

REVIEW OF CO₂ STORAGE IN LOW PERMEABILITY STRATA

Report: 2013/TR7 October 2013

INTERNATIONAL ENERGY AGENCY

The International Energy Agency (IEA) was established in 1974 within the framework of the Organisation for Economic Co-operation and Development (OECD) to implement an international energy programme. The IEA fosters co-operation amongst its 28 member countries and the European Commission, and with the other countries, in order to increase energy security by improved efficiency of energy use, development of alternative energy sources and research, development and demonstration on matters of energy supply and use. This is achieved through a series of collaborative activities, organised under more than 40 Implementing Agreements. These agreements cover more than 200 individual items of research, development and demonstration. IEAGHG is one of these Implementing Agreements.

DISCLAIMER

This report was prepared as an account of the work sponsored by IEAGHG. The views and opinions of the authors expressed herein do not necessarily reflect those of the IEAGHG, its members, the International Energy Agency, the organisations listed below, nor any employee or persons acting on behalf of any of them. In addition, none of these make any warranty, express or implied, assumes any liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product of process disclosed or represents that its use would not infringe privately owned rights, including any parties intellectual property rights. Reference herein to any commercial product, process, service or trade name, trade mark or manufacturer does not necessarily constitute or imply any endorsement, recommendation or any favouring of such products.

COPYRIGHT

Copyright © IEA Environmental Projects Ltd. (IEAGHG) 2013.

All rights reserved.

ACKNOWLEDGEMENTS AND CITATIONS

This report describes research sponsored by IEAGHG. This report was prepared by:

James Craig

The principal researchers were:

• James Craig

To ensure the quality and technical integrity of the research undertaken by IEAGHG each study is managed by an appointed IEAGHG manager.

The IEAGHG manager for this report was: Tim Dixon

The report should be cited in literature as follows:

'IEAGHG, "Review of CO2 Storage in Low Permeability Strata, 2013/07, October, 2013.'

Further information or copies of the report can be obtained by contacting IEAGHG at:

IEAGHG, Orchard Business Centre, Stoke Orchard, Cheltenham, GLOS., GL52 7RZ, UK Tel: +44(0) 1242 680753 Fax: +44 (0)1242 680758 E-mail: <u>mail@ieaghg.org</u> Internet: <u>www.ieaghg.org</u>



REVIEW OF CO2 STORAGE IN LOW PERMEABILITY STRATA

Executive Summary

 CO_2 Capture and Storage (CCS) from large point source emissions has tended to concentrate on depleted oil and gas reservoirs and deep saline basins. Reservoir conditions are favourable for large scale injection and retention of CO_2 , however these repositories may not necessarily be in close proximity to emission sources. There are countries, notably South Africa and India, which are heavily reliant on coal-fired power generation where oil and gas fields, and deep saline aquifers, are hundreds of kilometres from CO_2 sources. The viability of alternative geological options, with low matrix permeability, is therefore warranted especially if alternative reservoirs are located in close proximity to point sources of CO_2 .

This review has summarised a detailed assessment of South Africa's geological storage potential which is the most comprehensive for a country with both conventional and alternative (low permeability) options. The relevance of the experimental Longyearbyen site has been reviewed partly because of its relevance to South Africa. Brief consideration of India and South Korea has also been included because they too face the dilemma of limited, or unproven, alternatives to large scale conventional reservoirs.

A comparison of low permeable lithologies including coal and gas shale with conventional oil and gas reservoirs shows that they have permeabilities that are four to five orders of magnitude lower than conventional hydrocarbon reservoirs. A hypothetical exercise which compared a site with low porosity / permeability (0.1-10 mD) 100 km from a large point source with a good quality site (100 mD) 1,000 km from the same source has been attempted. The model showed that the avoided cost of CO_2 storage for the low permeability site was double the value for the high-permeability site.

The potential for CO₂ storage will depend on a number of properties including the presence of reactive minerals and microporous organic material which can trap CO₂ at a molecular scale. Lithologies with low permeabilities, including basalt and organic rich shales, have been identified as storage alternatives because of their compositions. It is also possible that clay minerals have adsorption and reactive properties that trap CO₂. There is some evidence from natural gas fields containing CO₂ that migration can occur over geological time scales without significant impact. Evidence from the Muderong Shale in Australia indicates that dissolution and gas sorption does occur despite very low permeabilities of ~10⁻²¹ m² (1 nD). Strong anisotropic differences in permeabilities of between three and four orders of magnitude have been observed in the same shale samples. This phenomenon is attributed to the orientation of clay minerals.

Injecting CO_2 into lithologies which have low matrix permeabilities, especially those with high organic carbon such as coal and organic rich shale, has been of interest because of their



retention potential. CO_2 storage in unmineable coal beds might be a more viable prospect in countries like South Africa which have large coal fields but less accessible large-scale saline aquifers and oil fields. Carbon rich material such as bituminous coal will preferentially retain CO_2 provided CH₄ has been displaced. Supercritical CO₂ is also known to mobilise liquid hydrocarbons from coal under laboratory conditions. It should be stressed that the behaviour of CO_2 injected into coal is not fully understood.

 CO_2 retention in organic rich shales is dominated by adsorption. It is also known that there is a correlation between Total Organic Carbon (TOC) and CH₄ sorption capacity. Other factors, particularly stress conditions and the presence of micro-fractures, are known to influence gas permeability. The mineral content, particularly the proportion of clay minerals, and their composition, will influence the extent to which shales fracture and therefore either release or absorb gas. There is some evidence that gas permeability within organic rich shales is also influenced by the presence of mobile hydrocarbon liquids.

Some attempts have been made to quantify the CO_2 storage capacity of basins with organic rich shales. The quantity of CO_2 that could be stored across the Illinois and Appalachian Basins, within organic rich Devonian Huron shales, has been estimated to be 25Bt. A re-evaluation by Midwestern Regional Carbon Sequestration Partnership (MRCSP), which covers this basin, has revised the capacity down to 2.2Bt assuming a 3% efficiency analogous to estimated efficiencies for saline aquifers. If storage efficiencies analogous to those calculated for coals are assumed (40%) as much as 29.68Bt could be stored.

There is a lack of detailed information on the potential storage capacity of gas shales, particularly the optimum conditions for CO_2 adsorption. Although organic material offers microporosity shales have low permeabilities (0.001mD - 0.1mD) consequently the injection rate is the biggest limiting factor for storage. The widespread use of horizontal wells and hydraulic fracturing for gas and oil from organic rich shales would need to be applied to CO_2 storage. Consequently, there are significant logistical implications notably the proximity of large point sources of CO_2 and sufficient water for drilling and hydraulic fracturing.

A detailed reconnaissance of South Africa's CO_2 storage potential has been completed. It estimates that an estimated 320 Mt (72%) of South Africa's 444Mt of annual CO_2 emissions could be stored. However, the most promising CO_2 storage sites are located hundreds of kilometres away within the offshore Mesozoic Basins and offshore oil and gas fields that fringe the continent. The largest storage potential (90%) is in large offshore deep saline aquifers. Despite the geological challenges within the Karoo Supergroup an estimated 7.42% could be stored in this stratigraphic unit but only a further 0.78% if coal is also included. The challenge presented by the Karoo Supergroup, which dominates much of the centre of the country, is the prevalence of low porosity / permeable sediments including sandstones. This broad stratigraphic unit is also heavily intruded by dolerite which has the effect of compartmentalising successions and potentially limiting lateral CO_2 storage sites.



Despite the abundance of coal, and proximity to large point sources of CO_2 , Coal Bed Methane (CBM) is not regarded as a prospective technology for South Africa. Tests in the country, and neighbouring Botswana, reveal coal with very low permeabilities. Large scale injection would therefore be reliant on a large number of wells.

The widespread presence of dolerite intrusions could have both positive and negative effects for CO_2 storage. Contact thermal metamorphism has destroyed primary porosity and permeability, but these intrusions have also created secondary porosity by fracturing adjacent shale. One of the significant challenges posed by CO_2 storage in basalts is the ability to use seismic monitoring techniques to delineate between separate flows and between basalt and overlying sediments. Other geophysical techniques such as Time Domain Electromagnetic (TDEM) surveys have been used effectively for groundwater prospecting but only to depths of 600m. TDEM and other techniques might be more effective for deeper surveys but more research is needed. Monitoring CO_2 induced mineral reaction, and the related compositional change, will be difficult for the same reason. Despite the presence of basic (Ca, Mg, Fe rich) igneous intrusions (dolerite), and extruded basalt, no attempt has been made to quantify the South African CO_2 storage potential in these formations. The country's water resources might also limit onshore storage if extensive drilling and hydraulic fracturing is required.

The Norwegian test site of Longyearbyen, on the island of Svalbard, is highly relevant to the evaluation and potential development of reservoirs with low matrix permeabilities. The sandstone reservoir has moderate porosities of 5 - 18%, but low permeability values (1 - 2 mD). Despite these properties water-injection tests have indicated good results (45 mD). The comparatively good fluid flow observed is attributed to fractures created by dolerite intrusions and tectonic stress. Modelling suggests that the most effective strategy to avoid exceeding fracture pressure is a gradual injection equivalent to a modest 17,500t per year. CO_2 injected at this rate would extend to 1 km from the well (assuming injection from a vertical well) over a timespan of 4,000 years. Modelling suggests fluid flow is also possible following initial pressure build up. The influence of the site's heterogeneity, and the presence of dolerite intrusions, will make monitoring and modelling CO_2 migration difficult.

Other countries with large point source emissions, particularly India, also face the challenge of limited or unproven reservoirs for CO_2 storage. There are conventional oil fields and deep aquifers but not in close proximity to coal fired power plants. Storage in basalts would offer the best alternative option for India. The challenge of CO_2 storage in an industrialised country such as South Korea are the limited number of onshore geological options. Despite the low permeability within the peninsula's sedimentary basins the nation's Korea Institute of Geoscience and Mineral Resources (KIGAM) has instigated a programme to identify pilot-scale test sites within three sedimentary basins. However, the largest estimated potential for CO_2 storage lies in deep saline aquifers within offshore basins.

This review has clearly shown that potential CO_2 storage in low permeability formations presents significant challenges. Preliminary evidence suggests there would be an economic



penalty. There is evidence that CO_2 could be retained within organic rich lithologies such as coal and organic rich shale, but there are a number of uncertainties that need to be resolved including high pressure injection. The most promising storage potential is likely to come from fracture permeability induced by igneous intrusions. Country-specific reviews suggest that South Africa and India have some low permeability storage potential, but South Korea would only have limited onshore capacity with much greater potential for offshore storage.



Contents

Exe	cutive	e Summary	1			
Con	Contents					
1	Introduction					
2	Technical / Economic considerations					
3	Petro	physical, mineralogical and organic properties that influence carbon dioxide	storage			
in lo	in low permeable lithologies					
	3.1	Australian / Chinese initiative to develop CO2 in organic rich shales	14			
4	Coun	try and location-specific examples	15			
	4.1	South Africa	15			
	4.2	Longyearbyen.	19			
	4.3	Indian subcontinent				
	4.4	South Korea.				
5	Conc	lusions				
6	References					



1. Introduction

The primary candidates for Carbon storage are depleted oil and gas reservoirs and deep saline basins. The geological characteristics, especially porosity and permeability properties of hydrocarbon reservoirs are generally well known. Detailed knowledge of reservoirs is necessary to optimise fluid extraction and injection to enhance oil recovery. Deep saline aquifers are also prime targets for Carbon storage because they have a tendency to have good porosity and permeability properties that extend over large areas. These formations are favoured provided suitable caprock is present to contain injected CO₂, and formation fluids can be displaced. However, one of the main limitations of these storage options is their proximity to large point sources of carbon emissions. CO₂ storage in countries like South Africa and India are good examples of where large point sources of carbon emissions are several hundreds of km from deep saline aquifers or oil fields. A potential alternative solution is to examine the prospects for low porosity / permeability geological storage in relatively close proximity to large point sources.

The potential for CO_2 storage will depend on additional properties including the presence of reactive minerals and microporous organic material which can trap CO_2 at a molecular scale. Lithologies with low permeabilities, including basalt and organic rich shales, have been identified as sequestration alternatives because of their compositions. It is also possible that clay minerals have adsorption and reactive properties that trap CO_2^{1} [1].

2. Technical / economic considerations

The prime candidates for CO_2 storage are oil and gas reservoirs and deep saline aquifers, which have relatively high porosities and permeabilities. These properties are fundamental to any form of fluid extraction, injection, migration and retention so it is helpful to compare porosity/permeability reservoir parameters if alternative options are to be considered. Table 1 provides a broad categorisation of permeability conditions that span conventional hydrocarbon reservoirs, low permeable formations and caprocks. The table shows that some lithologies (coal, gas shale), that are under consideration for CO_2 storage, have permeabilities that are four to five orders of magnitude lower than conventional hydrocarbon reservoirs.



Permeability	Qualitative	Comparative Formation (matrix)
(Darcy)	permeability category	porosity / permeability conditions
10 ⁻⁶ mD	Caprock Very low	
(nD 10 ⁻⁹)	permeability	
10 ⁻⁵ mD	Caprock	
10^{-4} mD	Caprock	
10 ⁻³ mD	Coal & gas shale	
(µD 10 ⁻⁶)		
10 ⁻² mD	Coal & gas shale	
10 ⁻¹ mD	Tight gas reservoir	Southern Karoo SG (<1mD) ϕ <2%
	Coal & gas shale	Ordos Basin caprock (organic rich shale and fine gained sandstone)
1 mD	Tight sandstone	South / Central Karoo SG (+2Md)
(mD 10 ⁻³)		<10%
		Longyearbyen CCS test site (1-2mD) $\oint 8 - 18\%$
10 ¹ mD	Oil Reservoir (fair)	North central Karoo 2-20 mD ¢ <10%
		Northern Karoo (>20 mD, >10%)
10^2 mD	Oil Reservoir (good)	Onshore Mesozoic Basins (South Africa) $(1 - 300 \text{ mD}) \oint 7 - 26\%$
10 ³ mD	Oil Reservoir (very good)	Offshore oil & gas reservoirs (\overline 10 - 30%)
		Offshore saline aquifers (South Africa) av ϕ 15% - 26% 470 - 700 mD
		Utsira sandstone (Sleipner oil field)
10 ⁴ mD	Oil Reservoir (excellent)	
	I	

 Table 1 Comparative Porosity / Permeability characteristics of CO2 storage reservoirs



Fine grained sandstones with low porosity and permeability properties will present greater challenges for CO_2 storage. Firstly, determining the lateral and vertical extent of suitable formations and, once characterised, applying higher pressures and well densities to achieve viable CO_2 concentrations. Selecting CO_2 storage sites will also depend on their suitability for storage and the proximity to large point sources of carbon emissions to achieve economies of scale. Ideally large scale deep saline aquifers or depleted oil and gas reservoirs need to be in relatively close proximity to point sources. However, comparing poorer quality CO_2 storage alternatives may help to provide a clearer perspective on the economic viability of poorer quality sites. A hypothetical exercise which compared a site with low porosity / permeability (0.1-10 mD) 100 km from a large point source with a good quality site (100 mD) 1,000 km from the same source has been attempted² [2].

In this comparison exercise an injection rate of 70Mt/y CO₂ was assumed based on a reservoir simulation model. To achieve this injection rate in the high permeability site 700 vertical wells were required. In contrast 15,000 wells were required to achieve the same rate in the low permeability site. The total number of horizontal wells is much lower, but the low permeability site still requires 731 wells each 5 km long whereas the high permeability site requires only 32 wells to achieve the same injection rate. Modelling suggests that fracturing can improve injection rates for low permeable formations by between 3 to 6 times for vertical wells and fourfold for horizontal wells. Pressure interference between wells, particularly where there is a high well density, could also become counter-productive.

The low permeability site requires higher pressures (22.7Mpa) and a disproportionate number of wells to match the injection rate of the high permeability site. Based on the assumptions made in this simulation the costs of injection into a low permeability site do not compensate for the lower cost of transporting the CO₂ over a much shorter distance. In this example rates of CO₂ capture, and injection in the range 10 to 40Mt/y, costs less than A\$50 per tonne of CO₂ avoided for the high-permeability storage site. This compares with over A\$100 per tonne of CO₂ avoided for storage into the low-permeability site. This example also reveals that costs are highly sensitive to permeability. In addition, reservoir pressure conditions have a significant effect. These variables can be highly uncertain and consequently reservoir characterisation is fundamental for site selection.

There are limits to CO_2 storage where permeability is extremely low, for example in caprocks. Even in these conditions CO_2 migration is possible. Caprocks are defined as low (μ D, 10⁻¹⁸ m²) or very low (nD, 10⁻²¹ m²) permeability formations, and sometimes, but not necessarily, with low porosity (<15%). Caprocks are generally defined as hermetic layers above the storage reservoir that inhibit CO_2 migration. However, there is some evidence from natural gas fields containing CO_2 that migration can occur over geological time scales without significant impact.³ [3]. At permeabilities of around 1 μ D very slow vertical transfer

² CO₂ Storage in Low Permeability Formations

³ Evaluating sealing efficiency of caprocks for CO2 storage: an overview of the Geocarbone Integrity program and results.



is possible. If a caprock formation is partially invaded by CO_2 , it may contribute to a faster decrease of the overpressure in the short term, and to the storage capacity in the long term over several thousand years⁴ [4].

The integrity of the caprock, and the suitability of CO_2 storage sites, depends partly on the permeability of the seal, but also on the lateral extent of the reservoir and its structural configuration. If the reservoir is compartmentalised by faults or impermeable barriers, such as igneous intrusions, then there is potential for a closed system to become established. In these circumstances CO_2 storage will be limited up to a level where the pressure in the formation approaches the caprock fracture pressure. This phenomenon becomes more important in closed systems where caprock permeabilities are very low (<10⁻⁵ mD) because of the potential for pressure build up. At higher permeabilities saline fluid migration into the caprock could limit pressure build up⁵ [5].

3. Petrophysical, mineralogical and organic properties that influence carbon dioxide storage in low permeable lithologies.

Clay rich lithologies such as shales are generally regarded as ideal caprocks because of their low permeabilities, but they may also act as potential repositories for injected CO_2 . Diffusion and gas sorption experiments on samples of the Muderong Shale from north-west Australia indicate that dissolution and gas sorption does occur despite very low permeabilities of ~10⁻²¹ m² (1 nD)⁶ [6]. A decrease in measured CO₂ diffusion after repeat experiments on the same samples has been interpreted as CO₂ retention within the sample. It is assumed that some of the gas has been adsorbed on to mineral surfaces or involved in geochemical reactions. The selected shale samples have low TOC contents (<0.5%) indicating that organic matter does not have a significant role in CO₂ retention. The extent of adsorption and reactivity depends on the clay mineral composition. For example, experimental observations suggest montmorillonite has a greater sorption capacity compared with kaolinite and illite. Mineral dissolution and carbonate precipitation is also likely to occur if Fe/Mg rich clay minerals such as Chlorite are present.

The experimental results of the Muderong Shale have been used to estimate the rate of CO_2 diffusion through a 100m thick shale caprock. By extrapolating the experimental CO_2 diffusion rates it would take approximately 0.3M years for the gas to migrate through this thickness of caprock⁷ [7]. It is possible that mineral dissolution of silicates, and carbonate

M. Fleury1(*), J. Pironon2, Y.M. Le Nindre3, O. Bildstein4, P. Berne5, V. Lagneau6, D. Broseta7, T. Pichery8, S. Fillacier9, M. Lescanne10, O. Vidal11. Oil & Gas Science and Technology — rev. IFP, Vol. xx (2009), No X, pp. 00-00

http://hal.archives-ouvertes.fr/docs/00/58/36/19/PDF/2010_Fleury_GHGT10.pdf

⁴ Int. J. Greenhouse Gas Cont., 2 (2008) 297-308. http://www.sciencedirect.com/science/article/pii/S1750583608000273

⁵ A method for quick assessment of CO2 storage capacity in closed and semi-closed saline formations. Quanlin Zhou *, Jens T. Birkholzer, Chin-Fu Tsang, Jonny Rutqvist. Earth Sciences Division, Lawrence Berkeley National Laboratory, University of California. http://esd.lbl.gov/files/about/staff/quanlinzhou/Paper14_PDF.pdf

⁶ Int. J. Greenhouse Gas Cont., 2 (2008) 297-308. http://www.sciencedirect.com/science/article/pii/S1750583608000273

⁷ Int. J. Greenhouse Gas Cont., 2 (2008) 297-308. http://www.sciencedirect.com/science/article/pii/S1750583608000273



precipitation, could affect the porosity and permeability characteristics of the formation and the retention of CO_2 .

Mineral orientation and compaction also influence matrix properties. For example, permeability in the Woodford Shales from Western Canada are controlled by mineralogy and bedding plane orientation but not TOC content⁸ [8]. The strong anisotropic difference of between three and four orders of magnitude in permeability measurements made parallel $(1.76 \times 10^{-3} - 3.71 \times 10^{-3} \text{ mD})$, and normal $(1.30 \times 10^{-5} - 8.79 \times 10^{-6})$, to bedding planes is attributed to the orientation of clay minerals. There is only a weak correlation between TOC content (1 - 14%) and permeability in these shales.

One of the main areas of interest for CO_2 storage are unmineable coal seams especially if there are prospects for coal bed methane (CBM) recovery. Carbon rich material such as bituminous coal will preferentially retain CO_2 provided methane has been displaced. CO_2 storage in unmineable coal beds might be a more viable prospect in countries like South Africa which have large coal fields but less accessible large-scale saline aquifers and oil fields. The concept of using CO_2 to enhance CH_4 recovery from coal Enhanced Coal Bed Methane (ECBM) has been evaluated in a number of laboratory and small-scale field trials in the United States. For example, an ECBM trial into a coal seam at a depth of 900m within the Allison Unit of the San Juan Basin, recovered $45Mm^3 CH_4$. 335,000t of CO_2 was injected of which 80% (270,000t) was retained. There was an initial reduction by an order of magnitude in permeability as the CO_2 induced swelling in the coal, but reservoir pressure declined and then gradually increased⁹ [9]. This phenomenon is attributed to initial adsorption near the injection site followed by desorption as the CO_2 displaced CH_4 . The study has indicated that the most favourable conditions for CO_2 ECBM are at depths of >900m in high rank coals with permeabilities of 50-250mD.

There is limited evidence from a study conducted in the Highveld Coalfield that contact thermal metamorphism, caused by dolerite intrusions, has increased the adsorption capacity of adjacent $coal^{10}$ [10]. The CO₂ adsorption capacity in a sample 4.6m from a dyke is approximately double the capacity of a sample 57m from the intrusion. There is also evidence that the adsorption capacity of CO₂ declines more than the capacity for CH₄. The increase in storage capacity and coal gas diffusivity in this case could be the result of an increase in pore volumes and internal surface areas which in turn is a consequence of increasing coal rank. However, another study of three coalfields in China revealed that the

In the faculty of graduate studies (geological science), The university of British Columbia (Vancouver). October, 2008

 $https://circle.ubc.ca/bitstream/handle/2429/5302/ubc_2008_fall_pathi_venkat_suryanarayana_murthy.pdf?sequence=1$

⁸ Factors affecting the permeability of gas shales. A thesis submitted in partial fulfillment of The requirements for the degree of Master of science By Venkat suryanarayana murthy pathi

⁹ Investigating the prospects for Carbon Capture and Storage technology in India. Rudra V. Kapila, School of Geosciences, University of Edinburgh. Hannah Chalmers and Matt Leach Centre for Environmental Strategy, University of Surrey. http://carbcap.geos.ed.ac.uk/website/publications/sccs-wp/wp-2009-04.pdf

implications of Gas Production from Shales and Coal for CO₂ Geological Storage. IEA/CON/11/199, August 2012,

¹⁰ CO2 storage potential of South African coals and gas entrapment enhancement due to igneous intrusions. International Journal of Coal GeologyVolume 73, Issue 1, 7 January 2008, Pages 74–87. http://www.sciencedirect.com/science/article/pii/S0166516207000857



adsorption capacity of coal can be reduced closer to intrusions¹¹ [11]. In this instance the distance from intrusions has no direct correlation with the changes in adsorption capacity. Intrusions can induce a number of changes including coal rank, ash, moisture, volatile matter, coal structure and pore characteristics all of which influence the adsorption capacity of the coal.

It is clear from these studies that CO_2 adsorption capacity can be influenced by a number of factors. The level of organic maturity, sediment compaction and volume of pore water are critical factors which influencing the degree of alteration produced by an intrusion. The pre-intrusion coal rank as well as the post-intrusion coal rank need to be taken into consideration. Detailed site-specific investigations also reveal that complexities caused by intrusions will make reservoir capacity estimates more challenging.

Supercritical CO_2 is also known to mobilise liquid hydrocarbons from coal under laboratory conditions. The range and concentration of organic compounds that are mobilised depends on the coal rank but not necessarily porosity. The solubility of organic compounds in supercrital CO_2 , and the preferential retention of some compounds within the coal matrix and the aspheltene faction, influence the relative mobility of different compounds¹² [12]. The extent to which observations from laboratory analyses translate to field conditions needs to be further investigated, but they do suggest that large scale CO_2 entrapment in coal needs much greater evaluation to minimise uncertainty.

It should be stressed that the behaviour of CO_2 injected into coal is not fully understood. Further research is necessary to:

- Improve current models of multi-component sorption, diffusion and phase conditions so that they replicate reservoir conditions more accurately.
- The phenomenon of coal swelling cannot be adequately modelled dynamically.
- Improve the understanding of CO₂ interactions with coal during initial injection, and in the longer term, and the processes involved in CO₂/CH₄ exchange.

Organic rich shales might also offer CO_2 storage potential, although this will depend on the injection rate of CO_2 into formations with very low permeabilities. An experimental evaluation of CO_2 retention in the organic rich Barnett shale indicated that adsorption is the dominant mechanism¹³ [13]. As pressure increases more free gas (CH₄) is released into pores¹⁴ [14]. It is also known that there is a correlation between TOC and CH₄ sorption

¹¹ Influences of igneous intrusions on coal rank, coal quality and adsorption capacity in Hongyang, Handan and Huaibei coalfields, North China. International Journal of Coal Geology 88 (2011) 135–146

¹² A Geochemical Investigation into the Effect of Coal Rank on the Potential Environmental Impacts of CO2 Sequestration in Deep Coal Beds ," in Rubin, E.S., Keith, D.W., Gilboy, C.F., Wilson, M., Morris T., Gale, J. and Thambimuthu, K., eds., *Greenhouse Gas Control Technologies 7*, Elsevier Science Ltd, Oxford, 2005. <u>http://seca.doe.gov/publications/proceedings/04/carbon-seq/089.pdf</u>

¹³ Carbon Dioxide Storage Capacity of Barnett Shale. A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the Degree of Master of Science by Seung Mo Kang Norman, Oklahoma, 2011.

http://mpge.ou.edu/research/documents/2011%20thesis/Seung%20Mo%20Kang.pdf

¹⁴ New Evaluation Techniques for Gas Shale Reservoirs. Reservoir Symposium 2004 Schlumberger.



capacity¹⁵ [15]. Other factors, particularly stress conditions and the presence of microfractures, are known to influence gas permeability. The mineral content, particularly the proportion of clay minerals, and their composition, will influence the extent to which shales fracture and therefore either release or absorb gas.

Up to 50% of the injected gas was adsorbed within organic material (kerogen). Kerogen is a nanoporous material with micropores ($\leq 2nm$) and mesopores (2 - 50 nm). The Barnett Shale experimental study revealed that kerogen acts as a molecular sieve preferentially retaining CO₂ by a factor of two to four times greater than CH₄. This study also showed that there was no significant correlation between TOC, or pore size, and storage capacity, although other studies suggest there is a correlation¹⁶ [16]. What could also be significant is the nature of the pore structure formed by compacted kerogen. A detailed petrological investigation using a series of SEM images to build up a 3D image of pore structures (Figure 1) shows that organic rich rocks have inter connected and highly irregular shaped pores ($\leq 100 nm$). It is possible that free and adsorbed gas in mature gas shales is retained within these structures whereas the water is preferentially adsorbed on to the surfaces of clay minerals¹⁷ [17].

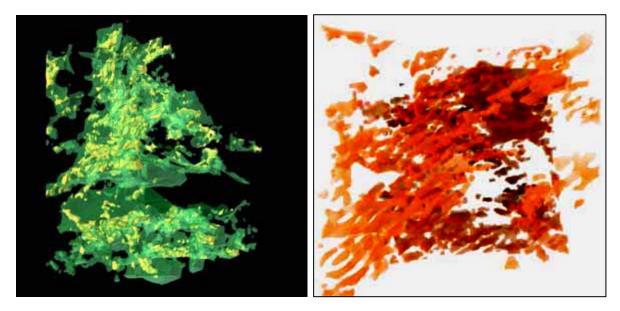


Figure 1aFigure 1bFigure a) 3D visualization of the organic network (green) and porosity (yellow)18 [18]

¹⁵ Rock Matrix as Reservoir: mineralogy & diagensis. Hans-Martin Schulz & Brian Horsfield. DeutschesGeoForschungsZentrumGFZ, Potsdam Presentation on March 1, 2010, AEON, University of Cape Town, Rondebosch 7701, South Africa. http://www.gfzpotsdam.de/portal/gfz/Struktur/Departments/Department+4/sec43/Breaking+news/Capetown-workshoppresentations/GASHsa+Rock_matrix;jsessionid=ED1EEF5204118133B554AB1A7C5D0656?binary=true&status=300&language=en

¹⁶ Rock Matrix as Reservoir: mineralogy & diagensis. Hans-Martin Schulz & Brian Horsfield. DeutschesGeoForschungsZentrumGFZ, Potsdam Presentation on March 1, 2010, AEON, University of Cape Town, Rondebosch 7701, South Africa. http://www.gfzpotsdam.de/portal/gfz/Struktur/Departments/Department+4/sec43/Breaking+news/Capetown-workshoppresentations/GASHsa+Rock_matrix;jsessionid=ED1EEF5204118133B554AB1A7C5D0656?binary=true&status=300&language=en

¹⁷ From Oil-Prone Source Rock to Gas-Producing Shale Reservoir – Geologic. and Petrophysical Characterization of Unconventional Shale-Gas Reservoirs. SPE 131350. Q. R. Passey, K. M. Bohacs, W. L. Esch, R. Klimentidis, and S. Sinha, ExxonMobil Upstream Research Co. Copyright 2010, Society of Petroleum Engineers. Paper presented at the CPS/SPE International Oil & Gas Conference and Exhibition in China held in Beijing, China, 8–10 June 2010. http://www.fossilfuel.co.za/articles/2012/SPE-131350-FINAL-Low_Passey-et-al_.pdf

¹⁸ From Oil-Prone Source Rock to Gas-Producing Shale Reservoir – Geologic. and Petrophysical Characterization of Unconventional Shale-Gas Reservoirs. SPE 131350. Q. R. Passey, K. M. Bohacs, W. L. Esch, R. Klimentidis, and S. Sinha, ExxonMobil Upstream Research Co.



b) Image of the connected pore network from the sample shown in (a)¹⁹ [19]

There is some evidence that gas permeability within organic rich shales is also influenced by the presence of mobile hydrocarbon liquids²⁰ [20]. Permeability measurements as low as 0.1 µD were recorded from core samples taken from the Devonian Huron Shale in eastern Ohio. There was evidence of free (i.e. liquid hydrocarbons) within these samples. The lowest permeabilities, recorded under more recent laboratory conditions, are within the oil-window $(R_o 0.85 - 1.05\%)^{21}$ [21]. In contrast, an organic rich sample of Marcellus Shale, with a higher permeability $(5 - 50 \mu D)$, appeared to have no mobile hydrocarbons. Observations from the Huron Shale showed that permeability was initially sustained but then declined. This phenomenon is attributed to the re-adsorption of free liquid hydrocarbon (oil) molecules plugging micro pores²² [22]. It is also possible that the formation permeability could be modified post injection by induced swelling of coal or kerogen, adsorption, desorption and possibly longer term mineral dissolution or carbonate formation if CO₂ forms carbonic acid²³ [23]. Further research is necessary to determine how significant these processes might be.

The potential for CO₂ sequestration has been estimated for Devonian organic rich shales which are present in the Illinois and Appalachian basins of the eastern United States²⁴ [24]. This study was based on side core samples from wells in a comparatively small region of the Illinois Basin in Kentucky. Extrapolation to the rest of the basin is therefore tentative. Laboratory analysis of organic rich samples (0.5 - 15% TOC) revealed a good linear correlation with CO₂ adsorption capacity in this instance. At a constant pressure of 2.8MPa the adsorption capacity ranges from $0.4 - 4.2 \text{ m}^3/\text{t}$ under experimental conditions. CO₂ is preferentially adsorped on to the organic matter (kerogen) present in the rock. At this pressure CO₂ adsorption exceeds CH₄ adsorption by a factor of five. Experimental studies on core samples indicate that 50% of the CO_2 is adsorbed. In this study vitrinite reflectance measurements ranged for R_0 0.78 – 1.59% indicating that the organic rich shales are

Copyright 2010, Society of Petroleum Engineers. Paper presented at the CPS/SPE International Oil & Gas Conference and Exhibition in China held in Beijing, China, 8–10 June 2010. http://www.fossilfuel.co.za/articles/2012/SPE-131350-FINAL-Low Passey-et-al .pdf. (courtesy FEI Company).

¹⁹ From Oil-Prone Source Rock to Gas-Producing Shale Reservoir – Geologic. and Petrophysical Characterization of Unconventional Shale-Gas Reservoirs. SPE 131350. Q. R. Passey, K. M. Bohacs, W. L. Esch, R. Klimentidis, and S. Sinha, ExxonMobil Upstream Research Co. Copyright 2010, Society of Petroleum Engineers. Paper presented at the CPS/SPE International Oil & Gas Conference and Exhibition in China held in Beijing, China, 8–10 June 2010. http://www.fossilfuel.co.za/articles/2012/SPE-131350-FINAL-Low Passey-et-al .pdf.

²⁰ Porosity and permeability of Eastern Devonian Gas Shale. (courtesy Mark Knackstedt and Trondt Varslot, ANU).

Danial J Soeder, SPE Formation Evaluation, March 1988, Inst. Of Gas Technology

http://www.pe.tamu.edu/wattenbarger/public_html/selected_papers/--shale%20gas/spe15213.pdf

²¹ Geophysical Research Abstracts. Vol. 15, EGU2013-1058-1, 2013. EGU General Assembly 2013. © Author(s) 2012. CC Attribution 3.0 License. Lithological controls on matrix permeability of organic-rich shales: An experimental study http://meetingorganizer.copernicus.org/EGU2013/EGU2013-1058-1.pdf

²² Energy Minerals Division website viewed on 8/07/13. A Division of the American Association of Petroleum Geologists. http://emd.aapg.org/technical areas/gas shales/index.cfm

²³ Potential implications of Gas Production from Shales and Coal for CO₂ Geological Storage. IEA/CON/11/199, August 2012

²⁴ Analysis of Devonian Black Shales in Kentucky for potential Carbon Dioxide sequestration and enhanced natural gas production. http://www.uky.edu/KGS/emsweb/devsh/final report.pdf



thermally mature and generating free hydrocarbons in the form of oil and gas^{25} [25]. Although there is a wide distribution of organic rich shales they exhibit low porosities (average 0.9%) and permeabilities (5 x 10⁻⁴ mD). CO₂ could be injected but as an EOR or EGR fluid medium combined with formation fracturing. The quantity of CO₂ that could be stored across the Illinois and Appalachian Basins, within organic rich Devonian Huron shales, has been estimated to be 25Bt. However, enhanced natural gas displacement using CO₂ injection has yet to be demonstrated at field scale although the technique is part of a research initiative being conducted by the Midwestern Regional Carbon Sequestration Partnership (MRCSP) which covers the Illinois and Appalachian basins. A re-evaluation by MRCSP revised the capacity down to 2.2Bt assuming a 3% efficiency analogous to estimated efficiencies for saline aquifers. If storage efficiencies analogous to those calculated for coals are assumed (40%) as much as 29.68Bt could be stored²⁶ [26]. Although not stated this implies very high organic rich shales are distributed across the basin which may not necessarily be the case.

There is a lack of detailed information on the potential storage capacity of gas shales, particularly the optimum conditions for CO_2 adsorption. Although organic material offers microporosity shales have low permeabilities (0.001mD – 0.1mD) consequently the injection rate is the biggest limiting factor for sequestration. The widespread use of horizontal wells and hydraulic fracturing for gas and oil from organic rich shales would need to be applied to CO_2 storage²⁷ [27]. Consequently, there are significant logistical implications notably the proximity of large point sources of CO_2 and sufficient water for drilling and hydraulic fracturing.

The experimental observations from the Barnett and Huron shales suggest that pore geometry, kerogen type and the relative thermogenic maturity, especially within the oil generation window, control CO_2 storage potential. It is conceivable that the higher the organic content the more permeable and therefore more favourable CO_2 storage conditions become provided thermal maturation has reached the gas window. If more accurate estimates of CO_2 storage in organic rich shales are required all these determinants will need to be quantified, ideally on a basin-wide scale.

3.1 Australian / Chinese Initiative to develop CO₂ storage in organic rich shales

There is an initiative between the China University of Geosciences and Tsinghua University, which is part of the China Australia Geological Storage of CO_2 (CAGS) co-operative

 $^{^{25}}$ The onset of oil generation is equivalent on an arbitrary vitrinite reflectance of 0.55%. Oil generation extends to 1.1%. The gas generation window is typically between 1.0 - 1.3% and extends up to 3%.

²⁶ MRCSP Phase II - Reassessment of CO2 Sequestration Capacity and Enhanced Gas Recovery Potential of Middle and Upper Devonian Black Shales in the Appalachian Basin. MRCSP Phase II Topical Report, October 2005–October 2010. Brandon C. Nuttal, Kentucky Geological Survey, Lexington, Kentucky. Midwestern Regional Carbon Sequestration Partnership (MRCSP). DOE Cooperative Agreement No. DE-FC26-05NT42589. OCDO Grant Agreement No. DC-05-13. http://addap.tk/userdata/phase_II_reports/topical_4_black_shale.pdf

²⁷ IEA Greenhouse Gas R&D Programme 42nd Executive Committee meeting. Potential implications of gas production from shales and coal for CO_2 geological storage. GHG/12/47



agreement²⁸ [28]. This initiative is highly pertinent to CO_2 storage in organic rich shales because it will assess the feasibility of using CO_2 for enhanced shale gas recovery (ESGR). The two Chinese universities are studying the interaction between CO_2 and shale formations within the Ordos Basin. The project is comprised of a comprehensive programme including:

- Evaluation of the formation's absorption equilibrium and kinetic parameters for CO₂ and CH₄ and the coefficient variations of the shale's expansion and permeability after absorption.
- Comparison between shale gas production using ESGR and conventional extraction using pressurised water. An ESGR numerical simulation will be developed to predict the efficiency of the process and CO₂ storage.
- Development of a model based on the geological conditions in the Ordos Basin to estimate the potential for shale gas production from ESGR and CO₂ storage including capacity.
- The potential detrimental as well as the beneficial properties of ESGR will be evaluated including technological, economic, safety and environmental parameters. The environmental impacts that will be covered include CO₂ and CH₄ leakage, soil and water course pollution and other non specified risks.

The ESGR and possibly the CO₂ storage potential might be significant. Mudstones with TOC contents of 2 - 3% extend across the basin. Favourable maturation levels of R_o 1.2% reportedly extend across 72% of the basin. High maturation levels can also be inferred from gas filled reservoirs. Very low permeabilities are also encountered $(10^{-1} - 10^{1} \text{ mD})$ in these lithologies which can form caprocks²⁹ [29]. This might restrict where CO₂ injection is possible. There are other basins in China, namely the Sichuan and Tarim, where extensive organic rich shales of marine origin, high thermal maturity and brittle mineralogy have been identified³⁰ [30]. However, the Ordos Basin is closer to large point sources of CO₂.

4. Country and location-specific examples

4.1 South Africa

The dilemma posed by the distance between large quantities of carbon emissions from point sources and suitable CO_2 storage sites is exemplified by South Africa. The country is heavily dependent on coal-fired power stations that use coal mined from seams within the Karoo Supergroup. An estimated 320Mt (72%) of South Africa's 444Mt of annual CO_2 emissions could be stored. However, the most promising CO_2 storage sites are located hundreds of

²⁸ China Australia Geological Storage of CO2 (CAGS) website accessed on 10/07/13. Possibility and Potential of CO₂ Enhanced Shale Gas Recovery in the Ordos Basin. http://www.cagsinfo.net/research_project_2.htm

²⁹ Tight sandstone gas reservoirs (exploration) in upper Palaeozoic of Ordos basin. YANG Hua FU JinHua WEI XinShan REN JunFeng. (PetroChina Changqing Oilfield Company, Xi'an, 710018, China

³⁰ World Shale Gas Resources: An Initial Assessment of 14 Regions Outside the United States. April 2011, US Energy Information Administration (EIA). XI China



kilometres away within the coastal Mesozoic Basins and offshore oil and gas fields that fringe the continent³¹ [31]. The challenge presented by the Karoo Supergroup, which dominates much of the centre of the country, is the prevalence of low porosity / permeable sediments including sandstones. The Karoo Supergroup is also heavily intruded by dolerite which has the effect of compartmentalising successions and potentially limiting lateral CO₂ storage sites (see Figure 2). The burial depth of some of the basins within the Karoo Supergroup, for example the Vryheid Formation, is <800m further restricting potential CO₂ sequestration.

A review of CO₂ storage within South Africa also highlights that porosity and permeability within the south and southwestern Karoo is very low (<2% porosity, <2mD) as a result of diagenesis and low grade metamorphism. More promising porosity (1.8 – 12.5%) and permeability (20 – 590 mD) has been recorded from the Vryheid Formation in the Northern Karoo Basin. The detection of gas shows within this basin suggests fluid retention is possible but CO₂ storage is unlikely to be considered unless gas is discovered in commercial quantities.

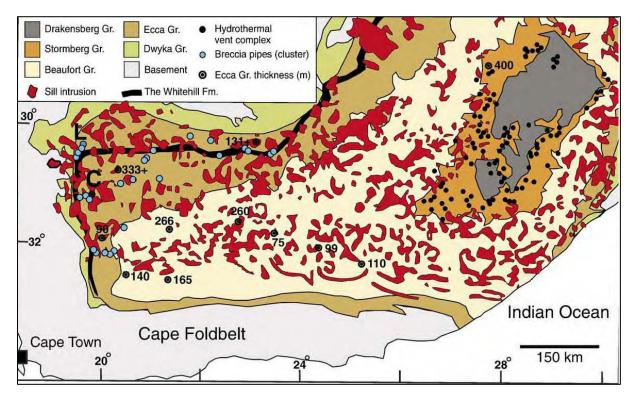


Figure 2. Igneous intrusions in the Karoo Basin, South Africa³² [32]

The most recent country-specific assessment of carbon storage potential clearly shows that the conventional options (oil and gas fields and large saline aquifers) far exceed the potential within the Karoo Supergroup³³ [33] (see Table 2). The review did evaluate storage potential

³¹ Technical Report on the Geological Storage of Carbon Dioxide in South Africa. Council for Geoscience South Africa, 2010.

³² Svensen, H., et al., "Hydrothermal Venting of Greenhouse Gases Triggering Early Jurassic Global Warming", Elsevier, Earth and Planetary Science Letters 256 (2007) 554-566

³³ Technical Report on the Geological Storage of Carbon Dioxide in South Africa. Council for Geoscience South Africa, 2010



in saline aquifers and coal within this stratigraphic unit. This assessment did not include basalts or organic rich shales.

Broad Geological Unit	Mt CO ₂	% Total
Onshore Karoo (within coal fields)	1,271.9	0.78
Onshore Karoo saline aquifers	12,163M	7.42
Onshore Mesozoic Basin	870M	0.53
Offshore Oil & Gas fields	1,835.6M	1.12
Offshore deep saline Mesozoic aquifers	147,772M	90
Total	163,912.6	100

Table 2 Estimated CO₂ capacity in South Africa

Broad estimates for CO_2 storage potential for countries with coal reserves have been published³⁴ [34] including South Africa (2.05Gt). A more detailed country-specific analysis, based on each coal field, estimates the potential for CO_2 storage to be much lower $(1.3Gt)^{35}$ [35].

Despite the abundance of coal, and proximity to large point sources of CO_2 , CBM is not regarded as a prospective technology for South Africa³⁶ [36]. Tests in the country, and neighbouring Botswana, reveal coal with very low permeabilities. Large scale injection would therefore be reliant on a large number of wells. The use of CO_2 with Underground Coal Gasification (UCG) is also unlikely to be considered because of environmental concerns particularly the leakage of CO_2 .

The presence of carbonaceous shales within the Ecca and Dwyka Groups within the Karoo Supergroup, might offer longterm storage potential. The TOC content is reported to be as high as 14.7%³⁷ [37]. The diagenetic history of these formations indicates decreasing

http://carbcap.geos.ed.ac.uk/website/publications/sccs-wp/wp-2009-04.pdf

³⁴ Investigating the prospects for Carbon Capture and Storage technology in India. Rudra V. Kapila, School of Geosciences, University of Edinburgh. Hannah Chalmers and Matt Leach Centre for Environmental Strategy, University of Surrey.

³⁵ Technical Report on the Geological Storage of Carbon Dioxide in South Africa. Council for Geoscience South Africa, 2010. 9. Storage potential and estimated CO2 storage capacity of unmineable coal seams in the Karoo Basins. 9.4 Estimated CO2 storage capacity in the coal fields of South Africa.

³⁶ CCS Global. Prospects of Carbon Capture and Storage Technologies. (CCS) in Emerging Economies. Final Report to the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU). Part IV: Country Study *South Africa*. GIZ-PN 2009.9022.6 Wuppertal, 30 June 2012. Wuppertal Institute for Climate, Environment and Energy.

³⁷ Hydrochemical and Hydrogeological Impact of Hydraulic fracturing in the Karoo, South Africa. G. Steyl and G. J. van Tonder. Intech science publications. <u>http://www.intechopen.com/books/effective-and-sustainable-hydraulic-fracturing/hydrochemical-and-hydrogeological-impact-of-hydraulic-fracturing-in-the-karoo-south-africa.</u>



thermogenesis towards the north and west of the Karoo Basin where conditions would be more favourable for CO_2 storage in terms of permeability. A country-specific estimate of CO_2 storage in these lithologies suggests South Africa has a potential capacity of 52Gt by comparison with Australia which has 39Gt. Both countries have much lower estimated capacities by comparison with the United States (134Gt)³⁸ [38].

The widespread presence of dolerite intrusions could have both positive and negative effects for CO_2 storage. Contact thermal metamorphism has destroyed primary porosity and permeability, but these intrusions have also created secondary porosity by fracturing adjacent shale. One of the significant challenges posed by CO_2 storage in basalts is the ability to use seismic monitoring techniques to delineate between separate flows and between basalt and overlying sediments. The strong contrast in acoustic impedance between these two lithologies also makes accurate stratigraphic interpretation difficult. Other geophysical techniques such as Time Domain Electromagnetic (TDEM) surveys have been used effectively for groundwater prospecting but only to depths of 600m. TDEM and other techniques might be more effective for deeper surveys but more research is needed.

Monitoring CO_2 induced mineral reaction, and the related compositional change, will be difficult for the same reason. Techniques need to be developed so that the effectiveness of mineral trapping can be quantified. Some experimental work is now attempting to simulate in-situ reservoir conditions that occur after CO_2 injection. By measuring the changes in the elastic properties caused by fluid substitution, and chemical alteration, it may be possible to detect these effects using seismic monitoring³⁹ [39]. Despite the presence of basic (Ca, Mg, Fe rich) igneous intrusions (dolerite), and extruded basalt, no attempt has been made to quantify the South African CO_2 storage potential in these formations.

Intermediate and plutonic equivalents of basalt, dolerite and gabbro, are less suitable because they lack porosity and fine gain size. Intrusions like dolerite can also form barriers potentially limiting the size of suitable reservoirs. However, dolerite intrusions may also create secondary fracture porosity and related permeability. The direct association between fracture zones created by thermal stress induced by igneous intrusions and country rock, and permeability, has been observed at the base of the Palisades sill near New York City⁴⁰ [40]. Geophysical logging, and other tests, have clearly shown that transmissivity levels are significantly higher along the contact zone by comparison with the sediments below the sill. This phenomenon has been more recently investigated as part of the Norwegian Longyearbyen carbon storage test site evaluation. This experimental facility, located on the island of Svalbard, is characterised by low permeable (1-2 mD) sandstones that have been

³⁸ Potential implications of Gas Production from Shales and Coal for CO₂ Geological Storage. IEA/CON/11/199, August 2012

³⁹ CO2 Sequestration in Basalt: Carbonate Mineralization and Fluid Substitution.

http://earth.boisestate.edu/pal/files/2011/04/FinalSEG2011Basalts.pdf

⁴⁰ Contact zone permeability at intrusion boundaries:new results from hydraulic testing and geophysical logging in the Newark Rift Basin, New Hydrogeology Journal (2006) 14: 689–699York, USA. *USGS Staff -- Published Research*.Paper 354. http://digitalcommons.unl.edu/usgsstaffpub/354



intruded by dolerite. Its relevance to the Karoo basin is therefore highly relevant and discussed below.

The supply of water for drilling, and to provide a medium for hydraulic fracturing, could potentially restrict large-scale CO₂ injection. South Africa faces a growing demand for water estimated to be 17.7Bm³ by 2030, but supply may only reach 15Bm³ by that date. There are also competing demands for water as the country's economy expands particularly from agriculture, power generation and mining. Rainfall is highly seasonal and comparatively low (annual average 18" (45.7cms))⁴¹ [41]. Climate change may also exasperate the situation leading to an estimated supply gap of 3.8Bm^{3 42 [42]}. Estimates for water demand for drilling and hydraulic stimulation vary widely but could be as much as $11,000 - 14,560m^3$ in total for each well⁴³[43]. Within the state of Texas the estimated water demand for shale gas extraction could reach nearly 150Mm³ by 2020⁴⁴[44]. Although this example may not be directly transferable to South Africa it does illustrate the degree of water intensity that drilling and hydraulic stimulation requires. An initial appraisal of the environmental impacts of hydraulic fracturing for gas states that there is sufficient water within the Karoo Basin for this application. Water resources would need to be obtained from local ground water sources and carefully managed⁴⁵[45]. The presence of dolerite intrusions, and thermal springs, indicates upward migration and potential contamination without adequate well control.

4.2 Longyearbyen

The Norwegian CO₂ storage demonstration site of Longyearbyen, on the island of Svalbard, is highly relevant to conditions within the Karoo supergroup. The Longyearbyen site was selected to evaluate CO₂ storage within a formation with comparatively low matrix (intergranular) permeability but good complementary permeability created by fractures⁴⁶ [46]. The target reservoir is a marginal-marine sandstone succession of the Upper Triassic–Middle Jurassic Kapp Toscana Group which is overlain by thick Upper Jurassic shales and younger shale-rich formations. This sandstone has moderate porosities of 5 – 18%, but low permeability values (1 – 2 mD). Despite these properties water-injection tests have indicated good results (45 mD m⁴⁷ [47]) in the lower part of the reservoir formation

⁴¹ "South Africa's water conundrum" Global Post website accessed 3/07/13 http://www.globalpost.com/dispatch/south-africa/090710/south-africa-water-shortages

⁴² "Confronting South Africa's water challenge". McKinsey & Company Website accessed 3/07/13

http://www.mckinsey.com/insights/sustainability/confronting_south_africas_water_challenge

⁴³ Resource and Environmental Studies on the Marcellus Shale Presentation by Daniel J. Soeder, NETL. Geology and Environmental Science. Morgantown, WV, 2008

http://www.mde.state.md.us/programs/Land/mining/marcellus/Documents/Marcellus GeoEnv Soeder.pdf

⁴⁴ Environmental Science & Technology: Water Use for Shale-Gas Production in Texas, US Bureau of Economic Geology, Jackson School of Geosciences, University of Texas at Austin, March 2012

 ⁴⁵ Hydrochemical and Hydrogeological Impact of Hydraulic fracturing in the Karoo, South Africa. G. Steyl and G. J. van Tonder. Intech science publications. <u>http://www.intechopen.com/books/effective-and-sustainable-hydraulic-fracturing/hydrochemical-and-hydrogeological-impact-of-hydraulic-fracturing-in-the-karoo-south-africa.</u>
 ⁴⁶ The Longyearbyen CO2 Lab of Svalbard, Norway—initial assessment of the geological conditions for CO₂ sequestration. Norwegian

⁴⁰ The Longyearbyen CO2 Lab of Svalbard, Norway—initial assessment of the geological conditions for CO₂ sequestration. Norwegian Journal of Geology. Vol 92, pp. 353–376. Trondheim 2012, ISSN 029-196X.

⁴⁷ P026 European Association of Geoscientists & Engineers. Outcrop-based reservoir modeling of a naturally fractured siliciclastic CO2 sequestration site, Svalbard, Arctic Norway. K. Senger (University of Bergen / CIPR), K. Ogata* (University Centre in Svalbard), J. Tveranger (CIPR), A. Braathen (University Centre in Svalbard), S. Olaussen (University Centre in Svalbard). http://co2-ccs.unis.no/Pdf/A9 EAGE SES2.pdf.



between 870-970m. Matrix permeabilities measured from cores are generally < 1 mD providing strong evidence that fracture permeability far exceeds the matrix permeability within the reservoir sandstone. The comparatively good fluid flow observed is attributed to fractures created partly by thin dolerite sills and dykes and tectonic stress induced during the Cenozoic. The potential effects of reservoir pressurisation on fractures that extend into the caprock has to be established. A detailed investigation of the location's fracture orientation, and related stress regime, suggests reactivation may lead to enhanced lateral migration within the caprock. Low vertical connectivity suggests upward propagation and dilation is unlikely. There is also evidence of compartmentalization inferred from the presence of under pressurised sections which are vertically isolated⁴⁸ [48]. This suggests that there is potentially good caprock integrity; however, the site's suitability for CO₂ storage has yet to be established.

The longer-term storage capacity of a low permeability reservoir has been evaluated at Longyearbyen test site by modelling⁴⁹ [49]. Two different scenarios were applied: firstly assuming vertical injection; and secondly assuming injection from a horizontal well. In both simulations injection pressure was held below (20.2MPa) to avoid fracturing the reservoir. The models showed that injection from a vertical well led a bottom hole pressure of 20.2MPa relatively quickly leading to a restrained injection rate. In contrast injection from the horizontal well led to a slower pressure build up that took three years to reach the same level. Modelling shows that the most effective strategy to avoid exceeding fracture pressure is a gradual injection equivalent to a modest 17,500t per year. CO₂ injected at this rate would extend to 1 km from the well (assuming injection from a vertical well) over a timespan of 4,000 years. Half the CO_2 would be dissolved in the formation brine. These results suggest that low permeability severely constrains the rate of CO₂ that can be injected and the scale of potential point sources. In the case of Svalbard there is a point source annual emission of 85,000t CO₂ from a local coal fired power plant that a low permeability reservoir might be able to accept assuming sufficient capacity and well density. It should also be stressed that these models do not include the effect of formation fractures.

The role of dolerite intrusions is also influential. Although they have induced fracturing they could act as conduits as well as barriers to fluid flow. Fracture frequencies within these, and Karoo, dolerites range from $5 - 20 \text{ m}^{50}$ [50]. Modelling suggests fluid flow is also possible following initial pressure build up. The influence of the site's heterogeneity, and the presence of dolerite intrusions, will make monitoring and modelling CO₂ migration difficult. The geological complexity at this site also highlights the difficulty of accurately quantifying

⁴⁸ Geometries of igneous intrusions in inner Isfjorden, Svalbard: implications for fluid flow and CO2 storage. LASI 5 Conference, 29 – 30 Oct 2012. Kim Senger1,2,3, Srikumar Roy2,3, Jan Tveranger1, Kei Ogata2, Sverre Planke4, Karoline Bælum5, Simon Buckley1, Alvar Braathen2, Snorre Olaussen2, Rolf Mjelde3 and Riko Noormets2http://co2-ccs.unis.no/Pdf/Senger_etAl_B_LasiV_submitted.pdf

Experimental and Numerical Simulation of CO2 Injection Into Upper-Triassic Sandstones in Svalbard, Norway. R. Farokhpoor,
 O.Torsæter, T.Baghbanbashi, NTNU, A. Mørk, SINTEF, NTNU, E. Lindeberg, SINTEF. SPE 139524 SPE International Conference on CO2
 Capture, Storage, and Utilization held in New Orleans, Louisiana, USA, 10–12 November 2010. http://co2 ccs.unis.no/Publications/SPE%20International%20Conference%20on%20CO2-2010-SPE139524.pdf

⁵⁰ Fluid flow around igneous intrusions: from outcrop to simulator. LASI 5 Conference, 29 – 30 Oct 2012. <u>http://co2-</u>ccs.unis.no/Pdf/Senger_etAl_LasiV_submitted.pdf



storage capacity. Characterisation of this site highlights the importance of structural assessments, and the influence of the stress regime, on geomechanical stability.

The importance of fracture porosity and permeability for CO₂ storage has been effectively demonstrated at the Lacq-Rousse site in southern France. Although the reservoir is a depleted gas field it has an average matrix permeability of <1mD and an average porosity of 3%. The dolomite formation is heavily fractured leading to locally high porosities of between $15 - 20\%^{51}$ [51]. Fracture permeability is not reported. The reservoir's initial abnormally high pressure (66MPa) indicates that this is a closed reservoir⁵² [52]. This example demonstrates that reservoirs with very low matrix permeabilities can be good CO₂ storage sites provided the fracture pattern and distribution can be characterised.

4.3 **Indian Subcontinent**

The Indian subcontinent is another region where there are significant point source emissions, largely from coal fired power stations, with comparatively limited geological options for CO₂ storage. Most of the subcontinent is comprised of crystalline metamorphic rocks with virtually no permeability. There are deep saline aquifers around the periphery of the land mass which offer the best prospects for storage based on current technology (360Gt). Depleted oil and gas fields are thought to have much lower storage capacities of only 3-7 -4.6Gt. If CO₂ storage could be successfully achieved in basalt as much as 200Gt could be stored⁵³ [53]. The country's National Geophysical Research Institute is currently assessing the feasibility of a demonstration project within the Deccan Traps, a series of basalt lava flows that extent over 500,000km² of western India and are within reasonable proximity to 25% of the country's coal fired power stations⁵⁴ [54]. There are other sedimentary basins such as the Cambay Basin and Krishna Godavari basin some of which have mature, organic rich shales. There are also basins including the Upper Assam Basin and the Southern Indus Basin in Pakistan which have commercial oil and gas fields⁵⁵ [55]. None of these basins have been evaluated for CO₂ storage potential which limits the alternative options for India until CO₂ storage can be shown to be viable in basalt and organic rich shale.

4.4 **South Korea**

The challenge of CO₂ storage in an industrialised country such as South Korea are the limited number of onshore geological options. The Korean peninsula is largely comprised of crystalline metamorphic and plutonic igneous rocks which have extremely low

⁵¹ Steam-Drive Pilot in a Fractured Carbonated Reservoir: Lacq Superieur Field. Journal of Petroleum Technology, Volume 34, Number 4, April 1982. <u>http://www.onepetro.org/mslib/servlet/onepetropreview?id=00009453</u> ⁵² Lacq Gas Field, France. The AAPG/Datapages Combined Publications

Databasehttp://archives.datapages.com/data/specpubs/fieldst2/data/a009/a009/0001/0350/0370.htm

⁵³ Investigating the prospects for Carbon Capture and Storage technology in India. Rudra V. Kapila, School of Geosciences, University of Edinburgh. Hannah Chalmers and Matt Leach Centre for Environmental Strategy, University of Surrey http://carbcap.geos.ed.ac.uk/website/publications/sccs-wp/wp-2009-04.pdf

⁵⁴ Planning of a CO2 Geological Sequestration Pilot Project in Basalt Formations of North Western India. Presentation - Balesh Kumar, National Geophysical Research Institute, Hyderabad, India K. Prasad Saripalli, Pacific Northwest National Laboratory; Richland, WA

⁵⁵ World Shale Gas Resources: An Initial Assessment of 14 Regions Outside the United States. April 2011, US Energy Information Administration (EIA). XII India/Pakistan



permeabilities. There are some onshore sedimentary basins including the Gyeongsang, Taebaeksan and the Pohang where potential storage sites are under investigation⁵⁶ [56]. The Gyeongsang is the largest basin and occupies the south east of the country. It is comprised of alluvial fan, fluvial and lacustrine successions interspersed with volcanic and volcaniclastic sediments of Cretaceous age. A combination of deep burial, tectonic activity, and subsequent low grade thermal metamorphism induced by granitic intrusions, has reduced permeability⁵⁷ [57]. Despite these conditions the Korea Institute of Geoscience and Mineral Resources (KIGAM) has conducted geophysical surveys and identified a series of sites in this basin for pilot-scale injection. Initial research suggests that there may be between 535 and 1,011Mt CO₂ storage capacity within sandstones of the Sindong Group within the basin⁵⁸ [58]. The Miocene Pohang Basin will also be investigated. The location for a storage site should be confirmed by mid 2015 according to the Korean National Roadmap for CCS⁵⁹ [59]. The country's longer term aim is to evaluate and develop deep saline aquifers in three offshore basins of which Ulleung is currently regarded as the most promising⁶⁰ [60]. It is possible that this basin has a potential storage capacity of 5,100Mt⁶¹ [61].

5 Conclusions

Locating suitable sites for CO₂ sequestration in low porosity / permeability formations presents a series of challenges:

- The identification and evaluation of suitable sites for CO₂ storage will need to be detailed and focused on sites with potentially limited capacity by comparison with depleted oil and gas reservoirs and deep saline aquifers.
- Detailed site characterisation could be challenging and expensive to ensure accurate quantification of capacity and compliance requirements by regulators.
- To store large quantities of CO₂ several different sites may need to be identified in one area.
- The economic viability of formations with low porosity / permeability properties, or restricted lateral homogeneity, needs to be determined. Research suggests that in comparison with sites that have good characteristics (high porosity / permeability) low porosity / permeability conditions require a higher well concentration and

⁵⁶ Site survey for pilot-scale CO₂ geological storage in the Korean Peninsula. Presentation by In Gul Hwang of KIGAM, 2012.

⁵⁷ Late Cretaceous volcanic rocks and associated granites in Gyeongsang Basin, SE Korea: Their chronological ages and tectonic

implications for cratonic destruction of the North China Craton. Journal of Asian Earth Sciences. Volume 47, 30 March 2012, Pages 252–264 http://www.sciencedirect.com/science/article/pii/S1367912011005074

⁵⁸ Preliminary evaluation of geological storage capacity of carbon dioxide in sandstones of the Sinddong Group, Gyeongsang Basin (Cretaceous). Journal of the Geological Society of Korea. V. 45, no 5, p 463-472, 2009.

⁵⁹ Current status of CCS in Korea. Presentation by Prof. Chonghun Han, Seoul National University, Chairman of KCCSA (Korean Carbon Capture and Storage Association), 30th January 2013

⁶⁰ A Preliminary Evaluation on CO2 Storage Capacity of the Southwestern Part of Ulleung Basin, Offshore, East Sea. Yulee Kim1, Keumsuk Lee2, Sohyun Jo1, Minjun Kim1, Jong-Soo Kim1 and Myong-ho Park. Econ. Environ. Geol., 45(1), 41-48, 2012.

http://koreascience.or.kr/search/articlepdf_ocean.jsp?url=http://ocean.kisti.re.kr/downfile/volume/kseeg/JOHGB2/2012/v45n1/JOHGB2 2012_v45n1_41.pdf

⁶¹ A Preliminary Evaluation on CO2 Storage Capacity of the Southwestern Part of Ulleung Basin, Offshore, East Sea. Econ. Environ. Geol., 45(1), 41-48, 2012



injection pressure leading to disproportionately higher development costs. This deduction needs to be treated with some caution because it is based on one study which assumed a permeability differential of an order of magnitude.

- Geophysical techniques will need to be tested or developed to improve resolution beneath sills. Without adequate interpretation it will not be possible to accurately delineate site characteristics.
- There is some experimental evidence that suggests clay minerals, and especially kerogen within organic rich shale formations, could adsorb injected CO₂. The retention capacity of organic rich shales depends on thermal maturity as well as the kerogen type. A major limitation of this lithology is its low permeability. CO₂ injection would require high pressure injection, fracturing and low rates that might be impracticable.
- The use of CO₂ for ECBM is potentially viable but more research, including field test evaluation, is necessary to monitor and quantify CO₂ retention in coal seams. The relatively rapid adsorption of CO₂ induces swelling in coal adjacent to injection points causing reservoir pressures to increase. Pressure drops can then occur as CO₂ displaces CH₄. The rate of this transition is likely to restrict the rate of CO₂ injection. The effects of free hydrocarbon mobilisation, caused by injection of supercritical CO₂ at field scale, also need to be understood.
- Extruded basalt is another low permeable lithology which has the potential for CO₂ storage. Its ferro-magnesium mineral composition reacts to form carbonate minerals causing effective mineral trapping.
- There is only limited experimental data on CO₂ diffusion and adsorption in low permeability lithologies. Initial conclusions suggest CO₂ could slowly diffuse through argillaceous caprocks over periods of thousands of years.
- The most promising reservoirs with low matrix permeability have significant fracture zones which do not compromise the caprock. Dolerite intrusions can induce fracture propagation but need to be differentiated to delineate a fracture dominated reservoir.
- The technical and economic constraints of formations with low matrix permeability may preclude them from CO₂ storage. Depleted oil and gas fields, and deep saline aquifers, may still be the only viable options especially for countries like South Africa and India which have limited, or unproven, geological conditions in close proximity to large point sources of carbon. Thorough research is needed to determine whether onshore and unproven reservoirs are technically and economically viable by comparison with offshore deep saline aquifers and depleted oil and gas reservoirs. Geological conditions in some countries, for example South Korea, suggest limited onshore CO₂ storage but much larger potential capacity offshore either in depleted oil and gas fields or saline aquifers.

Preliminary evidence suggests there would be an economic penalty if CO_2 was stored in low permeable formations by comparison with conventional depleted oil and gas fields or deep saline aquifers. There is evidence that CO_2 could be retained by adsorption within organic



rich lithologies such as coal and organic rich shale. The degree of retention depends on organic content, kerogen type, maturity and permeability. The estimated potential capacity varies by as much as an order of magnitude in the Huron Shale from the Appalachian Basin for example. There are a number of uncertainties that need to be resolved including high pressure injection. The most promising storage potential is likely to come from fracture permeability induced by igneous intrusions. Country-specific reviews suggest that South Africa and India have some low permeability storage potential, but South Korea would only have limited onshore capacity with much greater potential for offshore storage.



6 References

- 1. Int. J. Greenhouse Gas Cont., 2 (2008) 297-308.
- 2. CO₂ Storage in Low Permeability Formations. Y. Cinar, O. Bukhteeva, P. R. Neal, W. G. Allinson, and L. Paterson. Paper presented at 2008 SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA 19-23 April 2008. SPE 114028
- 3. Evaluating sealing efficiency of caprocks for CO2 storage: an overview of the Geocarbone Integrity program and results. M. Fleury1(*), J. Pironon2, Y.M. Le Nindre3, O. Bildstein4, P. Berne5, V. Lagneau6, D. Broseta7, T. Pichery8, S. Fillacier9, M. Lescanne10, O. Vidal11. Oil & Gas Science and Technology – rev. IFP, Vol. xx (2009), No X, pp. 00-00. http://hal.archivesouvertes.fr/docs/00/58/36/19/PDF/2010 Fleury GHGT10.pdf
- 4. Int. J. Greenhouse Gas Cont., 2 (2008) 297-308. http://www.sciencedirect.com/science/article/pii/S1750583608000273
- 5. A method for quick assessment of CO2 storage capacity in closed and semi-closed saline formations. Quanlin Zhou *, Jens T. Birkholzer, Chin-Fu Tsang, Jonny Rutqvist. Earth Sciences Division, Lawrence Berkeley National Laboratory, University of California. http://esd.lbl.gov/files/about/staff/quanlinzhou/Paper14 PDF.pdf
- 6. Int. J. Greenhouse Gas Cont., 2 (2008) 297-308. http://www.sciencedirect.com/science/article/pii/S1750583608000273
- 7. Int. J. Greenhouse Gas Cont., 2 (2008) 297-308. http://www.sciencedirect.com/science/article/pii/S1750583608000273
- 8. Factors affecting the permeability of gas shales. A thesis submitted in partial fulfillment of The requirements for the degree of Master of science By Venkat survanarayana murthy pathi. In the faculty of graduate studies (geological science), The university of British Columbia, (Vancouver). October, 2008. https://circle.ubc.ca/bitstream/handle/2429/5302/ubc 2008 fall pathi venkat survanaray ana murthy.pdf?sequence=1
- 9. Investigating the prospects for Carbon Capture and Storage technology in India. Rudra V. Kapila, School of Geosciences, University of Edinburgh. Hannah Chalmers and Matt Leach Centre for Environmental Strategy, University of Surrey. Implications of Gas Production from Shales and Coal for CO₂ Geological Storage. IEA/CON/11/199, August 2012. http://carbcap.geos.ed.ac.uk/website/publications/sccs-wp/wp-2009-04.pdf
- 10. CO2 storage potential of South African coals and gas entrapment enhancement due to igneous intrusions. International Journal of Coal GeologyVolume 73, Issue 1, 7 January 2008, Pages 74-87.

http://www.sciencedirect.com/science/article/pii/S0166516207000857



- Influences of igneous intrusions on coal rank, coal quality and adsorption capacity in Hongyang, Handan and Huaibei coalfields, North China. International Journal of Coal Geology 88 (2011) 135–146
- 12. A Geochemical Investigation into the Effect of Coal Rank on the Potential Environmental Impacts of CO2 Sequestration in Deep Coal Beds ," in Rubin, E.S., Keith, D.W., Gilboy, C.F., Wilson, M., Morris T., Gale, J. and Thambimuthu, K., eds., *Greenhouse Gas Control Technologies 7*, Elsevier Science Ltd, Oxford, 2005. <u>http://seca.doe.gov/publications/proceedings/04/carbon-seq/089.pdf</u>
- 13. Carbon Dioxide Storage Capacity of Barnett Shale. A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the Degree of Master of Science by Seung Mo Kang Norman, Oklahoma, 2011. http://mpge.ou.edu/research/documents/2011%20thesis/Seung%20Mo%20Kang.pdf
- 14. New Evaluation Techniques for Gas Shale Reservoirs. Reservoir Symposium 2004 Schlumberger. http://www.sipeshouston.com/presentations/pickens%20shale%20gas.pdf
- 15. Rock Matrix as Reservoir: mineralogy & diagensis. Hans-Martin Schulz & Brian Horsfield. DeutschesGeoForschungsZentrumGFZ, Potsdam Presentation on March 1, 2010, AEON, University of Cape Town, Rondebosch 7701, South Africa. http://www.gfzpotsdam.de/portal/gfz/Struktur/Departments/Department+4/sec43/Breaking+news/Capeto wn-workshoppresentations/GASHsa+Rock_matrix;jsessionid=ED1EEF5204118133B554AB1A7C5D0 656?binary=true&status=300&language=en
- 16. Rock Matrix as Reservoir: mineralogy & diagensis. Hans-Martin Schulz & Brian Horsfield. DeutschesGeoForschungsZentrumGFZ, Potsdam Presentation on March 1, 2010, AEON, University of Cape Town, Rondebosch 7701, South Africa. http://www.gfzpotsdam.de/portal/gfz/Struktur/Departments/Department+4/sec43/Breaking+news/Capeto wn-workshoppresentations/GASHsa+Rock_matrix;jsessionid=ED1EEF5204118133B554AB1A7C5D0 656?binary=true&status=300&language=en
- From Oil-Prone Source Rock to Gas-Producing Shale Reservoir Geologic. and Petrophysical Characterization of Unconventional Shale-Gas Reservoirs. SPE 131350.
 Q. R. Passey, K. M. Bohacs, W. L. Esch, R. Klimentidis, and S. Sinha, ExxonMobil Upstream Research Co. Copyright 2010, Society of Petroleum Engineers. Paper presented at the CPS/SPE International Oil & Gas Conference and Exhibition in China held in Beijing, China, 8–10 June 2010. http://www.fossilfuel.co.za/articles/2012/SPE-131350-FINAL-Low_Passey-et-al_.pdf
- From Oil-Prone Source Rock to Gas-Producing Shale Reservoir Geologic. and Petrophysical Characterization of Unconventional Shale-Gas Reservoirs. SPE 131350.
 Q. R. Passey, K. M. Bohacs, W. L. Esch, R. Klimentidis, and S. Sinha, ExxonMobil Upstream Research Co. Copyright 2010, Society of Petroleum Engineers. Paper presented at the CPS/SPE International Oil & Gas Conference and Exhibition in China



held in Beijing, China, 8–10 June 2010. <u>http://www.fossilfuel.co.za/articles/2012/SPE-131350-FINAL-Low_Passey-et-al_.pdf</u>. (courtesy FEI Company).

- From Oil-Prone Source Rock to Gas-Producing Shale Reservoir Geologic. and Petrophysical Characterization of Unconventional Shale-Gas Reservoirs. SPE 131350.
 Q. R. Passey, K. M. Bohacs, W. L. Esch, R. Klimentidis, and S. Sinha, ExxonMobil Upstream Research Co. Copyright 2010, Society of Petroleum Engineers. Paper presented at the CPS/SPE International Oil & Gas Conference and Exhibition in China held in Beijing, China, 8–10 June 2010. <u>http://www.fossilfuel.co.za/articles/2012/SPE-131350-FINAL-Low_Passey-et-al_.pdf</u>.
- 20. Porosity and permeability of Eastern Devonian Gas Shale. (courtesy Mark Knackstedt and Trondt Varslot, ANU). Danial J Soeder, SPE Formation Evaluation, March 1988, Inst. Of Gas Technology. http://www.pe.tamu.edu/wattenbarger/public_html/selected_papers/-shale%20gas/spe15213.pdf
- 21. Geophysical Research Abstracts. Vol. 15, EGU2013-1058-1, 2013. EGU General Assembly 2013. © Author(s) 2012. CC Attribution 3.0 License. Lithological controls on matrix permeability of organic-rich shales: An experimental study http://meetingorganizer.copernicus.org/EGU2013/EGU2013-1058-1.pdf
- 22. Energy Minerals Division website viewed on 8/07/13. A Division of the American Association of Petroleum Geologists. http://emd.aapg.org/technical_areas/gas_shales/index.cfm
- 23. Potential implications of Gas Production from Shales and Coal for CO₂ Geological Storage. IEA/CON/11/199, August 2012
- 24. Analysis of Devonian Black Shales in Kentucky for potential Carbon Dioxide sequestration and enhanced natural gas production. http://www.uky.edu/KGS/emsweb/devsh/final_report.pdf
- 25. The onset of oil generation is equivalent on an arbitrary vitrinite reflectance of 0.55%.
 Oil generation extends to 1.1%. The gas generation window is typically between 1.0 1.3% and extends up to 3%.
- 26. MRCSP Phase II Reassessment of CO2 Sequestration Capacity and Enhanced Gas Recovery Potential of Middle and Upper Devonian Black Shales in the Appalachian Basin. MRCSP Phase II Topical Report, October 2005–October 2010. Brandon C. Nuttal, Kentucky Geological Survey, Lexington, Kentucky. Midwestern Regional Carbon Sequestration Partnership (MRCSP). DOE Cooperative Agreement No. DE-FC26-05NT42589. OCDO Grant Agreement No. DC-05-13. http://addap.tk/userdata/phase_II_reports/topical_4_black_shale.pdf
- IEA Greenhouse Gas R&D Programme 42nd Executive Committee meeting. Potential implications of gas production from shales and coal for CO₂ geological storage. GHG/12/47.



- 28. China Australia Geological Storage of CO2 (CAGS) website accessed on 10/07/13. Possibility and Potential of CO₂ Enhanced Shale Gas Recovery in the Ordos Basin. http://www.cagsinfo.net/research project 2.htm
- 29. Tight sandstone gas reservoirs (exploration) in upper Palaeozoic of Ordos basin. YANG Hua FU JinHua WEI XinShan REN JunFeng. (PetroChina Changqing Oilfield Company, Xi'an, 710018, China
- 30. World Shale Gas Resources: An Initial Assessment of 14 Regions Outside the United States. April 2011, US Energy Information Administration (EIA). XI China
- 31. Technical Report on the Geological Storage of Carbon Dioxide in South Africa. Council for Geoscience South Africa, 2010.
- Svensen, H., et al., "Hydrothermal Venting of Greenhouse Gases Triggering Early Jurassic Global Warming", Elsevier, Earth and Planetary Science Letters 256 (2007) 554-566
- 33. Technical Report on the Geological Storage of Carbon Dioxide in South Africa. Council for Geoscience South Africa, 2010
- 34. Investigating the prospects for Carbon Capture and Storage technology in India. Rudra V. Kapila, School of Geosciences, University of Edinburgh. Hannah Chalmers and Matt Leach Centre for Environmental Strategy, University of Surrey. <u>http://carbcap.geos.ed.ac.uk/website/publications/sccs-wp/wp-2009-04.pdf</u>
- 35. Technical Report on the Geological Storage of Carbon Dioxide in South Africa. Council for Geoscience South Africa, 2010. 9. Storage potential and estimated CO2 storage capacity of unmineable coal seams in the Karoo Basins. 9.4 Estimated CO2 storage capacity in the coal fields of South Africa.
- 36. CCS Global. Prospects of Carbon Capture and Storage Technologies. (CCS) in Emerging Economies. Final Report to the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU). Part IV: Country Study South Africa. GIZ-PN 2009.9022.6 Wuppertal, 30 June 2012. Wuppertal Institute for Climate, Environment and Energy.
- 37. Hydrochemical and Hydrogeological Impact of Hydraulic fracturing in the Karoo, South Africa. G. Steyl and G. J. van Tonder. Intech science publications. <u>http://www.intechopen.com/books/effective-and-sustainable-hydraulic-fracturing/hydrochemical-and-hydrogeological-impact-of-hydraulic-fracturing-in-the-karoo-south-africa.</u>
- Potential implications of Gas Production from Shales and Coal for CO₂ Geological Storage. IEA/CON/11/199, August 2012



- 39. CO2 Sequestration in Basalt: Carbonate Mineralization and Fluid Substitution. http://earth.boisestate.edu/pal/files/2011/04/FinalSEG2011Basalts.pdf
- 40. Contact zone permeability at intrusion boundaries:new results from hydraulic testing and geophysical logging in the Newark Rift Basin, New Hydrogeology Journal (2006) 14: 689–699York, USA. USGS Staff -- Published Research.Paper 354. http://digitalcommons.unl.edu/usgsstaffpub/354
- 41. "South Africa's water conundrum" Global Post website accessed 3/07/13 http://www.globalpost.com/dispatch/south-africa/090710/south-africa-water-shortages
- 42. "Confronting South Africa's water challenge". McKinsey & Company Website accessed 3/07/13 http://www.mckinsey.com/insights/sustainability/confronting_south_africas_water_challe nge
- 43. Resource and Environmental Studies on the Marcellus Shale Presentation by Daniel J. Soeder, NETL. Geology and Environmental Science. Morgantown, WV, 2008. <u>http://www.mde.state.md.us/programs/Land/mining/marcellus/Documents/Marcellus_GeoEnv_Soeder.pdf</u>
- 44. Environmental Science & Technology: Water Use for Shale-Gas Production in Texas, US Bureau of Economic Geology, Jackson School of Geosciences, University of Texas at Austin, March 2012
- 45. Hydrochemical and Hydrogeological Impact of Hydraulic fracturing in the Karoo, South Africa. G. Steyl and G. J. van Tonder. Intech science publications. <u>http://www.intechopen.com/books/effective-and-sustainable-hydraulic-fracturing/hydrochemical-and-hydrogeological-impact-of-hydraulic-fracturing-in-the-karoo-south-africa.</u>
- 46. The Longyearbyen CO2 Lab of Svalbard, Norway—initial assessment of the geological conditions for CO₂ sequestration. Norwegian Journal of Geology. Vol 92, pp. 353–376. Trondheim 2012, ISSN 029-196X.
- 47. P026 European Association of Geoscientists & Engineers. Outcrop-based reservoir modeling of a naturally fractured siliciclastic CO2 sequestration site, Svalbard, Arctic Norway. K. Senger (University of Bergen / CIPR), K. Ogata* (University Centre in Svalbard), J. Tveranger (CIPR), A. Braathen (University Centre in Svalbard), S. Olaussen (University Centre in Svalbard). http://co2ccs.unis.no/Pdf/A9_EAGE_SES2.pdf
- 48. Geometries of igneous intrusions in inner Isfjorden, Svalbard: implications for fluid flow and CO2 storage. LASI 5 Conference, 29 – 30 Oct 2012. Kim Senger1,2,3, Srikumar Roy2,3, Jan Tveranger1, Kei Ogata2, Sverre Planke4, Karoline Bælum5, Simon Buckley1, Alvar Braathen2, Snorre Olaussen2, Rolf Mjelde3 and Riko Noormets2http://co2-ccs.unis.no/Pdf/Senger_etA1_B_LasiV_submitted.pdf
- 49. Experimental and Numerical Simulation of CO2 Injection Into Upper-Triassic Sandstones in Svalbard, Norway. R. Farokhpoor, O.Torsæter, T.Baghbanbashi, NTNU, A. Mørk,



SINTEF, NTNU, E. Lindeberg, SINTEF. SPE 139524 SPE International Conference on CO2 Capture, Storage, and Utilization held in New Orleans, Louisiana, USA, 10–12 November 2010. http://co2-ccs.unis.no/Publications/SPE%20International%20Conference%20on%20CO2-2010-SPE139524.pdf

- 50. Fluid flow around igneous intrusions: from outcrop to simulator. LASI 5 Conference, 29 30 Oct 2012. http://co2-ccs.unis.no/Pdf/Senger_etAl_LasiV_submitted.pdf
- 51. Steam-Drive Pilot in a Fractured Carbonated Reservoir: Lacq Superieur Field. Journal of Petroleum Technology, Volume 34, Number 4, April 1982. <u>http://www.onepetro.org/mslib/servlet/onepetropreview?id=00009453</u>
- 52. Lacq Gas Field, France. The AAPG/Datapages Combined Publications Database<u>http://archives.datapages.com/data/specpubs/fieldst2/data/a009/a009/0001/0350/0370.htm</u>
- 53. Investigating the prospects for Carbon Capture and Storage technology in India. Rudra V. Kapila, School of Geosciences, University of Edinburgh. Hannah Chalmers and Matt Leach Centre for Environmental Strategy, University of Surrey. <u>http://carbcap.geos.ed.ac.uk/website/publications/sccs-wp/wp-2009-04.pdf</u>
- 54. Planning of a CO2 Geological Sequestration Pilot Project in Basalt Formations of North Western India. Presentation - Balesh Kumar, National Geophysical Research Institute, Hyderabad, India K. Prasad Saripalli, Pacific Northwest National Laboratory; Richland, WA
- 55. World Shale Gas Resources: An Initial Assessment of 14 Regions Outside the United States. April 2011, US Energy Information Administration (EIA). XII India/Pakistan
- 56. Site survey for pilot-scale CO₂ geological storage in the Korean Peninsula. Presentation by In Gul Hwang of KIGAM, 2012.
- 57. Late Cretaceous volcanic rocks and associated granites in Gyeongsang Basin, SE Korea: Their chronological ages and tectonic implications for cratonic destruction of the North China Craton. Journal of Asian Earth Sciences. Volume 47, 30 March 2012, Pages 252– 264 <u>http://www.sciencedirect.com/science/article/pii/S1367912011005074</u>.
- 58. Preliminary evaluation of geological storage capacity of carbon dioxide in sandstones of the Sinddong Group, Gyeongsang Basin (Cretaceous). Journal of the Geological Society of Korea. V. 45, no 5, p 463-472, 2009.
- 59. Current status of CCS in Korea. Presentation by Prof. Chonghun Han, Seoul National University, Chairman of KCCSA (Korean Carbon Capture and Storage Association), 30th January 2013
- 60. A Preliminary Evaluation on CO2 Storage Capacity of the Southwestern Part of Ulleung Basin, Offshore, East Sea. Yulee Kim1, Keumsuk Lee2, Sohyun Jo1, Minjun Kim1, Jong-Soo Kim1 and Myong-ho Park. Econ. Environ. Geol., 45(1), 41-48, 2012.



http://koreascience.or.kr/search/articlepdf_ocean.jsp?url=http://ocean.kisti.re.kr/downfile/ volume/kseeg/JOHGB2/2012/v45n1/JOHGB2_2012_v45n1_41.pdf

61. A Preliminary Evaluation on CO2 Storage Capacity of the Southwestern Part of Ulleung Basin, Offshore, East Sea. Econ. Environ. Geol., 45(1), 41-48, 2012