

Report Title: Developing a Comprehensive Risk Assessment Framework for Geological Storage of CO₂

Type of Report: Final Scientific

Reporting Period Start Date: October 1, 2009

Reporting Period End Date: August 31, 2014

Principal Author: Ian J. Duncan

Date Report was Issued: December, 2014

DOE Award Number: DE-FE0001563

Name and Address of Submitting Organization: The University of Texas at Austin
Jackson School of Geosciences
Bureau of Economic Geology
University Station, Box X
Austin, Texas 78713

Submitted to: U.S. Department of Energy
National Energy Technology Laboratory

DISCLAIMER

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

ABSTRACT

The operational risks for CCS projects include: risks of capturing, compressing, transporting and injecting CO₂; risks of well blowouts; risk that CO₂ will leak into shallow aquifers and contaminate potable water; and risk that sequestered CO₂ will leak into the atmosphere. This report examines these risks by using information on the risks associated with analogue activities such as CO₂ based enhanced oil recovery (CO₂-EOR), natural gas storage and acid gas disposal.

We have developed a new analysis of pipeline risk based on Bayesian statistical analysis. Bayesian theory probabilities may describe states of partial knowledge, even perhaps those related to non-repeatable events. The Bayesian approach enables both utilizing existing data and at the same time having the capability to adsorb new information thus to lower uncertainty in our understanding of complex systems.

Incident rates for both natural gas and CO₂ pipelines have been widely used in papers and reports on risk of CO₂ pipelines as proxies for the individual risk created by such pipelines. Published risk studies of CO₂ pipelines suggest that the individual risk associated with CO₂ pipelines is between 10⁻³ and 10⁻⁴, which reflects risk levels approaching those of mountain climbing, which many would find unacceptably high. This report concludes, based on a careful analysis of natural gas pipeline failures, suggests that the individual risk of CO₂ pipelines is likely in the range of 10⁻⁶ to 10⁻⁷, a risk range considered in the acceptable to negligible range in most countries. If, as is commonly thought, pipelines represent the highest risk component of CCS outside of the capture plant, then this conclusion suggests that most (if not all) previous quantitative-risk assessments of components of CCS may be orders of magnitude to high.

The potential lethality of unexpected CO₂ releases from pipelines or wells are arguably the highest risk aspects of CO₂ enhanced oil recovery (CO₂-EOR), carbon capture, and storage (CCS). Assertions in the CCS literature, that CO₂ levels of 10% for ten minutes, or 20 to 30% for a few minutes are lethal to humans, are not supported by the available evidence. The results of published experiments with animals exposed to CO₂, from mice to monkeys, at both normal and depleted oxygen levels, suggest that lethal levels of CO₂ toxicity are in the range 50 to 60%. These experiments demonstrate that CO₂ does not kill by asphyxia, but rather is toxic at high concentrations. It is concluded that quantitative risk assessments of CCS have overestimated the risk of fatalities by using values of lethality a factor two to six lower than the values estimated in this paper. In many dispersion models of CO₂ releases from pipelines, no fatalities would be predicted if appropriate levels of lethality for CO₂ had been used in the analysis.

TABLE OF CONTENTS

EXECUTIVE SUMMARY.....	5
Section 1: Introduction, Nature of Risk, Objectives and Overview	7
Section 2: Subsurface Risks Associated with CO ₂ Sequestration	11
Section 3: Above Ground Risks of CCS Projects	50
Section 4: Mechanical Integrity CO ₂ -EOR wells and Implications for Long Term Risks of CO ₂ Sequestration in Brine Reservoirs	63
Section 5: Re-evaluating CO ₂ Toxicity and Lethality: Implications for Risk Assessments of Carbon Capture and Storage (CCS)	77
Section 6: Protocols for Monitoring Environmental Risk from Leakage of CO ₂ Sequestered in Deep Brine Reservoirs	108
Section 7: Application of Bayesian Inference to Risks Associated with CO ₂ Sequestration	138
Section 8: Programmatic Risks Faced by Carbon Capture and Storage Projects	162
Section 9: Estimating the Likelihood of Pipeline Failure in CO ₂ Transmission Pipelines: New Insights on Risks of Carbon Capture and Storage	191
Section 10: Evaluating the Likelihood of Pipeline Failures for Future Offshore CO ₂ Sequestration Projects	238
CONCLUSIONS.....	293
GRAPHICAL MATERIALS LIST.....	295
LIST OF ACRONYMS AND ABBREVIATIONS.....	297
Appendix: Papers from the Project	298

EXECUTIVE SUMMARY

The operational risks for CCS projects include: (1) The risks of capturing, compressing, transporting and injecting CO₂; (2) The risk of blowouts or very rapid CO₂ release from wells; (3) The risk that CO₂ put into long term geologic storage will leak into shallow aquifers and contaminate potable water; and (4) The risk that sequestered CO₂ (and possibly associated methane gas) will leak into the atmosphere. This report examines these risks by using information on the risks associated with analogue activities such as CO₂ based enhanced oil recovery (CO₂-EOR), natural gas storage and acid gas disposal. The four decade history of CO₂ injection involved in CO₂ based Enhanced Oil Recovery in the US represent the most tangible evidence available for understanding the risks of CO₂ sequestration in deep brine reservoirs. Where possible we have used this record to inform our risk estimates.

Geologic CO₂ sequestration in deep brine reservoirs is considered as a key technology for large scale mitigation of greenhouse gas emissions. Earlier risk assessments have identified a number of sub-surface related risks including: catastrophic leakage from fault zones; catastrophic CO₂ emulsion from slow leakage, and ground heave, that simply are not credible. They have overused the word catastrophic and presented an inflated impression of the subsurface risks associated with CCS. The short- and long- term risks of CO₂ leakage on drinking water resources, surface and subsurface ecosystems, and energy resources based on natural analogues are analyzed. Where careful studies have been able to quantify risks from sub-surface CO₂ utilizing analogues, they are on the order of 10⁻⁸, two orders of magnitude smaller than risks normally considered of societal concern.

We have developed a new analysis of pipeline risk based on Bayesian statistical analysis. Bayesian theory probabilities may describe states of partial knowledge, even perhaps those related to non-repeatable events. The Bayesian approach enables both utilizing existing data and at the same time having the capability to adsorb new information thus to lower uncertainty in our understanding of complex systems.

The potential lethality of unexpected CO₂ releases from pipelines or wells are arguably the highest risk aspects of CO₂ enhanced oil recovery (CO₂-EOR), carbon capture, and storage (CCS). Assertions in the CCS literature, that CO₂ levels of 10% for ten minutes, or 20 to 30% for a few minutes are lethal to humans, are not supported by the available evidence. The results of published experiments with animals exposed to CO₂, from mice to monkeys, at both normal and depleted oxygen levels, suggest that lethal levels of CO₂ toxicity are in the range 50 to 60%. These experiments demonstrate that CO₂ does not kill

by asphyxia, but rather is toxic at high concentrations. It is concluded that quantitative risk assessments of CCS have overestimated the risk of fatalities by using values of lethality a factor two to six lower than the values estimated in this paper. In many dispersion models of CO₂ releases from pipelines, no fatalities would be predicted if appropriate levels of lethality for CO₂ had been used in the analysis.

Incident rates for both natural gas and CO₂ pipelines have been widely used in papers and reports on risk of CO₂ pipelines as either implicit or explicit proxies for the individual risk created by such pipelines. Published risk studies of CO₂ pipelines suggest that the individual risk associated with CO₂ pipelines is between 10⁻³ and 10⁻⁴, which reflects risk levels approaching those of mountain climbing, which many would find unacceptably high. This report concludes, based on a careful analysis of natural gas pipeline failures, suggests that the individual risk of CO₂ pipelines is likely in the range of 10⁻⁶ to 10⁻⁷, a risk range considered in the acceptable to negligible range in most countries. If, as is commonly thought, pipelines represent the highest risk component of CCS outside of the capture plant, then this conclusion suggests that most (if not all) previous quantitative-risk assessments of components of CCS may be orders of magnitude to high.

This study also examined the likelihood of pipeline failures associated with offshore CO₂ pipelines for sequestration projects by evaluating the safety track record for offshore natural gas pipelines, using a 20-year detailed dataset available from the agency that regulates offshore pipelines in the US. Based on this analysis, it is concluded that the risks of future fatalities from offshore CO₂ pipelines are on the order of 10⁻⁷ km • yr., a level of risk that most authorities would see as negligible. The rate of serious incidents reported for offshore U.S. natural gas pipelines have been significantly increasing over the last decade. Our analysis suggests that this is an artifact correlated with increasing natural gas prices, which results in more incidents exceeding the \$US 50,000 damage criterion. The dominant risk of injuries and fatalities in offshore natural gas pipelines come from fires on offshore platforms. The rate of failure for offshore transmission pipelines is estimated as 5 x 10⁻⁴ versus 3 x 10⁻⁴ km • yr. for gathering pipelines. This may be explained by the difference in average age (27.7 for gathering and 32.9 years for transmission), or because transmission pipelines are operated closer to their maximum allowable operation pressures than are offshore gathering pipelines. The fatality rate for offshore natural gas pipelines is essentially the same as for those onshore however none of the recorded deaths in the data set were related to failures of pipeline integrity. As a result of the minimal exposure of workers (and the general public), to the impacts of CO₂ releases in the offshore environment it is argued that the fatality rate associated with CO₂ pipelines will likely be lower than for natural gas pipelines. Assuming that a future offshore CO₂ sequestration project is based on sea floor injection and control systems, risk mitigation efforts clearly should focus on the near shore portion.

Section 1.0: Introduction

The goal of this project was to develop a comprehensive analysis of programmatic (business) and technical risks associated with CO₂ storage in deep brine reservoirs. To meet this goal, objectives included quantifying these risks by: employing Bayesian inference to evaluate sequestration risks; utilize the safety record of the CO₂ based Enhanced Oil Recovery industry (CO₂-EOR) and pilot sequestration projects to identify and evaluate potential risks; develop and quantify the nature of programmatic risks; utilize diverse, highly qualified expert panels drawn from industry and nongovernmental organizations (NGO) to evaluate changing perceptions of programmatic risks; developing an understanding and quantify the role that a pressure field generated by injected CO₂ (and the dissolution of CO₂ from the plume into the brine phase) may play in risk; and assessing the possible consequences to water ecology and energy resources from potential leakage of CO₂ from deep brine reservoirs.

The project was structured into two major technical tasks to accomplish this goal and objectives:

Task 2: Development and Application of Conceptual Framework for Risk Assessment for CO₂ Sequestration Projects in Deep Brine Reservoirs

Task 3: Development of Protocols for Risk Assessment for Geologic Sequestration in Brines

The following report describes the research performed in each task and the results.

Nature of Risk

Risk is a measure of rates human fatalities, injuries, and/or property/environmental damage. Risk has two components, the likelihood or probability of a pipeline failure and the consequences (magnitude of the resultant damages). The consequences of a CO₂ pipeline failing for example can be economic losses, possibly serious injuries or fatalities, and more rarely environmental damages.

Geologic sequestration lacks a large historical data base that would enable computation of long term risks. Elkington (2007) has asserted that “Lack of actuarial data on integrated large scale projects coupled with an absence of uniform international regulation creates major obstacles to risk management, private investment and wide-scale deployment”. In the language of risk analysis (Ellsberg, 1961) such systems are “ambiguous”. In essence the term ambiguity refers to imprecisely specified probabilities. Decision makers are more adverse to ambiguous situations, than they are to risky ones. For example insurers are known to seek higher premiums for projects that are perceived as ambiguous, than for those known to be risk prone (Hogarth and Kunreuther, 1989).

Overview

The IPCC special report on carbon dioxide capture and storage (Benson et al. 2005) suggested that the above ground risks of CO₂ storage in brine reservoirs would be similar to the risks of analog industrial activities such as CO₂ based enhanced oil recovery (CO₂-EOR), deep injection disposal of acid (H₂S rich) gas, and natural gas storage in underground reservoirs. At the time the IPCC report was written quantitative evaluations of the risks of these analogue activities were not available to the authors. Over the last decade studies have been published on some aspects of the risks associated with these activities. Unfortunately some aspects of these analogue activities have limited relevance to CCS and should not be uncritically applied to inferring the risks associated with sequestration activities. As a result a comprehensive analysis of the above ground risks associated with future CCS projects is still lacking.

In conducting this project research to develop a comprehensive analysis of risk associated with CO₂ storage over the last four years, our project team has made a number of discoveries regarding both methodology and fact that have influenced modifying our originally proposed pathways. For example we discovered that CO₂ was toxic and killed only at high levels in air (on the order of 50%), rather than being non-toxic and killing by asphyxia at levels as low as 10%. This discovery led us to reevaluate the whole basis for previous risk analyses of CCS. We also discovered in this project that the data set for safety of CO₂ pipelines and for blowouts of CO₂ injection wells was too small to have any statistical reliability (and that previous analyses of these data were highly problematic). For examples, CO₂ pipelines in the US have not been associated with any fatalities, injuries or even pipeline ruptures. This made it impossible to apply bayesian inference without basing it on totally fabricated numbers. As a result we found it necessary to use data from analogues such as the safety record of natural gas pipelines that allowed examining much larger data sets.

In developing a new comprehensive framework for assessing both the programmatic and the technical risks associated with CO₂ sequestration in deep brine reservoirs the project set out to achieve a number of goals. In some cases the research has been published in international journals. In other cases, articles for journals are still being prepared and the material exists as unpublished reports. One goal was to establish a panel of experts to establish a measure of the relative and absolute programmatic risks and their linkages to technical risks by a formal process of elicitation. This was carried out via a meeting of experts held in the Federal Reserve Building in Houston. Based on this study a paper was prepared for publication. A report was prepared on a risk framework based on Bayesian inference to be used in the design, implementation, permitting and monitoring of projects to sequester CO₂ in deep brine reservoirs.

A major goal of the project was to utilize information from the safety record of the CO₂ EOR industry to infer the risks associated with future CO₂ sequestration in deep brine reservoirs. The success of using this kind of data has been mixed. The first data set examined was that of CO₂ pipelines. Unintentional releases associated with failure of

CO₂ pipelines is arguably the highest risk to public safety associated with CCS. We discovered early in the project that there were no significant accidents (no fatalities or injuries and no significant pipeline failures) associated with CO₂ pipelines. As a result our project has focused on the safety record of natural gas pipelines as an analog for CO₂ pipelines. Natural gas pipelines are an excellent analog as they follow the same design code, steel types, fabrication, and installation methods.

Another project goal was to compile and evaluate well integrity data for CO₂ injection wells including the likelihood of well blowouts and/or leakage. This Task has resulted in a paper for publication. Similarly our goal of exploring the role that the dissolution of CO₂ from the plume into the brine may play in risk resulted in a publication by Professor Hesse. Working on goal of developing a methodology of analyzing risk from CO₂ injection to inducing faulting that may breach a reservoir and cause associated seismic activity was terminated as a project decision point. Similarly using risk data from the natural gas storage industry was discontinues after it was determined that this was a poor analog for CCS. This is because natural gas storage is almost always in shallow reservoirs, often utilizes old wells, and in the US at least is not strongly regulated. The project has developed a toolkit of semi-automated mathematical models that will allow stakeholders to estimate risks.

Section 2: Subsurface Risks Associated with CO₂ Sequestration

Introduction

In the US and many other countries economic prosperity is currently linked in some part to the use of carbon based fuels. The use of such fuels is inextricably tied to CO₂ emissions. Addressing the concerns of climate impact atmospheric buildup of CO₂ in a timely manner, while maintaining economic health, may not be possible without implementing carbon capture and storage (CCS) as part of the solution. Geologic CO₂ sequestration in deep brine reservoirs is perhaps the key technology necessary to implement CCS successfully and concerns regarding the risks associated with this technology need to be fully assessed.

Geologic sequestration lacks a large historical data base that would enable computation of long term risks. Elkington (2007) has asserted that “Lack of actuarial data on integrated large scale projects coupled with an absence of uniform international regulation creates major obstacles to risk management, private investment and wide-scale deployment”. In the language of risk analysis (Ellsberg, 1961) such systems are “ambiguous”. In essence the term ambiguity refers to imprecisely specified probabilities. Decision makers are more adverse to ambiguous situations than they are to too risky ones. For example insurers are known to seek higher premiums for projects that are perceived as ambiguous, than for those known to be risk prone (Hogarth and Kunreuther, 1989).

The subsurface has been successfully used for the disposal of contaminated water and hazardous wastes for many decades in the US under the Underground Injection Control (UIC) program run by the EPA. This regulatory framework has been apparently successful in largely preventing these fluids from contaminating fresh water resources or creating other environmental problems. The question that needs to be answered is what additional issues and risks are posed by the injection of carbon dioxide.

Risk management is concerned with implementing processes and policies to both prevent and control risks. This is an approach widely used to manage hazards in oil and

natural gas fields, refineries, and chemical plants. Risk is composed of two elements, the likelihood (probability) of an adverse outcome (hazardous event) and the magnitude of its consequences that is:

$$\text{Risk} = \text{Likelihood} \times \text{Consequences}$$

Wilson et al. (2003) categorized the risks of CO₂ geologic storage into two classes: global (“uncertainty in the effectiveness of CO₂ containment”) and local (impacts on health, safety, and environment including impacts on human, animals and plants) risks. In local risks they also include chemical effects of dissolved CO₂ in subsurface (i.e. metals or contaminants mobilization, drinking water contamination, and impacts on deep-subsurface ecosystems), and displacement-related risks (i.e. ground heave, induced seismicity, brine displacement induced drinking water contamination, and damage to hydrocarbon or mineral resources). Saripalli et al (2004) have suggested that the “acute hazards” related to geologic CO₂ sequestration are “wellhead failure [blowouts], seismic hazard during injection, accumulation and explosion in lakes, and massive efflux in soils”. Wilson et al (2003) suggest that the “most obvious local [associated with the surface release of CO₂] risk” is related to “catastrophic leaks such as well blowouts...”. Similarly Stevens and van der Zwaan (2005) suggest that “the most frightening scenario [related to risks associated with geologic CO₂ sequestration] would be a large, sudden, catastrophic leak. This kind of leak could be caused by a well blowout or pipeline rupture”. Damen et al. (2006) further reviewed the risks of geologic sequestration, identifying five sources of risks: CO₂ leakage; CH₄ leakage; seismicity; ground movement; and displacement of brine. The general tone of these analyses is that CO₂ sequestration is a relatively high risk endeavor with potentially catastrophic consequences.

Despite the extensive research on CO₂ sequestration since Damen et al. (2006) there has been no comprehensive review publish of the nature of risks associated with CO₂ sequestration. In addition, as will be shown in this paper both the work of Wilson et al. (2003) and Damen et al (2006) suffer from significant misconceptions about the nature of

risks resulting from CO₂ injection. Therefore, this paper aims to provide an up-to-date overview of the nature of the below ground risks associated with geological sequestration of CO₂ in deep brine reservoirs. We also do not examine any risk mitigation strategies nor do we consider what Wilson et al describe as “options for mitigating the litigation … exposure”. The aim of the current study is not to attempt a quantitative risk assessment but rather to try and place some reasonable bounds on the risk posed by geologic CO₂ sequestration.

Nature of Risks Associated with Leakage of CO₂ from Deep Brine Reservoirs

Risk receptors

High concentrations of CO₂ can result in adverse impacts to humans, animals and biota, ecosystems, and resources including groundwater, oil and natural gas (Hepple, 2005; Carroll et al., 2009; Smyth et al., 2009; Apps et al., 2010). CO₂ is fundamental to respiration and a range of other physiological function through its mediation of pH in blood. However, leaked CO₂ at high concentrations can be harmful to human health and can potentially cause physiological effects including increased breathing rate and acidosis, dizziness, confusion, sweating, dim vision, unbearable dyspnea, possible coma, and death (Rice, 2003; Wilday et al., 2011). The acceptable limitation regulated by federal occupational safety and health regulations for average exposure to CO₂ at workplace is 5000 ppm (0.5%) over an eight-hour workday during a 40-hour workweek (NIOSH, 2007), however the CO₂ levels that present serious health hazards are considerably higher. At levels above 15% and higher, loss of consciousness can occur in response to short exposures (NIOSH, 1976, 1981). Some have suggested that death occurs within minutes at 30% CO₂ (Benson, 2005). In contrast Damen et al. (2006) state that “Prolonged exposure to high CO₂ levels, above 20-30%, will cause death by suffocation to humans”. More recently Duncan (2015) has shown that lethal levels of CO₂ are likely 50 to 60%; however the combined effects of reduced oxygen and CO₂ toxicity can kill at lower CO₂ levels. Except in confined spaces, the plausible scenarios for developing such high CO₂ levels from subsurface seepage are hard to envisage.

The CO₂ leakage can also deteriorate the quality of groundwater and in some cases release dangerous heavy metals and/or other contaminants. Dissolved CO₂ dissolves in water or brine to form carbonic acid, which initially lowers pH (Carroll et al., 2009; Kharaka et al., 2009; Humez et al., 2011; Trautz et al., 2013). Bruant et al. (2002) noted that pH is a key variable in “water-mediated chemical and biological reactions”, and suggested that a lower pH that “may cause undesirable changes in geochemistry, water quality, and ecosystem health”. Changes in the pH of groundwater can also lead to increased dissolution/desorption of trace elements (including potentially toxic metals) from mineral grains in the aquifers (Benson et al., 2002; Kharaka et al., 2010; Wilkin and Digiulio, 2010; Jun et al., 2013), leaching of important nutrients, and distortion of proton gradients across biological membranes such as the walls of bacteria (Bruant et al., 2002).

Leakage of CO₂

Keith and Wilson (2002) asserted that leaks are inevitable if large scale CO₂ sequestration is undertaken (and on geologic time scales this is certainly correct). They suggested that the understanding of the leakage processes was inadequate to make robust prediction of the potential risks posed by leakage. Damen et al. (2006) have asserted that there is “still a lack of understanding in the physics of CO₂ leakage (i.e. the processes that control leakage) through wells and faults”. This is perplexing as the physics of leakage in faults and up well bores is well established.

It is convenient to divide leakage into two end members: rapid and slow. In sequestration sites in regions of intense oil or gas drilling in the past, rapid leakage such as blowouts of poorly plugged and abandoned wells may occur early in the projects history and are highly unlikely post the closure period. Such leakage can be almost totally avoided by good site selection and careful, thorough site characterization. Leakage rates will undoubtedly vary from site to site with: the quality of the seal; the nature of the geology above the seal; and the location, characteristics and number of potential high permeability pathways (well bore holes, faults and fracture zones). The long term (hundreds to thousands of years) behavior of well bore casing steels, cements and plugs is

uncertain and cannot be readily studied in the laboratory. Some have suggested that leakage will be most rapid in the first 50 to 100 years off a projects life cycle when significant permeability, solubility, and mineralogic trapping are yet to occur (Oldenburg and Unger, 2003). Since Keith and Wilson's assessment there has been over half a decade of intense research, a number of pilot projects at a significant scale and two commercial scale projects.

Capillary Effects, Baffles and Seals; the Barriers to the Escape of CO₂

Cap rock (seal) integrity is crucial for preventing CO₂ escaping from deep saline aquifers. Damen et al. (2006) asserted that there are generally no cap rocks or seals associated with deep saline aquifers that "have stood the test of time in retaining gases". This is not correct. In Texas alone there are deep saline brines apparently saturated in CO₂ such as the deep Wilcox (Franks and Forester, 1984) where the CO₂ does not appear to have leaked through the overlying seal. A large amount of naturally generated CO₂ has been stored in sedimentary basins for millions of years, and has not leaked until oil and gas are exploited. In Australian sedimentary basins 500Mt of natural CO₂ has accumulated underground for up to 80 million years (Bradshaw et al., 2004). A number of gas fields have high CO₂ concentrations (>10%) within the conterminous U.S., which are mainly located in Texas, the Rocky Mountains, and the Gulf Coast; the CO₂ concentrations in parts of these fields can exceed 98% in the gas mixture, such as McElmo Dome of Colorado in the Paradox Basin within the Rocky Mountains (Pearce et al., 1996; Allis et al., 2001; Brennan et al., 2005).

Deep saline aquifers are promising for long-term geologic sequestration of CO₂. The injected CO₂ may dissolve with the formation waters (solubility trapping) and form the mineral carbonates (mineral trapping) eventually, reducing the leakage risks associated with geologic sequestration (Bruant et al., 2002; Bachu and Adams, 2003; Allen et al., 2005). Fault seals will also serve as baffles in some reservoirs by forming impermeable barriers for preventing lateral CO₂ migration. However, there are few reports on assessment of the across-fault leakage potential of faults in CO₂ storage sites (Bretan et al., 2011). Reveillere and Rohmer (2011) evaluated the feasibility of a hydraulic barrier

to prevent the CO₂ leakage at a case study of injection of CO₂ into a saline formation linked to a shallow aquifer. Their modeling results showed a hydraulic barrier could “prevent or stop the leakage in less than a few years instead of letting it continue in the long term, even with a low and declining flow rate”.

Leakage Pathways

CO₂ may migrate upward and finally to the atmosphere through/along a variety of natural and man-made pathways such as wells, faults and fractures, and cap rocks (IPCC, 2005; Oldenburg, 2008; Pruess, 2008; Sy et al., 2012). Moreover, the types of reservoirs and trapping mechanisms have significant effects on leakage potential. Generally the important leakage pathways are along/through the wells, faults and fractures (Benson et al., 2002; Gasda et al., 2004; Kopp et al., 2010). The leakage through faults and fractures is diffuse and more difficult to mitigate (IPCC, 2005). These faults and fractures can also alter the integrity of cap rocks, which thus increase the possibility of leakage. When the increased pressure caused by CO₂ injection exceed the capillary entry pressure threshold of the cap rocks, leakage can occur through the cap rocks (Rutqvist and Tsang, 2002; Rutqvist et al., 2007; Lemieux, 2011), however for most shale seals that have been characterized in the Texas Gulf Coast Basin this would represent a vanishingly small risk given the measured capillary entry pressures, shale permeability's and seal thicknesses (Dawson and Almon, 2000).

During the period of injection phase for a large sequestration project the leading edge of the CO₂ plume will typically advance many kilometers. The larger the plume the more probable that it will intersect a well that penetrates the reservoir seal. Various factors including post-injection stage plugging and abandonment procedure, plugging strategies, and types and properties of sealing and casing materials may affect the integrity of wells during long-term geologic storage periods (Mainguy et al., 2007; Guen et al., 2009; Pawar et al, 2009). There are no established models for the long-term corrosion of the steel casing (or presumably the leakage of other well components), that there under reservoir conditions for 1,000 year plus time scales involved in sequestration (Walton et al, 2004). Scherer et al. (2005) asserted that even wells that were properly plugged

initially may in the future act as high permeability pathways due to corrosion of well components and chemical degradation of cements. Ide et al (2006) concluded that even though there have been dramatic improvements in the technologies for plugging wells over the last 100 years the risk of CO₂ leaking through wells remains a “substantial risk” in geologic sequestration projects. However from a risk management view point these risks are not “substantial”, as a known potential leakage pathway such as an existing well can be neutralized as a risk by setting up appropriate monitoring and mitigation strategies.

The real risk would come from wells penetrating the reservoir seal that the project operator is not aware of. Nicot (2008) has addressed this issue, noting that his data from the Texas Gulf Coast show that the older wells, likely to be not accurately located or not recorded in modern databases, are invariably shallow in depth relative to likely sequestration reservoirs. In general the locations of all wells within and in the vicinity of the CO₂ plume are known. Even local of wells whose location has been lost can be cost effectively located using a combination of geophysical and geochemical approaches. Monitoring strategies can be readily tailored to the location of deeper wells and specifically those that penetrate the seal. With well-documented leakage control technologies and monitoring strategies the wellbore-risk can be effectively controlled or mitigated. Recent studies of behavior of cement during long term exposure to CO₂ suggest that cements may have far greater resilience to such exposures than earlier studies suggested (Rochelle and Milodowski, 2013).

Well bores can act as conduits, allowing rapid vertical transport of CO₂ and or brine. Parts of injected CO₂ may escape from the reservoirs to the atmosphere along/through the active wells together with industrial activities, while at the abandoned wells, leakage may occur due to deterioration of cements and casings, poor maintenance, and unknown abandonment conditions (Boukhelifa et al., 2004; Gasda et al. 2004; Zhou et al., 2005; Carey et al. 2007; Humez, et al, 2011; Lemieux, 2011; Zhang and Bachu, 2011; González-Nicolás et al., 2012; Nasvi et al., 2013a, b). The question of what roles well bores may play in acting as conduits for leakage is clearly a site specific issue. In areas that have never had oil and gas exploration this issue will be largely moot (with the

exception of deep water wells). As the CO₂ plume resulting from injection spreads there will be an increasing potential for CO₂ to encounter abandoned well bores that may or may not have been effectively plugged (Ide et al., 2006; Nicot, 2009). In Texas over 1.1 million (1 million) wells have been drilled; most of the wells (about 60%) are 1,500 to 3,000 m in depth (Nicot, 2009). If the location of a legacy well is known, then in general the risk is minimal as most old wells can be cost effectively mitigated (Guen et al., 2009).

Transmissive faults and fracture zones form the next most likely leakage pathways after well-bores. Modeling of the nature leakage of CO₂ along such faults and fracture zones has become a research topic of considerable interest. Birkholzer et al. (2008) have reported preliminary models (that include the effects of adiabatic cooling) of the upward migration of along such faults including the effects of the phase transition from super- to sub-critical CO₂. The case of CO₂ accessing a fault with very high permeability with a direct connection to the surface. As noted by Birkholzer et al. (2008) the key issue is under what (if any) circumstances can lead to very rapid, significant volume releases of CO₂. The nature of the factors controlling such events, even if they are of extremely low probability, could be a significant part of risk profile. Evaluation of this phenomenon can lead to both improved site evaluation criteria and risk management approaches. The simulations reported by Pruess (2011) show persistent flow cycling with fluctuating leakage rates at the land surface after a period of initial growth. He concludes that adiabatic cooling (and coupled effects) results in a self-limiting system with CO₂ migration slowing after over time.

Zhang et al. (2009) advanced a methodology through integration of percolation theory and fuzzy sets theory to estimate the connectivity of faults and the CO₂ leakage probability through faults or fractures at geologic sequestration sites. They concluded that the probability of CO₂ leakage into a compartment (i.e. potable groundwater) was dependent on distribution and connectivity of faults or fractures, and size and location of CO₂ plume. Their work was further improved by Smith et al. (2010) by considering potential geomechanical failure in post-injection fracture network risk analysis. They also pointed out that presence of a network of fractures in a caprock could generate a permeable pathway, consequently causing CO₂ leakage if the buoyancy pressure was

greater than capillary entry pressure for such a pathway. However Ellis et al. (2013) observed in a controlled laboratory high-pressure core flow experiment that fracture permeability as an important factor affecting CO₂ geologic storage may be reduced due to dissolution of critical asperities in a carbonate rock. Those contradict intuitive permeability evolution since dissolution generally causes an increase of porosity, consequently leading to increased permeability. Similar experimental results of self-sealing in the wellbore cements are demonstrated by Huerta et al. (2011, 2013), leading to decreased leakage rate over time along with wellbores.

Over the last 50 years the oil industry and associated academic researchers have developed a sophisticated understanding of the role of in controlling flow in deep reservoirs. Wiprut and Zoback (2002) investigated the effects of faults on the fluid flows in hydrocarbon reservoirs and evaluated the state of stress and pore pressure on major faults in four oil and gas fields in the northern North Sea. They identified three factors which caused fault reactivation and gas leakage along sections of previously sealing reservoir-bounding faults, including “(1) locally elevated pore pressure due to buoyant hydrocarbons in reservoirs abutting the faults, (2) fault orientations that are nearly optimally oriented for frictional slip in the present-day stress field, and (3) a relatively recent perturbation of the compressional stress caused by postglacial rebound”. They concluded that “leakage potential of reservoir-bounding faults appears to exert an important influence on potential hydrocarbon column heights”. Shipton et al. (2004) in their preliminary study built a conceptual model for the groundwater-CO₂ flow system by considering CO₂ source, leakage pathways, and flow rate to evaluate the leakage risk along the faults. They conclude that the faults are the conduit for CO₂ migration to the surface during the long-term injection into faulted geologic reservoirs. Regulatory controls over the maximum allowable injection pressure will be necessary to prevent fracturing of the seal or caprock during CO₂ injection. Ebigbo et al. (2010) suggested that “the caprock in the vicinity of the wells is particularly at risk of fracturing due to high pressure build-up during injection”.

The risk assessment for the FutureGen sequestration project concluded that a catastrophic failure and rapid release of CO₂ is highly improbable estimating that such an

event would be “vanishingly remote” with a probability of less than 5×10^{-9} per year (FutureGen Alliance, 2007).

Leakage through the Seal

Understanding of the nature and risk of leakage through the seal itself is perhaps the least characterized risk associated with sequestration. Understanding the nature of the seal and being able to accurately estimate its capacity to contain or perhaps retard CO₂ is a key to being able to predict leakage from the reservoir. Holloway (1996) pointed out that shale and anhydrite cap-rocks sealing the reservoirs were less affected by CO₂-water-rock reactions. Hovorka (1999) suggested that the thickness and continuity of top seal could have significant effects on CO₂ leakage at the reservoirs. Cartwright et al. (2007) defined seal bypass systems as “large-scale (seismically resolvable) geological features embedded within sealing sequences that promote cross-stratal fluid migration and allow fluids to bypass the pore network”, and classified them into fault bypass, intrusive bypass, and pipe bypass categories. The bypass systems have the potential to cause the failure of seals and accumulations; however, they will not inevitably lead to seal failure in the top seal. In many real-world reservoirs, bypass systems exist in the top seals of large petroleum accumulations. Such research outputs are helpful for assessment of potential risks of CO₂ leakage through the top seals. A seal could fail by pressure driven flow of brine, by pressure driven flow of CO₂ in two phase flow, or by flow of dissolved CO₂ through the seal.

Saripalli et al. (2004) in their analysis of seal integrity, assumed that 1% of the area of the seal contacted by the CO₂ plume was fractured and that another 1% was highly permeable. On the basis of these assumptions they calculated the risk of leakage through the seal as 2.0×10^{-2} and that this was the highest risk to all to the environment. However these calculations are based on ad-hoc assumptions and are inconsistent, assuming a carefully located/characterized site, with the extensive data bases on seal quality generated during oil exploration (c.f. Dawson and Almon, 2000).

Making generalizations regarding the risk of leakage from a hypothetical sequestration site is not useful. Leakage through the seal is inherently a site specific phenomenon.

Accidental Hydraulic fracturing of the Seal

Another possible CO₂ leakage pathway is hydraulic fractures formed during reservoir stimulation (or perhaps accidentally via excessive injection pressures). Caillet (1993) analyzed the seal integrity of shales at the oil and gas fields in the Norwegian North Sea, and suggested that hydraulic fracturing could induce leakage since it could re-open or initiate a fracture which could negatively affect the seal integrity of shale. Although this study focuses on leakage of hydrocarbons, it provides analogues on assessment of CO₂ leakage by hydraulic fracturing at geologic CO₂ sequestration sites. Liu et al. (2010) suggested that although hydraulic fractures together with natural fractures could help injected CO₂ move quicker and wider in the saline aquifer, they were also important potential leakage pathways.

A study whether hydraulic fracturing of shale gas reservoirs threatened the integrity of future CCS projects was conducted and published by Nicot and Duncan (2012). They found that the areal footprints of current and future hydraulically fractured oil-and-gas reservoirs and potential CO₂ geological sequestration intervals often overlap in sedimentary basins. However, they determined that vertical separation between prospective subsurface volumes will limit their interaction, particularly if the carbon storage site is deeper than the hydrocarbon resource. Recent intense development of shale resources also will translate into a reduced need for sequestration capacity. It has also resulted in technological innovations directly transferable to the carbon storage industry: progress on well completion such as new approaches to cementing, more mature horizontal drilling methods, and development of field treatment techniques for saline water. In addition, knowledge collected by operators on stratigraphy and faults, for example, using 3D seismic, and on abandoned wells is directly useful reducing risk for future carbon storage projects. Both industries can benefit from development of regional transmission pipelines, pipeline right-of-ways, and a trained workforce. Environmental

risks result mostly from abandoned wells and poorly-characterized faults for carbon storage and from defective well completions and surface spills for oil and gas production.

Risk to Drinking Water Resources from Leakage of CO₂

Brine is the most likely water contamination arising from geologic CO₂ sequestration in deep brine reservoirs. Brine may escape and contact fresh water aquifers via a variety of ways, and significantly increase the chloride contents of water above the standards for drinking water (Collins, 1971). The maximum limit of chloride concentrations is 250 mg/L in drinking water recommended by USEPA National Secondary Drinking Water Regulations. High chloride concentrations may seriously affect the functions of fresh-water aquifers as water supply sources, and aesthetic quality of water (USGS, 2011).

Geological history demonstrates that geologic reservoirs are capable of retaining natural gas in reservoirs on a time scale of millions of years. The IPCC (2005) report concludes it is likely 99% of the stored CO₂ will be retained over 1,000 years. Modeling of CO₂ leakage from deep brine reservoirs leads to the conclusion that, for carefully selected sequestration sites, slow leakage will likely be very slow with very low percentage leakage on a time scale of thousands of years (Lindeberg and Bergmo, 2003; Lindenberg 2003; Torvanger 2006). A similar conclusion has come from analysis of long term leakage risks for CO₂ for the Weyburn CO₂-EOR site (Zhou et al., 2004). Slow leakage does pose a threat to drinking water quality even though it does not impact on public safety.

Since the work of van der Meer (1992), a variety of studies have been conducted for addressing and assessing the impacts of CO₂ on groundwater resources (Holloway, 1996; Wang and Jaffe, 2004; Lewicki et al., 2007; Price et al., 2007; Carroll et al., 2009; Smyth et al., 2009; Apps et al., 2010; Newmark et al., 2010; Lemieux, 2011). Damen et al (2006) suggest that “fresh, potable groundwater, located in the top 100-200 m of the subsurface”, could be contaminated as a result of CO₂ leakage from the containment zone. Lemieux (2011) has asserted that the damages to the confined shallow aquifers are more serious than those to the unconfined aquifers since the leaked CO₂ can accumulate

at the top of the former, resulting in a larger volume of drinking water contamination. The relevance of such speculations to actual sequestration projects awaits site specific evaluation of actual sequestration sites. Damen et al (2006) also suggested that “Even small CO₂ leaks [from a geologic sequestration reservoir] may possibly cause significant deteriorations in the quality of potable groundwater”. These authors do not reveal what they regard as a small leak nor do they present any evidence to support this assertion.

Shallow drinking water aquifers can be directly affected by leaked CO₂ or indirectly by displaced brines entering the aquifers caused by CO₂ injection (IPCC, 2005; Kalunka et al., 2010). Water quality can be threatened by slow leakage in several ways: a) Lowering of pH from carbonic acid produced by interaction with the CO₂, b) Contamination of drinking water by metal enriched water formed by rock-water interaction with CO₂ saturated brines, and c) Migration of brine into USDW driven by anomalous pressures ultimately driven by CO₂ injection.

A number of authors have suggested that leakage of CO₂ from the reservoir can decrease pH (to values of 4-5 or lower), resulting in dissolution of Calcite, as well as increases in the hardness of the water and the concentration of trace elements trace elements such as metals and arsenic (Holloway, 1996; Damen et al, 2006; Kharaka et al., 2006, 2009). The geochemical process simulation by Humez et al. (2011) showed that pH of groundwater due to CO₂ intrusion to a shallow aquifer in the Paris Basin, France decreased from 7.3 to 4.9, leading to mineral dissolution in the formation and release of trace elements. The water acidification by dissolution of CO₂ could negatively affect the wells, pumps, pipes, and other equipment by corrosion, precipitation of scale, and lower well flow rates, leading to reductions of groundwater resources yield and economic losses (Ceron and Pulido-Bosch, 1996; Saripalli et al., 2004; Newmark et al., 2010). However these authors have not taken into account the buffering of the pH by ongoing water rock interactions so that they may have overstated the negative impacts of CO₂ on groundwater quality. Dissolution of alkaline minerals such as calcite could compensate the pH decrease in highly buffered aquifers, decreasing potential impacts caused by trace and metallic elements mobility on human health and environment at a certain degree

(Hovorka et al., 2006; Keating et al., 2010; Vong et al., 2011; Atchley et al., 2013; Navarre-Sitchler et al., 2013).

The simulation by Wang and Jaffe (2004), using greatly simplified host rock mineral compositions showed dissolved Pb concentrations in high buffered aquifers were lower than those in low buffered ones. In order to address the severity of CO₂ leakage in real worlds, Apps et al. (2010) evaluated the water quality changes in responses to CO₂ intrusion by using representative host rock mineralogy referred to Coastal Plain Sandstone in the US. They identified arsenic and lead as the trace elements of greatest concerns. Their modeling efforts showed although aqueous concentrations of arsenic and lead significantly increased as CO₂ intruded into a shallow confined aquifer, their maximum values were still below or close to specified maximum contaminant levels (MCLs). Karamalidis et al. (2013) reported that the amounts of dissolved trace metals were significantly affected by rock types in mineral dissolution and carbonate content buffering pH. Lu et al. (2010) investigated the variations of cations' concentrations to study the impacts of CO₂ on groundwater quality in a laboratory-batch experiment. Their results showed that the concentrations of some cations including Fe, Al, Mo, U, V, As, Cr, Cs, Rb, Ni and Cu initially increased (initial pH decrease resulted in metal desorption) and then declined to be lower than those before injection (adsorption replaced desorption due to mineral buffering causing the rebounded pH). They thus suggested for such type of cations risks are limited considering their self-mitigation capability.

Risk to Surface and Subsurface Ecosystems

It is well known from areas of high CO₂ seepage that at high concentrations it can do serious harm to overlying ecosystems, including reduction or even death of vegetation and animals (Williams, 1995; Benson et al., 2002; Price et al., 2007; Pierce and Sjogersten, 2009). Elevated soil CO₂ concentrations can decrease soil pH, thus adversely affecting plant growth (Saripalli et al., 2003; Patil et al., 2010). Wei et al. (2011) studied the effects of pure CO₂ on soil and plants in the laboratory-scale experiments. Their results suggested a positive correlation between soil moisture and CO₂ uptake during the reaction (i.e. greater soil moisture corresponded to higher CO₂ uptake). One of natural

analogue examples is at Mammoth Mountain, California where continuous CO₂ release due to volcanic activities since at least 1990 has caused the surrounding trees killed with the observed soil gas concentrations of 20-30% CO₂ (Farrar et al., 1995; Benson et al., 2002). However even in areas such as Mammoth with high CO₂ fluxes, ecosystem impacts are spatially limited to relatively small patches. The studies reviewed by Benson et al. (2002) indicated that plants were generally more tolerant than invertebrates to elevated CO₂ so that small-scale short-term leakage could have minimal impacts.

The long-term response studies of vegetation around natural CO₂ springs in Central Italy by Miglietta et al. (1993) showed some species (i.e. A. canina and S. lacustris) had positive responses including increased mean size to elevated CO₂ concentrations through generations. Although elevated CO₂ concentrations could inhibit root respiration of plants species in the proximity of natural CO₂ springs, a significant decrease was not common and only occurred under extremely high concentrations (Macek et al., 2005). The effects of high CO₂ concentrations on near-surface ecosystems are significant but spatially limited to fairly small areas, which were demonstrated by the real-world studies in Latera, Italy by Beaubien et al. (2008) and Lombardi et al. (2008), and in Laacher, Germany by Kruger et al. (2009).

Gough and Shackley (2006) suggested that “any impacts to the pristine ecosystems within an aquifer would be less acceptable than to an existing industrial site”. The knowledge on the effects of CO₂ on the microorganisms inhabiting the reservoir formations is very limited because the ecosystems either have been damaged by industrial activities including oil and natural gas exploitation or have achieved the adaptation capabilities (Gough and Shackley, 2006).

Seepage of CO₂ into Confined Spaces and Subsurface Gas Scavenging

Diffuse seepage of natural CO₂ from volcanic and geothermal from many of the locations in the world where substantial seepage rates of CO₂ pose a potential danger to man. The only documented cases of death or injury in such terrains have occurred when CO₂ had accumulated in confined spaces such as wells, ditches, and caves. In addition, a number of factors such as seep types, flux, temperature, local topography, wind speed,

and human behavior can affect the CO₂ seepage risks (Roberts et al., 2011). The higher concentrations of CO₂ occur in the seeps themselves and extend to a limited area away from the seeps at and near the ground level (BLM, 2006). Another example of CO₂ seepage is located in Salt Creek Oil Field, Wyoming, where a small portion (around 0.008%) was released to a small confined area within the Field's Phase I period during 2004-2005 (BLM, 2006). The field measurement shows the CO₂ concentrations at ground level are higher in limited depressions, drainages, and confined areas in still conditions, especially under no-wind nighttime conditions; however in the breathing zone of the population with a height of approximately 5 feet above the ground level the CO₂ concentrations are much lower and do not pose risks to a walking human in open areas. In both volcanic and geothermal areas there is typically a strong correlation between Radon and CO₂ levels in soil gases as well as gas accumulating in basements, cupboards and other confined spaces. CO₂ seepage through the shallow subsurface and soil, likely follows the same pathways as Radon. Beaubian et al. (2003) in a detailed geochemical survey in Italy suggested that CO₂ might act as a gaseous carrier to transport trace gases like radon along high permeable pathways such as faults and fractures, leading to soil-gas anomalies. In volcanic and structurally active areas the soil-gas method is useful for helping land-user planners assess possible health and safety risks of toxic gases.

Catastrophic Eruptions of CO₂: Lake Nyos Type Disasters?

It has been suggested that a “sudden leak” could be produced from a slow leak “if the CO₂ is temporarily confined in the near-surface environment and then abruptly released” (Stephens and van der Zwaan, 2005). Damen et al. (2006) suggest that “although a spontaneous release as occurred at Lake Nyos is no analogue for CO₂ leakage from a geological reservoir” that “a similar situation could occur in which anthropogenic CO₂ leaking from a geological reservoir accumulates in a deep lake”. They suggest that “this can be prevented by selecting reservoirs without any lakes in vicinity”. Wilson et al (2003) suggest that “Catastrophic events [associated with geologic CO₂ sequestration] maybe caused by slow leaks if the CO₂ is temporarily confined in the near-surface environment and then suddenly released”. Wilson et al (2003) then reference the Lake

Nyos incident, concluding that “while the specific mechanism active at Lake Nyos can occur only in tropical lakes (because they do not turn over annually), mechanisms may exist that could confine slowly leaking CO₂ in the subsurface, enabling sudden releases”. They suggest that “it is conceivable … that CO₂ leaking from deep underground could infiltrate karst caverns at shallow depths and that such CO₂ could then be rapidly vented …” Duncan (2013) has suggested that it is inconceivable that such phenomena could occur. It is true that CO₂ could leak from a sequestration reservoir up into karstic caverns and it is well known that some caverns have natural CO₂ accumulations. However because CO₂ is denser than air, a mechanism for “rapid venting” is lacking. Damen et al (2006) although they note that “a spontaneous release as occurred at Lake Nyos is no analogue for CO₂ leakage from a geological reservoir”, suggest that “a similar situation could occur in which anthropogenic CO₂ leaking from a geological reservoir accumulates in a deep lake”. They suggest that this “can be prevented” during site selection by choosing areas “without any lakes in vicinity”. Avoidance of lakes is not in any way necessary for locating low-risk sequestration sites. Duncan (2013) considered that such deep, stratified lakes that could create the physical conditions necessary to have a Lake Nyos type disaster are extremely rare and can be readily identified where they exist. Duncan (2013) also argued that there is no credible mechanism for creating a CO₂ release in any way similar to the Lake Nyos other than trapping in a deep, stratified lake.

Ground Movement/Ground Heave?

Keith and Wilson (2002) listed “ground heave” as one of the possible risks associated with CO₂ sequestration. Wilson et al (2003) suggested that “large volumes of any injected fluid impacts the subsurface environment by displacing the original material, sometimes causing local ground heave and inducing local seismic events”. Wilson (2004) asserted that “localized ground heave could result from improper maintenance of reservoir pressures”. Wilson further suggests that “[ground heave] can be controlled with proper operation of injection well fields, it could affect the rate at which CO₂ can be injected into a particular reservoir”. Ground heave was also identified as a risk related to CO₂ sequestration by, Wilson and Gerard (2007), Holloway et al (2007), Palmgren et al

(2004), Logan et al (2007) and others. Despite the large number of papers that suggest ground heave is a risk associated with CO₂ sequestration there appears to be no evidence to support this assertion.

Ground heave is a well-documented phenomena associate with permafrost and swelling clays. Ground heave involves short wavelength (on the scale of meters) and relatively high amplitude (centimeters to 10's of centimeters) surface deformation. Ground heave can crack and tilt foundations resulting in considerable damage to buildings. The probability that this kind of phenomena can be caused by CO₂ leakage is negligible.

Damen et al (2006) suggested that man-made pressure changes (caused by fluid injection) can cause “the earth’s surface will sink or rise” and that this “might cause damage to buildings and infrastructure”. CO₂ sequestration will almost certainly lead to a broad uplift of the land surface, just as extraction of fluids in oil and gas field leads to broad subsidence. The wavelength of this phenomenon will be scaled to the diameter of the CO₂ plume. A typical plume will have diameters on a scale of tens of kilometers, whereas the amplitude will likely be on a scale of less than a meter. Such ground motion would be unlikely to cause damage to buildings, unless the displacements are locally focused by reactivation of faults that cut the surface. Damen et al (2006) assert “that uplift will [not] take place in a CO₂ reservoir as long as the maximum storage pressure is kept below the geostatic pressure”. This statement is inconsistent with basic geomechanics.

Long wavelength low amplitude uplift driven by CO₂ inflating a deep subsurface reservoir is highly unlikely to lead to property damage except in some specific geologic settings. The possibility of such damages (if any), could be estimated on a site specific basis. Rutqvist et al. (2009) suggested through field observation and coupled reservoir-geomechanical modeling that the observed surface uplift (on the order of 5 mm per year above active injection wells during the first few years of injection) was consistent with volumetric expansion of CO₂ injection zone and/or adjacent formations, which was caused by pressure changes in the lower parts of the caprock formations (Rutqvist, 2012).

Degradation of the Quality of Energy Resources

Leakage of CO₂ from a sequestration reservoir can potentially lead to the degradation of the value of natural gas or oil reservoirs. Increasing the CO₂ content of natural gas decreases its heat content and may require it to be pipelined to a processing plant to reduce the CO₂ content. In the future, if it becomes illegal to vent CO₂, then leakage of CO₂ into an oil field would lead to a loss of value of the oil. Under common law in many US states, migration of CO₂ into an oil reservoir may be a basis for a law suit for fluid trespass. In some locations, degradation of natural gas quality by leakage of CO₂ may represent by far the largest financial risk faced by a CO₂ sequestration project. In general this risk can be readily identified and managed. Purchase of the mineral rights above the projected CO₂ plume, followed by production of any known gas reservoirs, would be a simple risk management strategy.

Discussion and Conclusions

It is disturbing that so many of the papers written on the subsurface risks associated with CO₂ sequestration use the word catastrophic in an almost gratuitous way. Webster defines catastrophe as: “a momentous tragic event ranging from extreme misfortune to utter ruin”, or “a violent and sudden change in a feature of the earth”, or “a violent usually destructive natural event”. It is difficult to find any factual justification for this word usage in the context of sub-surface leakage from CO₂ sequestration reservoirs.

The most robust evidence for the nature of the risks associated with subsurface leakage from CO₂ sequestration reservoirs come from studies of regions of naturally high CO₂ fluxes from subsurface CO₂ migration. In the Azores the town of Furnas, inside an active volcano, many of the houses have CO₂ concentrations of 10–15 volume% in closed in spaces on the ground floor. CO₂ abundances in some ditches in the area were measured at up to 50 vol. % CO₂ (Baxter et al, 1999). Although measured surges in emissions, recorded overnight in ground floor rooms in some houses resulted in CO₂ concentrations above the lethal levels noted above no deaths have been ascribed to CO₂ poisoning in

Furnas (Baxter et al, 1999). Deaths or near deaths have occurred indoors in confined spaces on Vulcano, an active volcano on an island north of Sicily (Baxter et al, 1990). The common factor in these incidents is the role of confined spaces and ditches where CO₂ levels tend to be highest. It has been reported by Baubron et al (1990) that CO₂ emissions were responsible for the deaths of two children as well as some incidents of dead small animals. Roberts et al. (2011) analyzed the long-term historic records in 286 CO₂ seep locations in Italy from 1990 to 2010, and concluded that the risk of death of populations exposed to natural CO₂ was negligible, on the order of 2.8×10^{-8} per year. Such risks are far lower than the risk of being killed by lightning.

The subsurface has been successfully used for the disposal of contaminated water and hazardous wastes for many decades in the US under the Underground Injection Control (UIC) program run by the EPA (USEPA, 2001; Rish 2005). Rish (2005) suggests that for hazardous waste injected in Class I wells the risk of leakage from containment is less than 10⁻⁶ (that is, 10⁻⁷ or lower). If this is the likelihood of loss of containment the risk of consequences from this leakage is likely substantially lower than this as the fluid has to be transported thousands of meters vertically and come into contact with a risk receptor such as domestic water wells.

This regulatory framework has been apparently successful in largely preventing these fluids from contaminating fresh water resources or creating other environmental problems. Recently, the EPA finalized the requirements for development of a new injection well class (Class VI) for geologic sequestration of CO₂ under UIC program to protect underground sources of drinking water (USEPA, 2010). Class VI wells have safety and well integrity specifications equal to or greater than Class I hazardous well. The core objective of UIC program is to protect current and potential drinking water resources. The question that needs to be addressed is “what issues and risks additional (to those in the current UIC program) are posed by the injection of carbon dioxide?”

CO₂-rich oil and gas reservoirs are good analogues to geologic sequestration since large amounts of CO₂ have been contained underground in these fields for much longer periods with no leakage. The operation and regulatory practices associated with the fields provide scientific bases for guiding CO₂ geologic sequestration practices and assessing

and mitigating the relevant risks. Some important factors or parameters in controlling CO₂ leakage and/or migration underground may be identified based on natural analogues, which are useful for site-specific risk assessment. Current methods for risk assessment in these fields can provide references for geologic sequestration of CO₂ in deep brine aquifers although the latters are analogues to but different from the former.

Since little data related to leakage is available in long-term containment of CO₂ in these reservoirs, the risk assessment methods and techniques developed are not successfully demonstrated in real-world applications. The risks are assessed and predicted based mainly on modeling of long-term transport and migration of injected liquids or gases in subsurface. Mathematical models are useful tools for prediction the fate and transport of CO₂ underground, which provides sound bases for risk assessment. Although the models are more and more advanced, they have the limitations due to knowledge gaps in understanding of processes of controlling the leakage and migration and characterization of heterogeneous subsurface conditions since the modeling outputs are only as good as the conceptual design of the models. Moreover, uncertainty inherently exists in the processes, systems, and factors, consequently affecting the accuracies of modeling and risk assessment results. Uncertainty may be reduced through better data collections and in-depth research; however, it is difficult to be eliminated. For example, some leakage inevitably exists in long-term geologic sequestration of CO₂.

Accumulation of CO₂ may lead to elevated pressures in the reservoirs, causing the variations of fault structures and networks, which consequently increase the uncertainties in characterization, modeling and assessment of leakage risks through the faults. UIC program provides good practices and experience to geologic sequestration of CO₂, especially in regulatory and technical aspects of hazardous waste underground injection. According to the regulations of UIC program by USEPA (2001), modeling the fate of injected hazardous wastes must demonstrate that migration out of zone will not occur during a period of 10,000 years. This is referred to as a “no-migration petition”. Natural and industrial analogues provide useful experience, but additional issues need to be considered in practical risk assessment of CO₂ sequestration in brine reservoirs. Continuous injection of CO₂ into the reservoirs may alter the geologic conditions of the

reservoirs, which are different from those with long-term containment of CO₂ in oil and gas fields. Little data is available on CO₂ dissolution rate in brine-filled reservoirs. In order to effectively and accurately assess the risks associated with CO₂ geologic sequestration in brine reservoirs, long-term in-situ monitoring, and site-specific modeling and risk assessment methods and tools are desired.

Given the current state of knowledge it is difficult to predict long term leakage rates from engineered brine reservoirs (Lindeberg, 1997; Holloway, 1997; Hepple and Benson, 2003; IEA, 2004). It could be argued that leakage rates from carefully screened and engineered geological reservoirs are likely to be very small. However there is no firm basis of relevant experience to calibrate expectations of outcomes based on existing data. Existing CO₂ injection projects either are EOR based (and have built in pressure relief through fluid extraction wells) and/or have insufficient length of injection history to infer long term risks. However the overwhelming evidence from natural CO₂ accumulations and CO₂ saturated brines in deep aquifers, is that carefully chosen reservoirs can and will retain CO₂ on a time scale of millions of years.

Summary

Geologic CO₂ sequestration in deep brine reservoirs is considered as a key technology for large scale mitigation of greenhouse gas emissions. Earlier risk assessments have identified a number of sub-surface related risks including: catastrophic leakage from fault zones; catastrophic CO₂ evulsion from slow leakage, and ground heave, that simply are not credible. They have overused the word catastrophic and presented an inflated impression of the subsurface risks associated with CCS. The short- and long- term risks of CO₂ leakage on drinking water resources, surface and subsurface ecosystems, and energy resources based on natural analogues are analyzed. Where careful studies have been able to quantify risks from sub-surface CO₂ utilizing analogues, they are on the order of 10⁻⁸, two orders of magnitude smaller than risks normally considered of societal concern.

References

Allen, D.E., Strazisar, B.R., Soong, Y., Hedges, S.W., 2005. Modeling carbon dioxide sequestration in saline aquifers: significance of elevated pressures and salinities. *Fuel Process. Technol.* 86, 1569-1580.

Allis, R., Chidsey, T., Gwynn, W., Morgan, C., White, S., Adams, M., Moore, J., 2001. Natural CO₂ reservoirs on the Colorado Plateau and Southern Rocky Mountains: Candidates for CO₂ sequestration. In: *Proceedings of the First National Conference on Carbon Sequestration*, Washington DC, May 2001.

Apps, J.A., Zheng, L., Zhang, Y., Xu, T., Birkholzer, J.T., 2010. Evaluation of Potential Changes in Groundwater Quality in Response to CO₂ Leakage from Deep Geologic Storage. *Transp. Porous Media* 82, 215-246.

Atchley, A.L., Maxwell, R.M., Navarre-Sitchler, A.K., 2013. Using streamlines to simulate stochastic reactive transport in heterogeneous aquifers: Kinetic metal release and transport in CO₂ impacted drinking water aquifers. *Adv. Water Resour.* 52, 93-106.

Bachu, S., Adams, J.J., 2003. Sequestration of CO₂ in geological media in response to climate change: capacity of deep saline aquifers to sequester CO₂ in solution. *Energ. Convers. Manage.* 44, 3151-3175.

Beaubien, S.E., Ciotoli, G., Lombardi, S., 2003. Carbon dioxide and radon gas hazard in the Alban Hills area (central Italy). *J. Volcanol. Geoth. Res.* 123, 63-80.

Beaubien, S.E., Ciotoli, G., Coombs, P., Dictor, M.C., Kruger, M., Lombardi, S., Pearce, J.M., West, J.M., 2008. The impact of a naturally occurring CO₂ gas vent on the shallow ecosystem and soil chemistry of a Mediterranean pasture. *Int. J. Greenhouse Gas Control* 2, 373-387.

Benson, S.M., 2005. Carbon dioxide capture for storage in deep geological formations - results from the CO₂ capture project. In *Geological Storage of Carbon Dioxide with*

Monitoring and Verification Vol. 2, Benson, S.M. (Ed.), pp. 654, Elsevier Publishing, UK.

Benson, S.M., Hepple, R., Apps, J., Tsang, C.F., Lippmann, M., 2002. Lessons learned from natural and industrial analogues for storage of carbon dioxide in deep geological formations. Lawrence Berkeley National Laboratory report LBNL-51170.

Birkholzer, J.T., Zhou, Q., Zhang, K., Jordan, P., Rutqvist, J., Tsang, C.-F., 2008. Research project on CO₂ geological storage and groundwater resources: large-scale hydrogeological evaluation and impact on groundwater systems, Annual Report October 1, 2007 to September 30, 2008, Lawrence Berkeley National Laboratory, Berkeley, CA

BLM (Bureau of Land Management), 2006. Salt Creek Phases III/IV Environmental Assessment. U.S. Department of the Interior, #WYO60-EA06-18. January 27, 2006.

Boukhelifa, L., Moroni, N., James, S.G., Le Roy-Delage, S., Thiercelin, M.J., Lemaire, G., 2004. Evaluation of cement systems for oil and gas well zonal isolation in a full-scale annular geometry. IADC/SPE Drilling Conference, March 2-4, Dallas, Texas, USA, SPE 87195.

Bradshaw, J., Boreham, C., La Pedalina, F., 2004. Storage retention time of CO₂ in sedimentary basins; examples from petroleum systems. In: Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), 1, 541-550.

Brennan, S.T., Hughes, A.V., Friedmann, S.J., Burruss, R.C., 2005. Natural gas reservoirs with high CO₂ concentrations as natural analogs for CO₂ storage. Greenhouse Gas Control Technologies 7, in: Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies, Vancouver, Canada, Vol. 2, pp. 1381-1387.

Bretan, P., Yielding, G., Mathiassen, O.M., Thorsnes, T., 2011. Fault-seal analysis for CO₂ storage: an example from the Troll area, Norwegian Continental Shelf. Petrol. Geosci. 17, 181-192.

Bruant, R.G., Celia, M.A., Guswa, A.J., Peters, C.A., 2002. Safe storage of CO₂ in deep saline aquifers. Environ. Sci. Technol. 36(11), 240A-245A.

Caillet, G., 1993. The caprock of the Snorre Field, Norway: a possible leakage by hydraulic fracturing. Mar. Petrol. Geol. 10, 42-50.

Carey, J.W., Wigand, M., Chipera, S., WoldeGabriel, G., Pawar, R., Lichtner, P., Wehner, S., Raines, M., Guthrie, Jr., G.D., 2007. Analysis and performance of oil well cement with 30 years of CO₂ exposure from the SACROC Unit, West Texas, USA. Int. J. Greenhouse Gas Control 1, 75-85.

Carroll, S., Hao, Y., Aines, R., 2009. Transport and detection of carbon dioxide in dilute aquifers. Energy Procedia 1, 2111-2118.

Cartwright, J., Huuse, M., Aplin, A., 2007. Seal bypass systems. AAPG Bulletin, 91(8), 1141-1166.

Ceron, J.C., Pulido-Bosch, A., 1996. Groundwater problems resulting from CO₂ pollution and overexploitation in Alto Guadalentin aquifer (Murcia, Spain). Environ. Geol. 28(4), 223-227.

Collins, A.G., 1971. Oil and gas wells: potential polluters of the environment?. J. Water Pollut. Con. F. 43, 2383-2393.

Cypser, D., 2012. Induced Earthquake Bibliography.

<http://www.nyx.net/~dcypser/induceq/induceq.bib.html>. Accessed on March 21, 2012.

Damen, K., Faaij, A., Turkenburg, W., 2006. Health, safety and environmental risks of underground CO₂ storage - overview of mechanisms and current knowledge. *Climatic Change* 74, 289-318.

Dawson, W.C., Almon, W.R., 2000. Top seal character and sequence stratigraphy of selected marine shales in Gulf Coast style basins.

<http://archives.datapages.com/data/HGS/vol42/no08/images/vol42no8p9.pdf>.

DOE (U.S. Department of Energy), 2007. Final Risk Assessment Report for the FutureGen Project Environmental Impact Statement. Contract No. DE-AT26-06NT42921, Revision 2 October 2007.

Duncan, I.J., 2015, Re-evaluating CO₂ toxicity and lethality: Implications for risk assessments of carbon capture and storage (CCS), submitted to *Int. J. GHG Control*.

Ebigbo, A., Helmig, R., Cunningham, A.B., Class, H., Gerlach, R., 2010. Modelling biofilm growth in the presence of carbon dioxide and water flow in the subsurface. *Adv. Water Resour.* 33, 762-781.

Ellis, B.R., Fitts, J.P., Bromhal, G.S., McIntyre, D.L., Tappero, R., Peters, C.A., 2013. Dissolution-driven permeability reduction of a fractured carbonate caprock. *Environ. Eng. Sci.* 30(4), 1-7.

Farrar, C.D., Sorey, M.L., Evans, W.C., Howle, J.F., Kerr, B.D., Kennedy, B.M., King, C.Y., Southon, J.R., 1995. Forest-killing diffuse CO₂ emission at Mammoth Mountain as a sign of magmatic unrest. *Nature*, 336, 675-678.

Franks, S.G., Forester, R.W., 1984. Relationships among Secondary Porosity, Pore-Fluid Chemistry and Carbon Dioxide, Texas Gulf Coast: Part 1. Concepts and Principles. In:

D.A. McDonald, R.C. Surdam (Eds.), *Clastic Diagenesis, Memoir 37*, American Association of Petroleum Geologists, pp. 63-79.

Gasda, S., Bachu, S., Celia, M., 2004. The potential for CO₂ leakage from storage sites in geological media: analysis of well distribution in mature sedimentary basins. *Environ. Geol.* 46(67), 707-720.

González-Nicolás, A., Cody, B., Baù, D., 2012. Stochastic analysis of factors affecting the leakage of CO₂ from injected geological basins. *XIX International Conference on Water Resources*, University of Illinois at Urbana-Champaign, June 17-22, USA.

Gough, C., Shackley, S., 2006. Towards a multi-criteria methodology for assessment of geological carbon storage options. *Climatic Change* 74, 141-174.

Guen, Y.L., Poupart, O., Loizzo, M., 2009. Optimization of plugging design for well abandonment-Risk management of long-term well integrity. *Energy Procedia* 1, 3587-3594.

Hepple, R., Benson, S.M., 2003. Implications of surface seepage on the effectiveness of geologic storage of carbon dioxide as a climate change mitigation strategy. *Proceedings of Sixth International Greenhouse Gas Control Conference*, in J. Gale and Y. Kaya (eds.), Elsevier, v.1, 261-266.

Hepple, R.P., 2005. Human health and ecological effects of carbon dioxide exposure. In: Benson, S.M. (Eds.), *Carbon dioxide capture for storage in deep geologic formations - results from the CO₂ capture project, Vol. 2: geologic storage of carbon dioxide with monitoring and verification*. London, UK, pp. 1143-1172.

Holloway, S., 1996. The underground disposal of carbon dioxide. Final report JOULE II project no. CT92-0031. Keyworth: British Geological Survey.

Holloway, S., 1997. Safety of the underground disposal of carbon dioxide. *Energy Convers. Manage.* 38(Suppl.), S241-S245.

Holloway, S., Pearce, J.M., Hards, V.L., Ohsumi, T., Gale, J., 2007. Natural emissions of CO₂ from the geosphere and their bearing on the geological storage of carbon dioxide. *Energy* 32, 1194-1201.

Hovorka, S.D., 1999. Optimal geological environments for carbon dioxide disposal in saline aquifers in the United States. Draft Final Contract Report to U.S. Department of Energy, Bureau of Economic Geology, The University of Texas at Austin, Austin, TX 78713.

Hovorka, S.D., Benson, S.M., Doughty, C., Freifeld, B.M., Sakurai, S., Daley, T.M., Kharaka, Y.K., Holtz, M.H., Trautz, R.C., Nance, H.S., Myer, L.R., Knauss, K.G., 2006. Measuring permanence of CO₂ storage in saline formations: the Frio experiment. *Environ. Geosci.* 13, 105-121.

Huerta, N.J., Bryant, S.L., Strazisar, B.R., Hesse, M., 2011. Dynamic alteration along a fractured cement/cement interface: Implications for long term leakage risk along a well with an annulus defect. *Energy Procedia* 4, 5398-5405.

Huerta, N.J., Hesse, M., Bryant, S.L., Strazisar, B.R., Lopano, C.L., 2013. Experimental evidence for self-limiting reactive flow through a fractured cement core: Implications for time-dependent wellbore leakage. *Environ. Sci. Technol.* 47, 269-275.

Humez, P., Audigane, P., Lions, J., Chiaberge, C., Bellenfant, G., 2011. Modeling of CO₂ leakage up through an abandoned well from deep saline aquifer to shallow fresh groundwaters. *Transp. Porous Media* 90: 153-181.

Ide, S.T., Friedmann, S.J., Herzog, H.J., 2006. CO₂ leakage through existing wells: current technology and regulations, 8th International Conference on Greenhouse Gas Control Technologies, Trondheim, Norway.

IEA (International Energy Agency), 2004. Prospects for CO₂ Capture and Storage. IEA/OECD, Paris, France, p. 94-97.

IPCC (Intergovernmental Panel on Climate Change), 2005. IPCC Special Report on Carbon Dioxide Capture and Storage.

Jun, Y.S., Giammar, D.E., Werth, C.J., 2013. Impacts of geochemical reactions on geologic carbon sequestration. *Environ. Sci. Technol.* 47, 3-8.

Kalunka, J.E., LaForce, T.C., Blunt, M.J., 2010. Effects of CO₂ storage in saline aquifers on groundwater supplies. SPE International Conference on CO₂ Capture, Storage, and Utilization, November 10-12, New Orleans, Louisiana, USA.

Karamalidis, A.K., Torres, S.G., Hakala, J.A., Shao, H., Cantrell, K.J., Carroll, S., 2013. Trace metal source terms in carbon sequestration environments. *Environ. Sci. Technol.* 47, 322-329.

Keating, E.H., Fessenden, J., Kanjorski, N., Koning, D.J., Pawar, R., 2010. The impact of CO₂ on shallow groundwater chemistry: Observations at a natural analog site and implications for carbon sequestration. *Environ. Earth Sci.* 60(3), 521-536.

Keith, D.W., Wilson, M., 2002. Developing Recommendations for the Management of Geologic Storage of CO₂ in Canada. University of Regina, Regina, SK, Canada.

Kharaka, Y.K., Thordsen, J.J., Kakouros, E., Ambats, G., Herkelrath, W.N., Beers, S.R., Birkholzer, J.T., Apps, J.A., Spycher, N.F., Zheng, L., Trautz, R.C., Rauch, H.W.,

Gullickson, K.S., 2010. Changes in the chemistry of shallow groundwater related to the 2008 injection of CO₂ at the ZERT field site, Bozeman, Montana. *Environ. Earth Sci.* 60(2), 273-284.

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 gases in sedimentary basins. *Geology* 34(7), 577-580.

Kharaka, Y.K., Thordsen, J.J., Hovorka, S.D., Nance, H.S., Cole, D.R., Phelps, T.J., Knauss, K.G., 2009. Potential environmental issues of CO₂ storage in deep saline aquifers: geochemical results from the Frio-I Brine Pilot test, Texas, USA. *Appl. Geochem.* 24, 1106-1112.

Kopp, A., Binning, P.J., Johannsen, K., Helmig, R., Class, H. 2010. A contribution to risk analysis for leakage through abandoned wells in geological CO₂ storage. *Adv. Water Resour.* 33, 867-879.

Kruger, M., West, J., Frerichs, J., Oppermann, B., Dictor, M.C., Joulian, C., Jones, D., Coombs, P., Green, K., Pearce, J., May, F., Moller, I., 2009. Ecosystem effects of elevated CO₂ concentrations on microbial populations at a terrestrial CO₂ vent at Laacher See, Germany. *Energy Procedia* 1, 1933-1939.

Lemieux, J.M., 2011. Review: The potential impact of underground geological storage of carbon dioxide in deep saline aquifers on shallow groundwater resources. *Hydrogeol. J.* 19, 757-778.

Lewicki, J.L., Birkholzer, J., Tsang, C.F., 2007. Natural and industrial analogues for leakage of CO₂ from storage reservoirs: identification of features, events, and processes and lessons learned. *Environ. Geol.* 52, 457-467.

Lindeberg, E., 1997. Escape of CO₂ from aquifers. *Energy Convers. Manage.* 38(Suppl.), 229-234.

Lindeberg, E., 2003. The Quality of a CO₂ Repository: What is the Sufficient Retention Time of CO₂ Stored Underground? In J. Gale and Y. Kaya (eds.), *Greenhouse Gas Control Technologies*, Elsevier, 255-260.

Lindeberg, E., Bergmo, P., 2003. The long-term fate of CO₂ injected into an aquifer. In *Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6)*, in J. Gale and Y. Kaya (eds.), 1-4 October 2002, Kyoto, Japan, Pergamon, v.I, 489-494.

Liu, X., Gong, B., Huo, D., 2010. Numerical simulation on CO₂ sequestration in saline formations with natural or hydraulic fractures using a discrete modeling approach. *Canadian Unconventional Resources & International Petroleum Conference*, October 19-21, Calgary, Alberta, Canada, CSUG/SPE 137621.

Logan, J., Venezia, J., Larsen, K., 2007. Opportunities and challenges for carbon capture and sequestration. *WRI Issue Brief* 1, 1-8.

Lombardi, S., Annunziatellis, A., Beaubien, S.E., Ciotoli, G., Coltell, M. 2008. Natural analogues and test sites for CO₂ geological sequestration: experience at Latera, Italy. *First Break*, 26, 39-43.

Lu, J.M., Partin, J.W., Hovorka, S.D., Wong, C., 2010. Potential risks to freshwater resources as a result of leakage from CO₂ geological storage: a batch-reaction experiment. *Environ. Earth Sci.* 60, 335-348.

Macek, I., Pfanz, H., Francetic, V., Batic, F., Vodnik, D., 2005. Root respiration response to high CO₂ concentrations in plants from natural CO₂ springs. *Environ. Exp. Bot.* 54, 90-99.

Mainguy, M., Longuemare, P., Audibert, A., Lecolier, E., 2007. Analyzing the risk of well plug failure after abandonment. *Oil Gas Sci. Technol.* 62(3), 311-324.

Miglietta, F., Raschi, A., Bettarini, I., Resti, R., Selvi, F., 1993. Natural CO₂ springs in Italy: a resource for examining long-term response of vegetation to rising atmospheric CO₂ concentrations. *Plant Cell Environ.* 16, 873-878.

Nasvi, M.C.M., Ranjith, P.G., Sanjayan, J., 2013a. The permeability of geopolymers at down-hole stress conditions: Application for carbon dioxide sequestration wells. *Appl. Energ.* 102, 1391-1398.

Nasvi, M.C.M., Ranjith, P.G., Sanjayan, J., and Haque, A., 2013b. Sub- and super-critical carbon dioxide permeability of wellbore materials under geological sequestration conditions: An experimental study. *Energy*, <http://dx.doi.org/10.1016/j.energy.2013.01.049>.

Navarre-Sitchler, A.K., Maxwell, R.M., Siirila, E.R., Hammond, G.E., Lichtner, P.C., 2013. Elucidating geochemical response of shallow heterogeneous aquifers to CO₂ leakage using high-performance computing: implications for monitoring of CO₂ sequestration. *Adv. Water Resour.* 53, 45-55.

Newmark, R.L., Friedmann, S.J., Carroll, S.A., 2010. Water challenges for geologic carbon capture and sequestration. *Environ. Manage.* 45, 651-661.

Nicot, J.P., 2008. Evaluation of large-scale CO₂ storage on fresh-water sections of aquifers: An example from the Texas Gulf Coast Basin. *Int. J. Greenhouse Gas Control* 2(4), 582-593.

Nicot, J.P., 2009. A survey of oil and gas wells in the Texas Gulf Coast, USA, and implications for geological sequestration of CO₂. *Environ. Geol.* 57, 1625-1638.

NIOSH (National Institute for Occupational Safety and Health), 1976. Criteria for a Recommended Standard, Occupational Exposure to Carbon Dioxide.

NIOSH (National Institute for Occupational Safety and Health), 1981. Occupational Health Guidelines for Chemical Hazards, DHHS (NIOSH) Publication Number 81-123.

NIOSH (National Institute for Occupational Safety and Health), 2007. NIOSH Pocket guide to chemical hazards, DHHS (NIOSH) Publication No. 2005-149, Department of Health and Human Services, Centers for Disease Control and Prevention.

Oldenburg, C., 2008. Screening and ranking framework for geologic CO₂ storage site selection on the basis of health, safety, and environmental risk. *Environ. Geol.* 54, 1687-1694.

Oldenburg, C.M., Unger, A.J., 2003. On leakage and seepage from geologic carbon sequestration sites: Unsaturated zone attenuation. *Vadose Zone J.* 2, 287-296.

Palmgren, C.R., Morgan, M.G., De Burin, W.B., Keith, D.W., 2004. Initial public perceptions of deep geological and oceanic disposal of carbon dioxide. *Environ. Sci. Technol.* 38(24), 6441-6450.

Patil, R.H., Colls, J.J., Steven, M.D., 2010. Effects of CO₂ gas leaks from geological storage sites on agro-ecosystems. *Energy* 35, 4587-4591.

Pawar, R.J., Watson, T.L., Gable, C.W., 2009. Numerical simulation of CO₂ leakage through abandoned wells: Model for an abandoned site with observed gas migration in Alberta, Canada. *Energy Procedia* 1, 3625-3632.

Pearce, J.M., Holloway, S., Wacker, H., Nelis, M.K., Rochelle, C.A., Bateman, K., 1996. Natural occurrences as analogues for the geological disposal of carbon dioxide. *Energy Convers. Manage.* 37, 1123-1128.

Pierce, S., Sjogersten, S., 2009. Effects of below ground CO₂ emissions on plant and microbial communities. *Plant Soil*, 325, 197-205.

Price, P.N., McKone, T.E., Sohn, M.D., 2007. Carbon sequestration risks and risk management. Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory report LBNL-513E.

Pruess, K., 2008. On CO₂ fluid flow and heat transfer behavior in the subsurface, following leakage from a geologic storage reservoir. *Environ. Geol.* 54, 1677-1686.

Pruess, K., 2011. Integrated modeling of CO₂ storage and leakage scenarios including transitions between super- and subcritical conditions, and phase change between liquid and gaseous CO₂. *Greenhouse Gas. Sci. Technol.* 1(3), 237-247.

Reveillere, A., Rohmer, J., 2011. Managing the risk of CO₂ leakage from deep saline aquifer reservoirs through the creation of a hydraulic barrier. *Energy Procedia* 4, 3187-3194.

Rice S.A., 2003. Health effects of acute and prolonged CO₂ exposure in normal and sensitive populations. Second Annual Conference on Carbon Sequestration, May 5-8, Alexandria, Virginia, USA.

Rish, W.R., 2005. A probabilistic risk assessment of Class I hazardous waste injection wells. *Dev. Water Sci.* 52, 93-135.

Roberts, J.J., Wood, R.A., Haszeldine, R.S., 2011. Assessing the health risks of natural CO₂ seeps in Italy. PNAS, 108(40), 16545-16548.

Rochelle, C.A., Milodowski, A.E., 2013. Carbonation of borehole seals: Comparing evidence from short-term laboratory experiments and long-term natural analogues. Appl. Geochem. 30, 161-177.

Rutqvist, J., 2012. The geomechanics of CO₂ storage in deep sedimentary formations. Geotech. Geol. Eng. 30(3), 525-551.

Rutqvist, J., Birkholzer, J., Cappa, F., Tsang, C.-F., 2007. Estimating maximum sustainable injection pressure during geological sequestration of CO₂ using coupled fluid flow and geomechanical fault-slip analysis. Energy Convers. Manage. 48, 1798-1807.

Rutqvist, J., Tsang, C.-F., 2002. A study of caprock hydromechanical changes associated with CO₂ injection into a brine aquifer. Environ. Geol. 42, 296-305.

Rutqvist, J., Vasco, D.W., Myer, L., 2009. Coupled reservoir-*geomechanical* analysis of CO₂ injection at In Salah, Algeria. Energy Procedia 1, 1847-1854.

Saripalli, K.P., Mahasenan, N.M., Cook, E.M., 2004. Risk and hazard assessment for projects involving the geological sequestration of CO₂, in: Gale, J., Kaya, Y. (Eds.), Sixth International Greenhouse Gas Control Conference, Kyoto, Japan, Volume I, pp. 511-516. Elsevier, Oxford, U.K.

Scherer, G.W., Celia, M.A., Prevost, J.H., Bachu, S., Bruant, R., Duguid, A., Fuller, R., Gasda, S.E., Radonjic, M., Vichit-Vadakan, W., 2005. Leakage of CO₂ through Abandoned Wells: Role of Corrosion of Cement. in S.M. Benson (ed.), Carbon Dioxide Capture for Storage in Deep Geologic Formations, Vol. 2.

Shipton, Z.K., Evans, J.P., Kirchner, D., Kolesar, P.T., Williams, A.P., Heath, J.E., 2004. Analysis of CO₂ leakage through “low-permeability” faults from natural reservoirs in the Colorado Plateau, southern Utah. In: Baines, S. J. & Worden, R. H. (eds.) Geological Storage of Carbon Dioxide. Geological Society, London, Special Publications 233, pp. 43-58.

Sminchak, J., Gupta, N., Byrer, C., Bergman, P., 2002. Issues related to seismic activity induced by the injection of CO₂ in deep saline aquifers. *J. Energy Environ. Res.* 2, 32-46.

Smith, J., Durucan, S., Korre, A., Shi, J.Q. 2010. Carbon dioxide storage risk assessment: Analysis of caprock fracture network connectivity. *Int. J. Greenhouse Gas Control* 5: 226-240.

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* 1, 1957-1964.

Stevens, J.C., van der Zwaan, B., 2005. The case for carbon capture and storage. *Issues in S. and T.* Fall 2005, 69-76.

Sy, S., Fabbri, A., Gravaud, I., Seyedi, D., 2012. Evaluation of the CO₂ leakage risk along the abandoned wells in the French context. *Energy Procedia* 23, 480-486.

Torvanger, A., 2006. Climate Impacts of Leakage from Geological CO₂ Storage. Presentation at the UNFCCC SB24 Meeting, May 20, 2006, Bonn, Germany.

Trautz, R.C., Pugh, J.D., Varadharajan, C., Zheng, L., Bianchi, M., Nico, P.S., Spycher, N.F., Newell, D.L., Esposito, R.A., Wu, Y., Dafflon, B., Hubbard, S.S., Birkholzer, J.T., 2013. Effect of dissolved CO₂ on a shallow groundwater system: A controlled release field experiment. *Environ. Sci. Technol.* 47, 298-305.

USEPA, 2001, Class I Underground Injection Control Program: Study of the Risks Associated with Class I Underground Injection Wells, US Environmental Protection Agency, Report EPA 816-R-01-007.

USEPA, 2010. Underground injection control program: protecting drinking water resources for over 30 years. Office of Water (4606M), 816-F-10-066, December 2010.

USGS (U.S. Geological Survey), 2011. Examination of brine contamination risk to aquatic resources from petroleum development in the Williston Basin. Fact Sheet 2011-3047.

Van der Meer, L.G.H., 1992. Investigations regarding the storage of carbon dioxide in aquifers in the Netherlands. *Energy Convers. Manage.* 33(5-8), 611-618.

Vong, C.Q., Jacquemet, N., Picot-Colbeaux, G., Lions, J., Rohmer, J., Bouc, O., 2011. Reactive transport modeling for impact assessment of a CO₂ intrusion on trace elements mobility within fresh groundwater and its natural attenuation for potential remediation. *Energy Procedia* 4, 3171-3178.

Walton, F.B., Tait, J.C., LeNeveu, D., Sheppard, M.I., 2004. Geological storage of CO₂: A statistical approach to assessing performance and risk. GHGT-7 Conference, Vancouver, B.C., Canada.

Wang, S., Jaffe, P.R., 2004. Dissolution of a mineral phase in potable aquifers due to CO₂ releases from deep formations; effect of dissolution kinetics. *Energy Convers. Manage.* 45, 2833-2848.

Wei, Y., Maroto-Valer, M., Steven, M.D., 2011. Environmental consequences of potential leaks of CO₂ in soil. *Energy Procedia* 4, 3224-3230.

Wesson, R.L., Nicholson, C., 1987. Earthquake hazard associated with deep well injection - a report to the U.S. Environmental Protection Agency. U.S. Geological Survey, Open-File Report 87-331.

Wilday, J., Paltrinieri, N., Farret, R., Hebrard, J., Breedveld, L., 2011. Addressing emerging risks using carbon capture and storage as an example. *Process Saf. Environ.* 89(6), 463-471.

Wilkin, R.T., Digiulio, D.C., 2010. Geochemical impacts to groundwater from geologic carbon sequestration: Controls on pH and inorganic carbon concentrations from reaction path and kinetic modeling. *Environ. Sci. Technol.* 44, 4821-4827.

Williams, S.N., 1995. Dead trees tell tales. *Nature*, 376, 644.

Wilson, E.J., 2004. Managing the Risks of Geologic Carbon Sequestration: A Regulatory and Legal Analysis. Ph.D. Thesis, Carnegie Mellon University, Pittsburgh, PA.

Wilson, E.J., Gerard, D., 2007. Geologic Sequestration under Current U.S. Regulations. In *Carbon Capture and Sequestration: Integrating Technology, Monitoring, Regulation*. Blackwell Publishing, Ames, IA.

Wilson, E.J., Johnson, T.L., Keith, D.W., 2003. Regulating the ultimate sink: Managing the risks of geologic CO₂ storage. *Environ. Sci. Technol.* 37, 3476-3483.

Wiprut, D., Zoback, M.D., 2002. Fault reactivation, leakage potential, and hydrocarbon column heights in the northern north sea. In: Norwegian Petroleum Society Special Publications Volume 11, pp. 203-219, *Hydrocarbon Seal Quantification*, Norwegian Petroleum Society Conference.

Zhang, M., Bachu, S., 2011. Review of integrity of existing wells in relation to CO₂ geological storage: What do we know?. *Int. J. Greenhouse Gas Control* 5, 826-840.

Zhang, Y.Q., Oldenburg, C.M., Finsterle, S., Jordan, P., Zhang, K., 2009. Probability estimation of CO₂ leakage through faults at geologic carbon sequestration sites. *Energy Procedia* 1, 41-46.

Zhou, W., Stenhouse, M., Arthur, R., 2005. Assessment of potential well leakage in the Weyburn site using a stochastic approach. In: *Proceedings of Fourth Annual Conference on Carbon Capture and Sequestration* DOE/NETL, May 2-5.

Zhou, W., Stenhouse, M.J., Arthur, R., Whittaker, S., Law, D.H.-S., Chalaturnyk, R., Jazrawi, W., 2004. The IEA Weyburn CO₂ monitoring and storage project - Modeling of the long-term migration of CO₂ from Weyburn. In: *Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies*.

Section 3: Above Ground Risks of CCS Projects

Introduction

The IPCC special report on carbon dioxide capture and storage (Benson et al. 2005) suggested that the above ground risks of CO₂ storage in brine reservoirs would be similar to the risks of analog industrial activities such as CO₂ based enhanced oil recovery (CO₂-EOR), deep injection disposal of acid (H₂S rich) gas, and natural gas storage in underground reservoirs. At the time the IPCC report was written quantitative evaluations of the risks of these analogue activities were not available to the authors. Over the last decade studies have been published on some aspects of the risks associated with these activities. Unfortunately some aspects of these analogue activities have limited relevance to CCS and should not be uncritically applied to inferring the risks associated with sequestration activities. As a result, a comprehensive analysis of the above ground risks associated with future CCS projects is still lacking.

Benson and Surles (2006) suggest that “analogous experience” from “seasonal storage of natural gas, disposal of liquid wastes, acid gas injection, and oil field operations” demonstrates that shows “injection activities can be carried out safely”. Extensive industrial experience with injection of CO₂ and gases in general indicates that risks from geologic storage facilities are manageable using standard engineering controls and procedures. Employed on a scale comparable to existing industrial analogues, the risks associated with CCS are comparable to those of today’s oil and gas operations. Elsewhere Benson (2006) asserted that “The cumulative experience from CO₂-EOR and natural gas storage provides the foundation for qualitatively and quantitatively assessing the risks of CO₂ storage”.

DNV (2010) suggested that CCS is “a mature technology” that is ready to be deployed on a large scale. DNV based this largely on empirical evidence from analog experience that comes from “almost 100 years of natural gas storage” from hundreds of storage sites in North America and Europe, 35 plus years of experience with CO₂-EOR largely in North America, 15 plus years of experience with acid gas (mixtures of H₂S and

CO₂) injection largely in Alberta, and 14 plus years of experience at dedicated CCS projects in the North Sea and Algeria.

The above ground elements of CCS arguably pose much higher risks in terms of fatalities and serious injuries than below ground risks. Surprisingly very little research has focused on above ground risks compared to those below ground. Above ground incidents will also attract more interest from the general public and have the greatest potential for impacting their health and safety.

To understand the nature of the magnitude of the risks posed on the surface of CCS projects it is first necessary to have some background on the nature of risks that the general public is exposed to in their normal lives. Individual risks for persons exposed to hazards, the likelihood of a fatality occurring per person per year range from (Fell, 1994) 3.0×10^{-4} for road travel to 1.0×10^{-5} for air travel. More risky activities bring a higher probability of death such as 1.9×10^{-3} for parachuting and 2.8×10^{-3} for working as a deep-sea fisherman. Whitman (2000) suggests that people, “implicitly accept a voluntary risk up to 10^{-3} and tolerate involuntary but recognized risks up to perhaps 10^{-5} ”. He notes however that the tolerance for risks suddenly discovered or not well understand is lower. In general risks experts assume that an imposed risk (such as construction of a CO₂ pipeline near your house) will be acceptable to the public only if it is one to two orders of magnitude lower than the highest voluntary risk they are exposed to.

There are a number of approaches to establishing the level of risk that is acceptable to the general public. The simplest is through legislation and/or regulation, as is done in the United Kingdom (UK). Under the UK system an individual risk of 1×10^{-6} is deemed acceptable and a risk of greater than 1×10^{-4} is unacceptable. Risks between these two values must be the subject of proactive mitigation to reduce them to a value as low as is reasonably possible (known as ALARP).

Critical Assessment of Industrial Analogues for Risk

CO₂-EOR as an Analogue

The thirty seven plus years of history of CO₂ injection involved in CO₂ based Enhanced Oil Recovery in the US represent the most tangible evidence available for understanding the risks of CO₂ sequestration in deep brine reservoirs. This section examines what can be learned from the record of risk management supplied by the CO₂-EOR industry.

Leakage and Blowouts of CO₂ Injection Wells

Blowouts are well-known but rare hazards associated with drilling, production from, and injection into oil and gas wells. A blowout of an oil or gas drilling operation occurs when the drillers lose control of the pressure in the well and natural gas, oil, drilling mud and/or formation water escapes. The main danger from blowouts of oil and gas wells comes from the fire or explosion that comes from ignition of the hydrocarbons, particularly natural gas. The typical trigger for blowouts is either mechanical failure and/or encountering unexpected gas pockets during drilling or unanticipated over-pressured zones. The risk of blowouts in CO₂ sequestration projects will differ significantly from those associated with oil and gas exploration and development. The brine reservoirs targeted by CCS drilling will initially contain no CO₂ and is not likely to contain unexpected natural gas. In general drilling into a CO₂ plume would not be planned. Most importantly CO₂ is not flammable or explosive.

A number of misleading statements occur in the CCS literature regarding the risks associated with blowouts. Damen et al (2006), quoting Holloway (1996) suggest that “the likelihood of a sudden escape of *all CO₂ stored* in an underground reservoir is *very small* due to the limited capacity of the injection system” (emphasis added). Even after long times only a portion of the CO₂ could escape due to residual trapping in the porous media. Damen et al also suggest that “in the majority of well failures, an amount equal to the content of the well tubing will be released”. This would only be true for a controlled venting of the well, not for a blowout.

The safety record of the CO₂-EOR industry is excellent. No records of deaths or serious injuries can be found (Duncan et al., 2009). DNV (2010) have pointed to “very similar industrial activities [to CCS] in the EOR industry, injecting CO₂ in large quantities” they suggest demonstrate that “industry and regulators have the necessary solutions to manage risks effectively”. Holloway (1997) suggested (without supporting references) that “although these EOR operations are on a smaller scale than envisaged for [CCS]”, they are “not considered to involve any undue risks to man or the natural environment”.

Regarding leakage of CO₂ to the surface, Damen et al. (2006) have suggested that based on the cumulative CO₂-EOR experience in the USA, “it has been concluded” that the reservoir seals “are maintaining their integrity” and that the CO₂ has been retained “in place”. Quoting an unpublished report by Grigg (2002) they suggest that “no significant leakages have occurred during CO₂ injection period”. Reading the publish version of the report (Grigg, 2005) Damen et al. have given this work more credibility than it deserves in this context. Griggs study was based on written replies to questionnaires sent to CO₂-EOR operators. The assertions by Damen et al. regarding seal integrity and CO₂ retention do not appear to be based on measurements or modeling. Grigg (2005) notes the uncertainty in operator’s statements on CO₂ retention, pointing out that “often the ratio of injection to production fluid has not been tracked as closely as it could be” and that this results in “mass balance uncertainty”. Another statement by Damen et al. (attributed to the Grigg study), is that “No significant leakages have occurred during CO₂ injection period; several operators mentioned that CO₂ migrated through fractures or via flanks of the structure to zones that are in communication with the injection zone”. Grigg (2005) pointed out that although “It is desirable to know how successfully CO₂ is delivered to the intended [oil reservoir] zone” this is often not clear. Grigg’s exact words are that “unexpected fractures, thief zones, and loss out of the flanks of the structure have been suspected as culprits of CO₂ loss”. Take in context Grigg is clearly referring to CO₂ loss from the reservoir zone the CO₂ is being injected into not leakage in the sense being used by Damen et al.

Information from at least one CO₂-EOR project provides evidence for significant diffuse leakage of CO₂ from the injection zone to the surface. Damen et al. (2006) suggested that Klusman (2003a) had measured a surface flux of CO₂ corresponding to roughly 0.1% of the annual injection volume of CO₂ in the at the Rangely CO₂-EOR operation in Colorado. They suggest that this data provides motivation “to assess the impact of reservoir over pressuring as a consequence of CO₂ injection more carefully”. However it is not clear from the information presented in Klusman (2003a) that any CO₂ is leaking from the reservoir to the surface. Klusman shows data that shows very low surface flux of CO₂ in the winter and high fluxes in the summer when microbial conversion of methane is at a maximum. Klusman (2003b) suggested that ¹⁴C data on shallow CO₂ confirms that up to 90% of the CO₂ is ancient. However, the ¹⁴C demonstrates that the carbon is ancient, not necessarily the CO₂. Methane with ancient carbon converted to CO₂ would inherit the carbon.

Deep Disposal of Acid Gas

In Alberta and the Rocky Mountains of the western US and elsewhere sour gas contains hydrogen sulphide (H₂S) and carbon dioxide (CO₂) that must be removed before the gas is sold. H₂S is highly toxic and must be handled with care. H₂S and CO₂ are the byproducts of processing sour gas. Because H₂S is a toxic gas deep well disposal is the safest and most cost effective option (Bachu and Gunter, 2004). Unfortunately there is very limited published information on the likelihood and consequences of accidents associated with acid gas injection projects. Although sour gas well blowouts in Alberta Canada have been estimated to occur with a probability of 3.55×10^{-6} blowouts per well year (Cornwell and Martinsen, 1994), estimates for the blowout rates of acid gas wells do not appear to be available. LeNeveu (2011) has noted that there have been no records of leakage of acid gas through wellbores. Similarly there seem to be no reports of failures of pipelines transporting acid gas.

Acid gas injection has the potential to be an excellent analog for the risk associated with CO₂ sequestration however little quantitative data on these risks is available. It is

likely that the number of well-years and pipeline-years are too small to reasonably expect any incidents.

Natural Gas Storage Fields as an Analog for CCS Risks

Many papers on CCS have suggested that natural gas storage is a useful analog for understanding risks of future CCS projects. Lewicki et al. (2007) suggested that “examples of CH₄ leakage from natural gas storage sites can serve as industrial analogues for CO₂ leakage”. Holloway et al. (2007) suggested that “Experience from natural gas storage operations suggests that fluxes to the biosphere might be expected from a proportion of man-made CO₂ storage sites”. Bachu (2008) suggested (quoting Damen, 2006) that “well-head and pipeline failures” may result in “relatively large flows of CO₂” that these will be “usually short lived”. Again quoting Damen et al. Bachu suggested that “based on statistics of underground gas storage, the frequency of such incidents is likely to be very low”. Damen (2006), quoting Benson et al. (2002) suggest that “there have been a number of documented cases where leakage [of underground gas storage reservoirs] has occurred”. Damen et al. also noted (quoting Perry 2004) that 9 of approximately 600 storage reservoirs globally “have experienced leakage”. DNV (2010) make an almost identical statement based on Perry (2005) but refer to the incidents as having “significant leakage”.

All of the above ultimately refer back to reports by Perry (see Perry 1975) or Benson et al. (2002). Perry’s analysis was based on a written questionnaire survey of 55 companies around the world engaged in natural gas storage that had a 75% response. Perry’s report also fails to make clear the nature of the nine failures that he documents. For example an undated incident in Kansas he lists as “well leakage” involved extensive lateral leakage of methane, explosions and two deaths. Benson et al. (2002) contains no quantitative analysis of failure rates, but rather contains some largely anecdotal information on significant storage failures. Neither this information nor the data provided by Perry (2005) are of the quality or granularity to draw conclusions as to the likelihood of “well head failures” or gas leakage.

A more quantitative approach to estimating risks for underground gas storage was attempted by Saripalli et al. (2002) who estimated the probability of “well-head failure” as 2×10^{-5} . They based this estimate on the fact that “over a period of 25 years, of 432 underground storage facilities”, five incidents “were reported to be U. S. Department of Transportation (DOT) with damages more than \$50,000, none of which were serious”. Unfortunately the incidents reported to the DOT were of failure of pipelines connecting the storage facilities to transmission lines, and thus this data is not relevant to blowouts. Several studies in the United Kingdom (funded by the IEAGHG and the HSE) have quantified risks associate with gas storage facilities (Papanikolau et. al., 2006; HSE, 2008; and Evans, 2009). HSE (2008) Papanikolau et al. (2006) “derived failure rates for the subsurface storage system and calculated it to be 2×10^{-5} per well year”. HSE (2008) estimated that the well failure rate for worldwide underground natural gas storage in depleted oil and gas reservoirs as 5.8 to 8.3×10^{-6} per well year. However consideration of the data presented in Evans (2009) which formed the basis for the HSE study, suggests that the well failures in these cases are major incidents that resulted in fire and explosions rather than well blowouts. The data presented by Evans lumps together blowouts with casing and plug leakage incidents. It seems that this reflects a lack of detail in the underlying data.

The available data on risks of blowouts and rapid leakage associated with underground gas storage projects is inadequate in detail to assess whether it is a useful analog for CO₂ sequestration. No details are available on the causes of the blowouts or the age and integrity of the well that failed. No information is available on the activities taking place at the well head (if any), the fluid pressure in the well, or whether any component such as a blowout preventer failed. As all the information appears to come from surveys of the operators of these facilities the quality and completeness of the data is open to question. Ultimately it seems likely that this kind of data is not of sufficient quality to provide useful input for risk assessments of CCS. In addition it is unlikely that the standards of well construction in underground gas storage sites are comparable to those contemplated for CCS wells. In many cases gas storage facilities used old existing

oil or gas wells. There appears to be little if any public information confirming the integrity of these wells.

Risks Associated with CO₂ Well Blowouts

As pointed out by Gale (2004), in his analysis of research gaps associate with CCS, large releases of CO₂ may occur in sequestration projects due to failure of a well bore. He noted that such releases can present a risk to the health and safety of workers around the well bore and/or nearby inhabitants. The empirical evidence from the CO₂-EOR experience appears to be that the risk presented by large releases of CO₂ by blowouts is small. There have been nearly 50 recorded blowouts in Texas and no fatalities or serious injuries.

Blowouts are a well-known risk in oil and gas development. A blowout of an oil or gas drilling operation occurs when the drillers lose control of the pressure in the well and natural gas, oil, drilling mud and/or formation water escapes. The main danger from blowouts of oil/gas wells comes from the fire or explosion that comes from ignition of the hydrocarbons, particularly natural gas. The typical trigger for blowouts is encountering unexpected gas pockets during drilling or unanticipated over-pressured zones. The risk of blowouts in CO₂ sequestration projects will differ significantly from those associated with oil and gas exploration and development. The brine reservoirs targeted by CCS drilling will initially contain no CO₂ and is not likely to contain unexpected natural gas. In general drilling into a CO₂ plume would not be planned. Most importantly CO₂ is not flammable or explosive. Holloway et al (2007) have asserted that the potential for blowout of CO₂ injection wells are a key risk for geologic CO₂ sequestration in deep brine reservoirs. They suggest that injection well blowouts are the “most likely scenarios in which a high flux emission from a man-made CO₂ storage site could occur”.

It has been suggested that blowouts of CO₂ injection wells are “particularly hazardous” as a result of “the tremendous expansion that can occur when containment is lost”. Near the critical point, even small pressure drops can produce large volume

increases, and CO₂ wells often operate with part of the well near the CO₂ critical point. Therefore, CO₂ wells are different from other wells, which can lead to behavior not expected by field personnel. With the rapid expansion of CO₂, correspondingly rapid cooling of the wellbore and fluid stream occurs. Cooling can reach the point at which solid dry-ice particles form, providing an additional hazard at the wellhead. After exiting the wellhead, the cold CO₂ condenses water from the atmosphere, creating a cloud of low visibility and water ice. After a blowout, the fluid accelerates until the pressure drop in the well matches the pressure drop between the reservoir and atmospheric pressure, limited by the sonic velocity. The sonic velocity is the maximum speed that fluids may attain. Blowouts can be simulated with numerical-flow models. In a blowout simulation, temperatures drop very rapidly to the point at which solid CO₂ (dry ice) is formed (−78°C, at atmospheric pressure). Even in the controlled release of CO₂ during a well test, dry ice can form downstream of the choke used to vent the CO₂.

There are five possible scenarios for blowouts of wells that are associated with CO₂-EOR activities:

- 1) Blowouts of exploration of production wells drilled into natural CO₂ reservoirs
- 2) Blowouts of CO₂ injection wells.
- 3) Blowouts of injector or production wells being drilled into a reservoir under active CO₂ injection
- 4) Blowouts of active oil production wells that are an integral part of the CO₂-EOR project, typically arranged around a CO₂ injection well in a “five spot” pattern.
- 5) Blowouts of inactive or plugged and abandoned wells within the area of increased pressure associated with CO₂ injection wells.

Of these, the second and fifth types are the most relevant to future CO₂ sequestration projects in brine reservoirs.

Using information supplied by the company data, the RRC files, and public reports, the nature of blowouts of CO₂ wells encompassing over 50 CO₂-EOR fields are compiled below as case studies.

Case Study One: Blowout of a CO₂ Production Well

The blowout at the Sheep Mountain Field in Huerfano County, Colorado, occurred March 17-April 3, 1982, during the drilling of CO₂ production well #4-15H, on the west slope of Little Sheep Mountain (Lynch, et al, 1983). The reservoir containing the CO₂ is at depths of 1000 to 1800 m depth in sandstones of Cretaceous and Jurassic age, sealed by fine grained marine sediments of Cretaceous age (Allis et al., 2001).

When the well lost containment, the resultant drop in pressure resulted in vaporizing the supercritical CO₂ to gaseous form. The expansibility of the CO₂ would have led to a highly energetic flow up the well bore. Lynch, et al. (1983) noted that the high CO₂ pressure in the reservoir and the limitations posed by the diameter of the casing pipe complicated attempts at well control. A contractor called in to “kill” the blowout initially had problems related to the high flow rate of CO₂ (estimated at 90 to 200 million cubic feet/day or 4,700 to 10,500 metric tons per day) out of the well. The CO₂ was blowing out the brine based “kill fluid” (and entrained drilling mud and debris). The well came under control the next month through the injection of drag-reduced, Calcium Chloride rich brine followed by mud (Lynch, et al, 1983). During the 17 days the well vented CO₂ before it was brought under control and the flow was stopped 80 to 180,000 metric tons per day. After killing the well, it was plugged and abandoned.

The following case studies of CO₂-EOR blowouts come from company data and the RRC. Over nine years of operation Company A experienced 7 blowouts, incidents where they temporarily lost control of a well. One of these incidents was associated with a CO₂ production well, when coiled tubing packing failed during well work. Two other incidents where associated with CO₂ injection wells. One was caused by leaking gasket at a well head. The other was not a problem with well itself but rather occurred when a

mechanical seal was blown on high-pressure, booster-pump. The other three incidents were associated with production wells. One incident occurred when a casing valve was accidentally left open during work-over operations. Another production well unexpectedly started to flow CO₂ before it was converted to an EOR producer. In the third incident, a problem occurred during the installation of a Blow-Out-Preventer (BOP) stack during work-over operations. There were no deaths or injuries associated with any of these events.

It is very difficult to determine with precision the amount of CO₂ that was released in each of these incidents due to the nature of the events. Company A's engineers have estimated that the release rates ranged from <1 mmcf per day to 10 mmcf per day. The largest event in one of the production wells, occurred over 4 days and Company A engineers have estimated that approximately 40 MMcf of CO₂ (an average of 10 MMcf per day was vented over four days).

Company A has begun to deploy fixed monitors strategically placed throughout their CO₂-EOR facilities. These monitors measure CO₂, O₂, LEL, and H₂S. The accuracy of the new monitors described is +/- 1000 ppm (0.1%). The blowout events discussed above were at wells not at the time equipped with fixed CO₂ monitors. CO₂ measurements were conducted during the accidental release at one of the producers was monitored by portable sensors. Two hundred feet from the release maximum concentrations recorded were approximately 4750 ppm (0.475%). The elevated concentrations dissipated quickly (within 30 minutes). This type of data will be extremely valuable in validating modelling of risks associated with accidental CO₂ releases.

Company A utilizes several safety and preventive measures monitor and mitigate potential blowouts. Company A uses alarms, automatic shutdowns, and human monitoring. Company A has converted sites to 24 hour manned operations in order to detect and respond to any abnormal conditions and to promote more effective risk mitigation.

As noted by Skinner (2003) the greatest danger for loss of well control is during work over operations. During such operations, Company A uses standard industry safeguards on their rigs. As part of their blowout prevention strategies, Company A does daily

monitoring of tubing, production casing and surface casing. Automatic reports are sent out if the pressure measured for production casing or surface casing is greater than zero.

Over the last fourteen years of operation Company B has experienced five blowouts, incidents in which they have temporarily lost control of wells. No injuries or deaths have resulted from any of these accidents. Four of these incidents were apparently caused by the failure of mechanical components (two due to valve failures, two due to failure of nipples). The fifth failure was not related to the well itself but rather was caused by failure of a pump component related to corrosion. None of the five incidents appear to have human error as the primary cause.

Over the past twenty years Company C has experienced twelve well blowouts involving temporary loss of control of CO₂ wells. Six of these incidents were associated with failure of physical components such as valves. One blowout occurred during the installation of a blowout preventer.

One incident that was clearly related to human error was caused by a truck running over an injection well. Another blowout occurred when CO₂ reached a planned production well before a well work over could be completed. Again one of the “blowout” incidents was caused by the failure of a pump component.

Only rarely do well integrity issues appear to play a role in well blowouts. However such incidents deserve closer attention.

CO₂ undergoing deep injections in sequestration projects typically have pressure and temperature conditions for at least a portion of the well near the CO₂ critical point. Decreasing pressure results in a large expansion in the volume of the gas. Thus such blowouts are associated with strong cooling related to adiabatic decompression of the released CO₂. This cooling often results in blowouts of CO₂ wells being characterized by high velocity ejection of solid CO₂ particles (dry ice) as has been described from CO₂- EOR blowouts by Skinner (2003). CO₂ blowouts may entrain sand and other solid debris as well as dry ice particles (Connelly and Cusco, 2007). These particles could have erosion effects, which can damage equipment around the well head, increasing the risks to workers near the well.

Above Ground Risks Associated with below-ground CO₂ Leakage

Gerstenberger et al. (2009) noted that for geologic CO₂ sequestration projects, the leakage of CO₂ to the surface “poses the most widely recognized risk to the success of the project”. They suggest that such leakage has “the potential” to impact health and safety, but do not suggest specific scenarios or likelihoods for such impacts.

The likelihood of leakage to the surface of CO₂ sequestered in deep brine reservoirs is generally expected to be very small (Bowden and Rigg have estimated probabilities in the range 10⁻⁴ to 10⁻⁶). Although research has focused on contamination of groundwater resulting from such leakage the key risk question is whether long term, slow leakage of CO₂ can result in fatalities or serious injuries.

High energy release of CO₂ during blowouts constitutes a low degree of hazard as noted above. However low-energy releases are more likely to form ground hugging plumes that will pond in topographic depressions. Oldenburg et al. (2009) have published some modeling results of the atmospheric dispersion of focused but low CO₂ flux releases. Such a release might be expected from a poorly plugged oil or gas well that has a connection to a deep porous zone above a leaky seal. Unfortunately Oldenburg et al.’s modeling results did not test realistic levels for CO₂ hazard as they used a 4.0% level for safe limit for CO₂ concentrations. Duncan (2015) has shown that 50% CO₂ is a more realistic value. The question of interest for modelling of the type performed by Oldenburg et al. is whether such levels can be reached in ponded CO₂ in topographic depressions given reasonable CO₂ fluxes. Unfortunately such calculations require estimating various factors. However if the probabilities estimated by Bowden and Rigg are reasonable the conditional probabilities of having risk receptors (humans) in a topographic depression in the vicinity of a focused source of leakage, and a sufficient CO₂ flux to build up lethal levels, would seem to be likely extremely small.

References

Aines, R. D., Leach, M. J., Weisgraber, T. H., Simpson, M. D., Julio Friedmann, S., Bruton, C. J., 2009, Quantifying the potential exposure hazard due to energetic releases of CO₂ from a failed sequestration well. *Energy Procedia*, 1 (1), 2421-2429.

Benson, S., 2006, Carbon Dioxide Capture and Storage: Assessment of Risks from the Storage of Carbon Dioxide in Deep Underground Geologic Formations, Lawrence Berkeley National Laboratory
http://www.uscsc.org/Files/Admin/Educational_Papers/AttachmentToUSCSCReportOnCSSafetyPaper_GeologicalStorageRiskAssessment.pdf

Benson, S. M., Surles, T., 2006, Carbon dioxide capture and storage: An overview with emphasis on capture and storage in deep geological formations. *Proceedings of the IEEE*, 94(10), 1795-1805.

Cornwell J. B., Martinsen W. E., 1994, Quantitative Risk Analysis of the Wahsatch Pipeline System, Sixth Annual International Pipeline Monitoring and Rehabilitation Seminar, Houston, Texas

Damen, K., Faaij, A., & Turkenburg, W. (2006). Health, safety and environmental risks of underground CO₂ storage—overview of mechanisms and current knowledge. *Climatic Change*, 74(1-3), 289-318.

DNV, 2010, CO₂ Storage - Is it safe? Towards large-scale implementation of CCS, Det Norske Veritas, Research and Innovation, Position Paper 06 - 2010

Gale, J., 2004, Geological storage of CO₂: What do we know, where are the gaps and what more needs to be done?. *Energy*, 29 (9), 1329-1338.

Gerstenberger, M., Nicol, A., Stenhouse, M., Berryman, K., Stirling, M., Webb, T., Smith, W., 2009, Modularized logic tree risk assessment method for carbon capture and storage projects, *Energy Procedia*, 1(1), 2495-2502.

Grigg R. B., 2005, Long-Term CO₂ Storage Using Petroleum Industry Experience, in Thomas, D. C., & Benson, S. M. (Eds.) *Carbon Dioxide Capture for Storage in Deep Geologic Formations-Results from the CO₂ Capture Project: Vol. 2-Geologic Storage of Carbon Dioxide with Monitoring and Verification*. Elsevier. Chapter 11

Holloway, S., Pearce, J. M., Hards, V. L., Ohsumi, T., Gale, J., 2007, Natural emissions of CO₂ from the geosphere and their bearing on the geological storage of carbon dioxide. *Energy*, 32(7), 1194-1201.

Klusman, R. W., 2003a, Evaluation of leakage potential from a carbon dioxide EOR/sequestration project. *Energy Conversion and Management*, 44(12), 1921-1940.

Klusman, R. W., 2003b, Rate measurements and detection of gas microseepage to the atmosphere from an enhanced oil recovery/sequestration project, Rangely, Colorado, USA. *Applied Geochemistry*, 18(12), 1825-1838.

Lewicki, J. L., Birkholzer, J., & Tsang, C. F. (2007). Natural and industrial analogues for leakage of CO₂ from storage reservoirs: identification of features, events, and processes and lessons learned. *Environmental Geology*, 52(3), 457-467.

Oldenburg C. M., et al., 2009, Model Components of the Certification Framework for Geologic Carbon Storage Risk Assessment, Chapter 21 of Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO₂ Capture Project, Volume 3 Advances in CO₂ Capture and Storage Technology Results (2004 – 2009), Eide L. I. (Ed) 289-316 http://www.co2captureproject.org/pdfs/advances_in_ccs_technology0409.pdf

Perry K.F., 2005, Natural gas storage industry experience and technology: potential application to CO₂ geological storage. In: Benson SM, editor. Carbon dioxide capture for storage in deep geologic formations—results from the CO₂ capture project, vol. 2: geologic storage of carbon dioxide with monitoring and verification. Oxford, UK: Elsevier; 2005. p. 815–25.

Wilson, E. J., Johnson, T. L., & Keith, D. W. (2003). Regulating the ultimate sink: managing the risks of geologic CO₂ storage. *Environmental Science & Technology*, 37(16), 3476-3483.

Section 4: Mechanical Integrity CO₂-EOR wells and Implications for Long Term Risks of CO₂ Sequestration in Brine Reservoirs

Introduction

This section attempts to document publicly available information relevant to understanding the integrity of wells used for CO₂ injection and the construction practices that have been developed by the oil and gas industry for injecting carbon dioxide (CO₂) for enhanced oil recovery (EOR) in large part in the Permian Basin of Texas.

These well construction practices were developed for CO₂ EOR but they clearly provide a direct analogue for the injection of CO₂ for the purpose of geologic sequestration as part of possible future Carbon Capture and Storage (CCS) projects. Wells penetrating the seal of the reservoir are widely regarded by experts as representing the highest risk for long term leakage of CO₂ out of the containment zone. For this reason the well integrity of CO₂ injection wells used in CO₂-EOR is of considerable interest for understanding the leakage risks associated with future CCS projects.

Well completions typically have several strings of steel casing, each cemented into place at least over some interval. During the completion cement is emplaced in the annulus between the casings as the well is drilled. Cementing the annulus provides structural support for the casing as well as protecting the outside of the casing from corrosive fluids (Nelson and Guillot, 2006). Inside the casing the CO₂ is injected through a metal “tubular” that can be replaced if corroded. Thus within a well there are a number of barriers to leakage. CO₂-EOR companies have developed approaches to monitor whether these barriers have been compromised. The main monitoring approach is to measure the pressure in the spaces between these barriers to check for leakage of CO₂. A number of issues can threaten wellbore integrity. Construction problems or difficulties can damage the steel casing. Defective steel pipe may also be an issue.

Unfortunately the current investigation has found that very limited information is available in the public record that would enable predicting future wellbore integrity of CCS projects based on the CO₂-EOR record. First the project team met with regulators at

the Texas Rail Road Commission (RRC). The commission has jurisdiction over the vast majority of CO₂ injection wells in the world. It was found that the RRC has essentially no information in its regulatory files that would help in understanding the nature of well bore integrity for CO₂ injection wells. Wells that fail mechanical integrity tests are remediated by the operators and as long as they pass the test after remediation no details are recorded of what caused the failure or what the remediation was. Anecdotal evidence suggests that in almost all cases the integrity issues are related to the tubulars within the well and not to the casing or cement sheath.

CO₂-EOR Record of CO₂ Injection

The CO₂-EOR industry has 37 years of experience in transporting and injecting CO₂. The first CO₂ pipeline was the 220 mile line constructed in 1972 to link the SACROC field in Scurry County Texas to a gas processing plant in the Val Verde basin. In the US alone the industry operates over 13,000 CO₂-EOR wells, over 3,500 miles of high pressure CO₂ pipelines, has transported over 600 MMtCO₂/yr. and injected approximately twice that amount through recycling. Over 120 active field projects are injecting approximately 52 MMtCO₂/yr. of CO₂. The vast majority are miscible in nature and range from 4000-12000 feet in depth below the surface. Many of the individual CO₂-EOR operations in the Permian Basin inject CO₂ on a scale equivalent to the production of this gas associated with coal burning power plants.

At the SACROC field Kinder Morgan currently injects ~18 MMtCO₂/yr. and captures/recycles ~13 MMtCO₂/yr., for a net storage of ~5 MMtCO₂/yr. For comparison, a 500 MW pulverized coal or Integrated Combined Cycle power-plant produces approximately 4 - 5 MMtCO₂/yr. As the project proceeds essentially all the CO₂ pipelined to the site is becoming sequestered in the reservoir. Kinder Morgan has calculated that well over 99% of the CO₂ transported is trapped in long term storage in the reservoir. Since beginning injection of CO₂ in 1972, the subsurface reservoir of the SACROC unit has accumulated more than 65 MMtCO₂. The injection reservoirs are

proven geologic traps little effort has been expended to date to document either the mechanics of storage or the ultimate fate of the CO₂ within the reservoir.

Monitoring, verification and accounting of stored volumes will be necessary as the EOR industry begins to move into concurrent EOR and storage. The thirty seven years of history of CO₂-injection involved in CO₂-EOR in the US represent the most tangible evidence available for understanding the issues that will arise from large scale sequestration of CO₂ in deep brine reservoirs. CO₂-EOR can also play a pivotal role in jump starting sequestration in the US.

Wellbore Integrity

Almost all risk assessments of CO₂ sequestration conclude that the largest risk is associated with leakage through existing wells and to a lesser extent, the project injection wells themselves. Unfortunately there limited available relevant quantitative data on the long-term wellbore integrity of wells exposed to CO₂. The only tangible data on the long term integrity of future injection wells for CO₂ sequestration projects comes from the experience of nearly four decades of CO₂ injection for enhanced oil recovery.

Wellbore integrity can be viewed as the capability of a well bore to prevent the contamination of potable water aquifers by brines (from deeper formations and/or the injection reservoir) injected CO₂. The Norwegians define wellbore integrity as the “application of technical, operational and organizational solutions to reduce risk of uncontrolled release of formation fluids throughout the lifecycle of a well.”

The improvements in the integrity of well bore over the last century have from the oil and gas industry in general and the CO₂-EOR industry specifically. In the case of CO₂ injection wells the experience comes exclusively from the CO₂EOR industry. Current well construction technologies will provide the basis for the design of CO₂ injection wells for geologic sequestration in brine reservoirs that are expected to provide the bulk of future Carbon Capture and Storage (CCS) projects.

Preexisting wellbores represent the most likely conduit for vertical CO₂ migration from sequestration reservoirs. Wells newly constructed wells also can be the site for CO₂ leakage and migration. Unfortunately field studies of real wells exposed to CO₂ that have

been conducted thus far have been inadequate to create a robust methodology to relate leakage risk to well-log data.

Well completions typically have several strings of steel casing, each cemented into place at least over some interval. During the completion cement is emplaced in the annulus between the casings as the well is drilled. Cementing the annulus provides structural support for the casing as well as protecting the outside of the casing from corrosive fluids (Nelson and Guillot, 2006). Inside the casing the CO₂ is injected through a metal “tubular” that can be replaced if corroded. Thus within a well there are a number of barriers to leakage. CO₂-EOR companies have developed approaches to monitor whether these barriers have been compromised. The main monitoring approach is to measure the pressure in the spaces between these barriers to check for leakage of CO₂.

Issues that influence the integrity of wellbores include: design problems, leaking along boundaries of the cement sheath around the casing due to poor quality cement job or degradation over time, corrosion particularly of casing exposed to acidic brine saturated in CO₂, leakage of tubing particularly at joints. Anecdotal evidence from CO₂ EOR companies suggests that tubing leakage is by far the most common reasons for well bore integrity problems in CO₂ injection wells. Such problems are also the easiest to detect, remediate and to prevent. Use of higher quality tubing and taking greater care in installation has been found to greatly reduce the frequency of leaks from tubing in CO₂ injection wells.

It is important to note that failure to contain CO₂ will only occur if there are multiple barrier failures during the same period of time. For example CO₂ leakage from the tubular is not a problem if the casing is intact. The casing will not leak if the cement sheathing is intact. Well cured cement has very low permeability, a typical value being 10⁻² m². CO₂ will not penetrate cement in the annulus to any extent unless it has been altered by corrosive fluids or is not properly cured. Issues that influence the integrity of wellbores include design problems, leaking along boundaries of cement due to poor quality cement job or degradation over time corrosion, leakage of tubing.

Cement Problems

Cementing wells can be either primary cementing (done immediately after setting casing) or secondary (remedial cementing such as squeezing). A number of techniques are available for primary cementing. Single-stage cementing is commonly used for oil and gas wells. In single stage cementing involves pumping a calculated volume of slurry displacing drilling mud through the casing, around the shoe (the base of a particular casing string) and up into the annulus.

Primary cementing is designed to seal the annulus between casing and formation, or between different casings. The cement sheaths provide structural for the casing that can prevent excessive stress being generated by pressure pulses in the well. In multi-stage cementing, cement slurry is pumped in two or more stages in order to effectively seal the annulus. First stage cementing is accomplished in the same manner as a single-stage, filling the lower casing. A collar is then hydraulically opened enabling cement to enter the remaining upper part of the casing interval. This approach can be used if the fracture gradient is problematic, or if a high quality cement-job is important for a long string of casing. Squeeze cementing is a remedial technique of forcing a cement slurry under pressure into splits in the casing, or through perforations into annular spaces that were inadequately cemented (Feder 2001; Farkas, 1999) . Squeeze jobs are mostly done during drilling and completion, but can also be important in the abandonment phase.

An important element of well bore integrity is the integrity of the cement sheath in the annulus between the casings. The cement sheaths may have cracks and/or tubular holes within them can provide pathways leakage of CO₂ to the surface or between formations.

Common well cement shrinks as it cures in the annulus of the well bore. If this results in the bond with the rock wall failing, this can result in open communication of fluids up the annulus. If the bond between the cement and the surrounding rock is strong negative dilatational strains may result in tensile failure of the cement-sheath.

The interaction of CO₂ and cement takes place via multiple steps: relatively rapid dissolution and carbonate replacement can be followed by leaching of the carbonate.

Calcite may create a mechanical instability of the cement sheath. Fissures in the cement sheath can result in enhanced fluid flow which in turn can result in leaching of the cement sheath.

The degradation of cement under sequestration-like conditions has been extensively studied in the lab and by theoretical modeling. Numerous experimental studies have been made of cement dissolution rates has been conducted by Kutchko et al., Duguid et al. and Barlet-Gouédard et al. who studied the effect of CO₂ on Portland cements in the Laboratory. Most of these studies did not buffer the fluid chemistry by including an appropriate wall rock such as shale and casing steel in the experiments. And in most cases the results have not been verified by studies of real well bores. The rate of degradation of the engineered components of a CO₂ well bore depends on the nature of the construction materials, the skill of the team performing the original cement job (and the adequacy of quality assurance). The older the well, the more likely that its sealing and casing components have degraded.

Methods of Monitoring Wellbore Integrity

A number of down-the-hole tools are available to evaluate the integrity of the casing and the cement-sheath. The cement bond log (CBL) is perhaps the most widely used technique currently in use. Pulse echo logs are less likely to be used. Although such approaches can give a general idea of the condition of a cement job, under some circumstances they fail to identify significant problems. Duguid and Tombari (2007) have noted that as CO₂ injection wells are a series of nested casings, each cemented, that a range of different types of measurements is required to properly evaluate well integrity. They suggest that such measurements should include wire-line-tools such as caliper-logs and some combination of sonic and ultrasonic tools to evaluate casing and cement sheath integrity.

Schlumberger's Isolation Scanner tool is a relatively new technology for measuring well bore integrity that has considerable promise for evaluating CO₂ injection wells. This tool combines the classic pulse-echo technology with a new ultrasonic technique known as flexural wave imaging. The ultrasonic transmitter in the tool creates an ultrasonic pulse

that induces flexural waves in the steel casing that are measured at two receivers. The attenuation of these waves between the two receivers provides an independent measure of material properties that can be paired with the pulse echo measurements and compared to a data base of lab measurements to identify material types on-the-fly and create image maps of the character of the material immediately behind the casing. Signals coming later than the casing arrivals from the interfaces between the cement sheath and the outer casing or the annulus and the borehole wall can be similarly mapped.

In addition to confirming the effectiveness of cement jobs for zonal isolation the tool pinpoints any channels in the cement. The tool's azimuthal and radial coverage differentiates low-density solids from liquids to distinguish lightweight and foam cements from contaminated cement and liquids. The Isolation Scanner can provide detailed images of casing centralization and identifies corrosion or drilling-induced wear on the casing.

The tool can be used to accurately characterize and map different variants of cement which may be related for example to impact of exposure to CO₂ and or CO₂ saturated brines. This is possible because the Isolation Scanner measures the acoustic impedance of the material behind the casing. As the acoustic impedance is the product of the ultrasonic velocity of the material and the density of the material it is a sensitive measure of material properties that we propose to relate back to experimental measurements that are an integral part of the proposed project. Measurements of wave attenuation made by the tool can be used to characterize the cement behind the casing. Class G cements have an attenuation similar to a liquid, an ambiguity that can be resolved by using the acoustic impedance, from the pulse echo technique. Light-weight and contaminated cements have a low impedance that can be readily distinguished from fluids. Unfortunately little if any scans of this sort for CO₂ wells are in the public domain.

Discussion and Conclusions

The CO₂-EOR industry has been injecting CO₂ for over 37 years and this experience represents the most tangible record that can be used to infer the risks that will be associated with future large scale injection associated with large scale geologic

sequestration of CO₂. In Texas alone the alone, the Rail Road Commission has permitted over 13,000 CO₂-EOR wells. The CO₂-EOR industry has transported over 600 million metric tons of CO₂ and has injected over 1,200 metric tons (assuming that on the average 50% of the CO₂ is recycled and reinjected as part of the CO₂-EOR process).

The well design, materials and operational methodologies developed and utilized by the CO₂-EOR industry will provide an invaluable resource in developing standards for CO₂ injection well for future CCS projects. Ultimately the integrity of CO₂ injection wells depend not only on the well design (and the operational practices for drilling and completing the wells), but also the skill of the well completion team. The most tangible data for the effectiveness of the well completion technologies used by the CO₂-EOR industry and their implementation is the fact that there are no known examples of contamination of USDW at any CO₂-EOR site. An extensive study of water chemistry in aquifers overlying the SACROC reservoir (the oldest CO₂-EOR project with injection of CO₂ beginning in 1972) by BEG scientists has failed to detect any evidence of leakage of CO₂ or contamination of USDW attributable to CO₂.

For CCS projects evaluation of the potential leakage risks for CO₂ leakage via well bores (both newly drilled and existing well bores) is essential. Comprehensive efforts should be made to evaluate mechanical integrity of existing wells prior to initiation of injection in a reservoir and of all wells prior to project closure. Technologies are readily available to identify and to remediate well bore integrity problems at any stage in the project.

An obvious question is how relevant is the CO₂-EOR experience (on the order of 35 years for the oldest CO₂ floods) to CO₂ sequestration where the time period of interest is on the order of hundreds to thousands of years. Following the closure of a CO₂ sequestration site, following the sealing of all injection wells, the greatest risk for leakage through the well bores is the time period before the significant additional pressures created by the injection have dissipated. Numerical simulations of multi-phase flow have led to the conclusion that this time period is relatively short, on the order of a few tens of years. For this reason we believe that the CO₂-EOR record does give some significant insights into the leakage risk of future CO₂ sequestration projects that inject into brine

reservoirs. Sealing of wells at the time of closure using contemporary industry best practices, should present a low risk of leakage of CO₂ during this period of higher reservoir pressures. In addition any wellbore leakage in this immediate closure period, after CO₂ injection has ceased, should be readily detectable and remediated.

The thirty seven plus years of history of CO₂ injection involved in CO₂ based Enhanced Oil Recovery in the US represent the most tangible evidence available for understanding the operational risks of CO₂ sequestration in deep brine reservoirs. In the case of blowouts; component failure rather than corrosion or human errors have resulted in the greatest loss of CO₂. The rarity of corrosion related incidents reflects the industries success in implementing anti-corrosion measures. In the case of blowouts, incidents related to CO₂ production wells from natural reservoirs and those that occurred during work over of production wells, resulting from unexpectedly early CO₂ breakthroughs are not directly relevant to understanding the risk of CO₂ sequestration in deep brine reservoirs. Although safety and health issues are always of paramount concern, the excellent safety and health record of the CO₂ industry in the Permian Basin of West Texas may suggest that these issues are not a major component of the operational risk faced by a putative carbon sequestration industry.

References

Bachu S, Bennion DB. (2008), Experimental assessment of brine and/or CO₂ leakage through well cements at reservoir conditions, Int. J. Greenhouse Gas Control (2008), doi:10.1016/j.ijggc.2008.11.002

Barclay, I., J. Pellenbarg, F. Tettero, J. Pfeiffer, H. Slater, T. Staal, D. Stiles, G. Tilling & C. Whitney (2002): The beginning of the end: A review of abandonment and decommissioning practices. Oilfield Review, winter 2001/2002, Schlumberger, UK

Barlet-Gouédard V, Ayache B, Rimmelé G, (2008b), Cementitious Material Behavior under CO₂ environment. A laboratory comparison. 4th Meeting of the Well Bore Integrity Network, Paris, France, 18-19 March.

Barlet-Gouédard V, Rimmelé G, Goffe B and Porcherie O (2006) Mitigation strategies for the risk of CO₂ migration through wellbores. SPE paper 98924.

Barlet-Gouédard V, Rimmelé G, Porcherie O, Quisel N, Desroches J, (2008), A solution against well cement degradation under CO₂ geological storage environment, Int. J. Greenhouse Gas Control, doi:10.1016/j.ijggc.2008.07.005

Beddoe RE, Dorner HW, (2005) Modeling acid attack on concrete: Part I. The essential mechanisms, Cement and Concrete Research 35, 2333-2339

Carey JW, Wigand M, Chipera SJ, Wolde G, Pawar R, Lichtner PC, Wehner SC, Raines MA, and Guthrie Jr GD, (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 1 75-85

Celia MA, Bachu S, Nordbotten JM, Gasda SE and Dahle HK (2004): Quantitative estimation of CO₂ leakage from geological storage: analytical models, numerical models and data needs. Proceedings of 7th International Conference on Greenhouse Gas Control Technologies. Volume 1: Peer reviewed papers and plenary presentations. IEA Greenhouse Gas Programme, Cheltenham, UK.

Dillenbeck RL, GoBoncan V and Rogers MJ, (2005), Testing cement static tensile behavior under down-hole conditions, SPE 97967.

Farkas, R.F., et al., *New Cementing Technology Cures 40-Year-Old Squeeze Problems*. SPE 56537, 1999.

Feder, J., *Casing and Cementing*. Rotary Drilling Series. 2001, Austin, Texas: The University of Texas.

Fernández-Carrasco L, Rius J, and Carles M, (2008), Supercritical carbonation of calcium aluminate cement, *Cement and Concrete Research* 38 1033–1037

Frisch G, Fox P, Hunt D, and Kaspereit D, (2005), Advances in Cement Evaluation Tools and Processing Methods Allow Improved Interpretation of Complex Cements, SPE paper 97186

Fujii K, Yasuda M, Cho B, Ikegami T, Sugiyama H, Imasato Y, Dallimore SR and Wright JF (2008), Development of a monitoring system for the JOGMEC/NRCAN/ AURORA Mallik gas hydrate production test program. *Proceedings of the 6th International Conference on Gas Hydrates (ICGH 2008)*, Vancouver, British Columbia, CANADA, July 6-10, 2008.

Heathman J, and Beck FE, (2006), Finite element analysis couples casing and cement designs for HP/HT wells in East Texas, IADC/SPE 98869.

Huerta NJ, Bryant SL, and Conrad L, (2008), Cement Core Experiments With A Conductive Leakage Pathway, SPE paper 113375

Huet B, Prevost J-H and Scherer GW, (2008), Influence of pH and CO₂ content of the brine on the degradation rate of cement, 4th Meeting of the Well Bore Integrity Network, Paris, France, 18-19 March, 2008.

Hunter S, et al., (2007), Thermal Signature of Free-Phase CO₂ in Porous Rocks: Detectability of CO₂ by Temperature Logging, SPE paper 109007

Krilov Z, et al., (2000) Investigation of a Long-Term Cement Deterioration under a High-Temperature, Sour Gas Downhole Environment, SPE paper 58771, 547-555

Kutchko BG., et al., (2008), Rate of CO₂ Attack on Hydrated Class H Well Cement under Geologic Sequestration Conditions, *Environ. Sci. Technol.*, 42 (16), 6237-6242 • DOI: 10.1021/es800049r

Kutchko BG, et al., (2007) Degradation of wellbore cement by CO₂ under geologic sequestration conditions, Environ Sci. Technol. 41(13), 4787-4792

Ladva HKJ, et al., 2005, The cement-to-formation interface in zonal isolation, SPE 88016, SPE Drilling & Completion, September 2005.

Loizzo M, (2008), Advances in cement interpretation, 4th Meeting of the Well Bore Integrity Network, Paris, France, 18-19 March, 2008.

Loizzo M, and Sharma S, (2008), Assessing Long-Term CO₂ Containment Performance: Cement Evaluation in Otway CRC-1, SPE paper 115707

Midgley HG, (1978), The use of thermoanalytical techniques for the detection of chemical attack on high alumina cement concrete, Thermochimica Acta, 27, 281-284

Milestone NB and Aldridge LP, (1990) Corrosion of Cement Grouts in Aggressive Geothermal Fluids, Geothermal Resources Council Transactions, 14, Part 1, 423-429

Milestone NB, et al., (1986) Carbonation of Geothermal Grouts - Part 1: CO₂ Attack at 150°C, Cement and Concrete Research, 16, 941-950

Mito S, Xue Z, and Ohsumi T, (2008), Case study of geochemical reactions at the Nagaoka CO₂ injection site, Japan, Int. J. Greenhouse Gas Control, 309-318

Moroni N, et al., (2007), Overcoming the Weak Link in Cemented Hydraulic Isolation, SPE 110523.

Moroni N, Repetto C, and Ravi K, (2008), Zonal Isolation in Reservoirs Containing CO₂ and H₂S, IADC/SPE 112703.

Morris C, et al., (2007), Application of Enhanced Ultrasonic Measurements for Cement and Casing Evaluation, SPE/IADC 105648

Nagelhout ACG, et al., (2005), Laboratory and Field Validation of a Sealant System for Critical Plug and Abandon Situations, SPE/IADC 97347.

Noik C, Rivereau A, and Bouygues CV, (1998) Novel Cement Materials for High-Pressure / High-Temperature Wells, SPE paper 50589, 189-194

Ogino T, Suzuki T and Sawada K, (1987) The formation and transformation mechanism of calcium carbonate in water. *Geochim. Cosmochim. Acta*, 51:2757-2767

Onan DD, (1984) Effect of Supercritical carbon dioxide on well cement, SPE paper 12593, 161-172

Orlic B and Benedictus T, (2008), Some geomechanical aspects of well integrity, 4th Meeting of the Well Bore Integrity Network, Paris, France, 18-19 March.

Pedersen RO, et al., (2006), Cementing of an offshore disposal well using a novel sealant that withstands pressure and temperature cycles, IADC/SPE 98891.

Randhol P, et al., (2007) Ensuring well integrity for CO₂ injection well, SINTEF-Report 31.6920.00/01/07, Unrestricted

Saint-Marc J, et al., (2008), Initial state of stress: the key to achieving long-term cement-sheath integrity, SPE paper 116651

Shen JC, Pye DS, (1989), Effects of CO₂ Attack on Cement in High-Temperature Applications, SPE/IADC

Shiraki R, Dunn TL, (2000), Experimental study on water-rock interactions during CO₂ flooding in the Tensleep Formation, Wyoming, USA, *Applied Geochemistry* 15 (3), 265–279

Spycher, N., Pruess, K., (2005). CO₂–H₂O mixtures in the geological sequestration of CO₂. II. Partitioning in chloride brines at 12–100°C and up to 600 bar. *Geochimica et Cosmochimica Acta* 69 (13), 3309–3320.

Sugama T, (2006) Advanced Cements for Geothermal Wells, BNL-77901-2007-IR, <http://www.pubs.bnl.gov/documents/35393.pdf>, July 2006

Sweatman R, (2008), CO₂ Resistant Cements and Chemical Sealants Influence of pH and CO₂ content of the brine on the degradation rate of cement, 4th Meeting of the Well Bore Integrity Network.

Vu-Hoang D, et al., (2006), Assessing the integrity of down-hole CO₂ Storage using in-situ sonic, advanced ultrasonic, and electromagnetic measurements, 2006 GHGT 8 Trondheim, Norway.

Wagh AS, et al., (2005a) New phosphate-based cement useful for drilling, completions in arctic, Oil & Gas Journal, May 9th 2005

Wagh AS, et al., (2005b) Ceramicrete blends produce strong, low-permeability cements for arctic use, Oil & Gas Journal, May 16th 2005

Section 5: Re-evaluating CO₂ Toxicity and Lethality: Implications for Risk Assessments of Carbon Capture and Storage (CCS)

Introduction

The health impact of the leakage of CO₂ transported or stored by carbon capture and storage (CCS) projects is a major part of the risk of such projects (Benson et al, 2002; Hepple, 2005; West et al, 2005) and is a concern of regulators and the public. Arguably by far the greatest risk of death will be associated with surface releases of CO₂ caused by failure of pipelines (Koornneef et al., 2010; Duncan and Wang, 2014) and the blowout of CO₂ wells (Duncan et al., 2009). Modelling of the dispersion of released CO₂ is a key tool in making risks assessments of such incidents (Mazzoldi et al., 2012; McGillivray et al., 2014). To estimate risks of fatalities from dispersion models, information on the lethality of CO₂ as a function of concentration and length of exposure is needed. Although McGillivray et al. (2014) suggest that “there are a number of different methods available to calculate levels of harm” it will be shown in this paper that these methods have failed to provide accurate information on the lethality of CO₂.

Another key need is knowledge of not only the lethal levels of CO₂ but also the level at which humans become impaired/incapacitated and the mechanism by which CO₂ kills. Benson and her co-workers have asserted that CO₂ is a “nontoxic inert gas” and “generally regarded as a safe, non-toxic, inert gas” (Benson and others, 2002; Benson, 2005; Hepple, 2005). Similarly, Stenhouse and Savage (2004), Heinrich et al (2004), BEST (2007), and Bachu (2008) have described CO₂ as a nontoxic substance. Benson (2005) and Hepple (2005) suggest that, at concentrations of CO₂ between 3 and 5%, humans experience discomfort and impacts on respiratory rate, followed by possible loss of consciousness at levels above 5%.

There is a large range in the supposedly lethal levels of CO₂ reported in the CCS literature. Benson (2005) suggests that “loss of consciousness occurs within seconds at concentrations above 25 to 30%, followed by imminent death”. Such assertions are common in older textbooks such as Henderson and Haggard’s (1943) hand book on Noxious Gases. They noted that for humans, levels of CO₂ higher than 10% can be lethal, and a few breaths at levels in the range 20-30% can lead to unconsciousness and death. Harper (2011) has recently published an analysis of

CO₂ lethality that suggested exposure to 10.5% CO₂ for 10 minutes would result in 50% fatalities. Similarly OSHA (2010) stated that being exposed to CO₂ concentrations “of 10% or more can produce unconsciousness or death”. In contrast Damen et al. (2006) stated that “Prolonged exposure to high CO₂ levels, above 20–30%, will cause death by suffocation to humans” and a French review of CO₂ toxicity (DMT, 1999) suggested that CO₂ is fatal for humans at levels of 30 -40%. Recent risk analyses of the release of CO₂ plumes from pipelines by McGillivray and Wilday (2009), McGillivray et al. (2014), Lisbona et al. (2014) used a lethal value for CO₂ of 17%, based on DNV (2008). Few, if any, of these reviews reference any primary data to support their assertions. A re-examination of the primary evidence (including animal experiments and accidental deaths) relevant to these issues has been made in the current study.

There is a consensus in the CCS literature that CO₂ kills by asphyxia. The Oxford Dictionary defines asphyxia as “a condition arising when the body is deprived of oxygen”. Bachu (2008) stated (referencing Hepple, 2005) that “Carbon dioxide acts as an asphyxiant at concentrations in the 7–10% range [of CO₂] and can be fatal”. A number of others have suggested that about 10% by volume of CO₂ would cause asphyxiation (Heinrich et al., 2004; BEST, 2007; OSHA, 1996; Luttrell and Jederberg, 2008). This paper will evaluate the evidence regarding the role of oxygen deficiency in CO₂ related deaths.

To enable a meaningful assessment of the risks associated with CCS it is essential to understand both the role CO₂ plays in human physiology, and its impact at increasing concentrations. This paper reviews: the nature and symptoms of Hypercapnia (the medical condition associated with excessive exposure to CO₂); the experimental data on the effects of exposure of small animals and primates to high concentrations of CO₂; and information from well documented incidents of CO₂ poisoning and accidental deaths of humans. After a review of available evidence on the lethal levels of CO₂ for humans it is concluded that notion that CO₂ is lethal at levels of 10% or 15% or even 30% is not supported by the available evidence. Rather it is likely that CO₂ at normal atmospheric oxygen levels is lethal at concentrations on the order of 50 to 60%. Thus lethal values of CO₂ are likely as much as a factor of three to six less than the values used in the published analyses of the risk of CCS.

The Nature and Effects of Hypercapnia

Human life depends on the difference in CO₂ pressure between the blood and the ambient pressure in the air to remove CO₂ produced in respiration (Nunn, 1987). As CO₂ levels in the air increases, human respiration becomes progressively less effective in removing excess CO₂ from arterial blood (West, 1985). As the body senses elevated CO₂ levels in blood, it involuntarily increases the ventilation rate (Askanazi et al, 1979). This response is so powerful that even an individual's conscious attempts to overcome it will fail.

The concentration of CO₂ in arterial blood reflects the net result from the bodies' production and elimination of CO₂; normally maintaining this value is within narrow limits. Hypercapnia is a condition characterized by unusually high concentrations of carbon dioxide in the blood (Gross and Hamilton, 1963; Reynolds et al 1972). CO₂ forms a weak dibasic acid in water and typically over 90% of the CO₂ is as bicarbonate ions. Spontaneous breathing requires feedback loops in which the body detects small variations in blood gas and responds with a change in ventilation rates (Feldman et al., 2003). These changes in ventilation appear to be controlled by recently discovered CO₂/pH sensing molecules that modulate the neural pathways in the brainstem (Jiang et al., 2005).

Our bodies have a chemoreceptor system, located in the carotid and aortic bodies, and in the ventral medulla as noted by Boggs (1991), that modulates ventilation proportional to level of CO₂ blood gas. These chemoreceptors respond to changing pH in the blood, a direct function of CO₂ levels. If CO₂ levels build up more rapidly than increases ventilation can handle, a cascade of negative physiological effects will ensue. Schneider and Truesdale (1922) showed that CO₂ levels of 10,000 ppm for 17-32 minutes stimulated an increase in ventilation of 32%. At 50,000 ppm breathing becomes difficult for some.

CO₂ plays an important role in cellular metabolism, and in the physiologic performance of the lungs, heart, intestines and other organs. Lower pH immediately affects a myriad of metabolic and membrane transport function in cells, as proteins and enzymes lose their catalytic functionality (Somero, 1986). Hypercapnia also has complex systemic effects mediated via the central and autonomic nervous systems (Kiely et al 1996). Halpern et al (2004) noted that during acute Hypercapnia (8.3% CO₂) blood flow velocity in the middle cerebral artery increases and has a distinct effect on the electroencephalogram (EEG). A study by Sechzer et al (1960)

identified a small incidence of cardiac arrhythmias as a result of exposure to between 7 and 14% carbon dioxide. The main physiologic effects of acute Hypercapnia are increases in: heart rate, cardiac output, average pressure in the pulmonary arteries, and pulmonary vascular resistance, all of which lead to an excessive load on the myocardium (Halpern et al, 2004). As the buildup of CO₂ increases a range of symptoms can result such as: loss of respiratory drive; increases in heart rate, cardiac output, mean pulmonary artery pressure, and pulmonary vascular resistance; followed by tachycardia, cardiac arrhythmias and impaired consciousness (Guillemin and Horisberger, 1994; Kiely et al, 1996; Mas et al, 2000; Gill et al, 2002; Langford, 2005).

The neurological effects of Hypercapnia have not been as intensively studied as the respiratory and cardiac effects. Lambertsen (1971) has suggested that the neurological consequences of a sudden exposure to high levels of CO₂ for one and a half minutes are:

- At 10% CO₂, psychomotor excitation, eye flickering, and myoclonic twitches.
- At 15%, the same as 10% but with increased muscle tone, perspiration, flushing, restlessness, dilated pupils, leg flexion, and torsion spasms.
- At 20 and 30% carbon dioxide, the same as 15% but with tonic (short epileptic) and tonic-clonic seizures (previously known as grand mal seizures) in some.

However Lambertsen's assertions are largely not documented by reference to primary literature and thus are difficult to evaluate. His assertions regarding seizures may represent a misunderstanding of the experimental data and this issue is explored later in this paper. Sieker and Hickam (1956) in their pioneering study of CO₂ intoxication noted that Hypercapnia correlates most closely with encephalopathy (malfunction of the brain). Ford et al (2000) noted that elevated levels of CO₂ in the blood result in narcosis preceded by delirium. CO₂ buildup in the blood acts as an anesthetic. Until the study of Kliefeth et al (1979) medical researchers had failed to demonstrate conclusively that hypercapnia impacted the cerebral metabolic rate for oxygen (CMRO) in humans or primates. Based on their study of the effects of hypercapnia in the rhesus monkey Kliefeth et al (1979) demonstrated that CO₂ has a depressant effect on the CMRO, in adult primates when the CO₂ content of arterial blood is acutely elevated.

Hypercapnia has secondary systemic effects that are mediated by the central and autonomic nervous systems (Kiely et al, 1996). Thus, when CO₂ builds up in blood it has psychological effects (Maresh et al, 1997). In humans, psychological effects typically include a degradation of

cognitive function, which can impair decision making. This is especially true in dealing with emergency situations. Cognitive degradation occurs at lower levels of CO₂ exposure than physical incapacitation (Maresh et al, 1997).

At elevated CO₂ levels, studies on small animals have provided key information on the physiological effects (Lai et al 1981; Bercovici et al 1983; Sakurai, 1989; Ikeda et al 1989; Gu et al, 2000). In a study of the brain in extreme respiratory acidosis based on a detailed analysis of changes in the brains of anesthetized rats Paljärvi et al. (1982) concluded that although short-term, moderate exposure to CO₂ had no measurable effect, high exposures resulted in a range of neural changes. Although human subject experiments (Sayers et al. 1987) showed that an increase in CO₂ levels up to 7.5 percent for 20 minutes had no significant impact on accuracy of reasoning or short-term memory. The speed of reasoning tasks was slowed significantly at the higher CO₂ levels.

There is a considerable body of evidence on human subjects that symptoms of anxiety (or panic) can result from short exposures to high doses of CO₂ (Van den Hout, et al 1984; Woods et al 1988; Coryell, 1997; Coryell et al 2001; Kaye et al. 2004). Hypercapnia is mildly to moderately anxiogenic in the case of average humans, however for those with a tendency to panic disorder exposure to CO₂ levels of 5% may result intense anxiety or full panic attacks (Woods et al, 1988; Kaye et al 2004). Exposure to CO₂ levels of 5-7.5% for 15 min resulted in an increase in symptoms of anxiety and panic proportional to CO₂ level in subjects of general good health (Van den Hout, et al 1984). Ironically single breath administration of 20 to 35% CO₂ is used as a treatment for panic attacks (Forsyth et al, 2000; Koszycki and Bradwejn, 2001). Disproportionately heightened anxiety and/or degradation of cognitive function can result in workers making poor decisions in emergency situations.

Toxicity of CO₂

Although there is a broad consensus in the CCS literature that CO₂ is non-toxic, the toxicology literature provides a very different view (Williams, 1958; Ikeda et al, 1989; Ernst and Zibrak, 1998; Gill et al, 2002; Stuhmiller and Stuhmiller, 2002; Langford, 2005). The toxic nature of CO₂ has been known for at least 50 years. Williams (1958) noted that of CO₂ has been considered to act both “as a simple asphyxiant”, and also by “a chemical action as a respiratory

stimulant and narcotic". Williams concluded that, in the cases he reported on, "the mode of action of carbon dioxide [is] as a poison".

The nature of lethal (and incapacitate) levels for CO₂ in humans are not well understood. Benson et al. (2002), quoting NIOSH (1976), NIOSH (1981), and ACGIH (1994), stated that "Death occurs within minutes at 30% CO₂". Neither NIOSH (1976) nor NIOSH (1981) make any statement regarding the lethal levels of CO₂, though they note that exposure to CO₂ levels of 25 to 30% "may cause convulsions". Death is probably due to loss of respiratory drive, resulting in rapid increase in CO₂ levels and pH in the victim's blood (Langford, 2005 and references therein). In humans the exact cause of death is not known and may well vary from case to case. This section examines the primary evidence that bears on the levels of CO₂ that are lethal to humans.

Information from Sub-lethal Experimental Exposures of Human Subjects

Limited data at the higher levels of non-lethal exposure are available from studies based on human volunteers. Dripps and Comroe (1947) described CO₂ as having a narcotic effect on medical student volunteers at levels of 7.6 or 10.4%. The students reported feelings of dizziness, faintness, and in some cases a "similarity to the onset of nitrous oxide anesthesia". Studies that are often referenced to suggest the range CO₂ levels that can lead to loss of consciousness include:

- At 7.6%, 1 out of 44 young males exposed levels of CO₂ for 2.5 to 8.5 minutes, studied by Dripps and Comroe (1947), became unconscious.
- At 10.4% CO₂ for 2.5 to 6 minutes, loss of consciousness was observed in 3 of 31 subjects (Dripps and Comroe, 1947)
- At 10 to 15% CO₂, 12 healthy male volunteers, exposed for ten to twenty minutes resulted in dizziness, drowsiness, severe muscle twitching, and unconsciousness in some subjects (Sechzer et al. 1960).
- At 17.0% CO₂ and 17.3% O₂ three subjects became unconscious after 16 to 35 seconds (Spealman, in Aviation Toxicology, 1953)
- At 27.9% CO₂ and 15% O₂ three subjects became unconscious after 20-52 seconds (Spealman, in Aviation Toxicology, 1953)

- At 30% CO₂ in 70% O₂, for 2 to 3 minutes resulted in unconsciousness and convulsions (reported by Lambertsen, 1971 but source and details of experiments not clear)
- At 30% CO₂ in 70% O₂, 37 young adult subjects exposed for 50-52 seconds resulted in “the average patient” losing consciousness within 24-28 seconds (Friedlander and Hill, 1954)

The three studies of humans exposed to 30% CO₂ (referenced by NIOSH, 1976) were not designed to establish the lethality of CO₂. At best, these may provide limited and fragmentary information on the propensity for loss of consciousness after short exposures to 30% CO₂ and 70% O₂. At least some of the studies of the effects of 30% CO₂ are inappropriate for the current purpose as they used subjects that were prone to seizures (see discussion section). Others were carried out in studies of the potential of CO₂ as an anesthetic, and thus likely to result in a different outcome than an emergency CO₂ incident which would release adrenaline into the body.

Information from Experimental Exposures of Animals

It is clearly too dangerous to test the limits of human tolerance to CO₂ on live subjects. The toxicity of CO₂ has been supported by clinical experiments using small animals (Sakurai, 1989; Watanabe and Morita, 1998; Ikeda et al 1989), as well as investigation of CO₂ based accidents (Guillemin and Horisberger, 1994; OSHA, 1996; Gill et al., 2002; Halpern, et al. 2004; Hsieh et al., 2005). Experimental studies on small animals have confirmed that breathing high concentrations of CO₂ (at normal oxygen levels) causes death by CO₂ poisoning rather than asphyxia. Experiments on rats have long shown that CO₂ acts in a different way to that of simple asphyxiants. Ikeda et al. (1989) conducted a study in which dogs breathed a mix of 80% CO₂ with 20% O₂. They observed that normal respiration ceased in one minute, with terminal respiration and circulatory breakdown soon thereafter. Ikeda et al. (1989) concluded that these observations demonstrated that the cause of death from high levels of CO₂ is not asphyxia but rather CO₂ poisoning. Watanabe and Morita (1998) have noted that in experiments on rats, respiratory arrest occurred at the concentration of 4–5% O₂ with non-toxic gases such as Nitrogen, Methane and Propane acting as diluents of air. In contrast, they noted that “toxic gases

[such as] CO₂” resulted in respiratory arrest within 30 minutes at higher levels of O₂ (6.6–8.0%) when CO₂ levels were 60–67%. They further note that with 80% CO₂ and 20% O₂ death occurred within 19–23 minutes.

Pryor et al (1969) studied the impact of toxic fire gases on mice exposed to various mixtures of gases and oxygen levels. In one set of experiments at 21% O₂ and 40% CO₂ none of ten mice exposed for 24 hours died. At 50% CO₂, again with 21% O₂, two of ten died. In another set of experiments under the same conditions for 4 hours, again two of ten rats died. Mitsuda et al. (1982) studied rats exposed to 40% CO₂ with normal oxygen levels for three hours and found a 21% mortality rate. In a series of experiments on the lethal effects of low oxygen environments on rats Watanabe and Morita (1998) found that death occurred within 30 minutes in an atmosphere of 60 to 67% CO₂ and 6% O₂.

In their study of the tolerance of the dog heart to CO₂ Brown and Miller (1952) conducted a series of experiments in which CO₂ concentration was gradually increased over 60 to 90 minutes. The dog’s blood pressure began to fall as CO₂ levels reached 50 to 70% and cardiac arrest followed. A study of Rhesus monkeys (Stinson and Mattsson, 1970), exposed to CO₂ (in an atmosphere controlled at 21% O₂), at a rate of increase of 30% CO₂ per hour, started exhibiting arrhythmias at approximately 26% CO₂ and died at 60% CO₂. A study of three chimpanzees (Stinson, and Mattsson, 1971) resulted in similar observations. This lead them to conclude that as monkey’s can survive in air with up to 51% CO₂, humans can survive similar exposures to this gas.

To extrapolate the information from animal experiments to humans, models have been developed to estimate the probability of lethality taking into account ventilation changes related to species, level of activity, and chemical response (Stuhmiller and Stuhmiller, 2002; Stuhmiller and Stuhmiller, 2005; Stuhmiller et al, 2006). A lethal concentration of CO₂ for humans of around 50% gave the best fit to the data sets used for calibrating the model (Stuhmiller and Stuhmiller, 2002).

Information from Accidental Human Deaths

Many reports in the emergency and forensic medicine literature document deaths related to high CO₂ exposures. Only a fraction of these reports contain measurements of the CO₂ and O₂

levels that proved lethal. Anselmo et al. (1951) described an incident where 2 of 5 workers who collapsed died working in a well 4.75 meters deep. Later analysis of the air found a CO₂ level of 12.5% and an O₂ level of 10.5% one meter above the surface of the water. In another incident three men consecutively descended into an open, “six-foot-deep” drainage-pit to recover a fallen grate lid. Each in turn, became unconscious and died within minutes. Analysis of air samples showed decreasing in oxygen levels, from 20% at the top to 3% at the bottom with CO₂ levels increasing to 22% at the 6-ft. depth of the pit (Manning et al., 1981). These incidents probably involve removal of oxygen from the atmosphere by bacterial action on organic matter.

NIOSH (1994) reported an incident where a 35 year old worker fell into a closed fermentation tank with an atmosphere with 49% CO₂ and 6% O₂ (as determined by an OSHA inspector after the accident). At some point after the worker’s fall, the foreman walked into the room and heard a thumping noise, which he discovered was the worker attempting to get out of the tank. The foremen failed to rescue the worker with a rope. Two hours after the accident the victim was found dead by the rescue squad. It is not known how long the worker remained conscious, nor at what time death occurred, however it seems likely from the anecdotal evidence that the workers was conscious for some minutes at a minimum.

Gill et al. (2002) describe the death of a 51-year-old research scientist, with a medical history of slight bronchial asthma, who entered a small cold storage room with no working ventilation system. At least 3 hours earlier, 15 one liter blocks of dry ice had been placed in the room. When the accident was recreated, a CO₂ level of 27.6% and an O₂ level of 13.6% were measured after 3 hours, with a room temperature of -15°C. In a similar accident, the San Diego Hazardous Materials Incident Response Team responded to an incident in which a 59-year-old man was found dead shortly after entering a walk-in freezer containing dry ice (Dunford et al., 2009). Initial measurements suggested a 13% O₂ concentration and that the CO₂ levels inside the freezer could be as high as 40%.

An interesting example of survival from high levels of CO₂ comes from the accidental release from a CO₂ fire suppression system in 1998 at Idaho National Lab described in government contracted investigation reports (AIB, 1998; LMITC, 1999) and in Shields (2006). On July 28, 1998, thirteen workers were shutting down electrical circuit breakers before beginning preventive maintenance of part of the Engineering Test Reactor Facility at the Idaho National

Engineering and Environmental Laboratory (INEEL). Just after the room went dark, after cutting off the electricity, a CO₂ fire suppression system was accidentally activated without warning (AIB, 1998). The system was designed to create a 50% CO₂ atmosphere. Eight workers escaped without assistance, probably because they were close to the exit door (LMITC, 1999). Several other workers collapsed before reaching the exit. During this accident Lab staff were exposed to the CO₂ enriched atmosphere, 3 for ten minutes, and 3 for 20 minutes (Shields, 2006). One victim died, and 5 survived. Three victims required hospitalization, one was initially comatose, and several of had long term symptoms.

There is also ample evidence in the data presented above that the impact of CO₂ is subject to significant differences between individuals. As noted by OSHA (1996) “The response to carbon dioxide inhalation varies greatly even in healthy normal individuals”. Rice (2004) has pointed out that the majority of studies of the physiological effects of CO₂ have been based on healthy young male subjects. Carbon dioxide tolerance may be different for children, the elderly, or people with respiratory deficiencies.

If CO₂ is Toxic then Does Asphyxiation Play a Role in Lethality of CO₂?

Given the evidence presented above that CO₂ is toxic, a logical question is whether asphyxiation will still play a role in death from CO₂ under plausible real world conditions. Rice (2004), in a review of the health effects of high CO₂ level in the context of CO₂ sequestration, suggested that signs of asphyxia will be observed in humans when oxygen levels in the atmosphere fall below 16%. Watanabe and Morita (1998) noted that, in their experimental study of asphyxia of rats, respiratory arrest occurred at oxygen levels of 4–5% when non-toxic gases (Nitrogen, Methane, Nitrous Oxide and Propane) acted as the asphyxiant. The text on Forensic Pathology by DiMaio & DiMaio (2001) suggests that for humans at oxygen concentrations [in air] of 4 to 6%, there is “loss of consciousness in 40 seconds and death within a few minutes” (see also USCSHIB, 2003). These conclusions are supported by Purser (1984) whose 4 monkeys remained conscious after exposure to 10% O₂ for 30 minutes. In addition, the model developed by Stuhmiller et al (2006) predicts that the average value for a lethal level of oxygen depletion for humans exposed for 30 minutes is 8.5%.

CO₂ and Occupational Safety

There are a large number of industrial, commercial and retail uses for CO₂, however by far the largest user is the CO₂-EOR industry. This industry has recorded no fatalities or serious injuries associated with handling over 1.2×10^9 metric tons of CO₂ (Duncan et al., 2009). Risks associated with other industrial and commercial uses of CO₂ are significant. For example, deaths from CO₂ accidental discharge of CO₂ fire extinguishing systems into confined areas from 1975 to 1999 totaled 72 deaths and 145 injuries (EPA, 2000). Sporadic deaths from CO₂ have also occurred over the last century in empty fermentation tanks in breweries and wineries. In all these cases CO₂ was contained in a confined space with no ventilation.

Recently Scott et al. (2008) have noted that many who are exposed to CO₂ in their work "believe it to be harmless" and therefore "neglect to recognize the dangers associated with this toxic gas". In this context it is disturbing to see statements such as the following by Halliday (2007): "Lowered oxygen levels associated with increased CO₂ can be lethal whereas increased CO₂ is merely distressing if adequate oxygen is present". Much of the information on the danger of CO₂ readily available to the general public is similar to the following from Iowa State Universities Agricultural and Biosystems Engineering Extension service web site who assert "CO₂ is not toxic. At high concentrations it can cause sleepiness, headache, and contribute to the "stuffy" feeling of closed houses".

This section looks at regulatory/worker safety issues related to CO₂ and reviews best practices in emergency response and treatment of hypercapnia.

Regulatory Issues

Strong occupational health standards to protect workers protective have been in place for many decades. A government agencies decision as to what is a level of acceptable human tolerance to CO₂ is in part a matter of policy rather than merely science. The first official safe limit for CO₂ was developed in 1946 by the American Conference of Governmental Industrial Hygienist (see ACGIH, 1994) who recommended that the Threshold Limit Value (TLV) should be 5.0%. From a safety/risk management perspective there are three key issues: 1) the CO₂ level that results in loss of effective decision making ability; 2) the level that causes loss of consciousness; and 3) the level that is immediately threatening to life (Speitel, 1995). OSHA and

ACGIH have set exposure limits for gaseous CO₂ as 0.5% for a time weighted average over 8-hours (OSHA, 1996). OSHA considers that concentration of CO₂ of 10% or more can be lethal. OSHA (1996) states: "Gaseous carbon dioxide is an asphyxiant. Concentrations of 10% (100,000 ppm) or more can produce unconsciousness or death." NIOSH states that the Immediately Dangerous to Life and Health (IDLH) concentration for CO₂ is 4%.

Emergency Response and Treatment of Hypercapnia

Humans may be unlikely to detect toxic exposure CO₂ until it is too late to escape. Initial signs of exposure to low levels of CO₂ may include coughing, labored breathing, headaches and lightheadedness. If those exposed are well trained, the occurrence of these symptoms may allow sufficient time for recognition of danger. However, a key observation made by responders to CO₂ related emergencies is that onset of respiratory arrest can occur in the absence of warning signs, making early recognition less likely (Hsieh et al, 2005). At higher levels of exposure to CO₂, symptoms can rapidly accelerate from significant depression of respiratory function to cardiac dysrhythmia. Wearing respirators with a positive pressure of breathable air is essential for avoiding injury or death to rescue workers responding to CO₂ emergencies because no filtration mask is effective to prevent CO₂ poisoning (Halpern, et al 2004). Unfortunately in incidents of death from CO₂, co-workers attempting to rescue victims are frequently incapacitated or killed themselves. It is essential that workers be trained not to attempt rescues without putting on respirators.

In enclosed spaces associated with CCS facilities it will be important to deploy carefully placed, well calibrated CO₂ detectors and monitoring systems linked to alarms. The CO₂ monitoring system should include both audible and visual warning systems to alert workers of dangerous conditions. It is also important to note that safe breathing conditions must be determined by monitoring CO₂ levels not just O₂ levels. For example, a reading of 19.5 percent O₂ (the OSHA established lower safe limit for oxygen in air) on an oxygen sensor would represent a CO₂ level of 7% (5 X 1.4%). As a result if a worker waits until an oxygen deficiency alarm is set off during a CO₂ leakage incident, he will have exceeded the OSHA 8 hour exposure limit for CO₂.

Workers need to be well trained to execute escape procedures as well as emergency response and urgent remediation. Rescue of CO₂ poisoning incidents starts with the removal of the victim from the CO₂ spill area, followed by administration of oxygen (Halpern et al, 2004). After hyperventilation, the rate of excretion of CO₂ from the lungs is rapid and pCO₂ in the blood returns to normal within minutes (Halpern et al, 2003). In severe cases, assisted ventilation (such as endotracheal intubation) may be required (Sieker and Hickham, 1956; Potkin and Swenson 1992; Nelson, 2000) and if clinically indicated, hemodynamic (blood circulation) support should be administered (Nelson, 2000). In general, the detrimental effects that result from low to moderate levels of exposure to CO₂ appear to be largely reversible. The rate of removal of excess CO₂ from the body is rapid. The typical human response hyperventilation is so effective that arterial CO₂ levels typically drop into the normal range within a few minutes (Halpern et al, 2003).

Perhaps the most common health issue to arise, in the unlikely event of a leak in surface equipment used for geologic CO₂ sequestration, is frostbite. When CO₂ under high pressure leaks the gas will cool adiabatically, resulting in the formation of particles of dry ice (or super-cooled CO₂ vapor). The US Government has warned of the hazards associated with dry ice (NIOSH, 1979) and has suggested that where appropriate gloves and aprons resistant to temperatures lower than -109 F, should be worn by workers potentially exposed to dry ice. Burns caused by contact of the skin with dry ice should be treated by thawing of affected tissue and pain medicine. Surgical intervention may be needed in severe cases (Biem J., et al., 2003).

Discussion

Knowledge of the levels of CO₂ at which humans become incapacitated or lose consciousness gives little insight into the levels at which CO₂ becomes lethal. The studies reviewed above that result in loss of consciousness by human subjects require careful interpretation. A wide variety of protocols were implemented in these studies and a range of criteria used to define “losing consciousness”, including the subjects feeling that this was likely. For example the study by Friedlander and Hill (1954) used young adult psychiatric patients and recorded the average time for “lost consciousness”. Lambertsen (1971) ascribed seizures, convulsions, and loss of consciousness at less than 2 minutes of exposure to 30% CO₂ but gave

no details on the subjects or the experimental design. In all these studies 70% O₂ was present and NIOSH (1976) suggested that the impact of such high oxygen levels on these subjects remains unresolved. Arieli and Ertracht (1999) noted that oxygen toxicity (manifested as convulsions and loss of consciousness) can occur in humans exposed to oxygen pressures above 180 kPa (just over twice the oxygen partial pressure in these 30% CO₂-70% O₂ experiments for example).

At least some of the suggestions that high CO₂ causes seizures have been based on misinterpreting the experiments. Rice (2004), quoting Pollock et al. (1949) and Gyarfas et al. (1949), suggested that “In several studies, intoxication leading to unconsciousness was evident in ≤30 s in patients inhaling 30% CO₂ in 70% O₂” and further that “some patients exhibited seizures that were characterized as decerebrate (no cerebral functioning)”. In Pollock et al.’s (1949) study, 18 patients were ventilated with up to 30% CO₂ (and 70% O₂) and then “stimulated with super-threshold shocking current”. They found that levels of CO₂ from 15-30% “routinely prevented electrically induced seizures” and that at 30% CO₂, “30 seconds of inhalation sufficed”; with slightly longer times required to prevent seizures at 15 to 20% CO₂. Clearly in this study the authors were investigating the prevention of seizures by use of CO₂. In a companion study Gyarfas et al. (1949) found that a “combination of E.S.T. with CO₂ inhibits the convulsion”. These studies simply do not address the issue of what CO₂ levels would cause unconsciousness or incapacitation in humans. It is possible, perhaps probable, that the symptoms of convulsion and loss of consciousness recorded in experiments with 30% CO₂ are a consequence of the very high oxygen levels in the experiments. This would suggest that the idea that 30% CO₂ is the lethal level is based on a misunderstanding of the experimental data.

It is clearly too dangerous to test the limits of human tolerance to CO₂ on live subjects. Estimating the lethal effects of many toxic gases can be made based on extensive data available from experiments with small animals, primarily mice and rats. To extrapolate the information gained in small-animal experiments to humans models have been developed to estimate the probability of lethality (accounting for the large differences in body mass and ventilation between these species and primates). Such models (Stuhmiller and Stuhmiller, 2002; Stuhmiller and Stuhmiller, 2005; Stuhmiller et al, 2006) take into account ventilation changes related to species, and level of activity. There is considerable variability within healthy human and animal subjects in their response to (or tolerance of) CO₂. As a result, the outcomes of human exposure

to toxic gases are best expressed as probability distributions. Unfortunately, small animal data on the effects of CO₂ is more limited than for other toxic gases and thus models of its lethality are not well constrained.

A re-examination of the primary evidence from animal experiments and from accidental deaths, as outlined above, suggests that lethal CO₂ levels at normal O₂ levels are in the range 50 to 60%. The experimental data on Rhesus monkeys quoted above suggest that primates can survive in a 50 to 60% CO₂ with 21% O₂ atmosphere, for as much as an hour. This is broadly consistent with the Idaho National Laboratory fire extinguisher incident described above where two of three accident victims survived in an approximately 50% CO₂ and 10.5% O₂ atmosphere for twenty minutes.

Most all CCS related incidents will involve O₂ levels that are reduced by dilution in response to CO₂ being added to the atmosphere. Normal room air is nearly 79% N₂ and 20.9 percent O₂ and 0.1% CO₂, by volume (together with water vapor, and traces of inert gases). As oxygen is approximately one-fifth of fresh air, every 5 percent of another gas introduced into a confined space lowers the oxygen level by 1 percent. If the oxygen level was reduced to 10% by influx of CO₂; then (assuming simple dilution), CO₂ would be 54.5% ($5 \times (20.9 - 10) = 5 \times 10.9\%$), a lethal level. To reach a level oxygen level of 8% by dilution by an influx of CO₂, the concentration of this gas would be 65%. This is beyond the lethal level of CO₂. These calculations do show that (despite frequent assertions to the contrary in the CO₂ sequestration risk literature) death from CO₂ influx incidents is most probably caused by dominantly by CO₂ toxicity and the added effects of reduced oxygen levels. These calculations are based on two assumptions. First, that the atmosphere in the room is well mixed during the release, and second, that no gas component is preferentially vented. In real situations some heterogeneity is almost certain. As noted previously, only a few examples of deaths related to oxygen displacement by CO₂ have been documented with measurements of the CO₂ and O₂ composition of the atmosphere involved in the death.

The best evidence of the impact reduced oxygen levels accompanying simple dilution of air by adding CO₂ comes from study of lethal accidents such as the one presented by Dunford et al. (2009). They estimated that death occurred at 13% O₂ and 40% CO₂.

Based on the examples of deaths related to CO₂ presented in this paper, three end member scenarios for CO₂ accidents can be distinguished:

- (1) CO₂ releases resulting in CO₂ diluting O₂ proportionally, for example release from a CO₂ fire extinguisher system in a confined space
- (2) Density stratified displacement enhanced by temperature contrast in CO₂ (such as sublimation of dry ice in a cold room); and
- (3) Isothermal, density stratified CO₂ driven by active fermentation or bacterial action, converting O₂ to CO₂ (such as in a fermentation tank or a well).

Little appears to be known of the mix of CO₂, N₂, and O₂ that would occur in an energetic, jet-like plume of CO₂ being released from a high pressure pipeline. Neither would CO₂ ponding in topographic lows match any of the above three scenarios. So, experiments and/or detailed modelling would be useful to help estimate likely CO₂ and O₂ levels for these scenarios.

One key observation that can be drawn from the case studies reviewed in this study is that all the reported CO₂ related deaths occurred in confined spaces with no (or very limited) ventilation. Deaths typically occurred in either airtight containers such as walk in freezers, fermentation tanks or wells, all difficult to escape from. Documented examples of deaths from accidental release of CO₂ into open or ventilated spaces are rare, if they exist at all.

As documented in this study, many of the occupational warnings promulgated by NIOSH and OSHA in the US are misleading and potentially dangerous in that they are based on dual misconceptions: that CO₂ is not toxic, and that death from exposure to CO₂ is a result of asphyxia. Worker safety agencies should: 1) require the use of CO₂ rather than O₂ sensors; 2) train emergency responders' use of respirators and treatment protocols for CO₂ poisoning; and 3) require screening workers who have the possibility of dealing with CO₂ releases for a predisposition to panic/anxiety disorders and/or respiratory disorders. Workers need to be well trained to execute escape procedures as well as emergency response, urgent remediation, and emergency notification plans.

One of the most important applications of the lethality of CO₂ is in making risk assessments. An increased potential for harm from CO₂ exposure will occur if large scale CO₂ sequestration proceeds. Worker exposure to CO₂ will center on CO₂ capture facilities, transportation pipelines, and surface injection facilities. Small leaks are unlikely to present a significant danger to workers

unless the CO₂ accumulates in confined spaces or holes/depressions. The likelihood that CO₂ pipeline failures, well blowouts or other unintentional releases of CO₂ will result in fatalities or serious injuries will be a key part of any risk assessment of CCS projects. A survey of the literature searching for the lethal levels of CO₂ used in such assessments is summarized in Table 1. It is clear that many of the risk assessments used values based on safety regulations, far lower than the magnitude of lethal CO₂ values suggested in the present study. McGillivray and Wilday (2009) quoting DNV (2008) stated that “Unconsciousness can result within a few minutes of exposure to 7% CO₂, while coma and death is possible within a few minutes of exposure to 17% CO₂”. Nyborg et al. (2011) noted that “risk analysis should be performed using the real lethal dose, not an allowable dose or a dose selected ‘on the safe side’.” A surprising number of the studies listed in Table 1 seem to have used CO₂ levels designed to be well on the safe-side.

Table 1: CO₂ lethality levels used in published risk analyses

Study	CO ₂ Concentration for 50% lethality	CO ₂ Concentration for 99% or 100% lethality
Vianello et al., 2013		11%, 15 min.
Mazzoldi et al., 2012		25%, 1 min.
Harper, 2012	11.5%, 5 min	
Bisschop, 2011		10%, 30 min.
Koornneef et al., 2010	8%, 4 hrs. 33%, 1 min	17%, 4 hrs. 37%, 5 min.
Tetra Tech, 2007		7%, 3 min.
Hooper et al., 2005		17 to 30%, minutes
Kruse and Tekiela (1996)		10%, 1 min.

In many, the results from modeling accidental CO₂ releases no fatalities would be predicted if appropriate levels of lethality for CO₂ had been used in the analysis.

Conclusions

The key conclusion from this study is that CO₂ is lethal only at levels up to six times higher than those assumed in previous evaluations of risk associated with CCS. The evidence on lethal levels of CO₂ is limited but does not support the widely quoted assertions that “death occurs

within minutes at 25-30% CO₂”. The preponderance of evidence is that CO₂ levels on the order of 50 to 60% appear to be lethal at normal oxygen concentrations. Previous assertions that CO₂ levels of 30% caused a loss of consciousness, seizures “and soon after death” (not observed in the experiments); are in large part based on experiments done at high O₂ levels in which oxygen poisoning may have been responsible for the first two symptoms.

There is a consensus in the toxicology and emergency medicine literature that CO₂ is toxic at high concentrations and is lethal even in the presence of normal oxygen levels. The widespread belief in the CCS research community that CO₂ is not toxic and that CO₂ kills by asphyxia, reflect outdated notions that could result in inappropriate safety monitoring, and emergency response strategies. CO₂ at high concentrations induces a range of toxic responses in humans and animals. The recognition of CO₂’s toxicity is important in designing appropriate monitoring (monitoring for CO₂ levels rather than just O₂ levels) and emergency response strategies. However, no changes in OSHA or NIOSH occupational safety levels for CO₂ are suggested.

The modeling approach used by Stuhmiller et al (2006) is the most promising approach to understanding the impact of reduced oxygen levels in lowering the lethal levels of CO₂. Some examples of deaths in fermentation tanks have occurred at lower CO₂ levels however these also are associated with greatly reduced oxygen levels, an outcome of the fermentation process. Similar effects probably occur in mines and subterranean voids where oxidation of organic matter has increased CO₂ at the expense of O₂.

Quantitative risk assessments of aspects of CCS have assumed much lower levels for the lethality of CO₂, than those proposed in this paper. This almost certainly resulted in significant overestimation of the risks from possible accidental CO₂ releases associated with future CCS operations.

7. Summary

The potential lethality of unexpected CO₂ releases from pipelines or wells are arguably the highest risk aspects of CO₂ enhanced oil recovery (CO₂-EOR), carbon capture, and storage (CCS). Assertions in the CCS literature, that CO₂ levels of 10% for ten minutes, or 20 to 30% for a few minutes are lethal to humans, are not supported by the available evidence. The results of published experiments with animals exposed to CO₂, from mice to monkeys, at both normal and

depleted oxygen levels, suggest that lethal levels of CO₂ toxicity are in the range 50 to 60%. These experiments demonstrate that CO₂ does not kill by asphyxia, but rather is toxic at high concentrations. Depleted O₂ levels will decrease the lethal level of CO₂; however available data provides only a general indication of the magnitude of this effect. It is concluded that quantitative risk assessments of CCS have overestimated the risk of fatalities by using values of lethality a factor two to six lower than the values estimated in this paper. In many dispersion models of CO₂ releases from pipelines, no fatalities would be predicted if appropriate levels of lethality for CO₂ had been used in the analysis.

References

ACGIH, 1971, Carbon dioxide. In: Documentation of the threshold limit values for substances in workroom air. 3rd ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists, p. 39.

Alberts W. M. 1994 Indoor air pollution: NO, NO₂, CO, and CO₂ J Allergy Clin. Immunol. 94, 2, 289-95

Anselmo, J. E., Pesigan, D. E., Dizon, G. D., Luciano, V. J., Navarro, J. Y., 1951, Fatal poisoning from carbon dioxide report of five cases with two deaths, J. Philipp. Med. Ass., 27, 102.

Arieli R., Ertracht O., 1999, Latency to CNS oxygen toxicity in rats as a function of PCO₂ and PO₂, Eur. J. Appl. Physiol. 80, 598-603

Askanazi, J.; Milic-Emili, J.; Broell, J. R.; Hyman, A. I.; and Kinney, J. M. 1979 Influence of Exercise and CO₂ on Breathing Pattern of Normal Man. J. Appl. Physiol., 47, 1, 192-196

Bachu S., 2008, CO₂ storage in geological media: Role, means, status and barriers to deployment Progress in Energy and Combustion Science 34, 254–273

Benson, S. M., 2005. Lessons learned from industrial and natural analogues for health, safety and environmental risk assessment for geologic storage of carbon dioxide. In Carbon dioxide capture for storage in deep geologic formations—results from the CO₂ capture project, vol. 2 (eds D. C. Thomas & S. M. Benson), pp. 1133–1142. Oxford, UK: Elsevier.

Benson, S.M. Hepple, R. Apps, J. Tsang, C.-F. Lippman, M. 2002, Lessons learned from natural and industrial analogues for storage of carbon dioxide in deep geologic formations, Lawrence Berkeley National Laboratory Report, LBL-51170, Berkeley, CA.

BEST 2007 Emergency and Continuous Exposure Guidance Levels for Selected Submarine Contaminants, Board on Environmental Studies and Toxicology

Biem J., et al., 2003, Out of the cold: management of hypothermia and frostbite, CMAJ; v168, p 305-311

Bisschop, R., 2011, Tailor-made conceptual design of CO₂ transport and injection facilities for the Barendrecht CO₂ storage project; minimizing risk and optimizing lifecycle value, Energy Procedia, 4, 2369-2376

Boggs, D. F., 1991, Comparative control of respiration. Comparative Biology of the Normal Lung. R. A. Parent (Ed.). Boca Raton, FL, CRC Press: 309-350.

Brown, E.B., Jr., 1956, Tolerance of the hyperthermic dog to carbon dioxide, School of Aviation Med., U.S.A.F. Rep. No 56-81, Randolph Field, Texas.

Brown, E.B., Jr. and Miller, F., 1952, Tolerance of the dog heart to carbon dioxide. Am. J. Physiol., 170: 550-554

Chow, F.K., Granvold, P.W., Oldenburg, C.M., 2009, Modeling the effects of topography and wind on atmospheric dispersion of CO₂ surface leakage at geologic carbon sequestration sites. Energy Procedia 1, 1925–1932.

Christensen HE, McMakin H, Silver SD, editors. NIOSH criteria for a recommended standard occupational exposure to carbon dioxide. Washington, DC: US Department of Health, Education and Welfare, 1976

Coryell, W., 1997, Hypersensitivity to Carbon Dioxide as a disease-specific trait marker, Biological Psychiatry, 41, 259–263, 1997.

Coryell, W., A. Fyer, D. Pine, J. Martinez, and S. Arndt, 2001, Aberrant respiratory sensitivity to CO₂ as a trait of familial panic disorder, Biological Psychiatry, 49, 582-587

Dalgaard J.B., et al., 1972, Fatal Poisoning and Other Health Hazards Connected with Industrial Fishing, Br J Ind. Med. 29, 307-316

Damen, K., Faaij, A., Turkenburg, W., 2006, Health, safety and environmental risks of underground CO₂ storage – overview of mechanisms and current knowledge, Climatic Change, 74, 289-318.

de Kort WL, Sangster B., 1988, Acute intoxications during work. Vet Hum Toxicol 1988; 30: 9-11

DiMaio V & DiMaio D., 2001, Forensic Pathology, Second Edition. Chapter 8, Asphyxia, p231 ISBN 0-8493-0072-X

DMT, 1999, Intoxication par inhalation de dioxyde de carbone, Dossier Medico-Technique, Documents pour le medecin du travail No 79,

<http://www.inrs.fr/accueil/produits/mediatheque/doc/publications.html?refINRS=TC%2074>

R.D. Dripps, and J.H. Comroe Jr, 1947, The Respiratory and Circulatory Response of Normal Man to Inhalation of 7.6 and 10.4 Per Cent CO₂ with a Comparison of the Maximal Ventilation Produced by Severe Muscular Exercise, Inhalation of CO₂ and Maximal Voluntary Hyperventilation," Am J Physiol. 149:43-51

Dunford J. V., et al., 2009, Asphyxiation due to dry ice in a walk-in freezer, The Journal of Emergency Medicine, Vol. 36, No. 4, pp. 353–356

EPA, 2000. Carbon Dioxide as a Fire Suppressant: Examining the Risks, U.S. Environmental Protection Agency, February 2000 <http://www.epa.gov/Ozone/snap/fire/co2/co2report.pdf>

Feldman, J.L., Mitchell, G.S., Nattie, E.E., 2003, Breathing: rhythmicity, plasticity, chemosensitivity. Ann. Rev. Neurosci. 26, 239–266.

Ford M, Delaney KA, Ling L, Erickson T., 2000, Clinical Toxicology. Philadelphia, PA: WB Saunders.

Friedlander WJ, Hill T., 1954, EEG changes during administration of carbon dioxide. Dis. Nerv. Syst., 15, 71-5

Gibbs F, Gibbs E, Lennox W, et al., 1943, The value of carbon dioxide in counteracting the effects of low oxygen. J. Aviat. Med. 14, 250-61

Gill JR, Ely SF, Hua Z., 2002, Environmental gas displacement: three accidental deaths in the workplace. Am. J. Forensic Med. Pathol.; 23: 26-30

Greiz E. et al., 1990, Response to 35% CO₂ as a marker of panic in extreme anxiety Am. J. Psychiatry, 145, 796-797

Greiz E. et al., 1990, Specific sensitivity of patients with panic attacks to carbon dioxide inhalation, *Psychiatry Res.*, 31 193-199

Gross, N.J., Hamilton, J.D., 1963, Correlation between the physical signs of hypercapnia and the mixed venous Pco_2 *Br. Med. J.* 2, 1096–1097.

Guillemin, M. P., Horisberger, B., 1994, Fatal intoxication due to the unexpected presence of carbon dioxide, *Annals of Occupational Hygiene*, 38, 6, 951-957.

Guillerm, R., Radziszewski, E., 1979, “Effects on man of 30-day exposure to a pCO_2 of 4 torr (2%): application to exposure limits,” *Undersea Biomedical Research, Submarine supplement*.

K. Gyarfas, G.H. Pollock, and S.N. Stein, “Central Inhibitory Effects of Carbon Dioxide. IV. Convulsive Phenomena,” *Proc. Soc. Exper. Biol. Med.* 70:292-293 (1949).

Glatte H.A., Hartman B.O., Welch B.E., 1967, Nonpathologic hypercapnea in man, San Antonia (TX): US Air Force School of Aerospace Medicine,

Glatte HA, Motsay G.J, Welch B.E. 1967, Carbon dioxide tolerance studies. San Antonia (TX): US Air Force School of Aerospace Medicine

Halpern P, Raskin Y, Sorkine P, et al., 2004, Exposure to extremely high concentrations of carbon dioxide: a clinical description of a mass casualty incident. *Ann. Emerg. Med.* 43, 196-9

Heinrich J. J., Herzog H. J., Reiner D. M., 2004 Environmental Assessment of Geologic Storage of CO_2 , MIT LFEE http://sequestration.mit.edu/pdf/LFEE_2003-002_RP.pdf

Hepple, R.P., 2005, Human health and ecological risks of carbon dioxide. In: Benson, S.M., Oldenburg, C., Hoverstein, M., Imbus, S. (Eds.), *Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project*.

Geologic Storage of Carbon Dioxide with Monitoring and Verification, vol. 2.
Elsevier Publishing, Oxford, 1143–1172.

Harper P., 2011, Assessment of the major hazard potential of carbon dioxide (CO₂). Paper for the Health and Safety Executive, www.hse.gov.uk/carboncapture/partners.htm

R. Hepple, S.M. Benson, 2005, Health, safety and environmental risk assessment for CO₂ exposure, Lessons Learned from Industrial and Natural Analogs for Health, Safety and Environmental Risk Assessment for Geologic Storage of Carbon Dioxide, Vol. 2. Geologic Storage of Carbon Dioxide with Monitoring and Verification, Elsevier Publishing.

Hsieh C-C, Shih C-L, Fang C-C, et al., 2005, Carbon dioxide asphyxiation caused by special-effect dry ice in an election campaign. Am. J. Emerg. Med., 23: 567-8

Ikeda, N., Hiroshi T., Umetsu K., Suzuki T., 1989, The course of respiration and circulation in death by carbon dioxide poisoning, Noriaki Forensic Science International 41, 1-2, 93-99

Jiang C., et al., 2005, CO₂ central chemosensitivity: why are there so many sensing molecules? Respiratory Physiology & Neurobiology, 145, 115–126

Kaye, J., Buchanan, F., Kendrick A., 2004, Acute carbon dioxide exposure in healthy adults: evaluation of a novel means of investigating the stress response. J. Neuroendocrinology, 16, 256–264.

Kety S, Schmidt C., 1948, The effects of altered arterial tensions of carbon dioxide and oxygen on cerebral blood flow and cerebral oxygen consumption of normal young men, J. Clin. Invest., 27, 484-92

Kiely DG, Cargill RI, Lipworth BJ., 1996, Effects of hypercapnia on hemodynamic, inotropic, lusitropic, and electrophysiologic indices in humans. *Chest*, 109, 1215-1221

Kliefeth A. B. Grurb R. L. Jr. Raichl M. E., 1979, Depression of cerebral oxygen utilization by hypercapnia in the Rhesus monkey *Journal of Neurochemistry*, 32, 661-663

Lambertsen, C. J., 1971, Carbon Dioxide Tolerance and Toxicity. Institute for Environmental Medicine, Univ. of Pennsylvania Medical Center

Langford, Nigel J., 2005 Carbon Dioxide Poisoning, *Toxicological Reviews*. 24, 4, 229-235

Lisbona, D., McGillivray, A., Saw, J. L., Gant, S., Bilio, M., & Wardman, M. (2014). Risk assessment methodology for high-pressure CO₂ pipelines incorporating topography. *Process Safety and Environmental Protection*, 92(1), 27-35.

LMITC, 1999, Identification of the Specific Mechanism by which the CO₂ System in Building TRA-648 Accidentally Discharged, Lockheed Martin Idaho Technologies Company INEEL/EXT-99-00669

Luttrell W. E., Jederberg W. W., 2008, *Toxicology Principles for the Industrial Hygienist* AIHA

Manning, T. J., Ziminski, K., Hyman, A., Figueira, G., & Lukash, L., 1981, Methane deaths?: Was it the cause?. *The American J. Forensic Med. Path.*, 2, 4, 333-336.

Maresh, C. M., Armstrong, L. E., Kavouras, S. A., Allen, G. J., Casa, D. J., Whittlesley, M., LaGasse, K. E., 1997, "Physiological and psychological effects associated with high carbon dioxide levels in healthy men," *Aviation Space and Environmental Medicine*, Vol. 68, pp. 41-45.

Mas A, Saura P, Joseph D, et al., 2000, Effect of acute moderate changes in pCO₂ on global hemodynamics and gastric perfusion. *Crit. Care Med.*, 28, 360-365.

McGillivray, A., Wilday, J., 2009. Comparison of Risks from Carbon dioxide and Natural Gas Pipelines, Health and Safety Executive Research Report 749,
<http://www.hse.gov.uk/research/rrpdf/rr749.pdf>

McGillivray, A., Saw, J. L., Lisbona, D., Wardman, M., Bilio, M., 2014, A risk assessment methodology for high pressure CO₂ pipelines using integral consequence modelling. Process Safety and Environmental Protection, 92(1), 17-26.

Mitsuda H., Ueno S., Mizuno H., Fujikawa H., Konaka K., Fukada C., 1982, Effects of various molecular oxygen levels in mixed gas on acute respiratory insufficiency induced with carbon dioxide inhalation in rats. Kankyo Kagaku Sogo Kenkyusho Nenpo 2: 35-46.

Nelson, L. 2000. Carbon Dioxide Poisoning, Emerg. Medicine 32, 5, 36-38.

Ng L. J., Stuhmiller L. M., Stuhmiller J. H. 2007 Incorporation of Acute Dynamic Ventilation Changes into a Standardized Physiologically Based Pharmacokinetic Model Inhalation Toxicology, Volume 19, Issue 3, pages 247 - 263

NIOSH, 1976, Criteria for a Recommended Standard: Occupational Exposure to Carbon Dioxide. National Institute of Occupational Safety and Health, NIOSH Publication No. 76-194.
<http://www.cdc.gov/niosh/docs/1970/76-194.html>

NIOSH, 1986, Alert : Preventing Occupational Fatalities in Confined Spaces, NIOSH Publication No. 86-110, www.cdc.gov/niosh/

NIOSH (Pettit T., Linn H.), A Guide to Safety in Confined Spaces, NIOSH Publication No. 87-113, U.S. GPO, Washington, D.C, 1987. www.cdc.gov/niosh/

NIOSH, 1994, Worker deaths in Confined Spaces, A Summary of NIOSH Surveillance and Investigative Findings, National Institute for Occupational Safety and Health, January.

Nunn J.F., 1987, Applied respiratory physiology London: Butterworths, 460-70

Nyborg M., et al., 2011, Risk analysis methodology for CO₂ transport including quantified risk calculation. Energy Procedia 4 2816-2823

OSHA, 1996, Potential Carbon Dioxide (CO(2)) Asphyxiation Hazard When Filling Stationary Low Pressure CO(2) Supply Systems OSHA Hazard Information Bulletins June 5, 1996 http://www.osha.gov/dts/hib/hib_data/hib19960605.html

OSHA. 1989. Carbon Dioxide, Industrial Exposure and Control Technologies for OSHA Regulated Hazardous Substances, Volume I of II, Substance A - I. Occupational Safety and Health Administration. Washington, DC: U.S. Department of Labor. March.

OSHA, 2010, Potential Carbon Dioxide CO2 Asphyxiation Hazard When Filling Stationary Low Pressure CO₂ Supply Systems http://www.osha.gov/dts/hib/hib_data/hib19960605.html

Paljärvi, L., Söderfeldt, B., Kalimo, H., Olsson, Y., Siesjö, B.K., 1982. The brain in extreme respiratory acidosis. A light- and electron-microscopic study in the rat. Acta Neuropathologica 58, 87–94.

Patterson J.L., Heyman A., Battey L.L., et al., 1955, Threshold of response of the cerebral vessels of man to increase in blood carbon dioxide. J Clin Invest. 34, 1857-64

Potkin R.T., Swenson E.R., 1992, Resuscitation from severe acute hypercapnia: determinants of tolerance and survival. Chest, 102, 1742-1745.

Pollock G.H., Stein S.N., Gyarfas K., 1949, Central Inhibitory Effects of Carbon Dioxide. III. Man," Proc. Soc. Exper. Biol. Med. 70, 291-292

Pryor et al., 1969, Hazards of smoke and toxic gases produced in urban fires, Final Report OCD Contract No. DAHC20-70-C-0212, <http://www.dtic.mil/cgi-bin/GetTRDoc?AD=AD0697839>

Purser D. A., 1984, A bioassay model for testing the incapacitating effects of exposure to combustion product atmospheres using cynomolgus monkeys. J. Fire Sci., 2, 20–36.

Reynolds W. J., Milhorn H. T., Jr. Holloman G. H., Jr., Roussos C., 1972, Transient Ventilatory Response to Graded Hypercapnia in Man. J. Appl. Physiol., 33, 1, 47-54.

Rice, S. A., 2003, Health effects of acute and prolonged CO₂ exposure in normal and sensitive populations. In Second Annual Conference on Carbon Sequestration pp. 5-8

Sakurai, T. 1989. Toxic gas tests with several pure and mixed gases using mice. J. Fire Sci. 7, 22–77.

Sayers, J.A.; Smith, R.E.A.; Holland, R.L.; Keatinge, W.R. 1987. Effects of carbon dioxide on mental performance. J. Appl. Physiol. 63, 1, 25-30.

Schaefer KE, Hastings BJ, Carey CR, et al., 1963, Respiratory acclimatization to carbon dioxide, J. Appl. Physiol., 18: 1071-8

Schneider E, Truesdale E. The effects on the circulation and respiration of an increase in the carbon dioxide content of the blood in man. Am J Physiol. 1922; 63: 155-75

Shields W. M., 2006, The Epistemic Value of Cautionary Tales, Journal of technology Studies, v 32, n2

<http://scholar.lib.vt.edu/ejournals/JOTS/v32/v32n2/shields.html>

Sechzer, P.H.; Egbert, L.D.; Linde, H.W.; Cooper, D.Y.; Dripps, R.D.; Price, H.L. 1960. Effect of CO₂ inhalation on arterial pressure, ECG and plasma catecholamines and 17-OH corticosteroids in normal man. *J. Appl. Physiol.* 15, 3, 454-458.

Speitel, L.C., 1995, Toxicity assessment of combustion gases and development of a survival model. U.S. Department of Transportation, FAA, Atlantic City International Airport, NJ. DOT/FAA/AR-95/5.

Sieker H., Hickam J. B., 1956 Carbon dioxide intoxication: the clinical syndrome, its etiology and management with particular reference to the use of mechanical respirators. *Medicine* 35, 389-423.

Sinclair, R.D., Clark, J.M., Welch, B.E., 1971, Comparison of physiological responses of normal man to exercise in air and in acute and chronic hypercapnia. *Underwater Physiology*, Ed. by C.J. Lambertsen. Academic Press: New York, NY, 409-417

Somero G.N., 1986, Protons, osmolvtes and fitness of internal milieu for protein function. *Am. J. Physiol.*, 251, R197-213

J.M. Stinson, and J.L. Mattsson, 1970, Tolerance of Rhesus Monkeys to Graded Increase in Environmental CO₂-Serial Changes in Heart Rate and Cardiac Rhythm," *Aerosp. Med.* 41, 415-418

Stinson J.M., Mattsson J.L., 1971, Cardiac depression in the detection of high environmental CO₂ – A comparative study in rhesus monkeys and chimpanzees, *Aerosp. Med.*, 42, 78-80

Stuhmiller, J. H., Stuhmiller, L. M., 2002, An internal dose model for interspecies extrapolation of immediate incapacitation risk from inhalation of fire gases, *Inhal. Toxicol.*, 14, 9, 929–957.

Stuhmiller, J. H., Stuhmiller, L.M. 2005. A mathematical model of ventilation response to inhaled carbon monoxide, *J. Appl. Physiol.* 98, 6, 2033–2044.

Stuhmiller J.H., Long D.W., Stuhmiller L.M., 2006, An Internal Dose Model of Incapacitation and Lethality Risk from Inhalation of Fire Gases, *Inhalation Toxicology*, 18, 347–364

Troisi F.M., 1957, Delayed death caused by gassing in a silo containing green forage. *Br. J. Ind. Med.* 14, 56-8

USCSHIB, 2003, Hazards of Nitrogen asphyxiation, U.S. Chemical Safety and Hazard Investigation Board Safety Bulletin No. 2003-10-B

Van den Hout M. A., Griez E., 1985, Peripheral Panic Symptoms Occur during Changes in Alveolar Carbon Dioxide. *Comp. Psych.*, 26, 4, pp. 381-7.

Van den Hout M. A., Griez E., 1984, Panic Symptoms After Inhalation of Carbon Dioxide. *Br. J. Psych.*, 144, 503-7.

Watanabe T., Morita M., 1998, Asphyxia due to oxygen deficiency by gaseous Substances *Forensic Science International*, 96, 47–59

West, J. B. 1985, *Respiratory Physiology – The Essentials*, 3rd edition. Williams and Wilkens, Baltimore, Maryland

White C.S., Humm J.H., Armstrong E.D., Lundgren N.P.V., 1952, Human tolerance to acute exposure to carbon dioxide. Report No. 1: Six percent carbon dioxide in air and in oxygen, *Aviation Med.* 439- 455.

Woods, S. W., Charney, D. S., Goodman, W.K., Sechzer, P. H., Egbert, L. D., Linde, H. W., Heninger, G. R., 1988, Carbon Dioxide-Induced Anxiety. *Arch. Gen. Psych.*, 45, 43-52.

Wong K.L., 1966, Carbon dioxide. In: Subcommittee on Spacecraft Maximum Allowable Concentrations. *Spacecraft maximum allowable concentrations for selected airborne contaminants*. Washington, DC: National Academy Press, 105-187

Section 6: Protocols for Monitoring Environmental Risk from Leakage of CO₂ Sequestered in Deep Brine Reservoirs

1. Introduction

Large-scale sequestration of carbon dioxide (CO₂) in deep brine reservoirs appears to be transitioning from pilot injection research to commercial scale projects. Transparent, reliable, scientifically sound, peer reviewed, risk based, monitoring protocols for CO₂ sequestration projects will be a key factor in assuring sound management of these projects and gaining public acceptance. In the US and in Europe there has been extensive experience with developing protocols for monitoring as a key part of the permitting and running of nuclear waste repositories. Although the consequences of CO₂ leakage are in no way comparable to migration of nuclear wastes; both share a common issue that of how to make the best regulatory decisions in the face of uncertainty. Systematic approaches to monitoring networks for high level waste included performance assessment tools and decision-under-uncertainty frameworks to create triggers for regulatory action (Helton, J., 1993; Ewing et al, 1999; Sandia National Laboratory, 2000). The knowledge gained during these endeavors can and should inform the approach taken to monitoring CO₂ injection projects (Stenhouse and Savage 2004). How large does a leak have to be before it is detected by the deployed monitoring network? Or perhaps more importantly what kind extent and intensity of monitoring would be needed to reliably detect a leak of a specific magnitude. As noted by Benson (2007) the technology exists to successfully measure leakage if its location is known and its magnitude is substantial.

Raupach et al. (2005) have asserted that uncertainty in data is as important as the magnitude of data because the uncertainties affect both the model, and the credibility of its predictions. The conceptual framework for uncertainty developed largely by the both the risk analysis and reliability engineering communities (Apostolakis, 1999; Aughenbaugh and Paredis, 2006), gives a comprehensive approach to understanding uncertainty that is summarized in the current paper. An understanding of the nature of uncertainty combined with the evolving science of decision theory (Yager, 2002; and Refsgaard et al, 2006) can provide a robust approach to examining the role of uncertainty in decision making based on the monitoring of CO₂ sequestration projects.

Rather than seeking scientific proof as the basis for decision making regulators and other professionals will have to develop a level of comfort in making decisions based on the basis of uncertain and imprecise information. Examples of such decisions are:

- At what point is a deep brine reservoir sufficiently well characterized to enable an injection project to be permitted?
- What is the minimum level of confidence in the integrity of the containment system to enable an injection project to be permitted?
- What is a reasonable threshold for determining that a reservoir is leaking CO₂?
- What degree of certainty should be required to trigger mitigation of a CO₂ leak from the containment zone?

This paper sets out to review the strategic approaches to monitoring sequestration of CO₂ in deep brine reservoirs in the context of uncertainty. This first paper first gives an overview of a conceptual framework for uncertainty of both models and measurement. The nature of uncertainty associated with the range of monitoring techniques being used for CO₂ sequestration projects is reviewed and discussed in the context of this conceptual framework.

A key question for monitoring CO₂ sequestration projects in deep brine reservoirs will be “what is the minimum size of a CO₂ leak that can be detected by a particular monitoring scheme deployed at a specific project”. Determining what level of concentration of CO₂ will be declared anomalous and represents significant leakage, represents a considerable challenge. Addressing these issues will require:

- An understanding of the magnitude of natural variability gained from measurement of baseline measurements
- Detailed modeling of the leakage process including the dispersion of the leakage signal
- Using modeling of both leakage dispersion and the response of deployed monitoring instruments to estimate the threshold for detection of leaks
- Developing sampling plans for monitoring networks to assure the effectiveness of leakage detection

Another way of conceptualizing this issue is to consider “what is the smallest leak rate that can be expected to be successfully detected by the monitoring system”.

As society (and its representatives, the regulatory agencies), contemplate the possibility of large scale sequestration of CO₂ in deep brine reservoirs, the prospect looms for having to make regulatory decisions in the face of considerable uncertainty. Issues of incomplete knowledge (epistemic uncertainty) will initially dominate at least until the evidence base expands proportional to the scale of the enterprise. The body of relevant data will grow from pilot projects and early entry commercial projects. In the case of decision making, particularly where decisions depend on the results of modeling complex natural systems, uncertainty related to random measurement error, bias, vagueness, context, ambiguity, over generalization and other types of imprecision must be evaluated. The need to make decisions in the face of uncertainty has been recognized for many decades (Tversky and Kahneman, 1974) and this paper begins to look at this approach in terms of models for leakage from deep brine reservoirs.

Monitoring data are subject to epistemic variability due to measurement error or systematic bias. Apostolakis (1994) amongst others has noted the importance of uncertainty in the models being used to make predictions based on the measured observational data set, not just the data alone.

This conceptual framework has the potential to provide a robust basis for informed regulatory decision-making under uncertainty. This kind of approach (combined with appropriate analytical tools) can identify potential pathways to lower uncertainty, help to guide early mitigation, and ultimately the lower the risk associated geologic sequestration.

One key question to be resolved either in rule making (or by adoption of agency policy) is what circumstances should trigger regulators to require preventive action? Tsang et al (2002) have asserted that action should be instigated “in the event of unanticipated leakage at unacceptable rates” but did not define an “unacceptable rate”. Going from detection of leakage to quantification of leakage rate presents a technical challenge. Rather than having a binary approach, that is a leakage or no-leakage determination. A possible graduated classification of leakage detection decisions is:

- 1) An anomaly (monitoring measurements that are larger than expected based on background measurements)

2) Possible leak detection (anomalous measurements that fit a pattern suggestive of leakage of CO₂)

3) Leak detection (a possible leak detection that is confirmed by carbon isotope tracers or some other definitive information or that has sufficient magnitude in the monitoring measurement that there is little if any ambiguity; corrective action will likely be required for such a leak if there is substantive evidence that such a leak will result in the contamination of USDW)

4) Significant leak detection (a leak that is estimated to have a magnitude equal or greater than a rate of loss from the reservoir of 1% or more of the accumulated CO₂ per thousand years or a leak that poses a significant threat to USDW; preventive action will be mandatory for significant leakage).

Successful, reliable leak detection will demand on understanding: the uncertainty in the measurements made by the monitoring system; the uncertainty in the models using to infer leakage rates from monitoring measurements; and the natural variation in background values of the parameters measured by the monitoring system. The next section summarizes the conceptual understanding of uncertainty that is required to realistically evaluate whether or not a particular set of monitoring measurements actually represents a robust detection of a leak of CO₂ from the containment zone.

Conceptual models for leak detection

Monitoring CO₂ sequestration projects (Winthaegen, Arts and Schroot, 2005; Hovorka et al 2006) can be divided into six domains:

- The Reservoir/Confinement Zone: including the injection zone, the target reservoir(s), and the geological seal.
- The Above Zone Monitoring targets: including any porous zones between the top of the primary seal and the base of USDW
- Deep aquifers: porous zones between the deepest water well and the base of USDW
- Shallow aquifers, shallower than the deepest water well currently being used for potable water or other purposes.

- Surface and near surface: soil gases, vadose zone, surface depressions, infrastructures (including tunnels and other confined spaces), and the area around wells penetrating the confinement zone.
- Atmosphere: including monitoring of the composition of the shallow atmosphere.

Surface and atmospheric monitoring may be important to assure the public of their health and safety. Assuring public acceptance is an important rationale for the implementation of monitoring networks. However if leaks are not detected until their effects can be observed at the surface, then perhaps decades of leakage from the reservoir may have occurred before mitigation (preventive action) and remediation (corrective action) can be instigated. With early detection of leakage at depth, preventive action could potentially prevent significant leakage out of the confinement zone. Above zone monitoring (monitoring deep groundwater in porous zones above the primary (and/or the secondary seal) is clearly an important strategy for early leakage detection (Hovorka, personal communication 2010).

Below the seal

In currently planned DOE Carbon Sequestration Partnership pilot injection projects in the US, the evolution of the CO₂ plume will be likely monitored using a combination of remote sensing (by seismic reflection) and direct observation in monitoring wells that penetrate the seal into the reservoir. In commercial sequestration projects it is unlikely that regulators will allow in-zone monitoring wells (Duncan, 2009). If this is the case then monitoring below the seal will be limited to attempting to track the evolution of the CO₂ plume using remote sensing approaches such as 4-D seismic imaging.

Above Zone

Above zone monitoring (monitoring deep groundwater in porous zones above the primary (and/or the secondary seal) should be an important strategy for early leakage detection (Hovorka, personal communication 2006). Possible CO₂ leakage could be detected by measuring the pressure of porous zones immediately above the seal (Benson, 2006; Hovorka personal communication, 2006) or water chemistry (pH, alkalinity, concentration of cations including

metals, carbon isotopes, as well as gases such as CO₂, CH₄, H₂S and related and aqueous species).

Measurements of pressure anomalies caused by leakage into a deep porous zone will be most effective if made in a closed system reservoir such as a sand lens surrounded by shale.

Geochemical monitoring may be more likely to be successful in an open system where regional aquifer flow disperses the leakage signal over a larger volume, making detection more likely. Detecting evidence of upward migration of brines including low pH water, metals dissolved by low pH related to CO₂ (as well as methane, hydrogen sulfide etc.) into aquifers above the confinement zone would also be very important.

One significant issue for above zone monitoring is establishing that the geochemical monitoring plan has a substantial likelihood of detecting any CO₂ leakage. More research into above zone detection to determine under what circumstances above zone pressure sensors can detect CO₂ leakage. This will require a combination of numerical modeling and understanding sensor capabilities and detection limits (preferably through field experiments).

Deep Aquifers

Deep aquifers can be defined as porous zones containing USDW below the depth of local water wells. From a regulatory viewpoint if CO₂ itself or other contamination caused by the CO₂ injection leaks into USDW is a violation of the conditions of the permit.

Shallow Aquifers

The technology is available for continuous collection of the chemistry of water (measuring pH, temperature, electrical conductivity, and dissolved CO₂).

Surface Flux

Monitoring for:

- rate of return to atmosphere
- health and safety

It is likely that the background values of CO₂ in shallow soil gases for example will vary with time of the year (season) and in some cases with weather (particularly rain fall but also ground temperature) or episodic events such as fertilizer application by farmers. In large part because of these fluctuations anomalous CO₂ levels associated with leakage will be difficult to detect in some parts of the natural environment surrounding the stored CO₂.

Atmospheric Monitoring Strategies

The wide fluctuations in levels of atmospheric CO₂ (reflecting seasonal and diurnal variations, as well as changes in levels with dominant wind direction in some areas (Leuning et al, 2008) present a challenge to monitoring for leak detection.

Monitoring for:

- rate of return of CO₂ to the atmosphere
- health and safety

Monitoring the atmospheric concentrations of CO₂ in the vicinity of seepage from subsurface CO₂ plumes potentially provides a direct measure of leakage to the atmosphere. Atmospheric monitoring is a relatively low cost approach and has the additional advantage that it can be deployed without impinging on farming or other land use. Unfortunately atmospheric concentrations of CO₂ and even the isotopic composition of the CO₂ can be highly variable (Ethridge et al, 2007; Leuning et al, 2008) making it difficult to detect anomalous CO₂ levels. A common approach to simulating the effects of the mixing and dispersion of CO₂ in the atmosphere is to use three dimensional Lagrangian particle modeling. Leuning et al (2008) have modeled the dispersion of CO₂ concentrations from point source leakage forward calculations of Lagrangian dispersion. They conclude that within 0–80 m downwind of the source, focused leaks above about 10 tonnes of CO₂ per year can be detected even with fluctuating background concentrations.

Concepts of Uncertainty, Imprecision and Accuracy

The term uncertainty is commonly accepted to be a general term that includes natural variability, random measurement error, imprecision, ambiguity, vagueness and lack of clarity.

Before any serious discussion of the issue of uncertainty in monitoring can take place a clear understanding of terminology is critical. Uncertainty can be simply defined as the difference between the present state of information and a state of certainty (Nikolaidis, 2005). Burgman (2005) has suggested that uncertainty is related to factors such as natural variability, insufficient data, errors in judgment, a lack of agreement amongst experts, and linguistic imprecision, as well as randomness and bias in measurements.

Epistemic uncertainty is associated with incomplete information and will be referred to in this study as imprecision/reducible uncertainty (Aughenbaugh and Paredis, 2006). If all reducible uncertainty was removed (to create a state of “precise information”) then the difference between this state and the present state of information can be identified as the as imprecision/reducible uncertainty. Webster defines the word precision as the state of being precise exactly or sharply defined. Where measurements lack specificity or are incomplete they are imprecise. Thus imprecision (reducible uncertainty) is the component of uncertainty that arises in part from insufficient information or knowledge, that is the finite spatial, temporal and measurement resolution at which monitoring observations are made (Parry 1996). Imprecision can be related to over simplified (or over generalized) conceptual models, limited sample sizes in statistical datasets, and incompletely elicited expert opinions. Imprecision is not to be confused with inaccuracy (more on this below). Expert judgment can in principle be used to reduce this component of uncertainty. Imprecision cannot be characterized by probabilistic measures (Duckham et al 2001).

Heterogeneity or natural variability in background CO₂ surface flux (an important factor in most if not all CO₂ monitoring deployments) is a component of reducible uncertainty. Increasing the spatial and/or temporal density of measurements will improve the characterization of this natural variability. Of course gathering more information may cost more than the benefit it brings in reduction of uncertainty or improved outcome.

The complementary component of uncertainty can be defined as irreducible uncertainty (Aughenbaugh and Paredis, 2006). Irreducible uncertainty is sometimes referred to as noise or stochastic uncertainty. Noise is an inherent property of measurement and monitoring systems and therefore cannot be reduced or eliminated. Measurement noise is uncorrelated (and independent), random error. More measurements can better characterize the random error but cannot reduce it.

In some cases it is possible to reduce measurement noise by modifying the methodology of measurement.

Another set of important concepts in the context of this paper are related to accuracy, error and truth. The accuracy of a measurement is its closeness to the true or reference value.

Measurement accuracy is not a quantity (Hauck et al, 2008), rather accuracy is a relative measure. Accuracy is the inverse of error. Error (and hence accuracy) can only be evaluated for measurements for which a true value is available (Zhang et al., 2002). For this reason error (and accuracy) in large part are generalized concepts where a measurement technique is characterized by having a particular accuracy (such as accuracy of CO₂ well-head flow meter which is often stated as $\pm 1\%$. See API Manual of Petroleum Measurement Standards, 1995, Chap. 14.3).

Truth is a commodity rarely seen in science and engineering. In fact it is arguably only found through arbitrary definitions. In the real world truth is typically defined through use of a measurement technique far more accurate than the one normally employed in field measurements. For example the accuracy of a wrist watch can be determined by calibration against the signal from a remote atomic clock. The accuracy of a mapping grade GPS for example, can be estimated by comparison with the results from a geodetic grade GPS. When applied to a set of measurements, accuracy refers to a combination of random (stochastic) and a systematic error (or bias) component (ISO 3 and ISO 5). The ISO concept of accuracy corresponds to the statistical concept of total error. Systematic error includes components such as instrumental bias in the measurement, calibration errors, as well as “the definitional uncertainty [component of measurement uncertainty resulting from the finite amount of detail in the definition of a measurand]” (Hauck et al, 2008).

As systematic components of error can only be identified in the rare cases when the reference value (truth) is available, they are typically not corrected for or included in formal analysis of uncertainty. In situations in which systematic error dominate measurement this is problematic. Traditional statistical analysis based on the frequentist approach can reveal useful information on random error but is not useful in understanding systematic errors. Both measurement error and systematic error are classified by Burgman (2005) as components of reducible (epistemic) uncertainty. In this context systematic error is unique in that more measurements of the same kind do not reduce it. Nor, in general, do more measurements better characterize the nature of the

systematic error. For example in measuring a distance of 4.5 feet with a one foot long wood ruler, let's suppose that the ruler is actually 11.75 inches long. In this case clearly no number of repeated measurements using this ruler is likely to improve our knowledge. Only better measurements based on improvement of the measuring process can decrease the level of systematic error. Unfortunately calibration data and the corrections made from them can themselves be highly uncertain. Even the sign of systematic errors can be uncertain. As a result data which have been corrected for systematic errors can have an additional random have a random component. Often systematic errors are ignored, or corrected for in an arbitrary fashion (and then ignored).

In traditional statistical approaches systematic errors are analyzed separately from random error (see for example Taylor 1997). For complex measurement systems (such as those involving time series formed by the convolution of multiple measurement streams/time series) methodologies may be required that, instead of distinguishing “random” and “systematic” error, evaluate errors at different time scales (Richardson et al, 2008).

Monitoring and modeling, used in tandem, are powerful tools to attempt to estimate leakage rates from the containment zone. The effectiveness of monitoring techniques is dependent on: their uncertainty, resolution and detection limit; the size of the signal produced by leaking CO₂; and the spatial and temporal nature of the deployment (Benson and Myer, 2002; Benson, 2006). The reliability and accuracy of CO₂ leakage detection is enhanced by the use of multiple measurement systems. For example a single geophysical technique may provide a non-unique measurement of CO₂ leakage, the use of electrical resistivity in conjunction with seismic could reduce ambiguity in the interpretation (Hoversten and Myer, 2000).

The uncertainty in estimates of the flux of CO₂ into the atmosphere depends in part on the scale of both temporal and spatial averaging. Eddy Covariance studies have been the subject of intense multi-decade research by some of the top research Universities in the world. Despite this effort, Hutyra et al (2008) recently concluded that “large biases can impact Eddy flux data if the measurements are not subjected to meticulous analysis, careful corrections, and rigorous error analysis”. Hutyra et al.’s statement largely referred to data collected by researchers at relatively optimal sites in terms of topography and flux heterogeneity. In the case of sequestration sites these variables may well be far from optimal. From a regulatory point of view if an operator

proposes to use eddy covariance as part of their monitoring strategy for leak detection they should demonstrate through careful error analysis of an extensive baseline data set that the uncertainty in the flux estimates (particularly the systematic errors) are sufficiently small that plausible leaks would be detected unequivocally. If this cannot be established then this technique should not be used as part of the monitoring program.

Assessment of uncertainty in the model calculations that are being used for regulatory decision making will be a critical aspect of regulatory oversight of CO₂ sequestration projects. Such decisions should be made in the context of an understanding of the imprecision, accuracy of the monitoring data. It is important that stakeholders believe that model predictions used in regulatory decisions have credibility. As noted by Duncan (2009) this will be particularly important when regulatory agencies issue orders for either preventive action (mitigation) corrective action (remediation). This type of issue involving environmental remediation has already been examined in terms of decision theory by Bonano et al (2000) amongst others.

The occurrence of false positives arising from a monitoring network can cause unnecessary expenditures by the operator. False positives are most likely to be caused by either by inadequate understanding of the natural variation of the background or from a failure to properly characterize uncertainty. There is also a potential problem of a false sense of security generated by monitoring schemes that seem comprehensive but in fact have a minimal chance of detecting leaks. Duncan (2009) refers to this situation as a false negative. The specific concern is that significant leaks may go undetected for considerable periods of time. Duncan (2009) suggested that the operator of a sequestration project should (as part of the permit application) be required to calculate the average annual leakage rate over a thousand years that would match the “1% leakage over a thousand years” performance standard, and then demonstrate that the detection limits, accuracy, precision and reliability of the proposed monitoring approach is appropriate to meaningfully measure this magnitude of leakage. This section represents a preliminary approach to addressing these issues.

Error and Imprecision in Modeling of the Fate of CO₂ from Deep Brine Reservoirs

In many, perhaps most, cases the parameters (such as leakage rates of CO₂ from the containment zone) cannot be measured directly. For CO₂ sequestration projects numerical

models will be necessary to relate monitoring measurements to the parameters of direct interest to regulators. Numerical models can be classified as either forward or inverse models. Forward modeling attempts to model observations of the real world by starting at some time in the past and trying to simulate how the observed situation evolved. Typically forward modeling is done sequentially, varying some input parameters in an attempt to match the observables. The downside to forward modeling is that this approach does not provide insight into the uncertainty inherent in the modeling. Inverse models are widely used in geophysics and have been increasingly applied to groundwater aquifer models (Neuman and Yakowitz, 1979; Gaganis and Smith, 2006). Inverse models provide a mechanism to calculate the optimal model that fits the available observations and constraints.

If the desired parameter is the flux of CO₂ from the ground into the atmosphere and the available measurements are Eddy-Covariance measurements of the atmospheric fluxes, then simulations of atmospheric flow (or an equivalent inverse model) are needed to estimate the flux into the atmosphere.

Unfortunately models are inherently a simplification (or more accurately an abstraction) of reality. The mismatch between the true nature of the natural system and the model, results in uncertainty in its predictions. The conceptual model must accommodate sufficient spatial and temporal granularity (or detail) to capture the key elements of the geology such as potential leakage pathways. Any conceptual model should the structure/geometry of the system and the dimensionality necessary to represent it, as well as the initial and boundary conditions. The complex nature of the natural systems being modeled makes them susceptible to multiple interpretations and thus a range of mathematical descriptions. Any conceptual model is inherently an inadequate simplification of the real world and will inevitably be proved false (Konikow and Bredehoeft, 1992) if tested against sufficient detailed and accurate new data.

Subsurface models can be decomposed into a static and a dynamic component. The static component is the reservoir model that portrays the geological structure, and the variation of porosity and permeability. A significant component of the uncertainty in the results of fluid flow simulations arises from the failure of the underlying static reservoir model to adequately represent the natural geologic heterogeneity (including variations in porosity, permeability, grain size, rock fabric, mineralogy, hydraulic conductivity, poroelastic properties, storativity etc. that

control multiphase flow, dispersion and transport. A three dimensional model of the subsurface geological depositional architecture can be created by combining data from well logs, 3-D seismic, together with regional geological data, in the context conceptual depositional facies models. Such an approach results in a single deterministic model of the architecture of the reservoir. Large scale (10's of meters) heterogeneity may be incorporated in static reservoir models but most often smaller scale heterogeneity is averaged out. The heterogeneity can be modeled by using geostatistical interpolation of porosity and permeability between measurements from wells.

Data sets for the static reservoir model are uncertain due to:

- natural variability (heterogeneity) not accounted for in the model
- imprecision related to the limited sampling provided by well data points and the limited ability to extrapolate geological features between the wells
- measurement error and uncertainty in the data used to construct the model

Dynamic reservoir models simulate the motion of fluids within a reservoir by solving the governing equations of a continuum given a static model of the reservoirs transport properties, equations of state for the relevant fluids, and appropriate boundary conditions. Methods to account for uncertainty in such models have typically focused on the effects of random or stochastic uncertainty on flow simulations (Gelhar and Axness, 1983; Zhang, 2002; Freeze, 2004).

Injection of CO₂ into porous rock result in complex coupled processes of multi-phase fluid flow, geomechanics, chemistry, and heat transfer that may be important to consider in monitoring CO₂ sequestration (Pruess et al, 2004). Failure to include the coupling between fluid flow, geomechanics, chemistry, and heat transfer introduces an unknown level of imprecision in the model simulations. In an inter-lab calibration study Pruess et al., (2004) found that uncertainties in the thermodynamic and physical properties of the CO₂-brine system and the reservoir, rather than inaccuracy in the numerical equation solvers, are the cause of most of the discrepancies between the results of different simulators. Validation of a numerical model is typically done by testing against observational data that can be predicted by the simulation. Even if a numerical model passes a validation test, this alone does not confirm the validity of the

conceptual model. For example the model simulation could give a correct match to the observables due to compensating errors.

The elements of uncertainty in a typical dynamic model include:

- 1) Uncertainty in boundary conditions or external driving forces
- 2) Uncertainty in the conceptual model due to incomplete understanding and the simplified nature of the descriptions of the modeled processes when compared to the real world
- 3) Uncertainty introduced by discretization and up-scaling
- 4) Uncertainty in model parameters particularly their finite resolution in space and time (Oberkampf et al, 2004)
- 5) Conceptual uncertainty in the model related an incomplete understanding and simplified descriptions of the underlying physical processes
- 6) Uncertainties in the values of parameter such as the Equations of State for the fluid and gas phases, the thermodynamic properties of the phase, and the transport parameters (Dou et al, 1995)
- 7) Uncertainty the numerical implementation of the model such as numerical approximations, issues with solvers and with the algorithms in general

It should be clear from the discussion above that the uncertainty in modeling is in some significant part imprecision/reducible uncertainty related to: the finite resolution of the model grid; the approximations involved in up-scaling transport properties; the finite spatial and temporal resolution of the boundary conditions. Unfortunately no robust, generic methodology exists for assessing the effects of the imprecision of the model. The assessment of the uncertainty in the results of model simulations is critical when these results are being used to support key regulatory decisions. Traditionally only the stochastic component of modeling uncertainty is assessed. New approaches are being developed to evaluate the impact of non- probabilistic uncertainty on numerical modeling (Moens and Vandepitte, 2005). At a minimum, as noted by Duncan (2009) the range of results from numerical models should be assessed when realistic variations of input parameters are used (Flett et al, 2003).

Understanding the imprecision inherent in the model simulation developed for a specific project is a significant challenge and to a large extent takes us into unexplored intellectual territory. The imprecision in the underlying conceptual model may be approached first by developing a range of different conceptualizations each one consistent with the known constraints. By using each conceptualization as the basis for a numerical simulation and comparing the results gives an estimate of the impact of this component of imprecision on the final results.

As noted by Duncan (2009) it is important to create appropriate performance standards for modeling. When does a model have sufficient accuracy, resolution to use as the basis for estimation of the magnitude of leakage? Typically a model has been assessed by comparing the models predictions with new field observations. If the model predictions have a larger mismatch with observations than the estimated uncertainties then the numerical model is typically adjusted or “calibrated” to remove or at least minimize the discrepancy.

Establishing Natural Variability through Baseline Data and Sampling Strategies

It has become apparent that background CO₂ concentrations and flux measurements in natural environments and in sites where natural accumulations of CO₂ leak vary over a wide range (West et al, 2005). Before initiating a CO₂ sequestration project based on injection into brine reservoirs, sources of anthropogenic and natural CO₂ in the local environment should be catalogued. Developing sufficient data on the natural variability (including their temporal and spatial variability) of background CO₂-fluxs (and for elements and compounds that may act as a proxy for CO₂ or that might be mobilized by CO₂) may take several years of measurements prior to initiation of CO₂ injection. Background measurements should include the full range of sampling sites and monitoring technologies that will later be relied on. A monitoring program can never be more accurate than the baseline measurements and an inadequate baseline will create a cloud of uncertainty over subsequent monitoring. The location of baseline surveys should be based on a risk analysis so that the focus is on the spatial distribution of possible leakage pathways and of risk receptors (such as aquifers with potable water, sensitive ecologies, and population). The expected range of background values (based on preliminary baseline studies and plausible natural variability) should be used to optimize the set-up and deployment of

monitoring instruments. At this stage modeling of leakage should be used to predetermine the lower bounds of anomalous values, the trigger for “leakage detection”.

As part of preparation for the baseline study, the operator should first identify the parameter(s) to be measured, and the anticipated range of values for plausible leakage scenarios. The monitoring strategies will be also influenced by the measurement resolution, detection limits, accuracy, precision and reliability of monitoring systems. At this stage a statistically based sampling plan should be developed before the starting the baseline measurement program.

Baseline measurements should not be restricted to CO₂. It is important to measure the spatial and temporal variations in background values of:

- any parameters that act as a proxy for leaking CO₂
- any chemical species that are likely highly correlated with leaking CO₂
- the chemistry of water in aquifers, particularly USDW
- baseline measurements for any physical properties that will later be relied on to detect the presence of CO₂

CO₂ is a commonly occurring gas in the environment. Atmospheric concentrations of CO₂ near to the ground tend to be larger at night due to respiration and lack of photosynthesis. Wind direction can be an additional source of variation particularly if there are fossil fuel fired power plants or cement plants in the vicinity. Biological activity of microorganisms in the soil is a large source of CO₂ flux into the atmosphere. The rate of CO₂ generation is highly variable both in space and time (Fóti et al, 2006), depending on the amount and chemical composition of organic matter, and the water content, nitrogen availability and temperature of the soil (Kowalenko et al., 1978).

In a study of agricultural soils in eastern Germany Reth et al (2005) a significant ranges of CO₂ fluxes in both brownfield (0.9 to 5.5 m. mol. CO₂ m⁻² s⁻¹), and meadow soils (1.1 to 12.6 m. mol. CO₂ m⁻² s⁻¹). In this study between 63% and 81% of the variation in CO₂ flux from brownfield soils was found to be correlated with variations in soil temperature, relative soil water content, pH, and Carbon to Nitrogen ratio in the soil. The background levels of CO₂ in soils and the fluctuations in these levels with season, weather and diurnal variation. As a result dispersed CO₂ leaks will likely be difficult to detect. Baseline data on soil CO₂ concentrations were

gathered by Van Bergen et al (2005) over a period of 7 days recorded near locations of wells at the Kaniow site (part of the RECOPOL project, Pagnier *et al.*, 2004) and taken by sensors in 2 meter deep tubes. The results show CO₂ concentrations varied from less than 0.1% to 2.5% at the same sampling site. Other significant concentrations of CO₂ in the natural environment include: groundwater that flows in part through limestone aquifers (or sandstone with carbonate cements); hydrothermal waters associated with volcanism; and formation water charged with CO₂ from deep gas reservoirs.

Storck et al (1997) have made an analysis of the optimal location of monitoring wells for detection of groundwater contamination in three dimensional heterogeneous aquifers. However, apart from shallow wells monitoring USDW, the number of observation wells is so limited that random placement of monitoring wells have low probability of detecting localized leakage plumes (Warner 1992). A superior approach is to use risk as the basis for location of monitoring sites.

The level of uncertainty in the baseline data is the key to the ultimate capability of the monitoring system to detect leaks from the containment system. Although this level of uncertainty will doubtless vary across the monitoring network there will obviously be some magnitude of leakage of CO₂, below which the measurement system is unlikely to detect as anomalous.

Frameworks for Risk Analysis and Decision Making for Brine Sequestration

In dealing with uncertainty in regulatory decision making applied to complex engineered natural systems such as deep brine CO₂ sequestration projects, it is important to bring to bear appropriate and robust conceptual/mathematical frameworks. Decision analysis theory has become an important part of scholarly effort in resource and environmental management (Dubois et al, 1999; Greening and Bernow, 2004; Zhou et al, 2006; and Refsgaard et al, 2006). Decision analysis approaches in the past have assumed that probabilities can be estimated precisely. In complex natural systems uncertainties cannot be represented as precise probability distributions. Natural variability is a significant component of imprecision that must be accounted for in any decision making process (Bogen and Spear, 1987). In regulatory decision-making the aim is to select the action that will result in the best outcome. Typically in regulatory decision making, the

probabilities of plausible outcomes of each action cannot be calculated. Often regulatory agencies must rely on the professional judgment of their technical staff to model uncertainty. Such inputs can be integrated into quantitative models for decision making under uncertainty (Adriaenssensa et al, 2004). These models can provide an estimate of the degree of subjectivity in the final results to decision-makers.

An important issue is the evaluation of uncertainty in the conceptual models that underlie the numerical simulations that link monitoring measurements to inference of CO₂ leakage rates from the brine reservoir. An inverse correlation might be expected between greater complexity of a model and the quality of its predictions. Some systems may have a complexity and unpredictability that make it difficult to estimate the uncertainty. George Box, in a much quoted statement asserted that “All models are wrong, some models are useful”. It is important to fully evaluate the magnitude uncertainties in each component of the analysis that results in the ultimate decision. For example the decision making chain could include: soil gas detections of anomalous CO₂ values and an aquifer model of dispersion in groundwater flow to infer the leakage rate from say a presumed fracture zone related to a fault that intersects the CO₂ plume. It is very useful understand the relative magnitude of the sources of uncertainty that affect the ultimate decision. This approach allows targeting the data or model components that have the greatest impact on the regulatory decision.

Another important issue for regulators of CO₂ sequestration is the amount of information (or the degree of certainty) that should be required to support a decision (see for example James and Gorelick, 1994). Clearly this is a question of considerable complexity that could affect the cost of sequestration. Information acquisition can be very expensive in the subsurface. Companies could make a strong argument that such data acquisition should only be required if the expected value exceeds the cost. In this case the value of the information should be viewed in the context of an improvement in the outcome arising out of the regulatory decision that was based on the acquired information.

In decision theory, Bayesian analysis is a tool that has been in use for over half a century (Wald, 1950). Bayesian modeling facilitates combining of results of monitoring with other relevant information (domain knowledge), and provides a methodology to deal with missing data.

Hobbs (1997) describes three key features provided by Bayesian analysis as a component of an approach to decision making under uncertainty:

- 1) Inferences of expected values for model parameters and prediction of credible intervals for such parameters that are analogous to, but not identical to, the confidence intervals of classical or “frequentist” statistics. These parameters can be used to project credible intervals or bounds for the future behavior of the system.
- 2) The Bayesian approach can be used to identify the best decision that can be made based on the uncertainty and the available information. The best decision is defined by Hobbs as one that “maximizes the expected value of one or more performance indices”.
- 3) Bayesian analysis can be used to evaluate the degree to which additional information can change the decision we would be made and thus improve the outcome from the decision. Hobbs (1997) suggests that this enables the “expected value of imperfect information” to be quantified. Evaluating the cost effectiveness of various monitoring strategies requires establishing the sampling density necessary to assure a high likelihood of leak detection.

Fuzzy logic/set theory has been applied to hydrology problems (Coppola et al 2002), subsurface contamination risk assessment problems, and in some cases specifically in the context of creating frameworks for decision-making under uncertainty. Typical applications of fuzzy logic/set theory analyze uncertainty the formulation of the problem this approach can also be used to understand the effects of fuzziness of model parameters such porosity, hydraulic conductivity and boundary conditions (Schulz and Huwe, 1997). Fuzzy logic based modeling approaches can be combined with probabilistic (including Bayesian) approaches to address the kinds of problems addressed in this paper. Such hybrid approaches are capable of using fuzzy logic to characterize model imprecision while using stochastic methods to model irreducible uncertainty.

A multiple attributes decision making technique has been employed by Morisawa and Inoue (1991) to select optimal locations for monitoring wells to detect leakage from a solid-waste landfill site. Chen et al (2003) have used hybrid fuzzy/stochastic modeling to assess the

environmental risks for contaminated groundwater systems. Adriaenssensa et al (2004) suggested that the key advantage of applying fuzzy modeling to environmental decision making is the ability to readily integrate expert knowledge.

Discussion and Conclusions

When a project operator, and insurance company or regulator looks at a proposed geologic CO₂ sequestration project several overarching questions should come to mind:

- What can go wrong (what are the possible adverse outcomes)?
- What is the likelihood of these outcomes?
- What would the consequences be at this site?
- In view of the uncertainty in the data used, how confident are we about the answers to these first three questions?

These four questions are the basis for any risk assessment for a sequestration project.

Much if not all of the science and engineering knowledge and protocols necessary for conducting comprehensive monitoring of CO₂ sequestration in deep brine reservoirs is either available or is being developed in pilot projects currently underway. However the capabilities to interpret and act on monitoring data in a regulatory context have not yet matured. Decision making under uncertainty is a relatively new field and its application to complex natural systems remains an area of active research. Although statistical tools for characterizing some components of uncertainty in such systems are available many components of the total uncertainty in such systems are difficult to quantify. If CO₂ sequestration in deep brine reservoirs becomes deployed on a large scale it will be critical that new methodologies are developed to assess uncertainties (both the irreducible uncertainty and the imprecision). It is important that these methodologies encompass not only in monitoring measurements but also in the conceptual and numerical models used to interpret these measurements. This approach can potentially give decision-makers the ability to both make better informed decisions and to recognize the role that uncertainties play in the decision making process.

The accuracy and uncertainty that should be demanded by regulators for modeling for a specific project will differ from case to case, dependent on the scale of the possible negative impacts of incorrect model predictions. Ultimately the perception of risk by concerned stakeholders may drive the performance criteria for uncertainty in modeling. The requirements for accuracy and uncertainty in modeling to be used for initial site screening are very different to the requirements for a model intended to evaluate the magnitude of leakage from a large scale sequestration project.

Natural systems are appropriate candidates for applying modeling approaches that combine both probabilistic and non-probabilistic techniques in uncertainty modeling (known as hybrid models). When sufficient information on the nature of imprecision and irreducible uncertainty is available then it is appropriate to use the new emerging methods in modeling these types of complex natural systems. Promoting the use of uncertainty concepts as the context for evaluating regulatory decisions related to CO₂ sequestration in deep brine reservoirs is going to be a major task. There is a clear need for developing new approaches and tools to evaluate the uncertainty in measurements and modeling of leaking from CO₂ sequestration projects. Ultimately explicit understanding of the nature and magnitude of uncertainty and its impact on decision making is a key to achieving robust and credible regulatory decisions.

References

Adriaenssensa, V., De Baetsb, B., Goethalsa, P. L.M., De Pauw N. 2004 Fuzzy rule-based models for decision support in ecosystem management The Science of the Total Environment 319 (2004) 1–12

Apostolakis G. The distinction between aleatory and epistemic uncertainties is important: an example from the inclusion of aging effects into PSA. Proceedings of PSA '99, International topical meeting on probabilistic safety assessment, Washington, DC, 1999. p. 135–42.

Apostolakis, G.A., 1994, A commentary on model uncertainty. In Proc. Workshop I in Advanced Topics in Risk and Reliability Analysis, Model Uncertainty: Its Characterization and Quantification, NUREG/CP-0138, October 1994.

Augenbaugh J. M., C. J. J. Paredis 2006 The Value of Using Imprecise Probabilities in Engineering Design Journal of Mechanical Design ASME JULY 2006, Vol. 128 / 969

Baldocchi, D.D., 2003. Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: past, present and future. *Global Change Biol.* 9, 479–492.

Bellman, R. E., and Zadeh, L. A. (1970). "Decision-making in a fuzzy environment." *Management Science*, 17(4), B-141 - B-164

Benson, S M 2007 Adequacy of Monitoring Methods and Strategies for Detecting Carbon Dioxide Leakage from Geological Storage Reservoirs AGU Fall meeting

Benson, SM L Myer 2002 Monitoring to ensure safe and effective geologic sequestration of carbon dioxide - IPCC Workshop for Carbon Capture and Storage, 2002

Benson, S. and P. Cook, 2005, Underground geological storage. IPCC Special Report on Carbon dioxide. Capture and Storage; 5:196-276.

Bogen, K. T., and Spear, R. C. (1987). "Integrating uncertainty and individual variability in environmental risk assessment." *Risk Analysis*, 7, 427-436.

Bonano, E. J., Apostolakis, G. E., Salter, P. F., Ghassemi, A., and Jennings, S. (2000) "Application of risk assessment and decision analysis to the evaluation, ranking and selection of environmental remediation alternatives." *Journal of Hazardous Materials*, 71, 35-57

Burgman, M., 2005. Risks and Decisions for Conservation and Environmental Management, Cambridge University Press, United Kingdom.

Carrera J, Alcolea A, Medina A, Hidalgo J, Slooten LJ. 2005 Inverse problem in hydrogeology. *Hydrogeol J* 13:206–22

Chen, Z., Huang, G. H., and Chakma, A. (2003). "Hybrid Fuzzy-Stochastic Modeling Approach for Assessing Environmental Risks at Contaminated Groundwater Systems." *Journal of Environmental Engineering*, 129(1), 79-88.

Coppola Jr, E. A., Duckstein, L., and Davis, D. (2002). "Fuzzy Rule-based Methodology for Estimating Monthly Groundwater Recharge in a Temperate Watershed." *Journal of Hydrologic Engineering*, 7(4), 326-335.

Davidson, E.A., Savage, K., Verchot, L.V., Navarro, R., 2002 Minimizing artifacts and biases in chamber-based measurements of soil respiration. *Agric. For. Meteorol.* 113 (1–4), 21–37.

Duckham, M., K. Mason, J. Stell, M. Worboys: A formal approach to imperfection in geographic information. In *Computers, Environment and Urban Systems*, 25, 2001, pages 89-103.

Dubois, D., Godo, L., and Prade, H. (1999). "On the possibilistic decision model: from decision under uncertainty to case-based decision." *International Journal of Uncertainty Fuzziness Knowledge-Based Systems*, 7(6), 631-670.

Ekel, P. Y. (2001). "Methods of decision making in fuzzy environment and their applications." *Nonlinear Analysis*, 47, 979-990.

Ekel, P. Y. (2002). "Fuzzy Sets and Models of Decision Making." *Computers and Mathematics with Applications*, 44, 863-875

Etheridge, D et al 2007 Monitoring of Geologically Stored Carbon Dioxide Using Atmospheric Techniques. Abstract, American Geophysical Union, 2007 Fall Meeting

Freeze, R. A. (2004). "The role of stochastic hydrogeological modeling in real-world engineering applications." *Stochastic Environmental Research and Risk Assessment*, 18, 286-289

Fóti, S., et al Spatio-temporal variability of ecosystem exchange in three non-arborescent temperate vegetations. – *Acta Biol. Szeged.* **46**: 239-241, 2002.

Gaganis P. Smith L. 2006 Evaluation of the uncertainty of groundwater model predictions associated with conceptual errors: A per-datum approach to model calibration
Advances in Water Resources 29 (2006) 503–514

Gelhar, L. W., and Axness, C. L. (1983). "Three dimensional stochastic analysis of macrodispersion in aquifers." *Water Resources Research*, 19(1), 161-180

Gorelick J. B.. When enough is enough: the worth of monitoring data in aquifer remediation design. *Water Resour Res* V 30(12), 3499–513.

Greening, L. A., Steve Bernow 2004 Design of coordinated energy and environmental policies: use of multi-criteria decision-making *Energy Policy* 32, 721–735

Guan, J. and Aral, M.: 2004, 'Optimal design of groundwater remediation systems using fuzzy set theory', *Water Resources Research* 40.

Hagen, S.C., Braswell, B.H., Linder, E., Frolking, S., Richardson, A.D., Hollinger, D.Y., 2006. Statistical uncertainty of eddyflux based estimates of gross ecosystem carbon exchange at Howland Forest, Maine. *J. Geophys. Res.–Atmos.* 111, Art. no. D08S03.

Hauck, W. W., William Koch, Darrell Abernethy, Roger L. Williams 2008 Making Sense of Trueness, Precision, Accuracy, and Uncertainty Pharmacopeial Forum Vol. 34(3)

Helton, J., 1993. Uncertainty and Sensitivity Analysis Techniques for Use in Performance Assessment for Radioactive Waste Disposal. Reliability Engineering and System Safety, 42, pp. 327-367.

Helton, J. C. (2004) "Alternative representation of epistemic uncertainty" Reliability Engineering and System Safety, 85, 1-10.

Helton, J. C., W.L. Oberkampf 2004 Alternative representations of epistemic uncertainty Guest Editorial Reliability Engineering and System Safety 85 (2004) 1–10

Hobbs B. F. 1997 Bayesian Methods for Analysing Climate Change and Water Resource Uncertainties Journal of Environmental Management 49, 53–72

Hollinger, D.Y., Richardson, A.D., 2005. Uncertainty in eddy covariance measurements and its application to physiological models. Tree Physiol. 25, 873–885.

Hora, S. C., 1996 Aleatory and epistemic uncertainty in probability elicitation with an example from hazardous waste management Reliability Engineering and System Safety 54 (1996) 217 – 223

Hutyra, L. R. et al. 2008 Resolving systematic errors in estimates of net ecosystem exchange of CO₂ and ecosystem respiration in a tropical forest biome Agricultural and Forest Meteorology 148 1266 – 1279

Kacprzyk, J., and Fedrizzi, M. (1990). "Multi-person Decision Making Models Using Fuzzy Sets and Possibility Theory." Theory and Decision Library, Series B: Mathematical and Statistical Methods, W. Leinfellner and G. Eberlein, eds.,

Kluwer Academic Publishers, Dordrecht, the Netherlands.

Kacprzyk, J., and Nurmi, H. (1998). "Group Decision Making Under Fuzziness." *Fuzzy Sets in Decision Analysis. Operations Research and Statistics*, R. Slowinski, ed., Kluwer Academic Publishers. Dordrecht.

Keeney, R. L. and H. Raiffa (1993). *Decisions with Multiple Objectives: Preferences and Value Tradeoffs*. New York, NY: Cambridge University Press

Khadam, I. M., and Kaluarachchi, J. J. (2003). "Multi-criteria decision analysis with probabilistic risk assessment for management of contaminated ground water." *Environmental Impact Assessment Review*, 23, 683-721.

Kitanidis PK, Vomvoris EG. 1983 A geostatistical approach to the inverse problem in groundwater modeling (steady state) and one dimensional simulations. *Water Resour Res* 19:677–90.

Konikow L. F. Bredehoeft J. D. 1992 Ground-water models cannot be validated *Advances in Water Resources* 15 (1992) 75-83

Kowalenko, C;G., Iverson, K.C. and Cameron, D.R., 1978. Effect of moisture content, temperature and nitrogen fertilization on carbon dioxide from fields soils. *Soil Biol. Biochem.*, 10: 417-423.

Kuuskraa V. A., 2007 OVERVIEW OF MITIGATION AND REMEDIATION OPTIONS FOR GEOLOGICAL STORAGE OF CO₂ Staff Workshop on Technical Papers for AB1925 Report to the Legislature Sacramento, CA, June 28, 2007

Leuning, R. David Etheridge, Ashok Luhar and Bronwyn Dunse 2008 Atmospheric monitoring and verification technologies for CO₂ geosequestration. International Journal of Greenhouse Gas Control Volume 2, Issue 3, Pages 401-414

Meyer, W.S., Reicosky, D.C., Barrs, H.D., Shell, G.S.G., 1987. A portable chamber for measuring canopy gas exchange of crops subject to different root zone conditions. Agron. J. 79, 181–184.

Moens, D., and Vandepitte, D. (2005). "A survey of non-probabilistic uncertainty treatment in finite element analysis." Computer methods in applied mechanics and engineering, 194, 1527-1555

Moncrieff, J.B., Malhi, Y., Leuning, R., 1996. The propagation of errors in long-term measurements of land-atmosphere fluxes of carbon and water. Global Change Biology. Vol. 2, no. 3, pp. 231-240. Jun 1996.

Molz, F. (2004). "A rational role for stochastic concepts in subsurface hydrology: a personal perspective." *Stochastic Environmental Research and Risk Assessment*, 18, 278-279
Gelhar, L. W. (1986). "Stochastic Subsurface Hydrology From Theory to Applications." *Water Resources Research*, 22(9), 135S-145S.

Morisawa, S. and Inoue, Y.: 1991, 'Optimum allocation of monitoring wells around a solid landfill site using precursor indicators and fuzzy utility functions', *Journal of Contaminant Hydrology* 7, 337–370.

Muhanna, R. L., and Mullen, R. L. 2001 "Uncertainty in Mechanics Problems - Interval-Based Approach." *Journal of Engineering Mechanics, ASCE*, 127(6), 557-566

Nay, S.M., Mattson, K.G., Bormann, B.T., 1994. Biases of chamber methods for measuring soil CO₂ efflux demonstrated with a laboratory apparatus. Ecology 75, 2460–2463.

Neuman, S. P., and Yakowitz, S. (1979). "A statistical approach to the inverse problem of aquifer hydrology." *Water Resources Research*, 15(4), 845-860

Nikolaidis, E. 2005 "Types of Uncertainty in Design Decision Making." In E. Nikolaidis, D. M. Ghiocel and S. Singhal (Eds.), *Engineering Design Reliability Handbook*. New York: CRC Press.

Norman, J.M., Garcia, R., Verma, S.B., 1992. Soil surface CO₂ fluxes and the carbon budget of a grassland. *J. Geophys. Res. Atmos.* 97, 18845–18853.

Oberkampf, W. L., Helton, J. C., Joslyn, C. A., Wojtkiewicz, S. F., and Ferson, S. (2004) "Challenge problem: uncertainty in system response given uncertain parameters." *Reliability Engineering and System Safety*, 85, 11-19

Ojima, D.S., Quegan, S., Schmullius, C.C., 2005 Model-data synthesis in terrestrial carbon observation: methods, data requirements and data uncertainty specifications. *Global Change Biol.* 11, 378–397.

Parry, G. W. 1996 The Characterization of Uncertainty in Probabilistic Risk Assessment of Complex Systems. *Reliability Engineering and System Safety* 54(2-3): 119-126.

Raupach, M.R., Rayner, P.J., Barrett, D.J., Defries, R.S., Heimann, M.,
Seth D. Humphries,¹ Amin R. Nehrir,¹ Charlie J. Keith,¹ Kevin S. Repasky,^{1,*} Laura M. Dobeck,² John L. Carlsten,³ and Lee H. Spangler 2008 Testing carbon sequestration site monitor instruments using a controlled carbon dioxide release facility *APPLIED OPTICS* Vol. 47, No. 4

Refsgaard J. C. , Jeroen P. van der Sluijs James Brown c, Peter van der Keur 2006 A framework for dealing with uncertainty due to model structure error Advances in Water Resources 29 1586–1597

Richardson A. D. et al 2006 A multi-site analysis of random error in tower-based measurements of carbon and energy fluxes Agricultural and Forest Meteorology 136 (2006) 1–18

Richardson A. D. et al. 2008 Statistical properties of random CO₂ flux measurement uncertainty inferred from model residuals Agricultural and Forest Meteorology 148 (2008) 38 – 50

Schulz, K., and Huwe, B. (1997). "Water flow modeling in the unsaturated zone with imprecise parameters using a fuzzy approach." *Journal of Hydrology*, 201, 211- 229.

Subke, J.-A. Ilaria Inglimaa, Alessandro Peressottib, Gemini Delle Vedoveb, M. Francesca Cotrufoa 2004 A new technique to measure soil CO₂ efflux at constant CO₂ concentration Soil Biology & Biochemistry 36 (2004) 1013–1015

Tsang, C.-F. S.M. Benson, B. Kobelski, and R. Smith (2002) "Scientific Considerations Related to Regulation Development for CO₂ Sequestration in Brine Formations," Environmental Geology, Vol. 42, No. 2-3, pp. 275-281.

Tversky, A. and D. Kahneman (1974). "Judgment under Uncertainty: Heuristics and Biases." *Science*, 185, 1124-31.

Van Bergen, F., Winthaegen, P., Pagnier, H., Jura, B., Kobiela, Z. and Skiba, J. (2005) Monitoring Techniques Applied for CO₂ Injection in Coal. Extended abstracts, 67th European Association of Geoscientists & Engineers Conference, A018 (quoted in Winthaegen, Arts and Schroot,2005).

Velthof GL, Oenema O (1995) Nitrous oxide fluxes from grassland in the Netherlands: Statistical analysis of flux chamber measurements. *Eur. J. Soil Sci.* 46: 533–540

Walker, W.E., et al, 2003 Defining uncertainty a conceptual basis for uncertainty management in model-based decision support. *Integrated Assessment* 4 (1), 5-17.

Weiss W, Smith L. Parameter space methods in joint parameter estimation for groundwater models. *Water Resour Res* 1998;24:647–61

Yager, R. R. (2002). "On the valuation of alternatives for decision-making under uncertainty." *International Journal of Intelligent Systems*, 17, 687-707

Zhang, D. (2002). *Stochastic Methods for Flow in Porous Media: Coping with Uncertainties*, Academic Press, San Diego, CA.

Zhou P, B.W. Ang, K.L. Poh 2006 Decision analysis in energy and environmental modeling: An update *Energy* 31 2604–2622

West J. M. et al 2005 Issue Profile: Environmental Issues and the Geological Storage of CO₂ *Eur. Env.* **15**, 250–259

Section 7: Application of Bayesian Inference to Risks Associated with CO₂ Sequestration

Introduction

In the US and many other countries economic prosperity is currently linked to the use and production of carbon based fuels. The use of such fuels is inextricably tied to CO₂ emissions. To address concerns with atmospheric buildup of CO₂ in the atmosphere in a timely manner, while maintaining economic health, may not be possible without implementing carbon capture and storage (CCS). CO₂ sequestration in deep brine reservoirs is perhaps the key technology necessary to implement CCS successfully. The risks associated with CO₂ sequestration in deep brine reservoirs are of three kinds (Stenhouse et al., 2004):

- operational risks, related to possible accidental release during carbon capture, transport, injection, and storage (including health and public safety risks, environmental damage, and remediation)
- in situ risks, related to impacts on public health and safety as well as environmental and ecosystem impacts caused by CO₂ leakage from the reservoir to the surface
- climate risks, related to possible breach of contract, associated with leakage to the atmosphere (presumably reversing the climate benefits of sequestration), where credit may have been awarded under emissions trading schemes.

How to handle these long-term risks has been a subject of considerable controversy. The following is a sampling of recent opinion (the last three quotes coming from Congressional testimony) on this topic:

“Because of the unknown risk — this could perhaps be catastrophic — you’d have to have some sort of overlying federal layer of protection... otherwise [carbon capture and storage (CCS) operators] wouldn’t do it ... they wouldn’t go forward and capture carbon and put it deep

underground unless they had some assurance that liability issues would not come back to bite them.” Tim Peckinpaugh, a lawyer for the nuclear industry

“My sense is that you run a risk if the government assumes too much of this liability.... If you insure someone against a risk, then they’re going to be less likely to take actions to reduce that risk.” Richard Newell, Professor of Energy and Environmental Economics at Duke University. Quoted in Wanted: 1,000-year insurance policy By Evan Lehmann Posted on August 19th, 2008, Climatewire

Geologic sequestration lacks a large historical data base that would enable computation of long term risks. Elkington (2007) has asserted that “Lack of actuarial data on integrated large scale projects coupled with an absence of uniform international regulation creates major obstacles to risk management, private investment and wide-scale deployment”. In the language of risk analysis (Ellsberg, 1961) such systems are “ambiguous”. In essence the term ambiguity refers to imprecisely specified probabilities. Decision makers are more adverse to ambiguous situations than they are to too risky ones. For example insurers are known to seek higher premiums for projects that are perceived as ambiguous, than for those known to be risk prone (Hogarth and Kunreuther, 1989).

In the real world, the most important risk assessments are often required in situations where empirical data are limited. Risk assessments are sometimes done for novel processes or systems that not only lack an actuarial data base but to some extent have not previously been studied. Risk analyses of Carbon Capture, Utilization, and Storage (CCUS), where there are very few if any actuarial data from historic activity and where some aspects are largely new, present such a challenge. Qualitative “engineering judgment” has often been applied to such situations in the past, sometimes formalized through the formalism of “expert systems”. Even in such cases a probabilistic risk analysis framework must be chosen.

Probability Models

Classical probability theory can be traced back more than three centuries to a series of letters exchanged between mathematicians Blaise Pascal and Pierre de Fermat over issues involving games of chance. Over a century later Pierre-Simon de Laplace showed that the techniques of

inference derived from dice could be applied to a variety of other problems. Clearly reflecting its roots in the analysis of gambling, classical (or frequentist) statistics views probabilities as the frequencies of repeatable observations of an event. To account for the uncertainties associated with parameters of a model, frequentists often resort to Monte Carlo simulation.

An alternative approach to evaluating probability and formulating risk issues began with the work of 18th century cleric and mathematician Thomas Bayes (1702–1761). Bayes discovered what we know recognize as a special case of what is now called Bayes' theorem in a paper titled "An Essay towards solving a Problem in the Doctrine of Chances". However it was not until Laplace developed what is now known as Bayesian probability that it became an established alternative. For two events A and B , with probabilities $P(A)$ and $P(B) =/ 0$ respectively, the conditional probability of A given B can be defined as $P(A | B) = P(A \& B) / P(B)$ where $A \& B$ denotes the event where both A and B occur and $P(A \& B)$ denotes that event's probability. The quantity $P(A | B)$ describes the likelihood that event A will occur, given that B has already occurred. If neither A nor B is impossible, i.e., if $P(A) =/ 0$ and $P(B) =/ 0$, then symmetry implies that the probability of the conjunction $A \& B$ is equal to two things, $P(A | B) P(B) = P(A \& B) = P(B | A) P(A)$, thus they must equal each other. Rearranging we get $P(A | B) = P(A) P(B | A) / P(B)$ which is known as Bayes' rule.

Bayes Rule serves as a way to convert a probability like $P(B | A)$ into one like $P(A | B)$. Thus, it converts the probability that B occurs, given A has occurred, to the probability that A occurs given B .

Bayesian theory probabilities may describe states of partial knowledge, even perhaps those related to non-repeatable events. Increasingly in risk studies, bayesian approaches are replacing those of classical or frequentist school.

Bayesian networks (BNs) have become a widely used approach to modeling risk in complex domains with considerable uncertainty. Bayesian approaches provide a coherent and robust framework for approaching such problems. Previous models utilized for risk assessments of CO₂ sequestration projects have focused on a series of single case assessments of hazard. Such approaches have tended to have inadequate analysis of uncertainty. They also are difficult to use

in the real world where adaptive techniques will be required as new data becomes available over the projects lifetime. The Bayesian approach enables both utilizing existing data and at the same time having the capability to adsorb new information thus to lower uncertainty in our understanding of complex systems. Bayesian networks are becoming extensively utilized in quantitative risk assessment analyses as they can provide predictive as well as diagnostic analysis. Bayesian networks have been used to study a wide range of technical problems.

Bayesian networks have a number of advantages over alternative approaches. They can be used for the analysis of data sets from small to large and those that are incomplete. BNs allow for uncertainty to be treated explicitly (Uusitalo, 2007).

The Monte Hall Problem

Most introductions to Bayesian inference fail to give any understandable examples of why the Bayesian approach works. An instructive example is the Monte Hall problem. Game show host Monte Hall was famous for the following challenge to winners on his show. The winner would be offered a choice between three doors (A, B, and C). Behind two of the doors, Monte would say, is a goat. The third door has a car. After choosing say Door C, Monte asks shows the winner what's behind one of the two gates they didn't select, in this case Door A. He invariably reveals the presence of a goat. Monte then challenges the winner.... “do you want to change your door or stay with the one you have”. Most competitors assume that their likelihood of winning the car has not changed and that is no advantage to changing their choice. Even professionals trained in frequentist statistics are likely to assert that the probability of selecting the door with the car was initially $1/3$ for each door, and becomes $1/2$ for each door when one door is removed from the game. They would be incorrect in this last assertion. In fact there is a $2/3$ probability of finding the car if you change your door choice and a $1/3$ if you stay with your initial door. Why is this? The reason is simple. Monte Hall has insider information. He knows which door hides the car and this is the door he will not open. He in effect conveys this information to you in his choice of doors to open. There is a $2/3$ chance that one of the two doors you have not chosen contains the car. As Monte will always chose the other door with the goat, the probability that the door that he does not chose has the car is $2/3$. In changing your door choice after receiving

new information you have in effect used a Bayesian updating scheme. The correct probability can be computed from Bayes' Rule.

An Overview of Bayesian Networks

Bayesian networks can be utilized to establish causal-relationships between key variables and the outcomes (representing cause-effect relationships). Bayesian network are sometimes referred to as causal-networks, or probabilistic-networks. Such networks can meaningfully incorporate information with a range of uncertainties. These uncertainties will ultimately be recorded in the outputs of the models. The nature of the variables in a BN may be continuous, discrete or categorical. To represent continuous relationships in a BN a continuous variable must be discretized.

To construct a BN one must first develop a conceptual-model that allows establishing a causal-structure by understanding the dependencies between variable of interest. These variables will become nodes in the final network. Bayesian network can be described qualitatively as a directed graph where the nodes (variables) are system variables the directed lines joining them may be used to represent the cause-effect relationships. Mathematically this kind of network is termed a directed graph. The relations between variables in a such a graph are “family relations” in the sense that line from X to Y means that Y is a child of X and thus X is a parent of Y (Jensen, 2001). There is a set of prior probabilities $P(X)$ attached to the parent node X, and a set of conditional probabilities $P(Y/X)$ associated with the node Y whose father is X. It defines the probability distributions over the states of Y given the states X.

In a Bayesian analysis a prior-probability (sometimes referred to as a “Bayesian Prior”) reflects the likelihood that a variable would have some specific value. Conditional-probabilities relate to the likelihood of a variable having a specific value given a set of input variables impacting it. Conditional probabilities are typically estimated from a variety of approaches including:

- Direct calculation from measurements
- Elicitation of expert opinion

- Established functional relationships between variables

The posterior-probability is the likelihood that a variable will be in a particular state, given the values of the input variables, the conditional-probabilities, and an associated set of rules governing how the probabilities are combined.

A very useful attribute of BNs is that Bayes' theorem can be used to update probabilities when new information is acquired. Such new information can be integrated into the analysis portrayed in the BN in the form of estimated posterior probabilities. Data sources may be assimilated into the BN in the form of a 'cases' each of which might represent monitoring data, or the results of a pilot project.

Bayesian networks can be utilized to codify complex cause-effect relationships and to derive causal inferences based on a range of assumptions. Such causal networks can also become tools that enable improved decision-making

Models based on Bayesian networks can be used to help make predictions of the future states of the systems and to understand the uncertainties in these predictions. They also can be utilized to test the validity of various options to manage the system and to identify gaps in available information.

Application of Bayesian networks to CO₂ Sequestration Issues

Using BNs for Interpreting CO₂ Monitoring Data

Yang et al. (2011) have presented a Bayesian based hierarchical model for soil CO₂ flux and leak detection at geologic CO₂ sequestration sites. These authors note that characterizations of background soil conditions, particularly CO₂ respiration rates, are the key to understand the significance of the results of CO₂ leakage monitoring in soils at CO₂ sequestration sites. Yang et al. (2011) note that CO₂ respiration is temperature-dependent and that this has to be taken into account in interpreting monitoring data for detecting leaks. The authors fit models using a Bayesian hierarchical method to get estimates for both site-specific and general situations. Their model predicts the observed range of background CO₂ fluxes from the soil as a function of

temperature. Detection of anomalous CO₂ fluxes obviously will only be possible if the values clearly exceed these background values.

Application of Bayesian to Risk of Leaking Abandoned Wells

Modeling the risk leakage from abandoned wells has been developed by DNV utilizing the BN approach. Their model utilizes a BN approach to “integrate leakage probability and the potential consequences” of possible leakage from a plugged and abandoned wellbore at a CO₂ sequestration site. Key issues are degradation of the wellbore cement and steel casing over time and the increase in fluid pressure in the reservoir as CO₂ injection proceeds. The model also depicts the consequences of CO₂ leakage, to both groundwater and to the atmosphere. A detailed analysis of this model was presented by Friis-Hansen et al (2010).

Modeling Risks of Future CO₂ Pipelines Based on Incident Record for Natural Gas Pipelines

Natural gas transmission pipelines can be used as an analogy to CO₂ pipelines. Wang and Duncan (In preparation) have analyzed the causes, failure modes and consequences of natural gas transmission pipelines using an up-to-date DOT database. The probabilities of different failing modes (leak, rupture or system component malfunction) conditioned on causing factors (internal/external corrosion, outside forces, material or construction defects) have been calculated. The occurrence probabilities of ruptures with different sizes were obtained. The natural of failure consequence were evaluated in different aspects: economic damage, unintended releases of natural gas, fatality/injury. The causes, failing modes and consequences, as shown in Figure 1, can be represented as random variables in BN. The causal relationship among these can be also well captured, whereas the conditional probabilities among them will be used as prior to drive the model.

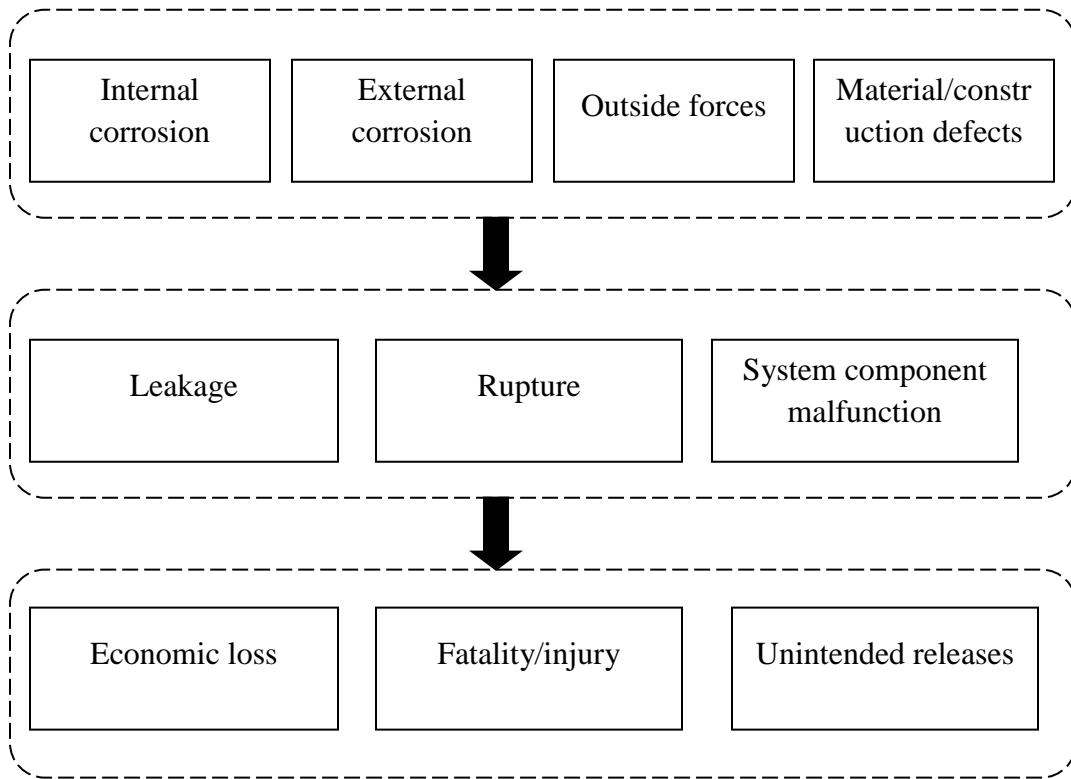


Figure 1: The random variables used to represent causes, failing modes and consequence of natural gas and CO₂ pipelines. The arrows denote the causal relationship among different groups of variables.

There are no serious incidents involving fatalities/injury in CO₂ transport pipelines but few cases where ruptures occurred. The constructed BN will be trained based on natural gas transmission pipelines and then updated based on limited CO₂ incident data.

Besides BN, Bayesian theorem can be utilized to update the probability distribution of failure rate of natural gas pipelines and CO₂ pipelines. We plan to first apply Bayesian theorem to update the failure rate of natural gas pipelines based on observed significant incidents during 1990~2009. Posterior distribution for natural gas pipelines is then used as priors for CO₂ pipelines. The proposed methodology for both is described as the following.

The number of incidents observed at each year is presented as x_i ($i=1990, 1991\dots 2009$). Assume that the number of incidents x_i occurred at each year follows a Poisson distribution with parameter λ . To find the posterior distribution based on observed incident data, the following is used:

$$p(\lambda | x_1, x_2, \dots, x_i, \dots) \propto p(x_1, x_2, \dots, x_i, \dots | \lambda) p(\lambda) \quad (1)$$

where $p(x_1, x_2, \dots, x_i, \dots | \lambda)$ is the likelihood term, $p(\lambda)$ is the prior probability and $p(\lambda | x_1, x_2, \dots, x_i, \dots)$ is the posterior distribution.

Assuming that any incident occurring in a year is independent, then the likelihood term can be represented as:

$$p(x_1, x_2, \dots, x_n | \lambda) = p(x_1 | \lambda) p(x_2 | \lambda) \dots p(x_n | \lambda) \quad (2)$$

Based on Poisson distribution, the likelihood term can be written as:

$$p(x_1 | \lambda) p(x_2 | \lambda) \dots p(x_n | \lambda) \propto \lambda^{\sum x_i} e^{(-n\lambda)} \quad (3)$$

where n is the number of years.

Gamma distribution has been demonstrated as a conjugate prior for Poisson distribution A. Gamma distribution with a shape parameter α and inverse scale parameter β has the following density function:

$$p(\lambda) \propto \lambda^{\alpha-1} e^{-\beta\lambda} \quad (4)$$

Combing Equations (1), (3) and (4), the following can be obtained:

$$p(\lambda | x_1, x_2, \dots, x_i, \dots) \propto \lambda^{\sum x_i} e^{(-n\lambda)} \lambda^{\alpha-1} e^{-\beta\lambda} \quad (5)$$

The posterior distribution of λ also follows Gamma distribution with shape parameter $(\alpha + \sum x_i)$ and scale parameter $(\beta + n)$. Thus the posterior distribution has been found in a closed form, as it remains a Gamma distribution, albeit with different parameters.

The obtained posterior distribution of λ can be used as priors in deriving the distribution function for CO₂ pipeline incidents.

Another alternative is to assign failure probabilities for pipelines with different conditions, e.g., diameter and age, using historical incident data. Based on pipeline size in diameter and pipeline age conditions, we have divided U.S. natural gas transmission pipelines into four subgroups: (old, small); (old, large); (new, small) and (new, large). Rather than assigning unified failure probability for pipelines in different groups, we calculate updated failure probabilities for different segments. Additionally, we have provided a small toolkit which demonstrates the use of Bayesian theorem.

According to Bayesian theorem,

$$P(S_{i,j} | D) = \frac{P(D | S_{i,j})P(S_{i,j})}{\sum_{i,j} P(D | S_{i,j})P(S_{i,j})} \quad (6)$$

Where $S_{i,j}$ represents a specific subgroup with i (i = old or new) and j (j = small or large); D is observed data of pipeline failures.

We have calculated pipeline statistics and incident statistics based on historical dataset during the period 1990-2009. Using Matlab software, we designed a toolkit to conduct Bayesian calculation for Eqn. (6) for different subgroups.

GUIs, known as graphical user interfaces, are a powerful tool in Matlab which provides point-and-click control of software applications. We selected GUIs to develop a toolkit primary based on two-fold reasons. Firstly, Matlab has a user-friendly development environment to design, implement and test GUIs. At the same time, it provides a packaging capacity that enables the developed GUIs work as a stand-alone software. This is favorable for users that have no

access to the software of Matlab. GUIs provide various components, including text box, editable box, push button, etc. A salient feature is one can design a call-back function for each box to activate a certain action, e.g., math calculation, figure generation, etc. A series of such actions aims to fulfill the software capacity. Details of the use of GUIs are omitted in this report as numerous resources are available in the literature.

There are several steps involved in the development of such an application, namely interface design, call-back function, application test and packaging. In the following, the four-step process of creating such a toolkit is described in details.

In the first step, we aimed to design the components and layout of the application. As we focus on updating pipeline failure probability of natural gas pipeline according to the above-mentioned equation, all the components in the equations are needed. These are pipeline statistics, incident statistics and prior probability of pipeline failures. We decided to group all of these into the input module. Accordingly, we added a module for output. To better present the results, we decided to add a figure that shows the prior and posterior probabilities. Additionally, to enhance its usability, we have decided to provide an instruction section in the interface which provides simple explanation of using it. The layout of GUIs is shown as in the following figure.

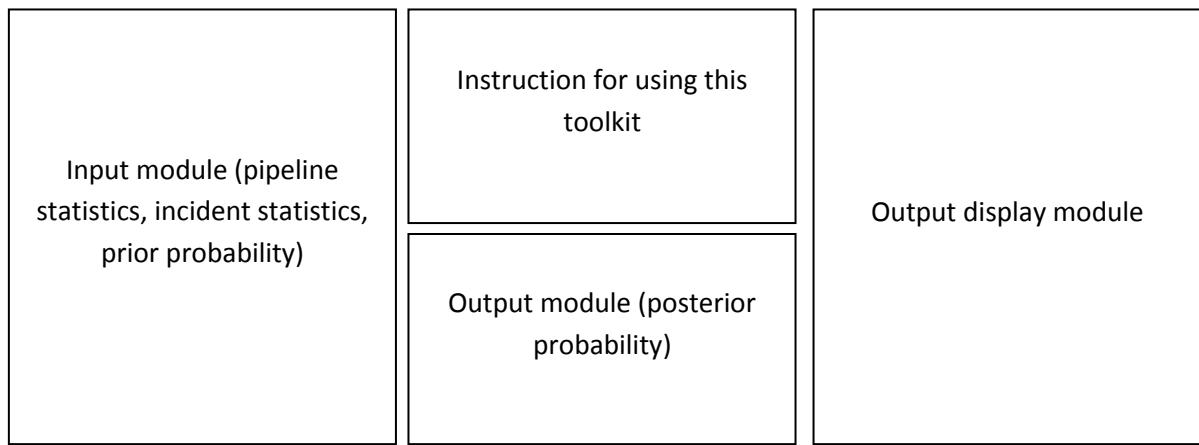


Figure 2: Interface design for the GUI toolkit in Matlab

In the second step, each component, including text box, push button or figures, should be placed properly and their call-back functions should be written. For the input module, all components are editable box as the users will provide the numerical value for each item (Figure 4). Note that the contents of each editable box can be pre-formatted by the GUI designer. In developing out toolkit, we didn't modify this setting and input of these boxes is considered as strings rather than numerical numbers. We later convert them to numbers when we design the call-back function for the output module.

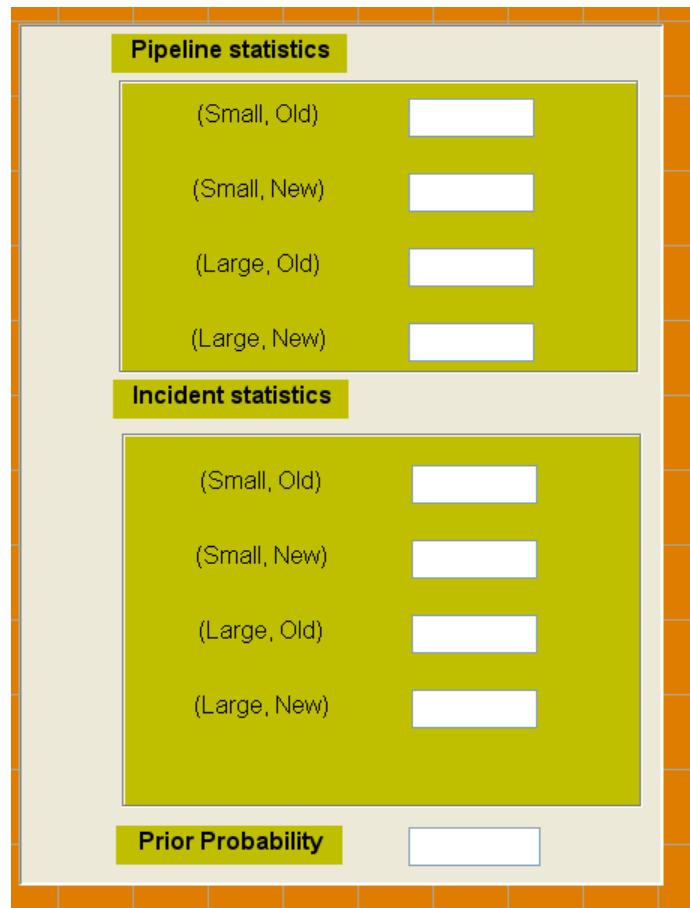


Figure 3: Editable boxes (blank) used in the input module of the toolkit.

In the output section, we design a push button that could be used to activate Bayesian calculation. Matlab code for this push button is listed below:

```
function pushbutton1_Callback(hObject, eventdata, handles)
% hObject    handle to pushbutton1 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
a_value = str2double(get(handles.edit1,'String'));
b_value = str2double(get(handles.edit2,'String'));
c_value = str2double(get(handles.edit3,'String'));
d_value = str2double(get(handles.edit4,'String'));
e_value = str2double(get(handles.edit5,'String'));
f_value = str2double(get(handles.edit6,'String'));
g_value = str2double(get(handles.edit7,'String'));
h_value = str2double(get(handles.edit8,'String'));
i_value = str2double(get(handles.edit9,'String'));
temp_1 = e_value*i_value./a_value;
temp_2 = f_value*i_value./b_value;
temp_3 = g_value*i_value./c_value;
temp_4 = h_value*i_value./d_value;
set(handles.edit10,'String',temp_1);
set(handles.edit11,'String',temp_2);
set(handles.edit12,'String',temp_3);
set(handles.edit13,'String',temp_4);
```

The call-back function of the push button implement the Bayesian calculation using input from pipeline statistics, incident statistics and prior probability.

The instruction module is relatively simple as it is comprised of text boxes. It is worth mentioning that the output display module could be more time consuming as it calls the value

from the input and output module. The following is the code of the call back function for the output display module:

```

function plot_button_Callback(hObject, eventdata, handles)
% hObject handle to plot_button (see GCBO)
% eventdata reserved - to be defined in a future version of MATLAB
% handles structure with handles and user data (see GUIDATA)
a_value = str2double(get(handles.edit1,'String'));
b_value = str2double(get(handles.edit2,'String'));
c_value = str2double(get(handles.edit3,'String'));
d_value = str2double(get(handles.edit4,'String'));
e_value = str2double(get(handles.edit5,'String'));
f_value = str2double(get(handles.edit6,'String'));
g_value = str2double(get(handles.edit7,'String'));
h_value = str2double(get(handles.edit8,'String'));
i_value = str2double(get(handles.edit9,'String'));
temp_1 = e_value*i_value./a_value;
temp_2 = f_value*i_value./b_value;
temp_3 = g_value*i_value./c_value;
temp_4 = h_value*i_value./d_value;
out(:,1)= ones(4,1)*i_value;
out(:,2)=[temp_1,temp_2,temp_3,temp_4];
bar(handles.axes2,out)
legend('prior probability','updated probability')
set(handles.axes2,'XTickLabel',{'small old','small new','large old','large new'})
set(handles.axes2,'FontSize',12)

```

The overall layout of the GUI is shown in Figure 5.

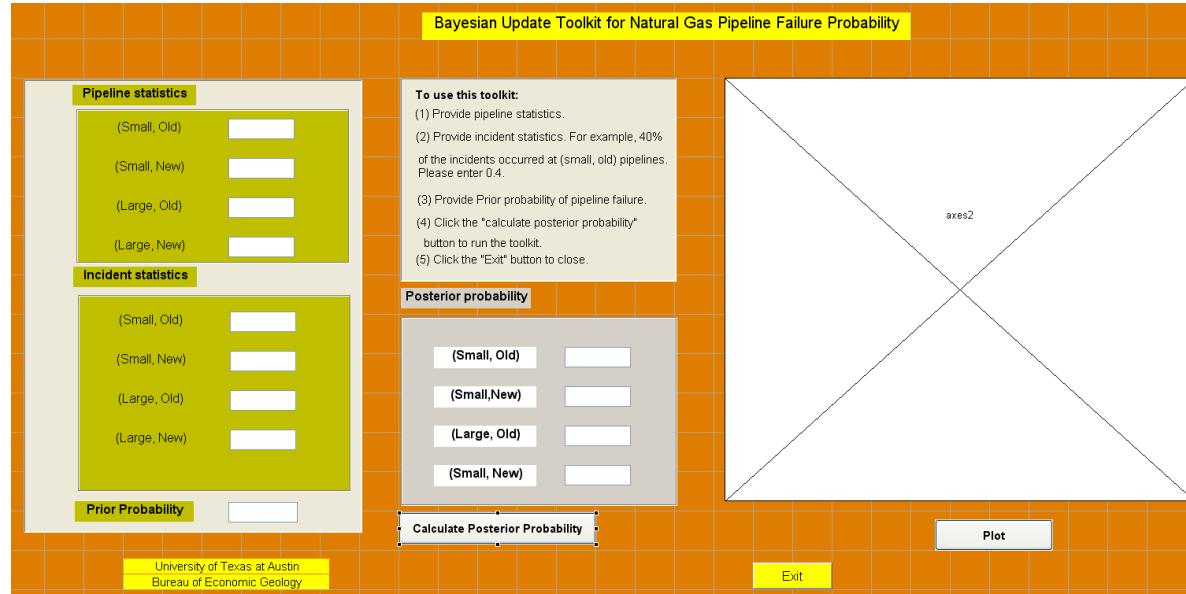


Figure 4: Layout of the GUI designed for updating pipeline failure probability using Bayesian rule.

In the third step, it is important to test the application and polish the design appropriately. In the testing phase, one may find and fix any programming bug and further improve its performance and change the layout. The purpose is to ensure that the application tool is function properly and user-friendly. The following figure shows a snapshot in our testing.

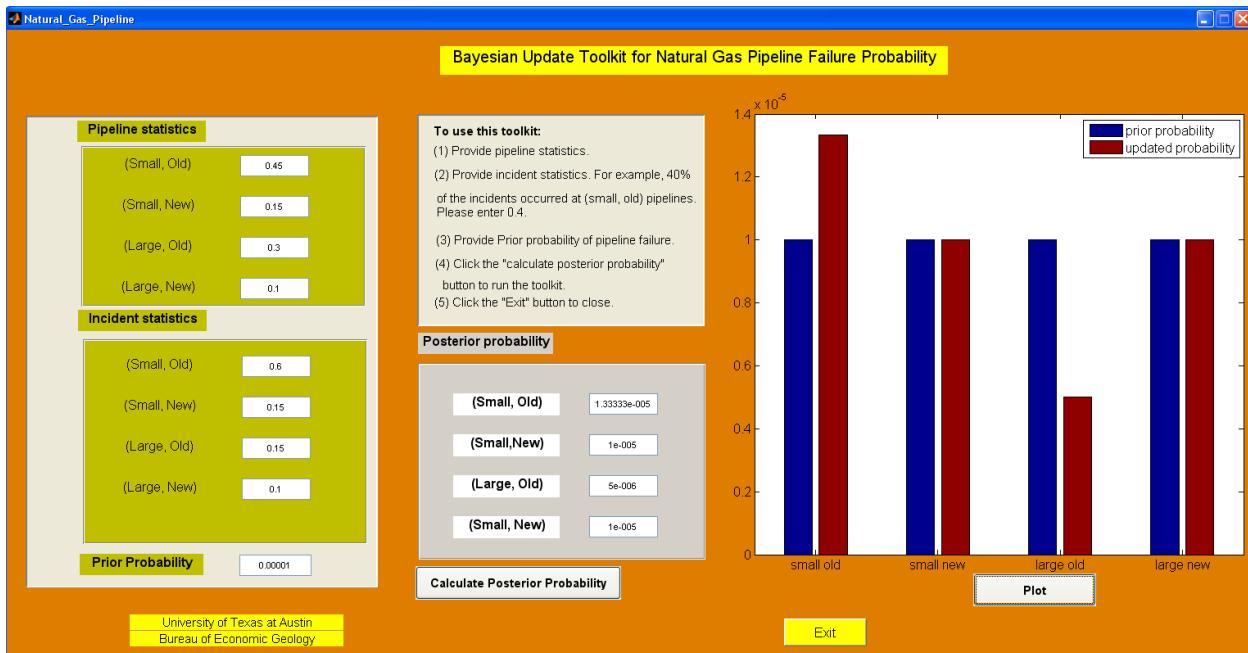


Figure 5: A snapshot of the application during the test phase.

The last step of developing such an application toolkit is to package and deploy it as stand-alone software.

Modeling Risks of Future CO₂ Pipelines Based on Incident Record for Natural Gas Pipelines

Natural gas transmission pipelines can be used as an analogy to CO₂ pipelines. Wang and Duncan (2014) have analyzed the causes, failure modes and consequences of natural gas transmission pipelines using an up-to-date DOT database. The probabilities of different failing modes (leak, rupture or system component malfunction) conditioned on causing factors (internal/external corrosion, outside forces, material or construction defects) have been calculated. The occurrence probabilities of ruptures with different sizes were obtained. The natural of failure consequence were evaluated in different aspects: economic damage, unintended releases of natural gas, fatality/injury. The causes, failing modes and consequences, as shown in Figure 1, can be represented as random variables in BN. The causal relationship among these can be also well captured, whereas the conditional probabilities among them will be used as prior to drive the model.

There are no serious incidents involving fatalities/injury in CO₂ transport pipelines but few cases where ruptures occurred. The constructed BN will be trained based on natural gas transmission pipelines and then updated based on limited CO₂ incident data.

Besides BN, Bayesian theorem can be utilized to update the probability distribution of failure rate of natural gas pipelines and CO₂ pipelines. We plan to first apply Bayesian theorem to update the failure rate of natural gas pipelines based on observed significant incidents during 1990~2009. Posterior distribution for natural gas pipelines is then used as priors for CO₂ pipelines. The proposed methodology for both is described as the following.

The number of incidents observed at each year is presented as x_i ($i=1990, 1991 \dots 2009$). Assume that the number of incidents x_i occurred at each year follows a Poisson distribution with parameter λ . To find the posterior distribution based on observed incident data, the following is used:

$$p(\lambda | x_1, x_2, \dots, x_i, \dots) \propto p(x_1, x_2, \dots, x_i, \dots | \lambda) p(\lambda) \quad (1)$$

where $p(x_1, x_2, \dots, x_i, \dots | \lambda)$ is the likelihood term, $p(\lambda)$ is the prior probability and $p(\lambda | x_1, x_2, \dots, x_i, \dots)$ is the posterior distribution.

Assuming incidents that occurred in each year are independent; then the likelihood term can be represented as:

$$p(x_1, x_2, \dots, x_n | \lambda) = p(x_1 | \lambda) p(x_2 | \lambda) \dots p(x_n | \lambda) \quad (2)$$

Based on Poisson distribution, the likelihood term can be written as:

$$p(x_1|\lambda)p(x_2|\lambda)\dots p(x_n|\lambda) \propto \lambda^{\sum x_i} e^{(-n\lambda)} \quad (3)$$

where n is the number of years.

Gamma distribution has been demonstrated as a conjugate prior for Poisson distribution A

Gamma distribution with a shape parameter α and inverse scale parameter β has the following density function:

$$p(\lambda) \propto \lambda^{\alpha-1} e^{-\beta\lambda} \quad (4)$$

Combining Equations (1), (3) and (4), the following can be obtained:

$$p(\lambda | x_1, x_2, \dots, x_n) \propto \lambda^{\sum x_i} e^{(-n\lambda)} \lambda^{\alpha-1} e^{-\beta\lambda} \quad (5)$$

The posterior distribution of λ also follows Gamma distribution with shape parameter $(\alpha + \sum x_i)$ and scale parameter $(\beta + n)$. Thus the posterior distribution has been found in a closed form, as it remains a Gamma distribution, albeit with different parameters.

The obtained posterior distribution of λ can be used as priors in deriving the distribution function for CO₂ pipeline incidents.

Estimating Risks from Surface Facilities

It is almost certain that the risks associated with surface facilities related to CCS and CCUS operations will dominate the total risks (see for example Duncan et al., 2009). Pipes and steel exposed to corrosive agents such as carbonic acid deteriorates over time and as the structural integrity of degrades with increasing age risks will increase. Thodi et al. (2009) have presented an analysis of risk based integrity modeling for natural gas processing plants that capture the elements needed for a similar analysis of CO₂ sequestration infrastructure. They create bayesian a framework to quantify the risks associated with an ageing plant subject to the flow of a mildly corrosive fluid. In risk based integrity assessments, the structural degradations are modeled using prior probability distributions. They suggest that plant inspection data, to create updated probabilities using Bayes theorem. Thodi et al. (2009) distinguish two types of structural degradations: corrosion; and cracking (or rupturing). The authors develop models for stochastic

degradation for corrosion (including uniform, pitting, and erosion corrosion). They also develop models to describe stress corrosion cracking, corrosion fatigue, and chemical induced cracking.

Thodi et al. (2009) note that risk based integrity modeling focuses on estimating both the likelihood of structural failures and the magnitude of the consequences of such failures. They suggest that the likelihood of failure can be estimated utilizing stochastic modeling of specific corrosion and cracking mechanisms. They then used case studies to validate the predictions from their stochastic models.

Risk Communication and Negotiation with Stakeholders

Henriksen et al. (2007) have used the BN approach to create an interactive forum for the public to participate in understanding groundwater contamination issues. In this approach BN allows stakeholders with divergent interests and beliefs express themselves and to be heard by competing groups. It provides a basis for negotiation between disparate participants even when data is insufficient for deterministic groundwater modeling to provide meaningful results. In the future this kind of approach could be a very useful tool for interacting with disparate stakeholders over how to deal with risk issues associated with sequestered CO₂.

Modeling Leakage Scenarios

Future applications of BN in CO₂ sequestration include quantification of the risk posed plausible scenarios for CO₂ leakage. This task will be particularly challenging as it requires predicting the performance of engineered geologic reservoirs over a time scale on the order of thousands of years.

Discussion and Conclusions

It is likely that Bayesian inference and Bayesian networks will play an increasing role in modeling, understanding and communicating risks associated with CCUS in general and CO₂ sequestration specifically. Although there seems to be a broad consensus in the scientific and engineering literature that the Bayesian approach is the most appropriate to tackle problems such as risks associated with CO₂ sequestration there are significant barriers to the implementation of such approaches. Because most aspects of CCS either lack a historical accumulation of data

relevant to risk or have very limited relevant information, coming up with reliable estimates of posterior probabilities is a challenge.

References

Borsuk ME, Stow CA, Reckhow K (2004) A Bayesian network of eutrophication models for synthesis, prediction and uncertainty analysis. *Ecol. Model.* 173: 219-239

Berger JO. Robust Bayesian analysis: sensitivity to the prior. *Journal of Statistical Planning and Inference* 1990;25:303–28.).

Brand, K.P., Small, M.J., 1995. Updating uncertainty in an integrated risk assessment: conceptual framework and methods. *Risk Analysis* 15, 719–731

Carlin, B. P. and Louis, T. A. 2009 *Bayesian Methods for Data Analysis*, CRC Press.

Castelletti A, Soncini-Sessa R (2007) Bayesian networks in water resource modeling and management. *Environmental Modeling & Software*, 22(8): 1073-1074.

Darwiche A (2009) *Modeling and Reasoning with Bayesian Networks*. Cambridge University Press

Elkington M. 2007 Options for managing liability in CCS Projects June 1st 2007

Ellsberg, D. (1961), Risk, ambiguity and the Savage axioms, *The Quarterly Journal of Economics* 75, 643–669

Friis-Hansen, P et al. 2010. Emerging Risks – Related Policies. SP1: Establishing the basis for the European Integrated approach to emerging risks: ERRAs – Emerging Risk Representative Industrial Applications. European Virtual Institute for Integrated Risk Management-EU-VRi.

Henriksen H. J. et al., 2007, Public participation modeling using Bayesian networks in management of groundwater contamination, *Environmental Modeling & Software* 22, p 1101-1113

Hudson L., Ware B., Laskey K., and Mahoney S. (2002). An application of bayesian networks to antiterrorism risk management for military planners. Technical Report, Digital Sandbox, Inc.

Jensen FV, 2001, Bayesian networks and decision graphs, Springer-Verlag

Miller, R., & Lessard, D. (2001). Understanding and managing risks in large engineering projects. *International Journal of Project Management*, 19(8), 437–443

Qian, S.S., Stow, C.A., Borsuk, M.E., 2003. On Monte Carlo methods for Bayesian inference. *Ecological Modeling* 159, 269–277.

Stenhouse, M.J., Wilson, M.; Herzog, H.; Cassidy, B.; Kozak, M.; Zhou, W.; Gale, J. 2004 “Regulatory Issues Associated With Deep (Geological) CO₂ Storage” GHGT7, Vancouver

Thodi P., et al., 2009, Risk Based Integrity Modeling of Gas Processing Facilities using Bayesian Analysis, *Proceedings of the 1st Annual Gas Processing Symposium*, Elsevier

Uusitalo, L. (2007). Advantages and challenges of Bayesian networks in environmental modeling. *Ecological Modeling*, 203(3/4), 312–318.

Xu J, Johnson MP, Fischbeck PS, Small MJ, VanBriesen JM (2010) Integrating Location Models with Bayesian Analysis to Inform Decision Making. *J Water Res Planning Manage*, 136(2): 209-216.

Yang Y. et al., 2011, Bayesian hierarchical models for soil CO₂ flux and leak detection at geologic sequestration sites, *Environ Earth Sci*, 64:787–798

Section 8: Programmatic Risks Faced by Carbon Capture and Storage Projects

Introduction

In arguing for the need for rapid commercialization of carbon capture and storage (CCS) Sheppard and Socolow suggested that deployment of this technology will “allow us to sustain many of the benefits of access to hydrocarbons even in a carbon constrained world” (Sheppard, M. and Socolow, R. 2007). Snyder et al have noted that carbon capture and storage (CCS) is “one of a limited set of large-scale options to enable an energy-rich, low-carbon future”. CCS is an umbrella-term that encompasses a range of types of projects, including the construction of new power stations using novel technology, retrofitting existing power stations for CO₂ capture, construction of pipeline networks, injection into deep brine reservoirs, and monitoring. The potential size of a future CCS industry is staggering. Morrison et al have noted that the global total volume of CO₂ that may be injected for sequestration by 2050 is as much as five times the current annual production of natural gas or over 100 Tcf per year (Morrison, H. et al. 2008). In most countries any implementation of CCS at a scale sufficient to meet typical proposed CO₂ reduction targets will only be accomplished through significant restructuring of the way society produces electricity. Kannan (2009) for example has noted that in the UK the government’s economy-wide reduction target for CO₂ of 60% by 2050 “requires a paradigm shift in the whole energy system.

Policy issues associated with CCS are complicated by: (1) the large projected financial impact on society of decarbonizing energy; (2) the requirement for such rapid implementation of carbon sequestration that a “learn-as-you-go” approach will be required to gaining the necessary scientific data to assure long term positive outcomes; (3) the assertion by many climate scientists that delay in taking action to lower the rate of CO₂ accumulation in the atmosphere may inevitably result in dangerous climate change; (4) the growing awareness and concern by the general public that climate change is a significant threat is driving politicians to develop legislative solutions; and (5) the realization by many corporations that only CO₂ sequestration in brine reservoirs has the capacity for making a large, cost effective impact on their CO₂ emissions within the next few decades. As a result of these realities corporations may well be faced with having to develop and implement CCS on a very short timeframe.

Managements of companies under pressure from stakeholders to adopt CCS are interested in understanding the associated business risks. . As no full scale CCS project with capture from a fossil fueled power plant has yet been built, the technology is striving to achieve the status of “commercially available”. In constructing (and operating) the first CCS projects industry will undertake “a significant amount of investment risk” (Snyder et al, 2008). A challenge to obtaining financing for CO₂ sequestration is identifying and quantifying these risks (Apt, J. et al. 2007). There are concerns that the technology is unproven, that key technical issues remain to be resolved, and that the financial stakes may be large than they first appear. There is uncertainty about the legal and regulatory framework for CCS, and even about basic political commitment. There are geological uncertainties related to proving up a sequestration site. For CCS projects to be viable commercial business models must be developed that give industry the incentives and confidence in the long term commercial viability of the technology to invest with confidence (Apt, J. et al. 2007). These issues are particularly important for early entry or first mover projects.

Electric utilities and merchant power generators are currently making resource planning and investment decisions that consider the possible implications in the face of uncertainty over the nature of future climate policy and carbon regulations. Van der Zwaan and Gerlagh have concluded that “much is left to be understood about the technical, economic and political dimensions of CCS” (van der Zwaan, B. and Gerlagh, R. 2009) if anything an example of understatement. If industrial corporations are to play a significant role in the implementation of CCS then an improved understanding of (and resolution of) the business risks associated with CCS will be necessary. Apart from the risks associated with a lack of public acceptance of CCS projects, the risks of greatest concern to business discussed in this paper arise predominantly in issues related to the storage part of CCS rather than capture or transport. We believe that capture, being comprised of a range of chemical engineering based industrial processes, is readily assessed by standard risk analysis and management strategies. Pipeline transport of compressed natural gas is also an everyday fact of life for modern societies and the risks associated with such pipelines have been well studied. In contrast geological storage is unfamiliar to most power utilities and other stakeholders.

Project Financing Issues, Business Models and Technological Risk:

With individual projects costing, in many cases, over one billion dollars, the total investment required for large scale implementation of CCS will be huge. The availability of project financing will be a crucial issue in determining the overall success of the move to a low carbon economy and issues related to project financing will play a major role in whether or not a specific project is constructed (O'Brien, J. et al. 2004). The key project finance related issues for CCS are the creation of a viable business model and the identification and analysis of project risk.

The significance of the choice of business model is that potential providers of project finance will want to assure themselves that a company that plans heavy investment in CCS has the technical and managerial capacity to deal with the problems it will encounter. The management capabilities that are required for today's typical utility business model are not necessarily those that will be needed in future.

Today CCS is not a business; rather it is a technology, or simply a solution to a problem. In the near future CCS may be implemented on a large scale and it is important that a viable business model be developed. Kheshgi et al suggested that CCS business models should be considered in the context of the following: (1) the relevant technological understanding lies mostly in the oil and gas sector, whereas the principal opportunity for CO₂ capture is in the power sector; (2) lack of process integration experience for capture schemes; (3) differing concepts of governments' roles in the CCS value chain; and (4) significant construction lead time and capital are required for infrastructure development (Kheshgi, H. et al. 2008).

It is likely that CCS economics will rely heavily on economies of scale (Kheshgi et al., 2008). In our view, scale economies will be a key driver in the choice of business model. They derive not so much from the technology of CCS but from the complexities of CO₂ gathering and the need to provide flexibility through operation of multiple CCS sites. Power generation is continuous and injection into storage must also be a continuous process: if for any reason CO₂ cannot be injected it must be vented to the atmosphere, presumably (in the future) at considerable expense as the emitter would be a distressed buyer of emission permits. A prudent operator would have several injection options ready for use. The capital required to develop multiple

injection sites and a pipeline network would be easier to justify if the system can serve a large number of CO₂ emitters. It would be technically possible for a generation plant to dispose of its CO₂ onsite using a dedicated injection well into a nearby aquifer, but we believe that scale economies and the need for flexibility make it unlikely that this arrangement would be viable in the long run.

A variation on the scale argument is implied by an amendment made to the EU emissions trading scheme (ETS) to incorporate CCS activities. The requirement to produce permits (EUAs) to cover emissions of greenhouse gases was extended to operators of CO₂ pipelines, storage facilities *and capture facilities*. The EU apparently sees a possibility that a firm could contract to process the flue gas from a power station, possibly operating a central processing facility serving several power stations or other emitters. This does seem possible, but we suspect that the number of locations where it could be appropriate would be very limited.

Given the need for scale and the range of competencies involved, the business model that is most likely to emerge in the short run will be a partnership between a CCS operator and other businesses operating in the relevant areas (Kheshgi et al. 2008). It will be essential that there should be a clear understanding of the value-sharing arrangements between partners in the value chain. The need for heavy financial investments points also to the need for a clear understanding of the long term basis of the value proposition – e.g. 20 years and beyond.

Operating risk issues may ultimately drive changes in the utility business model. The construction and operation of a thermo-electric fossil fueled power plant is not without risk, however the risks are well understood and have been successfully managed for many decades. The spot price of fuel can be volatile, but a utility can mitigate the risk by buying on term contracts, or hedging. Demand for electricity changes – can even fall sharply in a recession – but the overall trend is upwards. Regulation in many US states protects utilities and power producers from major losses. Even in a state like Texas, where the market is regulated by dispatching rules rather than by price, the rules are clear and their consequences are predictable. Technology change is slow – the operators of a coal-fired power station are unlikely to suddenly discover that new technology has made their business obsolete. In summary, there are

significant risks associated with electric power production but the utility business today knows how to manage them.

This may change in a carbon constrained world. The combination of an unfamiliar risk profile and new technology could create an opportunity for other types of firms to enter the power generation business. The IGCC technology presents complex process control problems that are not encountered in a traditional power plant, but are faced every day by firms in the oil refining and chemicals businesses. Some integrated oil companies are already in the power generation business through downstream integration from natural gas production, and some of them run IGCC plants in their refineries to process petroleum coke. If IGCC proves to be the economically most advantageous generation technology, these companies could become formidable competitors to the traditional utilities.

A significant challenge to obtaining project financing for CCS is the perception of high levels of technology risk. The technologies involved are not in general new or cutting edge, however, as noted by Bergerson and Lave, the choice of technology for new plants is unclear (Bergerson, J.A. and Lave, L.B. 2007). The consequences of making the wrong choice of technology would be serious for the utility involved. With none of these technologies yet operating at full commercial scale, we believe it would be very difficult to obtain project financing for a new plant incorporating carbon capture in the absence of a government guarantee that would limit the downside of a wrong choice. Kessels and Beck reported that a meeting of finance experts meeting in New York concluded that “currently in North America , from a private investment viewpoint , CCS remains a marginal financial option without Government loan guarantees and a legal framework in place to deal with liability issues” (Kessels, J. and Beck, B. 2008).

Even if the problem of choice of technology can be resolved in the reasonably near term, potential investors and providers of finance face the more traditional problem of uncertainty concerning the capital cost and operating performance of the technology selected. Rao and Rubin noted that although a “wide range” of existing technologies can be used to capture plant emissions, none had yet been proved at the scale of power plants (Rao, A.B. and Rubin, E.S. 2002). As of 2009, this is still true. De Coninck et al suggest that “technical maturity and reliability” are key issues that should be “fully addressed” before significant progress can be made in widespread implementation of CCS (de Coninck, H. et al. 2007).

A good deal is already known about the technology of CCS, but it is too early to say with any confidence how it will develop as a business. The best we can do at this stage is to lay out a number of scenarios. The key uncertainties that will determine, among other things, the availability of project finance, relate to the likely business model; the nature of the contractual relationships between the key players; and the availability of risk mitigation strategies (which encompasses the role of government).

- Business model:
 - The partnership model: a separate CCS operations business serving several independent power producers. We see this as the most appropriate model, at least in the short run.
 - Integrated power generation and CCS operations involving one company, or possibly a few companies with facilities located close together. We doubt that such a model would be long lasting due to lack of flexibility.
 - The power production business is partly taken over by integrated oil companies that run their own CCS operations, possibly linked with CO₂ EOR. In our view this is a viable model, but the need for economies of scale to achieve flexibility would push the company concerned to offer a carbon storage service to other power producers.
- Contractual relationships:
 - Take or pay vs flexible contracts for CO₂.
 - Utility insulated from downstream liability or not. Is it possible to design a contract between a power producer and a CCS operator that shields the power plant operator from legal liability for any damage done to third parties by the CO₂ post-transfer?
- Possibilities for risk mitigation, including government involvement:
 - Tax rebates, depreciation, tax exempt financing including Private Activity Bonds for CO₂ sequestration infrastructure projects such as pipelines.
 - Loan guarantees.
 - Creation of a Carbon Sequestration Trust Fund.
 - Availability of insurance for liability. A likely scenario for early entry projects might be blanket insurance or project guarantees provided by Government or a quasi-government

entity. This could meet the requirements of lenders and could be transferred to private insurance once the technology matures.

- Extended warranties (or wraps) to guarantee plant performance.

Regulatory Environment

It has been suggested that the “The real barrier to deployment of CO₂ capture and geological storage at the present time is the absence of a comprehensive policy, legislation and regulatory framework for implementation” (Bachu, S. 2008). If CCS is to have a significant impact on CO₂ levels in the atmosphere, on a time scale that will make a difference, an adequate regulatory framework must be put in place rapidly (Wilson et al, 2004). Many aspects of CCS can undoubtedly be permitted and regulated under current regulatory frameworks – this is the case for construction and running of gasification based power plants, CO₂ capture facilities and CO₂ pipelines, though de Figueiredo et al have asserted that transport of CO₂ by pipelines is “not (yet) governed by regulatory regimes similar to those that have governed oil and natural gas pipelines during much of the 20th century” (de Figueiredo, M. et al. 2007).

The greatest uncertainties concerning the regulatory framework for CCS relate to CO₂ sequestration. A viable and effective policy and regulatory framework for geologic carbon sequestration in deep brine reservoirs must strike a delicate balance. It must minimize the burden on companies involved (to encourage innovation and encourage involvement by private enterprise in implementing CO₂ sequestration), it must ensure that projects are actually effective in mitigating atmospheric CO₂ and it must have sufficient rigor to ensure the health and safety of the public and the environmental integrity of sequestration projects – these seem to be the minimum requirements for the policy to obtain public confidence and support. A key issue is how regulations can evolve in response to the rapid evolution of scientific knowledge related to CO₂ sequestration. Our scientific understanding of sequestration will always be imperfect but presumably improving over time.

In our view, such a policy should consider the following objectives:

- Establishing permitting procedures for CO₂ injection that minimize regulatory uncertainty, and enable competent enforcement.

- Creating incentives for locating injection sites that minimize risk and maximize permanence.
- Ensuring adequate monitoring, modeling and verification to establish risk and to project leak rates both pre and post project closure.
- Wilson et al (2003) have noted that “some leaks are inevitable if (geologic sequestration) is employed on a large scale. The challenge is to build a regulatory regime that works despite these uncertainties”.
- Regulatory flexibility to adapt to improved scientific uncertainties and/or new market conditions.
- Assuring adequate mitigation and/or remediation of CO₂ leakage that threatens underground sources of drinking water, both pre and post project closure.

The European Union took a major step towards putting such a regulatory framework in place by passing a Directive on CCS (dated April 23 2009) and implementing a number of changes to existing Directives including, most importantly, the Directive covering operation of the EU’s emission trading scheme (the ETS). A key point is that it is explicitly stated that CO₂ is not covered by a Directive concerning hazardous chemical substances. This comes very close to a declaration that CO₂ is not a serious hazard. Other important points include:

- The operating permit for an injection site is to be the principal means of control on CCS. This permit is issued after consideration of the Environmental Impact Assessment and covers site suitability, risk assessment and details of the proposed monitoring scheme.
- CCS is incorporated into the ETS from 2013. The ETS creates a chain of accountability for purposes of compliance, with injection facilities, pipelines and CO₂ separation units treated as separate entities for compliance purposes. The primary consequence of this provision is that CO₂ transferred from the original emitting facility would not count as emissions from that facility, while downstream facilities would have to account for CO₂ to the point of injection into storage and produce EUAs (EU Allowances – emissions permits issued under the ETS) to cover any volume not accounted for.
- However, the ETS chain of accountability is not capable of creating firm legal obligations concerning transfer of liability for health and safety or similar issues. The Directive makes no clear reference to this issue, probably because it is regarded as governed by the laws of the

member state(s) concerned. It may be that the EU will have to re-visit this question if cross-border transfers of CO₂ create legal problems.

- There are provisions for monitoring of the purity of streams of CO₂; for financial security on the operator's part; for transfer of responsibility for an injection site to the state concerned an unspecified number of years after injection has ceased and assuming that monitoring shows that the CO₂ stored underground is stable and unlikely to leak; for non-discriminatory access to pipelines and injection facilities and for all large combustion plants built after 2015 to have space set aside for CO₂ separation facilities.

In the US, the EPA has authority to regulate CCS under the Safe Drinking Water Act. A new regulatory framework for permitting injection of CO₂ for the purpose of sequestration is currently in the rule making phase. Legislation currently making its way through Congress would extend the EPA's responsibility by adding a new Title to the Clean Air Act that would require a new rulemaking process to be completed within two years of enactment. Until the final regulations are in place and sufficient experience develops in the nature of their implementation, it will be hard to evaluate the extent of regulatory risk on CCS operations.

In the EU (and possibly for the east coast of the US) most interest in sequestration is focused on subsurface injection offshore. The OSPAR convention and the London Convention (on dumping of waste materials at sea) have been amended to enable sub-surface storage of CO₂.¹

Legal Issues

Assertions (Kheshgi, H. et al. 2008) that “the legal framework (for CCS) is generally non-existent” are now not so applicable, although many issues remain.. A major risk element that will preoccupy potential providers of project finance is that of legal liability. There is a perception, in particular, of liability risks associated with post-injection leakage of CO₂. Objectively, these risks do not seem to be very large, but they are currently not well understood. These types of risks are unfamiliar to many of the companies most likely to become involved in CCS projects (such as power producers), and there is a perception among some stakeholders that such risks may be open ended.

¹ See http://www.unep.org/regionalseas/globalmeetings/9/inf.09_Storage_of_Carbon_Dioxide_Streams.pdf

It is generally true under common law that liability follows ownership, so clearly establishing the ownership of any CO₂ captured from power plants is important. CO₂ for use in EOR is typically sold at “the plant gate” to a pipeline company, which is effectively buying a commodity for use in its business. Under these circumstances, the exposure of the seller would be limited. However CO₂ captured from a power plant and sent for disposal is a form of process waste. Bachu has asserted that “some jurisdictions” have passed laws that designate CO₂ as “pollutant, toxic substance, waste (since it is injected) and even hazardous”. The power plant is in the position of paying for safe disposal rather than selling, and even if a contract of sale to a pipeline company or disposal operator exists, it might not in law constitute a clear transfer of liability for the consequences of any CO₂ leakage (Bachu, S. 2008). The classification of CO₂ either as a commodity or a waste (hazardous or non-hazardous) is perceived by the corporate counsels of many companies as very important. It has been suggested that liability associated with long term sequestration of CO₂ in deep brine reservoirs is analogous to the liability associated with underground storage of natural gas (de Figueiredo, M. et al. 2005), however it is not clear whether this would still apply if stored CO₂ were classified as a process waste.

If there is no effective legal barrier between the entity that captures the CO₂ and the entity that is responsible for its long term storage, the bank that provides project finance is in the same situation as a bank that provides finance for the establishment of a toxic waste dump, with the added problem that the waste in question has never before been stored in large volumes for long periods, and its behavior while in storage is hard to predict. Our view is that few, if any, banks would consider such a proposal.

Another key legal issue is ownership of the pore space occupied by the stored CO₂. Industrial scale CO₂ sequestration projects will typically result in creation of plumes of CO₂ in the deep brine injection zone that have large surface footprints. As a result the resolution of pore space ownership issues is important before commercial projects are undertaken. Although in most countries the subsurface is owned by the Crown (that is the national or state governments) in the US such ownership is in private hands. Apt et al have suggested that “It is currently unclear in many places who owns the rights to saline aquifer formations” and that “it is not readily apparent how a project should go about acquiring those rights to begin sequestration”

(Apt, J. et al. 2007). In contrast Duncan et al (2008a) have argued that the ownership of pore space under common law in the US is clear and consistent across the states.

The liability profiles for gasification installations, IGCC plants and post-combustion capture plants will be broadly similar to liabilities associated with chemical plants or similar industrial installations. Several studies have suggested that the liability for CO₂ pipelines is likely to be broadly similar to that for natural gas pipelines.

Apart from the direct financial impact of any major incident – verdicts of criminal or civil liability resulting in fines and awards of damages – the possibility of judicial interference in ongoing operations must be considered. Communities affected by an incident are likely to press for the closure of an injection site or even the cessation of activities over a wider area. Strongly expressed community concerns would undoubtedly result in a strong reaction from regulatory agencies. Until the industry is able to point to a long record of safe and incident-free operations, such pressures would be hard to withstand, and their financial consequences might be more harmful in the long run than the direct legal liabilities.

The evolution of common law through relevant court decisions regarding liability issues such as public nuisance and fluid trespass will inevitably influence future investment by industry in CCS. Some developers of CO₂ sequestration projects believe that they may be faced with either paralysis, extensive litigation over decades to achieve clarification through the courts, or achieving clarity through some combination of federal and state based legislation. On the other hand, de Coninck et al concluded that the “legal and regulatory issues (associated with CCS) are close to being resolved” (de Coninck, H. et al. 2007). Time will tell which view is correct.

Uncertainty in finding and proving up a sequestration site (or sites)

A key to successful implementation of commercial-scale sequestration projects will be the identification and acquisition of deep brine reservoirs suitable for injection and long term containment of CO₂. Some data will be available from regional geological compilations, from existing deep oil and gas wells and the results of any reflection seismic surveys. Core samples and cutting from deep well bores can provide measurements of the porosity and permeability of reservoirs. This information is essential to estimate the injectivity and to make a preliminary model of the evolution of the CO₂ plume that would result from CO₂ injection.

However, as noted by Morrison et al, many potential sequestration sites will be located in areas or formations that have never been of interest to oil and gas exploration (Morrison, H. et al. 2008). Even where drilling for oil or gas has taken place, information obtained from exploration wells often does not enable robust evaluation of the suitability of a brine reservoir for CO₂ sequestration. Morrison et al noted that typical oil and gas well data is characterized by limited availability of core samples (coring of the reservoir seals is rare); data is likely to be focused on areas with potential oil traps and largely absent from areas of greater interest for sequestration; and seismic data acquisition is often “tuned” to optimize information from formations deeper than those of interest for sequestration.

Once target reservoirs have been selected, permission to drill exploration wells and long term leasing of storage rights must be negotiated with land owners. It will be essential that the legal and regulatory status of the proposed injection should be clearly established before significant expenditure is made. This reservoir characterization phase is expensive (potentially costing tens of millions of dollars for a large multi-million ton annual injection rate project) and there will always be a risk that it will yield negative results. Reservoir properties (permeability and porosity) may not meet expectations and the injectivity of the well may be deemed inadequate; the seal may be deemed inadequate; faults or fracture zones may be identified in the 3-D seismic data that compromise the containment, or the 3-D seismic data may be of poor quality due to near surface caves and karst or some other issue.

Morrison et al have noted that it will not be commercially feasible to initiate a geologic sequestration project “if storage capacity and injectivity is not proven to a high level of certainty” (Morrison, H. et al. 2008). The risk is that, after carbon capture has begun, it is discovered that the reservoir has insufficient capacity to sequester the volume of CO₂ anticipated during the projects’ lifetime. Apt et al suggest that CCS projects that have not fully understood and quantified the risks and costs associated with sequestration “will simply not be financeable” (Apt, J. et al. 2007).

To minimize this risk, it is likely that a power producer contemplating an investment in CO₂ capture would contract with a specialist company to provide sequestration services. Such a

sequestration provider can lower the risks associated with site selection and characterization by aggregating demands for storage capacity.

THE OPERATIONAL/INJECTION AND MONITORING PHASES

The operational phase of CCS projects involves different risk receptors with a variety of possible consequences. The risks associated with the compression, pipeline transportation and injection of CO₂ are comparable to similar activities associated with the CO₂ EOR industry (Duncan et al 2008b). In the case of capture the likely processes are not currently being used at scales beyond pilot plant. As a result there is limited published, peer reviewed cost data. Building full-scale projects will be required to optimize plant efficiency through heat integration and other refinements. For example new compression technology under development could facilitate capturing the heat of compression and utilizing it to power CO₂ capture.

In the case of CO₂ pipeline transport, there is uncertainty as to what role government may take on both regulation (as pipelines start to be built in more populated areas) and possibly in financing regional pipeline infrastructure. In many areas integrated regional, pipeline-networks can provide lower costs per ton of CO₂ sequestered (Duncan et al 2007). Currently a rigorous understanding of the impact on pipeline safety of the variation of gas contaminants from industrial sources is lacking. Safety criteria for the transport of mixed gas streams will be required if it proves economically difficult for captured CO₂ to be cleaned up to the typically very high purity levels of natural CO₂ sources. More robust and reliable approaches to estimating the storage capacity of deep brine reservoirs are needed before large injection project are green lighted.

The initial stage of planning a large-scale carbon storage project requires evaluation of the relative risks associated with specific alternative sequestration sites – few risk studies have considered this issue. An important aim of designing large scale pilot injection programs such as Phase III of the Carbon Sequestration Partnership should be to gather information that will help companies to better evaluate the business risks associated with geologic CO₂ sequestration. The

identification of optimal sites for such large-scale demonstration projects provides a challenging test for the utility of available risk models and approaches.

Once injection at a site has ceased, monitoring for slow leakage and possibly for the continuing spread of the underground plume of CO₂ will have to continue for a period of time that will no doubt be stipulated by a regulator. Planning of a monitoring program for the injection phase should incorporate consideration of how this long term monitoring will be accomplished, and by whom. It is possible that some government agency will take on the task, no doubt on payment of a fee. As an aside, it is worth mentioning the view expressed by Kessels and Beck, who suggested that although insurance companies currently have risk models that can be applied to CCS, there is no model to cover the post operational liabilities of a sequestration project (Kessels, J. and Beck, B. 2008).

Operational Risks

The risks associated with CO₂ sequestration in brine reservoirs were perhaps first studied systematically over a decade ago in an EU funded study of geological CO₂ sequestration (Holloway, S. 1997). Many of these risks have also been analyzed in some detail in the environmental impact assessments completed for the four competing sites for the now revived FutureGen project. Despite these efforts the understanding of the operational risks of a future large scale, commercial sequestration industry is still subject to considerable uncertainty.

The operational risks for CCS projects (Duncan et al, 2008b) include: (1) The operational risks of capturing, compressing, transporting and injecting CO₂; (2) The risk of blowouts or very rapid CO₂ release from wells; (3) The risk that CO₂ put into long term geologic storage will leak into shallow aquifers and contaminate potable water; and (4) The risk that sequestered CO₂ (and possibly associated methane gas) will leak into the atmosphere. The final source of operational risk that must be considered is that of some change affecting the injection or storage qualities of the site, forcing its abandonment.

Of these risks the first two can be directly addressed by looking at the track record of the CO₂-EOR industry. Oil producers in the US have been using CO₂-EOR for more than thirty seven years. Over 600 million tons of CO₂ has been transported in pipelines and approximately 1,200 million tons has been injected (assuming that on the average 50% of the CO₂ is recycled).

The safety record has been excellent – during that period, no deaths or serious injuries have been ascribed to pipeline transportation of CO₂ or to injection and production activities. That is not to say that events causing even multiple fatalities are inconceivable. Any assessment of the risks of CCS must consider the impact of accidents such as rupture of a CO₂ pipeline or an injection well blowout.

Risks Associated with Possible Leakage of CO₂

Company's engaging in CCS projects will be concerned with the permanence of the CO₂ injected into a deep brine reservoir (or EOR field). Permanence has two key aspects to it. First if sequestration is not permanent and CO₂ leaks back to the atmosphere then the company may have to return the value of the credits originally gained for the sequestration of that amount of CO₂. This possibility raises a whole range of issues including what monitoring will be required to detect leakage into the atmosphere, who should conduct the monitoring, and will there be an end to this liability? The second concern is that leaking CO₂ will lead to adverse outcomes in terms of damage to water resources (or hydrocarbon resources), environmental damages or threats to health and safety. According to Bachu, “the primary (operational) risks associated with CO₂ leakage involve both acute (sudden, short and high rate) and chronic (slow, low rate and prolonged) leakage from the storage zone to the atmosphere or other subsurface zones containing resources that might be contaminated or biota that might be harmed” (Bachu, S. 2008). Acute leakage, in Bachu's terminology, could occur at any stage in the process of capturing, compressing, transporting and injecting CO₂, or post injection. It is essentially the risk of serious equipment failure or of a blowout or very rapid CO₂ release from a well. What Bachu calls chronic leakage poses almost no threat to public health and safety but could result in contamination of fresh water aquifers. This could result from direct contamination by CO₂ ingress to the freshwater aquifer, lowering pH and increasing dissolved metals and other components. It could also result from the displacement of brines or brackish water into fresh water zones.

Both acute and chronic leakage would result in sequestered CO₂ (and possibly associated methane gas) leaking into the atmosphere, reversing the climate change benefits of sequestration and perhaps requiring repayment of CO₂ sequestration credits. Hepple and Benson have noted

that over a time scale of hundreds of years (the time scale required for climate scale mitigation) even small leakage rates can add up to a significant loss of CO₂ back to the atmosphere (Hepple, R.P. and Benson, S.M. 2002). In some future cap and trade scheme, issuance of emissions permits might be made contingent on establishing that CO₂ placed into long term storage does not leak. Early detection of leakage would at least enable appropriate mitigation strategies to be implemented rapidly.

The risk of chronic leakage is addressed by the work that is currently being done in several parts of the world on mapping the spread of plumes of injected CO₂ through the subsurface. This work has direct relevance to the improvement of prediction methodologies and the design of monitoring programs. As an example of the type of problem that might be averted by means of careful site selection and high quality site characterization, let's assume that during the project planning phase a numerical fluid flow model of the evolution of the CO₂ plume is created. Based on the predictions of the surface footprint of the plume over time, a strategy is implemented to acquire the legal rights to allow sequestration. Suppose that as injection proceeds, monitoring reveals that the plume has evolved at an unexpectedly high rate and/or in an unanticipated direction. At this point in the project it may be difficult to negotiate for an enlarged area of pore space.

The Environmental Impact Assessment for a specific sequestration project should aim to assess the integrity of the saline reservoir, provide direct tangible evidence that leakage will not occur and present a monitoring plan customized to the nature of the site. Design of a monitoring plan for a first entrant, large scale CO₂ sequestration project should include development of an integrated multifaceted sampling strategy to evaluate techniques for the most cost effective detection of storage site leakage. Subsurface heterogeneities lead to dispersive processes: as a result CO₂ fluxes to the surface will typically be small and difficult to detect. Both technology choice and spatial /temporal deployment of monitoring should be dominantly based on risk based analysis of leakage pathways.

Injectivity Decline during Operational Phase:

The final operational risk that must be considered is that injection activities at some location will be brought to a close by some change affecting the injection or storage qualities of the site.

Experiments with CO₂ injection on a small scale indicate that a significant risk facing the operator of a sequestration project is that the injectivity of the wells will decrease over time and that this will threaten the project's capacity to deal with the contracted rate of CO₂ disposal. If the long-term injectivity rate for CO₂ can be maximized then the cost of sequestration in deep brine reservoirs can be reduced. Long term changes in injection rates for wells can be caused by several phenomena such as:

- Changes in permeability caused by dissolution or precipitation of minerals, driven by changes in the chemical environment within the pore spaces
- Motion of fine particles constricting pore throats and/or fracture permeability
- Multiphase effects on flow related to hysteretic effects in the relative permeability

These potential problems are in many ways similar to problems faced by reservoir engineers in CO₂-EOR projects (Bouchard, R. and Delaytermoz, A. 2004). The experience of long term injection in CO₂-EOR projects is the injectivity of CO₂ over time is more likely to reduce than to increase. The injectivity loss is site specific, and varies even within a single reservoir. It is apparently influenced by the specific nature of the mineralogy, fabric and pore structure of the reservoir rock; the chemistry of in-situ pore fluids; the composition of the injected fluid; and the thermodynamics of multi-phase fluid effects.

Typical injection rates for sequestration projects will be high compared with most CO₂-EOR injections wells. These high rates, which will be subject to inevitable frequent fluctuations, will likely have a mechanical impact on the reservoir near the well bore. Such damage is typically cumulative and can result in permanent decreases in long term injectivity.

Cailly et al. have reviewed the literature on declines in injectivity associated with CO₂-EOR. They note that EOR operators using CO₂ injection during a WAG (Water Alternate Gas) process, which involves alternating injection of CO₂ with injection of water, have experienced problems with multiphase flow (relative permeability effects related to the oil/water/CO₂ system). These authors also note that injectivity losses in CO₂-EOR are often explained by the CO₂ and oil interacting to cause swelling of the oil and clogging pore throats through formation of asphaltenes and other organic solids. On this basis it can be concluded that many (but not all)

of the phenomena that lead to injectivity decline in CO₂-EOR injection wells will not be likely to affect CO₂ injection into deep brine reservoirs (Cailly, B. et al., 2005).

PATH FORWARD FOR ADDRESSING RISKS

- Risk mitigation strategies for companies engaging in CCS should begin with choice of a business model. As noted above, we believe that the business model likely to emerge in the short run will be a partnership between a CCS operator and other businesses operating in the relevant areas (Kheshgi, H. et al. 2008). An alternative model is the creation an integrated CCS business that also offers a CO₂ storage service to emitters.
- The risks facing a project can be broadly categorized as political in nature, or linked to technological and operational factors. The technological and operational risks are known to be surmountable because practically all of the technologies concerned are proved and operating at a non-commercial scale or in a different context. However, the lack of a clear and credible political commitment to action against climate change magnifies the effect of these risks. A firm that invests in new technology ahead of the rest of the industry runs the risk of investing large sums prematurely in a technology that turns out not to be required at all due to a last-fence collapse of political commitment to action against climate change.

Another aspect of this risk of wavering political commitment is the possibility that political action to soften the impact of a carbon cap on the economy might lead to the carbon price falling below what business had been expecting. To create the incentive to invest in carbon capture, there must be confidence in the market place that the carbon price is reasonably predictable. Bergerson and Lave, in their analysis of the factors that a power company might consider before investing in an IGCC plant (despite the technology risk and a higher capital cost than alternatives), concluded that the earlier a utility “believes the carbon tax will be imposed and the higher the tax”, the more probable that it will invest in an IGCC with carbon capture and storage (Bergerson, J.A. and Lave, L.B. 2007).

For several years, a consensus has been growing among electric power producers and other stakeholders that the US Congress will soon pass legislation controlling emissions of CO₂, creating incentives for CCS through a cap-and-trade scheme, subsidies, and/or tax incentive. However, the current recession has made the task far more difficult and the passage of the House

version of a bill to do all of the above (the American Clean Energy and Security Act of 2009, or Waxman-Markey) has not fully dispelled the uncertainty on this issue.

- A characteristic of future commercial activity associated with CCS will be that the nature of the risks will change along the value chain. While considerable uncertainty currently attaches the legal and regulatory risks involved in sequestration, the key economic decisions, putting at risk capital sums an order of magnitude larger than those involved in the storage operation, concern power stations and pipeline networks. An important question is whether it is possible to keep the upstream (CO₂ capture and transportation) and downstream (injection into storage and long term monitoring) parts of the CCS value chain separate in terms of legal liability.

The power producers may well conclude that the greatest risk they face is the diffusion of the storage phase liability risks across the boundary between the two sectors. Our analysis of the risk situation of the power producer leads us to the conclusions that, if power producers are not liable for storage risks, possibly by virtue of a government guarantee or suitable insurance policy, their risk assessment task is tractable; however, if power producers can be held liable for accidents or legal eventualities affecting the storage phase, risk assessment becomes immensely more complex.

In these circumstances, the power producers' difficulties in obtaining project finance for retrofits or new plant would be magnified - Apt et al suggest that CCS projects that have not successfully understood and quantified the risks and costs associated with sequestration "will simply not be financeable" (Apt, J. et al. 2007). This is another area where government involvement may be required to kick start the industry by limiting the liability of power producers for the consequences of accidents that may occur at the storage phase. However, given the tendency of tort lawyers to go after innocent bystanders with deep pockets, we are not entirely sure that such government action would solve the problem.

A strategy for constructive corporate involvement

To develop projects and to secure financing corporations require a degree of policy and regulatory certainty. Recent political developments have brought this certainty closer, and many corporations may be seeing business drivers to becoming involved in implementing early entrant

CCS projects. These drivers may well be independent of the details of eventual climate change regulation and this is a situation where the first movers may gain an advantage.

- The image of a “Carbon Neutral” corporation may communicate an environmentally proactive stance that creates value in the eyes of shareholders. There is evidence from the news media that engagement in GHG reduction strategies can enhance the corporate brand, and consumers’ purchase choices may be increasingly affected by corporate reputation and attitudes regarding the environment. Corporations can achieve a positive public relations boost from being seen by the public as part of the solution rather than part of the problem.
- If we are indeed entering an age in which GHG mitigation strongly constrains energy usage developing corporate expertise and intellectual property in CCS and related technologies can have great strategic and financial value that might lead to real future business opportunities. The risk-limiting advantages of early entrance into this technological space are worthy of careful assessment. These activities can pay off if banks and investors view a reduction in the corporate carbon footprint as an indicative of sound management. Early movers can also gain business advantages such as avoiding rising insurance rates for industrial activities that create an exposure to future carbon reduction legislation (and possibly climate change related litigation).

Apt et al have suggested that “progressive firms” that are engaged in the engineering design phase of deploying clean coal projects (or are trying to finance a project) are motivated “to gain experience with CCS at commercial scales” before cap and trade or carbon tax legislation is passed (Apt, J. et al. 2007). As in the development of most new technologies, change results in unleashing the creativity of scientists and engineers to develop new and valuable intellectual property. This facilitates management of emerging risks and liabilities associated with societal expectations regarding climate change and changing regulatory requirements.

Carbon taxes or a cap-and-trade carbon credit program will result in an effective increase in the cost of fossil fuels, even if their market price actually decreases. Newell et al. have suggested that this can result at first in a decrease in energy consumption. In the long term however these authors believe that the result will be an increase in energy efficiency of the new technologies

developed and that, over several decades, innovation and optimization of technologies will lower costs (Newell, R.G. et al. 2006).

As corporations move to develop specific projects in response to forthcoming carbon legislation mandates in the US, several issues will be important to consider:

- As noted by Morrison et al the real (or perceived) technological risk that comes with a CCS project requires that the local community must be a key stakeholder (Morrison, H. et al. 2008). A key risk to specific CCS projects is a lack of acceptance by the local community (NIMBY or NUMBY). It is highly likely that the intensity and impact of local negative reaction will vary greatly regionally across the US: in regions that have extensive oil and gas production local residents are likely to be more accepting of pipelines and injection activity. In the absence of comprehensive opinion surveys we cannot be certain about public attitudes. In the UK, preliminary survey results gathered by the Tyndall Centre suggested that a majority of the public would accept CCS as part of a portfolio of measures for mitigation of climate change (Gough, C. et al. 2005). The clearest inference that can be drawn from the opinion polls taken thus far in the US is that the public has limited knowledge or understanding of CCS.
- Corporations that have a significant carbon footprint that do not become actively engaged in CCS and/or other approaches to lowering GHG emissions run the risk that they will not have any influence on legislative solutions. They may even become subject to negative publicity in the news media that could impact the value of the corporate brand and ultimately market capitalization. It is likely that GHG emissions will in the foreseeable future be required to be documented as liabilities on the corporation's balance sheet (O'Brien, J. and Dragan, M. 2003).
- Real opposition to CCS can be anticipated from the significant element in society that believes that a future without coal is not only feasible, but highly desirable. It is not clear who will take the lead in articulating the benefits that will accrue from large-scale deployment of CCS technologies (Dooley, J.J. et al. 2006), however, corporations that expect to be part of an energy future based on clean coal can minimize likely barriers to public

acceptance of the technology by pre-emptively taking responsibility for influencing public opinion, political actors and other stakeholders by adopting strategies such as:

- Constructive engagement - corporations that engage early in all facets of CCS will be best positioned to influence the development of the industry. By gaining a comprehensive understanding of the technical, legal and policy issues, they will be able to propose constructive changes to evolving public policy and regulatory frameworks.
- Developing “in-house” expertise – corporations that are able to develop and refine their own views on the development of CCS will have an advantage in navigating through the inevitable public policy turbulence that will accompany moves to a carbon constrained world. The transition will create business opportunities as well as threats - corporations that have appropriate technical expertise can garner valuable intellectual property and patents that may become increasingly valuable over time.
- Finally, insurance can play an important role in risk mitigation strategies: it might be used to cover risks of tort actions related to fluid trespass, public nuisance and other possible consequences of any CO₂ leakage, or the possibility of financial losses associated with project delays. An insurance policy may be required in order to obtain project financing. Although there has been a concern that insurance companies will be unwilling to quote reasonable rates for such coverage in the absence of government assurances Zurich Re has recently made such policies available. Kessels and Beck have suggested that “Quantifying the actual liability of CCS projects in dollar terms would assist and allow insurance companies a better means of assessing what underwriting is needed”. They further suggest that in the absence of such information on the possible future costs of leakage that insurance is for geologic sequestration projects will likely be limited to 1 -2 year rolling contracts (Kessels, J. and Beck, B. 2008).

CASE STUDIES

The FutureGen Project

In 2003, President George W. Bush announced the Department of Energy’s plans to build the FutureGen plant, presenting it as the world’s first coal-fueled electric power plant with near-zero

emissions. The plant was to be designed to demonstrate that carbon capture and storage could be used to decarbonize the electric energy produced from fossil fuels. The FutureGen project was to be designed, built and operated by the FutureGen Industrial Alliance - a non-profit consortium of 13 coal mining and electric utility companies from around the world, led by American Electric Power (AEP) and the Southern Company. The project was to be carried out under a cooperative agreement between DOE and the Alliance with the DOE providing 74% of the project's cost and the Alliance partners contributing the other 26%.

The FutureGen Request for Proposals (March 7, 2006) asked for applicants to establish “the extent to which it can or is willing to take title to the injected CO₂ and/or indemnify or otherwise protect the FutureGen Industrial Alliance and its members from any potential liability associated with the CO₂. Offerors may discuss other alternatives...” Mudd (2007), in his role as CEO of the FutureGen Alliance, emphasized that the request for indemnification in the RFP “is not due to lack of confidence in the safety of injection”, but rather is in recognition of the fact that the FutureGen project is a “First-of -a-Kind” (FOAK) demonstration and that “such indemnification will likely be required for early entrants in the future to commercialize CCS”. The FutureGen Alliance requested that the DOE indemnify the Alliance against any liability related to the CO₂ sequestration phase of the project (Mudd, 2007), however the DOE had no legislative authority to do so. Informal comments by Alliance staff suggested that the high priority placed on liability relief by the FutureGen Alliance was in some part driven by the fears of its foreign company members of what they perceived as a litigious American legal environment.

By April 2007, the FutureGen Alliance had completed the Final Risk Assessment Report for the four potential sites in Illinois and Texas (part of the FutureGen Project Environmental Impact Statement or EIS, completed under the National Environmental Policy Act). These studies concluded that overall, the likelihood and consequence of CO₂ leakage from the brine reservoir are not significant, although H₂S releases from abandoned, undocumented, or poorly constructed wells could lead to potential human health risks. The FutureGen risk assessment team concluded that the potential risks of transport and sequestration in the selected saline formations are quantifiable and manageable.

The FutureGen project was put on hold after the DoE decided in June 2008 that it would no longer provide partial funding, however the project has been reinstated with \$1bn of Recovery Act funding.

American Electric Power IGCC Projects

Another case study is provided by American Electric Power (AEP), which is committed to building commercial scale IGCC plants in Ohio and West Virginia. AEP based its original decision on several factors, including the likelihood of legislation creating a price for carbon emissions, the ability of IGCC plants to utilize a range of fuels including bituminous coal, sub-bituminous coal and biomass (fuel flexibility) and the ability of IGCC plants to produce chemicals (hydrogen, chemical fertilizers etc) as well as electricity. It was also concerned about possible future EPA action on mercury and other pollutants in coal that are more cheaply captured in IGCC plants.

Progress on these projects has been slow. As of today, the planned plant in Ohio is on hold after a decision of the Ohio Supreme Court that the state's Public Utilities Commission should review a decision that AEP could recover pre-construction costs for the project. Meanwhile, the planned Mountaineer plant in West Virginia is stalled after the refusal of regulators in Virginia (where part of the plant's output would be sold) to approve the plant based on current cost estimates.

This is a particular case of the political risk problem pointed to above: regulation redistributes risk between the power producer and the public. A commonly held view is that regulation by price reduces the producer's risk, enabling the latter to live with a lower rate of return and a higher level of debt financing, while the public pays a lower price for electricity (Taggart, R.A., Jr. 1985). The arrangement works well in a stable industry situation, but in the face of expected discontinuities in technology or in the basic economics of power production, the regulator may not be willing – or even legally able – to take part of the discontinuity risk onto the public. By setting a rate based on an expected change that might never happen, a state regulator might well be exceeding its legal powers. Until Congress passes a bill that will clearly and with reasonable certainty put a price on carbon emissions from some known date, it will be difficult to obtain regulatory authorization to build such a plant in a price regulation state.

Summary and Conclusions

Sixteen years ago Cavanaugh (1993) suggested that “with increasing risk that carbon dioxide emissions from new fossil-fueled power plants will be taxed or capped, the present value of CO₂ charges on output could substantially exceed plant construction costs”. This scenario may well be becoming a reality. A 2007 opinion poll (quoted in Barbose, 2008) of approximately 100 senior executives from the US electric generation industry revealed that half thought congress would enact climate change legislation within two years and nearly 90% anticipated expected such legislation within seven years. With the international community meeting to create a “post-Kyoto agreement” and the US Congress working on “cap and trade” legislation CCS has the potential to act as a bridge between the current energy paradigm based on relatively cheap fossil fuels and a possible energy paradigm for future generations powered by renewables.

Bachu has noted that the most significant gap in public policy and regulatory frameworks is in the post-operational, geologic sequestration area within CCS (Bachu, S. 2008). He suggests that this is because the bulk of current environmental laws and regulations (including international maritime treaties) were created before the current concerns over CO₂ emissions. Since 2008, some progress has been made, including amendments to the OSPAR treaty and the London convention on dumping waste at sea, and the issue of a CCS Directive by the EU. However even in the EU, detailed regulations must be promulgated to implement the new Directive, while in the US, Bachu’s analysis remains valid.

Risks that should be evaluated by both the direct participants in a CCS project (or the banks that provide project finance) include:

- Political risk, including doubts concerning the long term commitment of politicians to measures that mitigate climate change but entail significant costs to the community.
- The risks for existing utilities and independent power producers of a new business model based on unfamiliar technology, faster technological change and synergies that in some cases seem to favor competitors.
- Uncertainty as to which of several technologies to adopt, with the risk that choosing the wrong one could leave a firm locked into a large unprofitable investment.

- Uncertainty over the capital and operating costs of new technologies.
- Operating and legal risks arising from either acute or chronic escape of CO₂ such as:
 - fatalities or injuries and the attendant legal liability;
 - legal liability for damage to freshwater aquifers by the CO₂ plume or displaced brine.
- Regulatory action consequent on one or other of the above operational risks, potentially leading to closing down of activities at the locality concerned, or more widely.
- Geological problems such as deterioration of injectivity over time.

The nature of future regulation of carbon (and also mercury and heavy metals) make up a key component of the investment risk facing electric utilities and merchant power companies. Investments in new power plants and/or capture retrofits are the highest capital costs for implementing CCS.

Although it could be concluded that the main barriers to the broad scale implementation of CCS include uncertainties in regulatory/legal framework and technology costs, it may be that public acceptance is the most significant hurdle to be overcome. The public must be convinced not only that CCS is safe and effective but also that the transition to decarbonized fuels is necessary in the face of increased energy costs. Limited survey data on public acceptance suggests that in most areas of the US (and other countries). The public is largely unaware of CCS and has not formed an opinion, positive or negative. Getting an accurate assessment of the public's response to CO₂ sequestration will not become measureable until projects actually start construction.

Under current economic conditions CCS is not economically feasible and subsidies will be the key to building the first plants. This reality was recognized in the original FutureGen project in the US and now is being played out by plants being planned by AEP and other. Key developments for companies considering developing “early mover” projects: 1) the evolution of the willingness of insurance underwriters to take offer coverage for a broad range of the risks associated with CCS; the availability and structuring of Federal and state financial incentives (such as tax credits and loan guarantees and tax credits).

References

Apt, J., R. L. Gresham, et al. (2007). Incentives for Near-Term Carbon Dioxide Geological Sequestration. Washington D.C., The Gasification Carbon Management Work Group: 68.

Bachu, S. (2008). "CO₂ storage in geological media: Role, means, status and barriers to deployment." Progress in Energy and Combustion Science **34**(2): 254-273.

Bergerson, J. A. and L. B. Lave (2007). "Baseload Coal Investment Decisions under Uncertain Carbon Legislation." Environmental Science & Technology **41**(10): 3431-3436.

Bouchard, R. and A. Delaytermoz (2004). "Integrated path towards geological storage." Energy **29**(9-10): 1339-1346.

Cailly, B., P. L. Thiez, et al. (2005). "Geological Storage of CO₂: State of the Art of Injection Processes and Technologies." Oil & Gas Science and Technology - Rev. IFP **60**(3): 517-525.

de Coninck, H., J. Anderson, et al. (2007). "Is CO₂ capture and storage ready to roll?" Journal for European Environmental & Planning Law **4**: 402-414.

de Figueiredo, M., H. Herzog, et al. (2007). Regulating Carbon Dioxide Capture and Storage. Cambridge MA, Center for Energy and Environmental Policy Research, Massachusetts Institute of Technology.

de Figueiredo, M., D. Reiner, et al. (2005). "Framing the Long-Term In Situ Liability Issue for Geologic Carbon Storage in the United States." Mitigation and Adaptation Strategies for Global Change **10**(4): 647-657.

Dooley, J. J., R. T. Dahowski, et al. (2006). Carbon Dioxide Capture and Geologic Storage: a core element of a global energy technology strategy to address climate change. Washington D.C., Global Energy Technology Strategy Program.

Gielen, D. (2003). Uncertainties in Relation to CO₂ Capture and Sequestration: Preliminary Results. IEA/EET Working Paper. Paris, International Energy Agency.

Gough, C., C. McLachlan, et al. (2005). "The public perception of carbon dioxide capture and storage in the UK: results from focus groups and a survey." Climate Policy 4(4): 377-398.

Hepple, R. P. and S. M. Benson (2002). Implications of surface seepage on the effectiveness of geologic storage of carbon dioxide as a climate change mitigation strategy, eScholarship Repository.

Holloway, S. (1997). "An overview of the Joule II project [`]The underground disposal of carbon dioxide'." Energy Conversion and Management 37(6-8): 1149-1154.

Kessels, J. and B. Beck (2008). Financing carbon capture and storage projects the results of two expert meetings 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), Washington D.C., Energy Procedia.

Kheshgi, H., S. Crookshank, et al. (2008). Carbon Capture and Storage Business Models. 9th International Conference on Greenhouse Gas Control Technologies, Washington D.C., Energy Procedia.

Morrison, H., M. Schwander, et al. (2008). A vision of a CCS Business: the Zerogen Experience. 9th International Conference on Greenhouse Gas Control Technologies, Washington D.C., Energy Procedia.

Newell, R. G., A. B. Jaffe, et al. (2006). "The effects of economic and policy incentives on carbon mitigation technologies." Energy Economics 28(5-6): 563-578.

O'Brien, J., J. Blau, et al. (2004). "An Analysis of the Institutional Challenges to Commercialization and Deployment of IGCC Technology in the US Electric Industry: Recommended Policy, Regulatory, Executive and Legislative Initiatives." 2007, from <http://www.netl.doe.gov/energy-analyses/pubs/FinalReport2-20Vol1.pdf>.

O'Brien, J. and M. Dragan. (2003). "Corporate GHG Management: Review of International Best Practice Activities." from http://www.edf.org/documents/3190_GHGfinalObrien.pdf.

Rao, A. B. and E. S. Rubin (2002). "A Technical, Economic, and Environmental Assessment of Amine-Based CO₂ Capture Technology for Power Plant Greenhouse Gas Control." Environmental Science & Technology **36**(20): 4467-4475.

Sheppard, M. and R. Socolow (2007). "Sustaining fossil fuel use in a carbon-constrained world by rapid commercialization of carbon capture and sequestration." AIChE Journal **53**(12): 3022-3028.

Taggart, R. A., Jr. (1985). "Effects of Regulation on Utility Financing: Theory and Evidence." The Journal of Industrial Economics **33**(3): 257-276.

van der Zwaan, B. and R. Gerlagh (2009). "Economics of geological CO₂ storage and leakage." Climatic Change **93**(3): 285-309.

Wise, M. A. and J. J. Dooley (2004). Baseload and Peaking Economics and the Resulting Adoption of a Carbon Dioxide Capture and Storage System for Electric Power Plants. 7th International Conference on Greenhouse Gas Control Technologies, Vancouver, Pacific Northwest National Laboratory and Joint Global Change Research Initiative.,

Section 9: Estimating the Likelihood of Pipeline Failure in CO₂ Transmission Pipelines: New Insights on Risks of Carbon Capture and Storage

Introduction

Carbon capture and storage (CCS) is one approach to mitigating atmospheric CO₂ emissions. Apart from the CO₂ capture plant, the pipeline network for transporting CO₂ is by far the highest risk aspect of a future CCS industry. Pipeline networks required for a future CCS industry may eventually become substantial in total length. The integrity of pipelines and the resultant risk level are a key concern of regulators, as well as the general public.

As noted by Doctor et al. (2006), a pipeline infrastructure capable of transporting CO₂ in quantities sufficient to make a significant impact on climate mitigation will necessitate a large network. Studies of how long such pipeline networks might be have included both regional- and continent-scale studies. Johnson and Ogden (2011) estimated that in the southwestern U.S. approximately 100 km of pipeline per power plant would be required for effective sequestration. ICF (2009) suggested two bounding scenarios for possible CCS build-outs in the U.S. involving (1) 50% (1,000 million tonnes transported in 20,610 miles (33,168 km) of pipeline) and (2) 15% (300 million tonnes transported in 5,900 miles (9,495 km) of pipeline), respectively, of the capacity of existing coal-fired power plants being operated with CCS by 2030. Dooley et al. (2008) suggested that for their “most stringent” case a construction of CO₂-pipeline-network approximately 120,000 miles (193,121 km) in length would be required in the U.S. between 2010 and 2050. In Europe Neele et al. (2010) suggested that by 2050 a total of approximately 22,000 to 33,000 km of pipeline will need to be in place for the projected volume of CCS activity.

Before construction of a CO₂ pipeline network of unprecedented scale a comprehensive risk analysis will be essential. Although several recent papers provide interesting and useful initial contributions to the assessment and analysis of these risks (Koornneef et al., 2010; Vianello et al., 2012) the appropriateness of the data used for estimating the likelihood of significant pipeline failures in these papers is not clear. The current contribution does not attempt to carry out a risk

analysis. Instead this study focusses on evaluating one part of the risk, the likelihood of significant failures of CO₂ pipelines. The likelihood of pipeline failure can be estimated using a number of approaches, including (1) analysis of incident databases for national pipeline networks, (2) testing of individual components to failure, (3) modeling of processes such as internal corrosion, and (4) predictive analysis using a fault tree or something similar. Of these approaches, the most robust and reliable for estimating the likelihood of pipeline failure is likely analysis of large data sets of real incidents. Initial studies of the risk of CO₂ pipelines conclude that the number of incidents that have occurred in CO₂ pipeline networks is too small to make meaningful statistical estimates of risk (Vendrig et al., 2003; Gale and Davison, 2004). Subsequent researchers have followed Gale and Davison's lead and have used incident likelihood or probability data from natural gas pipeline networks to estimate risks of future CO₂ pipelines that may be built for development of large-scale CCS. Barrie et al. (2004) noted that although the number of incidents observed from CO₂ pipelines is small compared with those for natural gas pipelines that "it is reasonable to suggest" that statistically, "the number of incidents involving CO₂ should be similar to those for natural gas transmission." This approach will only be valid if the impact of internal corrosion in natural gas and CO₂ pipelines is equivalent and the failure mechanisms displayed by CO₂ and natural gas pipelines results in a similar spectrum of ruptures and other failures. There is a rich literature on the corrosion of carbon steel pipes carrying impure natural gas or CO₂ (from acids formed by combination of CO₂ and/or impurities such as H₂S) however this topic is outside the scope of the current paper and it will be assumed that future CO₂ streams carried in pipelines will be dehydrated.

Researchers have come to divergent conclusions as to the risk to the general public from future CO₂ pipeline networks associated with the development of CCS. Gale and Davison (2004) found that if the construction of large pipeline networks gains acceptance from the general public that "there would seem to be little reason for [the general public] to be concerned about the possible future presence of CO₂ pipelines." A similar assertion was made by Snyder et al. (2008), who suggested "transporting CO₂ is the least risky aspect of CCS ... and it is not a barrier to CCS implementation in Canada." In contrast, Doctor et al. (2006) suggested that "If CO₂ is transported for significant distances in densely populated regions, the number of people potentially exposed to risks from CO₂ transportation facilities may be greater than the number

exposed to potential risks from CO₂ capture and storage facilities.” Doctor et al. (2006) also suggested that “public concerns about CO₂ transportation may form a significant barrier to large-scale use of CCS.” The conclusions of Snyder et al. (2008) and Gale and Davison (2004) seem inconsistent with the conclusions of more recent modeling of the dispersion of CO₂ released by failed pipelines. For example, the modeling of Chow et al. (2009) suggests that even shallow topographic lows of 10 to 50 m in depth “can lead to accumulation of CO₂ at hazardous exposure levels.” Similarly, modeling by Mazzoldi et al. (2012) predicts that downstream lengths reached by hazardous concentrations of CO₂ resulting from full bore rupture of pipelines and the atmospheric conditions modeled “are on the order of a few tens to several hundreds of meters.”

Note that risk can be defined as the likelihood a hazardous event occurring convolved with the consequence of the event (such as risk of a fatality = individual risk). As a result, an understanding of the probability that a hazardous event will occur is the key to estimating risk. Thus far, analysis of natural gas pipeline statistics carried out in research on the risk of CO₂ pipelines has not been robust. If the natural gas pipeline safety record is the most tangible evidence bearing on the risk of CO₂ pipelines, then a more careful examination of this evidence is important. A recent detailed study of natural gas pipeline risk by Wang and Duncan (2013) shows that the incident rate for natural gas pipelines varies by an order of magnitude or more, depending on pipeline diameter, distribution network versus transmission pipelines, etc. The current paper attempts to build on this work by segmenting the natural gas pipeline population into subsets that provide more appropriate analogs for a future CCS-based pipeline network. The aim of this paper is to carefully examine the best available data on the safety of natural gas pipelines in the U.S. and to identify useful information bearing on an estimation of the likelihood of serious failure of current and future CO₂ pipeline networks. The paper first compares the nature of risks associated with natural gas and CO₂ pipelines. It assesses the differences in factors that influence the magnitude of risk and the causes of pipeline failure in each case. The paper then examines how risks associated with CO₂ pipelines might be mitigated in the future through risk-based pipeline design. Natural gas incident data are shown to provide robust information that establishes the success of pipeline design and factors of safety that are based on population density near pipelines. Previous studies of CO₂ pipeline risk that have been based on the record

of incidents in natural gas pipelines may have significantly overestimated the risks by using data that included incidents from categories of pipeline that are inappropriate.

1. Methodology

In the U.S. there are 321,000 miles (516,599 km) of onshore and offshore natural gas transmission and gathering pipelines. Of this network, 300,516 miles (483,633 km) of pipeline is used for gas transmission. It is these transmission pipelines that provide the best analog for a future CO₂ pipeline network for CCS. The Pipeline and Hazardous Materials Safety Administration (PHMSA) collected and classified incidents of U.S. natural gas transmission pipelines. In this study, significant incidents that occurred from 1990 through 2009 were analyzed. PHMSA defines *significant incidents* as those reported by pipeline operators that

1. involve fatalities or injury requiring in-patient hospitalization,
2. have \$50,000 or more in total costs measured in 1984 dollars,
3. result in releases of 50 barrels or more of product, and
4. result in an unintentional fire or explosion.

Table S1 lists annual pipeline length and number of significant incidents for each year. This table represents the data set used in our analysis. An analysis of the same data set emphasizing factors controlling natural gas pipeline incident rates and their associated risk was presented by Wang and Duncan (2013). The current analysis examines different aspects of this data set to attempt to predict the likelihood of incidents in a future large-scale CO₂ pipeline network.

2. Data Analysis

3.1 Estimating CO₂ Pipeline Failure Rates

In the U.S. a statistical database on both CO₂ and natural gas pipeline incidents is made available by PHMSA, which is part of the U.S. Department of Transportation (DOT). An early attempt to quantify the risks associated with CO₂ pipelines was the work of Gale and Davison (2004). Examining DOT incident data for CO₂ pipelines from 1990 through 2001, Gale and Davison (2004) noted that incident frequency was greater than that for natural gas pipelines. They also

noted that this conclusion was not robust because of the small number of incidents. However, Gale and Davison (2004) found that no injuries or fatalities were caused by the CO₂ pipeline incidents recorded in the PHMSA database. They further suggested that the cost of property damage “was significantly less” for CO₂ pipelines, compared with that for natural gas pipelines.

Although Kaufman (2008) referred to the experience base for evaluating the hazard potential of the existing CO₂ pipeline network in the U.S. as a “relative[ly] extensive,” detailed evaluation of this data set suggests that it is of limited value (Duncan, 2013). Thus far, quantitative risk assessments (QRA) of CO₂ pipelines, either site specific or generic, have relied on likelihoods (probabilities) derived from the occurrence of incidents either from the PHMSA CO₂ pipeline record or from natural gas pipeline incident data. Of the nine estimates of pipeline failure rates compiled by Koornneef et al. (2010), six were based on natural gas pipeline data, and three were based on the CO₂ pipeline record. The three values that these authors chose to use in their analysis were all based on data from natural gas pipelines.

As noted by Duncan (2013) the PHMSA data set for CO₂ pipelines used by URS (2009), Trabucchi et al. (2012), and DOE (2012) contains no information on significant ruptures or punctures. Because most incidents in the CO₂ pipeline data set record pinhole leaks and other minor incidents, their utility to an understanding of the likelihood of serious injury, deaths, or property damage is limited, if it exists at all. At the same time, risk analyses done by Hooper et al. (2005), Turner et al. (2006), and Koornneef et al. (2010) utilized an average incident frequency for natural gas pipelines from either DOT or European data (EGIG, 2011). In each case, the incident rate used was a broad average of transmission and distribution pipelines, small- and large-diameter pipes, and a range of incidents from pinhole leaks to full-bore ruptures. A compilation of incident probabilities from various sources has been used by previous QRA studies of CO₂ pipelines (Table 1). It can be seen in this table that five of these studies used US natural gas pipeline data from the US Department of Transportation’s Pipeline and Hazardous Materials Safety Administration (PHMSA), seven used CO₂ pipeline data from PHMSA, and four studies used data from the [European Gas pipeline Incident data Group \(EGIG\)](#). Values of natural gas pipeline incident rates in Table 1 range from 3.0×10^{-3} to 1.5×10^{-4} (per kilometer year), with a median of about 2.0×10^{-4} . These rates are not a good model for CO₂ transmission

pipelines because they include incidents for urban distribution networks that have higher incident rates. For example, PHMSA (2010) gave a recent incident rate for natural gas transmission pipelines of 1.2×10^{-5} per km per year. The natural gas incident data also include the influence of older, more incident-prone, pipeline segments dating back to the 1940's (Table 1).

The main problem with the probabilities in Table 1 is that although they represent the likelihood of natural gas or CO₂ pipeline incidents, they are described in the papers as representing "pipeline failure rate," "incident rate," or a generic "risk." In the PHMSA data base incidents involve either an injury, death or an event with more than \$50,000 of damages. In the EGIG data base an incident can range from a pinhole leak to a major rupture. Injuries and deaths are not recorded in the EGIG database. For both the PHMSA and EGIG data sets the vast majority of incidents are the result of pinhole leaks, small cracks, or damage to infrastructure such as valves that are unlikely to be life threatening. Such incident data does not seem to be appropriate for a proxy for individual risk. In QRA's, typical metrics for risk include individual risk, societal risk, and average individual risk of exposed population (or total population). Individual risk can be defined as the likelihood that death will occur within a year at a specific location as a result of all hazards. An individual risk is a geographic/spatial attribute that can be contoured to show its geographic variation. The societal-risk metric takes into account the risk of multiple fatalities and can be defined as the likelihood that an incident will result in a specific number of casualties. Societal risk is usually expressed in the form of cumulative frequency of fatalities per year (F) plotted against N (number of deaths in any particular incident) to form an "F-N" curve. Developing an evaluation of societal risk is a time-consuming and inherently site-specific process. For CO₂ pipelines, societal risk must take into account not only population density but also the topography that people live and work in. Note that a potentially impacted population in topographic lows will vary with time of day.

As noted earlier, because no deaths or serious injuries are recorded that are associated with CO₂ pipelines, no method can estimate individual risk directly from the CO₂ pipeline record. Natural gas pipelines do, however, have a record of casualties that can be used to estimate individual risks for these pipelines. Injury and fatality rates (per km per year) for natural gas transmission pipelines in the U.S. are available for the period 1990 through 2009 (Figure 1). Also available is

the total incident rate, the metric used by authors in CO₂ pipeline risk studies (Figure 1; Table 1). Note that the total incident rate for these data shows no correlation with either fatality or injury rate. Frequencies of significant incidents of natural gas transmission pipelines can be plotted against the sum of injuries and fatalities for each year from 1990 through 2009 (Figure 2). Note that, not only do the two not correlate, a weak anti-correlation actually is apparent.

With a few exceptions, fatality rates from 1990 through 2009 are lower than 2.0×10^{-6} . Average fatality rate is 3.2×10^{-6} for the time period. For the last 2 decades, annual injury rate has largely been in the range of 2.0×10^{-6} to 9.5×10^{-6} . Newer pipelines, built to higher standards, may have better outcomes. To test this assertion, we plotted fatality and injury rates for the natural gas transmission data set as a function of period of installation of the pipeline segment (Figure 3). For pipelines built between 1980 and 2000, fatality rate decreases from 2.0×10^{-6} to 8.5×10^{-7} . Average fatality rate for pipelines constructed over the last 3 decades is 1.0×10^{-6} . Note that these estimates of individual risk are values appropriate for use as an analog of CO₂ pipeline risks.

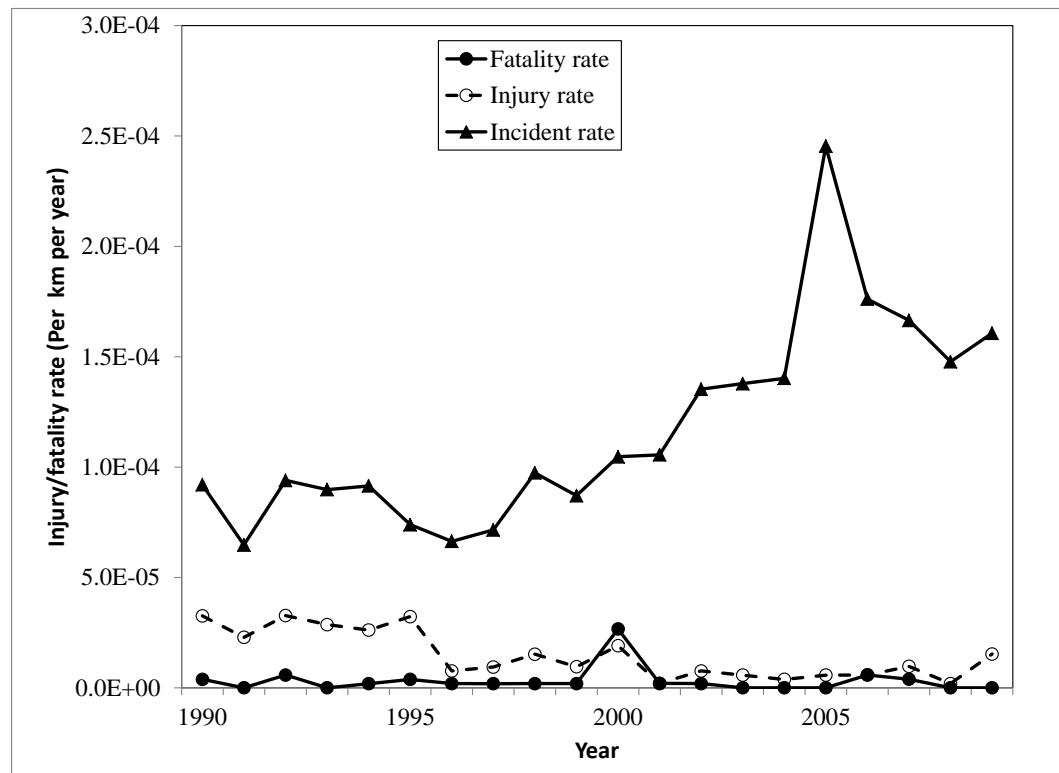


Figure 1: Total incident (dashed line), injury, and fatality rates (per km per year) for natural gas transmission pipelines from 1990 through 2009. Note that total incident rates are significantly lower than most of those for total natural gas pipeline networks shown in Table 1.

Table 1. Compilation of Failure Rates Used in the Literature to Represent the Risk of CO₂ Pipelines

Study	Failure Rate NG*	Source and Dates	Failure Rate CO ₂ ^a	Source and Dates
NEB, 1998	1.5×10^{-4}	EGIG/		
Gale & Davison, 2004	1.7×10^{-4}	PHMSA/1990– 2001	3.3×10^{-4}	PHMSA/1990– 2001
Turner et al., 2006	3.1×10^{-4} (24 in.)	EGIG/		
TetraTech, 2007	1.8×10^{-4}	PHMSA/1994– 2006		
Kaufman, 2008	2.0×10^{-5} (rupture rate, 24" pipeline)	EGIG/1970– 2004		
Grieb, 2009	2.1×10^{-4}	PHMSA/1988– 2008	2.3×10^{-4}	PHMSA/1988– 2008
URS, 2009	2.0×10^{-4}	EGIG/1970– 2001	1.69×10^{-4} per mile	PHMSA/1986– 2008
Koornneef et al., 2010	6.1×10^{-4}		4.1×10^{-4}	PMHSA/1994– 2007
Koornneef et al., 2010	1.5×10^{-4}			
Koornneef et al., 2010	3.0×10^{-3}			
Trabucchi, 2012			0.00131 per mile	PHMSA/2002– 2009
DOE, 2012	2.1×10^{-4}		2.3×10^{-4}	PHMSA/1988– 2008
Lisbona, 2012	1.92×10^{-4}	PHMSA/1986– 2009	5.10×10^{-4}	PHMSA/1986– 2009

^aAll likelihoods in this paper are normalized by distance and time and have units per km-year.

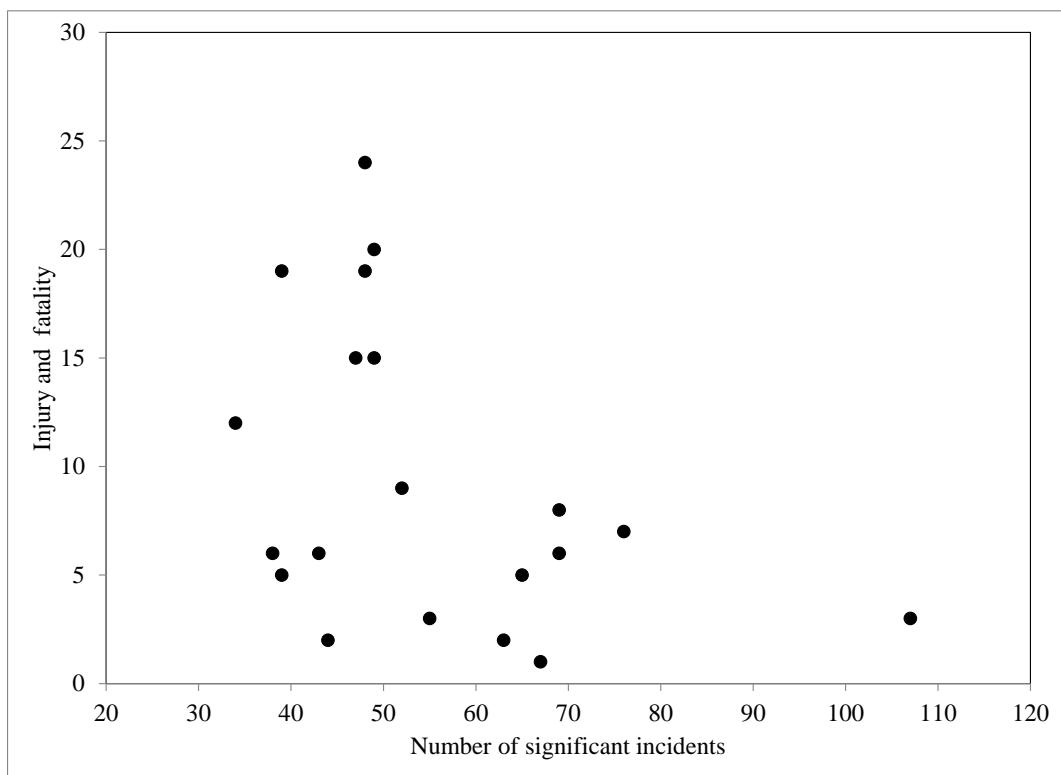


Figure 2: Plot of number of significant incidents (x axis) for natural gas transmission pipelines (Figure 1) versus number of injuries/fatalities for each year from 1990 through 2009.

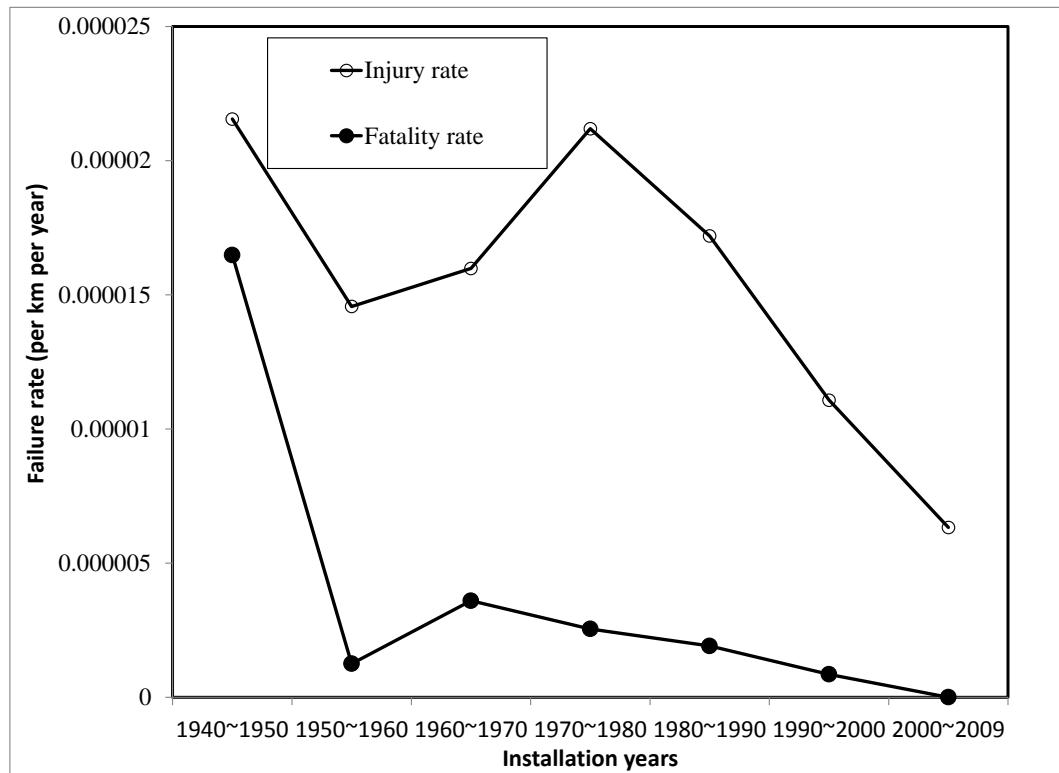


Figure 3: Injury and fatality rates for pipeline segments of particular installation years. Note that in general, the older the installation date of a pipeline segment, the higher the injury and fatality rates.

In risk analysis, distinguishing between accepted and imposed risks is important. If someone chooses to work for a gas pipeline company as an emergency responder to pipelines leaks, that person has accepted the risks that this job entails and presumably is financially compensated for taking on this risk. In general, when members of the general public are killed by a pipeline explosion, in the words of the UK safety authority they “have risks imposed on them in the wider interest of society” (HSE, 2001)

Injury and fatality rates for natural gas transmission pipelines (from 2002 through 2009) can be divided into public and nonpublic classes (Figure 4). Because of the nature of DOT’s regulations, this division does not correspond to “the general public” and “pipeline workers.” For example, independent contractors working on the pipeline are regarded as “the public.” In addition, not all members of the general public listed as pipeline fatalities are collateral damage from pipeline explosions. For example, a vehicle that loses control on a highway, killing the driver and eventually colliding with a pipeline facility, would be classified in the database as a *public fatality*. In any case, the average fatality rate for this period can be estimated at 7.2×10^{-7} . Note that the nonpublic fatality rate is even lower (4.8×10^{-7}) for this period.

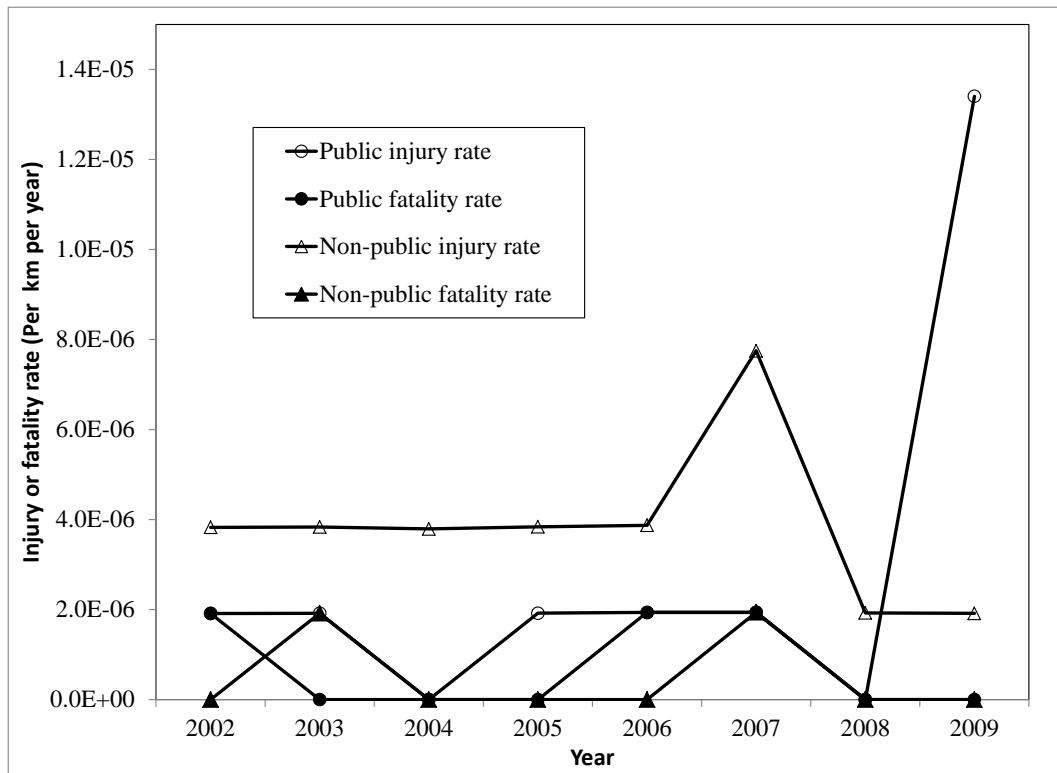


Figure 4: Public and nonpublic injury rate and fatality rate (per km per year) for transmission pipelines from 2002 through 2009.

3.2 Comparison of Causes of Failure in CO₂ versus Natural Gas Pipelines

Using comparisons between natural gas and CO₂ pipelines, several studies have pointed to key differences between the two. Establishing the nature and validity of these differences is a key to an understanding of how the likely portion of risks associated with CO₂ pipelines might be estimated from the natural gas pipeline record. Gale and Davison (2004) examined the causes of CO₂ pipeline incidents in the U.S. from 1990 through 2002. They found that failures resulting in CO₂ release resulted from relief-valve issues (four failures), weld/gasket/valve packing issues (three failures), corrosion issues (two failures), and outside-force incidents (one failure). Gale and Davison (2004) noted that for natural gas pipelines, DOT data list the main causes of pipeline incidents as outside force (35%), corrosion (32%), other (17%), weld and pipe failures (13%), and operator error (3%). DOT noted that for natural gas pipelines, outside force is the most common cause; however, the sample size for CO₂ pipelines is so small that comparison is unlikely to be meaningful. Using essentially the same data set as Gale and Davison (2004) analyzed, de Visser et al. (2008), Johnsen et al. (2009), EI (2010), and Koornneef et al. (2010) concluded that corrosion was the major cause of failure in U.S. CO₂ pipelines.

Det Norsk Veritas (DNV) (2010) suggested that “differentiating between external and internal threats, one may expect that the external threats related to CO₂ pipelines provide equivalent statistics as for hydrocarbon pipelines.” In other words, actions of external corrosion and excavators are not impacted by the contents of a steel pipeline. DNV (2010) also suggested that statistics for internal corrosion derived from natural gas pipelines can be applied to CO₂ pipeline water content if CO₂ is controlled to keep water levels below saturation (as is standard practice in the CO₂ EOR industry).

Distance-normalized annual frequencies of natural gas transmission pipeline failure from the PHMSA database are shown in Figure 4. Each cause of failure is shown separately. The proportion of incidents caused by internal and external corrosion, outside force, and construction/material defects are also shown. This data set is the same as that shown in Figure 1. Note that as the total number of incidents was increasing from 2004 through 2009 (as shown in Figure 4), the sum of injuries plus fatalities was largely decreasing. That incident rates are so

poorly correlated with injury/fatality rates demonstrates the problem of using data (such as that shown in Table 1) to represent risk.

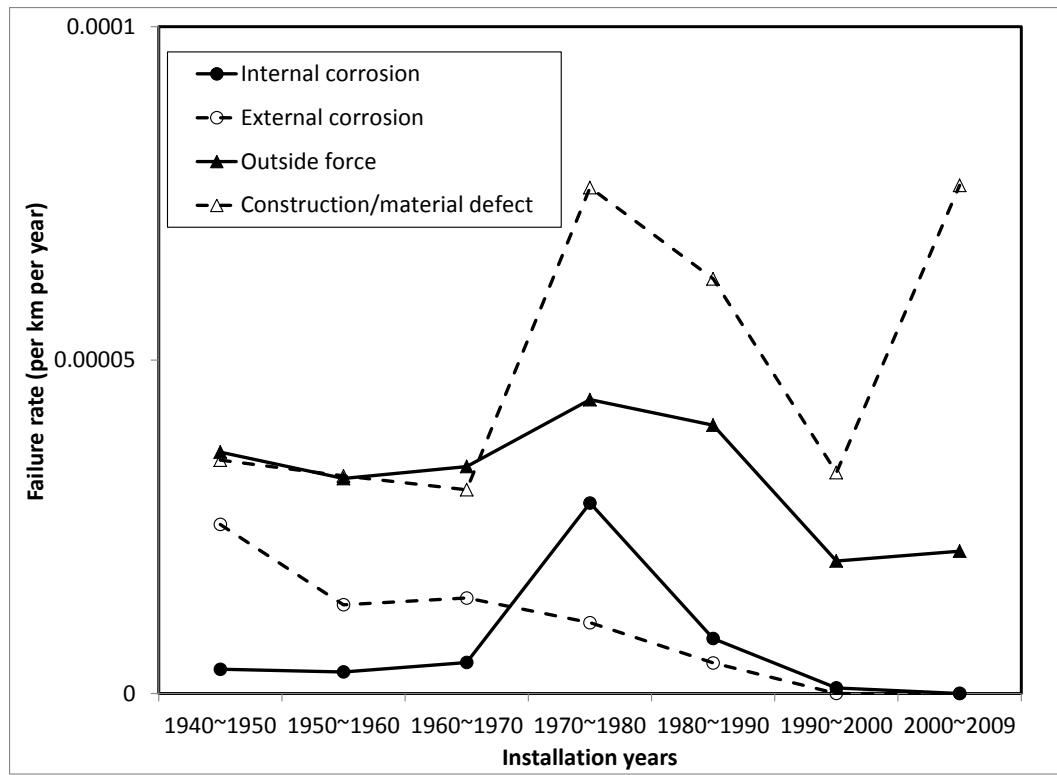


Figure 5: Normalized failure rate of different causal factors for U.S. natural gas transmission pipelines installed at different periods.

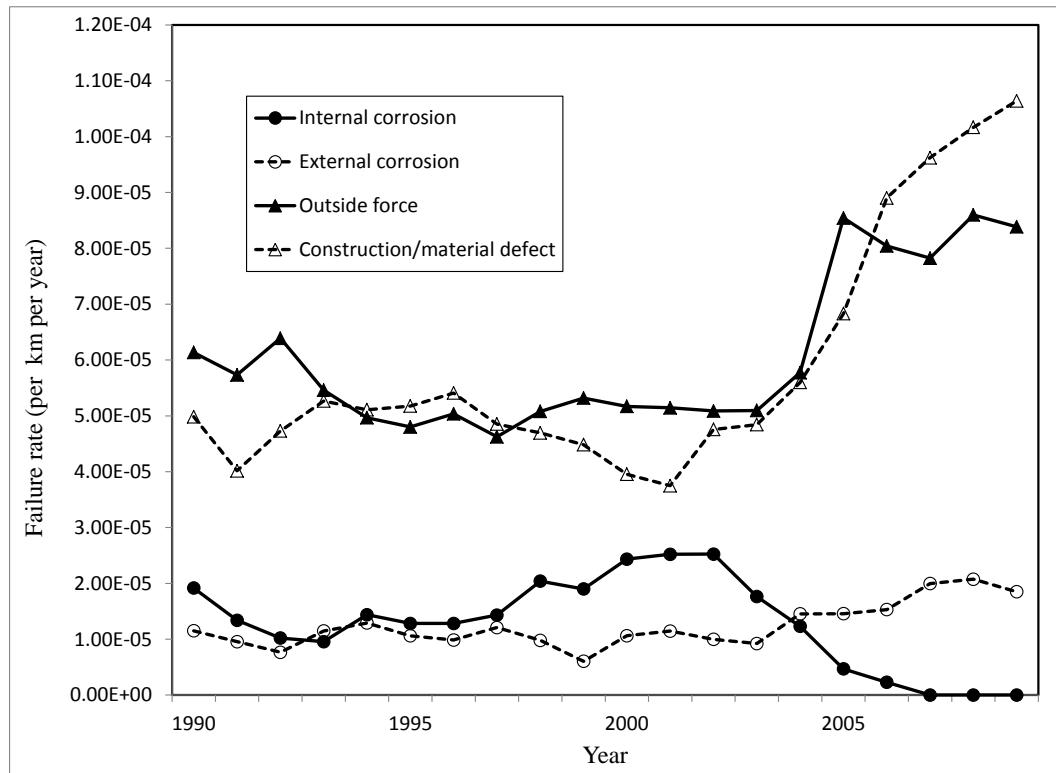


Figure 6: Normalized failure rate of different cause factors in U.S. transmission pipelines from 1990 through 2009. Note that incidents related to construction defects and, to a lesser extent, outside force have increased since 2004, whereas internal corrosion incidents have decreased.

Another issue significant to an understanding of the applicability of natural gas transmission pipeline data to risks that will be associated with future CO₂ pipeline networks is the impact of pipeline age on the data set. Figure 5 shows the distance-normalized failure rate for different causal factors of U.S. transmission pipelines from 1990 through 2009 for different ages of pipeline installation. As might be expected, the older the pipeline, the larger the impact from external corrosion (as noted by Wang and Duncan, 2013). The failure record of gas-transmission pipelines built over the last 30 years provides a better estimate of future CO₂ pipeline network than some average value calculated from the natural gas pipeline data set. Considering this fact in the context of the data (Figure 6) suggests that internal and external corrosion rates for CO₂ pipelines will be small. Note that failure rates for natural gas pipelines over the last 30 years are dominated by external force and material/construction defects—two issues that can potentially be effectively mitigated.

3.3 Risk of Serious Pipeline Punctures and Ruptures

Another way to approach estimating the likelihood of a dangerous incident occurring in a future CO₂ pipeline network is to use the natural gas transmission pipeline data to estimate the risk of a pipeline rupture occurring of sufficient length to release substantial volumes of CO₂. A key question is: what can be learned from the failure record of natural gas transmission pipelines that would inform our understanding of the risk from ruptures of CO₂ pipelines? In using incident data from natural gas pipeline statistics as a proxy for risk of CO₂ pipelines, several authors have implicitly assumed that all recorded incidents in the natural gas pipeline record were caused by either ruptures or punctures. Koornneef et al. (2009) asserted that “cumulative failure rates (puncture plus rupture) assumed within studies on risks of CO₂ pipelines show a range … from 1.6 to 6.1×10^{-4} / (km yr)” (see also discussion in Koornneef et al., 2010). This assertion appears to be far from the actual situation. On the basis of the 1990 through 2009 PHMSA database of all incidents, 41.9% were classified as leakage, 32.9% as ruptures, and 25.2% as system-component failures. Of leakage incidents (based on PMSHA data from 2002 through 2009) 65.1% of those recorded were pinholes, 19.8% were related to connection failures, and only 15.1% were caused by punctures. Figure 7 shows the probability of occurrence of the different types of leakage incidents from 2002 through 2009. The puncture rate is typically the lowest, averaging 1.0×10^{-7}

⁵, whereas pinholes are typically the highest rate, averaging 4.3×10^{-5} . Data from UK gas pipelines from 1992 through 2007 (Hopkins et al., 2009) show pinholes at approximately twice the frequency of punctures and an order of magnitude more frequent than ruptures.

Pinhole leaks can be dismissed as a significant safety concern for CO₂ pipelines. Such leaks are noisy and will result in an easily detectable plume of white frozen water vapor. The rate of puncturing of natural gas transmission pipelines in the U.S. from 2002 through 2009 is shown in Figure 7. The average rate of puncturing over this time period is 1.0×10^{-5} , a factor of 4 lower than the rate of pinhole leaks that averages 4.4×10^{-5} . The extent to which punctures may present a serious hazard for CO₂ pipelines depends on how large the punctures may be. The probability of occurrence of different-sized holes caused by punctures is shown in Figure 8. The size of a puncture-based leak that could create a serious hazard would require a site-specific evaluation. If it is assumed that a hole larger than 10 inches is required to pose a serious threat, the probability of such a hole computed from PHMSA data is 1.3×10^{-5} (Figure 8). The only practical experience with the rupture of a CO₂ pipeline comes from the cutting of an 8-inch pipeline delivering CO₂ to Tinsley oil field in southern Mississippi (Duncan, 2013) that caused little if any noticeable harm. A single 10-inch puncture would more likely release less CO₂ than the double 8-inch release from the severed Tinsley pipeline. Notwithstanding the preceding analysis, the impact of releases from small holes has some unexpected complexities. As noted by Gale and Davison (2004), small-leak depressurization of the pipeline (they suggested a 10-mm hole) will be slow, and the automatic safety-block valves may not activate for some time (Gale and Davison suggested 30 minutes). Gale and Davison (2004) also suggested that this timeframe “could allow a build-up of CO₂ in the ground or depressions of the ground.” However, Koornneef et al. (2010) came to the conclusion through their modeling that puncture contribution to risk is “expected to be limited.” The possible role of slow leaks resulting in gradual CO₂ accumulation in low-lying areas during periods of minimal or no wind deserves further analysis. If punctures are not a significant concern, another approach to calculating the likelihood of a dangerous incident occurring in a future CO₂ pipeline network is to estimate the likelihood of a pipeline rupture occurring of sufficient length to release substantial volumes of CO₂. Figure 9a shows the annual rate of leakage, rupture, system-component failure, and total failure rate of U.S. transmission pipelines from 1990 through 2009. Note that total incident rate and the three

failure mechanisms (leakage, rupture, and component failure) all show a general increase in normalized rates from the late 1990's through 2009. Figure 9b shows a 5-year moving average of rupture rate and total failure rate of natural gas transmission pipelines for the same data as plotted in Figure 6a. These data suggest that rupture rate increases slightly from 1990 through 2009 but, like fatality rate, is not strongly correlated with the increase in total incidents during the time period. However, before rupture rates (Figure 9 b) are used as an estimate of rupture rate in CO₂ transmission pipelines, two issues must be resolved. First, in general, the older the installation-date of a pipeline segment, the higher the injury and fatality rate (Figure 3). Distance-normalized rupture rates for natural gas transmission pipeline segments can be plotted as a function of installation period (Figure 10). Data show a strong decrease in rupture rate (by a factor of 6) as the age of the pipeline segment gets younger. Second, the majority of the ruptures are too short to be of concern. Figure 11 shows a histogram of rupture length for significant incidents in natural gas transmission pipelines which demonstrates that the population mode of rupture lengths is less than 2 inches.

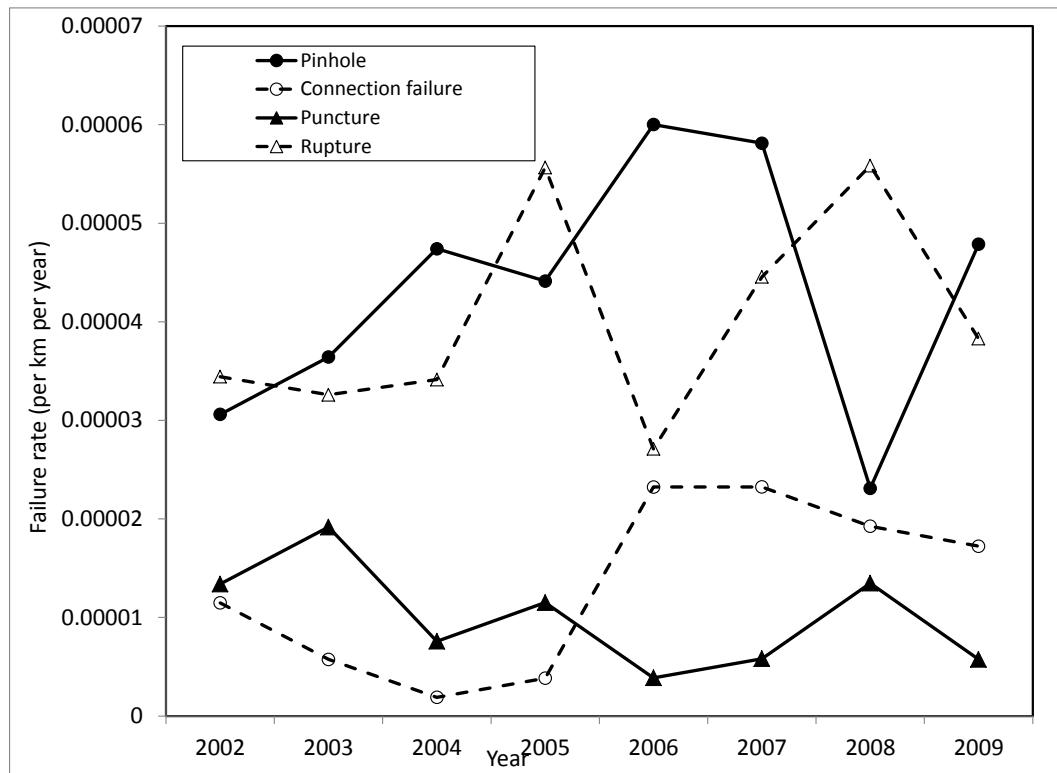


Figure 7: Comparison between rupture rate and normalized failure rate of different forms of leakage. For leakage incidents, category rupture should be interpreted as cracks or small fractures. Note that pinhole leaks are the largest type of failure except for a few years. Pinhole failures are undoubtedly underrepresented in the database because only incidents with greater than \$50,000 of damage are counted.

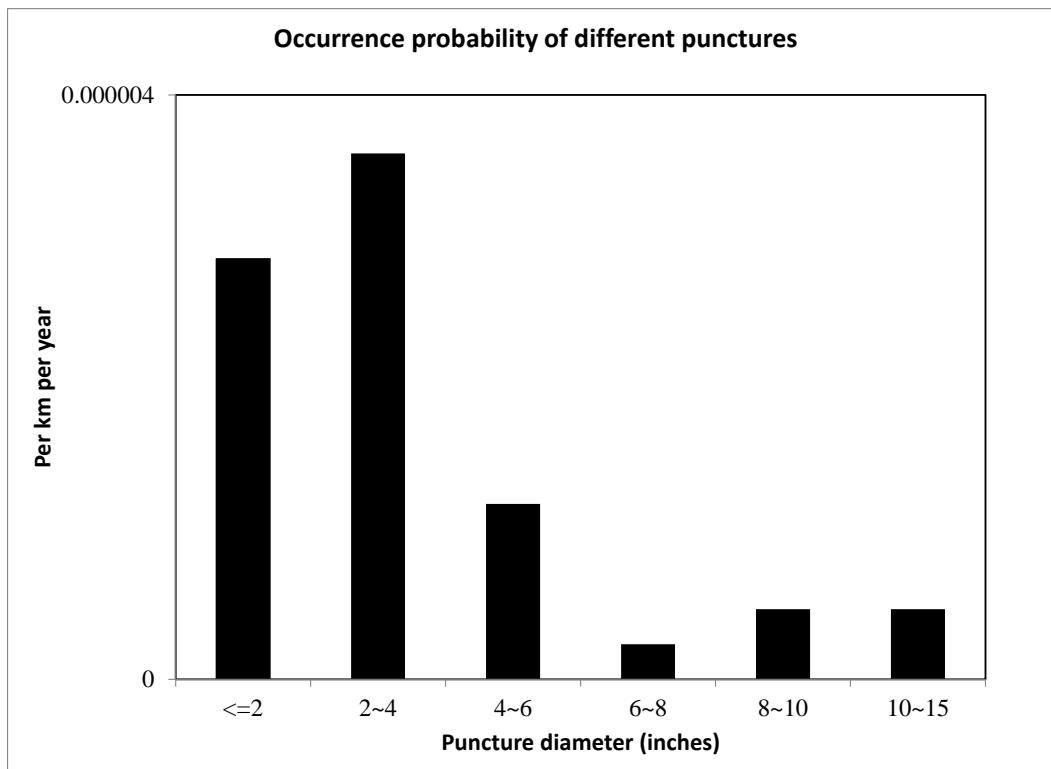
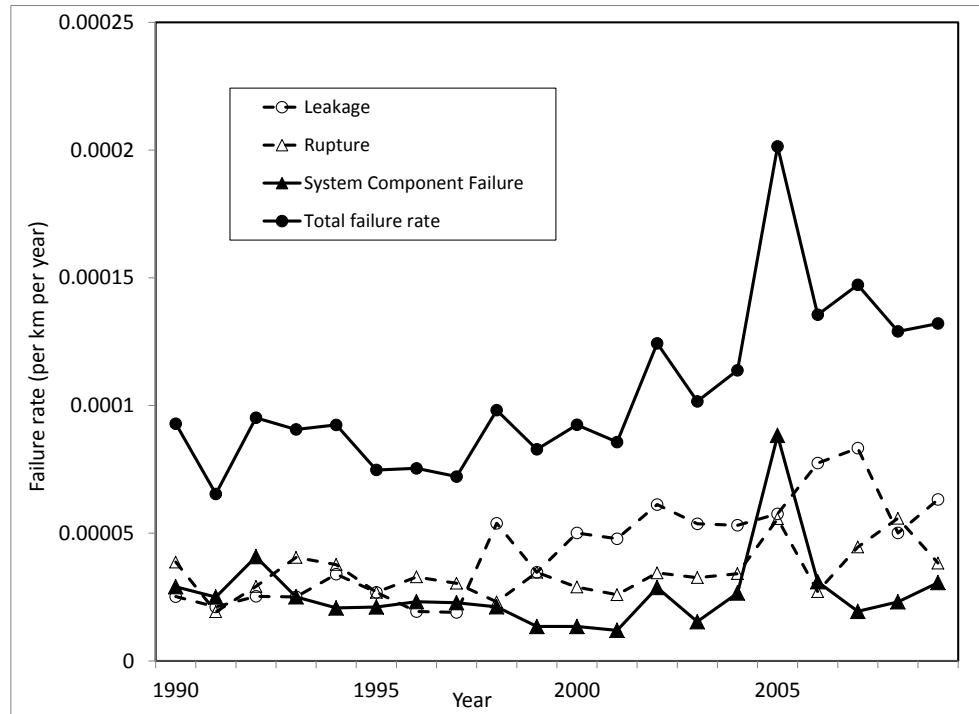
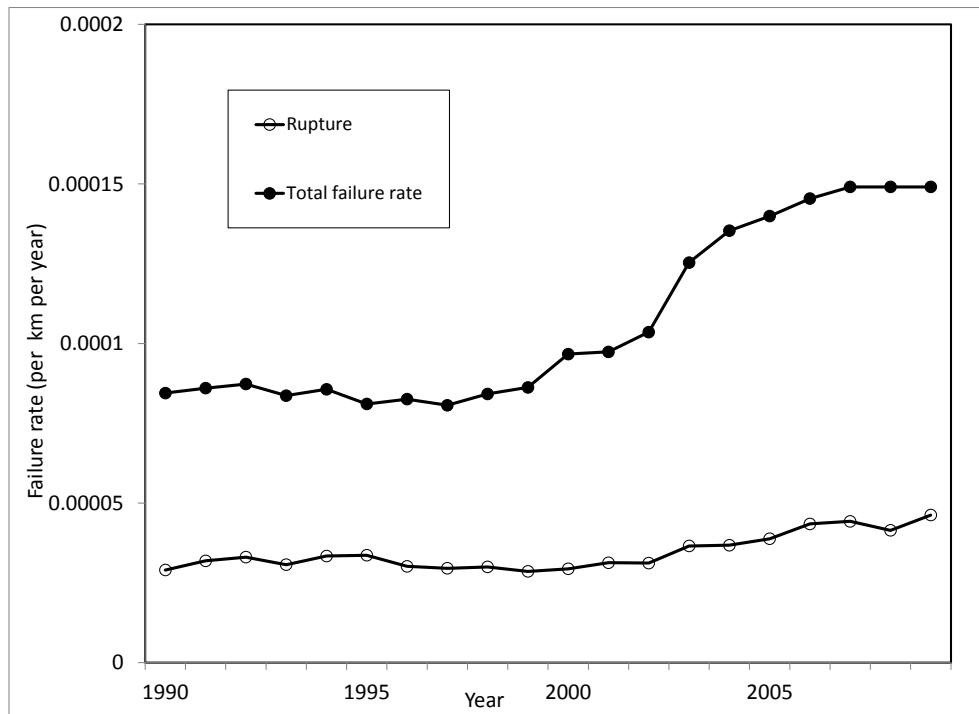


Figure 8: Occurrence probability of different diameter holes caused by punctures. Note that mode of puncture diameter is between 2 and 4 inches and that fewer than one-fifth of the holes are above 6 inches in diameter.



(a)



(b)

Figure 9: (a) Annual rate of leakage, rupture, system-component failure, and total failure rate for U.S. transmission pipelines from 1990 through 2009. Note that all incidents shown in Figure 7 are included in this graph as “leakage incidents.” Through most of the 1990’s leakage, rupture failure, and component failure were approximately the same magnitude. Since 1998, leakage rates (and, to a lesser extent, ruptures) have increased. Wang and Duncan (2013) attributed this increase to aging of the pipeline network (see Figure 10, for example). (b) 5-year average of rupture rate and total failure rate for transmission pipelines.

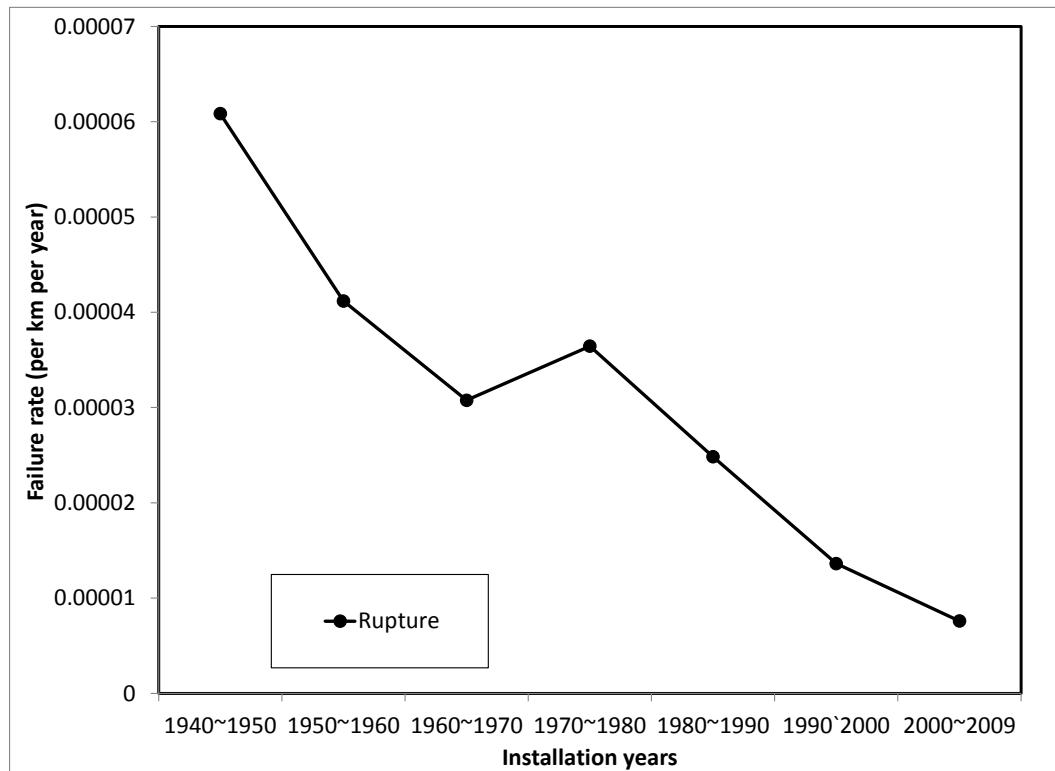


Figure 10: Distance-normalized rupture rate for natural gas transmission pipeline segments installed at different periods. Graph shows impact of old segments of U.S. pipeline network on rupture rates, with rupture rates (with one exception) decreasing with decreasing age of the pipeline segment. This decrease is presumably a compounding of several factors, such as newer pipelines being better fabricated from higher quality steel, newer pipelines being likely to have less corrosion, and newer pipelines having improved coatings to resist external corrosion in particular.

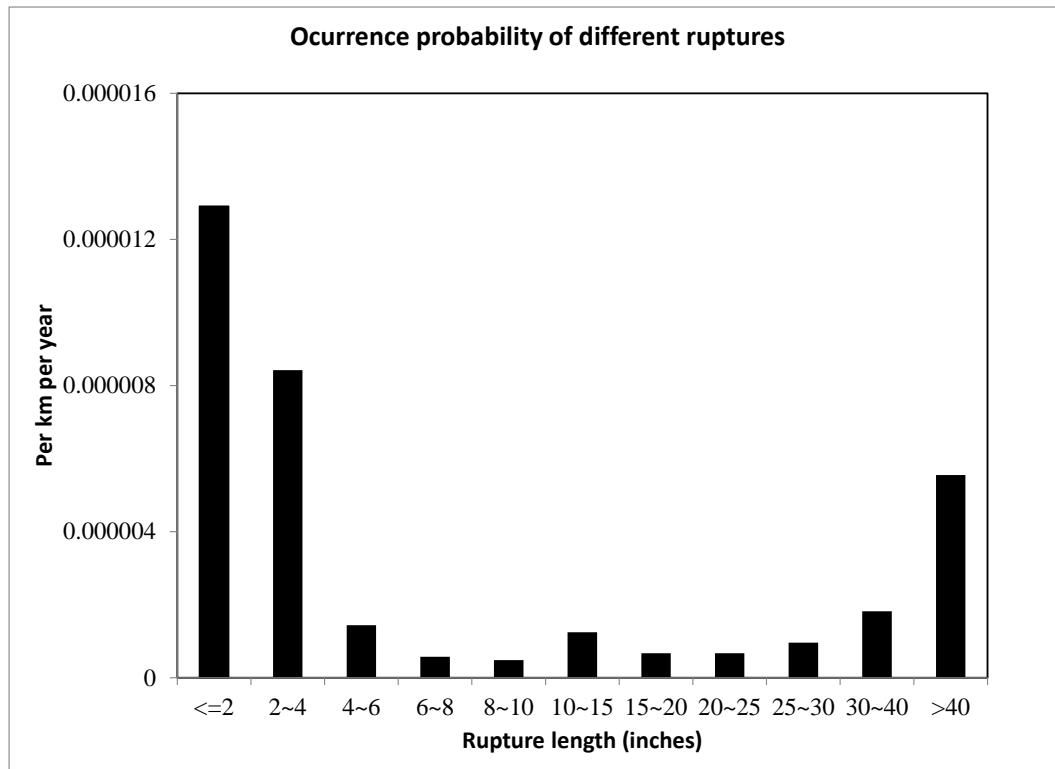


Figure 11: Histogram of rupture size for significant incidents in transmission pipelines; >40 bin includes some incidents in which ruptures exceed 40 inches. Note that mode of rupture lengths is less than 2 inches.

3.4 Risk Mitigation through Pipeline Design

Risk-mitigation strategies for CO₂ pipelines should focus on strategies to reduce the likelihood of significant-sized ruptures. Two basic approaches can mitigate these risks. The first is to reduce the likelihood that external force incidents (such as cutting by an excavating machine or backhoe) can initiate ruptures. The second is to use steel types and designs (such as crack-arresting hoops) to minimize the occurrence and propagation of ruptures (Cosham and Eiber, 2007). Both these approaches have been discussed extensively in pipeline-risk literature. Another approach to risk mitigation is to match the design factor for the pipeline to population density near the pipeline—a standard feature of most, if not all, pipeline design codes (Goodfellow and Haswell, 2006). In the U.S., classes are defined by ASME standard B31.8S (ASME, 2001) and are included in the Federal Code by reference. Class of pipeline segment is based on defining population-density-based class-location units (CLU's). A CLU is defined by population density in a 1-mile stretch, accounting for a swath of 220 yards on either side of the pipeline (ASME, 2001). Class 1 CLU's are defined as 0 to 10 ten buildings (a rural area); Class 2, 11 to 45 buildings (areas around towns); Class 3, more than 46 dwellings (suburban areas); and Class 4, multistory buildings (urban areas).

In ASME B31.8S, specified minimum yield strength (SMYS) of the pipe is used as the basis for adjusting the factor of safety of each pipeline segment that is based on CLU (ASME, 2001). Described as a design factor, a value of 0.5 would require maximum pressure in the pipeline to be half that of the theoretical maximum that the pipe could withstand. It is because the pipeline in practice has to be run in essentially the same pressure, in reality lowering the design factor is compensated for by using a thicker walled pipe with a proportionally higher SMYS. Such thicker walled pipelines have the additional benefit of having a lower propensity for being punctured by excavation equipment and a lower probability of compromise by corrosion. In ASME B31.8S sets, the design factor for Class 1 is 72% of SMYS, Class 2 is 60% of SMYS, Class 3 is 50% of SMYS, and Class 4 is 40% of SMYS. Most countries have a similar set of classes, or they use ASME B31.8S. In the U.S., as noted by GRI (2000), 49 CFR 192 requires that age-related deterioration be addressed by leaks and related strategies being tested for (see also ASME,

2004). As the density of population near the pipeline increases, replacement of existing pipe infrastructure with thicker walls is mandated.

Wang and Duncan (2013) showed that at a given diameter, as wall thickness of a pipeline increases, observed rate of failure (leakage and rupture) decreases (Figure 12). Minimal wall thickness for a CO₂ pipeline operating at 2,800 psi also changes for Classes 1, 2, and 3 (Figure 12). Note that wall thicknesses for typical CO₂ transmission pipelines (>20 inches in diameter) for all classes appear to be in a range of wall thickness that is protective for the reasons given earlier.

Thus far no direct evidence exists of the impact of the design-factor approach on consequences such as fatality rates or serious-injury rates. Design factors for Class 1 through 4 pipeline segments can be plotted against the fatality rate for these segments from the PHMSA database for 1990 through 2009 (Figure 13). The highest fatality rate of 4.0×10^{-6} per km per year is for Class 1 segments. For Class 2 segments, the rate decreases to 1.0×10^{-6} . Significantly fatality rate in Class 3 and 4 areas was effectively zero. Risks in urban areas are certainly nonzero but must be on the order of 10^{-7} per km per year or smaller. This risk range is similar to the chance of an airplane falling from the sky and destroying a house near an airport. These data, for the first time, demonstrate that the population-density-specific design code in ASME B31.8S is effective in controlling individual risks related to high-pressure gas-transmission pipelines.

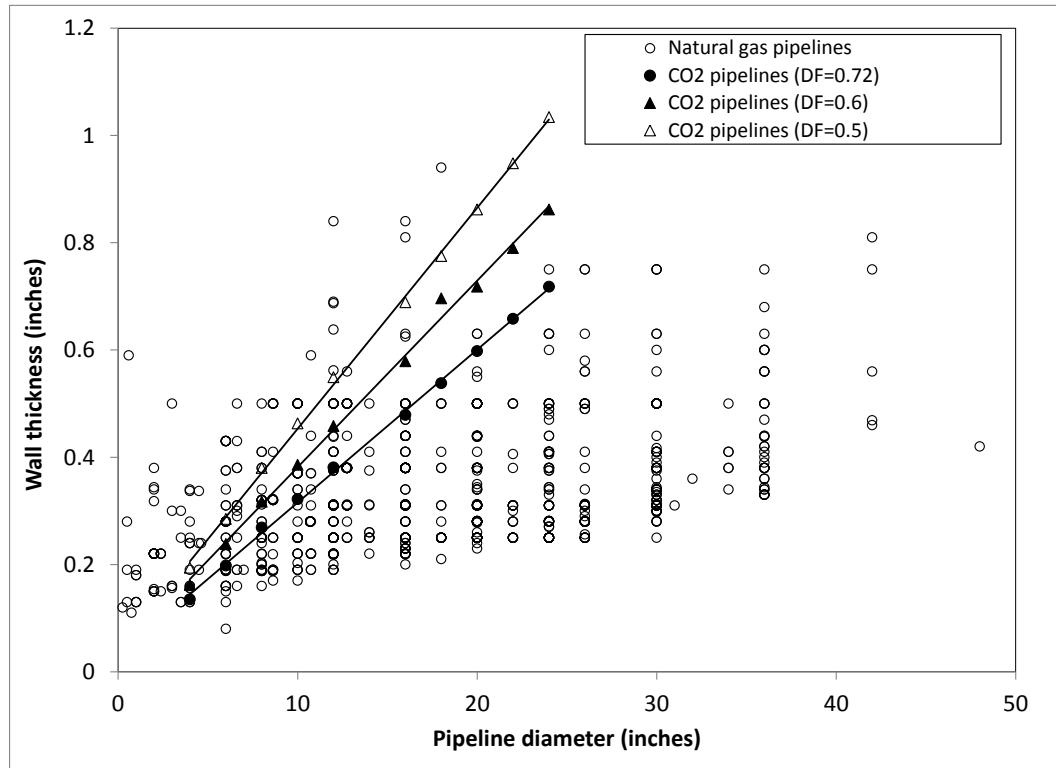


Figure 12: Black circles represent wall thickness for natural gas transmission pipelines recorded in the PHMSA incident database (from Wang and Duncan, 2013). The other symbols represent wall thickness required by ASME B31.8 for CO₂ pipelines fabricated from grade X65 steel and operated under 2,800 psig (from Nyman et al., 2004) when different design factors (DF) are used.

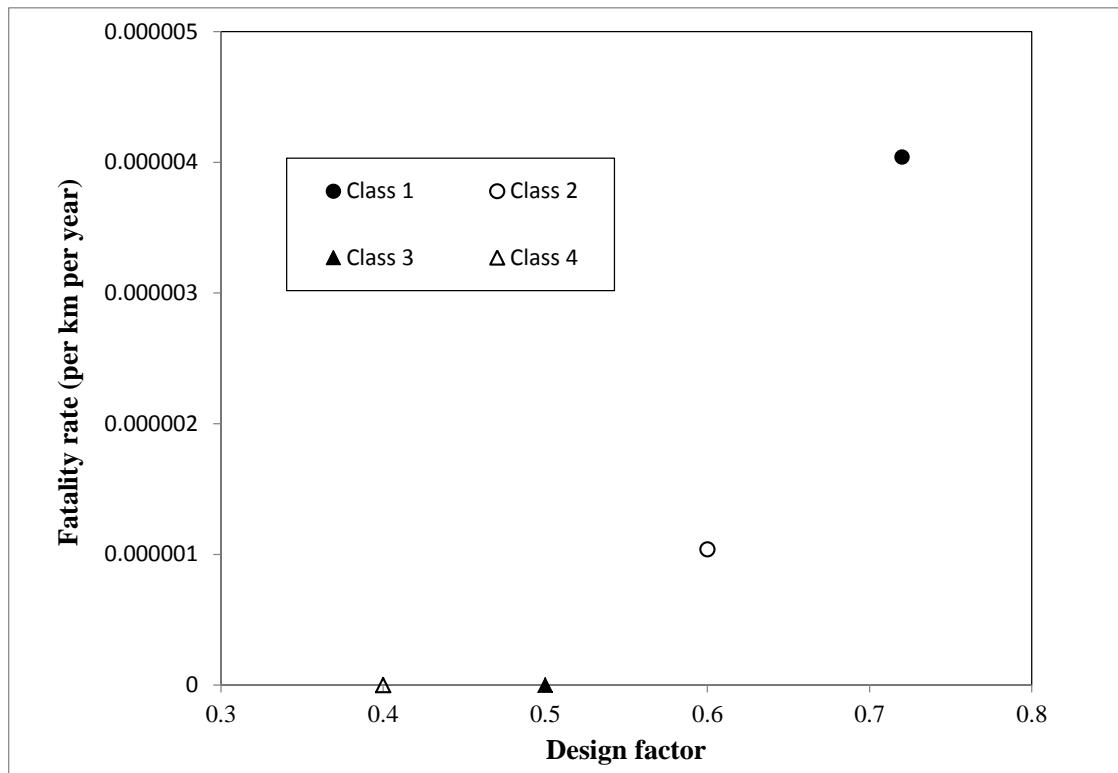


Figure 13: Design factor versus fatality rate for onshore natural gas transmission pipelines installed at different class location units (CLU) on the basis of PHMSA 1990 through 2009 database. This graph demonstrates the success of pipeline design codes in decreasing risk of fatality in suburban and urban areas.

3. Discussion

In making one of the first environmental assessments of CO₂ sequestration, Heinrich et al. (2003) suggested that “although pipeline failure [in CO₂ pipelines] does occur, technology, operational procedures and risks associated with CO₂ transport are well understood.” Barrie et al. (2004) were considerably more skeptical and warned that if new, longer CO₂ pipelines are built for CCS, with branch lines near populated areas, “there will be increased risk to the public.” Connolly and Cusco (2007) came to a conclusion from the CO₂ transportation record that differed considerably from that of Heinrich et al. (2003). Connolly and Cusco (2007) suggested that risks associated with handling high-pressure CO₂ in significant amounts were too small to establish a robust case for safety.

4.1 Estimating the Likelihood of Failure and Fatality Rates of Future CO₂ Pipelines

A key question is: what can be learned from the failure record of natural gas transmission pipelines that would inform our understanding of the risk from ruptures of CO₂ pipelines? The scientific literature on this point splits into three groups. One set of authors has concluded that the failure rate for CO₂ pipelines will be greater than that for natural gas pipelines because of its properties during transport. A second group explicitly or implicitly has assumed that the failure rate should be similar for both types of pipelines. A third group suggests that the failure rate of CO₂ pipelines is higher than natural gas.

Koornneef et al. (2009) suggested that common impurities in CO₂ pipelines “such as SO_x, NO_x, O₂ and H₂S” can increase corrosion rates, which, in turn “may lead to higher failure frequencies.” Some concerns with respect to CO₂ pipelines are legitimate. For example, Berstad et al. (2010) suggested that if a segment of a CO₂ pipeline is depressurized by an accident or for maintenance, rapid cooling can result in embrittlement of the metal and possible rupture damage to the pipeline.

Gale and Davison (2004) suggested that CO₂ pipelines, because of “the lack of fatalities or injuries, are safer than natural gas … pipelines.” Gale and Davison (2004) concluded from their “estimates of the risk of CO₂ releases from CO₂ transmission pipelines” that such pipelines “do not represent a significant risk” in terms of public hazard. The extensive literature on aspects of

risk associated with CO₂ pipelines published since 2004 has done little to resolve these issues. Gale and Davison (2004) suggested that, in general, it would be “reasonable to conclude” that CO₂ pipelines “are no less prone to incidents than natural gas pipelines.” This paper has set out to evaluate the nature of risks posed by future CO₂ pipelines and whether an increase in risk to the public is likely.

The pipeline industry has developed sophisticated approaches to ensuring the reliability of transportation of gas and liquids by pipelines. This paper has demonstrated the critical importance of design codes in interpreting failure-rate data. DNV (2010), in a recommended practice for design and operation of CO₂ pipelines, suggested that evaluating the risks associated with a specific CO₂ pipeline project should be based on examination of “available historical incident data in depth” to gather “the most relevant data.” DNV (2010), however, gave little indication as to how to identify the nature of the most relevant data. DNV (2010) noted that “one needs to consider pipelines designed according to equivalent codes.”

The current study contains an analysis of natural gas transmission pipeline that is directly applicable to the issues raised by DNV (2010) as to how to choose the “most relevant data.” Previous studies of the likelihood of CO₂ pipeline failure have stated that natural gas pipeline statistics are not appropriate as analogs for CO₂ pipelines. Most previous studies of CO₂ pipeline risk have simply used the average incident rate for natural gas pipelines from either the U.S. or Europe as an estimate of risk of CO₂ pipelines. Natural gas pipeline failure rates (Table 1) vary from 1.5×10^{-4} to 6.1×10^{-4} ; however, these data include both transmission and distribution pipeline systems. Transmission pipelines for CO₂ are much more likely to have failure rates similar to those of transmission pipelines for natural gas rather than urban distribution systems. Not surprisingly the pipeline incident rates are on the order of a factor of 5 to 10 higher than those computed for natural gas transmission pipeline in the U.S. constructed over the last 2 decades that are in the range of 4.0×10^{-5} to 6.0×10^{-5} per km per year (Wang and Duncan, 2013; Table 1). There is no correlation (at least for U.S. data from 1990 through 2009); however, between incident rate and fatality rate for natural gas transmission pipelines (Figure 2). The average fatality rate for natural gas transmission pipelines constructed over the last 3 decades (1.0×10^{-6}) is a metric that should be considered in the context of estimating individual risks for

CO₂ transmission pipelines. Note that this value forms an upper bound for estimating individual risks associated with CO₂ transmission pipelines. Data and modeling results are insufficient for a robust assessment to be made of the relative hazard of accidental releases of natural gas versus CO₂. However, this comparison is important and worth exploring.

CO₂ pipelines, in comparison with natural-gas transmission pipeline networks, have a fraction of the operating history in terms of pipeline kilometer years. The CO₂ incident record contains no ruptures or punctures of CO₂ transmission pipelines. Natural gas transmission pipelines in most cases operate at pressures of 60 to 80 bars, whereas CO₂ pipelines used for EOR typically operate at pressures of 85 to 150 bars. In addition, although natural gas is a pressurized gas, CO₂ is transported in pipelines in a supercritical state. In the US CO₂ and natural gas pipelines are constructed under the same design code standards where thicker pipe walls are required for higher pressure pipelines. Both CO₂ and natural gas pipelines are fabricated from carbon steel, typically API 5L Grades X65 or X70 grade (Seiersten and Kongshaug, 2005), and both are installed using the same equipment and practices. In comparing the failure mechanisms of natural gas and CO₂ transmission pipelines recent research has focused on the nature and controls of fracture propagation. For example Mahgerefteh and Brown (2011) modeling the factors controlling fracture in CO₂ pipelines constructed from X65 steel, found “highly temperature dependent propensity to fracture propagation” for pipelines with both high purity CO₂ and CO₂ streams typical of post-combustion capture. They also found that increasing the fluid temperature from 20 to 30 °C resulted in a “transition from a relatively short crack to a long running propagating fracture”. Mahgerefteh and Brown (2011) also found that for CO₂ streams predicted for capture from oxy-fuel capture, long running ductile fractures “are observed at all the temperatures under consideration”. Importantly they also noted that “counter intuitively” an increase in pipeline pressure decreased “the pipeline’s propensity to ductile fractures”. Recent research in CO₂ pipeline design has focused on mitigating the conditions that would result in fracture. Demofonti and Spinelli (2011) suggest that this can be achieved by: using high toughness steel; deploying crack arrestors; and/or using newly developed ultra-high “equivalent toughness” reinforced pipe. Similarly King and Kumar (2010) have explored the wall thickness, steel toughness, and limits on operating pressure that will minimize the probability of fracture in future CO₂ transmission pipelines. If the design code for CO₂ pipelines is adjusted such that the

fracture probabilities are similar in say an X65 steel to that for natural gas pipelines, then the use of natural gas transmission pipeline failure rates as an analogue for the behavior of future CO₂ pipeline networks should be valid.

4.2 Consequences of Pipeline Failure for Natural Gas versus CO₂ Pipelines

Comparison of the risks of failure of a pipeline containing natural gas with those of a CO₂ pipeline has to be used to evaluate the relative nature of consequences of a similar failure in the two different types of pipelines. Although both have the potential in theory to cause serious impacts to the population near the pipeline, the nature of the damages and factors controlling them are very different. Natural gas is less dense than air, and, as a result, it is buoyant and typically its leaks dissipate without ignition. Leaks from small-diameter, low-pressure natural gas pipelines are ignited in less than 10% of the incidents, whereas high-pressure, large-diameter-pipeline leak ignition occurs in over 80% of the incidents (Acton and Baldwin, 2008). When ignition of the escaping gas occurs, consequences are due primarily to thermal radiation from a fireball, crater fire, or jet fire. Even if ignition does not occur, rupture of a large-diameter, high-pressure pipeline can cause localized damages, forming craters up to 30 m in diameter and causing flying debris (Neurert, 2011). This phenomenon could clearly occur with both natural gas and CO₂ pipeline failures.

In contrast, CO₂ does not form a flammable mixture with air; it is, however, toxic at high concentrations. Leaks of supercritical CO₂ will be a mixture of cold gas (-78°C) and fine particles of dry ice. As noted by Barrie et al. (2004), for CO₂, “neither small nor large leaks” are dispersed in a fashion similar to releases of buoyant-in-air natural gas. CO₂ is denser than air, and, in the absence of winds, it will form cold, ground-hugging density flows that can accumulate in topographic depressions, displacing the ambient air. Because CO₂ is colorless and odorless, making clouds essentially invisible, it may remain undetected. The time required for CO₂ to disperse depends on wind speed, direction, and degree of instability in the air flow. Still conditions (no wind) are the most dangerous for CO₂ venting from pipelines.

For safety reasons, limiting the amount of CO₂ vented in a leak is necessary, and block valves must be installed at a spacing of 15 km or less along the line. In the U.S. this installation is

mandated by DOT regulations, and pipeline pressures are typically monitored at each block-valve location. As noted by Gale and Davison (2004), a key issue in the design of CO₂ pipelines is the spacing interval of these valves. Several studies have suggested reducing valve spacing in areas of higher population density. More closely spaced valves would appear to be more protective; however, this analysis may be too superficial. Mahgerefteh et al. (1997) pointed out that, at least for natural gas pipelines; the dynamic response to activation of emergency shutdown valves can create mechanical instabilities in the pipelines.

Observation of experimental releases of CO₂ has revealed that a part of the jet of CO₂ forms dry ice (CO₂ solids), which rains out of the vapor cloud, forming a blanket of frozen CO₂ solids (P. Cook, CO₂ CRC, Australia, personal communication, 2008). Using a model based on studies of the rupture of LPG pipelines (Morrow et al., 1983), Koornneef et al. (2009) predicted results of full-rupture failure of CO₂ pipelines. Their model includes a contribution to the vapor cloud from a bank of rained-out dry ice. The degree to which CO₂ freezes in the released fluid or in the breached pipeline itself may play a significant role in reducing the risk associated with such incidents. Unfortunately no experimental data or numerical modeling approaches currently can be used to make robust estimates of the proportion of leaked CO₂ that enters the vapor cloud versus that temporarily stored as dry ice. Turner et al. (2006), for example, in their modeling of pipeline rupture, assumed that the volume of fluid in the pipe is sufficient to justify their assumption of isothermal conditions, despite the adiabatic cooling in response to decompression. These authors assumed no freezing of CO₂ or blockage of the pipe.

The potential consequences of CO₂ pipeline incidents can be evaluated only on a site-specific basis. As a result, in some circumstances, with stable atmospheric conditions and low wind velocities, CO₂ could pond in a populated topographic low near a large CO₂ release from a pipeline and be lethal at a distance considerably larger than the danger zone for natural gas explosions. The probability of such an event, however, would be small. The possibility of this scenario taking place should be mitigated on a site-specific basis by judicious route selection and other strategies suggested later in this paper. No one has ever been killed by CO₂ venting from a pipeline; however, the current transmission-pipeline network is largely in regions with low population density, and no rupture events have been recorded.

One possible approach to estimating the likelihood of fatalities associated with a future larger CO₂ pipeline network is to use information of rupture rates. This paper, as well as Koornneef et al. (2010), has suggested that puncture incidents are unlikely to result in deadly CO₂ releases. In the FutureGen project's initial risk assessment of four proposed sequestration projects, TetraTech (2007) used rupture-failure frequencies of $5.92 \times 10^{-5}/(\text{km yr.})$ that were "based on data in Gale and Davison (2004)." Grieb (CERCDC, 2010) has described this value as representing the risk of "full bore rupture". These rupture rates were also used by Wade and Trabucchi (2009), Donlana and Trabucchi (2011), and Trabucchi et al. (2012) as the basis of their studies of risk consequences at FutureGen-candidate sites in Texas and Illinois. Curiously, Gale and Davison's paper contains no information on rupture or puncture rates. URS (2009), examining the same DOT data set as Tetra Tech (and Trabucchi and her colleagues), determined that "based on historical data obtained from the DOT's Office of Pipeline Safety covering the period 1986 to 2008...," there was "no record of catastrophic explosion or rupture ... recorded since the 1970s."

Given the information on rupture rates for natural gas transmission pipelines presented in the current study, the best estimate for rupture rate of the future CO₂ pipeline network is 1.4×10^{-5} (given by the average rupture rate of the last three most recent installation decades [Figure 10]). If one were to assume that only ruptures over 8 inches were likely to result in fatalities, the rate would be 4.6×10^{-6} . For a full bore rupture of pipelines equivalent to the proposed FutureGen pipelines, modeled by TetraTech (2007) and Donlana and Trabucchi (2011), with a likelihood of 5.92×10^{-5} , our data from natural gas pipelines (Figure 11) gives an estimate of 4.8×10^{-7} , essentially two orders of magnitude less likely. Rates for CO₂ transmission pipelines will almost certainly be lower than this rate because of the influence of pipeline-wall thickness (Figure 12). There is no basis on which to estimate a fatality rate for CO₂ pipelines from these data; however, it is likely to be a small fraction of the estimated rupture-failure rate, as it is for natural gas transmission pipelines.

Unfortunately the record of incidents in the CO₂ pipeline network in the US does not provide any information to evaluate the validity of two assumptions that are made in this paper. The first assumption is that that future CO₂ pipelines can be engineered to mitigate the likelihood of

fractures. The second assumption is that the consequences of pipeline failure, in terms of fatalities, is not greater for CO₂ compared to natural gas pipelines.

4.3 Hazard Distances around Natural Gas and CO₂ Pipelines

No consensus exists in the literature as to the relative distance from natural gas or CO₂ pipelines that constitutes a specific risk. One recent modeling study (McGillivray and Wilday, 2009) concludes that “distances to a similar level of risk are roughly comparable between CO₂ and natural gas.” However, these models were created at lower pressures, with CO₂ in a gaseous rather than a dense, supercritical state. This precaution was followed because of the “uncertainty when modeling dense phase CO₂,” which the researchers related to an uncertainty regarding formation of dry ice during venting of high-pressure CO₂. These authors noted that “risks are expected to be substantially larger for releases at higher pressure (... in the dense phase)” (McGillivray and Wilday, 2009).

Much remains to be learned about the accidental release and dispersion of CO₂ from high-pressure pipelines. The thermodynamic behavior of CO₂ near the critical point and the nature of two phases (and possibly three) is not well understood. The impact of significant pipeline ruptures is strongly influenced by the direction (horizontal, upward, downward) and momentum of the escaping jet of expanding fluid, horizontal, upward, downward (Molaga and Dam, 2011). As noted by Mohitpour et al. (2012), upward-directed, unimpeded jets generated from ruptures of larger-diameter, high-pressure CO₂ transmission pipelines will result in a high-energy jet that is more likely to disperse by entraining air (even in still air conditions) than an impinged, downward jet direction, in which momentum is lost in crater formation. This kind of phenomenon cannot be modeled by using Gaussian/dense-gas modeling codes that have been used in most studies of CO₂ dispersion from CO₂ pipeline failures.

Mazzoldi et al. (2011) noted that risk assessments of the consequences of pipeline failure that are based on simulations using Gaussian/dense-gas modeling codes can significantly overestimate the hazard that CO₂ presents. Mazzoldi et al. (2011) suggested that such misleading information can be used to support not-in-my-back-yard (NIMBY) stances. Perhaps a broader view would be

that scientists publishing modeling results (and risk studies in general) should be more careful in qualifying the uncertainties in their results and in the words they use to describe their work.

Mazzoldi et al. (2012) conducted CFD modeling of the dispersion of CO₂ jets from full-bore ruptures of high-pressure CO₂ pipelines with dimensions varying from 6 to 32 inches. They found that downstream distances reached by 25% CO₂ iso-concentration lines in plumes varied from tens to several hundreds of meters, from smallest- to largest-diameter pipes. Mazzoldi et al. (2012) model results also illustrate another feature of CO₂ plumes formed by ruptured high-pressure pipelines—they tend to be relatively small and narrow, impacting a small surface area. For example, they illustrate that the plume outlined by the more than 25% CO₂ contour at 1 m above the ground extends just over 100 m from the breach and is composed of a rather flat tongue approximately 20 m wide. This CO₂ hazard zone has a shape and areal extent different from those of the radial kill zones typically associated with natural gas explosions. For example, one researcher calculated that rupture of a 16-inch natural gas pipeline operating at 1,440 psi would have a potential impact radius (PIR) of 170 m (Kiefner, 2011). A person standing outside the PIR distance would have a 99% chance of surviving the natural gas leak were it to ignite.

These scenarios suggest that when detailed, site-specific risk modeling, including CFD modeling of CO₂ dispersion above real topography, is completed; risks associated with CO₂ pipelines will most likely have a character very different from those associated with natural gas transmission pipelines. The type of modeling done by Mazzoldi et al. (2012) should be extended to include the effects of topography, similar to the earlier studies by Chow et al. (2009), so that the potential for accumulation of lethal levels of CO₂ in topographic depressions might be better understood. Cowan (2012) has asserted that commercial CFD simulation packages are not able to correctly model stably stratified gases. Cowan warns that plumes may not disperse as rapidly if stable stratification exists but other effects are possible.

For natural gas pipelines, the spatial variation of societal risk is linked closely to that of individual risk, as computed using standard methodologies on contoured zones around the pipeline. In CO₂ pipelines, the spatial variation of societal risk is largely decoupled from the zone of individual risk around the pipeline, typical of natural gas pipeline risk assessments. Instead, CO₂-related risk assessments may begin to focus on topographic depressions as much as

hundreds of meters from the pipeline, with the potential for CO₂ accumulation during periods with minimal wind velocities. The traditional approach to evaluating and spatially mapping individual risks, results in contours of probability being drawn parallel to the pipeline route, with risk decreasing rapidly with increasing distance. This approach works well for natural gas when it mimics the behavior of fireballs and explosions. However, this approach will probably not ultimately be found useful for CO₂ pipelines.

4.4 Mitigating Risk of CO₂ Pipelines near Higher Populations

Some scientific literature suggests that CO₂ pipelines will have a greater probability of failure near urban areas. For example, Esteves and Morgado (2012) asserted that “accidents [associated with CO₂ pipelines] in densely populated areas represent a greater risk both in terms of probability and severity.” Wall thicknesses of pipes, required by design codes in the U.S. for CO₂ pipelines, are matched to the increased risk associated with higher population densities (Figure 12). Data on fatality rates for U.S. natural gas transmission pipelines demonstrate the effectiveness of increasing wall thickness of the pipeline to mitigate risk (Figure 13).

Unfortunately, a number of studies of the risk of CO₂ pipelines speculate, with little or no evidence, that future networks will have worse risk outcomes than current networks, given the rural nature of the current network. The opposite is more likely, however (Figures 12 and 13). Construction of pipelines in Class 2, 3, and 4 areas will most likely result in lower fatality rates for these pipeline segments because of their increased factors of safety created by greater pipe-wall thicknesses.

Even given the apparent success of design codes in protecting more densely populated areas it should be recognized as noted above that CO₂ pipelines present a distinctly different spatial risk profile to natural gas, a profile dominated by population in topographic lows. It would be important if future CO₂ pipelines are built near to denser population, that the risk to such endangered populations be mitigated by using some combination of physical barriers and alarm systems to guard against ground-hugging CO₂ accumulations in low-lying, populated areas.

4.5 Risk Communication

Improving scientific understanding of the risks associated with CCS is important; however, it is also important that risk information be communicated to the general public accurately and effectively. The general public has high levels of expectation in terms of minimizing hazards associated with pipelines. Complying with safety regulations may be regarded by NGOs as an inadequate response to risk on the part of industry. How effectively risk information is communicated will impact the approval of routes for future pipelines and is critical to public acceptance of future projects (NRC, 2003).

Many electric power plants are near population centers. If large-scale CCS is implemented in North America, Europe, or Asia, CO₂ transmission pipeline networks will by necessity be routed close to urban areas and through regions with higher population densities than those of the current EOR-oriented pipeline network. Public concerns centered on CO₂ transport may be a barrier to future implementation of CCS.

Effective communication of the nature and magnitude of risks associated with pipeline transport of CO₂ will be important. Risk analysis is complex, and the public's reaction to information is often emotional rather than rational. Distrust, misconception, and confusion about the facts are common (NRC, 1989). This paper has presented a number of lines of evidence that are based on a wealth of experience in natural gas transmission pipeline networks and provides a strong basis for concluding that properly designed, installed, and maintained transmission pipelines present very small risk to the general public, even in areas with higher population density. This paper has presented the case that CO₂ transmission pipelines have risks approaching the same level of likelihood as an airplane falling from the sky and hitting a house near an airport. However, small risk should not be portrayed as risk free.

4. Conclusions

A strong conclusion from examining the natural gas pipeline record in the U.S. over the 20-year period for which detailed records are available is that the incident rate is not correlated with the fatality rate. In other words, the frequency of minor accidents provides no basis for predicting rates of serious events. It is reasonable to conclude that the same is true for CO₂ pipelines.

Incident rates for both natural gas and CO₂ pipelines have been widely used in papers and reports

on risk of CO₂ pipelines as either implicit or explicit proxies for the individual risk created by such pipelines. Universally such papers and reports have used general averages for the entire natural gas pipeline network, including older pipeline segments that do not reflect the safety-level of modern pipeline technologies. Even when more careful analysis has been carried out (such as by Koornneef et al., 2010), a reasonable person reading the material might conclude that the individual risk associated with CO₂ pipelines is between 10⁻³ and 10⁻⁴, which reflects risk levels approaching those of mountain climbing, which would be regarded in most, if not all, countries as unacceptably high.

The analysis presented in this paper suggests that the likelihood of having significant (potentially lethal) releases of CO₂ from pipelines is likely in the range of 10⁻⁶ to 10⁻⁷. If these values can be used as a proxy for individual risk, these probabilities would be considered in the acceptable to negligible range where risk is regulated. The systemic overestimation of the risks associated with CO₂ pipelines found in this study may already have played a role in high-level decision making regarding CCS. If, as is commonly thought, pipelines represent the highest risk component of CCS outside of the capture plant, then most (if not all) previous quantitative-risk assessments of components of CCS may be orders of magnitude to high.

As discussed above the spatial variation of risk surrounding natural gas and CO₂ pipelines is likely to be very different. In this sense natural gas pipeline safety is an inadequate analogue for the risks associated with CO₂ pipelines. The conclusions derived in this paper must be tempered by this realization. This paper has suggested that the standard approaches to mapping individual risk contours for natural gas pipelines are not appropriate for CO₂ and that rethinking is necessary. The traditional approach to mapping individual risks, leads to the conclusions that risk decreases proportional to lateral distance from the pipeline, reflecting the impact of natural gas explosions. As noted in the Discussion section, for CO₂ pipelines mitigation strategies should focus on protecting vulnerable receptors in low lying areas near pipeline routes.

Further, this paper has presented new evidence that pipeline design standards for natural gas transmission pipelines that result in pipes with thicker walls being used in suburban and urban areas do have a significant impact on lowering fatality rates to levels so low that no deaths were recorded in incidents spanning 2 decades.

The validity of using statistical analysis of natural gas pipeline failure and risk data to predict the safety of current and future CO₂ pipeline networks, as noted in the Discussion section, depends in part on two assumptions, that fracture propensity in CO₂ pipelines can be successfully mitigated and that the consequences of in terms of deaths and injuries are not more likely than for natural gas releases. Assuming that these issues can be mitigated through engineering design, the very small likelihoods for significant leaks via rupture for CO₂ pipelines predicted in the current study support some degree of optimism for the safety of future CO₂ pipeline networks.

Summary

Previous studies of risks associated with CO₂ pipelines for future carbon capture and storage (CCS) activities have used either the frequency of incidents associated with existing CO₂ pipelines or from natural gas pipelines as a proxy. Risks of CO₂ pipeline failure have been estimated as in the range of 1.2×10^{-4} to $6.1 \times 10^{-4}/\text{km yr}$. This paper demonstrates that for U.S. natural gas pipeline data, incident/failure metrics are not correlated with fatality rates. Both CO₂ and natural gas pipelines are fabricated from the same grades of carbon steel, and both are installed using the same equipment and practices. However, natural gas is lighter than air and explosive in air, whereas CO₂ is nonflammable but toxic (and heavier than air). Their risk profiles are therefore not identical, and the differences in hazard certainly impact the nature of individual and societal risk. This study focuses on the likelihood of events that could result in fatalities or injuries. The average fatality rate for natural gas transmission pipelines constructed over the last 3 decades is $1.0 \times 10^{-6}/\text{km yr}$. This value can be viewed as an upper bound for estimating individual risks associated with CO₂ transmission pipelines. Use of incident rates to model individual risks for CO₂ pipelines, has overestimated these risks by two to three orders of magnitude. When pipelines are designed with factors of safety required by regulators for populated areas, analysis of natural gas pipeline data demonstrates that risks of significant accidental releases are extremely low. These results require a significant rethinking of previous notions of the risks associated with CO₂ pipelines.

References

Acton M.R., Baldwin P. J., 2008. Ignition probability for high pressure gas transmission pipelines, in: Proc. 7th International Pipeline Conference, v. 4, ASME 48609, p. 331.

ASME, 2001. Gas transmission and distribution piping systems, ASME B31.8.

ASME, 2004, Managing system integrity of gas pipelines, ASME Code for Pressure Piping, B31 Supplement to ASME B31.8S.

Barrie, J., Brown, K. Hatcher, P.R., Schellhase, H.U., 2004. Carbon dioxide pipelines: a preliminary review of design and risk, in: Greenhouse Gas Control Technologies 7, Vancouver, Canada.

Berstad, T., et al., 2010. CO₂ pipeline integrity: a new evaluation methodology. Energy Proc., GHGT-10.

CERCDC, 2010, Geologic Carbon Sequestration Strategies, Committee Workshop, California Energy Resources Conservation and Development Commission.
http://www.energy.ca.gov/2007_energypolicy/documents/2007-10-01_workshop/2007-10-01_TRANSCRIPT.PDF

Chow F.K., Granvold P.W., Oldenburg C.M., 2009. Modeling the effects of topography and wind on atmospheric dispersion of CO₂ surface leakage at geologic carbon sequestration sites. Energy Procedia, 1 (1), 1925-1932

Cleaver P., Hopkins H., 2012. The application of individual and societal risk assessment to CO₂ pipelines. The Journal of Pipeline Engineering, 3rd Quarter, p 191-199

Connolly S., Cusco L., 2007, Hazards from high pressure carbon dioxide releases, in: Loss Prevent & Safety Perform in Process: Ind. Symposium, IChemE Symposium Series 153:1–5.

Cosham A., Eiber R., 2007. Fracture control in carbon dioxide pipelines, Journal Pipeline Eng., 3rd Quarter, 147–158.

Cowan I., 2012. Dense gas dispersion for LNG plant... some recent findings, Presentation 18th October. <http://ukelg.ps.ic.ac.uk/49IC.pdf>

Demofonti G., Spinelli C.M., 2011, Technical challenges facing the transport of anthropogenic CO₂ by pipeline for carbon capture and storage purposes, PTC 6th Pipeline Technology Conference <http://www.pipeline-conference.com/abstracts/technical-challenges-facing-transport-anthropogenic-co2-pipeline-carbon-capture-and>

de Visser, E., Hendriks, C., Barrio, M., Mølnvik, M.J., de Koeijer, G., Liljemark, S., Le Gallo, Y., 2008. Dynamic CO₂ quality recommendations, Int. J. Greenhouse Gas Control, 2(4), 478–484.

DNV, 2010, Design and operation of CO₂ pipelines, Det Norske Veritas, Recommended Practice DNV-RP-J202, April.

Doctor R., et al., 2006. Transport of CO₂, Chapter 4, IPCC Report.

DOE, 2012. Mountaineer Project EIS.

Donlana M., Trabucchi C., 2011. Valuation of consequences arising from CO₂ migration at candidate CCS sites in the U.S., Energy Proc., 4, 2222–2229.

Dooley, J.J., Dahowski, R.T., Davidson, C.L., 2008. Comparing Existing Pipeline Networks with the Potential Scale of Future U.S. CO₂ Pipeline Networks, Pacific Northwest National Laboratory Report, PNNL-17381,
http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-17381.pdf.

Duncan I. J., 2013. Evaluating operational risks for carbon capture and storage I: CO₂ pipelines in North America, to be submitted.

EGIG, 2011, Gas Pipeline Incidents, 8th Report of the Eur0pean Gas Pipeline Incident Data Group. <http://www.egig.eu/uploads/bestanden/96652994-c9af-4612-8467-9bc6c2ed3fb3>

EI, 2010, Technical Guidance on Hazard Analysis of Onshore Carbon Capture Installations and Onshore Pipelines, Energy Institute. London, www.energyinstpubs.org.uk.

Esteves V., Morgado C., 2012. Carbon Capture and Storage – Technologies and Risk Management, Chapter 11, S. Khan (Ed.) Fossil Fuel and the Environment.
http://cdn.intechopen.com/pdfs/32337/InTech-Carbon_capture_and_storage_ccs_technologies_and_risk_management.pdf

Gale, J., Davison, J., 2004. Transmission of CO₂—safety and economic considerations, Energy 29(9–10), 1319–1328.

Goodfellow G., Haswell J., 2006. A Comparison of Inherent Risk Levels in ASME B31. 8 and UK gas pipeline design codes, IPC2006-10507, in: International Pipeline Conference, Calgary.

GRI, 2000, Natural Gas Transmission Pipelines: Integrity , Prevention, & Mitigation Practices, prepared by Hartford Steam Boiler Inspection Company, Gas Research Institute report, GRI-00/0193.

Grieb T., 2009, CO₂ Pipeline Transport Issues. Presentation at SPE International Conference on CO₂ Capture, Storage and Utilization, 2 – 4 November 2009, San Diego, California.
http://rd.tetratech.com/climatechange/projects/doc/SPE_CCS_Conference_2_4_November_2009_V4.pdf

Heinrich, J.J., Herzog, H.J., Reiner, D.M., 2003. Environmental assessment of geologic storage of CO₂, in: Second National Conference on Carbon Sequestration, pp. 5–8.

Hooper, B. Murray, L., Gibson-Poole, C., 2005. Latrobe Valley CO₂ Storage Assessment, CO₂ CRC, Report No. RPT05-0108, Melbourne, Australia.

Hopkins H., et al., 2009. Pipeline Risk Assessment: new Guidelines, WTIA/APIA Welded Pipeline Symposium, Sydney, Australia, April 3rd 2009.

HSE, 2001. Reducing Risks, Protecting People. UK Health and Safety Executive, London, Report R2P2

HSE, 2009. Comparison of risk from carbon dioxide and natural gas pipelines, Health and Safety Executive, London, Research Report RR749.

ICF, 2009. Developing a Pipeline Infrastructure for CO₂ Capture and Storage: Issues and Challenges, Report to INGAA Foundation.

IPCC, 2005. Special Report on Carbon Dioxide Capture and Storage, Cambridge University Press.

Johnsen, K., et al., 2009. Mapping of potential HSE issues related to large-scale capture, transport and storage of CO₂, DNV, report number 2008-1993.

Johnson N., Ogden J., 2011. Detailed Spatial Modeling of Carbon Capture and Storage Infrastructure Deployment in the Southwestern United States,
<http://steps.ucdavis.edu/Events/2011-steps-symposium/posters/Johnson%20-%20Jan2011.pdf>.

Kadnar J.O., 2008. Experience in CO₂ transportation via pipeline, in: CCS Web Conference on CO₂ Transport, Health and Safety Issues, International Energy Agency, Paris, France.

Kaufman K-D., 2008. Carbon Dioxide Transport in Pipelines- Under Special Consideration of Safety-Related Aspects, Pipeline Technology Conference 2008

Kelliher J.T., 2008. Testimony of the Honorable Joseph T. Kelliher, Chairman of the Federal Energy Regulatory Commission, Committee on Energy and Natural Resources of United States Senate.

Kiefner J., 2011, Pipeline Integrity Basics, Presentation June 22, 2011,
<http://springcreekhomesteading.files.wordpress.com/2013/04/pipeline-integrity-basics-kiefner.pdf>.

King, G., and Kumar, S. 2010, How to Select Wall Thickness, Steel Toughness, and Operating Pressure for Long CO₂ pipelines. *Journal of Pipeline Engineering*, 9(4), 253-264.

Koornneef J., Spruijt M., Molag M., Ramirez A., Faaij A., Turkenburg W., 2009, Uncertainties in risk assessment of CO₂ pipelines, Energy Proc., 1, 1587–1594.

Koornneef J., Spruijt M., Molag M., Ramirez A., Turkenburg W., Faaij A., 2010. Quantitative risk assessment of CO₂ transport by pipelines—a review of uncertainties and their impacts, *J. Haz. Mat.*, 177, 12–27.

Kruse H., Tekiela M., 1996. Calculating the consequences of a CO₂-pipeline rupture, Energy Convers. Mgmt., 37(6-8), 1013–1018.

Lisbona, D, 2012, Risk Assessment Methodology for CO₂ Pipelines, UK Health and Safety Laboratory, www.sieso.org.uk/Comah18_Lisbona_CO2.ppt.

Mahgerefteh H., Brown S., 2011, Influence of line pressure and temperature on fracture propagation behaviour in CO₂ pipelines. In: Proceedings of Brazilian Petroleum, Gas and Biofuels Institute. (pp. 1 - 10). Brazilian Petroleum, Gas and Biofuels Institute: Rio de Janeiro, Brazil.

Mahgerefteh, H., Saha, P., Economou, I.G., 1997. A study of the dynamic response of emergency shutdown valves following full bore rupture of gas pipelines, Proc. Safety & Env. Protect., 75.4, 201–209.

Mazzoldi A., Hill T., Colls J.J., 2011. Assessing the risk for CO₂ transportation within CCS projects, CFD modelling. Int. J. Green. Gas Cont. 5(4), 816–825.

Mazzoldi A., et al., 2012. Simulation-based estimates of safety distances for pipeline transportation of carbon dioxide, Greenhouse Gas Sci. Technol., 2, 1–18.

McGillivray A., Wilday J., 2009. Comparison of risks from carbon dioxide and natural gas pipelines, Health and Safety Laboratory, Health and Safety Executive, HSE Books, Sudbury, Suffolk, Research Report RR749.

Mohitpour M., et al. 2012. Pipeline Transportation of Carbon Dioxide Containing Impurities, ASME E-Book, DOI: 10.1115/1.859834.

Molaga M., Dam C., 2011. Modelling of accidental releases from a high pressure CO₂ pipelines, Energy Proc., 4, 2301–2307.

Morrow T. B., Bass R.L., Lock J.A., 1983. A LPG pipeline break flow model, J. Energy Res. Technol. 105 379–387.

NEB, 1998. National Engineering Board, Reasons for Decision, Souris Valley Pipeline Limited, MH-1-98, October, Calgary, Canada.

Neele, F., et al., 2010, Large-scale CCS transport and storage networks in North-west and Central Europe, GHGT-10.

Neurert U., 2011. Special considerations related to the quantitative risk assessment (QRA) of gas transmission pipelines, 3R International, Special Issue Pipeline Integrity,
http://www.ilf.com/fileadmin/user_upload/publikationen/3R_Special-Edition-1-2011_Editorial_CO2_QRA_AHF_Kaufmann_Neunert.pdf

NRC. 1989. Improving Risk Communication, National Academies Press, Washington, D.C.

NRC. 2003. Alerting America: Effective Risk Communication—Summary of a Forum, October 31, 2002. National Academies Press, Washington, D.C.

Nyman D. J., et al. 2004. Task 3: Assess Carbon Dioxide Transportation Options in the Illinois Basin, U.S. DOE Contract: DE-FC26-03NT41994, October 1, 2003–September 30, 2004.

PHMSA, 2010. The State of the National Pipeline Infrastructure, U.S. Department of Transportation,

http://opsweb.phmsa.dot.gov/pipelineforum/docs/Secretarys%20Infrastructure%20Report_Revised%20per%20PHC_103111.pdf

Seiersten, M., Kongshaug, K.O., 2005. Materials selection for capture, compression, transport and injection of CO₂. In: Thomas, D.C., Benson, S.M. (Eds.), Carbon Dioxide Capture for Storage in Deep Geologic Formations, vol. 2. Elsevier Ltd., Oxford, UK, pp. 937–953.

Serpa, J., Morbee, J., Tzimas, E., 2011. Technical and Economic Characteristics of a CO₂ Transmission Pipeline Infrastructure, EUR 24731 EN.

Snyder S., et al., 2008. Canada's Fossil Energy Future: The Way Forward on Carbon Capture and Storage Report to: The Minister of Alberta Energy and The Minister of Natural Resources Canada.

<http://www.nrcan.gc.ca/sites/www.nrcan.gc.ca/files/pdf/com/ressources/publications/fosfos/fosfos-eng.pdf>

TetraTech, 2007. Final Risk Assessment Report for the FutureGen Project Environmental Impact Statement. Lafayette, CA, USA,

Trabucchi C., et al., 2012. Valuation of Human Health and Ecological Risks Arising from Carbon Capture and Storage (CCS) Final Study Observations, Industrial Economics, Incorporated, Unpublished Report.

Turner, R., Hardy, N., Hooper, B., 2006. Quantifying the risks to the public associated with a CO₂ sequestration pipeline: a methodology & case study, in: Greenhouse Gas Cont. Tech., 8, Trondheim.

URS, 2009. Carbon Dioxide Pipeline Risk Analysis, HECA Project Site Kern County, California, Appendix E. Prepared for Hydrogen Energy International LLC, Long Beach, CA. http://www.energy.ca.gov/sitingcases/hydrogen_energy/documents/08-AFC-8/applicant/revised_afc/Volume_II/Appendix%20E.pdf

Vendrig, M., Spouge, J., Bird, A., Daycock, J., Johnsen, O., 2003. Risk analysis of the geological sequestration of carbon dioxide, in: Department of Trade and Industry's Cleaner Coal Tech Transfer Programme, DNV Consulting, London, Report R246 DTI/Pub URN 03/1320.

Vianello, C., Macchietto, S., Giuseppe Maschioa G., 2012, Conceptual Models for CO₂ Release and Risk Assessment: a Review, CHEMICAL ENGINEERING TRANSACTIONS VOL. 26, 573-578

Wade S., Trabucchi C., 2009. Understanding Potential GS Risk: A Multi-Disciplinary Framework to Foster Responsible Stewardship, Energy Proc. 1 (2009) 4567–4573.

Wang H., Duncan I. J., 2013. Likelihood, Causes and Consequences of Focused Leakage and Rupture of US Natural Gas Transmission Pipelines,

Section 10: Evaluating the Likelihood of Pipeline Failures for Future Offshore CO₂ Sequestration Projects

Introduction

Although the only operational commercial geologic storage projects in the world are Statoil's Sleipner (Hermanrud et al., 2009) and Snohvit projects, in the offshore North Sea, a number of countries are exploring possible offshore CO₂ sequestration projects. In Europe there is a strong interest in using North Sea brine reservoirs for sequestration (Chadwick et al., 2004; Lu et al., 2009). Recently McGillivray and Wilday (2009) asserted that all carbon capture and storage (CCS) projects (presumably in the United Kingdom) "are likely to involve onshore CO₂ capture, transport by pipeline and storage in an offshore storage facility". Recently ICF (2012) has made an assessment of the offshore sequestration potential the Atlantic, Gulf, and Pacific coasts of the U.S. They note that the largest potential is in the Gulf of Mexico because the Gulf has a wide shelf area less than 200 meters in water depth. They also note that most of the sequestration potential is in saline reservoirs, with some potential in depleted oil fields. Similarly, Brown et al. (2011) have made a preliminary assessment of CO₂ storage potential of the U.S.'s Atlantic Outer Continental Shelf. In Australia, offshore Victoria is being actively evaluated for possible sequestration projects (O'Brien et al., 2008). There is also a growing interest in offshore CO₂ sequestration in South East Asia, which has large gas reserves with high CO₂ content. These reserves are becoming economically viable as gas demand increases and new technologies become available for CO₂ separation (Shimekit and Mukhtar, 2012). For onshore CO₂ pipelines the consensus has been that pipeline transportation will be the highest risk aspect of CO₂ sequestration projects (Duncan and Wang, 2014). Thus far there have been little if any published quantitative evaluations of the risks that would be associated with future offshore sequestration.

Although they are rightly regarded as a relatively safe technology for the transport of both natural gas and CO₂, offshore natural gas pipelines have been associated with several disastrous accidents. The explosion of the Piper Alpha production platform in the North Sea in July 1988 cost 167 lives, the worst offshore accident in history. It was the natural gas from subsea pipelines

that caused the massive explosions leading to the catastrophic failure of the platform (Dhar, 2009). Such fatal incidents have focused public attention on the safety of offshore pipelines. This study was motivated in part by the observation that the annual rate of serious incidents associated with offshore natural gas pipelines had increased substantially over the decade from 2000 to 2009. This increase has raised the specter that an increased likelihood of failure may reflect an increased risk of fatalities. All of this also raises concerns regarding the safety of future offshore CO₂ pipelines constructed for sequestration projects.

Pipelines are the most economic means of large-scale transportation of natural gas and CO₂ (Lin et al., 2005; Thomas and Dawe, 2003). Globally Hopkins (2007) has estimated that 8,000 km of offshore natural gas and oil pipelines are being built per year. Because of the hostile corrosive sub-sea environment and the limited time span of production from offshore reservoirs, there is a continual process of building new offshore pipelines and decommissioning old ones. By the end of 2009, the length of offshore gas gathering and gas transmission pipelines in the offshore U.S. was 10,476 and 8,974 km, respectively. Gathering pipelines are generally run from production sites to centralized platforms, where the gas is processed and transmission pipelines carry the gas to the shore. Offshore natural gas pipelines in the North Sea range in diameter from 4 to 46 inches with modes at 24, 36 and 42 inches (OGUK, 2013). The current onshore CO₂ pipeline networks have a similar range in diameters (Duncan et al., 2009).

It has been projected that the demand for offshore CO₂ pipelines in the North Sea alone by 2050 may be nearly the same order of magnitude of length as the current offshore natural gas transmission pipeline system in the US. Neele et al. (2011) predict that as many as 32,000 km of pipeline may have to be built in their “offshore sequestration” scenario. Another study has suggested that the offshore option would require a “massive pipeline infrastructure” to be built by 2050 “adding up to a network of up to 15,900 km in 2050” (Mendelievitch et al., 2010). Neither report shows the portion of pipelines that are projected to be offshore, however the maps of pipeline routes presented in Neele et al. (2011) can be used to infer that 20 to 30% of the pipelines will be offshore. Most of these pipelines would be in relatively near to shore parts of the North Sea.

Installation of offshore pipeline can result in welded joins being stressed due to the mechanics of laying pipelines from lay barges. This becomes increasingly important as water depth increases. Offshore pipelines are typically constructed from pipe that has already been coated for corrosion protection and is often coated with concrete to provide negative buoyancy and to minimize physical damages during its installation (Kennedy, 1993). For both CO₂ and natural gas pipelines external and internal corrosion of the pipeline metal is a concern for safety. Mandke (1990) concluded that, based on data from prior to 1990, that corrosion caused “most [natural gas] pipeline failures in Gulf of Mexico”. When water dissolved in supercritical CO₂ saturates, it forms an aqueous phase containing corrosive carbonic acid (Sim et al, 2013).

Risk can be defined as the product of the likelihood of an unintended event occurring and the severity of the consequences of such an event. The acceptability of the risk can be assessed by evaluating the risks that individuals knowingly take-on (Dawotola et al., 2012). In practice in acceptable risk levels in many countries (the US being an exception) are set by government agencies. For example in the United Kingdom the Health Safety Executive (HSE, 2001) set a fatality rate of 10⁻⁶ per year as “broadly acceptable” whereas a fatality rate of greater than 10⁻⁴ per year is unacceptable.

Although there are about 6,000 km of CO₂ transmission pipelines installed onshore there has never been a significant injury or a fatality associated with this network (Duncan et al. 2009). As a result the consensus of risk analysis studies is that the track record of CO₂ pipelines is an inadequate basis for estimating risk. In the place of data from CO₂ pipelines most risk studies have used risk estimates from natural gas transmission pipelines. The use of safety record of natural gas pipelines as an analogue for future CO₂ pipelines is mainly based on the following observations:

- 1) Both utilize the same grades of carbon steel (typically API 5 X 55 to X70 or higher; Spinelli and Prandl, 2012)
- 2) Both are welded and installed using the same techniques (Akselsen et al., 2010; Demofonti and Spinelli, 2011).

- 3) Both use the same or similar internal and external coatings (Sorensen et al., 2009), although internal coatings are rarely used in practice.
- 4) Both are subject to the same corrosion issues related to formation of carbonic and other acids (such as sulfuric, and nitric) when the transported gas is not adequately dehydrated and contains CO₂, H₂S, NO₂ or other acid forming constituents (Hellevink and Langen, 2000; Nesic, 2007; Yahaya et al., 2009; Sim et al, 2013).
- 5) Both use the same types of cathodic protection to mitigate external corrosion

In addition, in the U.S. (and in many other jurisdictions) both pipelines are constructed according to the same ASME design code (Duncan and Wang, 2014). One of the main aspects of the ASME design code is a requirement that as the maximum internal design pressure increases (at a given pipeline diameter) the minimum wall thickness increases (Goodfellow and Haswell, 2006). In addition the minimum wall thickness must increase with increasing pipeline diameter. The requirements for natural gas and CO₂ pipelines however are not identical and Demofonti and Spinelli (2011) have provided a well-documented analysis of the key differences. For example they note that impurities likely to be found in anthropogenic CCS CO₂ streams could increase likelihood of stress corrosion cracking. They also note that “more stringent [temperature] requirements” are needed for welds “in anthropogenic CO₂ pipeline compared to those in natural gas pipelines”.

The majority of the studies on risk analysis of future CO₂ pipelines have implicitly assumed that the incident rate for natural gas transmission pipelines can be directly used as estimates for the risk of CO₂ pipelines (Koornneef et al., 2010; Duncan and Wang, 2014). Unfortunately, as demonstrated by Duncan and Wang (in press) the incident rates for natural gas pipelines, in some cases at least, are not correlated with the injury or fatality rates.

This paper is based on information from a detailed database on natural gas pipeline incidents that the U.S. Pipeline and Hazardous Materials Safety Administration (PHMSA) has made available. The objectives of this paper are to: (1) provide a basis for predicting the likelihood of incidents associated with future offshore CO₂ pipeline networks; (2) gain a better understanding of the probability of failure in offshore natural gas gathering and transmission pipelines using incident

data collected in the United States from 1990 through 2009; (3) examine the relative importance of the factors that cause pipeline failure; and (4) assess the consequences of pipeline failure with respect to property damage, fatality/injury rate, and volume of natural gas released. This paper does not attempt to evaluate environmental risks associated with future CO₂ pipeline networks as such an analysis will be published separately. The data and analysis presented below provides part of what is needed to quantify the risks associated with a future offshore CO₂ pipeline network but it does predict the risk. Understanding the risks associated with future offshore CO₂ pipeline networks is a significant challenge and this study is a first step towards evaluating them.

1. Methodology

Offshore natural gas pipelines are monitored for leaks using several approaches including: (1) visual inspection from helicopter or seaplanes routinely overflying the pipeline route for indication of a release; (2) monitoring using pressure sensors at both ends of the pipeline (leak detection is based on the pipeline pressure drops below expected values); and (3) using flow meters to measure the volume dispatched versus the volume received in the pipeline (flow rate monitoring is typically carried out by computer and can be combined with pressure analysis). Internal testing for extent of corrosion using ultra-sonic probes (Zhang et al., 2008) and calipers can be used to assess pipeline integrity. Remotely operated vehicles (ROVs) are sometimes used for: external ultra-sonic monitoring (Jeppesen et al., 2005); to identify the nature of leakage incidents; and to carry out repairs. In the future pipeline monitoring will likely be accomplished through wireless connected sensor networks (Mohamed et al., 2011). PHMSA, has maintained a database of such incidents in the offshore US since 1990 (U.S. Department of Transportation, 2013). This data comes primarily from the Gulf of Mexico (offshore Texas, Louisiana, Mississippi, and Alabama), which has the vast majority of offshore gas pipelines in the US with a minor number of data coming from offshore California. The PHMSA data base classifies pipeline incidents as significant (defined as those incidents that caused >\$50,000 in damage or led to fatality or injury requiring in-patient hospitalization) or non-significant. Three types of failure are defined by PHMSA: leaks, ruptures, and system-component failures. A *leak* refers to a pinhole or puncture failure. A *rupture* is a longitudinal or circumferential crack that results in a gas leak. *System-component failures* are defined as any malfunction of valves, failure of

mechanical joints, breaks in fittings, or flaws in compressors. The data base has useful information on the length of ruptures and the diameter of punctures where these were the failure type for a particular incident. The database is limited in three ways: (1) information about installation years of incident pipelines is incomplete, (2) subsea risers (vertical pipeline segments attached to platforms) have not been distinguished from pipelines, and (3) indirect cost associated with pollution of the environment is not included in the database.

Following investigations by the pipeline operator and/or PHMSA, failures of natural gas pipelines have been attributed in the PHMSA database to a number of causes, such as (1) internal corrosion, (2) external corrosion, (3) outside forces, or (4) defects in construction or materials. The magnitude of the consequences of a natural gas pipeline failure can be seen as a combination of three aspects: (1) human impact—number of people injured or killed, (2) property damage caused by the incident, and (3) released volume of natural gas.

Offshore gathering and transmission pipelines are the two subgroups. The frequency of occurrence of different failure modes for each subgroup can be calculated as

$$f_{i,j,k} = \frac{N_{i,j,k}}{L_{j,k}}, \quad (1)$$

where $f_{i,j,k}$ is the rate of failures with a certain failing mode ($i=1, 2, 3$) for subgroup j ($j=1, 2$) for year k ($k=1990, 1991, \dots, 2009$), $N_{i,j,k}$ is number of incidents of a certain failure mode ($i=1, 2, 3$) for subgroup j ($j=1, 2$) for year k ($k=1990, 1991, \dots, 2009$), and $L_{j,k}$ is pipeline length for subgroup j ($j=1, 2$) for year k ($k=1990, 1991, \dots, 2009$).

An important aspect of natural gas pipeline incidents is the volume of natural gas lost. PHMSA started collecting releases gas volume from 2010. Although such information is not recorded for the years 2002-2009 in the dataset, it can be estimated based using the value of lost natural gas and natural gas price at the time of pipeline incidents.

$$Q_{s,j} = \frac{L_{s,j}}{P_{s,j}} \dots (2)$$

Where $Q_{s,j}$ is estimated releases of natural gas in the s th incident in the year j ($j = 2002, 2003, \dots, 2009$); $L_{s,j}$ represents value-property damage in an individual incident and $P_{s,j}$ denotes price of natural gas at the specific month of incident. The validity of this approach has been checked by applying this approach to recent data from 2010 to 2012 where actual natural gas losses are available in the data base. Comparing the PHMSA data from 2010 to 2012 with estimates using equation 2 above shows good agreement with a few exceptions (Figure S1).

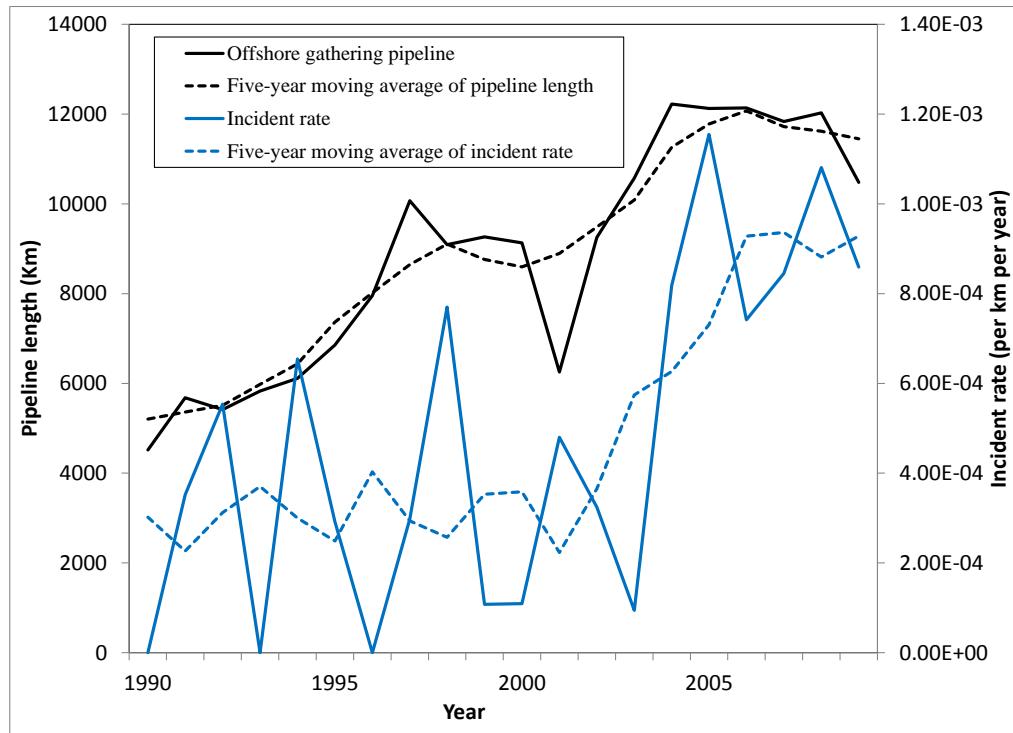
Note that such estimates are not provided for the period 1990-2001 because PHMSA doesn't have any information related to gas loss for incidents occurred in these years.

Considering limited data used in this analysis, the 95% confidence interval of fatality/injury rate is calculated (Ulm, 1990) with the assumption that the number of fatalities/injuries over the study period follows Poisson distribution. Statistical test (Sashi and Kurshid, 1996) is employed to compare fatality/injury rate between onshore gathering pipelines and onshore transmission pipelines. Detailed description of statistical methods and illustrative examples are provided in supplemental material.

2. Results and Analysis

3.1 Failure Rates

Records of pipeline failures and information on the causes of the failures are by far the largest risk-related dataset available for any pipeline system. In offshore gathering pipelines, among the 92 significant incidents recorded during 1990–2009, 59 were leakage incidents (64% of the total) and 15 were rupture incidents (16%). Among 254 significant incidents in offshore transmission pipelines during the same period, 144 were leakage incidents (57% of the total) and 43 were rupture incidents (17%). The remaining incidents, including weld, joint, and valve failures, were system-component failures.



(a)

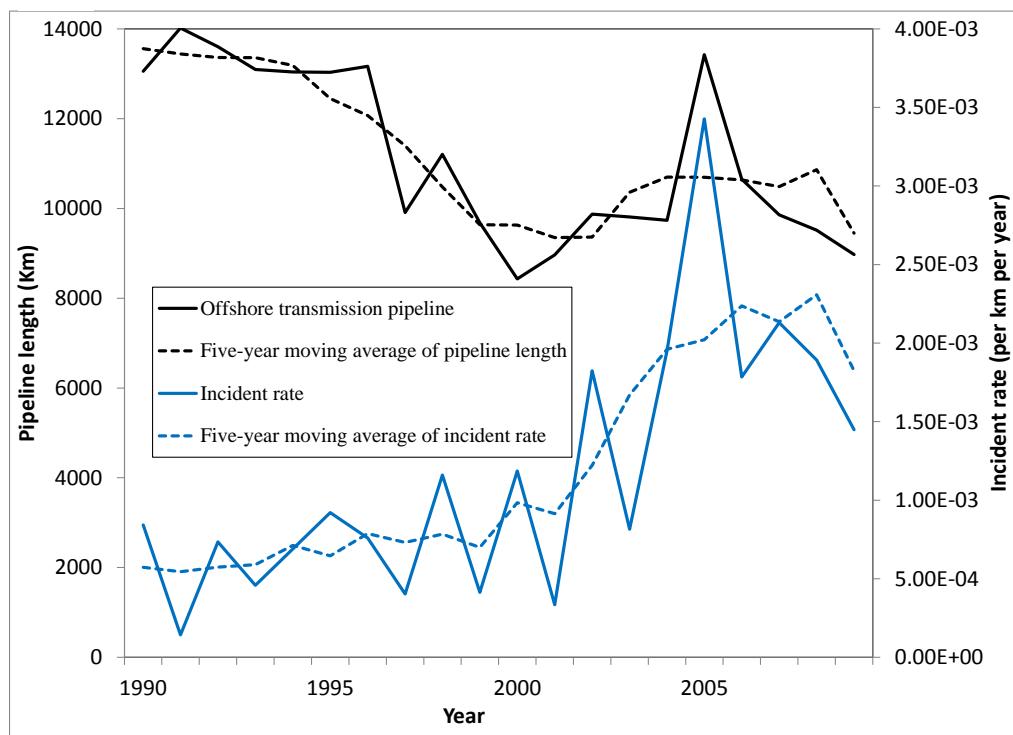


Figure 1: (a) Annual length and failure rate of offshore gathering pipelines over the period 1990–2009; 5-year moving average of pipeline length and failure rates also shown as dashed lines. (b) Annual length and failure rate of offshore transmission pipelines over the period 1990–2009; 5-year moving average of pipeline length and failure rates also shown as dashed lines. Note that there is an increasing trend of failure rate for both gathering and transmission pipelines. The spike in 2005 is related to Hurricane Katrina.

An upward trend in the normalized incident rate can be discerned (Figure 1a, b) in both offshore natural gas gathering and transmission pipelines. For instance, the total rate of serious failures of offshore natural gas gathering pipelines increased from 0 incidents per kilometer per year in 1990 to 8.6×10^{-4} incidents per $\text{km} \cdot \text{yr}$ in 2009.

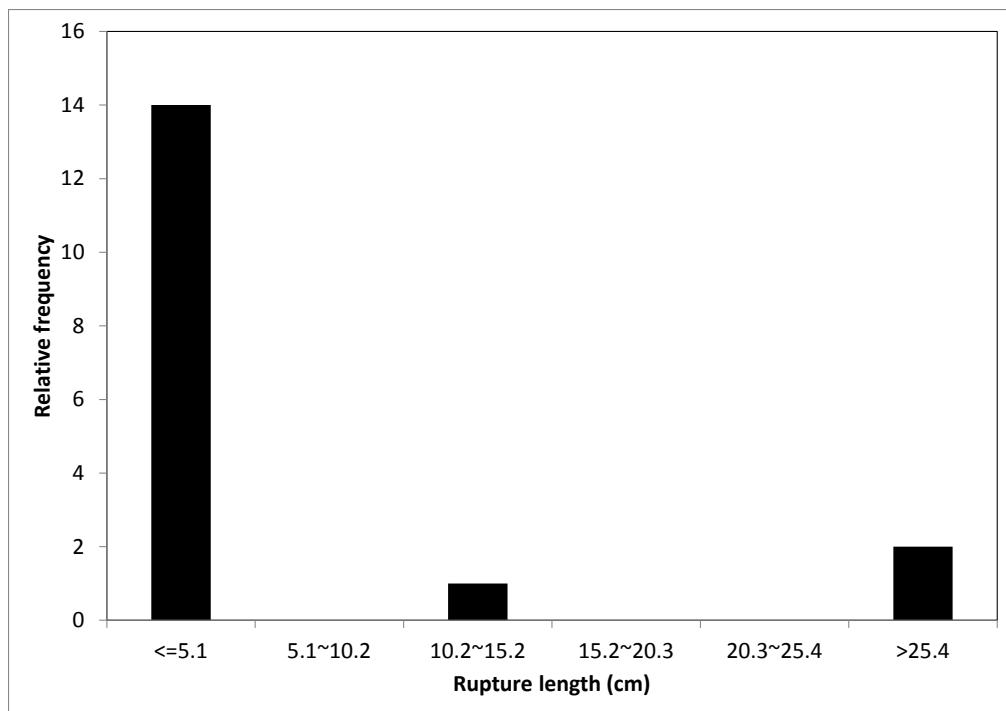
Table 1: Normalized failure rates of different types of failure mode, as well as total failure rates for different segment of natural pipeline system. The numbers shown in the brackets denote the 95% confidence interval.

Failure rate (per km per year)	Onshore transmission	Offshore transmission	Onshore gathering	Offshore gathering
Leak	2.7×10^{-5}	6.5×10^{-4}	2.3×10^{-5}	3.4×10^{-4}
Rupture	3.2×10^{-5}	1.9×10^{-4}	8.7×10^{-6}	8.5×10^{-5}
System- component failure				
	3.1×10^{-5}	3.1×10^{-4}	1.9×10^{-5}	1.1×10^{-4}
Average of failure rate between 1990 and 2009				
	9.0×10^{-5}	1.1×10^{-3}	5.1×10^{-5}	5.4×10^{-4}
Average of failure rate between 1990 and 2000				
	7.2×10^{-5}	0.7×10^{-3}	3.2×10^{-5}	2.9×10^{-4}

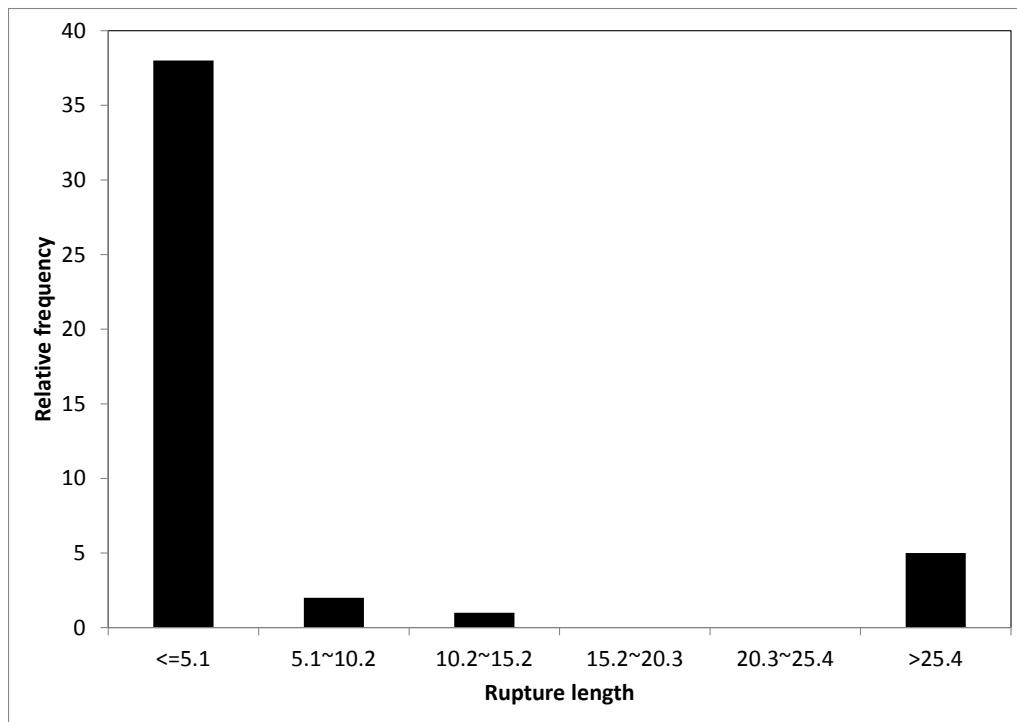
Offshore pipelines have higher total-failure rates than onshore pipelines by at least one order of magnitude (Table 1). For example, offshore natural gas transmission pipes have higher total-failure rate, 1.15×10^{-3} incidents per $\text{km} \cdot \text{yr}$. The larger failure rate of offshore transmission

pipelines can be partly explained by the fact that offshore pipeline systems are often more vulnerable to weather-related outages, even when no damage to equipment occurs (Muhlbauer, 2004).

Pipeline ruptures are of concern because they can result in much larger gas releases than punctures. We found that 82% of ruptures are <5.1 cm long and 12% are >25.4 cm long (Fig. 2a) in offshore gathering pipes. About 83% of ruptures are <5.1 cm and 11% of ruptures are >25.4 cm long (Fig. 2b) in offshore transmission pipes. The relative rates of incidents involving a rupture > 25.4 cm (10 inches) long are estimated at 1.1×10^{-5} per km • yr and 2.2×10^{-5} per km • yr in onshore gathering and transmission pipelines; for ruptures >5.1 cm (2 inches) long, the rate is 7.9×10^{-5} per km • yr and 1.7×10^{-4} per km • yr in offshore gathering and transmission pipelines, respectively.



(a)



(b)

Figure 2: (a) Histogram of rupture size for significant incidents in offshore gathering pipelines; >10 bin includes some incidents in which ruptures exceed 10 inches. (b) Histogram of rupture size for significant incidents in offshore transmission pipelines; >10 bin includes some incidents in which ruptures exceed 10 inches. It is observed that most rupture length is less than 5.1 cm.

To study significant incidents as a function of pipeline diameter, we examined failure rates in five categories of pipelines having diameters of (1) $D \leq 10.2\text{cm}$, (2) $10.2\text{ cm} < D \leq 25.4\text{ cm}$, (3) $25.4\text{ cm} < D < 50.8\text{ cm}$, (4) $50.8\text{ cm} < D \leq 71.1\text{ cm}$, and (5) $D > 71.1\text{cm}$ (Fig. 3). The total failure rate was 2×10^{-3} per $\text{km} \cdot \text{yr}$ in pipelines $< 10.2\text{cm}$ in diameter, whereas it was 5.0×10^{-4} per $\text{km} \cdot \text{yr}$ in pipelines having diameters between 50.8 (20 inches) and 71.1cm (28 inches). The failure rate of pipelines having diameters $\leq 10.2\text{ cm}$ (4 inches) is four times higher than that of pipelines having diameters $> 71.1\text{ cm}$ (28 inches).

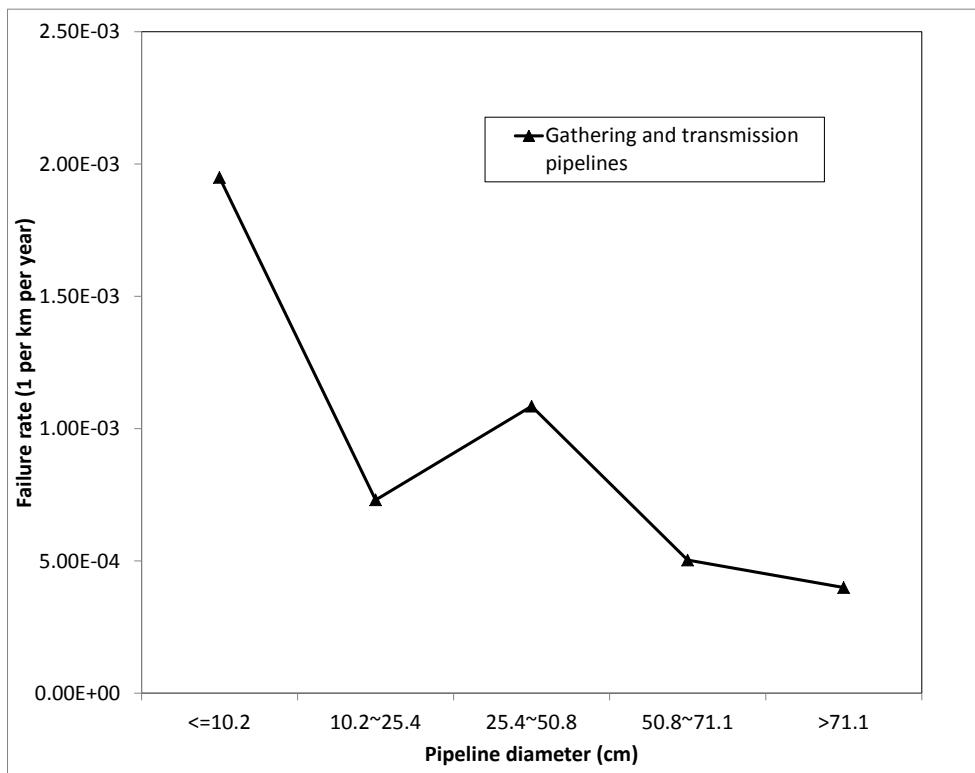
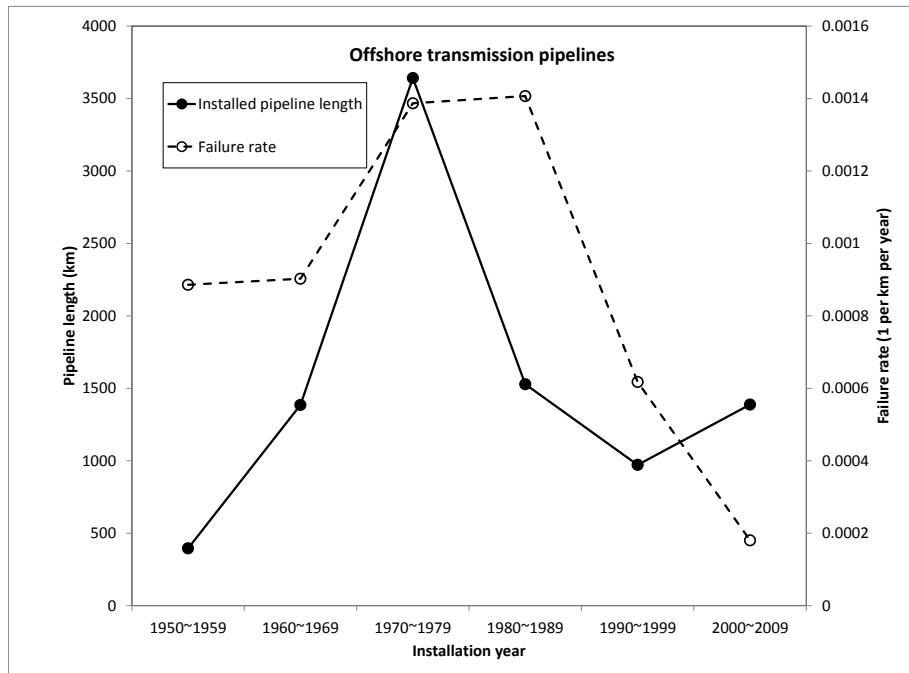


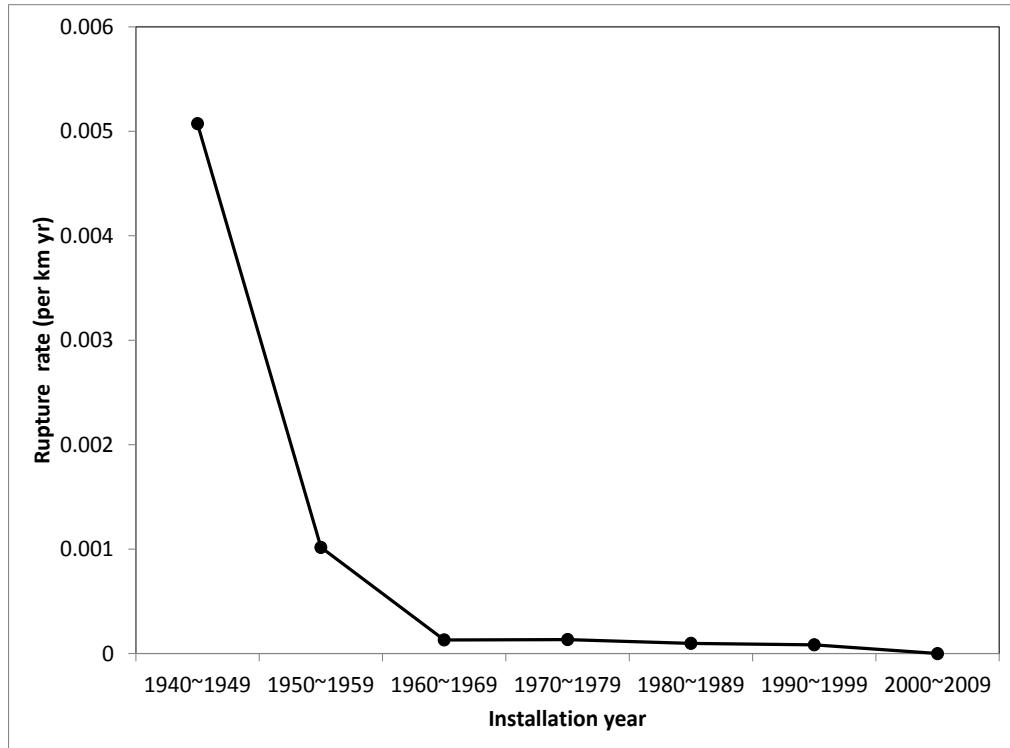
Figure 3: Distance-normalized failure rate for offshore gathering and transmission pipelines with different diameters based on incident records in offshore gathering and transmission pipelines during the period 1990–2009. It is observed that pipelines with diameter over 71.1 cm have the smallest failure rate.

To examine the impact of pipeline age on failure rates, we normalized the number of incidents by the cumulative length of pipeline installed in particular time periods. However, for offshore gathering pipes, installation-year data were missing for 40% (37 out of 92) of incidents. Therefore, we present results only from offshore transmission pipes. For pipelines installed in the 1950's, the failure rate was 8.0×10^{-4} incident per km •yr, contrasting with a rate ranging from 2.0×10^{-4} to 6.0×10^{-4} per km •yr in pipelines installed in the 1990's and 2000's (Fig. 4a). Figure 4b shows the rate of failure by rupture for pipeline segments with different installation ages. It is

interesting to note that the overall failure rates and rupture rates have a distinctly different relationship to the age of pipeline segments. The failure rates for pipelines increase with installation years from 2009 to the 1990s reaching a maximum in pipelines in the age range 1970 to 1989. The rates then decrease in pipelines constructed prior to 1970 (as shown in Figure 4a). Note that as the failure rate decreases from the 1970s to the 1950s the length of installed pipeline decreases substantially as shown in the Figure 4a. The increase in failure rate over the first few decades after a pipeline is installed is understandable as the design life of pipelines is typically 30 years. The correlation between the decrease in failure rate in older pipelines from 1950s and 1960s and the dramatic decrease in installed length, suggests that the most plausible explanation is survival of the fittest. It is not obvious why the rupture rate for pipeline segments of different ages varies in such a different way to that for total failure rates. The rupture rates decrease rapidly from a high of 5.0×10^{-3} per km •yr for pipelines from the 1940s to zero for pipelines constructed in the decade 2000 to 2009 (Fig. 4b).



(a)



(b)

Figure 4: (a) Length of offshore transmission pipelines installed in different decades and normalized failure rate for them during the period 1990–2009. Note that failure rates for pipelines installed during 1970s and 1980s are even higher than those installed in 1950s. This can be partially explained by the fact that design life of pipelines is often quoted 30 years. Hence, those from 1970s and 1980s exhibit the highest failure rate during the period 1990-2009. (b) Normalized rupture rate for offshore pipelines installed in different years. Rupture rate for pipelines installed in 1940s and 1950s is significantly higher than that of pipelines installed in later years.

3.2 Failure causes

The National Research Council (NRC) report on the safety of marine pipelines suggested that “reported causes of failures are not reliable” (NRC, 1994). They suggested that reported causes “are often determined by guesswork, without complete investigation”. Another issue is that causes are unlikely to fall neatly into distinct categories. Rather multiple linked causes are likely. A pipeline whose walls have been thinned by corrosion is ruptured by anchor damage, will likely as a failure caused by outside force rather by corrosion. Woodson (1991) noted that failures ascribed to corrosion are typically less for some time after a major storm. Both the critiques of Woodson (1991) and NRC (1994) largely refer to data collected prior to PHMSA being tasked to take over offshore pipeline regulation, with a mandate to improve such issues. Although PHMSA has done much to improve quality control and the accuracy of their data base information, much more could be done. For example in a review of their quality improvement efforts Kowalski (2009) noted that in 2008 PHMSA completed only 19 investigations of the 664 reported pipeline incidents (onshore and offshore) that occurred that year. Thus for the vast majority of incidents PHMSA relies on self-reporting by the companies. Given these caveats this section reviews the trends that are apparent in causes of failure recorded in the PHMSA data set.

Normalized failure rates for each failure mode, such as leakage, rupture, and system-component failure, are shown in Table 2. Construction/material defects are interpreted to be the primary

cause of failure in both gathering and transmission pipes. For example, 76% of leaks (45 out of 59) occurring in gathering pipes and 60% (86 out of 144) occurring in transmission pipes were caused by construction and material defects. Ruptures, occurring in gathering and transmission pipelines, were caused primarily by outside forces, which contributed to 87% (13 out of 15) of ruptures in gathering pipes and 81% (35 out of 43) of ruptures in offshore transmission pipes. System component failures are caused primarily by outside forces and construction/material defects in both gathering and transmission pipes.

Normalized rates of specific causes, particularly those related to construction/material defects, outside forces, and internal corrosion were significantly higher in offshore transmission pipelines than those in onshore transmission pipelines (Fig. 5). This difference undoubtedly reflects both the more complicated process of laying offshore pipe and the more dynamic nature of the seafloor environment.

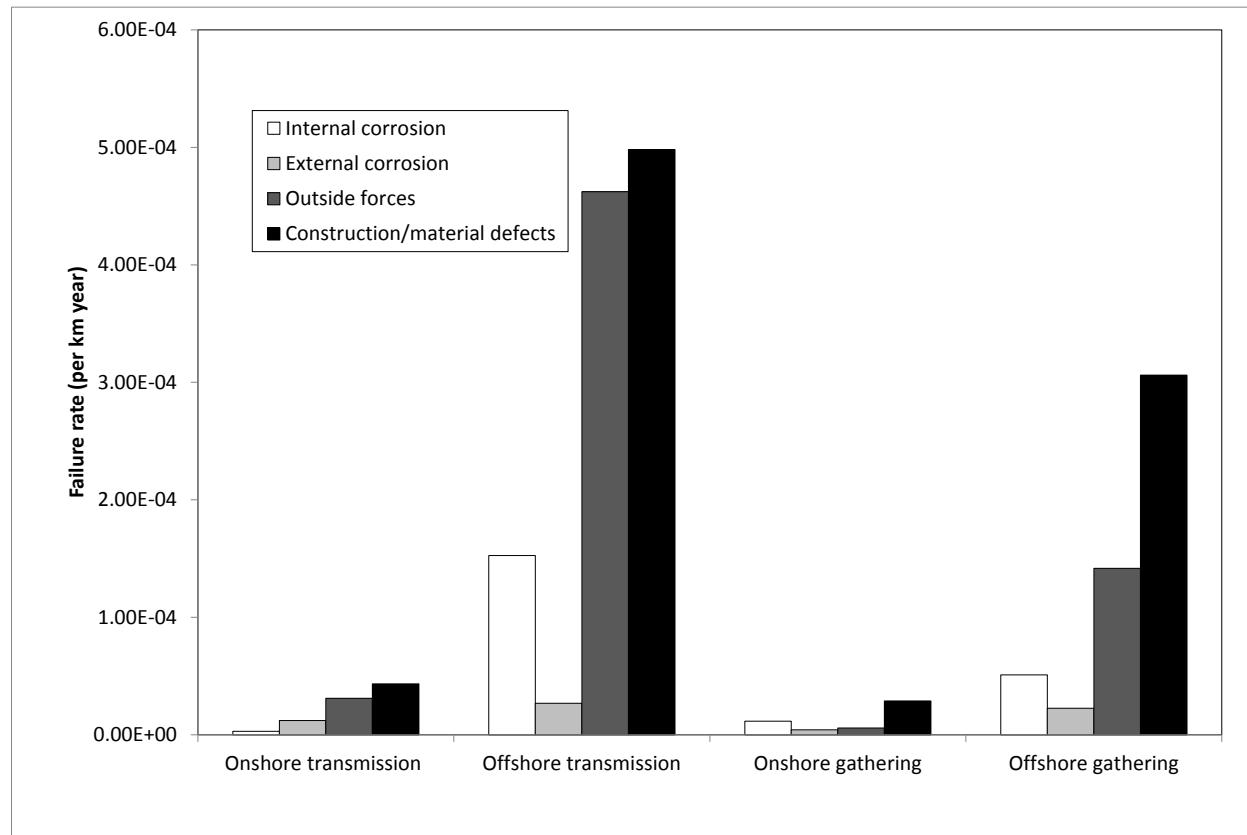


Figure 5: Comparison of normalized failure rates by different causes among four segments of natural gas pipelines: onshore transmission pipes, offshore transmission pipes, onshore gathering pipes, and offshore gathering pipes. Offshore transmission and gathering pipes have larger failure rates than onshore pipelines. Construction/material defects and outside forces are the two primary factors for offshore pipes.

		Internal corrosion	External corrosion	Outside forces	Component failure
Onshore transmission pipelines	Leakage	6.4×10^{-7}	4.0×10^{-6}	8.3×10^{-6}	1.4×10^{-5}
	Rupture	2.2×10^{-6}	8.0×10^{-6}	1.2×10^{-5}	9.3×10^{-6}
	System failure	1.1×10^{-7}	1.0×10^{-7}	1.0×10^{-5}	1.9×10^{-5}
Offshore transmission pipelines		Internal corrosion	External corrosion	Outside forces	Component failure
	Leakage	1.5×10^{-4}	2.7×10^{-5}	8.5×10^{-5}	3.9×10^{-4}
	Rupture	4.5×10^{-6}	0	1.6×10^{-4}	3.1×10^{-5}
Onshore gathering pipelines	System failure	0	0	2.2×10^{-4}	8.1×10^{-5}
		Internal corrosion	External corrosion	Outside forces	Component failure
	Leakage	1.0×10^{-5}	4.3×10^{-6}	0	8.7×10^{-6}
Offshore gathering pipelines	Rupture	1.4×10^{-6}	0	0	7.2×10^{-6}
	System failure	0	0	5.81×10^{-6}	1.3×10^{-5}
		Internal corrosion	External corrosion	Outside forces	Component failure
Leakage		4.5×10^{-5}	2.3×10^{-5}	1.1×10^{-5}	2.6×10^{-4}
	Rupture	0	0	7.4×10^{-5}	1.1×10^{-5}

System failure	5.7×10^{-6}	0	5.7×10^{-5}	4.0×10^{-5}
-----------------------	----------------------	---	----------------------	----------------------

Table 2. Normalized failure rate related to different causes for each type of failing mode in onshore/offshore transmission/gathering pipelines, which is based on PHMSA 90/09.

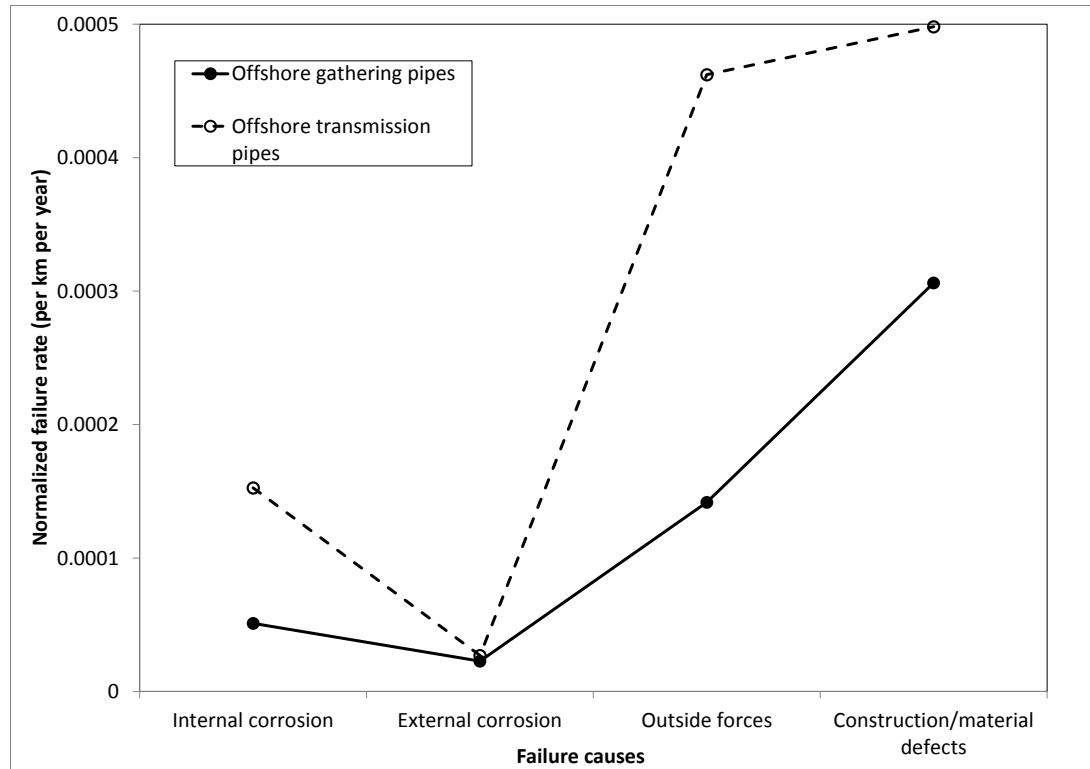


Figure 6: Normalized failure rate of different causes for offshore gathering and transmission pipelines based on significant incident records during 1990–2009. Except for external corrosion, offshore gathering pipes have larger normalized failure rate from all contributing factors, except external corrosion.

Figure 6 shows normalized failure rates of different mechanisms in both offshore gathering and transmission pipes. Except that the normalized rate of external corrosion is almost identical in both gathering and transmission pipes, all three other causes have a higher normalized failure rate in offshore transmission pipelines than those in offshore gathering pipelines. For instance, the failure rate of construction/material defects is nearly 5.0×10^{-4} per km • yr in offshore transmission pipelines, and it is 3.0×10^{-4} per km • yr in offshore gathering pipelines.

To investigate why the normalized failure rates of offshore transmission pipelines are higher than those of offshore gathering pipelines (Fig. 6), we examined the possible effects of pipeline age and operating pressure.

Average pipeline age was estimated on the basis of the length of pipelines installed in different years (Fig. 7). In offshore gathering pipelines, 63% are <30 years old; whereas 40% of offshore transmission pipeline segments are 30 years or younger. Because the design life of pipelines is often quoted as 30 years, this difference in pipeline-age distribution may partly explain the lower failure rates in offshore gathering pipelines.

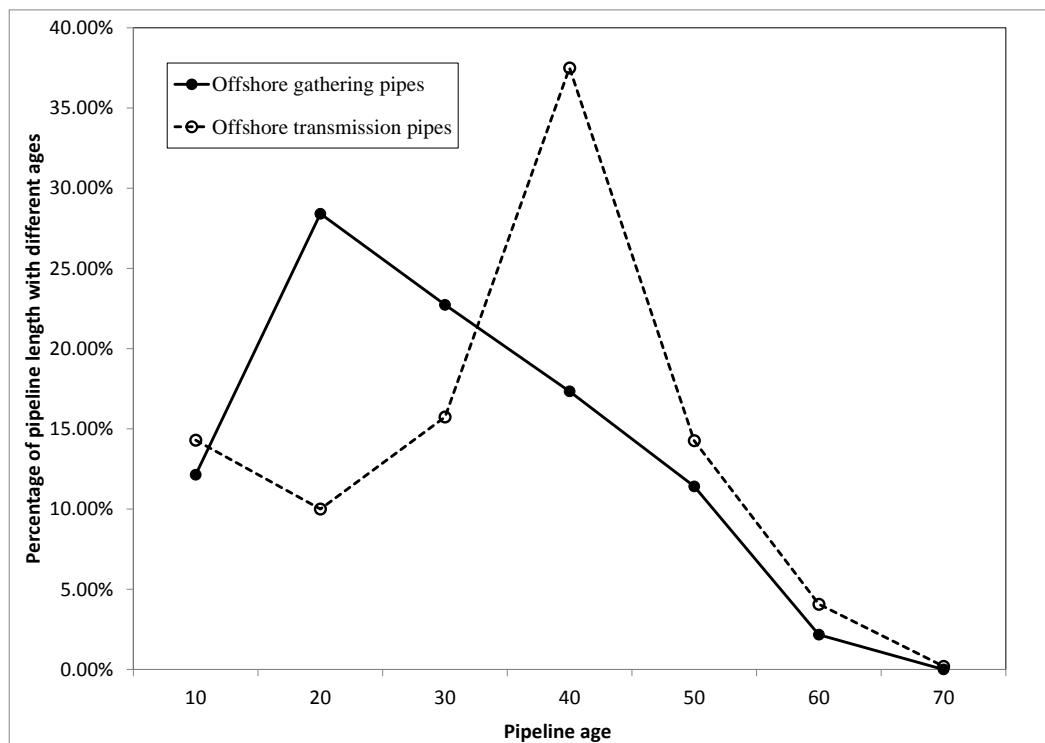


Figure 7: Percentage of segments of different pipe ages in offshore gathering and transmission pipelines. Note that average pipeline age for offshore gathering pipes is less than that for offshore transmission pipes. The average age for offshore gathering pipes is 28 years and for offshore transmission pipes is 33 years. This partially explains the difference in the failure rate between offshore gathering and transmission pipes.

Another key factor in controlling the variation in failure rates of offshore pipelines may be the operating pressure of the pipeline at the time of failure. Pipelines are often operated at pressures less than their maximum allowable operating pressure (MAOP) either because volumes being transported are lower, or the pipeline is being operated at a lower pressure as part of risk mitigation. The PHMSA database includes the operating pressure of the pipeline at the time of the incident, which is generally a fraction of MAOP. If a pipeline has been thinned by either internal or external corrosion and is operating at a high fraction of MAOP, the wall of the pipeline might be vulnerable to failure. The ratio of operating pressure to MAOP was calculated in offshore gathering pipelines and transmission pipelines (Fig. 8). The median ratio in offshore gathering pipelines was 0.66, compared with 0.77 in offshore transmission pipelines.

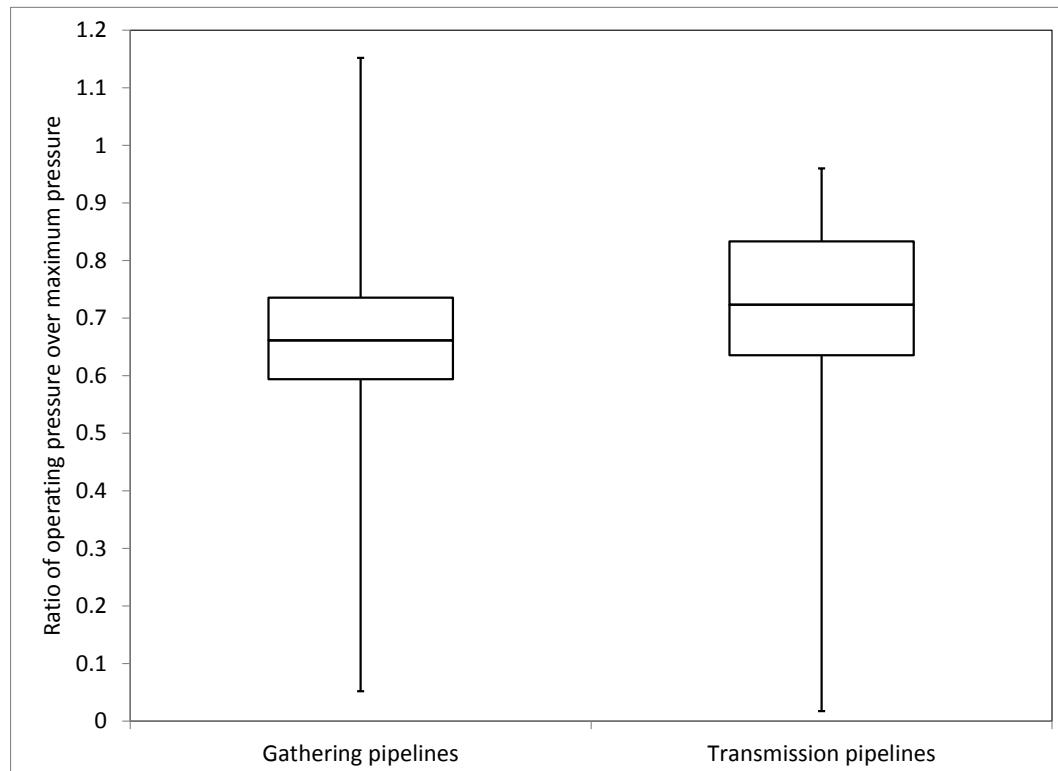


Figure 8: Box plots of ratio between operating pressure and maximum allowable operating pressure (MAOP) for offshore gathering pipeline and offshore transmission pipelines based on incidents in 1990–2009. The median of the ratio for offshore gathering pipelines is 0.66 and it is 0.72 for offshore transmission pipelines.

3.3 Pipeline Wall Thickness at Failure

An important aspect of designing pipeline for safety is the thickness of the wall of the pipeline. The ASME code specifies wall thickness depending on the diameter of the pipeline and the desired maximum operating pressure. It would be very useful to know the impact of corrosion on failure through information on the wall thickness of pipelines at failure. Unfortunately such data is extremely rare for onshore pipelines and does not appear to be available at all for offshore

pipelines. What is recorded in the PHMSA data base is the nominal (or installed) pipeline thickness of segment that fails. The available data is shown in Figure 9 as a function of pipeline diameter.

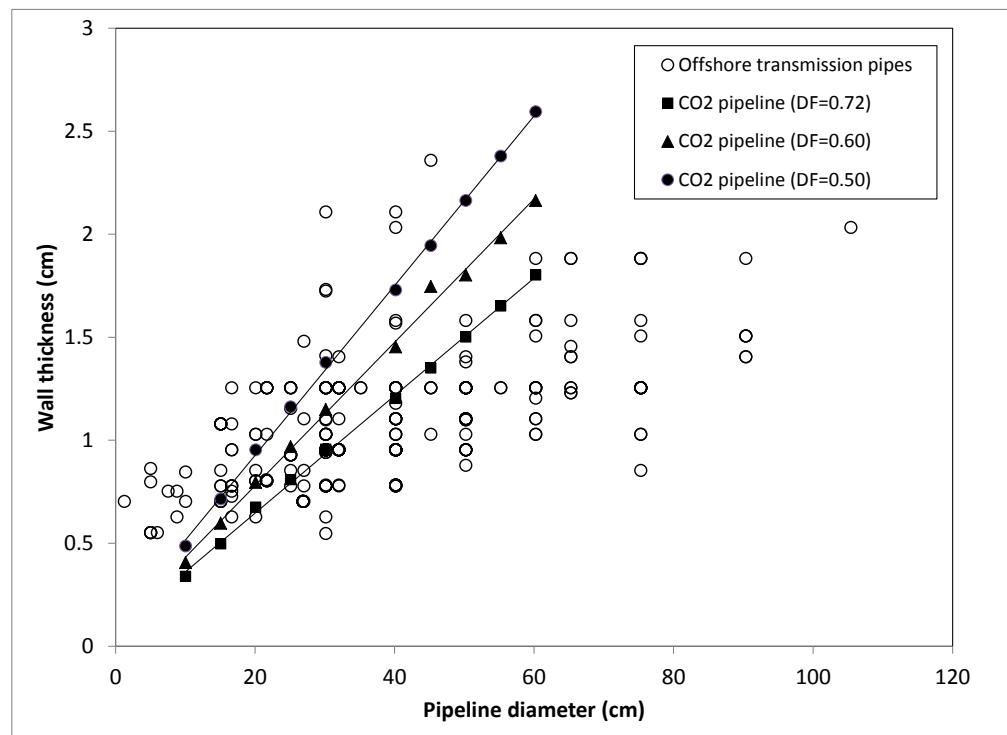


Figure 9: Scatter plot of pipeline diameter and wall thickness for failed pipelines. Black circles represent wall thickness for natural gas offshore transmission and gathering pipelines recorded in the PHMSA incident database. The other symbols represent wall thickness required by ASME B31.8 for CO₂ pipelines fabricated from grade X65 steel and operated under 2,800 psig (from Nyman et al., 2004) when different design factors (DF) are used.

3.4 Consequences

The following aspects of significant incidents are examined: (1) human impact (number of people injured or killed), (2) property damage associated with the incident, and (3) volume of natural gas released in the incident.

Injury and fatality rates of offshore gathering pipes and transmission pipes are distinctly different; however, this difference may exist because recurrence frequency is low (that is, the sample size is relatively small). From 1990 to 2009 2 fatalities and 9 serious injuries were recorded associated with offshore natural gas pipelines. Both 2 fatalities were associated with transmission pipeline failures. The 9 injuries were associated with failure offshore transmission pipelines. No injuries or fatalities were recorded for offshore gathering pipes from 1990 through 2009, and the associated injury/fatality rate was zero. Injury and fatality rates of offshore transmission pipelines were 3.45×10^{-5} per km • yr and 7.7×10^{-6} per km • yr, which were higher than those of offshore gathering pipelines. The 95% confidence interval of the estimated injury rate for onshore gathering pipelines is 1.8×10^{-5} to 7.7×10^{-5} per km • yr; whereas for the fatality rate for onshore pipelines, the uncertainty range is 1.1×10^{-6} to 3.2×10^{-5} per km • yr. Note that injury/fatality rates are dominated by rare but high-consequence incidents involving multiple injuries and/or fatalities. For instance, only two years (1990 and 1995) had nonzero injuries, and no injury was recorded for the rest of the years of offshore transmission pipelines. The seven injuries in one incident occurring in offshore transmission pipelines in 1995 were a statistic substantially higher than the average of annual injuries over the 1990 to 2009 period.

Due to the limited sample size of serious offshore incidents, we aggregated offshore gathering and transmission pipelines together to compare injury/fatality rates with onshore pipelines. Offshore pipelines have larger injury/fatality rates than onshore pipelines. The normalized injury for offshore pipelines is estimated as 2.30×10^{-5} per km • yr (with an uncertainty at the 95% confidence level of 1.0×10^{-5} to 4.3×10^{-5}). Similarly the estimated fatality rate for these pipelines is estimated to 5.0×10^{-5} per km • yr (with an uncertainty of 6.1×10^{-7} to 1.8×10^{-5}). The equivalent rates for onshore pipelines were estimated by Wang and Duncan (under review) as 1.90×10^{-5} per km • yr (with an uncertainty of 1.6×10^{-5} to 3.2×10^{-5}) for injuries and 3.5×10^{-6} per km • yr (with an uncertainty of 2.4×10^{-6} to 4.8×10^{-6}).

The volume of natural gas released in each incident on the basis of property cost of released natural gas recorded in the PHMSA 02/09 and natural gas price. Estimated average releases of natural gas in offshore pipelines were larger than those in onshore pipelines (Table 3).

Dispersion calculations by Dhar (2009) suggest that for sub-ocean releases, lateral dispersion will typically be effective in limiting methane levels to below danger levels and, therefore, that underwater fires are unlikely even if ignition is available. If the gas reaches the ocean surface in sufficient quantities, ignition may occur. Again, dispersion calculation reported by Dhar (2009) suggests that if no subsea isolation valves (SSIVs) are installed, then long periods of release of gas are likely as a result of the large volume in the pipeline. With SSIVs, major rupture releases were reduced to a few minutes.

The number of significant incidents that involved an ignition in onshore and offshore pipelines is shown in Table 3. Only one out of 162 incidents that occurred in offshore transmission pipes between 2002 and 2009 involved an ignition. Thus the conditional ignition probability is ~0.62% for transmission and is similarly small (1.45%) for offshore gathering pipes. These ignition probabilities are an order of magnitude or more less than those for their onshore equivalents (Table 3), reflecting the very low likelihood of igniting gas leaks subsea and why most of the fatality risk of offshore pipelines is on offshore platforms or where the pipelines come ashore.

Table 3: Total incidents, incidents with ignition, conditional ignition probability, and average release volume (in millions of cubic feet) for incidents that occurred in different pipeline segments of the natural gas pipeline system.

2002~2009	Onshore transmissio n	Offshore transmissio n	Onshore gathering	Offshore gathering
Total incidents	434	162	18	69
Incidents w/ignition	54	1	3	1
Conditional ignition probability	0.1	0.006	0.16	0.01
Average released volume (Mmcf)	26.2	27.6	6.9	16.3

In contrast to natural gas, CO₂ does not burn or explode so the consequences of a pipeline failure are very different for the two gases. CO₂ kills at relatively high concentrations (30% or more), that are most likely to occur in confined spaces or ponding in topographic lows. Such situations are much more likely onshore than offshore. The similarities and differences between the risks posed by CO₂ versus natural gas are reviewed in more detail in section 4.5 below.

4. Discussion

To assess the risks of operating offshore natural gas pipelines (and to estimate the risks associated with proposed offshore CO₂ pipelines) this study has attempted to use actuarial data from the PHMSA data base for offshore failure incidents. The implicit assumption in this approach is that historical incident rates (and the temporal trends in these rates) can be extrapolated to predict future outcomes. This approach assumes that a complete spectrum of types of accidents is represented in the data. The problem with this assumption is that the data sets may be too limited to accurately predict the future occurrence of low-frequency but high-

consequence events. These kinds of events that may not be represented in our actuarial data set are sometimes referred to as the “unknown-unknowns”.

There are also differences in design and operating conditions between pipelines, which can result in large differences in risk. Applying historical data to predict future events is also problematic when the materials and technologies are improving over time. Steel used for pipelines today has higher quality and less flaws than that used 40 years ago. Contemporary construction techniques and inspection protocols are superior. To some extent these issues can be accounted for by comparing the results of analysis of the small offshore pipeline data set with the much larger one available for onshore transmission and gathering pipelines.

A National Academy of Sciences report (NRC, 1994) suggested that it was clear that the risk of pipeline failure was higher in some areas of the Gulf of Mexico. They suggested that the high-risk areas were: (1) those with higher numbers of pipelines; (2) those where water is shallow and with large numbers of fishing boats; and (3) those close to platforms. NRC (1994) also identified zones of severe erosion and unstable sea floor, as well as areas susceptible to the impacts of hurricanes and large storms, as areas of greater concern. This kind of severe erosion can only occur in water shallower than the wave base. The NRC report was commissioned in response to a number of significant offshore pipeline accidents involving shallow water, erosion of pipeline cover and fishing boats. As noted below changes in regulations since the late 1980's appear to have been successful in mitigating these kinds of accidents. Our analysis has ignored such spatial variation in risk factors. There is insufficient data to segregate areas with differing risk profiles without the benefit of site specific investigation.

In this section we compare our results to information from other regions, evaluate the clear temporal trends apparent in the data set, and to apply the results of our study to attempt to predict the risks associated with a future offshore pipeline network developed for CO₂ sequestration.

4.1 Changing Causes and Consequences of Offshore Natural Gas Pipeline Failures over Time

The PHMSA database that we used in this study begins in 1990. In this section we compare our results with studies of risk for offshore US natural gas pipelines prior to 1990. This is important as there is good reason to believe that some of our results would be significantly different if our data set extended back even a few years. The 1980's was a time period with an unusual spate of offshore pipeline accidents in the Gulf. For example in October of 1989 the trawler Northumberland hit a 16-inch natural gas pipeline and was engulfed in fire. As a result of the accident, 11 of the 14 crew members died. The Northumberland was 0.8 km (1/2 mile) offshore, west of Sabine Pass in 278 meters (911 ft.) of water. This particular pipeline installed 15 years before the accident occurred, was initially buried under 2.5 to 3 meters (8 to 10 feet) of mud and sand. The National Transportation Safety Board investigators found sediment cover was completely gone by the time of the accident (NTSB, 1990). Two years earlier a similar accident occurred when another fishing boat, the Sea Chief ruptured a 203 mm (8-inch) natural gas liquids pipeline, and the resultant explosion resulted in the death of two of the crew. Investigators found that the 20 year old pipeline had only 152 mm (6 inches) of covering mud at the time of the accident (Joint Task Force on Offshore Pipelines, 1990). A third accident in 1989 occurred when the Sonat/Arco platform was engulfed in a flash fire and explosion during repair of an associated pipeline, resulting in deaths of seven of the platform-crew and injury of ten. Property damage totaled about \$70 million. It was determined that the incident was caused by human error, the pipeline being cut by a worker, resulting in the release of gas (U.S. Department of Transportation, 1989). The absence of such significant accidents since 1989 appears to reflect improved inspection of near shore pipelines and improved risk management strategies in general. Specifically four additions to Federal Regulations appear to have had a role in this improvement (PCCI, 2006): (1) 08/02, Rule defining high consequence areas (HCAs) for gas transmission pipelines (67 FR 50824); (2) 12/02, Rule to require integrity management programs for gas transmission pipelines in (HCAs); and (3) 12/03, Rule to require operators to make periodic inspections of pipelines in navigable waters (68 FR 69368); and (4) 8/04, Rule to require periodic inspections of gas and hazardous liquid pipelines in the Gulf of Mexico and its inlets in waters less than 15 feet deep (69 FR 48400). The change in accident rate from the 1980's to the

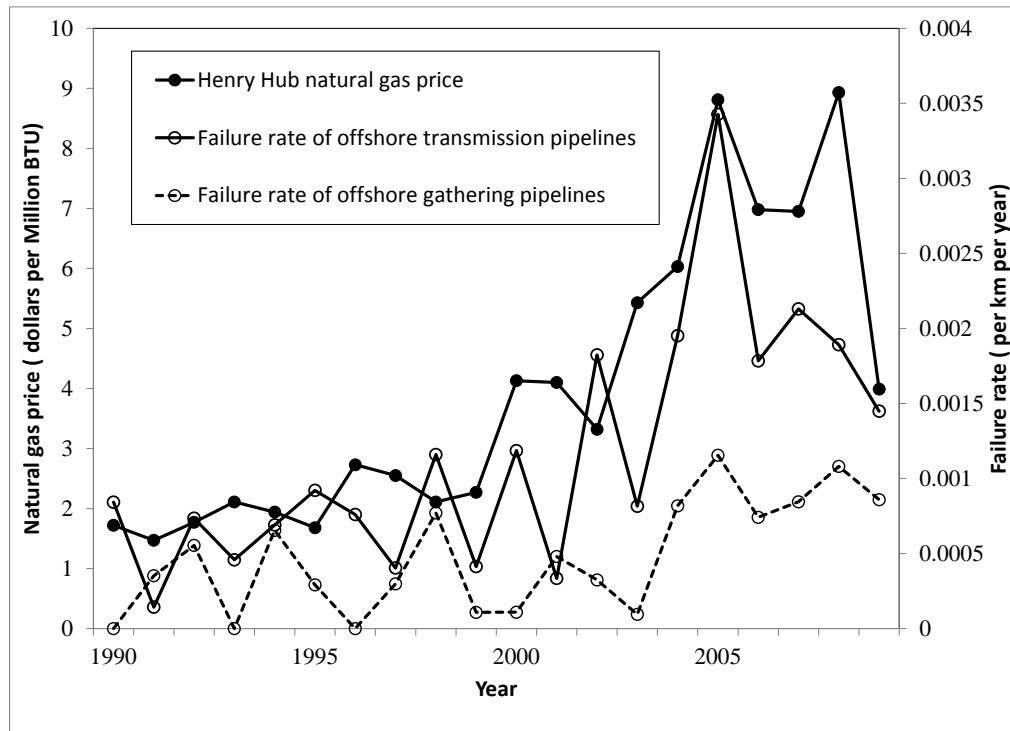
1990's demonstrates that introduction of best practices, targeted regulations, and proactive integrity management can have a significant positive impact on the safety of offshore pipelines. These lessons should be transferable to offshore CO₂ pipelines.

Prior to our current study perhaps the most comprehensive study of offshore pipeline risks was that of Woodson (1990) for the Gulf of Mexico. This study examined data from all federal sources on failures of gas, crude oil, or condensate pipelines occurring between 1967 and 1990, numbering just over a thousand incidents. However the Woodson study does not include accidents in state waters, which contain the oldest pipelines and the greatest risk to accidents involving fishing boats, as noted above (NRC, 1994).

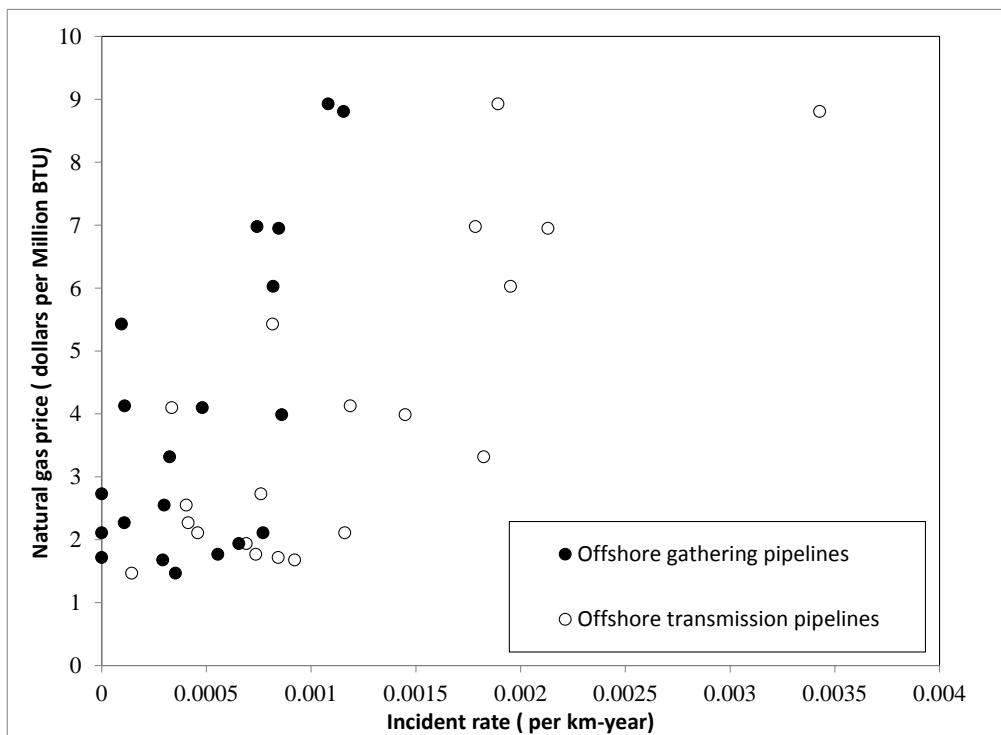
Woodson found that 50% of the pipeline failures in his data set were ascribed to corrosion (internal and external corrosion were not distinguished) whereas only 10% were related to material failure and 26% to outside force. Similarly, based on pipeline failure data from 1967-87, Mandke (1990) concluded that "corrosion is the leading cause of failures of subsea pipelines in the U.S. Gulf of Mexico". Mandke also noted that "In medium and large-size [pipe]lines; failures due to internal corrosion were more frequent than those due to external corrosion". The conclusions of Woodson and Mandke are in part divergent to our findings above based on the PHMSA (1990-2009) data base that, as noted above, has material failure as the dominant cause of failure in both gathering (76.3%) and transmission pipes (59.7%). Our interpretation of the PHMSA data (Figure 5) suggests that internal corrosion dominates over external corrosion as a failure cause, consistent with Mandke's conclusion. Some of the difference with Woodson's study may be because it includes oil and condensate pipelines as well as natural gas. The NRC (1994) report suggests that natural gas pipelines would be expected to have higher rates of internal corrosion (presumably because they are more likely to contain acid forming components such as CO₂ and H₂S. It is also important to note that post-1990 there was a significant and sustained increase in the number of new pipelines being built and the percentage of pipelines being decommissioned, such that it is likely that the pipelines studied by Woodson (1990) are a very minor portion of those represented in our data base. Unfortunately information on which pipelines have been taken out of service and when is not readily available.

4.2 Evaluating the Cause of Increasing Offshore Incident Rates

The total failure rate of transmission pipelines increased from 1.0×10^{-3} to 1.5×10^{-3} incidents per km • yr from 1990 to 2009. Note that property damage, which includes loss of natural gas, is one of the primary criteria in characterizing significant incidents. Hence, the number of significant incidents can be partly controlled by changes in the price of natural gas. As natural gas prices increases more incident get classified as significant rather than insignificant (that is more incidents exceed the \$US 50,000 threshold). This occurs even if the nature and rate of pipeline failures is actually unchanged. Because incident rate and natural gas price are highly correlated (Fig. 10a), the price of natural gas has played a dominant role in the upward trend of incident rates. Average failure rate for 1990–2000, when natural gas fluctuated little to distort the incident rate, was less than that for the 1990–2009 period (Table 1). The significant increase in the rate of failure of offshore pipelines therefore does not represent a sudden decline in pipeline safety. For example even the spike in incidents in 2005 (for both offshore gathering and transmission pipes) which correlates with Hurricane Katrina appears (on the basis of Figure 10b) to be in part to be an artifact of high natural gas prices.



(a)



(b)

Figure 10: (a) Annual variation of Henry Hub natural gas price and failure rate of offshore gathering/transmission pipes. The variation in incident rate is statistically significant correlated with natural gas price. (b) Scatter plot between incident rate and natural gas for offshore gathering/transmission pipelines during the period 1990-2009 in the US. The correlation between natural gas price and offshore gathering pipeline incident rate is 0.67 and it is 0.80 for natural gas price and offshore transmission pipeline.

The effect of gas prices also appears to distort the relationship between incident rates between offshore gathering and transmission pipelines. The average incident rate in offshore gathering pipelines was 4.76×10^{-4} per $\text{km} \cdot \text{yr}$ during 1990–2009, and it was 1.16×10^{-3} per $\text{km} \cdot \text{yr}$ in offshore transmission pipelines over the same period (Fig. 1) suggesting that offshore transmission lines have higher failure risks. However using the initial few years of the data set from 1990 (before the effect of gas prices starts to have a strong impact) the rate of incidents for transmission pipelines is 5×10^{-4} per $\text{km} \cdot \text{yr}$ (Fig. 1b) whereas for gathering pipelines the rate is about 3×10^{-4} per $\text{km} \cdot \text{yr}$ (Fig. 1a). This failure-rate difference may partly be explained by the difference in average age of offshore gathering pipelines (28 years) and offshore transmission pipelines (33 years). The difference can also be partly explained by the fact that offshore transmission pipeline's are operated under relatively higher pressures, on the average closer to the pipelines MAOP.

4.3 Comparison with North Sea Pipeline Risk

As noted by Stefani and Carr (2010) the U.S. offshore pipeline network totals twice the number of $\text{km} \cdot \text{yr}$ of operating experience as the North Sea pipeline system. Comparison of failure rates of offshore pipelines in the U.S. with those in the North Sea and is fraught with problems. Each area uses different definitions of what a significant incident is and different classifications of causes. In addition, because the raw data are not publicly available except in the U.S., comparisons to the North Sea data set are limited to the published metrics. In addition as noted by Mott MacDonald (2003) the oldest pipeline in their North Sea database was 35 years. And

they concluded that it was “difficult to draw firm conclusions on trends in loss of containment frequency with age”.

Pipeline and Riser Loss of Containment (PARLOC) is a dataset that contains details of all North Sea pipeline incidents (Robertson et al., 1996)]. Given pipeline and incident data collected until the end of 2000, frequency of loss in containment-loss incidents (Mott MacDonald, 2003) was within the range of 1.0×10^{-4} to 1.0×10^{-2} per km • yr. (in natural gas pipelines <2 km long). It was within the range of 1.0×10^{-3} to 1.0×10^{-5} per km • yr. in natural gas pipelines 2 to 5 km long. A key conclusion from the PARLOC dataset is that the rate of failure resulting in gas release in the risers is higher than that in the general pipeline population. The rate of loss of containment in risers is $\sim 1.0 \times 10^{-3}$ per km • yr. and it is these failures that are of greatest significance for an understanding of injury and fatality rates (Mott MacDonald, 2003). That the PHMSA database does not record riser incidents separately is unfortunate. Stefani and Carr (2010) found that failure frequency was 9.79×10^{-5} per km • yr in steel pipelines in the North Sea and 3.65×10^{-4} per km • yr in offshore pipelines in the U.S., based on data collected from 1984 to 2008. The lower failure rate in the North Sea may reflect different approaches to defining what a reportable incident is. It is not clear that this difference reflects a real difference in pipeline risk.

Understanding the role of environmental hazards such as hurricanes, tsunamis, soil liquefaction, slope failure and mass gravity flow in controlling pipeline failure rates is important in terms for taking risk estimates from one offshore area and applying them to other regions. Stefani and Carr (2010) note that the PARLOC database does not distinguish incidents associated with natural hazards. Stefani and Carr (2010), using a different and older version of the PHMSA data base than used in this study, estimated a leakage rate of 6.3×10^{-6} per km • yr, 4.19×10^{-5} per km • yr for ruptures. In the PHMSA database, a total of 16 incidents (2 associated with Hurricane Katrina) were found to have been caused by earth movement or hurricanes in 1990-2009 in offshore pipelines. Among these, only 1 was leakage, 3 were ruptures and 12 were system component failures. Correspondingly, the normalized rate of leakage is 2.5×10^{-6} per km • yr; the normalized rate of ruptures is 7.5×10^{-6} per km • yr and 3.0×10^{-5} per km • yr for system component failures.

Stefani and Carr (2010) have noted that construction and material defects (inherent in the steel or created during fabrication) contribute to 11% of incidents recorded in the PARLOC database and 9% of those in the PHMSA data set. They speculate that this difference may be explained by “the fact that in Europe there are much older onshore pipelines than offshore”.

In our analysis of the PHMSA database, we found that failure frequency appears to be correlated with the diameter and age of the pipeline. Similarly, Dhar (2009) showed that leak frequency of offshore pipelines is correlated with nominal pipeline diameter. For pipelines within 500 m of the platform, failure frequency is 1.26×10^{-2} per km • yr in pipelines having diameters of <4 inches (10.2cm) and 1.07×10^{-3} per km • yr in pipelines having diameters of >16 inches (40.6 cm). These are higher failure frequencies than in our study partly because Dhar (2009) combined both significant non-significant incidents.

Our analysis of the PHMSA data suggests that outside forces and construction/material defects are the two leading causes of offshore-pipeline failures. External forces contribute nearly 33% of all offshore incidents. Combined internal and external corrosion contributes 17%, and construction/material defects play the largest role, contributing to almost half of the incidents. For North Sea offshore pipelines (Mott MacDonald, 2003), internal and external corrosion contributes 40.0% of offshore pipeline incidents, external forces contribute 18% of the total incidents, and material/construction defects contribute 15%. The difference in the contribution of construction/material defects is due partly to PARLOC differentiating between incidents occurring in the body of the pipeline and other parts of the pipeline system. For instance, an incident caused by a fitting defect was counted as fitting failure rather than a pipeline incident in PARLOC, but it was included in PHMSA as a pipeline incident.

4.4 Comparison between Offshore and Onshore Pipelines

The average incident rate in onshore transmission pipelines (calculated from the PHMSA data base) from 1990 through 2000 (thus avoiding the influence of gas-prices on incident rates found in this paper) was 7.2×10^{-5} per km • yr, and it was 7.0×10^{-4} per km • yr in offshore transmission pipelines (Wang and Duncan, under review). The 95% confidence interval of incident rate for onshore transmission is 2.4×10^{-5} to 3.1×10^{-5} per km • yr, compared to $5.4 \times$

10^{-4} to 7.6×10^{-4} per km • yr for offshore transmission pipelines. Failure rate of onshore transmission pipelines is 7%-9% of that of offshore transmission pipelines. This order of magnitude difference can partly be best explained by the following:

- (1) Offshore pipelines are subjected to external pressures and forces from the nature of the installation process and from ongoing stress of waves and currents. These issues are reflected in much higher failure rates related to mechanical integrity and outside forces in offshore versus onshore pipelines (see Fig. 5).
- (2) As might be expected, offshore pipelines have higher external corrosion rates (2.5×10^{-5} per km • yr) than do onshore pipelines (1.2×10^{-5} per km • yr), presumably because seawater is more corrosive than typical groundwater.
- (3) Rates of internal-corrosion-related failures experienced by offshore gas pipelines are higher than for onshore pipelines (Fig. 5). This difference presumably reflects a more effective removal of water and components such as CO₂ and H₂S from onshore natural gas prior to transmission.

For onshore CO₂ transmission pipelines Duncan and Wang (2014) concluded that ruptures (specifically full bore ruptures greater than 25.4 cm or 10 inches) presented the greatest risk. Offshore pipelines have a higher rupture rate than onshore pipelines (Table 1). The relative frequency of incidents involving a rupture ≤ 5.1 cm (2 inches) long is estimated at 1.7×10^{-5} per km • yr in onshore and 1.7×10^{-4} per km • yr in offshore transmission pipelines. For ruptures > 25.4 cm (10 inches) long, the frequency is 1.1×10^{-5} per km • yr and 2.2×10^{-5} per km • yr in onshore and offshore transmission pipes, respectively. Based on rupture rates calculated for onshore natural gas transmission pipelines Duncan and Wang (2014) estimated that for “full bore” rupture, the rupture-rate of the future CO₂ pipelines would be 4.8×10^{-7} per km • yr. The overall full bore rupture rate computed in the current study of offshore pipelines is 1.5×10^{-5} per km • yr. For ruptures > 5.1 cm (2 inches) long, the frequency is 1.7×10^{-5} per km • yr and 3.6×10^{-5} per km • yr in offshore gathering and transmission pipes, respectively. Only 2 ruptures over 10 inches are recorded in the PHMSA data set for offshore transmission pipes constructed since 1980s, giving a rupture rate of 9.1×10^{-6} per km • yr. In comparison for onshore transmission pipelines, 5 ruptures over 10 inches are recorded in the PHMSA data set. For these pipelines the

rate of rupture over 10 inches over the last 30 year (since 1980s) is 1.9×10^{-6} per km • yr, Although the differences between all the rate comparisons in this paragraph are statistically significant at a 95% confidence level based on our statistical analysis (See Supplemental material S1) we are reluctant to make much of these differences due to the very small numbers of offshore rupture incidents.

Wang and Duncan (under review) noted that for onshore gas pipelines, failure rates decrease with increasing pipeline diameter. The failure rate in offshore pipelines having diameters <4 inches (10.2cm) was $\sim 2.0 \times 10^{-3}$ per km • yr (Fig. 4), and it decreased to 4.0×10^{-4} per km • yr in pipelines having diameters of >28 inches (71.1cm). Injury/fatality rates in offshore natural gas pipelines are higher than those in onshore natural gas pipelines. The normalized injury rate for offshore natural gas pipelines was 2.3×10^{-5} per km • yr, with an uncertainty range of 4.3×10^{-5} to 5.0×10^{-6} per km • yr at the 95% confidence level. Similarly the fatality rate is estimated to be 1.0×10^{-5} per km • yr, with an uncertainty range of 6.1×10^{-7} to 1.8×10^{-5} per km • yr. In comparison, the equivalent rates for onshore natural gas pipelines were 1.9×10^{-5} per km • yr (with an uncertainty of 1.6×10^{-5} to 2.2×10^{-6}) for injuries, and for fatalities the estimated rate is 3.5×10^{-6} per km • yr (with an uncertainty of 2.4×10^{-6} , 4.8×10^{-6}). It is also important to note that not all fatalities assigned to offshore, natural gas transmission pipelines are associated with failure of the pipeline itself. For example the only fatalities recorded in the PHMSA data set occurred in a 1995 accident in which two employees opened a trap door that was under pressure while working on pipeline monitoring equipment (INGAA, 2004). Thus no fatalities associated with natural gas offshore pipelines (in our data set) can be attributed to failures in pipeline integrity.

Although the failure rates of offshore natural gas transmission and gathering pipelines are higher compared with those onshore, the injury risks are broadly similar and the fatality rates are lower. Given the generally higher hazards of operating in the offshore environment (Ponsonby et al.,

2009; Cruz and Krausmann, 2009), this is in part explained by the ignition rates of gas releases being two orders of magnitude lower offshore than onshore. In addition the exposure of workers and the general public to subsea pipelines is much more limited than to those onshore. Thus higher failure rates do not translate into larger numbers of injuries and fatalities.

4.5 Implications for Risk in Future Offshore CO₂ Pipelines

A number of countries are considering offshore CO₂ sequestration projects and Norway has two active offshore sequestration projects underway, the Sleipner and Snohvit projects. Only the Snohvit project involves a CO₂ pipeline. No information is available on the risks associated with these pipelines. Duncan and Wang (2014) have argued that estimating likelihood of failure of future onshore CO₂ transmission pipelines is best based on the basis of analysis of data for onshore natural gas transmission pipelines. Similarly understanding the potential risk of offshore CO₂ is best based on the safety record of natural gas pipelines. Following the lead of Duncan and Wang (2014) it is useful to explore how the nature and rate of failure of natural gas pipelines can be applied to estimating the rate of failure for CO₂ pipelines. To answer this question we must first understand the similarities and differences between pipelines carrying natural gas and CO₂. As noted in the introduction both CO₂ and natural gas pipelines: utilize the same types of carbon steel; are welded and installed using the same techniques; utilize the same types of external coatings; are subject to the same corrosion issues; use the same types of cathodic protection to mitigate external corrosion; and are constructed according to the same ASME design code.

The rupture rates could be lower if future offshore CO₂ pipelines, as dictated by the ASME code for higher pressure pipelines, are proportionally thicker walled than current offshore natural gas pipelines. An additional caveat in applying natural gas pipeline risk estimates to offshore CO₂ pipelines is the fraction of the MAOP that these pipelines will operate at. In the current study it was found that the median ratio of operating pressure over MAOP for failures of offshore gathering pipelines was 0.66, and 0.77 for offshore transmission pipelines. If future CO₂

pipelines are operated at a higher ratio of then the failure rates established in this study would be underestimates.

CO₂ pipelines will almost certainly be constructed with a wall thickness greater than the minimum specified by the ASME code for a particular diameter and operating pressure. For example in the proposed North Sea CO₂ pipeline designed by WorleyParson, an increased wall thickness 3 mm corrosion allowance was proposed for a 711 mm diameter pipe (Drennan and Smith, 2008). Thicker walled pipes are generally less likely to fail or rupture than thinner ones, however because they are heavier, installation will be more difficult in an offshore environment and bending stresses during installation may become an issue of concern. As shown in Figure 6 above, corrosion is a relatively minor failure mechanism for the failure of natural gas pipelines compared with external force and construction/material defects. As noted by Duncan and Wang (2014) the analogy between natural and CO₂ pipelines breaks down if CO₂ transported to offshore projects is not dehydrated to the level typically achieved for onshore pipelines (60% of water saturation is often used as a rule of thumb). If appropriately dehydrated corrosion rates for CO₂ pipelines should not be appreciably different to that observed for natural gas pipelines. However, dehydration is an expensive process, and offshore operators may not achieve the recommended levels. In such cases, corrosion may be inevitable given natural fluctuations in industrial process and contaminate levels of the CO₂ coming from capture plants.

A recent literature review of corrosion on CO₂ pipelines by Cole et al. (2011) comes to essentially the same conclusion. These authors suggest that if conditions in a pipeline are maintained such that the water content and other contaminant levels are kept extremely low”, then corrosion rates in CO₂ pipelines “are also likely to be sufficiently low {to avoid corrosion issues threatening pipeline safety], as suggested by empirical evidence. However Cole et al. (2011) express a concern regarding the possible deleterious effects of residual contaminates (such as H₂S and O₂ that may be in the CO₂ stream from capture from electric power plants. Yahaya et al. (2009) have suggested that CO₂ is the predominant corrosive agent in many offshore oil and gas pipelines and is the “most significant degradation mechanisms in pipelines” (Hellevink and Langen, 2000). They further suggest that the prediction corrosion rates associated

with CO₂ and the residual strength of corroded pipelines are uncertain. This may become a significant issue limiting the long-term transport capacity of offshore CO₂ pipelines. Industry's approach to this issue has been to de-rate the MAOP of the pipeline to account for the projected thinning of the pipeline wall by corrosion. This lowering of the transmission pressure over time may not be a significant issue in gas production due to the decline in production rate (and pressure) over time from gas fields. However for CO₂ sequestration, the economics of any sequestration project would suffer if rates of CO₂ delivery to the injection site were reduced.

Beyond estimating failure and rupture rates of future offshore CO₂ pipelines, examining the safety record of offshore natural gas pipelines can aid in understanding the potential consequences of pipeline failures. Rabindran et al. (2011) suggested that for offshore pipelines "the water surrounding the pipeline will to some extent absorb or disperse the CO₂" that would minimize the area "where it could cause harm". Modeling of scenarios involved boat anchors cutting CO₂ pipelines in shallow coastal water would help evaluate the degree to which water depth mitigates risks of CO₂ outbursts. As with natural gas pipelines, the main source of risk for injuries and fatalities associated with CO₂-pipelines will be on manned offshore injection platforms. CO₂, because it is neither explosive nor flammable, in most cases will pose a significantly lower risk than natural gas. Also, because CO₂ is denser than air, it is unlikely to build up to dangerous levels in an elevated platform, except under exceptional circumstances. However Connolly and Cusco (2007) warned that in confined spaces on an offshore platform, a rapid release of CO₂ (such as from the large rupture of a riser) may cause workers to be harmed when being "sand blasted" by a mix of vented CO₂ and dry-ice particles. Unfortunately, until 2010 PHMSA did not distinguish between failures in the pipeline itself or in the riser to the platform (or within the confines of the platform structure). Any future design for an offshore CO₂ sequestration project based on a platform with CO₂ being transported via a riser should take into account the type of hazards that concerned Connolly and Cusco (2007) in the platform layout and design.

An obvious question is does the data from offshore natural gas pipeline failures provide any insights as to the probability of significant pipeline failure associated with platforms compared to the rest of the pipeline system? PHMSA has recently (2012) started collected information on the

nature of the location of offshore pipeline failures (shown in Table 4). Thus far the data reveals no near shore incidents and only a few associated with the platform or riser. However this information is too limited to draw conclusions. The results of a larger sample is available for two decades of offshore Gulf of Mexico pipeline data from 1967 to 1987, regarding which Mandke (1990) concluded that “a majority of failures, about 64% (439)” took place at “the platform deck, the riser section, or the seabed within 500 ft. [152 meters] of a platform”. For steel risers in the North Sea the failure rate is 1.2×10^{-4} per year for pipe diameters > 16 inch (40.6 cm) and for 9.1×10^{-4} per year for pipe diameters ≤ 16 inch (40.6cm) (OGP, 2010). The riser components of offshore pipelines are also significantly more susceptible to ruptures. For example for the North Sea data set, the number of large (> 80 mm equivalent diameter) hole failures was 4 compared to 1 for pipeline segments, over the same time period (Mott McDonald, 2003). Similarly the North Sea data reveals that 25% of the rupture failures in riser segments are full-bore whereas only 8% of the sub-sea segments are full-bore.

Location of the incident	Number of significant offshore incidents	Relative frequency
Shoreline/Bank crossing	0	0
Below water, pipe buried or jetted below seabed	51	0.75
Below water, pipe on or above seabed	11	0.161764706
Splash zone of riser	2	0.029411765
Portion of riser outside of	1	0.014705882

splash zone		
Platform	3	0.044117647

Table 4: The location distribution of offshore incidents based on 68 significant incidents during 2010-2013.

It is likely however that in many, if not all, offshore CO₂ sequestration projects in the future, operation of CO₂ injection wells will be done utilizing sub-sea installations rather than permanent platforms. For example, this approach is used in the North Sea CO₂ injection project design by WorleyParson outlined in Drennan and Smith (2008). In this case the subsea equipment would include included sea-bottom Christmas Trees for each injection well, together with a manifold, and a control system, are all proposed to be on the sea floor, under protective structures (Drennan and Smith, 2008). Although these installations would be installed using divers the design anticipates that subsequent inspections, maintenance and other intervention would be accomplished primarily by diverless technologies. With such automated subsea injection systems the risk to the day-to-day operators would be eliminated.

The second highest risk for hazards associated with offshore pipelines is likely associated with the point at which the pipeline crosses the coast. That is the region between the land pipeline and the subsea pipeline system. In many countries the pipeline will have to traverse shallow bays or coastal wetlands before becoming a truly subsea installation. The potential hazard to local population in this zone will be a highly site specific issues. As noted above natural gas pipelines in the shallow water zone along the coast prior to regulatory changes in the late 1990's to 2004 proved a hazard to fishing vessels. As previously noted this risk appears to have been mitigated successfully. Rabindran et al. (2011) suggested that "compared to an onshore pipeline the consequence for an offshore pipeline failure is likely to be much lower". The key question is how much lower? The conclusion of the analysis of Duncan and Wang (2014) that only full bore rupture of a CO₂ pipeline presents a significant risk for fatalities points to a strategy for estimating the likelihood of such an outcome. Taking an estimate for the full bore rupture rate as being 1.5×10^{-5} per km • yr pipelines (computed in this study) can be multiplied by the fraction

of the length of the pipeline network that has available risk receptors (such as people living close to the shallow water where the pipeline crosses the coast. If this fraction is on the order of .01 then the likelihood of an individual fatality would be on the order of 10^{-7} per km • yr. This is an order of magnitude lower than the level that is typically taken as an acceptable risk, and lower than the estimated individual risk for onshore CO₂ transmission pipelines estimated by Duncan and Wang (2014). However as noted by Palmer (2012) risks this small have high uncertainties as a result of the inherently small sample size.

A future offshore CO₂ pipeline network would likely be built using enhanced safety features that are just starting to be introduced into natural gas pipeline systems. As compiled by Purvis (2010) these include: (1) “Real-time” monitoring of temperature, flow rates and pressure in the pipeline linking operational with integrity monitoring; (2) use of “Permanently installed monitoring systems” for “components that require frequent monitoring”; and (3) use of fiber optic based smart instruments for real time monitoring.

5 Conclusions

In the absence of any information on pipeline failures for the one existing offshore CO₂ pipeline (the Snohvit pipelines owned and operated by STATOIL), the use of information from an analogue such as offshore natural gas pipelines seems the most useful approach to understanding the likelihood and consequences of failure of future sub-sea CO₂ pipelines for sequestration. In this paper we have concluded that although the incident rate for natural gas accidents is approximately an order of magnitude higher for offshore than onshore pipeline networks, the injury and fatality rates for natural gas are roughly equivalent. Duncan and Wang (2014) have argued that the individual risk of CO₂ pipelines onshore is likely in the range of 10^{-6} to 10^{-7} per km • yr, lower than the risk estimated for natural gas pipelines. Offshore CO₂ pipelines will have a significantly lower risk of injuries and fatalities per kilometer given the limited exposure to potential CO₂ venting from the leakage or rupture of sub-sea pipelines. In addition as CO₂ does not form an explosive mixture with air and is non-flammable, it would seem reasonable that the

individual risk to workers would be even lower for offshore than for on-shore pipelines. The two high risk areas, for both natural gas and CO₂ pipeline networks in the offshore areas are: 1) on offshore platforms (served by pipelines); and 2) in the shallow waters, near-shore, and where the pipelines cross onto land. Recent designs for offshore sequestration projects have been CO₂ being injected via sub-sea completions rather than on platforms. If the near shore risks are well mitigated and managed and the, then the risks of offshore pipelines are almost certainly well into the acceptable range. An important caveat to this conclusion comes from our concern that the data sets may be too limited in terms of number of incidents and time scale of observation, to accurately predict the future occurrence of low-frequency but high-consequence events.

The data for rupture, injury and fatality rates for offshore natural gas pipelines is the most tangible basis to predict the likelihood of ruptures capable of causing serious injuries or fatalities associated with a future offshore CO₂ pipeline network. Rabindran et al. (2011) have suggested that consequence for the failure of an offshore CO₂ pipeline failure is likely to be “much lower” than its onshore equivalent. The current study generally supports this contention though when risks are on the order of 10⁻⁷ the uncertainties in risk estimates intrinsically have large uncertainties.

Summary: This study sets out to understand the likelihood of pipeline failures associated with offshore CO₂ pipelines for sequestration projects by evaluating the safety track record for offshore natural gas pipelines, using a 20-year detailed dataset available from the agency that regulates offshore pipelines in the US. Based on this analysis, it is concluded that the risks of future fatalities from offshore CO₂ pipelines are on the order of 10⁻⁷ km • yr., a level of risk that most authorities would see as negligible. The rate of serious incidents reported for offshore U.S. natural gas pipelines have been significantly increasing over the last decade. Our analysis suggests that this is an artifact correlated with increasing natural gas prices, which results in more incidents exceeding the \$US 50,000 damage criterion. The dominant risk of injuries and fatalities in offshore natural gas pipelines come from fires on offshore platforms. The rate of failure for offshore transmission pipelines is estimated as 5 x 10⁻⁴ versus 3 x 10⁻⁴ km • yr. for gathering pipelines. This may be explained by the difference in average age (27.7 for gathering

and 32.9 years for transmission), or because transmission pipelines are operated closer to their maximum allowable operation pressures than are offshore gathering pipelines. The fatality rate for offshore natural gas pipelines is essentially the same as for those onshore however none of the recorded deaths in the data set were related to failures of pipeline integrity. As a result of the minimal exposure of workers (and the general public), to the impacts of CO₂ releases in the offshore environment it is argued that the fatality rate associated with CO₂ pipelines will likely be lower than for natural gas pipelines. Assuming that a future offshore CO₂ sequestration project is based on sea floor injection and control systems, risk mitigation efforts clearly should focus on the near shore portion.

References

Akselsen et al., 2010, Mechanical Properties of Hyperbaric Gas Metal Arc Welds In X65 Pipeline Steel, International Journal of Offshore and Polar Engineering, volume 20, (2), 110-117

Brown, A. L., Berlin, E. H., Butsch, R. J., Senel, O., Mills, J., Harichandran, A., and Wang, J. 2011. Carbon Capture and Sequestration: Ascertaining CO₂ Storage Potential, Offshore New Jersey, USA, Paper OTC 21995, Offshore Technology Conference held in Houston, Texas, USA, 2–5 May 2011

Connolly, S., Cusco, L. 2007, Hazards from high pressure carbon dioxide releases during carbon dioxide sequestration processes, loss prevention, in 12th International Symposium on Loss Prevention and Safety Promotion in the Process Industries, IChemE Symposium Series No 153

Chadwick, R. A., Zewig, P., Gregersen, U., Kirby, G. A., Holloway, S., Johannessen, P. A. 2004. Geological reservoir characterization of a CO₂ storage site: The Utsira Sand, Sleipner, northern North Sea, *Energy* 29: 1371-1381

Cole, I. S., Corrigan, P., Sim, S., Birbilis, N., 2011, Corrosion of pipelines used for CO₂ transport in CCS: Is it a real problem? International Journal of Greenhouse Gas Control 5 (2011) 749–756

Cruz, A. M., Krausmann, E., 2009, Hazardous-materials releases from offshore oil and gas facilities and emergency response following Hurricanes Katrina and Rita, *J. Loss Prev. in Proc. Ind.*, 22, 59–65.

Dawotola, A. W., Gelder, P. V., & Vrijling, J. K. (2012). Design for acceptable risk in transportation pipelines. *International Journal of Risk Assessment and Management*, 16(1), 112-127.

Demofonti, G., & Spinelli, C. M., 2011, Technical challenges facing the transport of anthropogenic CO₂ by pipeline for carbon capture and storage purposes, 6th Pipeline Technology Conference, <http://www.pipeline-conference.com/sites/default/files/papers/Spinelli.pdf>

Drennan F., Smith D., 2008, London Office Studies CO₂ Capture and Storage for Cootes, Worley-Parson Quarterly Journal, Q2-2008

Duncan, I. J., Wang, H. 2014, Estimating the Likelihood of pipeline failure in CO₂ transmission pipelines: new insights on risks of carbon capture and storage, *Int. J. Green. Gas Cont.*

Duncan, I. J., Nicot, J. -P., and Choi, J. -W., 2009, Risk assessment for future CO₂ sequestration projects based on CO₂ enhanced oil recovery in the U.S., *in Energy Procedia* (v. 1, no.1), Proceedings of 9th International Conference on Greenhouse Gas Control Technologies GHGT9, November 16–20, Washington D.C., p. 2037–2042.

Dhar, R., 2009, Risk assessment as a tool in estimating the requirement of subsea isolation valves in subsea pipelines, *in SPE Americas E&P Environmental and Safety Conference*, San Antonio, Texas, USA, 2009.

Goodfellow G., Haswell J., 2006, A comparison of inherent risk levels in ASME B31. 8 and UK gas pipeline design codes, *IPC2006-10507*, International Pipeline Conference, Calgary

Hermanrud, C., Andresen, T., Eiken, O., Hansen, H., Janbu, A., Lippard, J., Bolas, H. N., Simmenes, T. H., Teige, G. M. G., Østmo. S. 2009, Storage of CO₂ in saline aquifers – Lessons learned from 10 years of injection into the Utsira Formation in the Sleipner area. *Energy Procedia*, 1, pp 1997-2004

Helleink, S. G., Langen. I. 2000, Optimal design-phase inspection and replacement planning of pipelines subjected to CO₂ corrosion. *International Journal of Offshore and Polar Engineering*, 10, pp 123-130

Hopkins P., 2007, Oil and Gas Pipelines: Yesterday and Today
<http://www.penspen.com/Downloads/Papers/Documents/OilandGasPipelines.pdf>

HSE, 2001, R2P2 Reducing Risks, Protecting People, UK Health and Safety Executive

ICF, 2012, Analysis of the Costs and Benefits of CO₂ Sequestration on the U.S. Outer Continental Shelf, OCS Study BOEM 2012-100 ICF International.

http://www.boem.gov/uploadedFiles/BOEM/Oil_and_Gas_Energy_Program/Energy_Economics/External_Studies/OCS%20Sequestration%20Report.pdf (July 2013)

INGAA, 2004, Risk of a Gas Transmission Pipeline, INGAA Pipeline Safety Committee
http://www.p-pic.com/files/whitepapers/paper_riskofapipeline.pdf

Jeppesen L., Dam J., Olsen H., 2005, Subsea Automated Ultrasonic Inspection, 3rd Middle East Nondestructive Testing Conference & Exhibition - 27-30 Nov 2005 Bahrain,
<http://www.ndt.net/article/mendt2005/pdf/35.pdf>

Joint Task Force on Offshore Pipelines, 1990, Joint Task Force Report on Offshore Pipelines. Washington, D.C.: U.S. Department of Transportation, Research and Special Programs Administration.

Kennedy, J. L. 1993, Oil and Gas Pipeline Fundamentals, second ed., Pennwell, Oklahoma, USA, 1993.

Koornneef J., Spruijt M., Molag M., Ramirez A., Turkenburg W., Faaij A., 2010. Quantitative risk assessment of CO₂ transport by pipelines—a review of uncertainties and their impacts, *J. Haz. Mat.*, 177, 12–27.

Kowalski R., 2009, A Data Quality Assessment Evaluating the Major Safety Data Programs for Pipeline and Hazardous Materials Safety, *Pipeline and Hazardous Materials Safety*

Administration,

<http://phmsa.dot.gov/staticfiles/PHMSA/DownloadableFiles/Files/DQA%20Report.pdf>

Lin, L., Guo, B., Song, S., Chacko, J., Ghalambor, A. Offshore Pipelines, Elsevier, 2005.

Lu, J., Wilkinson, M., Haszeldine, R. S., Fallick, A. E. 2009, Long-term performance of a mudrock seal in natural CO₂ storage. *Geology*, 37, pp 35-38

Mandke J. S., 1990, CORROSION CAUSES MOST PIPELINE FAILURES IN GULF OF MEXICO 10/29/1990 Oil and Gas Journal, <http://www.ogj.com/articles/print/volume-88/issue-44/in-this-issue/pipeline/corrosion-causes-most-pipeline-failures-in-gulf-of-mexico.html>

McGillivray, A., Wilday, J. 2009, Comparison of risks from carbon dioxide and natural gas pipelines. HSE report rr -749 .

Mendelevitch, R.; Herold, J.; Oei, P-Y; Tissen, A., 2010, CO₂ highways for Europe modeling a carbon capture, transport and storage infrastructure for Europe, Discussion papers, German Institute for Economic Research, No. 1052

Mohamed, N., Jawhar, I., Al-Jaroodi, J., Zhang, L. (2011). Sensor network architectures for monitoring underwater pipelines. *Sensors*, 11(11), 10738-10764.

Mott MacDonald, 2003. The update of Loss of Containment Data for Offshore Pipelines, <http://www.hse.gov.uk/pipelines/parloc-2001-report.pdf> (May 2013).

Muhlbauer, W. K., 2004, Pipeline Risk Management Manual: Ideas, Techniques and Resources, Gulf Professional Publishing

National Transportation Safety Board. 1990. Pipeline Accident Report. The F/V *Northumberland* and Rupture of a Natural Gas Transmission Pipeline in the Gulf of Mexico Near Sabine Pass, Texas, October 3, 1989. Report PB90-916502 NTSB/PAR-90/02. Washington, D.C.

Neele, F., Koenen, M., van Deurzen, J., Seebregts, A., Groenenberg, H., & Thielemann, T. (2011). Large-scale CCS transport and storage networks in North-west and Central Europe. *Energy Procedia*, 4, 2740-2747.

Nesic S. 2007 Key issues related to modelling of internal corrosion of oil and gas pipelines - A review, *Corrosion Science* 49 4308-4338

NRC, 1994, Improving the Safety of Marine Pipelines. National Research Council, Washington, DC: The National Academies Press, 1994.

O'Brien, W. G., Tingate, R. P., Divko, G. L. M., Harrison, L. M., Boreham, J. C., Liu, K., Arian, N., Skladzien, P. 2008, First order sealing and hydrocarbon migration processes, Gippsland Basin, Australia: implication for CO₂ geosequestration. *Third Eastern Australasian Basins Symposium*, J. E. Blevin, B. E. Bradshaw and C. Uruski (eds): pp 1-28

OGP, 2010, Riser and pipeline release frequencies, International Association of Oil and Gas Producers, Risk Assessment Data Directory, Report No. 434-4. March 2010.

OGUK, 2013, Decommissioning of Pipelines in the North Sea Region, Oil and Gas UK, www.oilandgasuk.co.uk/cmsfiles/modules/publications/pdfs/OP083.pdf

Palmer A., 2012, 10⁻⁶ and all that: what do failure probabilities mean? *Journal of Pipeline Engineering*, 12 (4), 269-272

PCCI, 2006, Study on Burial of Submerged Pipelines, Report to PHMSA, US Department of Transportation,

<http://www.phmsa.dot.gov/staticfiles/PHMSA/DownloadableFiles/NTSBOIGRecommendation%20Report%20to%20Congress%2008%20part%202.pdf> (July 2013)

Ponsonby, W., Mika, F., Irons, G., 2009, Offshore industry: medical emergency response in the offshore oil industry, *Occ. Med.*, 59, 298–303.

Purvis 2010, Pipeline integrity monitoring – what's the present situation for offshore pipelines and the future? Paper Number IPC2010-31449 Proceedings of the 8th International Pipeline Conference

Rabindran, P., Cote, H., & Winning, I. G. Integrity Management Approach to Reuse of Oil and Gas Pipelines for CO₂ Transportation. 6th Pipeline Technology Conference 2011,

http://www.pipeline-conference.com/sites/default/files/papers/Rabindran_0.pdf

Robertson, JLM, Smart, D., Al-Hassan, T. 1996, Offshore North Sea Pipeline and Riser Loss of Containment Study (PARLOC)—applications and limitations in the assessment of operating risks, *J. Offshore Mech. Arct. Eng.* 118, 115–220.

Shimekit B., Mukhtar H., 2012, Natural Gas Purification Technologies – Major Advances for CO₂ Separation and Future Directions, in Advances in Natural Gas Technology, Dr. Hamid Al-Megren (Ed.), InTech, <http://www.intechopen.com/books/advances-in-natural-gastechology/natural-gas-purification-technologies-major-advances-for-co2-separation-and-future-directions>

Sim, S., F. Bocher, I.S. Cole, X-B. Chen, and N. Birbilis (2013) Investigating the effect of water content in supercritical CO₂ as relevant to the corrosion of carbon capture and storage pipelines, *Corrosion*, In-Press.

Sørensen, P. A., Kiil, S., Dam-Johansen, K., & Weinell, C. E. (2009). Anticorrosive coatings: a review. *Journal of Coatings Technology and Research*, 6(2), 135-176.

Spinelli, C. M., and L.Prandi. (2012) High Grade Steel Pipeline for Long Distance Projects at Intermediate Pressure 7th Pipeline Technology Conference 2012, http://www.pipeline-conference.com/sites/default/files/papers/ptc_2012_Prandi.pdf

Stefani, V. D., Carr, P. 2010, A model to estimate the failure rates of offshore pipelines, in Proceedings of the 8th International Pipeline Conference, Albert, Canada.

Thomas, S., Dawe, R. A. 2003, Review of ways to transport natural gas energy from countries which do not need the gas for domestic use, *Energy* 28, 1461–1477.

U.S. Department of Transportation, 2013, URL: <http://www.phmsa.dot.gov/> (May 2013).

U.S. Department of Transportation. 1989. Accident Report, Southern Natural Gas Company (Sonat), Arco South Pass 60 Baker Offshore Production Platform, Outer Continental Shelf, Gulf of Mexico. March. Washington, D.C.

Wang, H., Duncan, IJ. Likelihood, causes, and consequences of focused leakage and rupture of U.S. natural gas transmission pipelines, *Journal of Loss Prevention in the Process Industries*, Volume 30, July 2014, Pages 177–187.

Woodson R. D., 1990, Offshore Pipeline Failures, M.E. thesis, University of California, Berkeley, <http://www.dtic.mil/cgi-bin/GetTRDoc?Location=U2&doc=GetTRDoc&ADNumber=AD-A259708> (July 2013)

Yahaya, N., et al., 2009, Prediction of CO₂ corrosion growth in submarine pipelines. *Malaysia Journal of Civil Engineering*, 21, pp 69-81.

Zhang Q., Que P., Lei H., 2008, Corrosion Assessment of Offshore Oil Pipeline Based on Ultrasonic Technique, 17th World Conference on Nondestructive Testing, 25-28 Oct 2008, Shanghai, China

CONCLUSIONS

Geologic CO₂ sequestration in deep brine reservoirs is considered as a key technology for large scale mitigation of greenhouse gas emissions. Earlier risk assessments have identified a number of sub-surface related risks including: catastrophic leakage from fault zones; catastrophic CO₂ evulsion from slow leakage, and ground heave, that simply are not credible. They have overused the word catastrophic and presented an inflated impression of the subsurface risks associated with CCS. The short- and long- term risks of CO₂ leakage on drinking water resources, surface and subsurface ecosystems, and energy resources based on natural analogues have been analyzed. Where careful studies have been able to quantify risks from sub-surface CO₂ utilizing analogues, they are on the order of 10⁻⁸, two orders of magnitude smaller than risks normally considered of societal concern.

The thirty seven plus years of history of CO₂ injection involved in CO₂ based Enhanced Oil Recovery in the US represent the most tangible evidence available for understanding the operational risks of CO₂ sequestration in deep brine reservoirs. In the case of blowouts; component failure rather than corrosion or human errors have resulted in the greatest loss of CO₂. The rarity of corrosion related incidents reflects the industries success in implementing anti-corrosion measures. In the case of blowouts, incidents related to CO₂ production wells from natural reservoirs and those that occurred during work over of production wells, resulting from unexpectedly early CO₂ breakthroughs are not directly relevant to understanding the risk of CO₂ sequestration in deep brine reservoirs. Although safety and health issues are always of paramount concern, the excellent safety and health record of the CO₂ industry in the Permian Basin of West Texas may suggest that these issues are not a major component of the operational risk faced by a putative carbon sequestration industry.

The potential lethality of unexpected CO₂ releases from pipelines or wells are arguably the highest risk aspects of CO₂ enhanced oil recovery (CO₂-EOR), carbon capture, and storage (CCS). Assertions in the CCS literature, that CO₂ levels of 10% for ten minutes, or 20 to 30% for a few minutes are lethal to humans, are not supported by the available evidence. The results of published experiments with animals exposed to CO₂, from mice to monkeys, at both normal and depleted oxygen levels, suggest that lethal levels of CO₂ toxicity are in the range 50 to 60%.

These experiments demonstrate that CO₂ does not kill by asphyxia, but rather is toxic at high concentrations. Depleted O₂ levels will decrease the lethal level of CO₂; however available data provides only a general indication of the magnitude of this effect. It is concluded that quantitative risk assessments of CCS have overestimated the risk of fatalities by using values of lethality a factor two to six lower than the values estimated in this paper. In many dispersion models of CO₂ releases from pipelines, no fatalities would be predicted if appropriate levels of lethality for CO₂ had been used in the analysis.

The analysis presented in this report suggests that the likelihood of having significant (potentially lethal) releases of CO₂ from pipelines is likely in the range of 10⁻⁶ to 10⁻⁷. If these values can be used as a proxy for individual risk, these probabilities would be considered in the acceptable to negligible range where risk is regulated. The systemic overestimation of the risks associated with CO₂ pipelines found in this study may already have played a role in high-level decision making regarding CCS. If, as is commonly thought, pipelines represent the highest risk component of CCS outside of the capture plant, then most (if not all) previous quantitative-risk assessments of components of CCS may be orders of magnitude to high.

The spatial variation of risk surrounding natural gas and CO₂ pipelines is likely to be very different. In this sense natural gas pipeline safety is an inadequate analogue for the risks associated with CO₂ pipelines. The conclusions derived in this report must be tempered by this realization. The traditional approach to mapping individual risks, leads to the conclusions that risk decreases proportional to lateral distance from the pipeline, reflecting the impact of natural gas explosions. For CO₂ pipelines mitigation strategies should focus on protecting vulnerable receptors in low lying areas near pipeline routes. This report has presented new evidence that pipeline design standards for natural gas transmission pipelines that result in pipes with thicker walls being used in suburban and urban areas do have a significant impact on lowering fatality rates to levels so low that no deaths were recorded in incidents spanning 2 decades.

Overall this report has marshalled a wide array of evidence that supported the notion that risk to the general public from CCS development is sufficiently low that it can be effectively mitigated to acceptable levels.

GRAPHICAL MATERIALS LIST

Section 7

Figure 1	Causes, failing modes and consequence of natural gas and CO ₂ pipelines	148
Figure 2	Interface design for the GUI toolkit in Matlab	152
Figure 3	Editable boxes (blank) used in the input module of the toolkit	153
Figure 4	GUI designed for updating pipeline failure probability	156
Figure 5	A snapshot of the application during the test phase	157

Section 9

Figure 1	Injury and fatality rates for natural gas transmission pipelines	199
Figure 2	Significant incidents versus number of injuries and fatalities	201
Figure 3	Injury and fatality rates for particular installation years	202
Figure 4	Public and nonpublic injury rate and fatality rate	204
Figure 5	Normalized failure rate of different causal factors	206
Figure 6	Normalized failure rate of different causation	207
Figure 7	Comparison between rupture rate and normalized failure rate	211
Figure 8	Probability of different diameter holes caused by punctures	212
Figure 9	Annual rate of leakage, rupture, system-component failure	213
Figure 10	Distance-normalized rupture rate	215
Figure 11	Histogram of rupture size for significant incidents	216
Figure 12	Pipeline wall thickness versus diameter at failure	219
Figure 13	Design factor versus fatality rate	220

Section 10

Figure 1	Annual length and failure rate of offshore gathering pipelines	247
Figure 2	Histogram of rupture size for significant incidents	251
Figure 3	Distance-normalized failure rate versus diameter	253
Figure 4	Length of offshore transmission pipelines installed in different decades	255
Figure 5	Normalized failure rates by different causes (incident age)	258
Figure 6	Normalized failure rate of different causes (installation age)	261
Figure 7	Percentage of segments of different pipe ages	262
Figure 8	Box plots of ratio between operating pressure and MAOP	264
Figure 9	Pipeline diameter and wall thickness for failed pipelines	265
Figure 10	Annual variation of Henry Hub natural gas price and failure rate	273

LIST OF ACRONYMS AND ABBREVIATIONS

BEG Bureau of Economic Geology the University of Texas

CBL Cement bond log.

CCS Carbon Capture and Storage

CO₂-EOR Carbon dioxide based enhanced oil recovery

DOE Department of Energy

EPA Environmental Protection Agency

EOR Enhanced oil recovery

GHG Greenhouse Gas

md. Millidarcy

Mt million metric tons

MIT Mechanical Integrity Test

MMV Monitoring, Modeling, and Verification for CO₂ sequestration

NETL National Energy Technology Laboratory

pH The measure of hydrogen ion activity

ppm parts per million

psi pounds per square inch

UIC EPA Underground Injection Control program

UIC Class VI well EPA designation for permitting a CO₂ GS injection well

USDWs Underground Sources of Drinking Water

Appendix: Papers from the Project

Published Papers:

- 1) **Duncan I. J. Wang H.**, 2014, Estimating the Likelihood of Pipeline Failure in CO₂ Transmission Pipelines: New Insights on Risks of Carbon Capture and Storage *International Journal of Greenhouse Gas Control*, 21, 49-60.
- 2) **Duncan, I., Wang, H.** 2014, Evaluating the likelihood of pipeline failures for future offshore CO₂ sequestration projects. *International Journal of Greenhouse Gas Control*, 24, 124-138.
- 3) **Wang H., Duncan I. J.**, 2014, Likelihood, Causes and Consequences of Focused Leakage and Rupture of US Natural Gas Transmission Pipelines, *Journal of Loss Prevention in the Process Industries*, Volume 30, July 2014, Pages 177–187
- 4) **Wang, H., Duncan, I. J.**, 2014, Understanding the nature of risks associated with onshore natural gas gathering pipelines. *Journal of Loss Prevention in the Process Industries*, 29, 49-55.
- 5) **Zhang, X., Duncan, I. J.**, Huang, G., and Li, G. C., 2014, Identification of management strategies for CO₂ capture and sequestration under uncertainty through inexact modelling: *Applied Energy*, v. 113, p. 310-317.
- 6) MacMinn, C. W., Neufeld, J. A., **Hesse, M. A.**, & Huppert, H. E., 2012, Spreading and convective dissolution of carbon dioxide in vertically confined, horizontal aquifers. *Water Resources Research*, 48(11).
- 7) **Duncan, I.** 2013, The Bubble/Slug Flow Model for Methane Leakage from natural Gas Wells as an Analogue for Shallow CO₂ Migration. *Energy Procedia*, 37, 4692-4697.
- 8) **Duncan, I.**, 2013, Suicide by Catalytic Converter and Deaths at Lake Nyos; Is Carbon Monoxide the Toxic Agent? Implications for Leakage Risks from CO₂ Pipelines. *Energy Procedia*, 37, 7696-7701.

- 9) Adelman, D. E., **Duncan, I. J.**, 2012, The limits of liability in promoting safe geologic sequestration of CO₂: Duke Environmental Law & Policy Forum, v. 22, no. 1, p. 1-66.
- 10) Nicot, J. -P., and **Duncan, I. J.**, 2012, Common attributes of hydraulically fractured oil and gas production and CO₂ geological sequestration: Greenhouse Gases Science and Technology, v.2, p. 352-368
- 11) Ambrose, W. A., Breton, C., Hovorka, S. D., **Duncan, I. J.**, Gülen, G., Holtz, M. H., and Nuñez-López, V., 2011, Geologic and infrastructure factors for delineating areas for clean coal: examples in Texas, USA: Environmental Earth Science, v. 63, p. 513?-532.

Submitted Papers:

- 1) **Duncan Ian J., Wang H.**, 2015, Unravelling the Impact of Age on the Risks Associated with Natural Gas Transmission Pipelines, [Submitted to Journal of Risk Analysis]
- 2) **Duncan Ian J., Wang H.**, 2015, Risk of Fatalities and Serious Injuries Associated with Unconventional/Shale Gas and other Gas Gathering Pipelines, [Submitted to Journal of Risk Analysis]
- 3) **Duncan Ian J.** 2015, Re-evaluating CO₂ Toxicity and Lethality: Implications for Risk Assessments of Carbon Capture and Storage (CCS), Submitted to International Journal of Greenhouse Gas Control