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GEOLOGICAL, OCEAN, AND MINERAL CO₂ SEQUESTRATION OPTIONS: A TECHNICAL REVIEW

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SUMMARY

Of the six greenhouse gases (GHG) covered by the Kyoto protocol, carbon dioxide (CO₂) is the greatest contributor to Canada's total GHG emissions. Fossil fuel combustion is the main source of anthropogenic CO₂, and it currently supplies over 85% of the global energy demand. Worldwide, an effort for reduction of CO₂ emissions aims at increased efficiency of fossil energy usage, development of energy sources with lower carbon content and increased reliability on alternative energy sources such as wind, solar, geothermal and

nuclear. However, to meet the objectives of the Kyoto agreement, CO₂ sequestration methods may be needed. In this review, the methods that we will cover are storage in oil and gas reservoirs, in deep coal seams, in deep saline aquifers, in deep ocean, in salt caverns, and mineral carbonation. Each of these methods has its weaknesses and strengths.

RÉSUMÉ

Des six types de gaz à effet de serre (GES) dont il est question dans le traité de Kyoto, le gaz carbonique (CO₂) est celui qui contribue le plus aux émissions totales de GES au Canada. La combustion de carburants fossiles qui répond présentement à 85 % des besoins d'énergie de notre monde, constitue la principale source de CO₂ anthropogénique. L'effort mondial de réduction des émissions de CO₂ vise à augmenter l'efficacité de l'utilisation des énergies fossiles, à développer des sources d'énergie contenant moins de carbone et à augmenter l'apport d'autres sources d'énergie comme le vent, le soleil, l'énergie géothermique et l'énergie nucléaire. Cependant, pour atteindre les objectifs du traité de Kyoto, on devra peut-être recourir à des méthodes de séquestration du CO₂. Dans la présente étude rétrospective, les méthodes considérées sont les suivantes : le stockage dans des réservoirs de pétrole et de gaz, dans des couches de charbon en profondeur, dans des aquifères salins profonds, dans le fond des océans, dans des cavernes de gisements de sel, ainsi que par carbonatation de minéraux. Chacune de ces méthodes présentent des avantages et des inconvénients.

INTRODUCTION

Canada's Kyoto commitments are to reduce its annual greenhouse gas (GHG)

emissions levels by 6% relative to its 1990 levels (Environment Canada, 2002). Although Canada contributes only about 3% of total global GHG emissions (Table 1), it is one of the highest per capita emitters (23.6 tonne CO₂ equivalent per year), largely because of its resource-based economy, cool climate (*i.e.*, the need for heating) and travel distances (Environment Canada 2002). Of the six GHGs covered by the Kyoto protocol, CO₂ is the greatest contributor to Canada's total GHG emissions (Table 2). Fossil fuel combustion is the main source of anthropogenic CO₂, and it currently supplies over 85% of the world's energy demand (Fig. 1). The main engineering effort for reduction of CO₂ emissions is aimed at increased efficiency of fossil energy usage, development of energy sources with lower carbon content, and increased reliance on alternative energy

Table 1 Canada's total CO₂ emissions for 2000 as compared to global emission estimates. Numbers for emission levels are in Megatonnes (Mt) of CO₂ equivalent (source: Environment Canada, 2002)

CO ₂ emissions	Mt	%
World total (1999)	23900.00	100.00
Canada total (1990)	601.00	2.51
Canada total (2000)	726.00	3.04
Alberta	223.00	0.93
Ontario	207.00	0.87
Quebec	90.40	0.38
British Columbia	65.90	0.28
Saskatchewan	61.80	0.26
Nova Scotia	21.50	0.09
Manitoba	21.40	0.09
New Brunswick	20.20	0.08
Newfoundland	8.80	0.04
Prince Edward Island	2.10	0.01
North West Territories	1.80	0.01
Yukon	0.53	0.00

Table 2 Canadian greenhouse gas emissions. Carbon dioxide (CO₂) is the main contributor to Canada's total greenhouse gas emissions (source: Environment Canada, 2002)

Gas	%
Carbon Dioxide (CO ₂)	78.90%
Methane	12.40%
Nitrous Oxide	7.40%
Other (HFCs, PFCs and SF6)	1.30%

sources such as wind, solar, geothermal and nuclear. It is not likely that the reduction of CO₂ emissions required to meet targets set by the Kyoto agreement could be met using these measures alone. Thus a need for geological, mineral or deep ocean sequestration of carbon dioxide (CO₂) may arise. For the purpose of this paper, the term "CO₂ sequestration" refers to the capture, separation, transportation and storage of CO₂. The storage is expected to be permanent (on the order of thousands to millions of years). Methods of sequestration that are currently being considered by industrialized countries include enhancement of terrestrial carbon sinks (not covered in this study) as well as geological, ocean and mineral sequestration. Each method has its weaknesses and strengths. The methods that we will cover in this review are:

1. Storage in oil and gas reservoirs
 2. Storage in deep coal seams
 3. Storage in deep saline aquifers
 4. Storage in deep ocean
 5. Storage in salt caverns
 6. Mineral carbonation
- Geographic relationships between the main stationary point CO₂ sources and sinks are an essential piece of the puzzle for CO₂ sequestration planning, since transportation of the CO₂ is one of the most important cost factors. Voormeij and Simandl (2003) and Bachu (2001b) have identified the main stationary point sources of CO₂ emissions and the main potential carbon or CO₂ sinks for British Columbia and Alberta, respectively.

Physical Properties of Carbon Dioxide

It is important to know the main properties of carbon dioxide in order to understand the different sequestration methods. CO₂ is an odourless, colourless gas that occurs naturally in the atmosphere at current ambient concentrations of around 370 ppm (0.037%). The effects of high concentrations of CO₂ on humans and other life forms are beyond the scope of this paper and are summarized by Benson et al. (2002).

Depending on pressure and temperature, CO₂ can take on three separate phases (Fig. 2). CO₂ is in a supercritical phase at temperatures

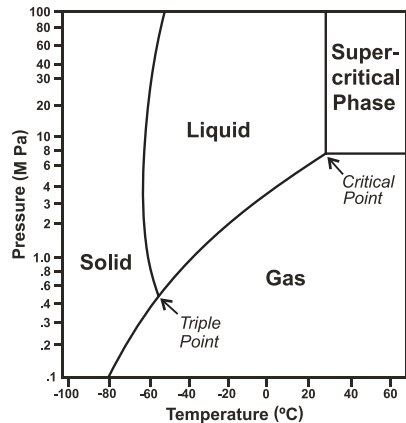


Figure 2 Carbon dioxide phase diagram. CO₂ reaches a supercritical state at 31.1°C and 7.38 MPa (adapted from Koide et al., 1996).

greater than 31.1°C and pressures greater than 7.38 MPa (critical point). Below these temperature and pressure conditions, CO₂ will be a gas, liquid or a solid. Depending on in situ temperature and pressure, CO₂ can be stored as a compressed gas or liquid, or in a supercritical (dense) phase.

CO₂ STORAGE IN OIL AND GAS RESERVOIRS

Both depleted and active fossil fuel reservoirs are potential storage spaces for CO₂ in underground formations. For the purpose of this paper, the term "depleted fossil fuel reservoirs" refers to abandoned oil or gas reservoirs. These reservoirs have undergone primary and secondary recovery and CO₂-enhanced oil recovery is not currently envisaged to generate positive cash flow. Thus CO₂ may be injected directly into a depleted or inactive hydrocarbon reservoir without expectation of any further oil or gas production, resulting in the permanent storage of CO₂. CO₂ may also be injected into producing oil and gas reservoirs, where CO₂-enhanced oil recovery (EOR) and CO₂-enhanced gas recovery (EGR) will offer an economic benefit. Alberta currently has about 26,000 gas pools and more than 8,500 oil pools in various stages of production and completion (Thambimuthu et al., 2003). CO₂ storage capacity in these reservoirs is estimated at 637 Megatonnes of CO₂ in depleted oil pools; 2.2 Gigatonnes of

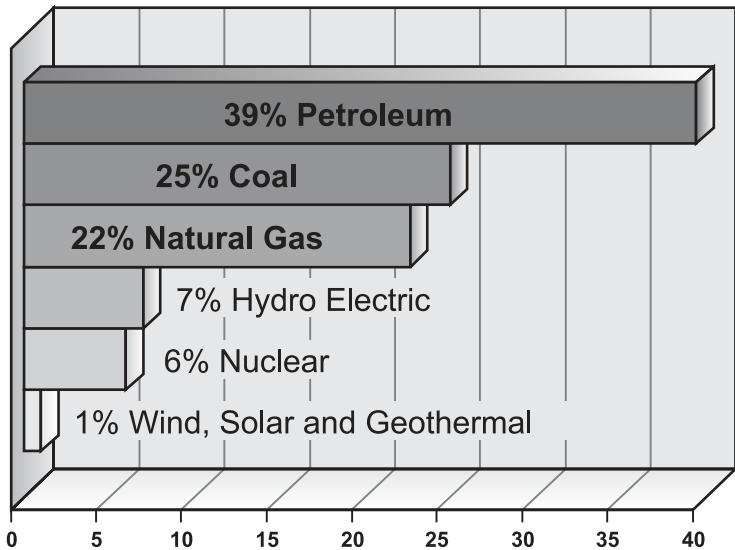


Figure 1 Global energy demands, showing that fossil fuels supply over 85% of the world's energy (McKee, 2002).

CO₂ in gas caps of approximately 5,000 oil reservoirs and 9.8 Gigatonnes of CO₂ storage capacity in gas reservoirs that are not associated with oil pools (Thambimuthu et al., 2003). Of the more than 8,500 oil pools in Alberta, 4,273 reservoirs were identified as suitable for CO₂-EOR.

Typically, oil reservoirs have undergone a variety of production and injection processes during primary and secondary recovery (e.g. gas, water or steam injection), as described by Jimenez and Chalaturnyk (2003). As a tertiary recovery process, CO₂ can be injected into the reservoir to improve the mobility of the remaining oil, thereby extending the production life of the reservoir. Injection of CO₂ into producing gas reservoirs for EGR was previously believed to risk contaminating the natural gas reserve (Stevens et al., 2000). However, recent studies by Oldenburg et al. (2001) and Oldenburg and Benson (2002) suggest that mixing of the CO₂ and methane (CH₄) in a gas reservoir would be limited because of the high density and viscosity of CO₂ relative to the natural gas. Furthermore, significant quantities of natural gas can be produced by repressurization of the reservoir. It is possible that improved gas recovery could more than offset the cost of CO₂ capture and injection (Davison et al., 2001).

Depleted Oil and Gas Reservoirs

Following more than a century of intensive petroleum exploitation, thousands of oil and gas fields are approaching the ends of their economically productive lives (Davison et al., 2001). Some of these exhausted fields are potential sites for CO₂ sequestration. The concept of CO₂ disposal in depleted oil and gas reservoirs is that the hydrogeological conditions that allowed the hydrocarbons to accumulate in the first place will also permit the accumulation and trapping of CO₂ in the space vacated by the produced hydrocarbons (Hitchon et al., 1999; Gentzis, 2000). The caprock that prevented the escape of oil and gas over geological time should retain the sequestered CO₂ for thousands of years (Bachu, 2001a), as

long as it is not damaged as a result of overpressure during the CO₂ injection (van der Meer, 1993), or by the presence of unsealed, improperly completed or abandoned wells (Hitchon et al., 1999). Depleted hydrocarbon reservoirs that are filled with connate water (fully water-saturated reservoirs) offer limited storage capacity. Storage of CO₂ in water-saturated reservoirs would, in practice, amount to aquifer storage (Bachu, 2000; van der Meer, 2003).

Closed, underpressured, depleted gas reservoirs are excellent geological traps for CO₂ storage. Firstly, primary recovery of gas fields usually removes as much as 95% of the original gas in place (Bachu, 2001a), creating large storage potential. Secondly, the injected CO₂ can be used to restore the reservoir to its original pressure (Bachu et al., 2000), thereby preventing possible collapse or man-induced subsidence. Thirdly, the trapping mechanism that retained hydrocarbons in the first place should ensure that CO₂ does not reach the surface. And lastly, the existing surface and down-hole infrastructure used for production of gas may be modified for transportation and injection of supercritical CO₂. About 80% of the world's hydrocarbon fields are at depths greater than 800 m (IEA, website), thus meeting the pressure and temperature requirements needed to store CO₂ as a supercritical fluid (van der Meer, 1993). Spatial association between hydrocarbon production and the presence of reservoirs suitable for CO₂ sequestration may result in shared infrastructure and reduction of transportation costs. Furthermore, depleted hydrocarbon fields commonly have an established geological database and as such, reservoir characteristics are well known. Currently, the petroleum industry is reluctant to consider storage of CO₂ in depleted hydrocarbon reservoirs, because abandoned fields will still contain oil and gas resources (U.S. Dept of Energy, 2002), which potentially have economic value if oil prices were to rise enough or new EOR technologies were developed in the future (Davison et al., 2001; Bachu et al., 2000).

Acid gas injection operations in the Western Canada Sedimentary Basin are a useful small-scale analogue for storage of CO₂ into depleted oil or gas reservoirs. Acid gas is a product of oil and gas processing and consists of a combination of CO₂ and hydrogen sulphide (H₂S). It is either injected into depleted hydrocarbon reservoirs or into saline aquifers for the purpose of reducing atmospheric H₂S emissions. The technology used in acid gas injection in terms of transportation, injection and storage may be comparable to that of geological sequestration of CO₂ (Bachu and Gunter, 2003).

Active Oil Reservoirs

The petroleum industry has been injecting CO₂ into underground formations for several decades (Gentzis, 2000) to improve oil recovery from light and medium oil reservoirs, even before climate change became an issue (Bachu, 2000). CO₂ injected into suitable oil reservoirs can improve oil recovery by 10 to 15% of the original oil in place in the reservoir (Davison et al., 2001). When CO₂ is injected into a reservoir above its critical point (typically a reservoir depth greater than 800 m), the fluid acts as a powerful solvent. If the pressure is high enough and the oil gravity is greater than 25° API, the CO₂ and oil become completely miscible (Bachu, 2001a). According to Aycaguer et al. (2001), the miscible flood reduces the oil's viscosity, thereby enabling the oil to migrate more readily to the producing wells (Fig. 3). At lower pressures CO₂ and oil are not completely miscible, and only a fraction of the CO₂ will dissolve in the oil. This is known as immiscible displacement and it also enhances oil recovery. CO₂ enhanced oil recovery is now considered as a mature technology (Gentzis, 2000). Much of the CO₂ will remain stored in the reservoir, but a significant part ultimately breaks through at the producing well, together with the recovered oil. As a result, the residence time is relatively small, on the order of months to several years (Bachu, 2000). If EOR is the main objective of CO₂ injection, then the operation is optimized to minimize the cost of CO₂

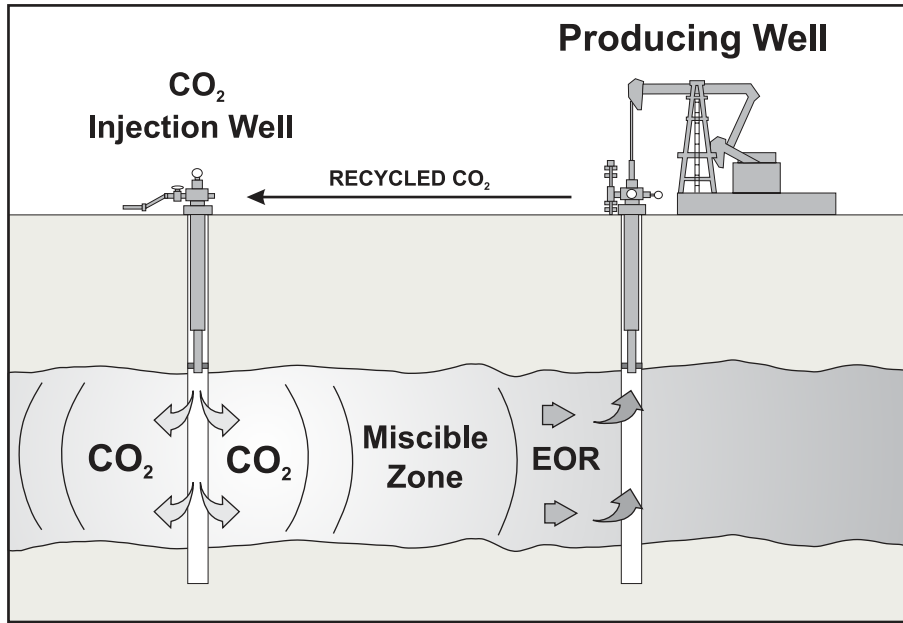


Figure 3 Simplified diagram showing a CO₂-enhanced oil recovery (EOR) operation (modified from IEA R&D Programme, 2001).

used and maximize the oil recovery. An example of this is Pan West Petroleum's Joffre Viking EOR field in Alberta. However, CO₂ sequestration differs from CO₂-EOR: its main objective is to sequester as much CO₂ in the reservoir as possible and to keep it underground thousands if not millions years (van der Meer, 2003; Benson, 2000).

A life cycle assessment study on EOR with injection of CO₂ in the Permian Basin of West Texas (Aycaguer et al., 2001) suggested that the amount of CO₂ injected, not including recycled CO₂, may balance the amount of CO₂ in emissions that ultimately are produced by combustion of the extracted hydrocarbon product. Most of the existing CO₂-EOR projects in the world use naturally occurring sources. CO₂ from natural carbon dioxide reservoirs, where the infrastructure for distribution is already present, provide delivery without major capital costs (Aycaguer et al., 2001) and without processing (Smith, 1998). To help mitigate the release of CO₂ to the atmosphere, the source of CO₂ for EOR should come from anthropogenic (man-made) sources. A Canadian study done by Tontiwachwuthikul et al. (1998) on the economics of CO₂ production from coal-fired power plants concluded that flue gas extraction could be an

economically viable CO₂ supply source for CO₂-EOR projects in Western Canada, should oil prices increase substantially.

Canada is the forerunner in the technology of using anthropogenic CO₂ emissions in a large-scale EOR project at the Weyburn oil field in Saskatchewan. The ongoing project aims at implementing a guideline for geological storage of anthropogenic CO₂ by EOR (Moberg, 2001; Whittaker and Rostron, 2003). Although natural sources can supply CO₂ at a lower cost (Bachu, 2000), funding provided for research makes it feasible to use anthropogenic sources. CO₂ is captured from the Great Plains coal-gasification plant at Beulah, North Dakota, USA and transported through a 320 km pipeline to the Weyburn Pool. The injected CO₂ is 95% pure and initial injection rates are 5000 tons/day (Moberg et al., 2003). The reservoir is located within the Williston Basin and has temperatures near 65°C and pressures around 14.5 Mpa, which indicate that the injected CO₂ will likely exist as a supercritical fluid (Whittaker and Rostron, 2003). The CO₂ from the produced oil will be captured and re-injected into the reservoir so that most of the anthropogenic CO₂ used for EOR will ultimately be sequestered

(Whittaker and Rostron, 2003). An estimated 20 Megatonnes of CO₂ will be injected over the project life (Moberg et al., 2003). Potential future sources of CO₂ include the purified flue gas from Saskatchewan coal-fired thermal plants, such as those at Boundary Dam, Poplar River and Shank (Huang, 2001).

CO₂ STORAGE IN COAL SEAMS

Coal beds are a potential storage medium for CO₂. Canada has abundant coal resources; some of them lie at depths too great to be considered for conventional mining. CO₂ can be injected into suitable coal seams where it will be adsorbed onto the coal and stored in the pore matrix of the coal seams for geological time. Since flue gas, a mixture of CO₂ and nitrogen (N₂) accounts for 80% of CO₂ emissions in western Canada (Reeve, 2000), an alternative to CO₂-only storage is injection of flue gas into coal beds, which may avoid the high cost of CO₂ separation (Law et al., 2003).

CO₂-Enhanced Coalbed Methane Recovery

CO₂ sequestration in coal seams has the potential to generate cash flow through enhanced coalbed methane (CBM) recovery, a process similar to the practice of CO₂-EOR. Recovery of CBM is a relatively well-established technology used in several coalfields around the world (Schraufnagel, 1993; Ivory et al., 2000). A number of companies are looking at producing CBM in Western Canada. Primary CBM recovers about 20 to 60% of the gas in place (Gentzis, 2000; van Bergen and Pagnier, 2001); some of the remaining CBM may be further recovered by CO₂ enhanced CBM recovery. A study done on the Alberta Sedimentary Basin estimated a potential capacity for CO₂ sequestration by enhanced CBM recovery at nearly 100,000 Mt (Fig. 4). To put this storage capacity into perspective, CO₂-enhanced CBM recovery could potentially sequester Metropolitan Toronto's CO₂ emissions (City of Toronto, 1991) for more than 3000 years.

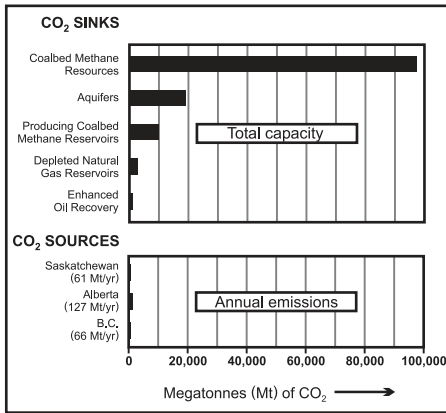


Figure 4 Total CO₂ sink capacity for the Alberta Sedimentary Basin and annual CO₂ emissions for provinces near the basin (modified from Gentzis, 2000).

The disposal of CO₂ in methane-rich coal beds, where applicable, is expected to increase drive pressure and the CBM recovery rate (Hitchon et al., 1999). Thus, injection of CO₂ should enable more CBM to be extracted, while at the same time sequestering CO₂. CO₂ has a higher affinity with coal, about twice that of methane (Fig. 5), just below the critical point (~7.38 Mpa). In theory, injected CO₂ molecules displace the adsorbed methane molecules (Wong et al., 2001; Ivory et al., 2000; Hitchon et al., 1999), which desorb from the coal matrix into the cleats (Fig. 6) and flow to the production wells. However, limited data at pressures exceeding the critical point of CO₂ indicate that the extrapolation of the CO₂ adsorption curve above 7.38 Mpa is not justified (Krooss et al. 2002) and that we do not really know what is happening above this pressure.

CO₂-enhanced CBM production could be achieved by drilling wells into the coal deposits, typically a five-spot pattern, with the centre well as the injector and the four corner wells as the producing wells (Wong et al., 2001). After discharging formation waters from the coal, CO₂ is injected into the coal seam. CO₂-enhanced CBM extraction may achieve up to 72% recovery (Wong et al., 2000). A CO₂-enhanced CBM production project terminates at CO₂ breakthrough in one or more of the production wells (Wong et al., 2001).

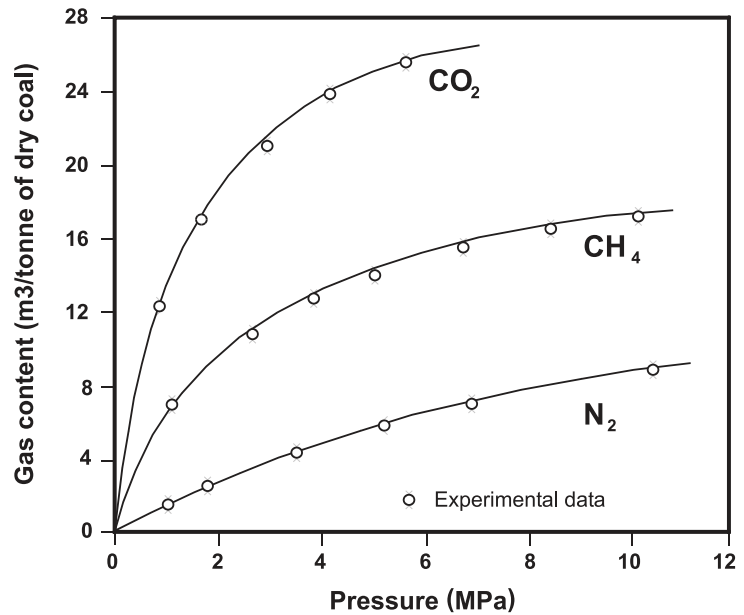


Figure 5 Adsorption isotherms for carbon dioxide (CO₂), methane (CH₄) and nitrogen (N₂) on coal (adapted from Arri et al., 1992). Limited data is available for CO₂ adsorption at pressures in excess of 7.38 MPa (Krooss et al., 2002).

Flue gas injection may enhance methane production to a greater degree than CO₂ alone (Ivory et al., 2000). However, N₂ has a lower affinity for coal than CO₂ or methane (Fig. 5). Therefore, injection of flue gas or CO₂-enriched flue gas will probably result in rapid nitrogen breakthrough at the producing wells (Macdonald et al., 2003; Law et al., 2003). In such cases, N₂ waste could be reinjected into the coal seam (Wong and Gunter, 1999).

Sequestration of CO₂ in coal seams, while enhancing CBM recovery, is an attractive option, but the most suitable physical characteristics of the coals for the purpose of CO₂-enhanced coalbed methane recovery (ECBM) are largely unknown. Recent studies (Fokker and van der Meer, 2003; Reeves, 2003) have shown that continued injection of CO₂ in coal beds induces a decrease in the permeability of the cleat system surrounding the injection well area. In general, desorption of methane induces shrinkage of the coal matrix that results in widening of the cleats, thereby allowing the CO₂ injection rate to increase and methane to flow to the producing well. However, replacement of the methane by the injected CO₂ is

believed to cause the coal matrix to swell. This swelling will partially close the cleat system and reduce permeability. The fracturing and swelling of the coal have opposite effects on the CO₂ injectivity (Fokker and van der Meer, 2003). One possible solution to achieve an acceptable CO₂ injection rate would be to allow the gas pressure in the cleat system to exceed the hydraulic fracturing pressure (Fokker and van der Meer, 2003; Shi et al., 2002), essentially fracturing the coal bed

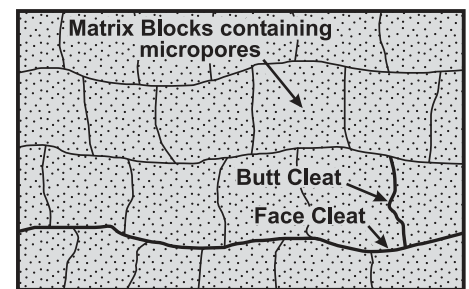


Figure 6 Coal beds contain both primary and secondary porosity systems. The coal matrix (primary porosity system) contains the vast majority of the gas-in-place volume, while the cleats (secondary porosity system) provide the conduits for mass transfer to production wells (adapted from Rice et al., 1993).

in the vicinity of the injection well to enhance permeability. However, if repeated hydraulic fracturing is necessary to maintain connectivity between the well bore and the permeable areas of the coal seam, this may result in over/under burden fracturing (Gale, 2003), and subsequent CO₂ leakage.

The Alberta Research Council (ARC) has done extensive applied research in the field of CBM and some of the outstanding contributions were published by Wong et al. (2000), Law et al. (2003), and Mavor et al. (2002). There are currently several CO₂-ECBM recovery field projects studying sequestration of CO₂ and flue gas in deep coal seams. These projects range in depth from 760 to 1100 metres:

1. Alberta Research Council under an international project, facilitated by the IEA Greenhouse gas R&D Programme, has established a pilot site at Fenn-Big Valley, Alberta, Canada (Fig. 7). The project is looking at the enhancement of CBM production rates in low permeability CBM reservoirs using mixtures of CO₂ and N₂ while sequestering CO₂ into coal beds (Law et al., 2003; Reeve, 2000; Ivory et al., 2000).
2. In October 2000 a three-year government-industry project in the San Juan Basin (USA), known as the Coal-Seq project, was launched. The project studies the feasibility of CO₂-sequestration in deep, unmineable coal seams using enhanced CBM recovery technology (Reeves, 2003).
3. In November 2001, the RECOPOL project (Reduction of CO₂ emission by means of CO₂ storage in coal seams in the Silesian Coal Basin of Poland), funded by the European Commission, started with aims to develop the first European field demonstration of CO₂ sequestration in subsurface coal seams (van Bergen et al., 2003).

The industrial and scientific community will carefully scrutinize the results from these deep field tests, particularly since they may provide empirical data on CO₂ adsorption behaviour above its critical point (7.38 MPa).

CO₂ STORAGE IN DEEP AQUIFERS

Worldwide, deep saline aquifers have larger geological storage capacity than hydrocarbon reservoirs and deep coal seams (Table 3). Deep aquifers are found in most of the sedimentary basins around the world (Bachu, 2001a) and typically contain high-salinity connate water not suitable for human consumption or agricultural use. Deep saline aquifers have been used for injection of hazardous and non-hazardous liquid waste (Bachu et al., 2000) and as such provide viable options for CO₂ sequestration. Approximately 2% of the total effective volume in a deep aquifer can be made available for CO₂ storage (van der Meer, 2003; 1993). Thus, from a capacity perspective, deep saline aquifers offer significant potential for CO₂ storage (Gale, 2003).

Suitable aquifers must be capped by a regional aquitard (*e.g.* shale), which should not contain any fractures or

uncompleted wells (Bachu et al., 1994). The top of the aquifer must be at a minimum depth of 800 metres (van der Meer, 2003), ensuring that the injected CO₂ will be stored in supercritical state. A suitable aquifer should have high permeability locally, for injection purposes, but regional-scale permeability should be low, to ensure long-term disposal of CO₂ (Bachu et al., 1994). When the CO₂ is injected into an aquifer it will rise up as a result of buoyancy effects and gradually spread out, forming a layer of CO₂ under the cap rock (Gale, 2003). In the early stages of geochemical reactions, dissolution of CO₂ into formation water is expected to be the predominant process (Gunter et al., 1997). The surface area of CO₂ in contact with the formation water will control the rate of dissolution. It is believed that during an injection period of 25 years, between 10 and 25% of the CO₂ will be dissolved (Gale, 2003). The undissolved



Figure 7 Carbon dioxide injection test into a coal bed, central Alberta, 1998. **A**=CO₂ cisterns, **B**= compressor and **C**= injection well (courtesy of Bernice Kadatz, Alberta Research Council).

Table 3 Global CO₂ storage capacity of geological reservoirs (source: IEA Greenhouse Gas R&D Programme, 2001).

Storage option	Global capacity	
	Gigatonnes CO ₂	% of Emissions to 2050
Depleted Oil and Gas Fields	920	45
Deep Saline Aquifers	400-10,000	20-500
Unmineable Coal Seams	>15	>1

portion of the injected CO₂ will segregate and form a plume at the top of the aquifer as a result of density differences (Bachu, 2001a). The CO₂ plume will be driven by both hydrodynamic flow and by its buoyancy (Bachu et al., 2000). The greater the density and viscosity differences between the CO₂ and the formation fluid, the faster the undissolved CO₂ will separate and flow upwards in the aquifer in a process similar to oil and gas migration (Bachu, 2001a). Thus, CO₂ should be injected under high pressures to ensure a high density of the CO₂ and a high CO₂ solubility rate in formation water.

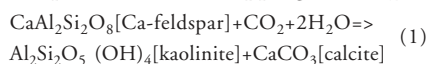
Injection of CO₂ into deep, saline aquifers relies on existing technology. Since 1996, Statoil injects about 1 Megatonne of CO₂ per year into a deep aquifer offshore Norway (Chadwick et al., 2003). Sequestration of the CO₂ waste, a by-product of natural gas production, saves the company from paying a Norwegian CO₂ tax (Gunter et al., 2000).

Hydrodynamic Trapping

Outside the radius of influence of the injection well, both dissolved and immiscible CO₂ will travel at the same velocity as the formation water (Gunter et al., 1997), termed hydrodynamic trapping. Regionally, the velocities of formation water in deep aquifers are expected to be around 1 to 10 cm/year (Bachu et al., 1994), suggesting a basinal residence time for CO₂ of tens to hundreds of thousands of years (Gunter et al., 1997).

Mineral Trapping

The injected CO₂ may be sequestered permanently by undergoing geochemical reactions with silicate minerals, resulting in carbonate production whereby CO₂ is fixed as a carbonate mineral (e.g. calcite, dolomite and siderite). This is known as mineral trapping (Bachu et al., 1994; Gunter et al., in press) and is based on a similar rock-weathering reaction as mineral carbonation, which will be discussed in the last section of this paper. The following chemical reaction is an example of mineral trapping of CO₂:



Experiments carried out to test the validity of mineral trapping of CO₂, by Gunter et al. (1997), concluded that these reactions are expected to take hundreds of years or more to complete. Because of the long residence time of CO₂-charged formation waters within the aquifer, these reactions may eventually trap over 90% of the injected CO₂ (Gunter et al., 1997). Mineral trapping will not greatly increase the CO₂ storage capacity of the aquifer; rather its advantage lies in the permanent nature of CO₂ disposal (Bachu et al., 1994).

DEEP OCEAN DISPOSAL OF CO₂

The ocean is the largest sink available for disposal of CO₂, with a residence time of four to five hundred years (Gentzis, 2000). The oceans contain a stratified thermocline, which is situated between the surface layer and the deep ocean. Its waters circulate between surface and deep layers on varying time scales, from 250 years in the Atlantic Ocean to 1000 years for parts of the Pacific Ocean (Mignone et al., 2003; Ormerod et al., 2002). The atmosphere and the ocean are in contact over 70% of the globe and there is a continuous exchange of inorganic carbon between them. Oceans are, at the present time, removing about six Gigatonnes of CO₂/year from the atmosphere (Ormerod et

al., 2002). Disposing anthropogenic CO₂ in the deep ocean would accelerate a natural process. CO₂ could be injected as a liquid below the thermocline at depths greater than 1500 metres and be sequestered either by dissolution in the water column or by formation of CO₂ hydrates.

Storing CO₂ by Dissolution

One approach involves transporting liquid CO₂ from shore by pipeline and then discharging it from a manifold lying on the ocean bottom, forming a droplet plume (Fig. 8). Since liquid CO₂ is less dense than seawater, the CO₂ droplets will rise until they are dissolved into the seawater and the CO₂-charged solution spreads laterally into the (stratified) surrounding seawater. The dissolved CO₂ may travel in the thermocline, and eventually (after hundreds of years) circulate back into the atmosphere. The deeper the CO₂ is injected, the more effectively it is sequestered, but injecting deeper requires more advanced technologies (Ormerod et al., 2002). The oil and gas industry have established technologies to construct vertical risers in deep water and to lay seabed oil and gas pipelines at depths down to 1600 metres (Ormerod et al., 2002), suggesting that this method is technically feasible.

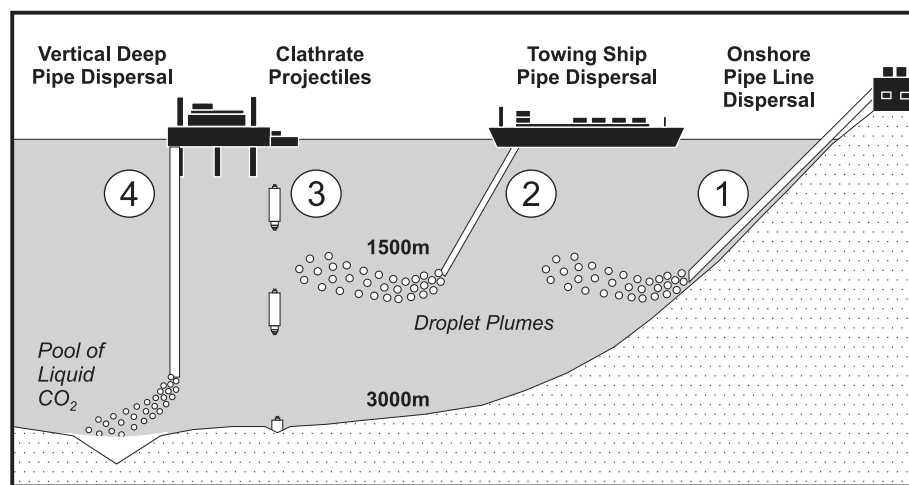


Figure 8 Compilation diagram of proposed methods for ocean disposal of CO₂. Methods 1 and 2 dispose of CO₂ by injecting a droplet plume below 1500 m depths, either through onshore pipeline or via a pipe towing behind a ship. The buoyant CO₂ droplets dissolve into the water column before reaching the surface. Methods 3 and 4 involve sequestration of CO₂ as clathrate hydrates, which are denser than the surrounding seawater and either penetrate into the seabed as streamlined blocks (3) or generate a dense pool on the ocean floor or filling a trench (4).

Alternatively, liquid CO₂ could be transported by a tanker and discharged from a pipe towed by a moving ship (Fig. 8). The Japanese R&D program for ocean sequestration of CO₂ is currently in phase II of a large-scale “moving-ship” scheme in the western North Pacific to assess environmental impact and CO₂-plume behaviour (Murai et al., 2003). Studies by Ozaki et al. (2001) have shown that CO₂ injection would be most effective at relatively slower rates (larger droplet size) and at depths greater than 1500 metres. Such a depth is well within the capability of present-day subsea pipeline technology and CO₂ could be transported by tankers, similar to those used for transportation of liquid petroleum gas (Ormerod et al., 2002).

Storing CO₂ as Clathrates

Another method for ocean disposal of CO₂ involves sequestration of CO₂ at depths in excess of 3000 metres. At these depths, because of the high pressure and low temperatures, CO₂ exists in the form of a clathrate hydrate, an ice-like combination of CO₂ and water (Brewer et al., 2000). Pure CO₂-hydrate is denser than seawater and will generate a sinking plume, settling on the bottom of the ocean (Brewer et al., 2000). CO₂ sequestered in this way would form submarine pools in hollows or trenches in the deep sea. Dissolution of CO₂ into the overlying seawater would be reduced significantly because of formation of the CO₂-hydrates. Direct disposal of CO₂ at great depths is currently not technically feasible, however, it may be possible to send cold CO₂ (dry ice) from mid-depth to the ocean floor (Aya et al., 2003). With a density greater than seawater, cold CO₂ will sink to the ocean bottom and be effectively stored. The Monterey Bay Aquarium Research Institute (MBARI) has recently conducted a series of controlled experiments that involve release of cold CO₂ slurry at depths of 350 to 500 metres (Aya et al., 2003).

Yet another method proposes disposal of CO₂ as clathrate blocks. Studies on this disposal method confirm that streamlined blocks have higher terminal velocity and thus reach the seabed faster than equidimensional blocks (Guever et al., 1996). As large as

1000 tonnes and shaped like a projectile, these blocks could penetrate into the deep seabed where the solid CO₂ would physically and chemically interact with the sediments before reacting with the ocean water (Fig. 8). The retention times could, therefore, be significantly increased as compared to the gaseous or liquid CO₂ disposal methods (Guever et al., 1996). According to the IEA this method is currently not economically feasible (Ormerod et al., 2002).

Further studies on ocean disposal of CO₂ include *fertilizing the oceans* with additional nutrients to increase draw-down of CO₂ from the atmosphere (Ormerod et al., 2002). Addition of nutrients such as nitrates and phosphates or iron may increase production of biological material, thereby drawing down additional CO₂ from the atmosphere through photosynthesis of the phytoplankton. Should this method prove to be feasible, the fishing industries may benefit from the resulting increase in the fish population, with atmospheric CO₂ sequestration as a secondary benefit. However the overall impact on the marine ecosystem is not well understood.

All the above-described ocean disposal methods could potentially cause at least a local change in pH of the ocean water. Marine populations are, in general, intolerant to changes in the pH. Thus, because of environmental impacts on the marine ecosystem and associated public disapproval, ocean sequestration of CO₂ is not currently considered as an attractive option.

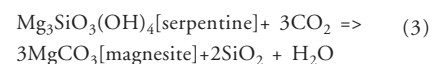
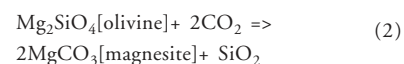
STORAGE IN SALT CAVERNS

Salt can be found as evaporite beds or as intrusive (domal or ridge) deposits where salt from a major underlying source has been forced up into overlying formations. The Western Canada Sedimentary Basin contains several regionally extensive salt deposits, contained primarily within strata of the Devonian Elk Point Group (Grobe, 2000). Large cavities are created by solution mining, whereby water is injected into a salt bed or dome and the brine solution is pumped out. These caverns can be up to 5x10⁵ m³ in volume (Bachu, 2000), and since salt is

highly impermeable (Murck et al., 1996), these spaces could provide a long-term solution to CO₂ sequestration. The technology has been developed and applied for salt mining and underground storage of liquid petroleum gas (LPG), compressed air and petrochemicals (Bachu, 2000; Crossley, 1998; Istvan, 1983). Solid CO₂ (dry ice) could also be stored in these repositories, surrounded by thermal insulation to minimize heat transfer and loss of CO₂ gas (Davison et al., 2001). Although salt and rock caverns theoretically have a large storage capacity, the associated costs are very high and the environmental problems relating to the mined rock and disposal of large amounts of brine are significant (Kolkas-Mossbah and Friedman, 1997). Using current technology, storage of CO₂ in underground salt caverns is uneconomical.

MINERAL CARBONATION

Based on a natural rock-weathering reaction, mineral carbonation is a sequestration concept whereby CO₂ is chemically combined in an exothermic reaction with readily available Mg or Ca-silicate minerals to form carbonates (Lackner et al., 1997; O'Connor et al., 2000; Gerdemann et al., 2003). The products are stable on a geologic time-scale, potentially storing CO₂ for millions of years. Mg-silicates are favoured relative to Ca-silicates because they are more widespread, form larger bodies and contain more reactive material per tonne of rock (Lackner et al., 1997; Kohlmann et al., 2002). A wide variety of Mg-bearing materials, such as enstatite, fly ash and other industrial residues were investigated as potential starting materials for the industrial carbonation process. Recent laboratory tests however, indicate that olivine [(Mg,Fe)SiO₄] and serpentine [Mg₃Si₂O₅(OH)₄] are the most promising raw material (e.g. Lackner et al., 1997; O'Connor et al., 2000). The two reactions below illustrate the basic CO₂ carbonation principle using olivine and serpentine as examples:



In nature, carbonation reactions involving silicates are slow (Kohlmann and Zevenhoven, 2001). A sequestration plant can be visualized as a blender operating at high temperature and pressure conditions (Fig. 9). For industrial CO₂ sequestration applications, carbonation reactions have to be accelerated. This can be achieved by increasing the surface area of the Mg-silicate (crushing and milling), agitating the slurry (O'Connor et al., 1999; Dahlin et al., 2000) and by adding catalysts (for example, NaCl and NaHCO₃ and HCl) to the solution/slurry prior to the carbonation process (Dahlin et al., 2000; Goldberg and Walters, 2003; Jia and Anthony, 2003; Fauth and Soong, 2001; Lackner et al., 1998). Optimization of the carbonation process by controlling temperature and partial pressure of CO₂ (P_{CO₂}) may be also a major factor (O'Connor et al., 1999; Dahlin et al., 2000). In the case of serpentine, an energy-intensive heat pre-treatment (activation-destabilization of the crystal structures) at temperatures of 600 to 650°C is required (O'Connor et al., 2000). Such pre-treatment removes chemically bound water and increases overall porosity (Gerdemann et al., 2003; Kohlmann et al., 2002; Goldberg and Walters, 2003), thereby enhancing its mineral carbonation potential.

There is currently no mineral sequestration plant in operation, however members of the Mineral Sequestration Working Group, a multi-laboratory team managed by the National Energy Technology Laboratory (NETL) of the Department of Energy (DOE) are developing pilot-scale mineral carbonation units and according to their plan a 10 MW demonstration plant will be operational by 2008 (Goldberg and Walters, 2003). Their current research includes the design and operation of a first prototype high temperature-high pressure (HTHP) flow loop reactor by the Albany Research Center (Fig. 10), with the aim to develop a transition from batch experiments to continuous operation.

The mineral sequestration concept is currently incorporated into the design of the coal-fuel electricity generating plant of the Zero Emission Coal Alliance (ZECA), an international

consortium of utilities, mining companies, engineering firms and government laboratories; however it may be also applied elsewhere.

Advantages of Mineral Carbonation

Serpentine and olivine are the two most likely silicates that could be used as

starting materials in mineral sequestration. Olivine is favoured because it reacts better without the energy-intensive pre-treatment that serpentine requires. In contrast to the previously described methods, once the CO₂ is locked into a carbonate (a mineral stable on a geological time scale), there is no possibility for an

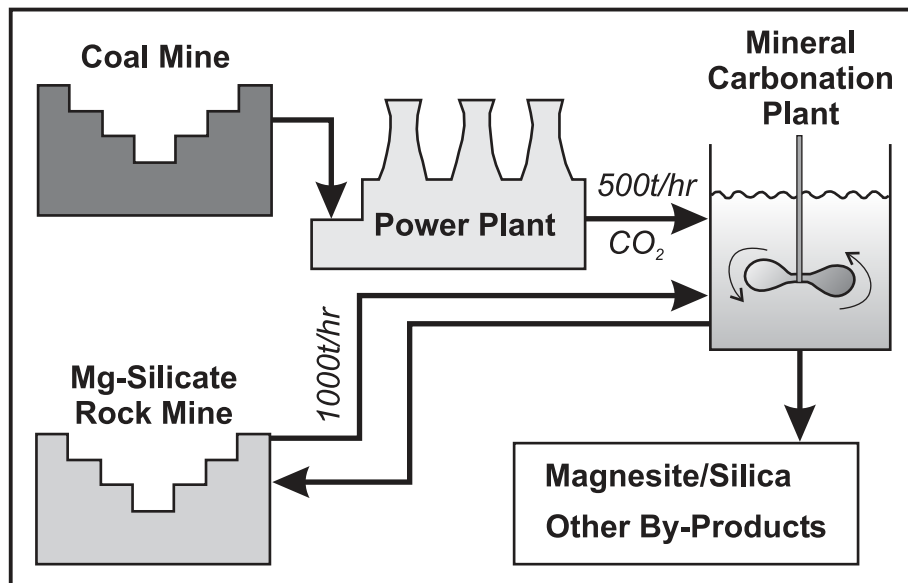


Figure 9 Idealized view of a mineral carbonation plant. The coal is mined for energy, and the waste CO₂ emissions are combined with finely ground Mg-silicates in a temperature and pressure controlled slurry. The resulting carbonate and silica may have industrial applications. Other by-products may include strategic minerals typically associated with serpentinite and dunite deposits, such as Ni, Co, Cr, Fe and Mn (modified from Bauer, 2001).

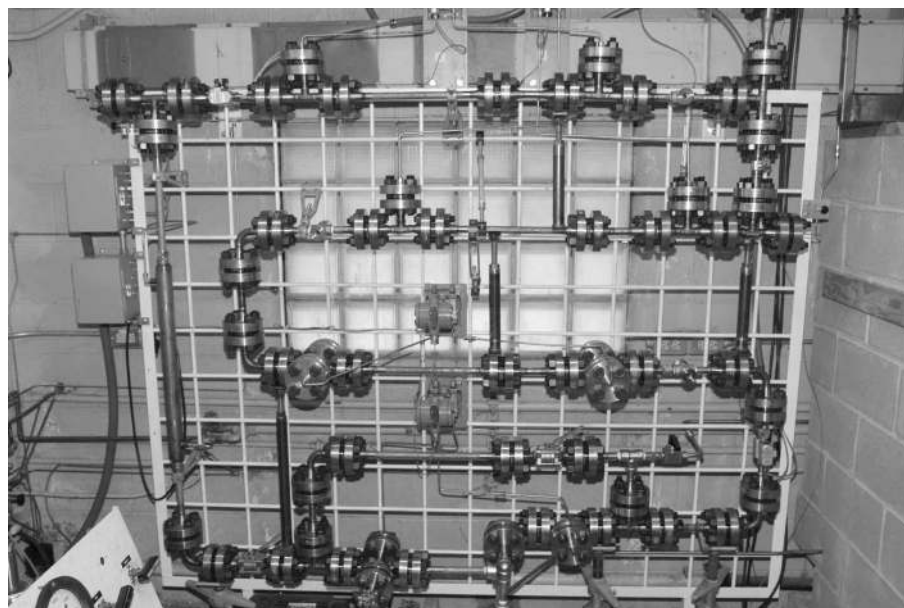


Figure 10 Flow loop test-bench reactor at Albany Research Centre used for mineral carbonation tests. The apparatus is 2 metres high by 2 metres wide, with an ~1.25 cm diameter stainless steel pipe and rated to 150 atm at 200°C (photo is the courtesy of Thermal Treatment Technology Division; Albany Research Center; Office of Fossil Energy, US DOE).

accidental release of CO₂. As well, direct carbonation does not lead to problematic by-products (Lackner et al., 1998). Furthermore, should fibrous serpentine tailings (chrysotile) be considered as raw material for the process (e.g. Huot et al., 2003), then mineral sequestration would help dispose of unwanted asbestos waste. Mineral carbonation may, therefore, benefit from public acceptance.

The costs of the CO₂ disposal could be higher than for the injection of CO₂ into oil and gas reservoirs or deep coal seams, for example. However, these costs may be reduced if the potential for industrial applications of the product (depending on acceptable purity, grain size, particle shape and chemical properties). Magnesite has a wide variety of industrial applications (Simandl, 2002) and the same applies for silica. The carbonation process may also become a new source of Fe, Mn, Co, Cr and Ni recovered during the breakdown of Mg silicate's crystal structure (Haywood et al., 2001; O'Connor et al., 2000).

Large-scale CO₂ sequestration into carbonates will require enormous amounts of raw material (Kohlmann et al., 2002). For a typical power plant, the mass flows of fuel and carbonated mineral will be of the same order of magnitude. For example, studies suggests that for a single 500 MW coal-fired power plant, generating approximately 10 000 tons of CO₂ per day, more than 23 000 to 30 000 tons per day of Mg-silicate ore would be required (Dahlin et al., 2000; O'Connor et al., 2000). Thus, under ideal conditions, coal and Mg-silicate mines should be located close to each other. No shortage of starting material is likely to occur if mineral sequestration becomes a reality and serpentine becomes a workhorse of mineral CO₂ sequestration (Goff et al., 1997). However, if forsterite (Mg-end member of olivine) is used as starting material, supplies are limited and geographically constrained. In most cases, serpentine is an unwanted by-product of metal and chrysotile mining, but in some locations, this waste may become a sought after commodity when its potential for CO₂ sequestration is realized. Should mineral sequestration

of CO₂ become an established technology, then new opportunities will arise for potential producers of magnesium silicates and owners of magnesium silicate-rich tailings.

CONCLUSIONS

This paper presents descriptions of the main geological, ocean and mineral CO₂ sequestration methods that are currently the focus of intensive research by industrialized nations worldwide. At first glance, the most technologically mature methods are storage in active and depleted oil and gas fields, though most of the emphasis lies on maximizing oil and gas recovery rather than sequestration potential. Research relating to injection of CO₂ into deep coal seams is rapidly advancing, with CO₂-enhanced CBM recovery potentially offsetting sequestration costs. Saline aquifers provide huge storage potential in terms of volume for CO₂ sequestration, but they are much more difficult and expensive to characterize than hydrocarbon reservoirs because of the lack of an existing exploration database. The methods that currently encounter the most resistance from the public are storage in salt caverns and ocean sequestration. Mineral sequestration is the only method that truly disposes of CO₂ on geological time scale, with a minimum risk for an accidental CO₂ release.

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