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A review and assessment of technologies for the geological storage of CO_2 as gas hydrate in aquifers

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FOREWORD

This report contained herein was prepared for the Geological Survey of Canada (GSC), a branch of Natural Resources Canada (NRCan) by the Alberta Research Council (ARC), which is currently known as Alberta Innovates – Technology Futures. The research presented in the report was conducted under a formal Letter of Agreement between NRCan's Office of Energy Research and Development (OERD) and ARC, covering fiscal years 2005-06 and 2006-07. Primary funding for the study was provided by Canada's Climate Change Action Plan 2000 (CCAP 2000), with limited in-kind support provided by both the GSC and ARC. The ARC report is presented in its entirety, as delivered by ARC to GSC, without changes or editorial comment by the GSC Scientific Authority.

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A REVIEW AND ASSESSMENT OF TECHNOLOGIES FOR THE GEOLOGICAL STORAGE OF CO_2 AS GAS HYDRATE IN AQUIFERS

Final Report for Geological Survey of Canada

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EXECUTIVE SUMMARY

Governments from around the world have expressed an interest in taking action to address the risks of global climate change. One recent approach for preventing large volumes of CO_2 from being released into the atmosphere is the capture of CO_2 from industrial facilities and storing it in deep geological formations. One CO_2 storage application could involve the capture, transport and storage of CO_2 as a hydrate in aquifers in locations where CO_2 hydrate formation is possible or methane hydrates already exist. This paper outlines the technologies that would be associated with this CO_2 storage application.

Gas hydrates or clathrate hydrates are ice-like solids, non-stoichiometric compounds of gas molecules and water. They form when low molecular guest molecules such as CH_4 or CO_2 come into contact with water under certain thermodynamically favourable conditions (typically, temperature less than 300K and pressure more than 0.6 MPa).

Three specific reservoir types have been identified by the Geological Survey of Canada as having the appropriate pressure and temperature conditions to maintain stable CO_2 hydrates:

1. sub-sea sediments
2. sub-permafrost aquifers in the far north
3. sub-lake sediments below Lake Superior

In some cases, these technologies will be similar to other CO_2 storage applications. Perhaps CO_2 hydrate formation is most similar to CO_2 storage associated with coalbed methane except that in coals, the CO_2 is sorbed to the coal as a dense phase. Certain conditions for storing CO_2 in hydrate form are quite different from other CO_2-storage applications such as CO_2 enhanced natural gas recovery or CO_2 enhanced oil recovery. Hydrate conditions may require different technologies to be considered in the capture, transport, injection and monitoring of CO_2. Additionally, numerical studies will be important for providing an integrated understanding of the process mechanisms in predicting the potential and economic viability of methane production and CO_2 storage in a hydrate geological reservoir.

With respect to the capture of CO_2 that could ultimately be stored as a hydrate, the feasibility and likelihood of commercial application of CO_2 capture technology depends very much on the industrial process from which the waste CO_2 stream is produced. There are a number of processing options available for separation of CO_2 from produced gas streams containing CO_2, including gas separation membranes, chemical absorption, physical absorption and cryogenic systems. All of these have been used commercially. Mackenzie Valley gas could also be handled using commercially available processes if they contain sufficient CO_2 for a large scale hydration operation. Final selection of capture technology would depend on process specifics, such as gas stream composition, pressure, flow rate, and operating costs.

The location of storage opportunities somewhat limits the potential sources of CO_2 and suggests that relatively long CO_2 pipelines may be required. CO_2 can be pipelined in dense phase at temperatures from –25°C to 0°C, thereby reducing the impact in permafrost areas. As a general rule, transportation costs still are only 5-15% of overall projects costs with capture being the vast majority (80%) of overall costs. The risks associated with the handling and transport of pure CO_2 are technically manageable and low, relative to the risks associated with many other industrial gases and chemicals. Properly designed and operated, a high-pressure CO_2 pipeline should present minimal health and safety risk. Further, the risks associated with operating a high-pressure CO_2 pipeline are significantly less than those associated with produced hydrocarbon streams containing H_2S.

Operations where CO_2 is injected into subsurface aquifers to form stable hydrates in the reservoir face some unique challenges in designing and operating the transportation and well systems. For example, warm gas (above the hydrate stability temperature at the injection pressure) may need to be injected to ensure hydrates do not form near or in the wellbore. As well, shut down scenarios for the CO_2 pipeline transportation system must minimize the volume of cold gas that would be injected into the wells at restart to minimize the risk of forming hydrates in the well and reducing injectivity. Wells that penetrate permafrost zones must be insulated to prevent gas cooling and thaw of the permafrost. Injection pressures must be managed to prevent hydraulic fracturing in the reservoir and to minimize formation movements that could impact the well seal integrity. Ultimately, casing and cement corrosion downhole can be minimized with appropriate selection of materials.

Reservoir modelling was the prime objective of an accompanying report. Results were promising for CO_2 hydrate storage. Future focus should be on: evaluating accompanying ice formation in the lower temperature reservoirs; injection of hot CO_2 into 100% water saturated aquifers near 0^oC; co-production of methane from existing hydrates and CO_2 storage in hydrates; geomechanics of permeability changes during hydrate formation; competing carbonate mineral reactions with CO_2 hydrate formation; slurry injection of hydrates; and horizontal well placement.

Monitoring and verification are an integral part of the performance assessment of a geological storage project. As such, the implementation of an appropriate monitoring scheme is the core of a monitored decision framework. The focus of monitoring depends on the phase of monitoring (operational, verification or environmental) and the particular mechanism (i.e. migration, leakage or seepage) being measured. The monitoring systems will be different for each reservoir situation and reservoir type. There are a variety of effective tools and methods for monitoring the injection of CO_2 underground that will delineate how the fluid is migrating, and whether or not the sink is leaking. These monitoring techniques combined with analytical and numerical techniques will help to either validate or adjust the predicted migration of the CO_2 plume, and the soundness and robustness of the properties input into the models, as well as to take any mitigation activity if the facility underperforms. The cost versus benefit must be weighed in deciding which monitoring techniques to apply.

1. INTRODUCTION

Governments from around the world have expressed an interest in taking action to address the risks of global climate change. Typically, governments, including the Canadian federal government as well as several provincial governments are pursuing a portfolio of actions. This portfolio usually includes energy conservation, renewable energy and fuel switching (e.g. moving from coal to natural gas for power generation). Over the past several years, governments have begun working with industry, academia and non-government organizations to pursue another option for reducing greenhouse gas emissions – Carbon dioxide (CO_2) capture and geological storage. CO_2 capture and storage is a process for reducing greenhouse gas emission into the atmosphere by first extracting CO_2 from gas streams typically emitted during electricity production, fuel processing and other industrial processes. Once captured and compressed, the CO_2 can be transported to a storage site, often to be injected into a geological formation where it can be safely stored for the long-term.

The most common geological storage applications have been using CO_2 to enhance the recovery of oil. This practice has been used in the United States since the 1970s. More recently, industry and the research community are exploring other CO_2 storage applications such as CO_2 enhanced coalbed methane recovery and CO_2 enhanced natural gas recovery. Storage of CO_2 in deep saline formations represents another application for storing large quantities of CO_2.

While the focus of most deep saline aquifer storage projects has been on storing CO_2 in a liquid or supercritical phase, there may be opportunities for CO_2 to be stored as a hydrate in certain formations. This paper will review and discuss the technologies that would be needed for such a form of CO_2 storage.

Gas hydrates or clathrate hydrates are ice-like solids, non-stoichiometric compounds of gas molecules and water. They form when low molecular guest molecules such as CH_4 or CO_2 come into contact with water under certain thermodynamically favourable conditions (typically, temperature less than 300K and pressure more than 0.6 MPa) (Sloan, 2003). Host water molecules form a hydrogen-bonded cubical cavity around gas molecules and are the basic building block for gas hydrates. Within the cavity, gas molecules are held in place by Van der Waals forces with limited translation but substantially more spin and vibrational mobility. The gas molecules trapped into cavities are effectively compressed with an average gas density many times greater than would be predicted for the ambient pressure.

When pressures and temperatures are changed, which places the hydrates outside their stability zone, they are prone to decompose at rates that depend on many factors, including hydrate structure and composition, and the physical state and properties of the hydrate and its surroundings. The technologies for recovering CH_4 from hydrates are very challenging and are still under development. The three most practical methods are: (1) depressurization, in which the pressure of an adjacent gas phase is lowered to cause decomposition; (2) thermal stimulation, in which an external source of energy is used; and (3) inhibitor injection, in which CH_4 or some combination of inhibitors is used to de-equilibrate the system. The process of injecting CO_2 into the hydrate reservoir for the purpose of CO_2 sequestration and CH_4 recovery will be more complex. CH_4 and CO_2 hydrate stability conditions will allow the possibility of storing CO_2 in a hydrate reservoir and at the same time enhancing CH_4 recovery.

Aquifers would be selected so that the CO_2 hydrate is stable without requiring intervention or maintenance. As long as the CO_2 hydrate does not decompose, the CO_2 will remain immobile in the aquifer, greatly reducing the potential for the CO_2 to leak from the aquifer. Three specific reservoir types have been identified by the Geological Survey of Canada as having the appropriate pressure and temperature conditions to maintain stable CO_2 hydrates:

1. sub-sea sediments
2. sub-permafrost aquifers in the far north
3. sub-lake sediments below Lake Superior

There is also potential to store CO_2 in formations that already contain methane hydrates. The side benefit of these CO_2 storage operations would be the production of methane.

This paper will examine the technologies needed for the capture, transport, injection and monitoring of CO_2 being stored in hydrate form. In some cases, these technologies will be similar to other CO_2 storage applications. Certain conditions for storing CO_2 in hydrate form are different from other CO_2 storage applications such as CO_2 enhanced coalbed methane recovery or CO_2 enhanced oil recovery. These conditions may require different technologies to be considered in the capture, transport injection and monitoring of CO_2. Additionally, numerical studies will be important for providing an integrated understanding of the process mechanisms in predicting the potential and economic viability of methane production and CO_2 storage in a geological reservoir.

Section 2 will discuss technologies for CO_2 capture, including pre-combustion or non-flue gas alternatives and post-combustion (flue gas) alternatives. Where available, this section will also describe the extent to which these technologies are being commercially utilized.

Pipelines are the most likely method of transporting large volumes of CO_2. Section 3 will discuss design and economic costs associated with CO_2 transport, particularly in cold northern climates where the initial CO_2 hydrate applications are expected to occur.

Section 4 will discuss CO_2 injection and sub-surface technologies. This section includes a discussion of technology performance under cold weather conditions. Critical in the determination of appropriate technologies is an understanding of the geomechanical impacts of CO_2 injection on casing design, casing and cement corrosion in the presence of $CO_{2,}$ and wellbore hydraulics and heat transfer for CO_2 injection.

Section 5 summarizes current approaches for reservoir monitoring, and documents possible modelling approaches and geochemical and geomechanical interactions.

Section 6 will discuss areas for future technology research related to CO_2 hydrate storage.

For the purposes of this study, a number of key assumptions have been made to facilitate the analysis. First, while there may be a range of national and international opportunities for storing CO_2 in hydrate form, the technology review will focus on applications similar to those being pursued at the Mallik reservoir in northern Canada. Other opportunities may exist in northern Alberta and possibly under Lake Superior. Technologies that may be unique to these opportunities are not discussed in detail in this paper.

With respect to the CO_2 being captured, pipelined and injected, it is assumed that it will have a purity of at least 95%. While lower concentrations of CO_2 can be injected into formations, it is most likely that CO_2 would need to be pipelined in a dense liquid phase. CO_2 at lower concentrations would present significant obstacles with respect to its safe and efficient transport.

2. TECHNOLOGIES FOR CO_2 CAPTURE

The purpose of this chapter is to provide an overview of the technologies currently available for capture of CO_2 from industrial sources. It also provides an overview of CO_2 pipeline transportation considerations. The content of the chapter is based on literature and internet surveys and on non-confidential knowledge acquired through carrying out several confidential studies over the past three years. The content is intended to be used for screening evaluation purposes and should not be used for definitive technology selection.

2.1 BASE ASSUMPTIONS

CO_2 Purity

As discussed in section 1, a key assumption related to the utilization of CO_2 for methane hydrate production and CO_2 storage is that CO_2 purity as delivered to the injection site must be 95%+ pure. There are three reasons for this:

1. This level of purity allows the CO_2 to be pipelined in dense phase rather than as a gas. The result is a much higher pressure but substantially smaller diameter pipeline and the ability to use booster pumps rather than compressors to move the fluid. This appears to be the form in which all existing CO_2 is transported over long distances.
2. The lower limit of CO_2 gas stream purity that would allow effective hydrate formation is unknown.
3. High levels of impurities (such as would be the case if untreated dry flue gas with high N_2 content were to be transported) results in high transportation costs for non-greenhouse gases and loss of reservoir space for CO_2 storage.

Storage Site Locations

Another key consideration is the potential locations for subsurface storage of CO_2 in hydrate form. Based upon direction from the Geological Survey of Canada and on current research related to methane hydrate occurrences in Canada, the locations under consideration are:

- Northwest Territories
- Northern Alberta
- Under Lake Superior

CO_2 Recovery Options:

The report reviews the following CO_2 recovery options:

- Pre-combustion or non flue gas alternatives
- Post-combustion (flue gas) alternatives

Economics

The report contains no detailed economic analyses. In categorizing technologies "commercially available" is defined as presently existing in a business-driven application. "Commercially ready" means that a process has undergone pilot and demonstration unit testing at conditions and sizes that allows for a reasonably accurate prediction of operating conditions and performance in business-driven applications.

The use of the word “commercial” does not imply that a technology would be found to be economically attractive in any application in comparison to others. Where business-driven applications exist, it may be assumed that the business entity has likely undertaken economic analyses and that in their particular circumstances the technology has been deemed to be more economically attractive than the alternatives.

A benchmark of five years from now has been set as the time frame in which opinions expressed here on commercial availability or readiness are likely to remain valid. Beyond that point, it is possible that research and development presently underway may result in a wider range of available technologies being commercially available or ready. The report explores some of these possibilities as well.

Any CO_2 recovery costs quoted in this report should be used only to compare the relative cost of each technology. Both the figures from the International Energy Agency (IEA) study referenced and from the work used as a basis for the comments made here are for the most part based on CO_2 recovery from coal-fired utility power generation.

Further, energy cost (electricity and natural gas) is a key component of the recovery cost of virtually all the technologies reviewed. The IEA study was based on energy costs of $2.5/GJ and other work has generally been based on energy costs ranging from $1.5/GJ - $2.5/GJ. These costs are now out of date.

All cost numbers are quoted in US Dollars.

References

It is beyond the scope of this survey to review or provide detailed analysis of the large body of literature that exists discussing CO_2 capture processes. Most of the material used comes from internal non-confidential records associated with various studies performed for clients. There are two overview papers that contain more detailed discussions and address some of the more speculative and long-term prospects for technology innovation. Neither report addresses pipeline transportation of CO_2:

- *White et al; Separation and Capture of CO_2 from Large Stationary Sources and Sequestration in Geological Formations – Coalbeds and Deep Saline Aquifers, Journal of the Air and Waste Management Association, June, 2003*.

  This paper provides more in-depth analysis of present and emerging CO_2 capture technologies and projects into the area of processes in the pure or theoretical research stage. It does not discuss transportation of CO_2.

- *Wong et al; CO_2 Separation Technology in Enhanced Oil Recovery: A State-of-the-Art Technical & Economic Review, Alberta Research Council, March, 2002.*

  This report covers similar ground to that of the White paper, and adds more specific cost detail.

- *Stobbs et al; Clean Coal-Fired Power Plant Technology to Address Climate Change Concerns, Canadian Clean Power Coalition presentation to Gasification Technologies 2003, San Francisco, CA, October, 2003.*

  This presentation provides cost analyses for various CO_2 capture technologies, all based on coal as a fuel. The value of the report is its basis on detailed and plant-specific engineering calculations. The presentation can be found at: www.canadiancleanpowercoalition.com.

2.2 CO_2 CAPTURE PROCESSES

Table 2.1 on the following page summarizes the findings of the CO_2 capture section and compares key parameters for each technology.

Generally, processes for separating CO_2 from other gases fall into the following categories:

Pre-Combustion Schemes:

These involve fundamental changes to the way the CO_2 is produced in the first place. Examples are firing a furnace with oxygen and recycled CO_2 instead of air to eliminate nitrogen in the flue gas stream (oxy-fuel), or partial oxidation of hydrocarbons to produce a synthetic gas that has a higher CO_2 content and is at a higher pressure (gasification). These options are reviewed in sections 2.2.1 and 2.2.2.

Non Flue Gas Alternatives:

Two possible non-flue gas alternatives might prove attractive in the present circumstances:

- Physical absorption of high CO_2 content acid gas produced in conventional sour gas sweetening operations using Flexsorb™ or similar processes. Recovery of CO_2 from arctic gas produced in conjunction with the proposed Mackenzie Valley pipeline could be an ideal source for this approach. It is discussed in Section 2.2.8.
- Chemical absorption of pressure swing adsorption (PSA) purge gas from large hydrotreating or hydrocracking operations that produce their hydrogen via steam methane reforming. A significant volume of CO_2 is available in the Ft. McMurray area from sources associated with oil sands bitumen upgraders. This is discussed in Section 2.2.5.

Post-Combustion Alternatives:

A range of post-combustion recovery technologies, including chemical absorption, membranes, cryogenic separation and adsorption can be used for the separation of CO_2 from flue gas stream. These are described in sections 2.2.4 to 2.2.10.

Table 2.1: Summary of CO_2 Recovery Technology Issues

Parameter	Chemical Absorption	Gas Absorption Membranes	Gas Separation Membranes	Physical Absorption	Cryogenic Separation	Adsorption	O_2-Enriched Combustion
CO_2 Purity, %	+ 99.9%	+ 99.9%	45% (1-stage) 90-95% (2-stage)	96 - 98%	99.9%	75%	99%
Cost, \$/tonne CO_2 (from IEA report; based on flue gas source)	35	45	47	not calc.	not calc.	84	16
Cost, \$/tonne CO_2 (previous SNC-Lavalin work)	47	56	109	not calc.	not calc.	not calc.	31
Cost, \$/tonne CO_2 (CCPC Study, based on flue gas)	45-55						110
Status of Technology	Proven, some concerns re scale-up	One system in use for prod. gas, none for flue gas	Proven for produced gas, lab scale only for flue gas	Proven for acid gas, not used for flue gas	Proven for inlet CO2 >90% not widely used otherwise	Proven for acid gas, but much lower CO2 content	Lab scale only
Advantages	Proven technology, PG avail., low CO2 cost	Compact, may be good for off-shore	Low energy & operating costs	Proven technology, PG avail.	Proven technology, PG avail. at lower volumes	Not suitable for flue gas	Simple concept, potential to reduce CO2 cost
Disadvantages	Energy costs, amine make-up	Energy, amine make-up, PG likely not avail.	Recycle needed for purity, PG not available	High cost due to high inlet pressure	Prohibitive CO2 cost	Prohibitive CO2 cost, PG not avail.	Very high technical risk, PG not avail.
Potential for improvement	Good	Good	Promising	Limited	Limited	Limited	Promising
Recommendation	Basis for comparison	Monitor developments (short-run)	Monitor developments (long-run)	Suitable for natural gas applications	Not suitable	Likely not suitable	Monitor developments (long-run)

Notes:

1. PG = performance guarantee
2. CO_2 costs expressed in \$/ton CO_2 "avoided", or "net" - considers additional CO_2 emitted during capture process.
3. CO_2 costs based on coal-fired utility power generation using medium-sulphur coal.
4. IEA costs from "Carbon Dioxide Capture from Power Stations" (www.ieagreen.org.uk/sr2p.htm), +/- 30% accuracy.
5. IEA costs include compression but not transport.
6. Both SNC-Lavalin & IEA costs for Gas Separation Membranes based on 45-55% pure CO2 - may not be suitable for hydration.
7. SNC-Lavalin costs from previous studies. Include compression & transport. Costs estimated to be +/- 35 % accuracy.

2.2.1 Oxygen enriched combustion

Two of the defining characteristics of flue gas from conventional boilers are low CO_2 content and high gas volume. This is largely due to combustion of the hydrocarbon stream in air, which consists of roughly 80% inert nitrogen. The inert component must be cooled, handled, and separated from the CO_2. Separation of nitrogen and CO_2 is relatively difficult and the presence of 80% nitrogen results in large volumes of gas being handled.

Oxygen enriched combustion ("Oxy-fuel") uses combustion in an oxygen enriched stream as opposed to air, to obtain a flue gas stream with a much higher concentration of CO_2 and a much smaller volume. This process is shown in Figure 2.2.

Because combustion in oxygen results in a much higher temperature in the boiler versus combustion in air, under an oxy-fuel scenario a portion of the flue gas is recycled back to the boiler to control flame temperature. The most significant drawback to oxy-fuel systems is the cost and parasitic power demand of the oxygen production. Cryogenic separation is typically used for production of very large volumes of oxygen, particularly where oxygen purity is not a critical requirement. These systems are commercially available from several suppliers. The air separation technology is mature and significant reductions in costs are not expected.

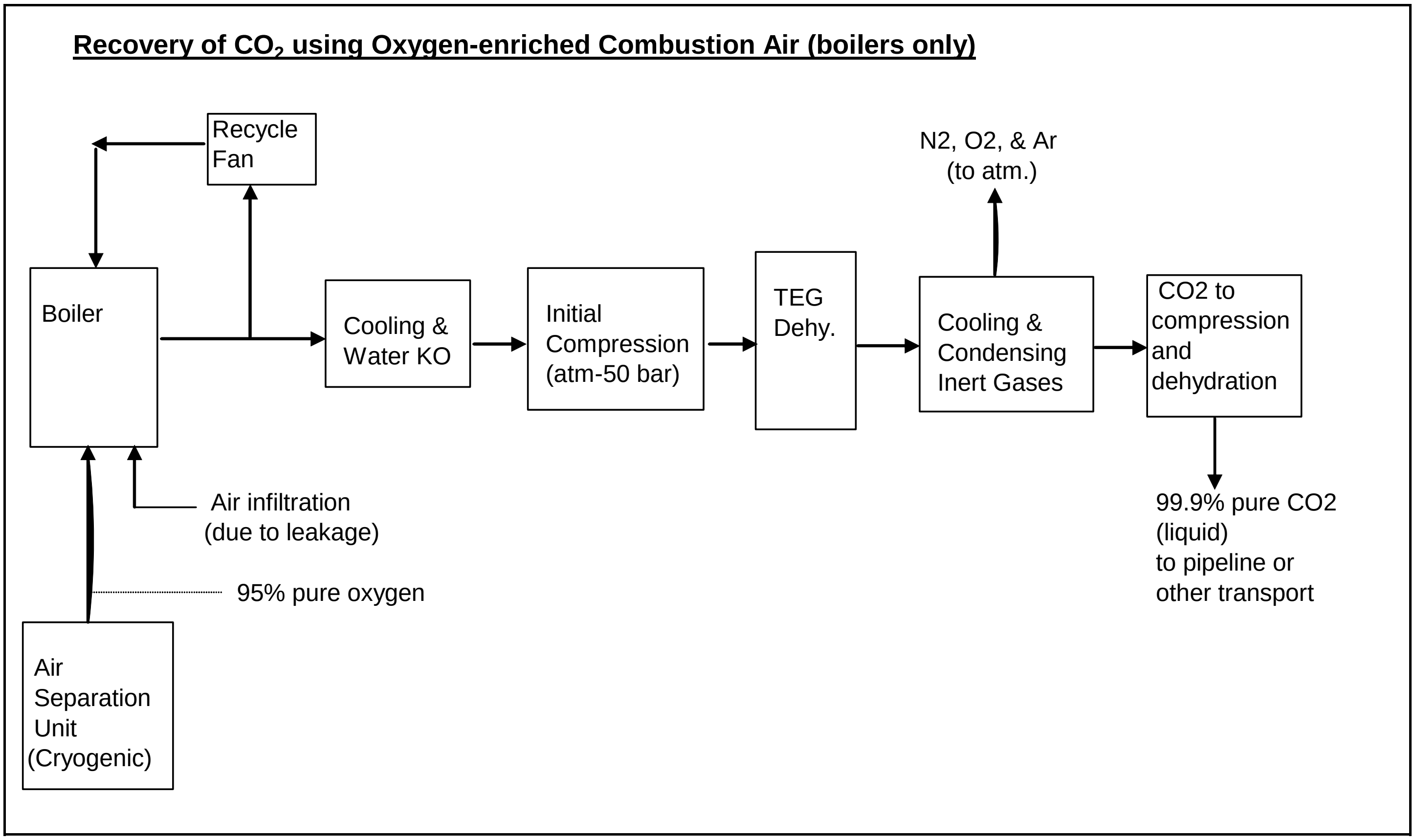

Figure 2.2: Recovery of CO_2 using Oxygen-enriched Combustion Air

In addition to the high capital and operating costs associated with an oxygen plant, significant modifications would be required to any existing boiler and its flue gas handling systems to accommodate the different flame characteristics and flue gas recycling required for an oxy-fuel system.

It is not clear from published studies, however, that oxy-fuel operation would necessarily result in a lower overall CO_2 recovery cost compared to conventional air combustion systems, due mainly to the high oxygen production cost.

There are several initiatives underway to explore possible commercialization of Oxy-fuel combustion. Some of these are driven by industry and others by government research. One U.S. company, Jupiter, has been using oxy-fuel principles in aluminium production for several years and claims to have tested their process successfully in small scale coal fired test equipment.

A previous study (2001) estimated the cost of CO_2 recovery using oxy-fuel at around $31/t CO_2 avoided, compared to about $47/t for amine-based chemical absorption. A recent study by the International Energy Agency's Greenhouse Gas R&D Programme (IEA), entitled "Carbon Dioxide Capture from Power Stations" (www.ieagreen.org.uk/sr2p.htm) estimated recovery costs using oxy-fuel at $16/t CO_2 avoided, versus $35/t for amine-based systems.

While these studies have indicated very promising CO_2 costs (i.e. – lower than conventional amine-based flue gas CO_2 recovery systems), there is a high degree of uncertainty associated with these estimates. For example, another study commissioned by the Canadian Clean Power Coalition appears to indicate a cost per tonne of CO_2 avoided in the neighbourhood of $110/tonne (http://www.canadiancleanpowercoalition.com).

Because the technology has not been demonstrated at large scale, design considerations such as burner modifications, amount of recycled gas required, and start-up considerations do not appear to have been well thought out yet, and lend uncertainty to the costs. The technology needs to be developed beyond the present laboratory and pilot scale, including the need to build and operate demonstration and semi-commercial units that generate power.

Bearing in mind the strong need for reliability of power supply in very cold climates, the virtual re-design of the boiler and the additional complications of flue gas recycling and oxygen generation for oxy-fuel systems might significantly compromise power generation operations and availability.

The issues with the use of oxy-fuel for CO_2 hydrate storage as presently conceived are as follows:

- No commercial experience with technology - no demonstration units have been built to date;
- High technology risk. Significant design issues must still be resolved;
- High capital and operating costs associated with oxygen separation units;
- High level of uncertainty associated with cost studies to date. There is no guarantee this unproven technology would in fact lead to a lower CO_2 recovery cost;
- Not acceptable in prototype or first commercial installation situations where high power system reliability is required.

CO_2 capture using oxy-fuel systems may offer some long-term promise, particularly if significant reductions in oxygen production costs can be achieved, or if the technology can be established at commercial scale and reliability and potential cost savings borne out. These reductions would likely occur through the development of radically different air separation technologies (e.g. – oxygen membranes) rather than through improvements in cryogenic oxygen separation. None of these technologies are close to being commercially ready at this point.

While CO_2 recovery using oxy-fuel is promising in the long run, the technology has not been developed to a level where it could be recommended to be further investigated with respect to storing CO_2 in hydrate form.

2.2.2 Gasification

Gasification involves partial oxidation of a hydrocarbon stream, using either air or oxygen resulting in a synthesis gas (syngas) stream that is rich in hydrogen, carbon monoxide and CO_2. This stream is typically treated to remove acid gases (H_2S and CO_2) and burned in a gas turbine to generate power. Under a CO_2 recovery or hydrogen production scenario however, carbon monoxide in the synthetic gas is converted to CO_2 using a “water gas shift” reaction, and the CO_2 is recovered. A physical absorption system is generally used, as the syngas stream is typically at a pressure (around 20 bar or 300 psia) where physical absorption is cost effective.

Gasification is a well-understood and commonly used technology for many refinery and petrochemical applications as the synthesis gas can be used as a basis for manufacturing other products such as hydrogen, methanol, ammonia, etc. It has not been used extensively for base-load utility systems due to its high cost and historically low availability compared to conventional boilers.

For power generation under a CO_2 capture scenario, gasification has some attractive features and may be more widely used in the future, particularly as more systems come on stream and problems with low availability are resolved. For power applications, we would expect it to be considered only where the fuel source is coal, petroleum coke, or heavy fuel oil. The likely configuration would be a gasifier producing synthesis gas, integrated with CO_2 capture and a integrated gasification combined cycle (IGCC) power plant.

There is at least one gasification plant in the construction stage in the Ft. McMurray area (OPTI/Nexen), gasifying asphaltene byproducts from the bitumen upgrading process. When started up in approximately 2009, it will represent an attractive CO_2 source along with others from different processes in that area.

The likely long gestation time associated with implementing CO_2 hydrate storage may well result in IGCC being commercially ready in isolated, high-reliability applications at about the same time.

2.2.3 Recovery of Co_2 from gas processing plant acid gas using Flexsorb™ or similar process

Previous studies have identified the acid gas streams from many sour gas processing plants as potentially attractive sources of CO_2. CO_2 content varies widely from plant to plant. Presently these streams are either being fed to sulphur recovery facilities, in which the CO_2 becomes part of the flue gas, or injected directly into depleted gas reservoirs in acid gas injection schemes. In the past few years these have become increasingly popular in Alberta and British Columbia with over 40 such facilities in operation.

For this scheme, acid gas streams being directly injected are probably less attractive, as the focus is on sources of CO_2 not presently being captured and the presence of significant H_2S in the injected stream may render sour an otherwise sweet gas deposit.

Technology is commercially available and in use for the purpose of controlling the amount of CO_2 "slipped" to the sales gas stream, and at least one Alberta operation is currently recovering CO_2 for commercial sale.

Flexsorb^{TM} is a commercially used chemical absorption system designed for selective removal of H_2S in the presence of CO_2. The solvent is described as a "severely hindered amine", and was developed as an alternative to MDEA-based solvents, which are more limited in their capacity to absorb H_2S. Flexsorb^{TM} is licensed by ExxonMobil. ExxonMobil indicated that based on operating conditions at other plants they have typically designed a maximum recovery of about 60% of the available CO_2. In connection with another project, ExxonMobil expressed an opinion that Flexsorb could be appropriate for this kind of application. Installation of an Exxon Flexsorb™ unit or similar technology that selectively removes H_2S from the acid gas would produce a relatively pure stream of CO_2 that could be sent directly to compression. This stream would likely contain about 0.5% H_2S, depending on the design specification.

Other solvents were not investigated for this report. It may be possible that there are other solvents that are appropriate for this application that can improve on CO_2 recovery. Depending on the specification for H_2S in the CO_2 stream, it may be possible that MDEA-based solvents could also be used.

This absorption process operates in a similar manner to the amine-based chemical absorption systems used for flue gas. The acid gas stream is fed to an absorber at close to atmospheric pressure. H_2S is absorbed by solvent, then regenerated from the solvent through the addition of heat in a second column. The system can be designed to meet a very low H_2S content in the treated gas (i.e. - CO_2) stream, resulting in over 99% of the H_2S going to the sulphur plant or separate acid gas injection operation. If enhanced oil recovery (EOR) or CO_2 storage in a sour reservoir were to be contemplated, because the produced hydrocarbons would already contain H_2S, and because H_2S can improve CO_2 miscibility in certain reservoirs, it may be possible that a relatively high level of H_2S (up to 5% based on pipeline requirements) in the CO_2 can be tolerated, leading to a less demanding absorber design.

This alternative could have the following advantages for post-combustion CO_2 recovery:

- Likely much lower CO_2 recovery cost than post-combustion chemical absorption from flue gas;
- Simpler equipment logistics and construction; and
- Less disruption of processing plant operations.

If the CO_2 content of raw gas from Arctic areas associated with the proposed Mackenzie Valley Pipeline is sufficiently high, this would represent an ideal source of CO_2 for storage opportunities in the Northwest Territories, owing to proximity of the source and potential sinks.

2.2.4 Recovery of Co_2 from PSA purge gas using chemical absorption

In this configuration, CO_2 is recovered directly from the Pressure Swing Adsorber (PSA) purge gas stream at a steam methane reformer used for hydrogen production. Typical sources would be refineries, heavy oil and bitumen upgraders and ammonia-based fertilizer plants not in the business of producing urea. The PSA purge gas contains about 45% CO_2 along with hydrogen, methane, and carbon monoxide. It is not vented but returned to the reformer burners. The stream would be amenable to some type of chemical absorption.

The absorber for PSA purge gas would be much smaller than that required for recovery of CO_2 from steam methane reformer flue gas. This is due to the much smaller gas volume (about 15% of that of the flue gas). Unlike flue gas, inlet gas cooling would not be required, as the PSA purge gas is at ~50°C.

One of the well-known processes associated with enriching synthesis gas streams is Benfield. After discussion with the Benfield system licensor, it was tentatively concluded that the hot carbonate-based Benfield process may not be an economically feasible alternative. This is due to the requirement to raise the pressure of the purge gas to the point where the Benfield system would operate effectively, around 7 – 15 bar (100 – 200 psia). This situation is similar to that outlined for physical absorption, and is described in more detail in section 2.2.9.

Recovery of CO_2 from the PSA purge gas could have the following advantages versus post-combustion recovery:

- Potentially lower recovery cost;
- Much smaller CO_2 absorber;
- Less potential impact on reformer operations; and
- Replacing the inert portion of the purge gas stream from the reformer fuel gas system could provide opportunities for simpler operation (one burner system vs. two) and a possible opportunity to de-bottleneck the reformer if it is limited by flue gas back pressure constraints.

2.2.5 Chemical absorption

All commercial installations in existence today recovering CO_2 from flue gas are based on chemical absorption using amines. Chemical absorption has been used extensively in the gas processing industry to remove CO_2 from hydrocarbon gas streams, generally using some form of alkanolamine solvent. The CO_2 in the gas reacts with the amine in an absorber column and then is stripped from the amine through addition of heat in a regenerator column. Absorber columns generally operate in a counter-current fashion: the CO_2-rich gas enters the absorber column at the bottom and flows upward, and the lean amine solution enters near the top and flows downward, usually over trays or packing. The CO_2-rich amine is pumped from the absorber tower bottom to the regeneration column. For flue gas applications the incoming gas is generally cooled to about 50°C. Figure 2.3 describes this process.

Costs for this type of system are reported to be in the range of \$30-50/t CO_2 avoided. The IEA report quoted earlier estimated \$35/t CO_2 avoided. The studies used as the background for this report have indicated similar or higher costs, but costs are very project and site specific, and are very sensitive to the energy costs used and opportunities for heat integration with other local users of thermal energy.

One recent site specific study indicated that the cost per tonne of CO_2 captured from post combustion sources increases by about $5.00 for every $1.00 per thousand standard cubic feet (mcf) of natural gas price increase.

Each amine has different process characteristics with respect to CO_2 (or other acid gases like H_2S), in terms of reaction rates, absorption capacity, and the amount of heat required to regenerate the amine. Other factors such as solvent stability and corrosion potential are also important. Generally a 15 – 30% solution by weight in water is used, to reduce corrosion potential and improve flow characteristics. Amines in this service can be divided into four general groups:

- Primary amines (monoethanolamine or MEA, diglycolamine or DGA);
- Secondary amines (diethanolamine or DEA);
- Tertiary amines (triethanolamine or TEA, methyl-diethanolamine or MDEA);
- Mixtures of the above.

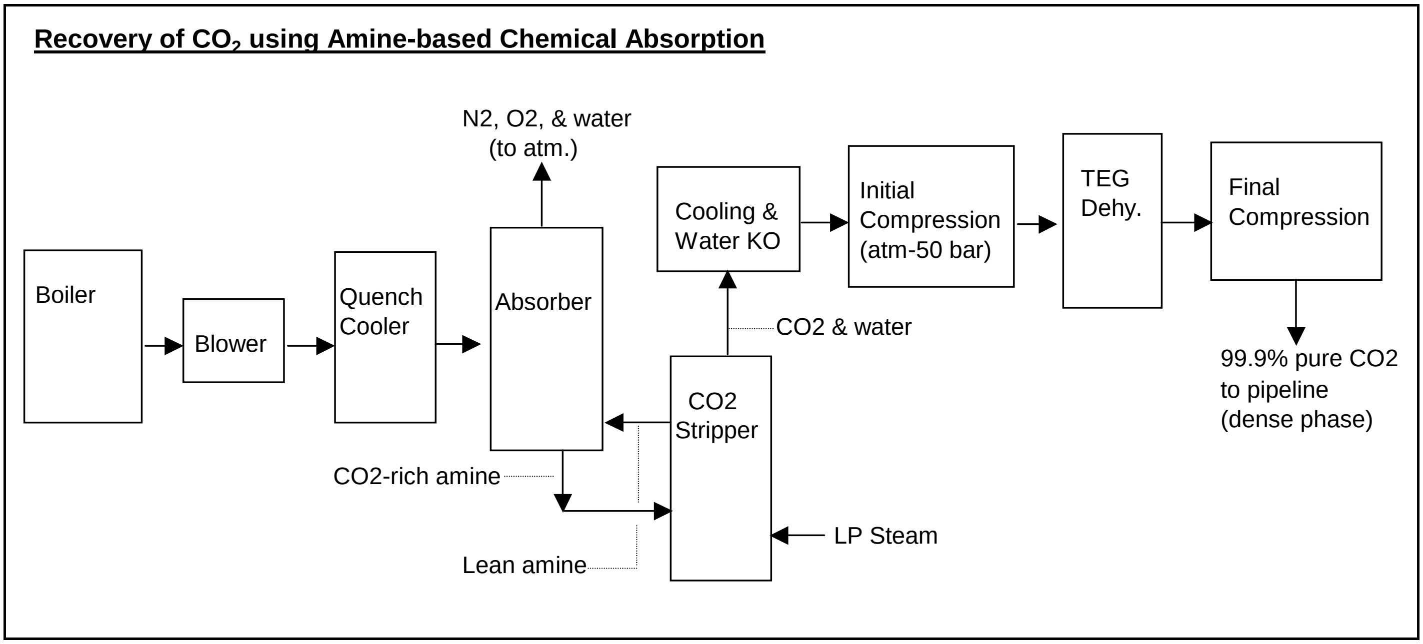

Figure 2.3: Recovery of CO_2 using Amine-based Chemical Absorption

MEA is most commonly used for CO_2 removal in both flue gas and other applications because (generally) compared to the other amines, it is the least expensive, has the highest absorption capacity, and has the fastest reaction rate. Although MEA has some disadvantages such as higher tendency for carryover and higher corrosion potential, for flue gas applications the overriding design consideration due to the high actual gas flow rates has been the reaction rate. Therefore MEA has been used almost exclusively for flue gas applications. Efforts have been made to improve the design to minimize the disadvantages compared to the other amines. Examples of this are the addition of corrosion inhibitors, and a water wash at the top of the absorber to minimize carryover and solvent loss.

Despite being the technology of choice for this application, there are significant drawbacks to using chemical absorption for recovery of CO_2 from flue gas:

- Degradation of the solvent due to the presence of trace contaminants in the flue gas such as SO_x, NO_x and particulates;
- Large low-grade heat requirements to strip the CO_2 from the amine solution;
- High corrosion potential, particularly in the presence of oxygen;
- Intolerance to high temperatures typically found in flue gas.

There appears to be significant research and development effort taking place to resolve these issues and lower the overall life-cycle cost of CO_2 recovery. It appears most of the effort is focused on increasing the rate of reaction during absorption, reducing the energy required during regeneration, and improving the effectiveness of corrosion inhibitors. Efforts have also been focused on finding other amine-based solvents that, when mixed with MEA, improve the performance.

Generally the degradation issue is addressed by removal of the contaminants from the flue gas prior to the absorber inlet, using processes developed largely for the power industry.

NO_x levels can be a concern, depending on the flue gas source. Typical flue gas “NO_x” consists of NO and NO_2 in a 90:10 ratio. NO is an inert gas that has no impact on the solvent, but NO_2 will contribute to the formation of heat stable salts. Licensors recommend that the NO_2 level should not be greater than 15 ppm in the flue gas.

There are currently at least six proprietary process licensors of commercial chemical absorption technologies:

- ABB Lummus Global (Kerr-McGee/Lummus);
- Cansolv®;
- Fluor Econamine FG PLUS^{SM};
- Mitsubishi (MHI) KS1/KS2;
- Praxair; and
- Universal Oil Products (UOP).

Fluor, MHI and ABB chemical absorption technologies are being used successfully at commercial installations.

A recent development is the announced startup of a 1 ton per hour amine-based CO_2 capture pilot plant attached to a coal-fired power station in Denmark. The technology supplier is IFP (Instituit Francais du Petrole). Because of the small size of this capture pilot, it cannot be considered as a fully integrated facility.

2.2.6 Gas absorption membranes

Gas absorption membranes employ a CO_2–absorbent solution and use the membrane as the mass transfer medium, where the CO_2 migrates across the membrane and into the amine solution for absorption. The membranes used for this application do not necessarily have any selectivity towards CO_2 over the other flue gas components. The selectivity is provided by the amine solution; the membrane is simply a mass transfer medium, substituting for the packing in a conventional packed absorption tower. This process is shown in Figure 2.4.

These systems appear to be a promising alternative to conventional packed towers, offering the possibility of significantly reduced equipment sizes. They may be more appropriate for offshore applications, where size and weight restrictions may make conventional packed columns required for CO_2 absorption at this scale not practical (i.e. >10 m in diameter). They may also lend themselves to modularization better than large conventional towers, again an advantage for offshore use.

This combined technology has been supplied by Kvaerner to StatOil in the North Sea to strip CO_2 from produced natural gas at the Sleipner West field for re-injection and storage in a deep saline aquifer. While no operating issues with this system appear to have been identified, it should be noted that this is a different application than recovery from flue gas due to the much higher operating pressures involved and the strong driving force for compact equipment occasioned by the offshore platform location.

A test application of one such membrane has been undertaken in 2002 by MHI in their CO_2 recovery pilot plant at Kansai, Japan. This technology apparently suffered plugging problems. This unit was being used in an application where the fuel source of the flue gas was liquefied natural gas (LNG). Gas absorption membranes do not appear to have been used commercially on flue gas from oil or natural gas combustion.

This hybrid membrane/chemical absorption technology could be commercially ready for a large-scale on-shore application in gas sweetening in a time period of 5-10 years.

The Alberta Research Council and others are engaged in research to improve the applicability of membranes in this application, particularly in the area of substitution of hollow fibres for sheets of membrane material.

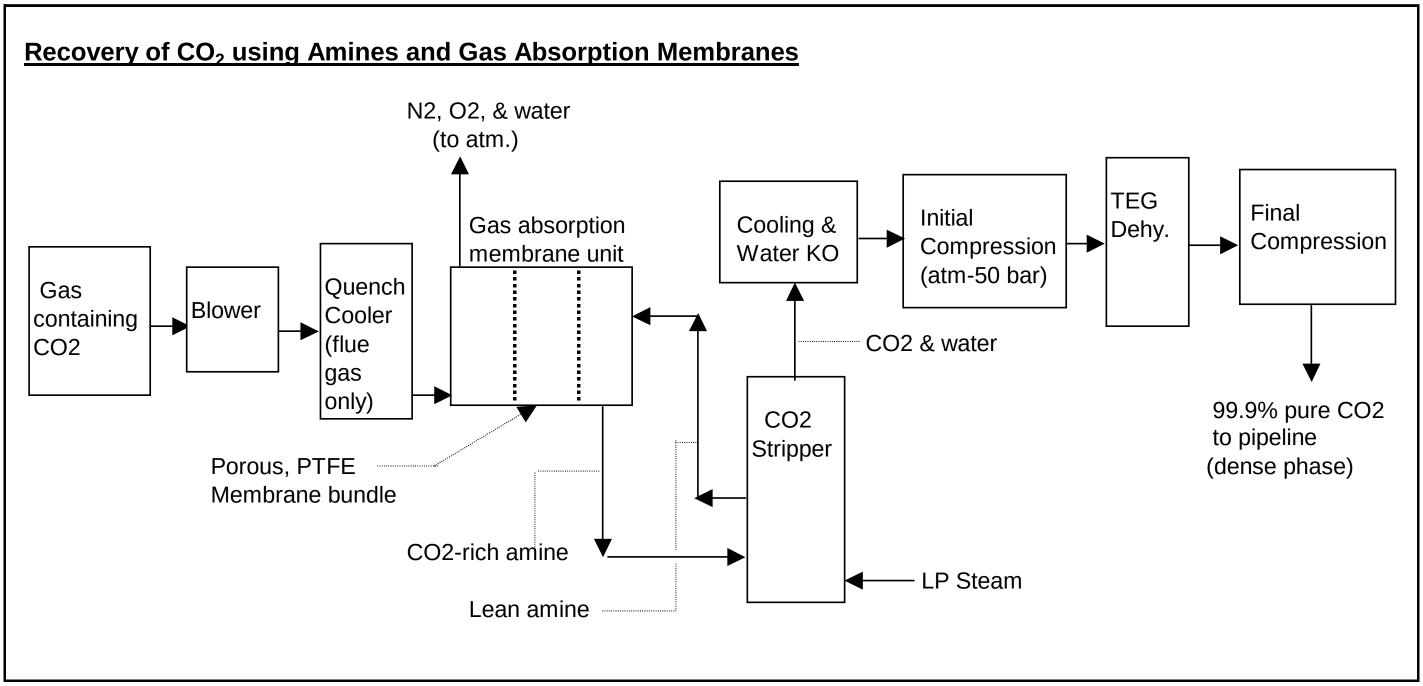

Figure 2.4: Recovery of CO_2 using Amines and Gas Absorption Membranes

A key difference between gas processing and flue gas applications is that even when burning LNG, combustion flue gas can contain a significant amount of soot, dust particles, pollen, etc., all of which can potentially plug the micron-sized pores in a gas separation membrane. None of these contaminants are present in produced hydrocarbon gas.

Due to the additional costs associated with the membrane units versus a conventional absorber, recovery costs for this system are presently estimated to be about 10-15% higher compared to conventional amine-based systems. This comparison should be treated as speculative, as there do not appear to have been any studies comparing the two technologies for use with flue gas.

As with gas sweetening, this application of membrane technology may offer the most likely route to success for membranes in CO_2 capture from low pressure sources. It is conceivable that over a 5-10 year horizon, such a process may be commercially ready in flue gas applications.

2.2.7 Gas separation membranes

Gas separation membranes are available and in use commercially both onshore and offshore for processing gas streams at high pressure and CO_2 content. The primary difference for produced gas separation versus flue gas recovery is that the inlet gas is at a much higher pressure and would likely have a higher CO_2 content than flue gas. The retentate (hydrocarbon) stream also remains at a relatively high pressure for further gas processing and clean-up.

In the southwestern United States, gas separation membranes are used as a means of recovering CO_2 from solution gas streams that are associated with CO_2 - EOR operations.

Gas separation membranes rely on differences in the rate of physical or chemical interaction between each component in the source gas and the membrane material. Membranes designed for the recovery of CO_2 ideally should have a high selectivity between CO_2 and other gas components. This means that the CO_2 permeates faster through the membrane than the other components, leaving the permeate stream more concentrated in CO_2.

Gas separation membranes, as they exist at present, appear to concentrate other pollutants such as SO_x and NO_x into the CO_2 stream. Low levels of these components in the CO_2 do not appear to have an adverse impact on EOR operations, but may influence hydrate formation. More laboratory work, however is required to better understand the impacts of contaminants on gas separation membranes.

The driving force for gas separation membranes is the difference in partial pressure across the membrane. This poses a challenge for flue gas applications because flue gas is at atmospheric pressure and must be compressed to a level that can provide an effective differential pressure across the membrane. The permeate is collected at the lower pressure, resulting in additional equipment and cost to compress the CO_2-rich permeate stream to the required pipeline pressure. This process is shown in Figure 2.5.

Using current membrane technology, it appears that a CO_2 purity of about 45% can be achieved without recycle, with a recovery efficiency of about 60%. This purity is not acceptable for long distance pipeline applications where >95% pure CO_2 is necessary and may not meet requirements for hydrate formation. Therefore a second set of membranes with recycle and secondary compression would likely be required to meet the requirements for storing CO_2 in hydrate form. Some of the required compression horsepower may be recovered through use of a turbo-expander on the high pressure side of the membrane.

Generally gas separation membranes are intolerant of elevated temperatures; another reason why they are less adaptable to flue gas applications.

Gas separation membranes are commercially available and should be seriously considered for CO_2 separation from higher pressure streams such as raw natural gas. They should also be considered as a future promising area for CO_2 recovery because if order-of-magnitude increases in membrane performance can be achieved through improvements in membrane selectivity and reducing the required inlet pressure, CO_2 recovery costs could be significantly lowered. There appears to be significant research and development activity occurring in this area.

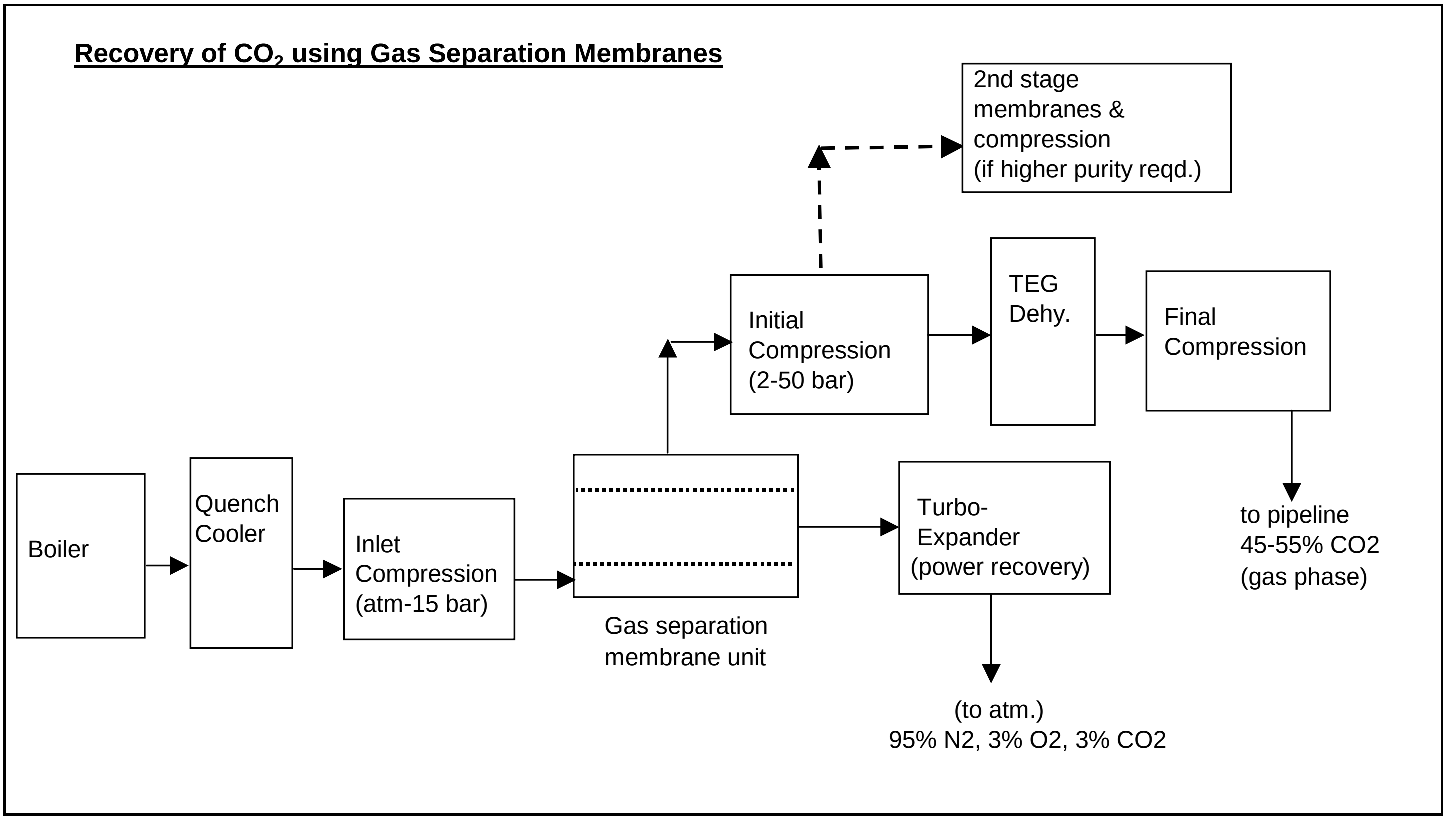

Figure 2.5: Recovery of CO_2 using Gas Separation Membranes

In the longer term, developments in gas separation membrane technology should continue to be closely monitored. If its use in gas processing applications were to expand to lower pressure and lower CO_2 content streams, it would be an indicator of possible emerging applications of interest in this area.

2.2.8 Physical absorption

Physical absorption of CO_2 is a well established method of removing CO_2 from gas streams. The CO_2 is physically absorbed by the solvent, with the CO_2 being more soluble as the pressure increases, and as the temperature decreases. The solvent is typically regenerated by pressure reduction, or by heating, depending on the process design and solvent being used. Physical absorption is commonly used in gas processing and would likely be the technology of choice for CO_2 capture in a hydrocarbon partial oxidation/gasification system, where the syngas is typically at about 20 bar (300 psia).

Solvents commonly used are Selexol (dimethylether of polyethylene glycol) and Rectisol (cold methanol). Selexol-based systems operate at about 20 bar and relatively low temperatures (0 - minus 5°C). The Exxon gas plant at La Barge, Wyoming, is reported to use Selexol to recover CO_2 from produced gas for use in EOR. Rectisol is used at the Great Plains Gasification plant in Beulah, North Dakota to recover CO_2, which is then transported by pipeline for EOR use at Weyburn, Saskatchewan. This process is shown in Figure 2.6.

The primary difficulty in using physical absorption to recover CO_2 from flue gas lies in the near-atmospheric pressure of the flue gas and the need to compress it to a level where the CO_2 solubility is such that the absorption tower can be sized effectively. As the pressure increases, the solubility increases and the volumetric gas flow decreases. Both of these effects result in smaller vessels and help make physical absorption a feasible option for higher pressure streams.

No studies evaluating the cost of recovering CO_2 from flue gas using physical absorption appear to have been undertaken. In gasification scenarios it appears to be the technology of choice. Previous studies have estimated the recovery cost for two processes that also involved significant inlet compression requirements (capture of the entire flue gas stream, and recovery using gas separation membranes). Due to the very large parasitic energy demands resulting from the compression of the large volume of atmospheric flue gas, neither option was close to being cost competitive with chemical absorption.

Hot potassium carbonate processes such as Benfield are also well established for CO_2 removal from streams with high partial pressure of CO_2 such as ammonia/urea production and older steam methane reformer applications. They are not directly suitable for flue gases, owing to the low pressure and low CO_2 concentrations of flue gases.

Compared to physical absorption, membranes have potentially greater interest for future applications than physical absorption, as they are an emerging technology undergoing significant research effort. As such, they would offer a greater chance for significant breakthroughs in performance, and hence a more realistic CO_2 capture opportunity.

The Alberta Research Council is involved in testing potassium carbonate as a CO_2 capture medium in conjunction with hollow fibre membranes. This offers some promise but should be seen from the standpoint of the membrane as the enabler of wider application as opposed to the carbonate itself.

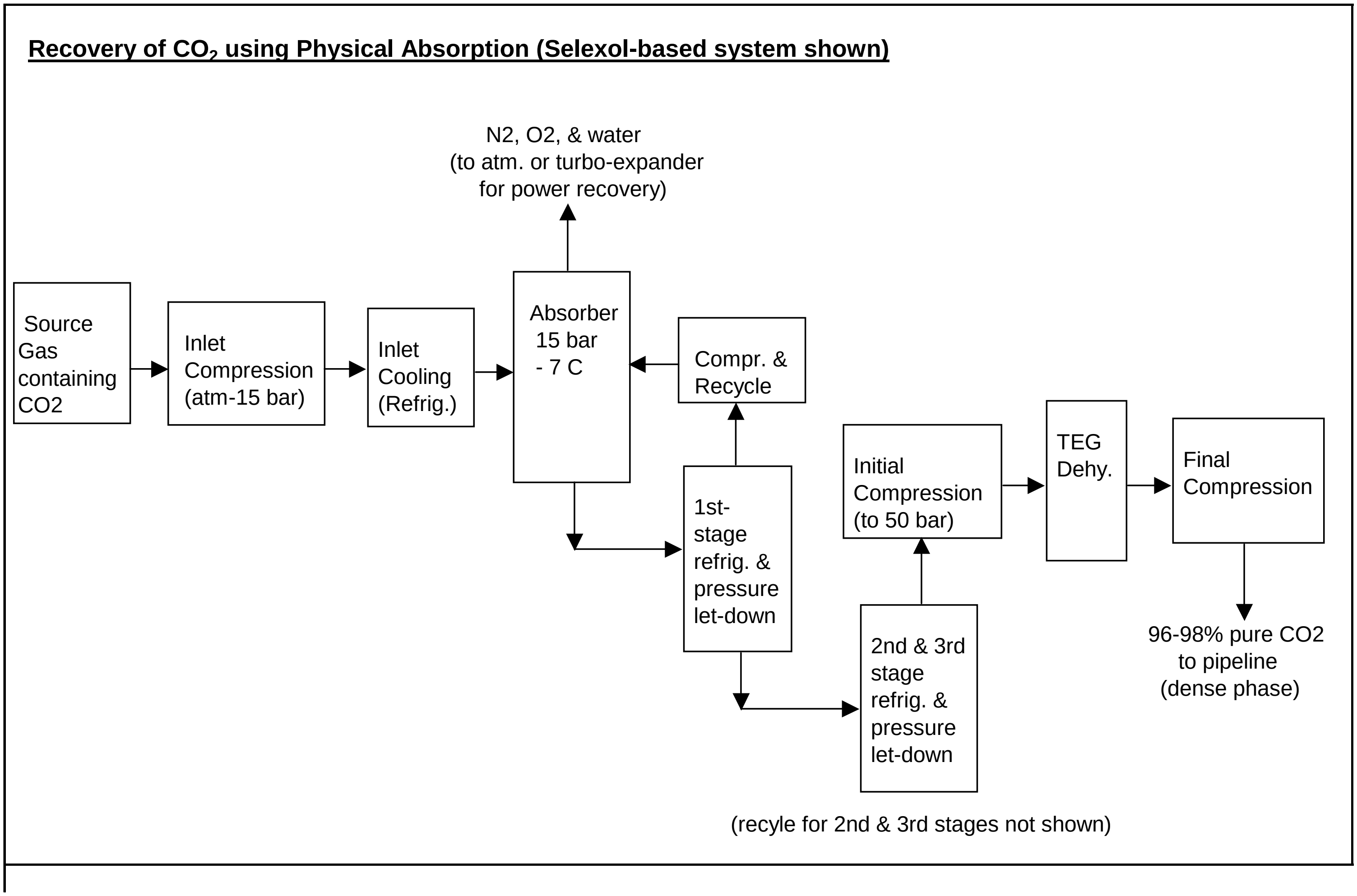
Recovery of CO_2 using Physical Absorption (Selexol-based system shown)

Figure 2.6: Recovery of CO_2 using Physical Absorption

2.2.9 Cryogenic separation

CO_2 can be separated from other gases through cooling and condensation, known as cryogenic separation. It is a well-understood commercial process widely used to purify CO_2 streams for food or industrial use, but generally only when the feedstock already has a CO_2 content in excess of 90%. It should be noted for reference that the boiling point of CO_2 is –78.5°C, and the boiling points of oxygen and nitrogen are –183°C and –196°C, respectively.

Most studies have generally given minimal consideration to this option for flue gas applications, due to the following issues:

- Cooling and compression energy requirements are prohibitive due to the large gas volume. Virtually the entire gas stream must be cooled, as nitrogen is the main contaminant, and it has a lower boiling point than CO_2;
- The gas stream must be thoroughly dried, as the presence of water and other higher boiling point impurities tend to freeze and plug equipment;
- Cryogenics is considered a mature technology that is not expected to yield further significant reductions in cost or efficiency.

The semi-cryogenic Ryan/Holmes process is in commercial use recovering CO_2 from produced gas streams in EOR applications in the southwestern United States.

This technology has not been considered a viable flue gas capture alternative, except when used in conjunction with other technologies, such as purification of the relatively pure CO_2 stream produced under an oxy-fuel scenario.

Cryogenic separation does have the advantage that the CO_2 is produced as a liquid, making it amenable to transport by truck, ship or by cylinders, and thus appropriate for food grade CO_2 applications.

In summary, this technology is confined to high-purity, low volume CO_2 applications and perhaps those where the CO_2 stream is contaminated with something whose boiling temperature is much higher than CO_2, so the CO_2 is produced as a gas rather than a liquid.

2.2.10 Adsorption

Adsorption is a process where solid materials with very high surface areas can be used to separate gas mixture components. There are two steps and typically two or more parallel trains involved. In the first step the gas stream flows through a bed of the solids where the CO_2 (in our case) is adsorbed onto the solid. The solids used are typically zeolites (molecular sieves), alumina, or activated carbon. When the solid bed is fully loaded, the gas stream is switched to a second solid bed and the first bed is regenerated and the CO_2 is released. Molecular sieves have been proposed for CO_2 applications because their absorption capacity for CO_2 is much higher than alumina or activated carbon.

The regeneration can be achieved using either pressure or temperature. In pressure swing adsorption (PSA), the pressure of the regeneration unit is reduced and the CO_2 is released. In temperature swing adsorption (TSA) the CO_2 is released by raising the temperature of the second bed. Both processes are commonly used, depending on the solid, gas and relative operating costs. In general, PSA cycle times are much shorter, resulting in smaller vessels and lower adsorbent volumes than TSA systems. This process is shown in Figure 2.7.

More distant possibilities in the area of electrical swing adsorption (ESA) have also been proposed.

Adsorption is a well-understood commercial process used for separating CO_2 from produced hydrocarbon gas streams. It is generally used at higher pressures and much lower CO_2 concentrations (generally 400 ppm to 1.5% maximum). Its most common commercial use is in the purification of hydrogen for oil hydrotreating or ammonia manufacture. In these applications the CO_2 appears in a waste stream that is about 45% CO_2 and therefore in need of further purification if long distance transportation is contemplated. See section 2.2.7 for additional discussion of this stream as a potential CO_2 source.

Some research is being done in this area to improve both the selectivity and capacity of adsorbents. It is possible that adsorbents could be developed with order-of-magnitude improvements over current materials, which would help reduce cycle times and equipment sizes. Despite possible improvements, however, low initial source gas pressure may prevent this option from being considered for anything but high pressure gas applications.

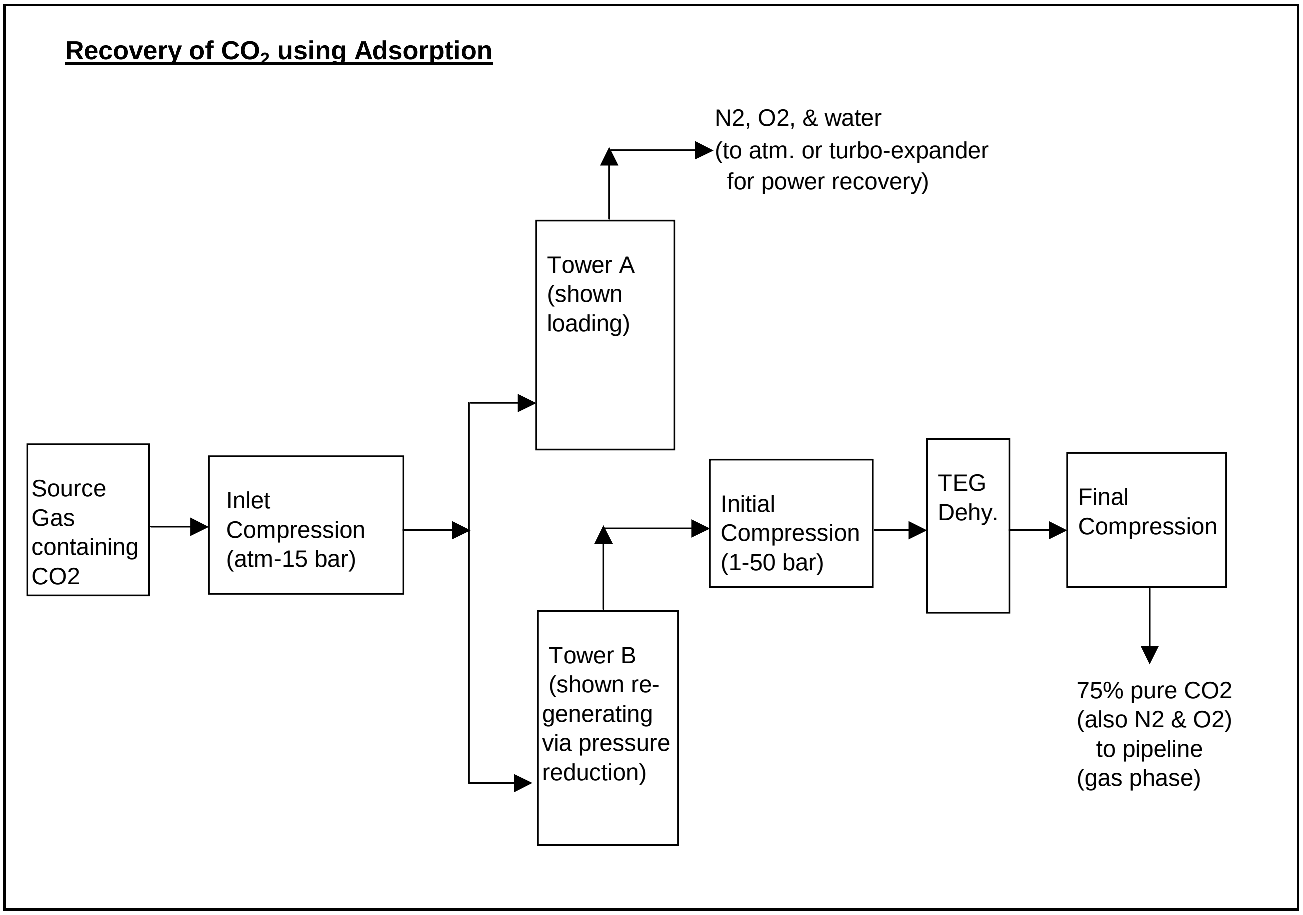

Figure 2.7: Recovery of CO_2 Using Adsorption

2.3 CONCLUSIONS

Following are conclusions regarding technology for recovery of CO_2:

- The feasibility and likelihood of commercial application of CO_2 capture technology depends very much on the pressure of the raw gas stream from which the CO_2 is to be removed.
- Based on a plant start-up within five - ten years, amine-based chemical absorption is the only feasible option for CO_2 recovery from flue gas or other near-atmospheric pressure streams. All current flue gas CO_2 recovery systems in commercial operation use this technology. Such processes can expect to see continuing incremental improvements in unit cost of CO_2 captured;
- Gas absorption membranes are a subset of chemical absorption that offers promising benefits. They are in commercial use in certain specialized clean services with high pressure inlet gas sources; notably offshore. They offer the best possibility for membranes, and for larger improvements in the efficiency of chemical absorption processes for both high- and low-pressure source streams.

- Gas separation membranes offer promise as an eventual alternative to chemical absorption but are commercially available today mainly for specialized applications associated with EOR.
- Other processes such as cryogenic separation, physical absorption and adsorption are possibilities for specialized niches but their situation is unlikely to see significant improvements.
- Pre-combustion options such as oxygen-enriched combustion or gasification do not appear suitable unless used in conjunction with new fossil fuel power generation opportunities, and premised on greater reliability than is presently experienced.
- Recovery of CO_2 from PSA purge gas streams or Benfield off-gas streams at refineries and heavy oil and bitumen upgraders represents an attractive source of CO_2 in relatively large volumes.
- Recovery of CO_2 from the acid gas feed to some sour gas plants could be attractive, using the commercially-proven Flexsorb™ or similar process. It is in commercial use in central Alberta. This opportunity may be somewhat limited by the fact that many gas processing plants are considering or already have abandoned sulphur production and are directly injecting their acid gas into depleted gas reservoirs, thus taking them out of play as CO_2 sources. Mackenzie Valley gas could also be handled using these commercially available processes if they contain sufficient CO_2 for a large scale hydration operation.
- There are a number of processing options available for separation of CO_2 from produced gas streams containing CO_2, including gas separation membranes, chemical absorption, physical absorption and cryogenic systems. All of these have been used commercially. Final selection would depend on process specifics, such as gas stream composition, flow rate, and operating costs.

3. TECHNOLOGIES FOR CO_2 TRANSPORT

3.1 BACKGROUND

This chapter provides an overview of CO_2 pipeline transportation considerations. When considering the amount of CO_2 to be moved, it is presumed that pipelines will be used.

CO_2 is a colourless, odourless, non-combustible gas, generally considered to be non-toxic except at high concentrations when it can cause asphyxiation and death. Physical discomfort has been reported starting at a concentration of 5%. Concentrations greater than 10% can lead to difficulty in breathing, impaired hearing, nausea, stupor within ten minutes and loss of consciousness within fifteen minutes. Deaths have been attributed to exposure in excess of 20%. At higher concentrations some of these effects can also be attributed to accompanying oxygen deficiency.

During an accidental release of pure CO_2, a dilution factor of about 20:1 would be required to lower the CO_2 concentration in air to a level where one would not expect any short-term health impact. While one would generally expect CO_2 leaks to be dispersed in the atmosphere to the point where they would not be considered a health threat, because CO_2 is denser than air, under certain atmospheric conditions CO_2 could collect in low-lying areas in dangerous concentrations. Cold, calm climates increase these risks.

Therefore, the risks associated with the handling and transport of pure CO_2 are technically manageable and low relative to the risks associated with many other industrial gases and chemicals. Properly designed and operated, a high-pressure CO_2 pipeline should present minimal health and safety risk. Further, the risks associated with operating a high-pressure CO_2 pipeline are significantly less than those associated with produced hydrocarbon streams containing H_2S.

Existing CO_2 pipelines

There are two areas where CO_2 pipelines exist:

1. Southwestern United States

   There is a sizeable CO_2 gathering and distribution network in the southwestern United States (Colorado, New Mexico, Texas), focused on collecting CO_2 from naturally occurring underground sources and transporting it over long distances to oil fields where it is used as an agent for enhanced oil recovery (EOR). The system has been in existence since the 1970's and has performed well.

2. North Dakota/Saskatchewan, USA/Canada

   A 320 km single CO_2 line was constructed in 1999 from the coal gasification plant at Beulah, North Dakota to Weyburn, Saskatchewan, for the purpose of transporting byproduct CO_2 to an EOR operation in Weyburn.

3.2 CO_2 PIPELINE DESIGN

Without knowing the actual volumes and pipeline length, the key design parameters that can be stated are:

- CO_2 purity of 95% - 99.9%;
- Water content of 0.176 g/Nm3 (11 lb/MMSCF);
- CO_2 in dense phase (as a general rule, but liquid-phase pipelining could be possible for extremely cold climate applications)

As an example, CO_2 recovered from flue gas using an amine-based system produces a water-saturated CO_2 stream of +99.9% purity. Although other gases such as nitrogen tend to change the phase behaviour of CO_2, making it more difficult to keep the CO_2 in the dense phase, this phenomenon would be expected to occur only if the contaminant content was 5% or more.

In a typical application, the water content of the CO_2 is reduced through compression, cooling and free-liquid removal. After the third stage of compression, there is a dehydration unit that reduces the water content below the dew point of water at the operating conditions.

This small amount of water in the CO_2 will not change the behaviour of the gas or increase the pressure loss significantly. However, CO_2 in the presence of water can form carbonic acid, which is very corrosive to standard carbon steel. Conservatively, actual design moisture content should be a maximum of 40-60% of the upper limit. If the CO_2 is not thoroughly dehydrated then the pipeline would need to be made from stainless steel, which would be prohibitively expensive.

The critical point of CO_2 occurs at 31°C and 73 bar (88°F and 1070 psig). Pipeline design aims to maintain the operating pressures comfortably above that at operating temperatures.

The initial pressure and delivery pressure and number of booster stations required will be determined by the specific circumstances, in the same way as would be used for any pipeline design. As CO_2 is significantly more dense than natural gas, it will have an advantage in deep well injection as it can help to reduce the required well head injection pressure (WHIP).

The required WHIP for the hydration storage is unknown. As an example, a recent study of a 100 km pipeline in a warmer climate indicated that an inlet pressure of approximately 2100 PSIG (144 bar) and a WHIP of approximately 2000 PSIG (136 bar) yielded a design that did not require booster or injection pumps on a 100-km pipeline. Figure 3.1 presents a phase diagram for CO_2 and includes a likely operating envelope for CO_2 pipelines. Inlet, in line, booster suction and delivery pressures and temperatures should fall within this envelope for all flowing and shut in states. The dotted section to the left of the chart that indicates a possible lower pressure regime if the maximum expected temperature of the pipeline under all flowing and shut in conditions and all seasons can be maintained below 20°C.

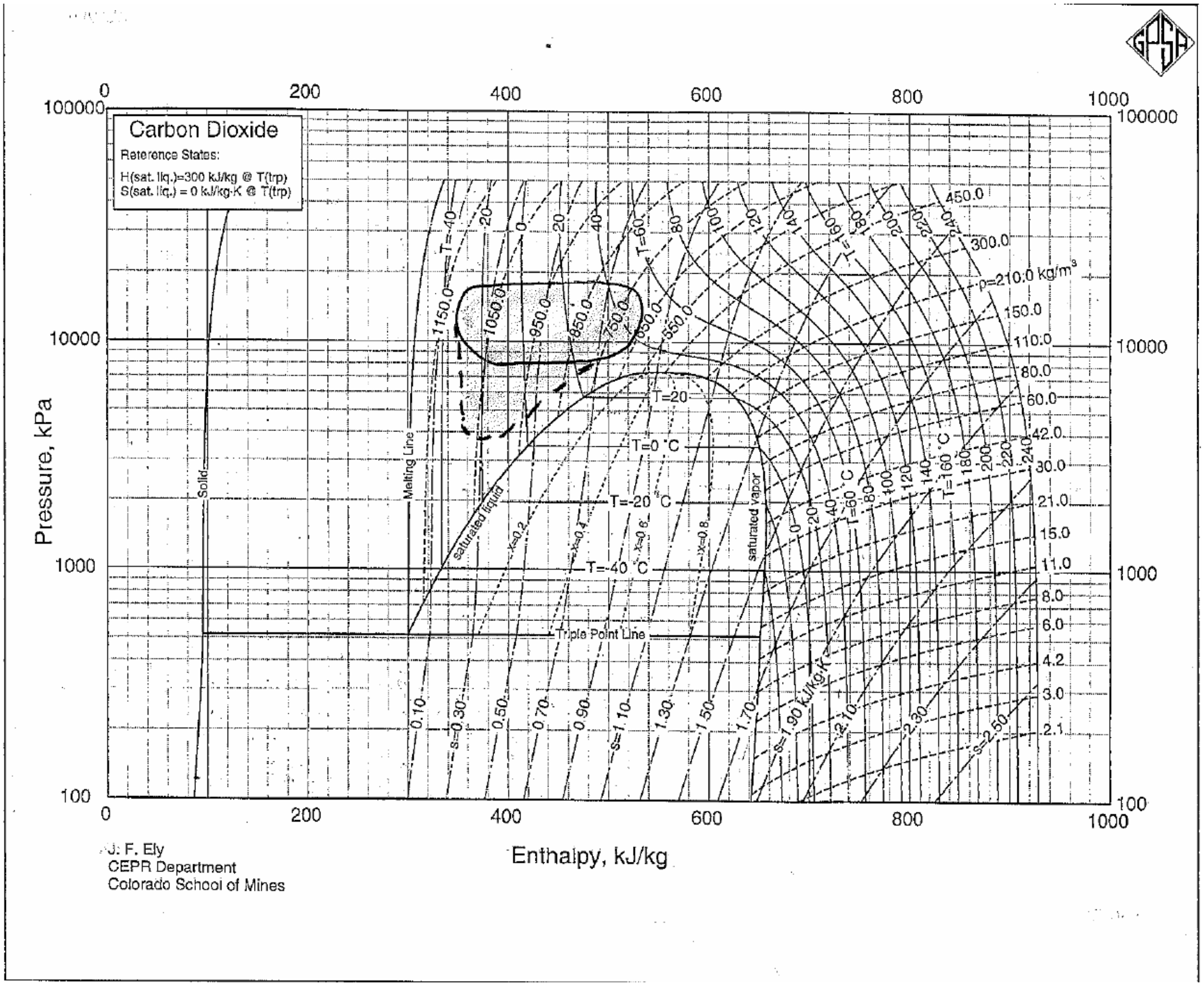

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Figure 3.1 CO_2 Phase Diagram

Material selection is important for CO_2 pipelines, due to the potentially hazardous nature of the gas, high potential for corrosion, possibility of fracture propagation, decompression potential, and other safety issues associated with operation at high pressures. In general, relatively standard carbon steel can be used but certain parameters do need to be confirmed. The pipe should be made of low alloy, high strength steel to withstand the internal pressures, thermal stress and external loads and pressures anticipated. Pipe specification must also address chemical requirements, carbon equivalent, hardness and fracture strength.

Special attention is required for valves and fitting selection. Sour service should be specified for valve trim. All valve parts in wetted service should be made of materials that are compatible with CO_2. All non-metal components such as teflon, nylon, or polyurethane need to be acceptable for CO_2 service. O-rings, seals and valve seats need to be designed to resist deterioration in the presence of CO_2, and need to withstand potentially explosive decompression if the line pressure is reduced rapidly. Specially selected inorganic sealing materials and greases must be used for CO_2 service, as petroleum-based greases and other synthetic greases can harden and become ineffective if deteriorated by CO_2.

For applications in permafrost, the CO_2 fluid temperature can be practicably kept below 0°C. The pipeline should be insulated in any case. Chapter 4 refers to a likely required wellhead injection temperature of 6°C. The decision as to whether to operate a relatively warmer pipeline or install a reheat facility at the wellhead involves economic tradeoffs and is beyond the scope of this report.

Although the CO_2 is dehydrated to below the water dew point, the potential for water drop-out still exists. CO_2 in the presence of water can form highly corrosive carbonic acid which can promote internal corrosion of the bare steel pipe, especially at low points where water could accumulate. For these reasons a CO_2 pipeline could be protected from internal corrosion by using a shop - applied Fusion Bond Epoxy (FBE) coating.

Although standard carbon steel is recommended, there are certain metallurgical parameters that need to be considered. If a high-pressure CO_2 pipeline bursts, the high vapour pressure of the CO_2 prevents depressurization. Such an occurrence, however, can promote long ductile fractures in the pipe, and this needs to be considered in the steel specification and additional (but relatively minor) costs should be included.

3.3 CO_2 TRANSPORTATION COSTS

Previous studies have evaluated the cost of transporting CO_2 from sources to sinks in the Western Canada Sedimentary Basin. In all cases, it was determined that the cost of transportation of the CO_2 is a minor part of full cycle CO_2 capture, transportation and injection cost; perhaps about 10%. These studies generally presume a coal – fired flue gas source of CO_2.

One study estimated pipeline transportation to cost (CDN) $6/tonne CO_2 for 650 kilometers transported in a common carrier network with a capacity of 14.5 Mt CO_2/yr (Thambimuthu, 2004). Many factors, however, will play into the economics of the transportation options for specific pipeline projects. The cost of pipeline transport depends on its length, the physical geography of the route taken and whether or not the route is heavily populated. Northern pipelines would likely have additional costs due to the more extreme weather conditions pipelines would have to withstand. In any case, transportation is still not the major determinant of overall project costs.

3.4 CO_2 SOURCES

The following represent possible sources of CO_2, arranged generally in order of their ease of capture. Ease of capture equates roughly but not exactly to CO_2 concentration in the source stream:

- Ammonia-based fertilizer plants not producing urea
- Plants producing ethylene oxide/ethylene glycol
- Benfield off-gas from refinery or upgrader hydrogen plants
- Acid gas streams from gas processing plants
- PSA off gas from refinery or upgrader hydrogen plants
- Coal, coke or ashpaltene gasification operations
- Cement kilns
- Coal fired power stations
- Oil fired power stations
- Gas fired power stations

- Gas turbine applications

This places central and northern Alberta in the position of having the largest number and widest range of large volume potential CO_2 sources, and Ft. McMurray/Peace River as key locations to be considered. No existing transportation facilities exist in any of the areas close to potential sinks, and few facilities emitting large amounts of CO_2 exist elsewhere close to the sinks.

3.5 CONCLUSIONS

Compared to other technologies that would be needed for CO_2 capture and injection into hydrate producing formations, CO_2 transport technologies are already relatively established and understood. Key conclusions related to CO_2 transportation technologies include:

- The location of the storage opportunities somewhat limits the potential sources of CO_2 and suggests that relatively long CO_2 pipelines may be required;
- CO_2 can be pipelined in dense phase at temperatures from –25°C to 0°C, thereby reducing the impact in permafrost areas; and
- Transportation costs represent only 10-15% of overall projects cost with capture being the vast majority (80%) of overall costs.

4. CO_2 INJECTION AND SUB-SURFACE TECHNOLOGIES

4.1 TECHNOLOGY PERFORMANCE UNDER COLD WEATHER CONDITIONS

Sequestering CO_2 in the far north will require operating the CO_2 transportation and injection system in extreme cold conditions. This may raise issues of material embrittlement and special insulation needs to avoid gas hydrate or ice formation in the transportation system.

Material embrittlement issues are addressed in the pipeline design standard CSA Z662-03 Oil and Gas Pipeline Systems and material standard CSA Z245.1-02 Steel Pipe. These standards specify the design basis and testing requirements to ensure that the selected pipe material retains sufficient notch toughness to operate at the specified operating temperature (i.e., standard test temperatures range from 0°C to -45°C). Pipelines transporting CO_2 fall into a category with special requirements for notch toughness testing.

The notch toughness performance requirements, however, are not required for pipelines where one of the following applies:

- pipe diameter is smaller than 114.3 mm OD
- pipe nominal wall thickness of less than 6.0 mm
- design operating stress is less than 50 MPa

Therefore, the notch toughness requirement may apply to large diameter, high pressure, long distance transmission lines but may not apply to small diameter, low pressure local distribution lines running to the wellheads.

Based on this cursory review it appears that the design of a CO_2 transportation and distribution system in the far north can be covered by the existing pipeline design codes.

As discussed in Section 3 of this report, ensuring that the supplied CO_2 is dewatered would allow the use of carbon steel materials for building a transmission and distribution pipeline system. This dewatering process would also alleviate concerns regarding hydrate formation in the pipeline and distribution systems. However, to ensure that the injected CO_2 does not form hydrates in, or immediately adjacent to, the wellbore, the temperature of the gas must be maintained above a certain level at the wellhead to account for heat loss as the gas flows down the wellbore. This minimum wellhead temperature suggests that insulated/heated distribution lines may be required depending on the temperature of the CO_2 supply following dewatering.

The critical design condition for the distribution system will likely be related to restarting injection following a shut-down. Injecting CO_2 that has cooled while sitting stagnant in the distribution system could form hydrate plugs with water that backflows into the wellbore during the shutdown. Removing these plugs would be a costly operation and may be hampered by well accessibility issues associated with operating in the far north. Insulating the lines would reduce the sensitivity of the system to moderate duration shut downs. Heat tracing (that is only activated during a shut down) could extend the allowable shut down time so that required repairs can be made before the CO_2 becomes too cold to inject safely.

One alternative to heat tracing might be to design the distribution system so that it can be blown down to minimize the volume of cold CO_2 that would contact the reservoir during a restart.

4.2 GEOMECHANICAL IMPACTS OF CO_2 INJECTION ON CASING DESIGN

Changes in the reservoir pore temperature and pressure during injection cause changes in the stress acting on the reservoir sand. Preliminary modeling of CO_2 injection to form hydrates in sandstone aquifers by Uddin (2005) showed that the reservoir temperature does not change significantly during injection so that thermally induced strains should not affect the well casing. On the other hand, the modeling shows that reservoir pore pressure may reduce over time as the hydrate forms. Virgin aquifers would be assumed to be initially saturated with water at the depth (300 m) considered in this analysis. The initial injection of CO_2 into a virgin reservoir would tend to cause the reservoir pressure to increase. The rate and magnitude of increase would be a function of the: reservoir volume and permeability; reservoir matrix compressibility; and rate of gas injection. The injection pressure would have to be managed to ensure the fracture pressure of the reservoir is not exceeded, since fracturing the reservoir may result in compromising the integrity of the reservoir cap rock and allowing the injected gas to contact overlying strata.

The reservoir pressure drop predicted by Uddin appears to be due to the uptake of CO_2 in the reservoir as hydrates form. Such a pressure reduction would cause the effective stress acting on the sand to increase, which can result in consolidation of the sand. Zoback (2002) also notes that pore pressure reductions in reservoirs can activate normal faulting in and above the reservoir which could compromise the reservoir cap rock seal or damage the wellbore.

The degree of reservoir compaction that can occur is a function of the: magnitude of the pressure drawdown; areal extent of the drawdown; and the stiffness of the reservoir materials. The stiffness of sandstones is shown by Kosar (1989) to be a function of the confining stress on the reservoir rock. The modeling performed by Uddin (2002) considered reservoirs at a depth of approximately 300 m in which the lithostatic confining stress would be approximately 6 MPa. Kosar (1989) reports the bulk modulus of clean, over consolidated reservoir sands to be in the range of 500 to 1,000 MPa at confining stresses ranging from 3 to 8 MPa, respectively.

Goldberg et al. (2004) report that log data suggests that the dynamic stiffness of geologic materials may increase as much as 50% where high concentrations of natural gas hydrates fill the pore spaces instead of water. Therefore, the compressibility of the formation may decline (bulk modulus of the sand increases) as hydrates form, so that the effects of pore pressure reduction may be reduced.

A simplified reservoir compaction model was used to assess the degree of reservoir compaction that may be encountered in a CO_2-hydrate injection well. The reservoir compaction analysis was based on the modeling presented by Uddin (2005) where the pore pressure declined by 1.5 MPa as a result of hydrate formation. This pore pressure decline was assumed to extend throughout the reservoir so that uniform consolidation occurs throughout. It was also assumed that the magnitude of the consolidation was small enough that the overburden materials subside uniformly as the reservoir consolidates, with no arching or bridging effects to reduce the overburden stress applied to the reservoir. The bulk modulus of the reservoir material was assumed to range from 500 MPa (soft material) to 2,000 MPa (stiff sand with hydrate pore filling) and the reservoir pressure drawdown was assumed to range from 0.5 to 2.0 MPa. The resulting vertical strain estimated in the reservoir is shown in Figure 4.1.

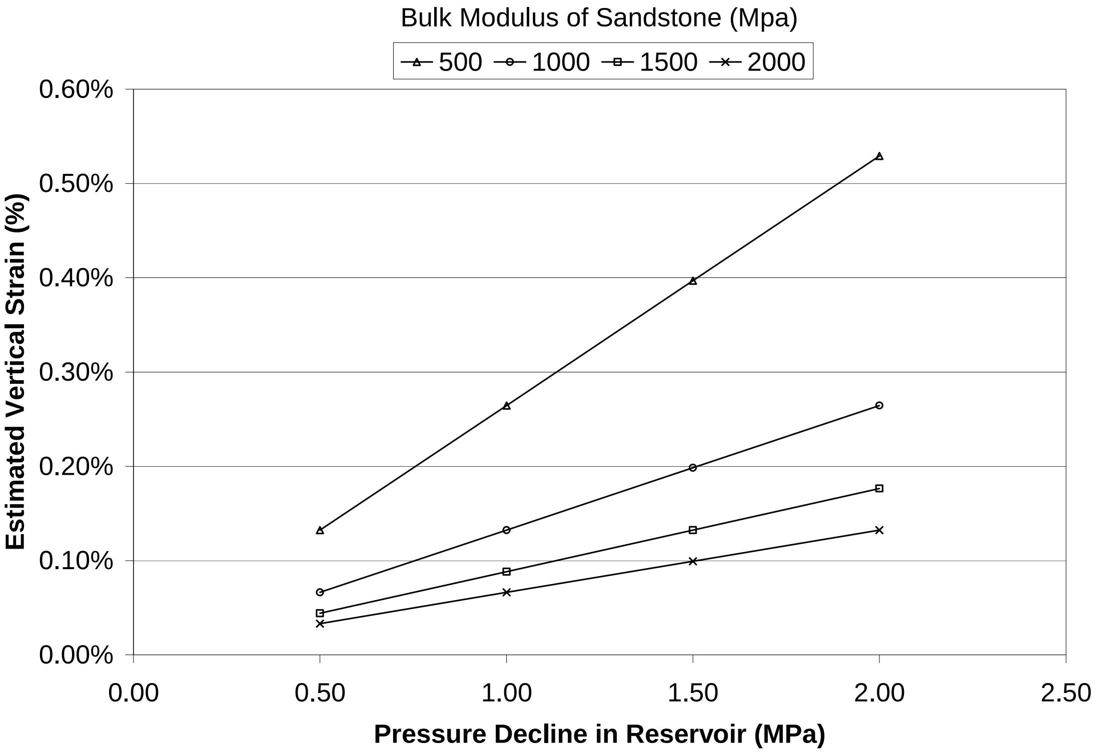


Figure 4.1 Estimated Vertical Strain (Consolidation) in the Reservoir Caused by the Pressure Decline Associated with CO_2 Hydrate Formation.

The vertical strain in the geologic column is transferred to the well casing through the annular cement. Conventional well casing design approaches limit the stresses in the casing to below yield, which is generally considered to correspond to approximately 0.2% strain. Figure 4.1 shows that this strain level is likely to be exceeded in softer formations and at higher pressure drops. This indicates that the casing yield strength could be exceeded in some cases, suggesting that special issues related to designing casing for high stress environments will likely have to be addressed.

Casing stresses in excess of yield also have a significant impact on the collapse resistance of the casing. The well configuration (especially the placement of injection packers at the top of the injection zone) must consider scenarios where near wellbore fluid pressures due to injection may exceed the collapse resistance of the casing. When the casing is subjected to high longitudinal stresses due to reservoir compaction, the collapse resistance of the casing can decline significantly.

The magnitude of pressure reduction in the reservoir can likely be managed by balancing the CO_2 injection rate with the rate of hydrate formation in the reservoir. Injecting CO_2 at a rate higher than the hydrate formation rate would tend to cause the formation pressure to increase. Injecting CO_2 at a rate slower than the hydrate formation rate would cause the formation pressure to stabilize where the CO_2 partial pressure reaches the critical point where no further hydrates will form. The preliminary analysis by Uddin suggests that this stabilized pressure may be lower than the original reservoir pressure. This condition may occur if CO_2 injection is curtailed for an extended period of time and the formation of hydrates continues until the equilibrium pressure is reached in the reservoir.

One of the sites identified by the Geological Survey of Canada that could be used for CO_2 sequestration is in Canada's far north. These injection wells would pass through massive permafrost zones above the CO_2 disposal zone. This raises the potential for heat from the injected gas to radiate from the wellbore to thaw the permafrost surrounding the well. Permafrost thaw and water migration leads to ground movements that result from ice-to-water phase change contraction and consolidation of fine soils. The magnitude of these movements can vary considerably, depending on such factors as soil type, depositional history, and the amount of ice initially present. The soil movements can impose loads on the casing string that are compressive in some intervals of the casing and tensile in others. Tensile loads may be sufficient to pull apart casing connections, while compressive loads can cause casing buckling. Buckled casing can impair well access and cause connections to leak due to high curvatures.

Another critical design condition associated with wells through permafrost is collapse loading that may occur due to freeze back of the thaw zone when the well is shut in. In such cases, the thawed permafrost and water-based pore fluids outside the casing refreeze and the confined expansion of the frozen water generates inward radial loads on the casing string. The magnitude of the freeze-back pressure is a function of depth, time, initial thawed soil state, water salinity, saturation, etc. and will thus vary from field to field. Freeze-back would be a much slower process than ground thawing since the thermal gradients during freeze-back would be significantly smaller than the thermal gradients imposed during injection. Therefore, freeze-back induced casing collapse may only be an issue for extended shut-in periods but should be assessed for each application.

Conventional casing design approaches such as described in American Petroleum Institute Recommended Practice 5C2 that are based on limiting the stress to below the yield strength of the material may not be applicable if the imposed casing stresses exceed the yield strength of the material. The alternative is a strain-based casing design approach which considers the post-yield behaviour of the casing material to ensure that the structural integrity of the well is maintained for the life of the project. The strain-based approach considers the combinations of longitudinal, radial and hoop strain that can be tolerated without a failure occurring in the casing body and connection. This requires detailed analysis of specific connection designs subjected to the estimated strains since the strain in the casing body can be magnified several times in the connection due to strain localization in various areas of the connection. In general, only buttress and premium connections have sufficient strength to tolerate stresses in excess of the pipe body yield strength. Material selection is also a critical component of the strain based design approach. Generally a strain hardening material such as K55 or L80 are required to ensue that the structural integrity of the connection can be maintained at loads beyond the yield strength of the material.

For wells in very large strain environments some operators have incorporated a strain-absorbing device in the casing string. Schwall et al (1996) describe such a casing design for compacting chalk reservoirs in the North Sea. In this application, the longitudinal strain absorbing devices were designed to accommodate up to 10% reservoir compaction, which is significantly higher than anticipated in the proposed CO_2 injection scheme.

4.3 CASING AND CEMENT CORROSION IN THE PRESENCE OF CO_2

The interaction between CO_2 and cement is termed carbonation and involves the degradation of several different constitutive minerals. The agent for this reaction is carbonic acid, which is formed when carbon dioxide is dissolved in water (Neville 1981). Although it is a relatively weak acid, carbonic acid can nevertheless be quite damaging to cement. Aqueous CO_2 can change hydrated wellbore cement to a soft, silica gel with very little structural integrity and low compressive strength (Bruckdorfer 1986). It was noted that several efforts to develop new formulations or mixtures which prevent or reduce the damaging effects of CO_2 on cements have been met with varied levels of success. For instance, tests have shown that increasing the ratio of cement to water improves the cement resistance to CO_2 attack. However, the use of standard cement additives in low concentrations apparently does not affect CO_2 resistance, nor does relative salinity of the formation water. Additives that are used to dilute cement (e.g. lost-circulation additives, and silica) tend to decrease cement resistance to carbonic acid attack in applications below 100°C (Bruckdorfer 1986).

The principal approach to minimizing corrosion damage of steel components is to limit the water content of the CO_2 stream to minimize the corrosive nature of the fluid. This allows conventional carbon steel materials to be used for most pipeline networks. However, downhole, the CO_2 stream will mix with water at some point. During injection very little water may be present in the wellbore above the injection zone but the sump of the well (the section below the injection zone) would likely eventually fill with water. Outside the casing, the injected gas would mix with formation water to form a corrosive environment for the well casing. In addition, during shutdown periods, the wellbore pressure would equilibrate with the near-well reservoir pressure, likely resulting in water filling part of the well. Consequently, the casing in the reservoir section of the well will likely be exposed to a very corrosive environment. It is assumed that a packer would be set in the well near the top of the reservoir section so that reservoir fluids could not rise up the wellbore, thus protecting the majority of the well from corrosion. The Sleipner CO_2 injection project in the North Sea (Baklid et al., 1996) used solution annealed 25% Cr duplex stainless steel for the casing material. For production tubing, where only the interior surface of the pipe is exposed to the CO_2, various linings such as plastic, cement and fiber-glass have been tried to prevent corrosion. Of these, fiberglass lining is reported to provide the best service life (CO_2 Norway, 2006) however, no data is provided in the article regarding the cost of the fiberglass lined pipe compared to the other options. The same article indicates that packers may be coated with nickel or plastic to provide long service lives.

CO_2 injection projects where existing wellbores are used for enhanced oil recovery may control corrosion of the original carbon steel casing strings by injecting corrosion inhibitors with the CO_2. Some types of corrosion inhibitor contain methanol and ethylene glycol which also form the key components of hydrate inhibitors, making them inappropriate for this application where stable hydrates are the desired outcome. The ongoing cost of corrosion inhibitors might also outweigh the cost of installing corrosion resistant downhole equipment in new wells or even retrofitting existing wells.

4.4 WELLBORE HYDRAULICS AND HEAT TRANSFER FOR CO_2 INJECTION

In the sequestration scenario where CO_2 is to be injected below permafrost, issues related to permafrost thaw and CO_2 cooling as it is injected must be addressed.

Two basic approaches may be considered for limiting permafrost thaw around injection wells: passive, using insulation; and active, using cooling. The passive approach is to construct the well with thermal barriers (insulation) between the injected fluid and the surrounding permafrost. Options for insulating include:

- Fill well annulus with insulating fluids such as: gas, glycol-water mixture; or gelled diesel
- Use light weight cement
- Use vacuum insulated tubing for the injection string

Wells can be actively cooled by circulating a chilled glycol-water mixture in the annulus between conductor pipes installed over the permafrost interval. Active cooling systems have the advantage of being able to handle larger heat loads, and thus higher injection rates than passive insulation systems but do require ongoing operating costs that passive systems do not require.

A wellbore injection system through permafrost must also be designed such that the temperature of the CO_2 entering the formation is slightly higher than the hydrate stability temperature at the injection pressure to ensure that hydrates do not form in, or immediately adjacent to, the wellbore. The CO_2 will cool due to heat transfer to the surrounding formation but will also warm slightly as it compresses (due to the Joule-Thomson effect) from the increase in pressure with depth along the wellbore. Therefore, the wellbore design must balance the need to keep the permafrost cool and the injected gas warm. This suggests that active wellbore cooling systems may not be appropriate since they would tend to cool the injected CO_2 as well as the permafrost, thereby increasing the probability that hydrates would form in, or near, the wellbore.

A simplified analysis was performed of the heat loss from the injected CO_2 in the wellbore to the formations overlying the injection zone. The analysis focused on the change in the gas temperature and assumed that the temperature of the overburden in contact with the wellbore does not change with the input of heat from the wellbore. The model assumed that the overburden temperature increased from -4°C at surface to +6°C in the reservoir at 300 m depth. A CO_2 injection rate of 4,000 standard m^3/day was assumed. It was also assumed that it would be desirable to deliver the CO_2 to the well perforations above the hydrate formation temperature of approximately +12°C at the assumed injection pressure of 6 MPa. Given this downhole constraint on the injected CO_2 temperature, the model was used to estimate the minimum wellhead gas temperature required to ensure the gas is outside of the hydrate stability envelope when it enters the formation.

Three wellbore scenarios were considered:

- injection down the 139.7 mm casing (no tubing string or packer)
- injection down 88.9 mm bare steel tubing with brine in the well annulus above a packer at the top of the injection zone
- injection down 88.9 mm vacuum-insulated tubing with brine in the well annulus above a packer at the top of the injection zone

The analysis showed that heat loss from the CO_2 was considerable if the gas is injected down the well casing, requiring a wellhead CO_2 temperature of approximately 90°C. Using bare steel tubing with a packer reduces the required wellhead gas temperature to 53°C. The vacuum insulated tubing results in very small heat loss, requiring only 13°C wellhead gas temperature compared to a bottomhole gas temperature of +12°C. Special tubing configurations for CO_2 injection such as fiberglass lined pipe would provide some degree of insulation that would likely fall somewhere between the bare steel pipe and vacuum insulated tubing.

This constraint on wellhead gas temperature may impose special gas treatment requirements for certain gas supply options and may make some applications impractical to implement (i.e. where the gas must be heated prior to injection).

4.5 CONCLUSIONS

Sequestration operations where CO_2 is injected into subsurface aquifers to form stable hydrates in the reservoir face some unique challenges in designing and operating the transportation and well systems. The key conclusions reached in the review of these challenges include:

- Warm gas (above the hydrate stability temperature at the injection pressure) must be injected to ensure hydrates do not form near or in the wellbore.
- Shut down scenarios for the CO_2 pipeline transportation system must minimize the volume of cold gas that would be injected into the wells at restart to minimize the risk of forming hydrates in the well and reducing injectivity.
- Wells that penetrate permafrost zones must be insulated to prevent gas cooling and thaw of the permafrost.
- Injection pressures must be managed to prevent hydraulic fracturing in the reservoir and to minimize formation movements that could impact the well seal integrity.
- Casing and cement corrosion downhole can be minimized with appropriate selection of materials.
- The use of corrosion inhibiting chemicals may be limited since components of these chemicals may also inhibit the formation of hydrates.

5. RESERVOIR PERFORMANCE AND CO_2 MONITORING TECHNOLOGIES

5.1 GEOCHEMICAL REACTIONS

Carbon dioxide hydrates are much more stable than methane hydrates at equivalent pressures of CO_2 and CH_4 for a given salinity and temperature. As well, hydrate solutions of methane and CO_2 mixtures exist stably in the field at pressures above the CO_2 hydrate stability curve but below the methane hydrate stability curve. Consequently injection of CO_2 into a CH_4 reservoir in a drive situation (i.e. injecting in one well and producing from another) would tend to breakdown the methane hydrates by lowering the P_{CH4} in the reservoir (by displacing the gaseous CH_4 with the injected CO_2) and replacing the CH_4 hydrates with CO_2 hydrates. This could have a dual advantage: if the methane could be recovered and used as an energy source; and by trapping the CO_2 in the hydrate reservoir, the GHG emissions to the atmosphere would be lowered.

Compared to carbon dioxide hydrates, methane hydrates have a fairly simple geochemical framework being mainly restricted to synthesis from methane gas and water or the reverse decomposition reaction. Carbon dioxide, besides the relatively simple direct synthesis and decomposition hydrate reactions, can be involved with complex carbonate and silicate reactions depending on pressures, temperatures and cation availability. Calcite and dolomite dominate the carbonate geological record and are even more plentiful than methane hydrates. They also are a potential source of CO_2. Under normal conditions imposed by a seawater chemistry of the formation water, they would precipitate long before CO_2 hydrates. In the inset of Figure 5.1, the change in the composition of seawater is plotted as CO_2 is added to the seawater in the absence of any calcite reaction. This causes the P_{CO2} to increase as shown by moving up along the solid black line (in the inset); and the pH of the seawater to become more acid by the reaction:

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$$

The calcite stability curve is also plotted for ideal CO_2 as a dashed line in the inset. Calcite is close to equilibrium with sea water but will dissolve in seawater as the P_{CO2} is elevated. Calcite, when present, will dissolve and slow the decrease in pH of the seawater by the reaction:

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{++} + 2HCO_3^-$$

as the P_{CO2} rises. In this case the pH will be forced to remain in equilibrium with the calcite and will be determined by the calcite equilibrium where calcite is stable on the high P_{CO2} side of the stability curves (i.e. dashed line in inset; also see Uddin and Coombe, 2006 for a simulated example).

As discussed, the dashed line of the inset is the calcite equilibrium curve and is for the condition that CO_2 behaves ideally, and is equivalent to the fat solid negatively sloping line in the main graph (i.e. enlargement of the inset) of Figure 5.1. However, at the low temperatures of hydrate formation, CO_2 behaves non-ideally. The effect of this on calcite stability is shown by the other three negatively sloping curves which successively reduce the calcite stability field below that of the calcite stability curve for ideal CO_2 on Figure 5.1. The real behavior of pure CO_2 is accounted for as shown by the thin black line. Mixtures of CO_2 and methane reduce the stability of calcite further at the same total gas pressure as shown by the dash dot (2/3 CO_2, 1/3 CH_4) and dashed curves (1/3 CO_2, 2/3 CH_4). The pure CO_2 hydrate stability curves (dash dot line for

1^oC and dashed line for 10^oC) are a function of CO_2 pressure predominantly and appear as horizontal lines on Figure 5.1 with the CO_2 hydrate being stable at higher CO_2 pressures. The stability field of mixed CO_2-CH_4 hydrates would shrink and the boundary would move to higher pressures compared to the pure CO_2 hydrate stability curves shown here.

Consequently, if high P_{CO2} is imposed on a pore water which is the composition of seawater in the presence of calcite and other carbonate minerals (i.e. a limestone), then calcite will dissolve and as the P_{CO2} increases, the composition of the altered seawater will remain on one of the calcite stability curves (see Figure 5.1) depending on the quantity of methane present until CO_2 hydrate starts to precipitate at which point the P_{CO2} will be buffered by hydrate synthesis. If no carbonate minerals are present, and no other mineral reactions take place, then only the pH of the seawater will shift as the P_{CO2} rises until the hydrate stability curve is intersected.

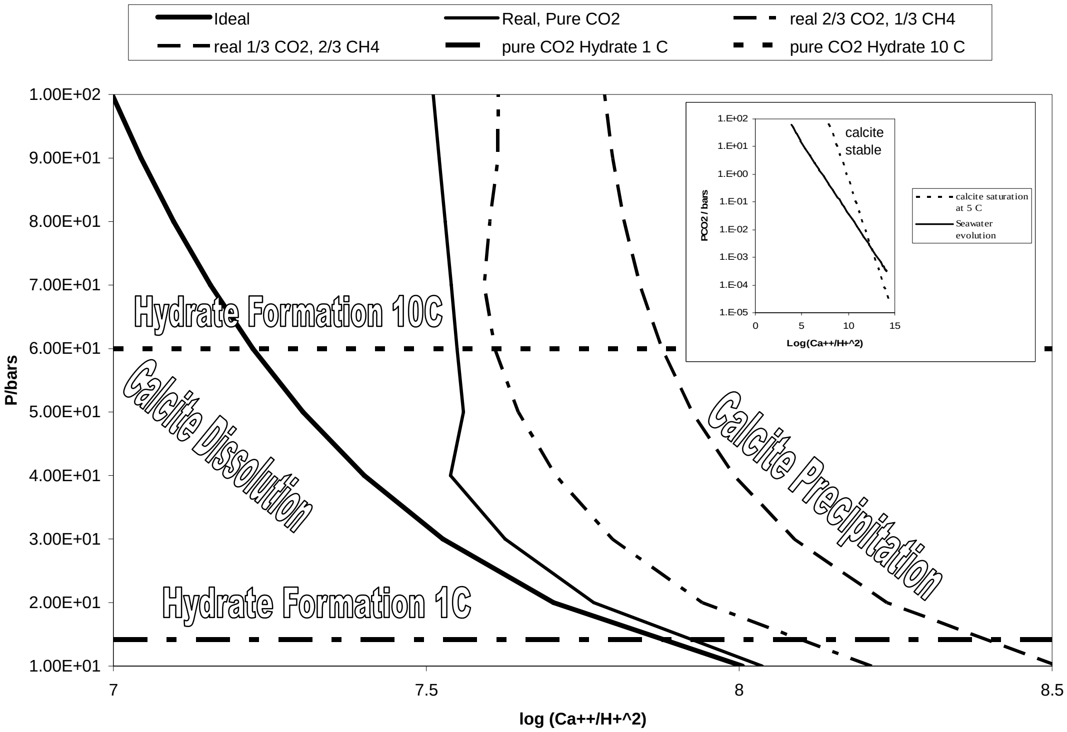


Figure 5.1 Stability curves as a function of T & P for pure CO_2 hydrates (P_{co2}) at 1 and 10°C and calcite (P_{co2}, P_{CH4} and a_{Ca++}/pH) at 1°C. Inset shows seawater evolution as CO_2 pressure is increased relative to the ideal gas calcite stability curve. (Courtesy of Stephen Talman, ARC).

However, if reactive basic silicate minerals are present such as the feldspars and clays (which can serve as a source of Ca^{++} and/or hydroxyl ions), carbonate mineral forming reactions can compete with the hydrate forming reactions by reactions of the form (e.g. anorthositic component of plagioclase breaks down to kaolinite):

$$CaAl_2Si_2O_8 + 3H_2O \rightarrow Ca^{++} + 2OH^- + Al_2Si_2O_5(OH)_4$$

$$Ca^{++} + 2OH^- + CO_2 \rightarrow CaCO_3 + H_2O$$

Even if these basic silicate minerals are present, their kinetics of reaction are so slow compared to hydrate formation, they would only be effective in buffering the seawater-like chemistry over the long term. The result would be that the CO_2 hydrates would form metastably and over time would be converted to the more stable carbonate mineral form, either calcite or dolomite.

5.2 RESERVOIR FLOW BEHAVIOR

Formation of either CO_2 or methane hydrates has a similar effect to freezing of water. The reservoir changes from a permeable media where the formation water is free to percolate through pore throats in an aquifer-like behavior to an aquitard or aquiclude due to the blocking of pore throats by the ice-like hydrates. Methane hydrate reservoirs can be compared to the oil sands where the solid bitumen plugs pore throats reducing the permeability to low values. In this application, heat in the form of steam is transferred to the bitumen causing the bitumen to melt and enhancing the permeability to Darcies. Heat can also decompose ("melt") the CH_4 hydrates to CH_4 and water, thereby enhancing the permeability significantly.

As discussed above, hydrate synthesis reactions in a closed system result in a significant decrease in the porosity of the system. These hydrate synthesis reactions can also result in significant heating of the reservoir (due to their negative heat of reaction = exothermic reaction). Since the stability of the hydrates is favored by cooler temperatures, as the reaction proceeds, it requires increasingly higher P_{CO2} or P_{CH4} pressures due to the temperature increase to precipitate a hydrate. The heating also leads to an incremental volume increase of the solid phases, further decreasing the porosity. Formation of CO_2 hydrates by injection of CO_2 assumes that due to the high mobility of the injected gas, it cannot displace the water and hydrates will form. In this case, the resulting dilatancy could lead to shearing which may effectively increase the permeability as seen in the anthropogenic domain fracturing carried out in tight sands and gas shales. This could partially counter the reduction in permeability (i.e. porosity) caused by hydrate formation and heating. The theory to predict permeability modifications by domain shearing is being developed and cannot be modeled at this time. These geomechanical effects due to volume changes from temperature, pressure and mass changes are expected to be important to the development strategy of the reservoir and should not be neglected. Some preliminary approaches to this are illustrated in Uddin and Coombe, 2006)

5.3 MODELLING APPROACHES

Optimizing CO_2 storage will involve recovering any remaining methane in the reservoir and replacing it with CO_2 hydrates. The consideration of the geochemical and geomechanical effects leads to a strategy for modelling. This is guided by past experiences in the oil and gas industry starting out with primary depletion where pressure drive is the sole production mechanism. It is expected that this strategy would leave a cooler and depressurized reservoir with substantial methane hydrates remaining with the temperature and pressure gradients sloped positively away from the well bore. Since it is desired to recover the remaining methane in the hydrate reservoir and replace it with CO_2, the enhanced recovery process should focus on sweeping the remaining methane out of the reservoir with CO_2 but not allowing CO_2 to be produced from the production well. For CO_2 injection, higher temperatures and lower pressures in the near well region would minimize CO_2 hydrate formation and the resultant near well damage. Since higher pressures are required at the wellbore to inject the CO_2 further into the reservoir, it is impossible to keep lower CO_2 pressures at the wellbore relative to the rest of the reservoir and consequently CO_2 hydrates would form near the injection wellbore first, reducing the permeability and injectivity. Consequently, a temperature strategy is needed to heat the area around the wellbore which can be accomplished by the injection of hot CO_2 thereby reversing both the temperature and pressure slopes. The goal is to achieve initial formation of CO_2 hydrates far from the injection well bore where the temperature is cooler while recovering methane. However, reservoir simulation by Uddin, 2005 for injection only, predicted that at low CO_2 injection rates, the average field temperature and pressure dropped significantly with the formation of CO_2 hydrates. This was unexpected since the hydrate formation reaction is exothermic and, in addition, the addition of CO_2 to the system through injection would be expected to increase the pressure. If this effect was correctly modeled, it may offer some interesting alternative strategies for exploitation of CO_2 hydrate storage. These could be tested by using reservoir simulators which can model the stability of hydrates such as documented most recently by Uddin and Coombe, 2006.

5.4 FRAMEWORK FOR MONITORING

Monitoring provides the confidence that the CO_2 has been injected and stored in an environmentally sound and safe manner and provides the necessary accounting metrics for emissions offset/trading scenarios based on geological storage.

Discussion on the monitoring of the fate of injected CO_2 will adopt the following definitions:

- Migration: refers to movement of fluids (including injected CO_2) within the injection formation. This can involve movement both vertically and horizontally within the designated injection horizon. The fluids remain “trapped” by both the upper and lower bounding seal layers;
- Leakage: refers to movement of fluids (including injected CO_2) outside the injection horizon. This can involve movement through the upper and lower bounding seals or through wellbore pathways. Leakage includes all pertinent pathways through the geosphere. Monitoring for leakage is important as it includes all processes leading to CO_2 movement towards and possibly into the envirosphere; and
- Seepage: refers to movement of fluids (including injected CO_2) from the geosphere to the envirosphere. Monitoring programs aimed at seepage processes are primarily focused on limiting any health, safety or environmental issues. Envirosphere is defined based on specifics conditions of a site. For the development of generic monitoring programs, envirosphere is defined as the region from the deepest potable water horizon up to and including the atmosphere (and here envirosphere is used interchangeably with biosphere).
- Catastrophic: refers to uncontrolled release to the atmosphere.

The following sections describe the relevant issues in establishing a monitoring framework for geological storage; and draws largely on previous work (Chalaturnyk and Gunter, 2005; Chalaturnyk et al., 2005). The framework can be used to guide effective decisions about monitoring approaches and the integration of monitoring in the overall geological storage project performance assessment process. A monitoring framework must be designed such that the level of complexity will be commensurate with the level of risk that a “site” poses. For this report, risk will not be computed specifically but it will be assumed that risk can be assessed generically based on characteristics of each site (depth, reservoir thickness, etc.) and speaks generally to the potential for CO_2 leakage.

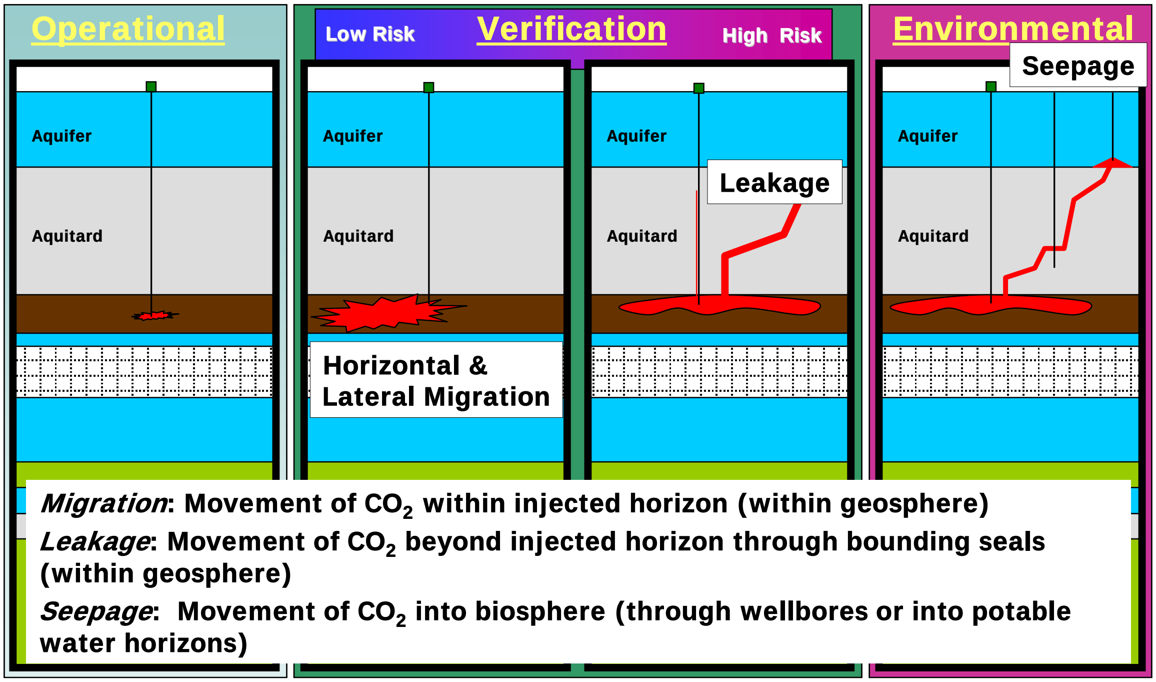
The framework also needs to efficiently and economically address existing and anticipated regulatory performance objectives for CO_2 storage. Uncertainty in predicting the fate of CO_2 in reservoirs cannot be eliminated. The challenge is to build a regulatory regime that works despite these uncertainties; and the monitoring framework discussed in this paper is designed to evolve with development of these regulations.

The purpose of monitoring is to “truth” the predictive capability of the simulators, validate the physics of the storage process, mitigate uncertainty associated with reservoir parameters, identify and validate different categories of storage mechanisms in geological formations, correlate operational issues with aquifer and caprock response, trigger contingency plans and mitigation activities, and to satisfy regulatory response.

These general attributes of monitoring can be classed into three distinct mandates:

1. Operations - monitor/control actual in situ processes by changes in injection/production strategy based on the measured variables. Minimal requirements are specified by regulatory requirements; and additional operations monitoring is guided by the complexity of injection/production scenario. It is generally concerned with migration;
2. Scientific or Verification – measurements that improve the understanding of complex processes occurring in situ. This level of monitoring is generally linked intimately to predictive modelling where important mechanisms are hypothesized, history matching on basis of the measured variables is conducted to improve the modelling capability and future behavior is predicted. It is generally concerned with migration and leakage. This currently is a major focus of effort in geological storage research; and
3. Environmental – monitoring aimed at safeguarding against health, safety and environmental risks. Depending on the risk level of the project, aspects of environmental monitoring may be part of operational monitoring scenarios. It is generally concerned with seepage.

Figure 5.2 provides a schematic illustration showing the progression from operational monitoring through to environmental monitoring. Inherent within the framework of a monitored decision approach, is an effective, fully integrated monitoring program, whether for operational, verification or environmental reasons. Planning a monitoring program should be a logical and comprehensive engineering process that begins with defining objectives and ends, and planning how the measurement data will be implemented. The following sections provide a brief description of the steps that should be followed in developing the monitoring programs embodied within the monitored decision framework.



Migration: Movement of CO_2 within injected horizon (within geosphere)

Leakage: Movement of CO_2 beyond injected horizon through bounding seals (within geosphere)

Seepage: Movement of CO_2 into biosphere (through wellbores or into potable water horizons)

Figure 5.2 Operational, verification and environmental monitoring levels (adapted from Chalaturnyk and Gunter, 2005).

5.5 SYSTEMATIC APPROACH TO GEOLOGIC STORAGE VERIFICATION

A monitored decision process is not simply long-term monitoring. It is a planned approach to decision-making over time that draws on long-term field measurements for input, with planned analysis of the measurements and appropriate contingent actions (D'Appolonia, 1990). Its framework is one of recognizing uncertainties in the geological storage system and making design decisions with the knowledge that planned long-term observations and their interpretation will provide information to decrease the uncertainties, plus providing contingencies for all envisioned outcomes of the monitoring program. It is important to highlight the fact that this tenet for a monitored decision framework conforms naturally to monitoring (observations), mitigation (contingencies) and verification (interpretation).

With respect to geotechnical design practice, Terzaghi, 1948 commented that "the inevitable uncertainty involved in fundamental design assumptions, the conception on which the design is based is often no more than a crude working hypothesis". The scientific basis and rigor for interpreting the "science" of geological storage is improving rapidly but because we are inherently dealing with the subsurface, Terzaghi's comments equally apply to the design of geological storage projects. Consequently, long-term monitoring requires integration with a "working hypothesis" of the storage mechanisms.

The monitoring results combined with their analysis or interpretation serve to support the hypotheses of storage processes or aid in improving our predictive capabilities. Monitoring, its frequency, longevity, and scope is part of the approach, as are the evaluations of the monitored results and actions to be taken based on the evaluations. It includes routine or operational monitoring and analysis and actions for special circumstances such as unanticipated reservoir response to injection of CO_2.

Most elements of the monitored decision approach are already implemented as normal practice in subsurface waste disposal or oil and gas activities. The difference in the context of geological storage of CO_2 is the need (and more often, a requirement) to confirm the “science” of storage and to ensure adequate storage permanence. These drivers demand monitoring programs that inform operating practices, but provide value-added knowledge on the evolution of the CO_2 storage processes.

5.5.1 Definition of project conditions

The regulatory process can provide a majority of the information required to plan the monitoring program. Depending on the reasons for monitoring, however, additional information may be required and should be collected at this stage in the planning process.

5.5.2 Technical questions to be answered

This step is perhaps the most critical step in the systematic development of a monitoring program for a particular geological storage project. Critical because selection of an appropriate measurement method and/or the selection of instrumentation are based on whether it can provide the data necessary to answer a particular technical question – if there is no question, there should be no instrumentation. This applies equally to all three monitoring scenarios: operations, verification and environmental. Operational questions can be as simple as “what are the wellhead injection pressures?” to “what is the distribution of CO_2 within the reservoir?” A focus on verification issues may pose an identical question of “what is the distribution of CO_2 within the reservoir?” with the only distinction being the degree of resolution required to answer the question. Detailed and substantive recording of technical questions or objectives to be answered from the monitoring program and their ranking in terms of importance to meeting project objectives will provide a solid foundation for the design of an effective monitoring program. The overwhelming nature of selecting a particular technology to assist in answering a technical question is evident in Table 5.1 which is a summary of significant monitoring practices that could be applied to monitoring CO_2 injection and storage sites (Clifton Associates Inc., 2004).

Table 5.1 Monitoring methods applicable to capture, transportation, injection and geological storage of CO_2 (Clifton Associates Inc., 2004).

Target for Monitoring	Current Monitoring Approaches
CO_2 Plume Location	- Two and three dimensional time-lapse seismic reflection surveys - Vertical seismic profiling and cross wellbore seismic surveys - Electrical and electromagnetic surveys - Satellite imagery of land surface deformation - Satellite imagery of vegetation changes - Gravity measures - Reservoir pressure monitoring - Wellhead and formation fluid sampling - Natural and introduced tracers - Geochemical changes identified in observation or production wells
Early warning of storage reservoir failure	- Two and three dimensional time-lapse seismic reflection surveys - Vertical seismic profiling and cross wellbore seismic surveys - Satellite imagery of land surface deformation - Injection well and reservoir pressure monitoring - Pressure and geochemical monitoring in overlying formations - Microseismicity or passive seismic monitoring
CO_2 concentrations and fluxes at the ground surface	- Real time infrared based detectors for CO_2 concentrations - Air sampling and analysis using gas chromospectrometry - Eddy flux towers - Monitoring for natural and introduced tracers - Hyperspectral imagery
Injection well condition, flow rates and pressures	- Borehole logs, including casing integrity logs and radiotracer logs - Wellhead and formation pressure gauges - Wellbore annulus pressure measurements - Well integrity tests - Orifice or other differential flow meters - Surface CO_2 measures near injector points and high risk areas
Solubility and mineral trapping	- Formation fluid sampling using wellhead or deep well concentrations of CO_2 - Major ion chemistry and isotopes - Monitoring for natural and introduced tracers
Leakage up faults and fractures	- Two and three dimensional time-lapse seismic reflection surveys - Vertical seismic profiling and cross wellbore seismic surveys - Electrical and electromagnetic surveys - Satellite imagery of land surface deformation - Reservoir and aquifer pressure monitoring - Microseismicity or passive seismic monitoring - Groundwater and vadose zone sampling - Vegetation changes
Groundwater quality	- Groundwater sampling and geochemical analysis of monitoring wells - Natural and introduced tracers

5.5.3 Prediction of mechanisms that control behavior

This third step involves developing working hypotheses about the important mechanisms that control the behavior of injected CO_2. This has been studied extensively over the last decade and from a risk assessment perspective; this step is similar to the features, events and processes (FEPs) identification stage prior to performing risk analyses. Table 5.2 provides a brief listing of some of the important mechanisms for geological storage of CO_2 (Stenhouse, 2001). Currently, these “lists” are exhaustive and identifying the critical mechanisms for monitoring, while time consuming, is an important exercise to ensure the monitoring programs represent a value-added component of a storage project.

Table 5.2 Processes associated with geologic storage of CO2 (after Stenhouse, 2001).

SYSTEM FEPs	
Rock properties	
	Mechanical properties of rock (including stress field)
	Mineralogy
	Organic matter (solid)
	Presence and nature (properties) of faults / lineaments
	Presence and nature (properties) of fractures
	Cap-rock integrity
Hydrogeological properties	
	Cross-formation flow
	Fluid characteristics of rock
	Geometry and driving force of groundwater flow system
	Groundwater flow (including rate and direction)
	Hydraulic pressure
	Hydrogeological properties of rock
	Pore blockage
	Saline (or fresh) groundwater intrusion
	Transport pathways
Chemical/Geochemical	
	Carbonation
	Colloid generation
	Degradation of borehole seal (cement / concrete)
	Dissolution of minerals/precipitates/organic matter
	Dissolution / exsolution of CO2
	Dissolved organic material
	Groundwater chemistry (basic properties)
	Methanogenesis
	Microbial activity
	Mineral surface processes (including sorption/desorption)
	Precipitation/Coprecipitation/Mineralisation
	Reactive gaseous contaminants
	Redox environment / heterogeneities
	Salinity gradient
CO2 Properties and Transport	
	Advective flow of CO2
	Colloid transport
	Diffusion of CO2
	Dispersion of CO2
	Gas flow
	Source term (CO2 distribution)
	Thermodynamic state of CO2
	Transport of CO2 (including multiphase flow)
SYSTEM FEPs (continued)	
Other gas	
	Gas pressure (bulk gas)
	Release and transport of other gases
Geology	
	Seismicity (local)
	Temperature / thermal field
	Uplift and subsidence (local)
Abandoned Wells	
	Annular space (quality / integrity)
	Boreholes - unsealed (extreme case)
	Corrosion of metal casing (abandoned wells)
	Expansion of corrosion products (abandoned well metal casing)
	Incomplete borehole sealing / Early seal failure
	Incomplete records of abandonment / sealing
NON-SYSTEM FEPs	
EFEPs	
	Artificial CO2 mobility controls
	Climate change
	Cross-formation flow (fast pathways)
	Depth of future wells drilled
	Earthquakes
	EOR-induced seismicity
	Exreme erosion
	Fault activation
	Future drilling activities
	Glaciation
	Hazardous nature of other gases
	Hydraulic fracturing (EFEP?)
	Hydrothermal activity
	Igneous activity
	Major rock movement
	Metamorphic processes
	Mining and other underground activities
	Monitoring (future)
	Regional uplift and subsidence (e.g. orogenic, isostatic)
	Rock properties - undetected features (e.g. faults, fracture networks, shear zone, etc.)
	Sea-level change
	Seismic pumping
	Seismicity (EXTERNAL)

The mechanisms that control past and future behavior need to be understood through reservoir simulation which is guided by the injection/production and monitoring data as it becomes available. Simulations are utilized to predict temporal and spatial development of the injected gas “bubble”, the effect of geochemical reactions on trapping of CO_2 on long term porosity and permeability, caprock and wellbore integrity, impact of thermal/compositional gradients in the reservoir, pathways of the CO_2 out of the reservoir, the importance of secondary barriers, unplanned hydraulic fracturing, upward migration of CO_2 along the outside of the well casing, cement dissolution, wellbore failure and hydrogeological disruptions.

For example, CO_2 can exist as a liquid or a gas depending on the depth of injection. In addition, geochemical traps will render the CO_2 dissolved or as an ionic species in the formation water, or as a solid carbonate mineral or as a hydrate. Within the context of CO_2 injection, Gunter et al., 2004 provide valuable descriptions of the salient geochemical reactions expected in situ, except for hydrates. Changes in pressure, temperature, synthesis of hydrates, rate of movement and size of the “bubble”, thickness of the solubility front, dilation of the reservoir, permeability and porosity all influence the movement of injected CO_2.

5.5.4 Parameters to be measured and role in answering technical questions

The range of physical processes active in geological storage is large and identifying measurable parameters to help elucidate these processes is difficult. Parameters such as pressure, temperature, load, deformation, acoustic velocity, and resistivity are common while rock-fluid parameters such as conductivity, pH, ionic strength, stable isotopes, and mineralogy begin to identify more complex parameters that aid in answering specific questions. These parameters are referred to as “performance measures”. Pressure transient testing is an example of a monitoring system or method, not a measured parameter - bottomhole pressure (ideally) would be the measured parameter during a pressure transient test.

5.5.5 Magnitude of change expected in parameters

Predictions or estimates of the maximum possible value of a parameter provide limits on the instrument range and an estimate of the minimum value of a parameter leads to a selection of instrument sensitivity or accuracy. Parametric studies with the models or analysis tools that will be used throughout the project can provide valuable input to assist in establishing range, accuracy and sensitivity of an instrument. The uncertainty and variability expected in a performance measure must also be quantified. This is necessary because parameter uncertainty is a function of the amount and variability in data used to support the parameter values, the uncertainty in the interpretation of those data, as well as uncertainty in the data values themselves. Parametric analyses can also assist in this exercise.

If the primary reason for measuring a particular variable is for environmental or safety purposes, in addition to calculating the anticipated value of a variable based on a working hypothesis, one should also calculate the values of the same quantities under the most unfavorable conditions. This allows performance objectives to be established for each variable and monitoring technology capable of satisfying these performance objectives to be identified. A performance objective is a threshold value that defines acceptable performance with respect to movement of injected CO_2.

5.5.6 Select instrumentation and monitoring approaches

There is a wide array of instrumentation available for monitoring:

- The sensitivity of seismic technologies has been steadily improved from 2D to 3D, so that it is now can be used for monitoring fluid movement through 4D (time dependent) seismic using surface deployed geophones and sources. There are also a variety of downhole techniques which could be used, including: crosswell seismic profiling (CSP), where the source is in one well and the receivers in the other); and VSP (vertical seismic profiling) where the receivers are in the well and the source is at the surface). When the receivers are deployed in the well, they also can be used for micro or passive seismic which records the sonic signals generated by deformational events in the reservoir or overlying layers. For the best resolution, seismic surveys combine both surface deployed and well deployed geophones. Seismic has been used to detect occurrence of hydrates in the subsurface.
- Tiltmeters measure deformation or changes in volume by production or injection of fluids or phase changes. They are passive and can be located at the surface or in wellbores.

They have been used successfully to measure progress of steam floods and fracs. They are being tested in coals to detect swelling caused by CO_2 injection and should be tested in hydrate reservoirs to measure dilatency during CO_2 injection.

- Microgravity surface measurements can be used to detect changes in density. It may be most useful to detect large volumes of liquid to gas changes where the density change is large.
- Electromagnetic field propagation measurements are made at the surface but may not be useful if the hydrates are not conductive replacing the conductive pore water.
- Electrical resistance tomography uses well casings as electrodes to measure the changes in electrical resistance in the reservoir, and is particularly sensitive to water composition and saturation.
- Geochemical analyses are based on collecting and chemically analyzing fluids from observation and/or producing wells. These represent specific sample points in the reservoir or overlying formations. To be more definitive, sometimes, in addition to the natural tracers, anthropogenic tracers are introduced into the reservoir to tag the fluids being introduced. Tracers to be considered are in situ, radioisotopes, gases, water soluble salts, fluorescent dyes, water soluble alcohols and isotopes. Fluids may be sampled at the surface or downhole. When sampled downhole, they are normally part of a drill stem test.
- Atmospheric boundary layer measurements are made at the earth’s surface through soil gas and shallow atmospheric by point measurements (e.g. chromatography, infra red, eddy flux towers) or average path measurements (e.g. ground laser, aircraft).
- Well logs have been developed to a fine art by the oil and gas industry and can compile a continuous record of the subsurface properties of formations as the logging tool is lowered on a wireline. Common logs used are pressure, temperature, flow, gamma ray, caliper, density porosity, neutron porosity, induction, spontaneous potential, sonic, cement bond and noise logs. Each log measures a different attribute of the formation as it passes through it. Repetitive runs will record changes in the formation properties due to phase changes or introduction or removal of material. Since each log measures a specific property of the formation, a suite of logs is needed to help quantify the nature of the change.
- Well test analyses are based on the pressure response of a reservoir to injection or production of a small amount of fluid and are used to measure permeability and saturations.
- Interference testing is recording the change in pressure in offset wells due to changes in rates of production or injection in a nearby well.

Instrument selection should recognize any limitations in skill or quantity of available personnel and should consider construction, installation and long-term needs and conditions. Criteria established for operations monitoring may be quite different from environmental monitoring and may entail selection of two different monitoring methods for the same “performance measurement”. Monitoring approaches involves the selection of techniques rather than instruments themselves that provide information to assist in answering the technical questions posed for the project. Within a particular approach, however, instrument selection remains an important step. For instance, surface seismic acquisition requires a decision to use either analogue or digital geophones (the “instruments”).

Instrument selection and location depends on the parameter being measured and the sensitivity required detecting the change. Changes are more detectable if the monitoring instrument can be located as close to the volume where the change is occurring. Monitoring, can be split into *surface monitoring* of sonic, deformation, tilt, pressure, temperature, rate, composition and tracers; and *downhole monitoring* of sonic, deformation, tilt, pressure, temperature, rate, composition. Surface data is generally the least expensive to collect but is less diagnostic than downhole data.

5.5.7 Instrument/monitoring locations

Instrument locations should reflect the hypothesized behavior of the injected CO_2 and should be compatible with the method of analysis that will subsequently be used to interpret the data. Particular attention should be paid to zones within the geological storage system which are critical or are zones of particular concern. For instance, if reservoir or geological characterization indicates the possible presence of a fault and its ability to conduct fluids is uncertain, this would be a region of concern for a geological storage project. Identifying that a fault may exist does not necessarily mean the geological storage project cannot proceed. Appropriately installed instrumentation can provide a monitored decision approach during operation of the project.

Based on previous experience or numerical simulation predictions, zones should also be identified where the behavior within these zones could be considered representative of the behavior as a whole. These sections or zones would be considered as primary instrumented sections and instruments would be located to provide comprehensive performance data.

5.6 TIMEFRAMES AND DEPTH OF MONITORING

Issues arising from the following discussion are the assessment of the monitoring tools (geophysical versus geochemical), the depth of monitoring, the type of monitoring (remote versus in situ), the location of the monitoring tools and the definition of the frequency of monitoring.

The frequency with which monitoring is undertaken is an important design element in the monitored decision framework. Currently, regulatory agencies focus mostly on the time period approved for waste fluid injection into depleted hydrocarbon reservoirs or deep saline aquifers, on the order of 25 years. The lifetime of the injection operation is limited by the reservoir capacity and the injection rate. During injection and abandonment, issues are safety, well integrity, caprock integrity and monitoring. Operating, shut-in and abandoned wells in the vicinity of the injection well which may be contacted by the waste fluids have to be identified and assessed for leakage potential both in the short term (during injection) and the long term (after abandonment of the reservoir or aquifer). The definition of long term is based on perceived risk of leakage, which is expected to decrease as the pressure decays (after injection ceases) towards a stable condition. As this point, if leakage has not occurred, the storage container is quite secure against geomechanical failure due to internal forces. This timeframe is in the order of 100 years. Geochemical reactions can operate on a longer time scale. They may neutralize the acid CO_2 by the formation of carbonate minerals through reaction with the silicate minerals in the reservoir, or the reactions may dissolve the carbonate or other basic minerals in the caprock or wellbore cement resulting in leakage. This timeframe is on the order of 1000s of years. For wellbore cements, new formulations may be required. Carbonate mineral reactions take place in a tens-of-years timeframe, while silicate minerals react over hundreds of years. Although currently not performed, the assessment of whether short term or long term geochemical reactions, or both are important can be made through geochemical modeling (if the reservoir and cement mineralogy and reaction kinetics are known). Such calculations could be the basis for the length of monitoring requirements, which could range from 25 to 1000 years, depending on the nature of the geochemical reactions.

Monitoring Techniques

Monitoring Depth	Baseline	Injection	Pressure Equilibration	Long Term Storage
Surface	Aircraft Soil Gas Insitu Tracers	Aircraft Soil Gas Insitu Tracers	Aircraft Soil Gas Insitu Tracers	Aircraft ------------- Insitu Tracers
Subsurface	3D-Seismic Tilt Meter Pressure Insitu Tracers Logs Passive Seismic	3D-Seismic Tilt Meter Pressure Insitu Tracers Logs Passive Seismic	3D-Seismic Tilt Meter Pressure Insitu Tracers Logs Passive Seismic	3D-Seismic Tilt Meter ------------- ------------- ------------- -------------
Reservoir	3D-Seismic Passive Seismic X-Well Seismic Tilt Meter Pressure ------------- Insitu Tracers Logs -------------	3D-Seismic Passive Seismic X-Well Seismic Tilt Meter Pressure Injected Tracers Insitu Tracers Logs Injection Rates	3D-Seismic Passive Seismic X-Well Seiemic Tilt Meter Pressure Injected Tracers Insitu Tracers Logs -------------	3D-Seismic ------------- ------------- Tilt Meter ------------- ------------- ------------- ------------- -------------
	0.1	1	10	100 — 1000

*Assumes wellbores are abandoned after 100 years

Time Years

Figure 5.3 Range of monitoring technologies over depth (y axis) and a complete timeframe of geological storage (adapted from Chalaturnyk and Gunter, 2004)

Figure 5.3 provides an alternative approach for illustrating the range of monitoring technologies and their applicability for monitoring geological storage sites. Within Figure 5.3, the change in technologies with increasing time reflects the inability of a particular technology to provide meaningful monitoring information and the decreasing access to the reservoir due to abandonment procedures. Prior to injection, a baseline set of monitoring data is collected for Operational monitoring, for Verification monitoring and for Environmental monitoring. During injection of CO_2 (i.e. 10 year time frame), normally, the pressure in the reservoir is steadily increasing and the risk of leakage is the highest. Consequently, the highest frequency monitoring should be used. After the end of injection, the reservoir pressure will decay as fluids disperse through the reservoir and the reservoir comes to pressure equilibrium (i.e. the 100 year time frame). As the reservoir pressure decreases, the frequency of monitoring is steadily decreased. At the end of this stage, abandonment takes place where the wellbores are sealed and abandoned; and monitoring may be restricted to surface methods (1000 year time frame). In some cases, the downhole monitoring tools may be cemented in and still be useable in this longer term. As well the frequency of monitoring is substantially lowered.

5.7 MONITORING SYSTEMS

5.7.1 Reservoir types

Monitoring technologies will have a range of applicability for different reservoir types into which CO_2 injection could occur. The adoption of a systematic approach to the planning and development of a monitoring program for any particular reservoir type is CRITICAL to identify the appropriate technology to be utilized. Although the recommended monitoring tools are the same for the different reservoirs, the responses are different due to the different fluid phases present (i.e. aquifers - water, oil reservoirs - oil & water, gas reservoirs -gas & water). However, if CO_2 is injected into a potential hydrate reservoir, the degree of formation swelling (formation displacements) that occurs upon CO_2 hydrate formation may be significantly higher than formation deformations that would occur for CO_2 injection into a saline sandstone aquifer. Identifying this controlling mechanism would clearly suggest technologies that enable formation deformations to be monitored would be a valuable component of a CO_2 hydrate storage reservoir monitoring program. And this would lead to the observation that for the technologies identified earlier, the use of tiltmeters would become extremely valuable for this application. This is an example of where the application of the systematic approach to developing a monitoring plan enables the most appropriate technologies to be adopted for monitoring the specific mechanisms identified for a particular reservoir type.

The following sections provide additional discussion concerning the selection of monitoring technologies for each of the main injection scenarios: (1) single injection well with no offset observation wells; (2) single injection well with at least two offset observation wells; and (3) an injection-production operation.

5.7.2 Single Injection Well – No Offset Wells

With the absence of offset wells for monitoring, spatial (and by default, temporal) distribution of the injected CO_2 plume is difficult to directly monitor. Consequently, reliance is placed on time-lapse cased hole logging to ascertain near well behavior with time. Time-lapse seismic surveys (we suggest high resolution 2D seismic lines as a technical and economic compromise to 3D surveys) to monitor movement of the CO_2 plume and some level of environmental monitoring to confirm no biosphere impacts. For this scenario, it is critical that numerical modeling is highly integrated with these activities. Based on the original investigations to develop the CO_2 project, a geological/reservoir model is constructed. In most cases, this geological/reservoir model is based on limited data and for this scenario, will generally not have any offset well control on the model development. Consequently, the modeling and model improvement must occur currently with the monitoring program to ensure that the performance observations can be reliably modeled. For the single injection well case, a higher degree of reliance is placed on the modeling predictions since it is not possible to obtain direct measurements of the CO_2 plume position at some distance from the injection well.

For all the scenarios presented, including this one, the deployment of downhole pressure/ temperature measurement technology within the injection well will be challenging. It is speculated that given the safety requirements for CO_2 injection wells, special designs are required for tubing conveyed pressure/temperature gauges. Careful material selection and a gauge carrier design that incorporates a downhole fail-safe design are possible and could be constructed to allow cost-effective, real-time downhole pressure/temperature measurement throughout the life of the operations.

The application of 2D high resolution seismic surveys for monitoring the movement of the plume instead of 3D surveys is recommended for the following reasons:

- Economics: The cost of running three 2D seismic lines (each at 60 degrees to each other) less expensive than a 3D survey. This is important since many repeat surveys inherently provide increasing levels of confidence in the CO_2 plume behavior.
- Resolution: Within a single seismic line, improved resolution can be obtained for the vertical and horizontal position of the CO_2 plume;
- Footprint: 2D seismic lines require less environmental disturbance; and

- Integration: The three lines offset at 60 degrees to each other still provides six (6) measurement points, spatially and temporally, that can be used in the performance modeling to predict the evolution of the CO_2 plume within the injection horizon.

5.7.3 Single Injection Well –Offset Wells

For this scenario, it has been tacitly assumed that the offset wells are available as permanent observation wells and that monitoring strings can be installed within the wells. In the baseline stages for this scenario, the presence of the offset wells provides an opportunity to conduct pressure interference tests with the injection well to improve reservoir characterization.

Offset wells also permit vertical (VSP) and crosswell (CSP) seismic profiles to be measured within the project. The implementation of these programs, however, requires careful planning. For VSP surveys, the placement of a geophone string within the offset well and the alignment of one of the 2D seismic lines with this offset well will allow repeat VSP surveys to be obtained easily. The value of these surveys will depend on the distance the offset well is from the injection well because the VSP only provides data very near the offset well.

The offset well distance from the injection well is also an issue for the CSP surveys. If a monitoring program adopts CSP surveys within the program, it is likely best applied as an environmental monitoring tool. In this case, the baseline CSP survey would be run between the injector and the offset well prior to injecting any CO_2, with the source run in the injection well and the multi-point geophone string cemented in the offset well serving as the receiver. If unintended migration is detected during the monitoring program, the injection well can be shut-in, the source re-run in this well. Interpretation of this second CSP survey may provide an indication of the CO_2 plume location within any formations above the injection horizon.

A specific benefit of this scenario to the assessment of geological storage processes is the ability to sample reservoir fluids as the CO_2 plume approaches and passes by the offset well. Again, it is assumed the offset well is reasonably close (within 250 m) to the injection well. Clearly, geochemical analyses of these fluids will provide a measure of not only the position and timing of the plume movement but along with reservoir mineralogy will provide quantitative data on the geological storage trapping mechanisms. The design of the downhole fluid sampling system requires special care and attention, especially for the surface pressure systems used in the sampling device.

5.7.4 Injection Well – Production Wells

For this scenario, the monitoring technologies intended for application within an injection well can also be applied to the production well, such as cased-hole logs, etc. The presence of the production well also provides an opportunity to collect and analyze reservoir fluids over time to monitor fluid movement within the injection horizon. It is anticipated that most production wells will be sufficiently far from the injection well as to preclude conducting VSP or CSP surveys as a regular component of a monitoring program. As discussed in previous sections, the option exists to acquire a baseline VSP survey near the injection or production wells which includes the entire injection horizon. Upon completion of the wells and initiation of CO_2 injection, repeat VSP surveys would only be available within formations above the injection horizon due to the presence of the packer in the wellbore - this may still be a valuable component of an environmental monitoring program.

5.8 CONCLUSIONS

The focus of monitoring depends on the phase of monitoring (operational, verification or environmental) and the particular mechanism (i.e. migration, leakage or seepage) being measured. Although, in this case, the focus of monitoring is for a hydrate reservoir, the phases with potential to escape from the reservoir will be liquids or gases. Consequently, they are no different than the phases that would be subject to escape from an oil or conventional gas reservoir or aquifer, and similar monitoring tools can be used in all cases, depending on the required sensitivities of the tools. The monitoring systems will be different for each reservoir situation and reservoir type.

Operational monitoring focuses on the storage reservoir; verification monitoring between the storage reservoir and the shallow subsurface; and environmental monitoring into the shallow subsurface or into the atmosphere. All three have consequences in addition to loss of CO_2 from a geological storage project. Migration in the storage reservoir can result in updip migration of the CO_2 plume and weakening of the seals and opening of fractures. Leakage above the storage reservoir can mobilize metals or other contaminants, contaminate energy or mineral resources and potable water. Release to the surface or atmosphere will result in build up of greenhouse gases in the atmosphere, potential suffocation of humans and animals above ground, effects on plants above ground, effects below ground on plant roots, microbes, insects and burrowing animals, and potential contamination of potable water. Consequently, monitoring at all three levels should be carried out.

Monitoring and verification are an integral part of the performance assessment of a geological storage project. As such, the implementation of an appropriate monitoring scheme is the core of a monitored decision framework. There are a variety of effective tools and methods for monitoring the injection of CO_2 underground that will delineate how the fluid is migrating, and whether the sink is leaking or not. These monitoring techniques combined with analytical and numerical techniques will help to either validate or adjust the predicted migration of the CO_2 plume, and the soundness and robustness of the properties input into the models, as well as to take any mitigation activity if the facility underperforms. Consequently, the cost versus benefit must be weighed in deciding which monitoring techniques to apply. In order to achieve that optimum cost/benefit it is necessary to be familiar with the most common monitoring techniques available nowadays, their applicability, pros, cons and shortcomings, and to use this knowledge to design monitoring systems for the specific purpose in mind.

6. AREAS FOR FUTURE TECHNOLOGY RESEARCH

Following are areas for further research related to CO_2 storage in hydrate form and the associated sub-surface technologies:

1. Complete a detailed review of existing Arctic/permafrost activities in Prudhoe Bay and the Mackenzie Delta to describe the current situation and mitigating measures for wellbores. Based on these results, analyze thaw subsidence potential for injection wells through permafrost and develop appropriate casing design options.
2. Model initial CO_2 injection in virgin, water-saturated aquifers to estimate allowable injection rates such that hydraulic fracturing does not occur.
3. Evaluate the placement of horizontal wells to assist in development of a CO_2 hydrate storage reservoir.
4. Model heated CO_2 injection cases where ambient CO_2 injection temperatures cause decrease of injectivity due to permeability reduction in the reservoir adjacent to the wellbore.
5. Integrate the geomechanical implications of hydrate formation into future reservoir simulations.
6. Integrate the geochemical implications of carbonate and silicate mineral reactions on hydrate formation into future reservoir simulations.
7. Further model the interplay between ice and hydrate formation.
8. Determine the impact of gas impurities such as other gases (e.g. H_2S) and chemical additives (e.g., mercaptan, corrosion inhibitors) on CO_2 hydrate formation and stability.
9. Examine reaction speed and control methods to allow forming CO_2 hydrates on surface, prior to their injection in a water slurry by forming fractures in the subsurface. In support of this, establish basic data for CO_2 hydrate size at expected surface and downhole conditions, establish physical pumping characteristics of hydrates and examine potential viscosity modifiers.
10. Examine the use of microbiological enhancements to aid in the displacement of methane/gas from methane hydrates using CO_2; and in the conversion of CO_2 hydrates back to methane hydrates.
11. Conduct a detailed review of acceptable locations in Canada where CO_2 hydrates could be stored but where CO_2 dense phase storage could not occur. Pinpoint shallow reservoirs or aquifers where CO_2 cannot be stored in dense phase because the reservoirs are too close to the surface but the pressure temperature conditions are favourable for CO_2 hydrate formation. Follow-up activities would be to match these reservoirs to nearby potential CO_2 anthropogenic sources.

7. SUMMARY OF CONCLUSIONS

CO_2 Capture

The feasibility and likelihood of commercial application of CO_2 capture technology depends very much on the pressure and the CO_2 content of the raw gas stream from which the CO_2 is to be removed, and consequently is related to the industrial process. There are a number of processing options available for separation of CO_2 from produced gas streams containing CO_2, including gas separation membranes, chemical absorption, physical absorption and cryogenic systems. All of these have been used commercially. Final selection would depend on process specifics, such as gas stream composition, flow rate, and operating costs.

Coal-fired Power Plants: Based on a plant start-up within five - ten years, amine-based chemical absorption is the only feasible option for CO_2 recovery from flue gas or other near-atmospheric pressure streams. All current flue gas CO_2 recovery systems in commercial operation use this technology. Such processes can expect to see continuing incremental improvements in unit cost of CO_2 captured.

Offshore Gas Purification: Gas absorption membranes are a subset of chemical absorption that offers promising benefits. They are in commercial use in certain specialized services with high pressure inlet gas sources; notably offshore. They offer the best possibility for membranes, and for larger improvements in the efficiency of chemical absorption processes. Gas separation membranes offer promise as an eventual alternative to chemical absorption but are commercially available today mainly for specialized applications associated with EOR. Other processes such as cryogenic separation, physical absorption and adsorption are possibilities for specialized niches but their situation is unlikely to see significant improvements.

Oxy-fuel & Gasification: Pre-combustion options such as oxygen-enriched combustion or gasification do not appear suitable unless used in conjunction with new fossil-fuelled power generation opportunities, and are premised on greater reliability than is presently experienced.

Refineries & Upgraders: Recovery of CO_2 from PSA purge gas streams or Benfield off-gas streams at refineries and heavy oil and bitumen upgraders where the CO_2 streams are more concentrated and are at higher temperatures and pressures represents an attractive source of CO_2 in relatively large volumes.

Gas Plants: Recovery of CO_2 from the acid gas feed to some sour gas plants could be attractive, using the commercially-proven Flexsorb™ or similar process. It is in commercial use in central Alberta. This opportunity may be somewhat limited by the fact that many gas processing plants are considering or already have abandoned sulphur production and are directly injecting their acid gas into depleted gas reservoirs, thus taking them out of play as CO_2 sources. Mackenzie Valley gas could also be handled using these commercially available processes if they contain sufficient CO_2 for large scale storage.

CO_2 Transportation

CO_2 can be pipelined in dense phase at temperatures from $-25^{O}C$ to $0^{O}C$, thereby reducing the impact in permafrost areas. The location of the storage opportunities somewhat limits the potential sources of CO_2 and suggests that relatively long CO_2 pipelines may be required. Ocean transport in tankers over long distances greater than 1000 miles may be competitive.

CO_2 Injection and Sub-Surface Technologies

Storage operations where CO_2 is injected into subsurface aquifers to form stable hydrates in the reservoir face some unique challenges in designing and operating the transportation and well systems. The key conclusions reached in the review of these challenges include:

- Warm gas (above the hydrate stability temperature at the injection pressure) must be injected to ensure hydrates do not form near or in the wellbore
- Shut down scenarios for the CO_2 pipeline transportation system must minimize the volume of cold gas that would be injected into the wells at restart to minimize the risk of forming hydrates in the well and reducing injectivity
- Wells that penetrate permafrost zones must be insulated to prevent gas cooling and thaw of the permafrost
- Injection pressures must be managed to prevent hydraulic fracturing in the reservoir and to minimize formation movements that could impact the well seal integrity
- Casing and cement corrosion downhole can be minimized with appropriate selection of materials
- The use of corrosion inhibiting chemicals may be limited since components of these chemicals may also inhibit the formation of hydrates

Monitoring

The focus of monitoring depends on the phase of monitoring (operational, verification or environmental) and the particular mechanism (i.e. migration, leakage or seepage) being measured. Although, in this case, the focus of monitoring is for a hydrate reservoir, the phases with potential to escape from the reservoir will be liquids or gases. Consequently, they are no different than the phases that would be subject to escape from an oil or conventional gas reservoir or aquifer, and similar monitoring tools can be used in all cases, depending on the required sensitivities of the tools. The monitoring systems will be different for each reservoir situation and reservoir type.

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Monitoring and verification are an integral part of the performance assessment of a geological storage project. As such, the implementation of an appropriate monitoring scheme is the core of a monitored decision framework. There are a variety of effective tools and methods for monitoring the injection of CO_2 underground that will delineate how the fluid is migrating, and whether the sink is leaking or not. These monitoring techniques combined with analytical and numerical techniques will help to either validate or adjust the predicted migration of the CO_2 plume, and the soundness and robustness of the properties input into the models, as well as to take any mitigation activity if the facility underperforms. Consequently, the cost versus benefit must be weighed in deciding which monitoring techniques to apply. In order to achieve that optimum cost/benefit it is necessary to be familiar with the most common monitoring techniques available nowadays, their applicability, pros, cons and shortcomings, and to use this knowledge to design monitoring systems for the specific purpose in mind.

Modelling

Although reservoir modelling of CO_2 hydrates is examined in an accompanying report (Uddin and Coombe, 2006), both reports identified areas for improvements in treating geotechnical aspects, effects of other accompanying water- solid (i.e. mineral) geochemical reactions, ice formation and different CO_2 injection scenarios to minimize permeability impairment and optimize CO_2 hydrate formation and methane production from existing hydrates.

Fresh Technologies

Applications in other oil and gas subsurface operations, suggest newer technologies which may have a role in exploitation of hydrates for CO_2 storage and methane production. These are injection of CO_2 hydrate slurries, placement of horizontal wells and bacterial process modifiers.

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