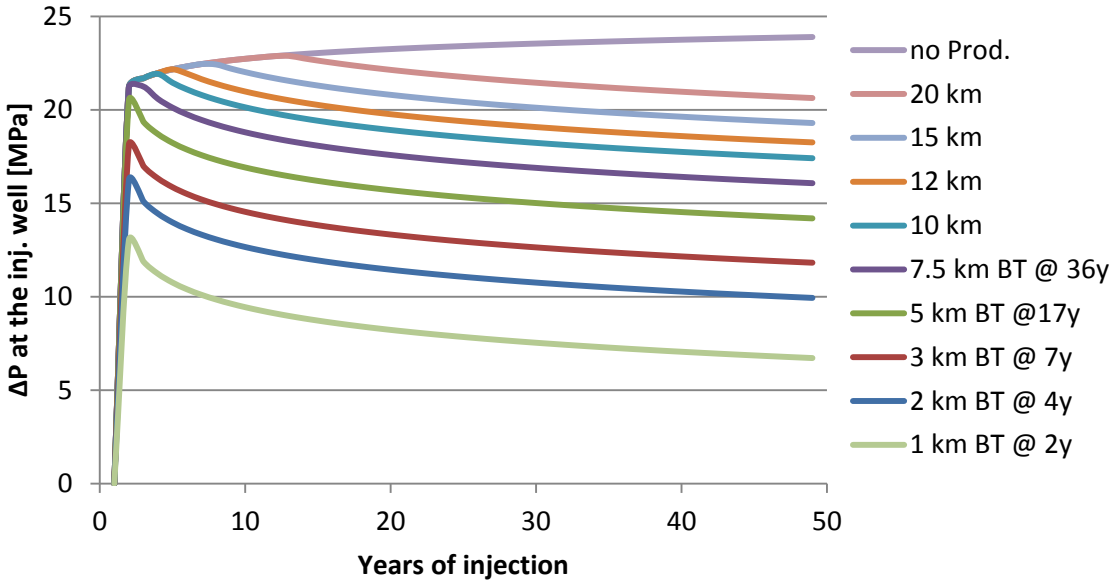


Figure 6.1: Impact of pressure control distance on the injection well pressure. BT stands for "breakthrough", defined here as the arrival of the CO_2 plume at the location of the fixed pressure outer boundary condition before the end of the 50 years of injection, with time of occurrence indicated next to it.

It is clear from Figure 6.1 that brine production can control the build-up of pressure at the injection well. At 50 years it can reduce the injection well pressure by almost 30 % between the no production case and the first case without breakthrough (10 km case). It is also important to remember that the main limiting constraint on injection rate is driven by the need to remain below the fracture pressure of the overlaying aquitard. The transient pressure decrease at the injection well pressure can therefore provide the potential for higher injection rates at later times. See Buscheck et al. (2011a) for more details about possible optimized injection rates through time. Note also that reduced pressure at the injection well would allow injection at a constant rate with a lower compression cost.

In conclusion, brine production has the ability to significantly reduce injection well pressure build-up and therefore provides the potential for higher injectivity.

6.2.4. Result: brine production can significantly reduce the AoR

Table 6.2 compares the areal footprint of the CO_2 plume and the areal extent of the critical pressure for the simulations plotted in Figure 6.1 without CO_2 breakthrough. These results show that brine production can reduce the AoR from 4000 km^2 when no pressure control is imposed to an area very close to the size of the CO_2 plume, which is 16 times smaller. Clearly, brine production has the ability to significantly decrease the AoR.

Fixed Pr. Boundary Location	**10 km**	**12 km**	**15 km**	**20 km**	**No P. control**
CO_2 Area [km^2]	250				
Critical Pr. Area [km^2]	190	275	430	765	4000

Table 6.2: Comparison of CO_2 and critical pressure (Bandilla et al., 2011) areal extents after 50 years of injection for the simulations plotted in Figure 6.1 without CO_2 breakthrough.

For CCS operators this reduction potential would allow much smaller unitization for each CCS operation, reduce the area where monitoring and potential remediation will be necessary, and enable multiple independent injections in a given basin to avoid operationally constraining each other. This AoR reduction would also facilitate independent assessment and permitting by convincing regulators that each project is spatially distinct and that each operator is responsible for only one well-defined and non-overlapping AoR. Buscheck et al. (2011a) also presents analysis demonstrating the beneficial reduction in post-injection residual pressure build-up that results from brine production in the injection formation, which could have a positive impact on monitoring requirements and on the cost of liability insurance.

Through all of these mechanisms, AoR reduction will provide better assurance to local communities about the limited areal pressure perturbation and reduction of the associated risks including leakage to USDW, thereby increasing public confidence. Considering an average

abandoned well density over a given area (see Gasda et al. (2004)), it is important to note that AoR reduction will also decrease, as quantified in Section 6.3, the number of wells contacted by the critical pressure, thereby concurrently reducing brine leakage

6.3. CO_2 and brine leakage reduction from brine production

This section quantifies the impact of brine production on CO_2 and brine leakage risk. The main physical drive of leakage through abandoned wells for both brine and CO_2 is the pressure difference across a given well segment perforating an aquitard, with an additional buoyant drive for the CO_2. Because brine production reduces the injection formation pressure, it is expected to reduce this leakage risk. The goal here is to quantify this reduction of risk.

The authors are not aware of any modeling studies quantifying the reduction in leakage risk by brine production from the injection formation. We acknowledge here complementary earlier work by Guswa and Celia (2001) and Réveillère and Rhomer (2010), who considered a higher-pressure hydraulic barrier preventing upward leakage via brine injection into the overlaying aquifer.

6.3.1. Model choice: sharp-interface semi-analytical multi-layer model

The multi-layer model is based on vertical equilibrium equations in each of the permeable formations in the vertical sequence, with the assumption of a sharp interface between the CO_2 and brine. The permeable layers are assumed to be horizontal and homogeneous, and are separated by impermeable aquitards. The domain is assumed to have a high number of existing wells through which leakage of both brine and CO_2 can occur. Each well is characterized by effective permeability values assigned across each aquitard formation. Analytical solutions, like those used in Section 6.2, are used to model each plume of CO_2. The model is semi-analytical because all of the plumes and the associated pressure fields are coupled together into a

nonlinear computational model that combines analytical spatial models with discrete time stepping. Details of the model can be found in Nordbotten and Celia (2006), Celia et al. (2011), and references therein.

Leakage along well segments is modeled using a standard two-phase Darcy equation, with the relative permeability along the wells taken to be linear in phase saturation. Leakage of both brine and CO_2 is tracked along all wells, and leaked fluids can enter any of the other formations along the wells. In the calculations, leakage into each of the layers is tracked. In the following simulations, the total amount of leakage out of the injection formation is calculated and reported as the main output from the models.

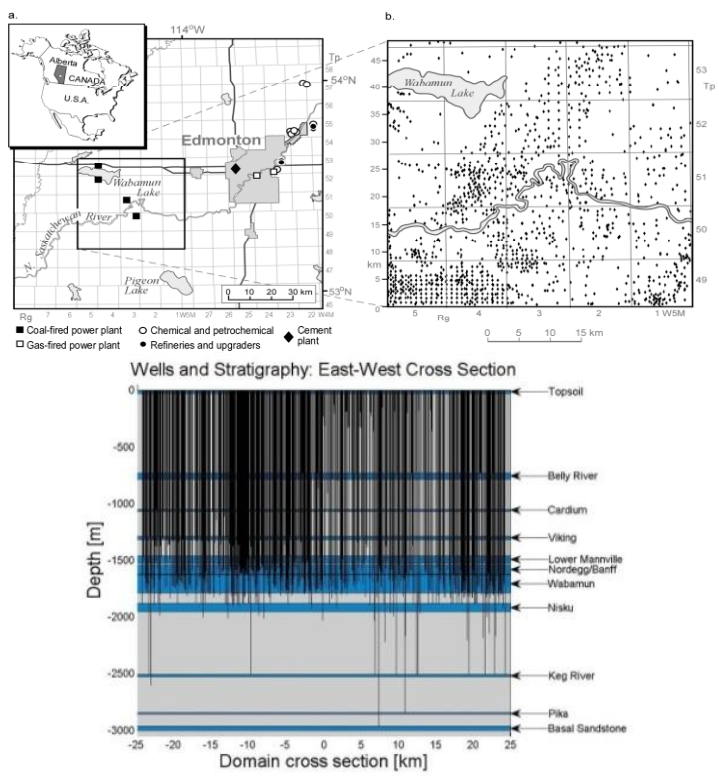


Figure 6.2: Wabamun Lake area study site in Alberta, Canada with both a top view and vertical section of all wells in the domain. (Figure adapted from Celia et al. (2011)).

Aquifer Name*	Top depth [m]	Thickness [m]*	Intrinsic permeability [mD]*	Porosity*	Wells ending in layer
Belly River	728.8	56	86	0.15	1146
Cardium	1051.8	15	7	0.19	1131
Viking	1287.8	30	53	0.11	878
Mannville	1461.8	65	7	0.14	874
Nordegg/Banff	1537.8	80	4	0.10	719
Wabamun	1628.8	160	4	0.12	136
Nisku	1881.8	72	170	0.12	39
Keg River	2506.8	22	3.5	0.12	11
Pika	2844.8	14	16	0.12	2
Basal Sandstone	2964.8	38	23	0.12	1

Table 6.3: Characteristics of permeable layers in the study area. The shaded row corresponds to the formation into which injection is simulated. Data in columns marked with * are from Michael et al. (2009c). (Table adapted from Celia et al. (2011)).

6.3.2. Case study 2

The leakage results presented below are a continuation of the work presented in Chapter 3 (based on Celia et al. (2011)), focusing on a case study in Alberta, Canada where data have been collected for site characterization in a 50 km × 50 km area containing four large coal-fired power plants that currently emit about 30 million tons of CO_2 per year (Mt CO_2/yr), and where 1,146 existing oil and gas wells have been identified over 10 aquifers (see Figure 6.2 and Table 6.3). The study focused on the impact of the uncertainty in abandoned well parameters on CO_2 and brine leakage risk. We refer to Celia et al. (2011) and references therein for further details.

In this section we model a CO_2 injection into the Nisku aquifer, which is 72 m thick and has a permeability of 170 mD. Similar to Case 2 in Celia et al. (2011), we inject 12.3 MtCO_2/y CO_2 based on the maximum allowable injection pressure of 90 % of the fracture pressure using a 20 kPa/m gradient. We consider residual brine saturation of 0.3 and the associated end-point CO_2 relative permeability of 0.55. Four brine production wells are located at 17 km from the injection well (they are outside of the 50-year CO_2 plume outer radius) and cumulatively extract the same volume as is injected. For all simulations, values of density and viscosity are set to 479 kg/m^3 and 0.0395 mPa·s for CO_2, and 1045 kg/m^3 and 0.2535 mPa·s for brine. To avoid non-physical interactions with the outer boundary of the domain, we set the outer boundary (with a fixed hydrostatic pressure condition) at a radius of 130km from the injection well. The effective compressibility coefficient for the fluid and the solid matrix is assumed to be fixed and equal to the compressibility of brine (4.2e-10 Pa^{-1}), since most of the computational domain is filled with brine. As in Celia et al. (2011), the effective permeabilities of abandoned wells are sampled 1000 times from a lognormal bimodal distribution with one mode corresponding to intact cement and the other corresponding to degraded or otherwise damaged cement regions; the two mean values were set to 0.1 mD and 1 D, respectively, and 50% of the wells, chosen randomly, are assumed to have ‘good cement’ with the remaining 50% having ‘bad cement’. Each mode is assigned a unit variance in log space. In order to represent the worst leakage case, as in complementary work of Nogues et al. (2011), well permeabilities are fully correlated so that if one well segment is

leaky the whole well is leaky (see Celia et al. (2011) for investigation of fully uncorrelated permeabilities).

Injection rate	12.3 $MtCO_2/y$
Thickness	72 m
Permeability	170 mD
Porosity	0.12
Top depth	1881.8 m
CO_2 density*	479 kg/m^3
CO_2 viscosity*	3.95e-5 Pa.s
Brine density*	1045 kg/m^3
Brine viscosity*	2.35e-4 Pa.s
Compressibility	4.2e-10 Pa^{-1}

Table 6.4: Parameters used in case study 2. Data in rows marked by * are from Celia et al. (2011).

6.3.3. Result: brine production can significantly reduce CO_2 and brine leakage

As observed by Celia et al. (2011), the larger spatial footprint associated with the critical pressure, as compared to the footprint of the CO_2 plume, tends to drive brine leakage through many more wells (39) than those wells contacted by the injected CO_2 (17) when there is no brine production. Less brine than CO_2 reaches the top aquifer, highlighting the important role played by buoyancy as well as the importance of intermediate permeable formations between the injection formation and the shallow subsurface (often referred to as secondary barriers to leakage; see Nordbotten et al., 2004; Oldenburg , 2008).

Figure 6.3 presents results from 1000 simulations, showing the distributions of total CO_2 fractional mass leakage (total mass leaked out of the injection formation / total mass injected) and total brine fractional volume leakage (total brine volume leaked out of the injection formation / total CO_2 volume injected). It shows that brine production reduces the total leakage of brine out of the injection formation, on average, by more than one order of magnitude, while the CO_2 leakage is reduced by about half an order of magnitude, both measured after 50 years of simultaneous injection and production. The smaller reduction in CO_2 leakage can be explained by three reasons.

First, Figure 6.4 compares two single-run pressure profiles showing the impact of brine production on the injection formation pressure after 1, 10, 25 and 50 years of injection. It can be observed that the pressure reduction in the CO_2 plume region (the CO_2 plume outer extent is marked by the dot/cross on the curves) only becomes significant late (after 25-30+ years), while the difference is significant at much earlier times for the brine region outside of the CO_2 plume. This difference partly explains why the reduction in CO_2 leakage is smaller than the reduction in brine leakage.

Secondly, for the brine production case, the outer extent of the critical pressure is reduced from about 55 km to about 15 km. Therefore fewer wells (17) are contacted than when no brine is produced (39), which clearly reduces the risk of brine leakage. The number of wells contacted by the CO_2 plume (17), however, does not change by producing brine.

Finally, CO_2 leakage through abandoned wells is both density- and pressure-driven while brine leakage is only pressure-driven. Brine-production-driven pressure relief therefore reduces the only driving force of brine leakage but only one of the two driving forces for CO_2 leakage. The buoyancy difference thus also contributes to the smaller reduction of CO_2 leakage than brine leakage shown in Figure 6.3.

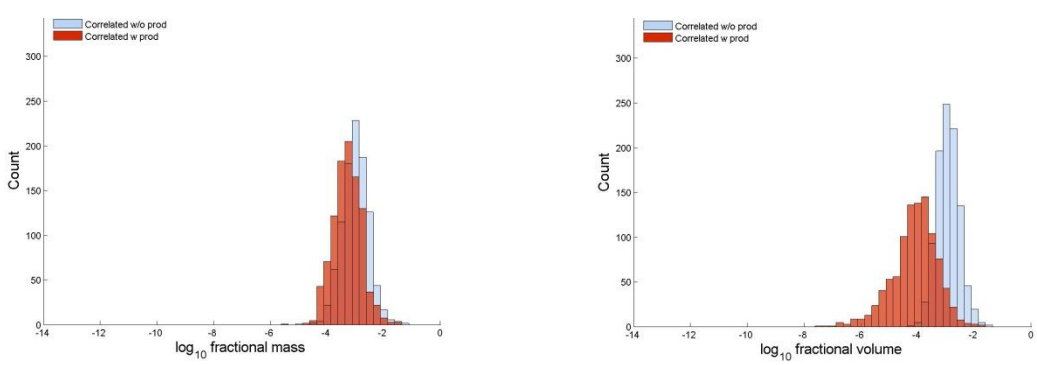


Figure 6.3: Total CO_2 fractional mass (left) and brine fractional volume (right) leakage out of the injection formation for 1000 simulations sampling bimodal fully correlated well segment effective permeabilities. Both graphic compare the scenario (red) with and (blue) without brine production.

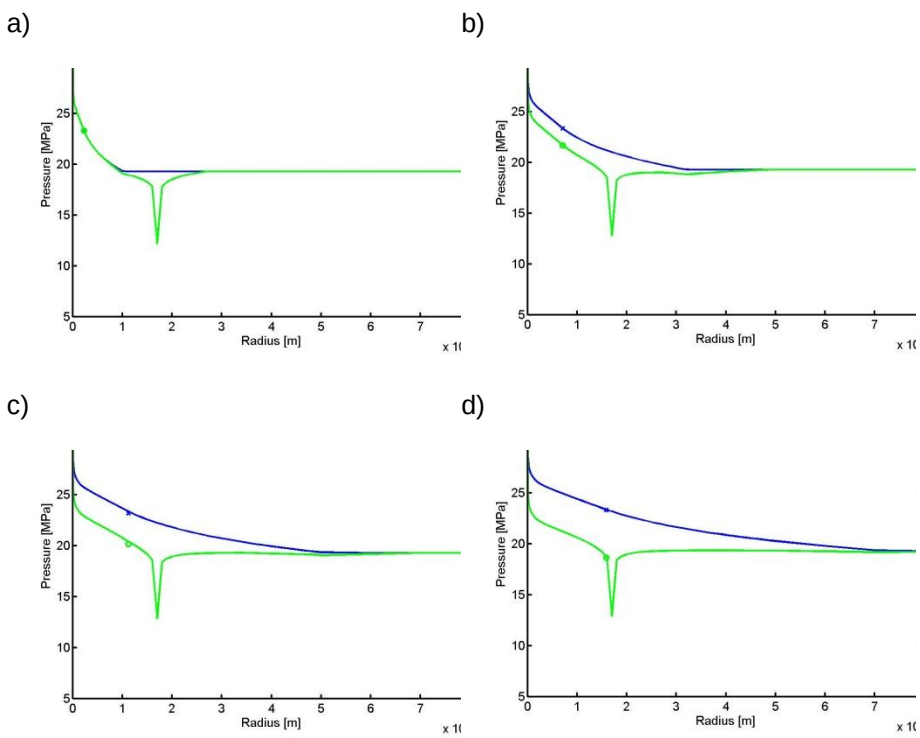


Figure 6.4: Single-run pressure profile comparison at 1, 10, 25 and 50 years (a-d respectively) between CO_2 injection (green) with and (blue) without brine production. The outer extent of the CO_2 plumes are marked with the cross/dot.

As described in Section 6.3.1, the brine production wells were placed 17 km from the injection well in order for them not to be contacted by the CO_2 plume during the 50-year injection period. The results show that they were too far away to have a major impact on CO_2 leakage, suggesting the investigation of more sophisticated case scenarios with, for example, horizontal production wells or sequential rings of inverted 5-spots, as recently investigated by Buscheck et al. (2011a). Future work should also include diffuse brine leakage through the overlaying aquitards, which could have a significant impact on the pressure profile as shown in Janzen (2010).

6.4. Impact of a single ring of 4 vertical brine production wells on the CO_2 plume

While the simulations in Sections 6.2 and 6.3 focused on the impacts of brine production on fluid pressure, this section examines its impacts on the shape of the CO_2 plume. We do this for two reasons. The first is related to the issue of breakthrough of the CO_2 at the production wells; to avoid breakthrough (further discussed in section 5.2), any brine production strategy will have to be adapted to the expected CO_2 plume shape. The second reason is the practical question of "plume steering." The plume steering concept could be of interest in remediation strategies; for example, in the case of a plume migrating toward undesirable locations, including possible leakage into overlying formations. It is therefore important to quantify the extent to which brine production can impact the shape and extent of the CO_2 plume.

Because the horizontal movement of the plume when it is being "steered" will lead to plume shapes that are not radially symmetric, use of a radially-symmetric simulator is not appropriate. As such, we choose to use a more general numerical model that is based only on the assumption of buoyant segregation and vertical equilibrium of pressures. We then apply the model to investigate the impact of brine production on the CO_2 plume and gain insights into the effectiveness of plume steering strategies in different formations.

6.4.1. Model choice: vertically-integrated numerical model

The concept of vertical equilibrium, which is assumed for all models used in this chapter, is based on the assumption that the significant density difference between the two fluids leads to relatively fast vertical segregation. Given competent aquitard formations above and below the injection formation, the buoyantly segregated fluids achieve pressure equilibrium with negligible vertical flows after the segregation occurs. As long as the time scale of the simulation is large compared to the segregation time, this is a good approximation. We refer to Lake (1989), Yortos (1995), Gasda et al. (2009), Class et al. (2009), Pruess and Nordbotten (2011), Celia and Nordbotten (2011), Nilsen et al. (2011), and Nordbotten and Celia (2011) for details on and application of

vertically-integrated models, and to Court et al. (2011a) and Norbotten and Dahle (2011) for a recent detailed discussion of the segregation timescale, which is mainly controlled by the formation vertical intrinsic permeability but also impacted by capillary pressure, local brine relative permeability, formation thickness, porosity, and fluid density and viscosity.

Under the assumption of vertical equilibrium, the phase pressures vary linearly in the vertical direction, each with slope of $-\rho g$ with the appropriate density (ρ) used for each fluid. The capillary pressure is the difference between the two phase pressures. Vertically-integrated models allow for these linear pressure profiles to be calculated, and from them, given information about the relationship between capillary pressure and saturation, the vertical saturation profile can be calculated (see Court et al. (2011a), Norbotten and Dahle (2011), and Nordbotten and Celia (2011) for details on the saturation reconstruction). This saturation profile will exhibit a "capillary transition zone" which is governed by the capillary pressure – saturation relationship. When this transition zone is very small compared to the injection formation thickness, the assumption of a sharp interface is appropriate. This corresponds to the case of negligible capillary effects. When the capillary transition zone is large, capillary pressure forces are not negligible and should therefore be included in the analysis.

For the results presented in this section, we will investigate questions associated with occurrence of breakthrough and plume steering using both sharp-interface and finite-capillary-transition-zone vertically-integrated numerical models (Gasda, 2008; Gasda et al., 2009; Janzen, 2010; Nordbotten and Celia, 2011). We use both because the underlying behavior of systems with and without significant capillary effects can be considerably different, as shown in the recent work of Court et al. (2011a), among others. In order to have a consistent metric for each of these models, we will always calculate the "vertically averaged" saturation, which is the fraction of pore space occupied by one phase, compared to the total available pore space, along any vertical line extending from the bottom to the top of the formation at a given (x,y) location. Figure 6.5provides a visual comparison of this metric and an illustration of reconstructed saturation profiles from both

sharp-interface and finite-capillary-transition-zone vertically-integrated numerical models. We refer to Court et al. (2011a) for additional details.

The sharp-interface vertically-integrated numerical model (Figure 6.5a) assumes constant full saturation of CO_2 and brine on their respective sides of the front (brine residual saturation assumed to be zero), and a negligible capillary transition zone. The CO_2 effective uniform thickness is the depth-averaged CO_2 saturation, varying between 0 and 1, multiplied by the injection formation thickness. This effective uniform thickness is shown as the white line in Figure 5a and exactly matches the reconstructed CO_2-brine interface. This is not the case for results from finite-capillary-transition-zone vertically-integrated numerical models because the CO_2 saturation distribution based on reconstruction will vary vertically behind the interface. Figure 6.5b and 6.5c show CO_2 saturation distribution profiles using two nonlinear capillary pressure-saturation curves for the reconstruction. The CO_2 effective uniform thickness essentially "compresses" the saturation profile into a single line, which allows us to compare resulting curves from different simulations with variable production rates in Sections 6.4.3 and 6.4.4 without having to plot the entire saturation profile. It is important to note that a comparison of this finite-capillary-transition-zone vertically-integrated model with a three dimensional reservoir simulator showed close agreement of the two for cases similar to the ones modeled here (see Chapter 4 based on (Court et al., 2011a)).

(a) Linear k_{rel} - No P_c

(negligible capillary transition zone)

(b) Ebigbo k_{rel} & P_c

(small capillary transition zone)

(c) Zhou k_{rel} & P_c

(large capillary transition zone)

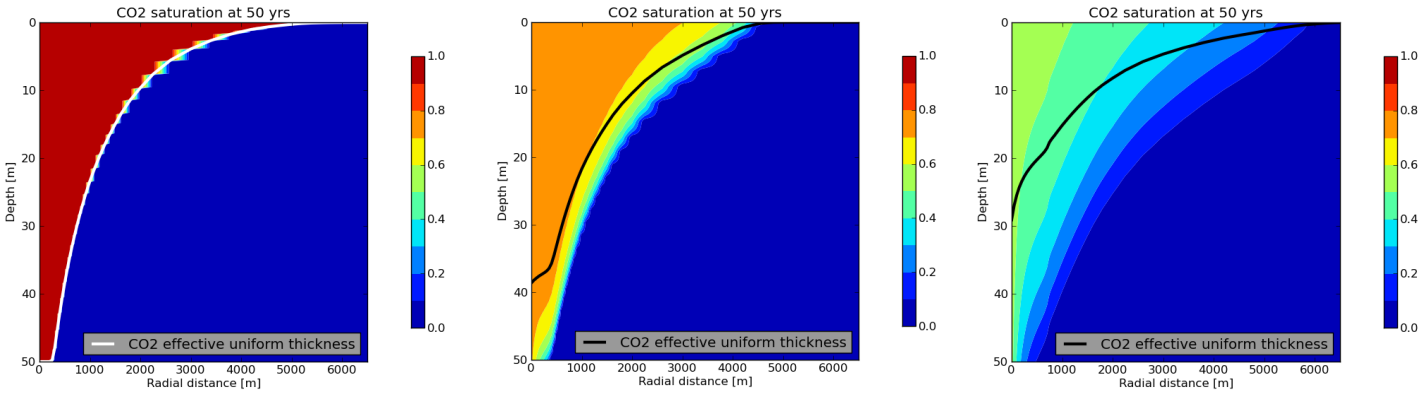


Figure 6.5: (a) CO_2 effective uniform thickness [Depth-averaged CO_2 saturation varying between 0 and 1 multiplied by the injection formation thickness] superimposed on the reconstructed CO_2 saturation profile for (a) linear k_{rel} and no P_c from the sharp-interface vertical-equilibrium numerical model and for (b-c) Ebigbo, Zhou cases (see Figure6.6) from the vertical-equilibrium numerical model with finite capillary transition zone.

6.4.2. Case study 3

We examine the impact of a single ring of 4 vertical production wells in a 5-spot pattern for a system with 50 years of CO_2 injection at a rate of 1 $MtCO_2$/y. The five wells are perforated over the entire thickness of the target formation. The hypothetical formation is horizontal, homogeneous and isotropic, and is 50 m thick with a 100 mD permeability and 15 % porosity as summarized in Table 6.5. The domain considered is 40 km by 40 km with the injection well located at the center. The focus of this study is on the injection period therefore only primary drainage is considered here; this means that CO_2 residual saturation is not relevant.

Injection rate	1 $MtCO_2$/y
Thickness	50 m
Permeability	100 mD
Porosity	0.15
Top depth	2000 m
CO_2 density**	800 kg/m^3
CO_2 viscosity**	4.25e-5 Pa.s
Brine density**	1000 kg/m^3
Brine viscosity**	3.00e-4 Pa.s
Compressibility	4.2e-10 Pa^{-1}

Table 6.5: Parameters used in case study 3. Data in rows marked by ** are from the ECLIPSE study in Chapter 4.

The four production wells are located 8 km away from the injection well in a 5-spot pattern, with the location chosen so that the CO_2 plume does not contact them (without production) over the 50-year injection period. The no-production case represents the base-case scenario. In order to investigate the impact of brine production on the CO_2 plume, the sum of the four identical individual production rates is selected to produce cumulatively one, two and three times the volume of CO_2 injected (see discussion on management of brine disposal in section 6.5.1). We also use two different capillary pressure and relative permeability functions (see Figure 6.6) to examine their impact on the results.

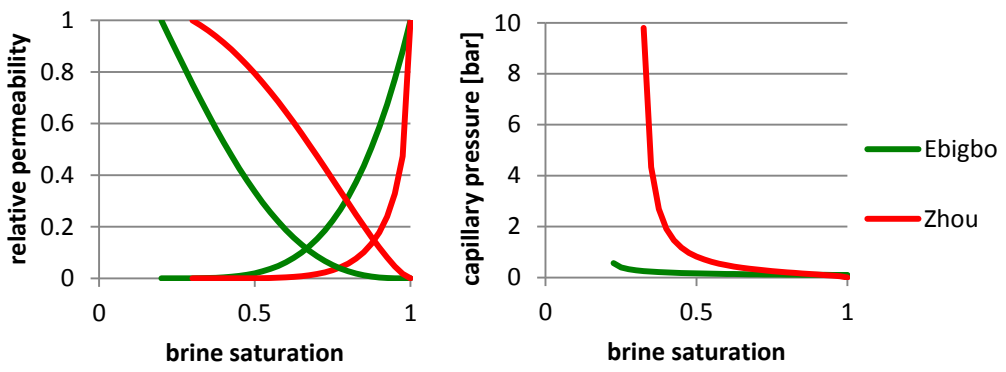
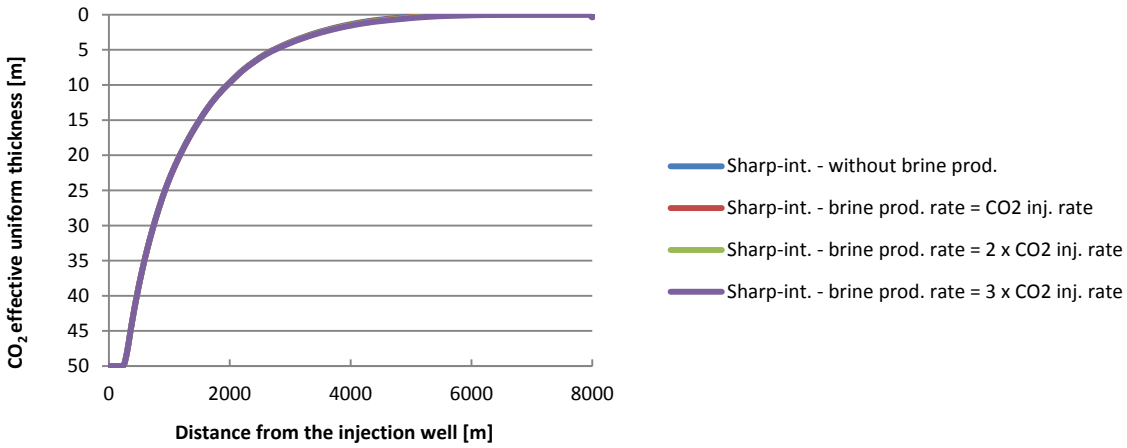


Figure 6.6: CO_2 and brine relative permeability (k_{rel}) and capillary pressure (P_c) curves used in the simulations taken from Chapter 4.

6.4.3. Results from vertically-integrated sharp-interface numerical model: brine production via a single ring of vertical production wells has limited impact on the CO_2 plume

We used the vertical equilibrium sharp-interface numerical model (with no brine residual saturation and end-point CO_2 relative permeability of 1) to investigate the impact of different brine production rates when capillary forces are negligible. The results presented in Figure 6.7 plot the inner 8 km of the cross-section taken from the injection well through a production well. Figure 6.7b zooms in on the upper 10 m of Figure 6.7a. The figures clearly show that brine production, even when producing three times the volume of injected CO_2, has essentially no impact on the plume vertical profile and only a small impact on the plume outer extent, with a small amount of the CO_2 reaching the production wells for the highest production rate. We note that sharp-interface models allow for very thin regions of CO_2 at the top of the formation, which explains the small amount of breakthrough.

a)



b)

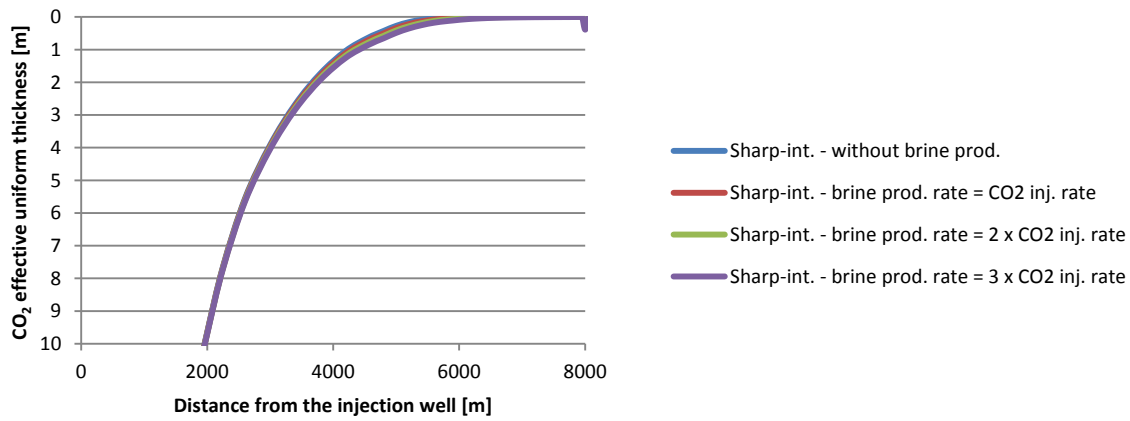


Figure 6.7: a) CO_2 effective uniform thickness [Depth-averaged CO_2 saturation multiplied by the injection formation thickness] after 50 years injection from the sharp-interface vertical-equilibrium numerical model for various brine production rates. Graphic b) is a zoom-in of graphic a) for the upper 10 m of the injection formation.

6.4.4. Results from vertically-integrated numerical model with finite capillary transition zone inclusion: formation characteristics (krel & Pc) have more impact on the CO_2 plume than brine production rates

In this section we explore, for the same set of brine production rates, the impact of two different sets of formation parameters plotted in Figure 6.6. We use the finite-capillary-transition-zone vertically-integrated numerical model described in Section 6.4.1. Similar to Figure 6.7b, only the

CO_2 effective uniform thickness results, zoomed in the upper 10 m of the injection formation, are presented in Figure 6.8 (negligible differences are seen in the plots over the full formation thickness). Their associated pressure profiles are plotted in Figure 6.9.

The first observation is that formations characteristics (k_{rel}, P_c) have more impact than the production rate on the CO_2 plume vertical profile and outer extent after 50 years. Figure 6.5 shows that for the base case without production, the vertical profiles of the CO_2 plume vary significantly across the various sets of formation parameters (k_{rel}, P_c) examined, especially for the high capillary pressure Zhou case (c). Similarly Figure 6.5 and 6.8 show that the outer radii of the CO_2 plumes without brine production range from about 4 km to 6.2 km. Figure 6.8 shows that an increase in production rates has essentially no impact on the Ebigbo cases. Production rates only have a noticable impact on the Zhou cases, where the outer extent of the CO_2 plume is increased from 6.2 to 8 km, and breakthrough occurs when 3 times the volume of CO_2 injected is produced.

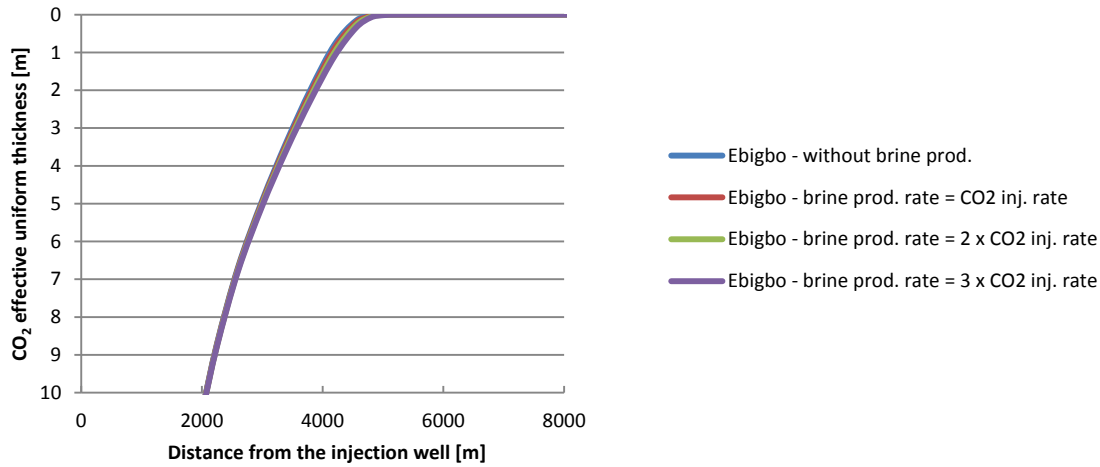
The second observation is that the pressure response is the opposite of the CO_2 response. Figure 6.9 shows that relative permeability and capillary pressure have a very small impact on the overall pressure profile after 50 years of injection in the entire domain, while the production rates have, as expected, a significant impact.

These results can be explained by the fact that the plume's vertical profile is driven to the first order by the mobility ratio (relative permeability over viscosity), as discussed in Nordbotten and Celia (2006), and thus is impacted more by the relative permeability than by the brine production rate, whereas the pressure profile is mostly driven by the the formation intrinsic permeability and advective forces (injection/production), and is therefore impacted more by varying production rates than by injection formation characteristics (k_{rel}, P_c).

Clearly understanding the impact of key parameters affecting a CO_2 plume is a prerequisite for accurate modeling of large-scale CO_2 injection coupled with brine production. These results indicate that a single ring of production wells in an inverted 5-spot pattern located

outside of the 50-year CO_2 injection plume has limited-to-negligible impact on the CO_2 plume profile, which is impacted more by the formation relative permeability and capillary pressure curves. High production rates, when close to the outer extent of the CO_2 plume, will decrease breakthrough time; however, our general conclusion is that steering potential appears limited with single vertical wells across the parameters and conditions investigated. We refer to the complementary work of Buscheck et al. (2011a) for modeling of multiple rings of vertical production wells sequentially coming online as the plume progresses, horizontal well strategies, and consideration of formation heterogeneity. It is also worth noting that brine production is not the only means of manipulating CO_2 migration. As described in Court et al. (2011b), Buscheck (2010), and Buscheck et al. (2011b), the plume could also be impacted by brine re-injection and hydraulic barriers in the same formation, which has not been investigated to the authors' knowledge.

a)



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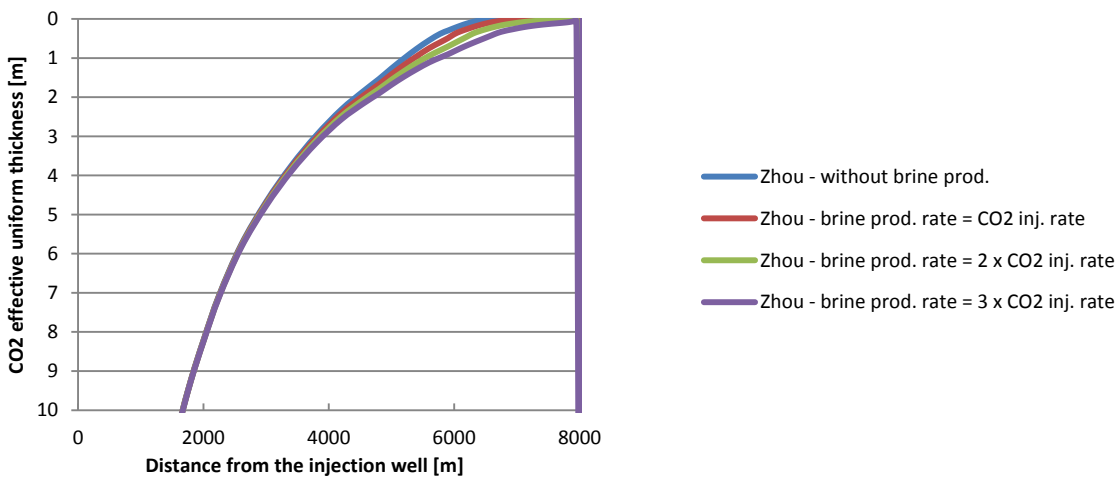
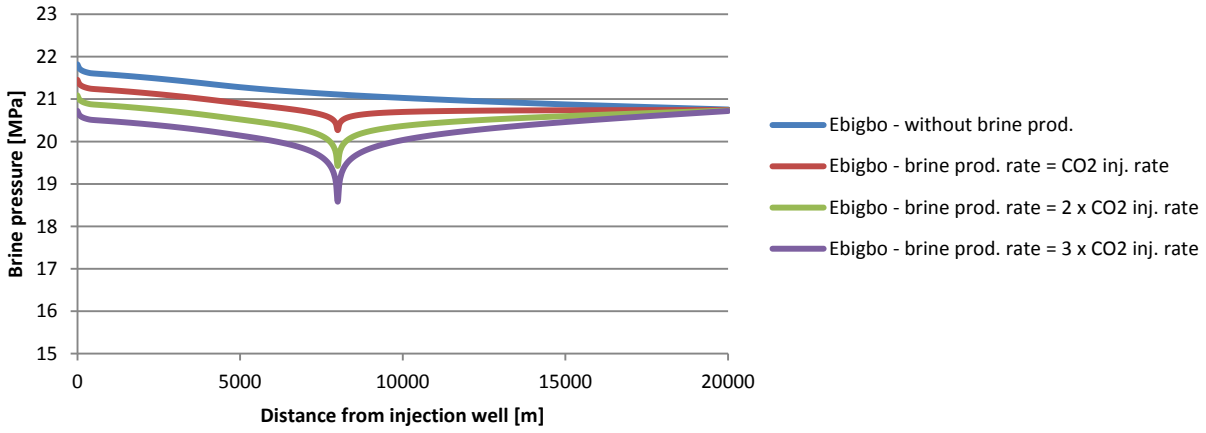


Figure 6.8: CO_2 effective uniform thickness zoomed in the upper 10 m of the injection formation, after 50 years injection from the finite-capillary-transition-zone vertically-integrated numerical model with saturation reconstruction for (a) Ebigbo and (b) Zhou formation parameters (see Figure 6.6) for various brine production rates.

a)



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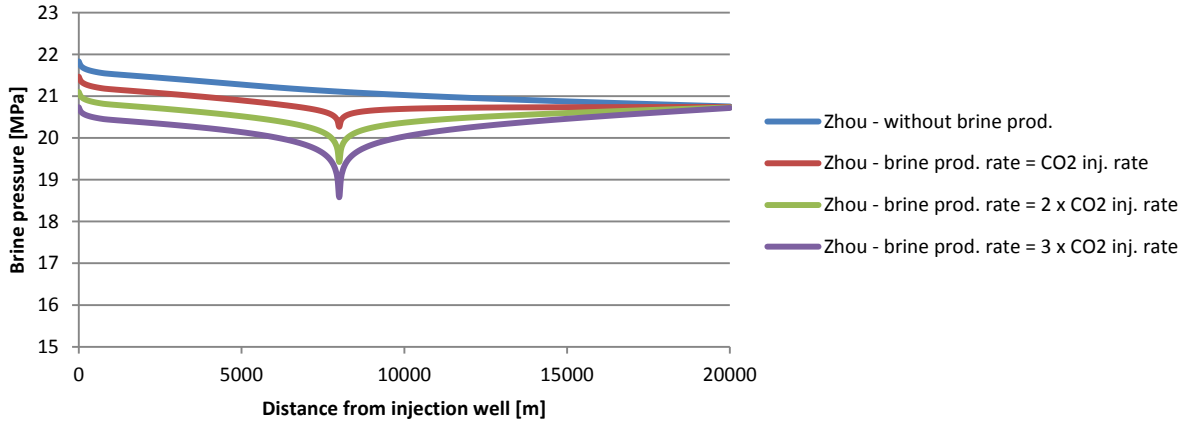

Figure 6.9: Pressure profile after 50 years injection from the finite-capillary-transition-zone vertically-integrated numerical model with saturation reconstruction for (a) Ebigbo and (b) Zhou formation parameters (see Figure 6.6) for various brine production rates.

6.5. Discussion

6.5.1. Management of brine disposal through potential advantageous uses

Chapter 5 (based on Court et al. (2011b)) indicated that water management is a newly identified challenge to the large-scale CCS implementation described in the introduction and should be actively and carefully considered across all CCS operations. Court et al. and several references therein proposed that water management should include both freshwater resources and brine management. The motivation for considering the integration of water management with CCS arises from the fact that CCS-retrofitted coal-fired power plants require about twice the cooling water of the original plant. Considering the required CCS implementation ramp-up described in introduction, this additional water need could put a significant strain on freshwater resources, especially in water-limited areas. However, a broader view of reservoir management leads to the possibility of brine production from the injection reservoir, which can provide cooling water while also allowing for significant reductions in pressure build-up in the injection reservoir. Such a strategy avoids additional stresses on local water resources, and also provides large-scale pressure management of the injection formation, as quantified in Sections 6.2 and 6.3, that can increase CO_2 injectivity potential, reduce the Area of Review (AoR), and decrease CO_2 and brine leakage risk.

However, unless beneficial brine-utilization options can be found that result in significant consumption of the produced brine, the production of brine volumes on the same order of magnitude (or larger) than the volume of CO_2 to be sequestered will present an important disposal challenge because traditional methods such as evaporation ponds or discharge to surface waters represent significant environmental risks. Therefore, a range of advantageous brine-utilization options coupled to surface use should be considered.

In regions with scarce water supplies and sufficiently low salinity brine formations, brine production coupled with desalination may constitute a viable source of cooling water to cover the additional water requirement associated with the CO_2 capture retrofitting process. It may also

provide freshwater or "greywater" suitable for irrigation or other industrial processes. These benefits could prevent water availability, already a sensitive public issue, from becoming a new barrier to CCS implementation.

Produced brine might also be used directly for cooling purposes, such as in saltwater or brackish-water cooling towers. Compared to desalination, this option requires less costly brine treatment, and because of the inherent evaporative losses, zero liquid discharge approaches for cooling towers can be useful by reducing (or even eliminating) the volume of residual brine requiring re-injection or disposal. In addition, produced brine will carry significant heat (which may be viewed as conflicting with its use as a coolant) that can have beneficial uses, such as capturing the heat , for example in a district heating system. Such a system could provide a significant benefit to the local community, thereby improving the CCS operation's public acceptance. Alternatively, if the temperatures are sufficiently high, an electricity-generating geothermal unit could cover part of the treatment plant energy penalty. It must be noted that some brines are of high salinity and include undesirable trace metals; these brines are not suitable for treatment and use and therefore should be fully re-injected or not produced. Such considerations may be part of the overall site characterization and suitability assessment.

Re-injection of either the untreated brine or the output of the treatment plant (more concentrated brine) could be advantageous in several ways. Injecting it in the CO_2 injection well could help immobilize and dissolve the injected CO_2, and injection in an additional, optimally-located well could reinforce a steering effort of the CO_2 plume in a "push-pull" injector/producer-well-pair strategy. Reinjection into an overlying aquifer could create a beneficial hydraulic barrier through over-pressurization, thereby reducing CO_2 and brine leakage risk. Because they have complementary requirements, the integration of CCS with geothermal energy recovery presents several interesting synergistic opportunities in these multiple-well reservoir management strategies. These complementary requirements come down to the fact that geothermal energy production is limited by pressure depletion, whereas pressure build-up limits CO_2 sequestration injectivity and increases leakage risk (see Buscheck (2010) and Buscheck et al. (2011b) for more details). It is worth noting that re-injection of the residual brine into the original CO_2 sequestration

formation or into oil, gas, or geothermal reservoirs will not necessitate additional geological characterization, while re-injection into a new formation will incur additional cost, and present additional leakage risk which needs to be considered.

6.5.2. CO_2 management to include or avoid breakthrough

Results in Sections 6.2.3 and 6.2.4 demonstrate that brine production well(s) can provide increased injectivity potential and can greatly reduce the AoR. Yet in order to have the largest possible impact, these wells may have to be close to the CO_2 injection well(s), thereby increasing the risk of CO_2 breakthrough. In this context, two possible scenarios may be discussed.

One scenario would be to actively incorporate CO_2 breakthrough in the CCS operation planning. One could envision including CO_2 breakthrough purposefully after 10 or 25 years of a 50-year injection to provide assurance to regulators that CO_2 is where it is supposed to be at a given time. The challenge would be that the operator would effectively "sacrifice" the first brine production well(s). Turning these production well(s), now monitoring well(s), into additional injection well(s) is an option that would represent a significant cost but, if carefully planned, could contribute to the required injection ramp-up described in the introduction. Another factor to consider is that brine production and the timing and location of CO_2 breakthrough, particularly when combined with "smart-well" technology with down-hole sensors and multiple independently-controlled production intervals, would provide valuable information about hydrogeological heterogeneity for history matching and reservoir management that would otherwise not be available (Buscheck et al., 2011a).

The second scenario would require the operator to avoid CO_2 breakthrough. This will be a requirement for systems where desalination or geothermal units are coupled to the CCS brine production infrastructure because of the technical incompatibility of the membranes and heat exchangers with the presence of CO_2 (Court et al., 2011b). Also if carbon credits are included in the financing of the CCS operation, CO_2 breakthrough will pose accounting challenges. Both of

these possible scenarios will have to be specifically adapted to the expected CO_2 plume vertical profile and outer extent, which motivated us to work on this initial quantification of brine production impacts on the plume in Section 6.4.

6.6. Conclusion

In order to have a significant effect on global atmospheric carbon emissions, the scale of CO_2 capture and geological sequestration in deep saline formations must be expanded by several orders of magnitude over the next two decades. This introduces a number of challenges, including those associated with water management, risk assessment, and public acceptance. These challenges lead to opportunities for a more active and integrated management approach, with potential synergies in resource use.

This Chapter, based on (Court et al., 2011d), investigates four specific synergies associated with coupled CO_2 injection and brine production. Our results demonstrate that brine production can provide an important pressure-control benefit by reducing both the injection well pressure, which enables higher injectivity potential, and reducing the extent of the AoR. For operators the AoR reduction potential allows smaller unitization for each CCS operation, reduces the area where monitoring and potential remediation will be necessary, and enables multiple independent injection operations to avoid operationally constraining each other. This AoR reduction also facilitates independent assessment and permitting by convincing regulators that each project is spatially distinct, can be independently operated, and that each operator is responsible for only one well-defined and non-overlapping AoR. AoR reduction also decreases the number of wells contacted by the critical pressure, thereby concurrently reducing brine leakage risk. Through all of these mechanisms, AoR reduction provides better assurance to local communities about the limited areal pressure perturbation and reduction of the associated risks including leakage to USDW. Our results also show that brine production can significantly reduce

the risk of CO_2 and brine leakage, especially in fields like those found in North America where a significant number of leakage pathways (in our case, abandoned wells) may exist within the AoR. We also conclude that effective steering of the CO_2 plume will require more sophisticated brine-production strategies, such as horizontal producers, than a single ring of vertical producers located outside of the 50-year CO_2 injection plume.

Coupled brine management and CO_2 injection provides clear benefits in terms of pressure management in the injection formation. Brine production can also provide important secondary benefits when coupled to water needs at the land surface or the beneficial use of extracted heat from the produced brine. Therefore, brine production should be included in the management of both basin-scale and single project local-scale CCS operations.

6.7. References

Abramson, E.H. 2009, "Viscosity of carbon dioxide measured to a pressure of 8 GPa and temperature of 673 K", *Phys.Rev.E,* vol. 80, no. 2, pp. 021201.

Bandilla Karl W., Kraemer Stephen R. & Birkholzer, J. 2011, "Using the concept of critical pressure to define the Area of Review for CO2 injection", *International Journal of Greenhouse Gas Control. in review.*

Birkholzer, J.T., Nicot, J.P., Oldenburg, C.M., Zhou, Q., Kraemer, S. & Bandilla, K. 2011, "Brine flow up a well caused by pressure perturbation from geologic carbon sequestration: Static and dynamic evaluations", *International Journal of Greenhouse Gas Control,* vol. In Press, Corrected Proof.

Birkholzer, J.T. & Zhou, Q. 2009, "Basin-scale hydrogeologic impacts of CO2 storage: Capacity and regulatory implications", *International Journal of Greenhouse Gas Control,* vol. 3, no. 6, pp. 745-756.

Buscheck, T. 2010, "Active Management of Integrated Geothermal-CO2-Storage Reservoirs in Sedimentary Formations: An Approach to Improve Energy Recovery and Mitigate Risk", *DE-FOA-0000336.*

Buscheck, T.A., Sun, Y., Chen, M., Hao, Y., Wolery, T.J., Bourcier, W.L., Court, B., Celia, M.A., Friedmann, S.J. & Aines, R.D. 2011a, "Active CO_2 reservoir management for carbon capture, utilization, and storage (CCUS): extracting brine to increase storage capacity, reduce risk, and generate useful products", *International Journal of Greenhouse Gas Control, submitted,*

Buscheck, T.A., Sun, Y., Hao, Y., Chen, M., Court, B., Celia, M.A. & Wolery, T.J. 2011b, "Geothermal energy production from actively-managed CO_2 storage in saline formations ", *Proceedings for the Geothermal Resources Council 35th Annual Meeting: 23-26 October 2011, San Diego, CA, USA.*

Buscheck, T.A., Sun, Y., Hao, Y., Wolery, T.J., Bourcier, W., Tompson, A.F.B., Jones, E.D., Julio Friedmann, S. & Aines, R.D. 2011c, "Combining brine extraction, desalination, and residual-brine reinjection with CO2 storage in saline formations: Implications for pressure management, capacity, and risk mitigation", *Energy Procedia,* vol. 4, pp. 4283-4290.

Celia, M.A. & Nordbotten, J.M. 2011, "How simple can we make models for CO2 injection, migration and leakage?", *Energy Procedia,* vol. 4, pp. 3857-3864.

Celia, M.A. & Nordbotten, J.M. 2009, "Practical Modeling Approaches for Geological Storage of Carbon Dioxide", *Ground Water,* vol. 47, no. 5, pp. 627-638.

Celia, M.A., Nordbotten, J.M., Court, B., Dobossy, M. & Bachu, S. 2011, "Field-scale application of a semi-analytical model for estimation of CO2 and brine leakage along old wells", *International Journal of Greenhouse Gas Control,* vol. 5, no. 2, pp. 257-269.

Class, H., Ebigbo, A., Helmig, R., Dahle, H., Nordbotten, J., Celia, M., Audigane, P., Darcis, M., Ennis-King, J., Fan, Y., Flemisch, B., Gasda, S., Jin, M., Krug, S., Labregere, D., Naderi Beni, A., Pawar, R., Sbai, A., Thomas, S., Trenty, L. & Wei, L. 2009, "A benchmark study on problems related to CO2 storage in geologic formations", *Computational Geosciences,* vol. 13, no. 4, pp. 409-434.

Court, B., Bandilla, K.W., Celia, M.A., Janzen, A., Dobossy, M.E. & Nordbotten, J.M. 2011a, "Applicability of the vertically-integrated approach and the sharp-interface assumption in carbon sequestration modeling", *International Journal of Greenhouse Gas Control, submitted.*

Court, B., Dammel, J.A., Elliot, T.R., Rohmer, J., Buscheck, T.A. & Celia, M.A. 2011b, " Promising synergies to address water, sequestration, legal, and public acceptance issues associated with large-scale implementation of CO2 sequestration", *Special Issue on Carbon Capture and Storage of The Journal for Mitigation and Adaptation Strategies for Global Change, in review.*

Court, B., Celia, M.A., Nordbotten, J.M. & Elliot, T.R. 2011c, "Active and integrated management of water resources throughout CO2 capture and sequestration operations", *Energy Procedia,* vol. 4, no. 4221, pp. 4229.

Court, B., Bandilla, K.W., Celia, M.A., Buscheck, T.A., Nordbotten, J.M., Dobossy, M.E. & Janzen, A. 2011d, "Initial evaluation of advantageous synergies associated with simultaneous brine production and CO2 geological sequestration", *International Journal of Greenhouse Gas Control, submitted.*

Federal Register 2010, "Federal Requirements Under the Underground Injection Control (UIC) Program for Carbon Dioxide (Finalized and Published rule)", *(75 FR 77230 (2010)) available at http://www.federalregister.gov/articles/2010/12/10/2010-29954/federal-requirements-under-the-underground-injection-control-uic-program-for-carbon-dioxide-co2#h-34.*

Fenghour, A., Wakeham, W.A. & Vesovic, V. 1998, "The Viscosity of Carbon Dioxide", *Journal of Physical and Chemical Reference Data,* vol. 27, no. 1, pp. 31-44.

Gasda, S., Nordbotten, J. & Celia, M. 2009, *Vertical equilibrium with sub-scale analytical methods for geological CO_2 sequestration*, Springer Netherlands.

Gasda, S.E., Bachu, S. & Celia, M.A. 2004, "Spatial characterization of the location of potentially leaky wells penetrating a deep saline aquifer in a mature sedimentary basin", *Environmental Geology,* vol. 46, no. 6-7, pp. 707-720.

Gasda, S.E. 2008, "Numerical Models for Evaluating CO2 Storage in Deep Saline Aquifers: Leaky Wells and Large-scale Geological Features", *Ph.D Thesis available at http://arks.princeton.edu/ark:/88435/dsp01j098zb09n.*

Guswa, A.J. & Celia, M.A. 2001, "Hydraulic Controls on Injection of Carbon Dioxide into Deep Saline Aquifers", *available at http://arks.princeton.edu/ark:/88435/dsp01d791sg17d.*

Janzen, A. 2010, "Development and Application of a Multi-scale, Multi-layer Numerical Model for CO2 Injection", *Master's Thesis available at http://arks.princeton.edu/ark:/88435/dsp01np193917f.*

Lake, L. 1989, *Enhanced Oil Recovery,* Prentice Hall.

McPherson, B.J.O.L., Han, W.S. & Cole, B.S. 2008, "Two equations of state assembled for basic analysis of multiphase CO2 flow and in deep sedimentary basin conditions", *Computers & Geosciences,* vol. 34, no. 5, pp. 427-444.

Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L. & (Eds.) 2005, *IPCC Special Report on Carbon Dioxide Capture and Storage,* New York, NY: Cambridge University Press.

Michael, K., Bachu, S., Buschkuehle, B.E., Haug, K. & Talman, S. 2009, "Comprehensive Characterization of a Potential Site for CO2 Geological Storage in Central Alberta, Canada.",

In: Grobe, M., Pashin, J., Dodge, R., (Eds.), Carbon Dioxide Sequestration in Geological Media – State of the Art, AAPG Studies in Geology, vol. 59, pp. 227-240.

Nilsen, H., Herrera, P.A., Ashraf, M., Ligaarden, I., Iding, M., Hermanrud, C., Lie, K., Nordbotten, J.M., Dahle, H.K. & Keilegavlen, E. 2011, "Field-case simulation of CO2 -plume migration using vertical-equilibrium models", *Energy Procedia,* vol. 4, pp. 3801-3808.

Nicot, J., Oldenburg, C.M., Bryant, S.L. & Hovorka, S.D. 2009, "Pressure perturbations from geologic carbon sequestration: Area-of-review boundaries and borehole leakage driving forces", *Energy Procedia,* vol. 1, no. 1, pp. 47-54.

Nitao, J.J. 1998, "Reference manual for the NUFT flow and transport code, version 3.0", *Lawrence Livermore National Laboratory, UCRL-MA-130651-REV-1.*

Nogues, J.P., Court, B., Dobossy, M., Nordbotten, J.M. & Celia, M.A. 2011, "Quantifying CO2 Leakage in a Geological Sequestration Operation under Parameter Uncertainty", *International Journal of Greenhouse Gas Control, in review.*

Nordbotten, J.M. & Celia, M.A. 2011, "Geological Storage of CO2: Modeling Approaches for Large-Scale Simulation", *with John Wiley and Sons, Inc., in press.*

Nordbotten, J.M., Celia, M.A., Bachu, S., 2004. Analytical solutions for leakage rates through abandoned wells. Water Resour. Res. 40 (4), W04204.

Nordbotten, J.M., Celia, M.A. & Bachu, S. 2005, "Injection and storage of CO2 in deep saline aquifers: Analytical solution for CO2 plume evolution during injection", *Transport in Porous Media,* vol. 58, no. 3, pp. 339-360.

Nordbotten, J.M., Celia, M.A., Bachu, S. & Dahle, H.K. 2005, "Semianalytical solution for CO2 leakage through an abandoned well", *Environmental science & technology,* vol. 39, no. 2, pp. 602-611.

Nordbotten, J.M. & Dahle, H.K. 2011, "Impact of the capillary fringe in vertically integrated models for CO2 storage", *Water Resources Research,* vol. 47, no. 2, pp. W02537.

Nordbotten, J.M. & Celia, M.A. 2006, "Similarity solutions for fluid injection into confined aquifers", *Journal of Fluid Mechanics,* vol. 561, pp. 307-327.

Oldenburg, C.M., 2008. Screening and ranking framework for geologic CO2 storage site selection on the basis of health, safety, and environmental risk. Environ. Geol. 54(8),1687–1694.

Pruess, K. 2004, "The TOUGH Codes—A Family of Simulation Tools for Multiphase Flow and Transport Processes in Permeable Media", *Vadose Zone J.,* vol. 3, pp. 738-746.

Pruess, K. & Nordbotten, J.M. 2011, "Numerical simulation studies of the long-term evolution of a CO2 plume in a saline aquifer with a sloping caprock", *submitted to Transport in Porous Media.*

Réveillère, A. & Rohmer, J. 2010, "Managing the risk of CO2 leakage from deep saline aquifer reservoirs through the creation of a hydraulic barrier", *to be submitted to the GHGT10 conference in Amsterdam.*

Schlumberger 2010, "ECLIPSE Technical Description".

USEPA (U.S. Environmental Protection Agency) 1994, "Determination of Maximum Injection Pressure for Class I Wells, United States Environmental Protection Agency Region 5—Underground Injection Control Section Regional Guidance #7", *EPA, Washington, DC, USA; available at http://www.epa.gov/r5water/uic/r5guid/r5_07.htm.*

White, M.D. & Oostrom, M. 1997, "STOMP, Subsurface Transport Over Multiple Phases", *Pacific Northwest National Laboratory Report PNNL-11218, Richland, WA, October 1997.*

Yortos, Y.C. 1995, "A theoretical analysis of vertical flow equilibrium", *Transport in Porous Media,* vol. 18, pp. 107-129.

Chapter 7

Concluding remarks and future research

7.1. Summary and conclusion

Stabilization of atmospheric CO_2 concentrations to current levels requires practical strategies to address society's dependence on fossil fuels. This dependence is particularly acute in the case of coal, which is projected to continue dominating worldwide baseload-electricity production in the following decades. CO_2 Capture and Sequestration (CCS) is currently the only technology that could allow the required transition period, of simultaneous continued coal burning and mitigation of the resulting high CO_2 emissions, until the necessary low-carbon energy infrastructure can be put in place. This mitigation will require CCS demonstration projects to increase by several orders of magnitude in both number and scale across the globe over the next two decades (as discussed in detail in Chapter 1). This task has several potential implementation barriers which will have to be taken into account. The two main objectives of this dissertation focused on the previously identified CO_2 sequestration safety implementation barrier, and the newly identified CCS water implementation barrier which is only starting to gain attention in the CCS community. The first objective was to advance the capability to model CO_2 injection, migration, and associated pressure field to quantify the CO_2 and brine leakage risk; and to identify the limitation of the modeling approach used. The second objective was to improve the current CCS paradigm

by considering both the surface and subsurface CCS systems and their implementation challenges more globally, and by integrating water management across all CCS operations.

The first part of this dissertation (Chapters 2 through 4) examined the primary risks of sequestration and required models to adequately address them, provided analysis to quantify the risk of CO_2 and brine leakage through abandoned wells, and investigated the applicability of the models and assumptions used.

Chapter 2 identified practical CO_2 sequestration safety questions facing almost all CCS operations, and reviewed the newly developed modeling approaches used to address them. CO_2 sequestration safety is impaired by numerous complex leakage pathways with often unknown locations and highly uncertain parameters. Traditional complex numerical tools are useful in providing physical insights into CO_2 behavior, but often inappropriate to investigate risk associated with leakage because the parametric uncertainty requires probabilistic assessments with prohibitive computational cost. Therefore, a hierarchy of vertically-integrated CO_2 injection and migration models, which become sequentially simpler as more restrictive assumptions are applied, was developed by our research group. These models can now provide accurate answers to all of the primary practical safety questions identified. This set of vertically-integrated models includes the sharp-interface semi-analytical/analytical models, and vertically-integrated numerical models including capillary forces via mathematical reconstruction, both of which were used in this dissertation.

Based on a specific field site in Alberta, Canada, and using the sharp-interface semi-analytical model, Chapter 3 provided the first quantification of field-scale CO_2 and brine leakage risks through abandoned wells during an industrial multi-million ton injection of supercritical CO_2. The probabilistic risk analysis focused on the parametric uncertainty associated with these abandoned wells during the injection period, when risk of leakage is expected to be largest. This leakage risk assessment used a novel dataset collected near Edmonton which includes the stratigraphy from a 50km x 50km field site and the properties of 1146 abandoned wells located within it. The simulations involved injection, migration, and leakage over a 50-year time horizon

for domains having multiple layers in the sedimentary succession. Thanks to the efficiency of the model, performing each simulation in a few minutes of computer time, probabilistic investigation results based on tens of thousands of simulations could be done. These established the importance of residual brine saturations, quantified the impact of leaky well properties, and examined the effects of depth of injection on CO_2 and brine leakage risk.

Chapter 4 investigated the applicability of vertically-integrated models and the validity of the sharp-interface assumption via direct comparisons with the ECLIPSE commercial simulator, for a range of injection rates, injection durations, and formation characteristics. Our findings demonstrated that the applicability of the vertically-integrated modeling approach depends on the time scale of the permeability-dominated vertical brine drainage within the CO_2 plume. The validity of the sharp-interface assumption was then shown to depend on the spatial scale of capillary forces. Simple metrics involving the time scale for this buoyant segregation and the spatial scale for the so-called Capillary Transition Zone (CTZ) provide valuable information about the way the system will behave and, more importantly, about the levels of simplification that can be used in modeling. Our finite-CTZ vertically-integrated numerical model results with saturation reconstruction closely matched 3D ECLIPSE model runs including capillary pressure, when fluids are fully segregated. Finally, the inclusion of drainage dynamics was identified as a promising improvement to both analytical and finite-CTZ vertically-integrated numerical models to provide accurate results in cases when fluids are not yet fully segregated.

The second part of this dissertation (Chapters 5 and 6) presented a paradigm shift in the way the CCS system is considered and argued that the newly identified CCS water management challenge should be carefully taken into account across all CCS operations. The CCS surface facility and subsurface environment ought to be viewed comprehensively and their respective implementation challenges examined collectively.

Chapter 5 provided a complete review of water, sequestration, legal, and public acceptance potential barriers to CCS implementation and proposed a novel active and integrated CCS operation management framework to address them. Our main finding was that, while

somewhat daunting in scope, some of these challenges can be addressed more easily by recognizing multiple potential advantageous synergies that can be exploited when these challenges are dealt with in combination. For example, the doubling of cooling-water required by the CO_2 capture retrofitting process was only recently identified as a significant challenge to CO_2 capture implementation. Supplying this additional water requirement from conventional water sources will be technically challenging and highly publicly sensitive in water stressed areas. At the same time, the extended area of pressure perturbation and CO_2 and brine leakage risks of the CO_2 sequestration operation will also present regulatory and public acceptance challenges. The likely pressure-buildup-control solution involving brine production is associated with a problematic disposal of the produced brine. We argued that, among other synergies, an active management of water resources can address both surface and subsurface challenges. Brine production and treatment can synergistically provide this additional cooling-water (and potential geothermal power / district heating) while simultaneously reducing the Area of Review and leakage risk, which will streamline regulatory permitting while furthering efforts toward public acceptance. The exploitation of the multiple promising synergies identified in the proposed active and integrated framework, increases the potential for successful large-scale implementation of CCS.

Finally, Chapter 6 quantified the advantageous impacts of three of these identified synergies through coupling simultaneous brine production to a large-scale CO_2 geological sequestration operation. Our results demonstrated that brine production can provide an important pressure-control benefit by reducing both the injection well pressure, which enables higher injectivity potential, and the extent of the Area of Review, which regulators may want to control and for which operators have to buy property rights, monitor, and potentially remediate. Our findings showed that brine production can also significantly reduce the risk of CO_2 and brine leakage through abandoned wells.

In summary, this dissertation provides novel and important contributions in advancing the fields of CO_2 sequestration safety modeling focusing on leakage risk, and in addressing CCS

potential implementation barriers with a specific focus on the new water challenge through the active and integrated framework proposed. By integrating the modeling progress, findings, and the broader considerations of the CCS surface facility together with the subsurface environment presented in this dissertation, future work has the potential to provide a more complete understanding of both the CCS system and implementation barriers. Future work can also make the presented hierarchy of very useful modeling tools available to CCS operators, regulatory agencies, and local communities. These modeling tools are going to be essential in CCS project screening and permitting. They can help justify additional data collection, more complex numerical modeling, or pilot testing; can aid in communication and public acceptance efforts; and may become a requirement for legal and regulatory purposes. The exploitation of the identified synergies provides the best possibilities for the required large-scale CCS implementation to be successful.

7.2. Future research directions

In the following section I will briefly highlight a few key future research directions to continue the work presented in this dissertation:

- Populate a database of abandoned well hydraulic properties (effective well segment permeability) through an experimental program in the field (see Gasda et al. (2010) and Gasda (2008)). This will be essential to improve our mapping of scores into permeabilities and the use of distribution like the bimodal distribution (see Chapter 3). Until this database is developed, these mappings/well treatments will remain hypothetical, constrained only by expert opinion and simple estimates associated with micro-annular flows

- Investigate the optimal number and location of injection well(s) depending on this improved abandoned well properties treatment (and cost) to minimize the number of very leaky wells

contacted; horizontal injection wells to address injectivity limitation; sequestration operation with multiple injection wells & multiple injection formation simultaneously; and the efficiency of abandoned wells remediation on leakage risk reduction.

- Include faults, fractures, and diffuse leakage in the leakage risk analysis.

-Treat fluid phases, and wells and/or formation properties dynamically through time when geochemical or geomechanical modeling codes, or appropriate experimental data, become available and possible to include in the model as additional modules. For example, in flow along poorly sealed abandoned wells shallower than 800m, complex nonisothermal effects may need to be coupled with the multi-phase flow along the wellbore. This would be a very involved calculation in full 3D numerical model. But in the multi-scale context it could be made manageable by only performing the calculation along the (one-dimensional) shallow well segment(s) of the leakiest wells across the aquitard of interest. Cement degradation will obviously impact well segment effective permeability through time and should be taken into consideration. Geochemistry of CO_2 and brine may impact formations permeability and porosity. Geomechanical effects close to the injection/production wells (during and after operations) may impact aperture of cracks inside wellbores or fractures and again impact the effective permeability.

- Increase the scope of application (when fluids are not fully segregated) of vertically-integrated models by including brine drainage dynamics. Determine capillary transition zone thickness threshold for sharp-interface assumption validity (see Chapter 4 and references therein for both).

- Pursue hybrid modeling for investigation of heterogeneity/sloping/non flat injection formation(s) while shallow formation are still considered horizontal, homogeneous and isotropic when appropriate (see future work section of (Janzen, 2010)).

- Include the presented findings into basin-scale analysis most likely based on multi-scale analysis which represent on-going work by Nordbotten and Celia, and into large field studies (Wyoming, Basal, Mont Simmons projects) pursued by Celia and Peters's groups in the CEE department.

- Couple subsurface CO_2 injection, migration, and CO_2 and brine leakage risk analysis to surface geospatial analysis of CO_2 capture and transport implementation; pore space competition (with shale gas, water pumping and storage, natural gas storage etc…); and regulation (AoR and leakage), insurance and public acceptance large scale studies.

- Do not ignore the water CCS challenges! Quantify the impact of large-scale CCS implementation on water resources in areas both promising CCS and water stressed such as the Midwest of the US, China, Australia, the Middle East etc…

- Examine full scale case studies to quantify CCS operation CO_2/ water / heat / cost budget analysis including the power plant (building on the work of Dr. Williams, Dr. Kreutz, Dr. Larson in Princeton), the subsurface sequestration operation (Chapters 5 and 6 and references therein), and the coupling of the two via brine production and likely brine treatment and/or geothermal unit (see work by Buscheck and Lawrence Livermore National Laboratory colleagues and references in Chapters 5 and 6).

- Explore cost benefit analysis of all the synergies identified in Chapter 5.

- Continue the investigation of more complex strategies of coupling of CO_2 injection and simultaneous brine production (horizontal wells, sequential rings of vertical brine production wells, heterogeneity, sloping/non flat injection formation, brine re-injection strategies in or above the injection formation etc..)

- Integrate the implication of the presented results and concepts in the CCS legal & regulatory (water rights implications) and public acceptance fields (brine utilization [cooling water, geothermal power, district heating, “grey water” for irrigation and other industrial uses] and CO_2 utilization [EOR]).

- Communicate the CCS system challenges more globally across fields (capture / sequestration), expertise (engineering, maths, modeling, legal, social sciences, policies), and institutions (industry, academia, government, NGO, start-ups, local community).

-Actively research arguments (air quality, job development, energy security) and synergies (see Chapter 5) that could facilitate the required implementation of CCS, understand and address potential barriers, and include external factors (financial crisis, japan nuclear disaster, shale gas boom…) into CCS implementation roadmaps and how they affect the portfolio of mitigation strategies (for example we must compare the cost of renewable to the cost of coal+CCS and not coal without CCS).

- Finally make sure that CCS demonstration projects are not only applied in the OECD countries and the power sector. The United Nation Industrial Development Organization held a workshop in September 2010 on their current effort to develop an Industrial Sector CCS Roadmap (see (UNIDO 2010)). Several points were highlighted at this workshop, which I believe should be a lot more present in the CCS industry and debates. Non-power sector industries (cement, iron&steel, refineries and biomass) represent 40% of global energy related CO_2 emissions. The majority of current CCS demonstration projects are occurring in the power sector and in developed countries. However, according to IEA (2010), of the 20% CO_2 abatement total mitigation effort that CCS is forecasted to contribute to, half of it to be provided by CCS will be in the non-power sectors, and much of it would occur in developing countries. And contrary to the power sector CCS alternatives do not exist for industrial processes (coal-fired electricity could be produced by switching to nuclear but there is no carbon free process to make iron, cement and steel). And

considering CCS in industrial sector would not come with coal industry/lobby/mining challenges and related strong public and activist oppositions. Decoupling and depolarization of CCS and coal could in my view be very beneficial. One can wonder what would have been the CCS development if industrial sources of CO_2 and not power sector had been the focus of early CCS development (the reason to start with power sector was likely because it is a better environment to secure decadal contracts and thus investment compared to non-power sector more prone to annual variation depending on demand).

In summary, this dissertation opens a large number and very diverse set of new and exciting topics in the vibrant field of CO_2 sequestration safety modeling, and new fields of CCS water challenges, integration, and global implementation.

7.3. References

Gasda, S.E. 2008, "Numerical Models for Evaluating CO2 Storage in Deep Saline Aquifers: Leaky Wells and Large-scale Geological Features", *Ph.D Thesis available at http://arks.princeton.edu/ark:/88435/dsp01j098zb09n*

Gasda, S.E., Wang, J.Z. & Celia, M.A. 2010, "Analysis of in-situ wellbore integrity data for existing wells with long-term exposure to CO2", *Proceedings of the GHGT-10 conf., Amsterdam, .*

Janzen, A. 2010, "Development and Application of a Multi-scale, Multi-layer Numerical Model for CO2 Injection", *Master Thesis available at http://arks.princeton.edu/ark:/88435/dsp01np193917f.*

UNIDO - United Nations Industrial Development Organization 2010, "Carbon Capture and Storage in Industrial Applications: Technology Synthesis Report Working Paper", available at http://www.unido.org/fileadmin/user_media/Services/Energy_and_Climate_Change/Energy_Efficiency/CCS/synthesis_final.pdf

IEA 2010, "World Energy Outlook 2010 Executive Summaries", available at http://www.worldenergyoutlook.org/,