The importance of confining strata integrity in mining, coal seam gas extraction and geological storage of industrial waste (CO_2 and nuclear): towards early detection indicators of potential groundwater contamination

S. Bouzalakos and W.A. Timms
National Centre for Groundwater Research and Training (NCGRT), Australia
Australian Centre for Sustainable Mining Practices (ACSMP), School of Mining Engineering, University of New South Wales, Sydney NSW 2052, Australia

ABSTRACT

Mining, coal seam gas extraction and geological storage of industrial waste all pose a potential risk of groundwater contamination. In many cases, geological confining strata (also known as aquitards, cap rock seals etc.) overlying or underlying these activities are the last resort of protection against groundwater contamination. Understanding the low permeability nature of confining strata is critical in assessing their integrity against long-term (centuries to millennia) migration and displacement of contaminants in fresh groundwater resources. Early detection indicators, such as dissolved gases (e.g., CH_4, CO_2), stable isotope tracers (e.g., $\delta^{18}O$, δD) and cations (e.g., Na^+, K^+), can be used to assess the importance of an initial appearance of a pollutant and allow for sustainable management steps to be taken to mitigate further contamination. An overview of factors governing contaminant transport through confining strata is provided for the aforementioned industrial activities, along with examples of leading practices and innovative physicochemical and hydromechanical methods of assessing the integrity of confining strata.

1. INTRODUCTION

The Earth's subsurface is in demand from new and potential developments such as mining for mineral and energy resources, coal seam gas (CSG) extraction, and deep geological storage of greenhouse gases (GHG) (e.g., carbon dioxide, CO_2) and nuclear waste.

Meeting the ever increasing energy and minerals demand while reducing GHG emissions will require a combination of exploitation of new energy resources or implementation of schemes that capture and store GHG emissions (e.g., CO_2 geological storage) (Ferguson, 2013). While coal remains the main source of energy for the largest economies around the world, it is likely that nuclear power will be required in the energy mix to ensure security of energy supply in the near future (IEA, 2011).

Although CSG and nuclear waste storage repositories could have the potential to avoid a significant amount of GHG emissions from burning coal, there is significant overlap between the geological environments that host these operations (Elliot and Celia, 2012).

Low permeability clay-rich sediments and rocks can form natural hydraulic barriers known as aquitards in sedimentary sequences. Aquitards often overlie aquifers that yield strategically important fresh water resources, and form important cap rocks or seals between shallow aquifers and deeper strata that are targeted for depressurization during CSG or mineral extraction (Timms et al., 2012).

Naturally occurring aquitards are also common and play a critical role in deep geological storage of CO_2 and nuclear waste, having the potential to limit impacts of contaminant transport (e.g., solutes).

Argillaceous materials can form effective aquitards provided that there is no loss of hydraulic integrity due to faults or geological structures, and where they are resistant to stress fractures from drilling or subsidence. Assessing the hydraulic characteristics and integrity of confining geological units is therefore critical to mitigate possible impacts of mining, CSG extraction and deep geological storage of CO_2 and nuclear waste on overlying fresh groundwater resources.

Possible contaminants can be effectively contained by an aquitard where solute fluxes are controlled by chemical gradients (diffusive transport), and less controlled by flow (advective transport), and geochemical reactions act to degrade or isolate salts, trace metal or organic constituents (Timms et al., 2012).

The objective of this paper is to discuss the importance of confining strata in new and prospective mineral/energy developments with regard to potential groundwater contamination. Emphasis is placed on hydraulic characteristics, particularly vertical hydraulic conductivity (K_v) and contaminant transport as a means of introducing the notion of early detection indicators. Examples of innovative methods, along with datasets of K_v values for argillaceous aquitards, are given as an example of leading practices for assessing the integrity of confining strata.

2. HYDRAULIC CHARACTERISTICS OF CONFINING STRATA IN EXTRACTIVE AND STORAGE OPERATIONS

Extractive (mining, CSG) and storage (CO_2, nuclear waste) operations exploit a wide range of depths within the Earth's crust (Fig. 1). While the optimal depths for each development differ, there is considerable overlap and the same confining units could have multiple possible uses. In other cases, use of one geological unit will rely on the integrity of the overlying units and an adequate assessment of their hydraulic integrity would be expected.

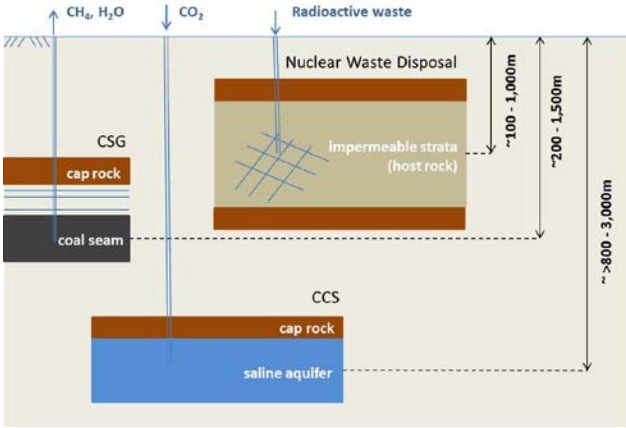

Figure 1: Illustrative examples of deep geological disposal of industrial waste (CO_2 and nuclear) and utilisation of energy resources (CSG).

K_v values are not readily available (from field and/or laboratory investigations) for cap rocks resulting in a lack of detailed understanding of their hydraulic integrity, mainly due to the practicalities of measurements in such low permeability materials. Low permeability material is commonly defined as $K_v < 10^{-8}$ m/s, although K_v as low as 10^{-14} m/s has been recorded for shale at greater depths (Neuzil, 1994). Figure 2 gives an illustrative representation of K_v versus depth footprints, further stressing the competition for tight confining strata at greater depths.

2.1 Mining and Coal Seam Gas Extraction

Mining methods and CSG extraction are distinctly different industrial operations; however, there are strong synergies concerning risk of groundwater pollution via vertical seepage (hydraulic connection or disconnection) of low permeability confining strata with overlying more permeable aquifers.

The volume of groundwater flow to underground mine works, and similarly during CSG production, can have implications for safe and efficient extraction and for potential impacts on

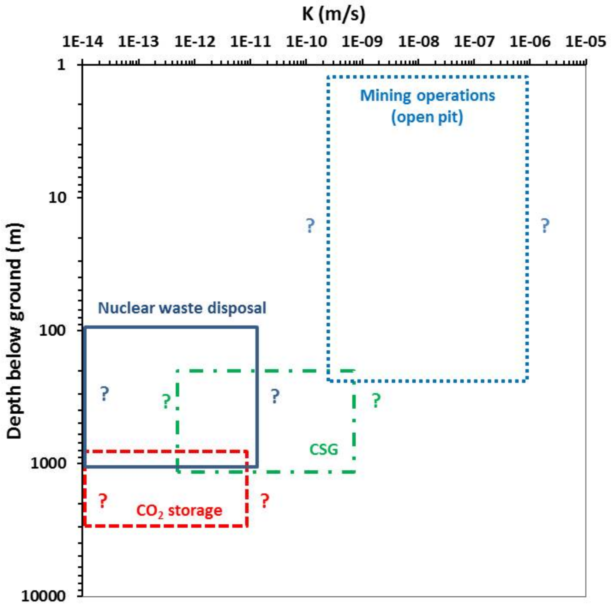

Figure 2: Illustrative examples of typical hydraulic conductivity (K) values vs. depth footprints of deep geological disposal of industrial waste (CO_2 and nuclear) and extraction of mineral (mining, hard rock) and energy resources (CSG and mining, coal).

shallow aquifers, or nearby rivers, lakes and wetlands. For example, tunneling and coal mining beneath large water bodies with negligible inflows is practiced where geological conditions are favourable (Timms et al., 2012).

The Queensland Water Commission (QWC), Australia, has recently released a report on groundwater quality impacts of CSG extraction in the Surat Basin, expressing a lack of K_v data for aquitards which is required to improve numerical models predicting long-term depressurization and dewatering impacts (QWC, 2012). Nevertheless, scarce K_v data have been estimated to vary from ~ 10^{-12} – 10^{-9} m/s from field test investigations of lateral conductivity (K_h).

2.2 Geological Storage of Industrial Waste

2.2.1 CO_2 Sequestration

In contrast to depressurization required for CSG development, injecting pressurized CO_2 in deep geological formations to permanently store GHG emissions could also put overlying groundwater resources at risk.

Geological storage of CO_2 in deep saline aquifers is currently regarded as the most technologically favourable option to minimize GHG emissions (e.g., IPCC, 2005). Approximately 1 Mt/yr of CO_2 are being injected at Sleipner in the North Sea since the mid-1990s and, similarly, at In Salah in Algeria since the mid-2000s. Further, there is extensive relevant experience to be gained from the petroleum industry (e.g., enhanced oil recovery, EOR). Much could also be learnt from the radioactive waste disposal experience (e.g., employing system-level models and the need to make maximum use of geological information).

The requirements for effective geological storage are: i) repository at >800 m depth (CO_2 in supercritical phase); ii) adequate porosity and thickness (i.e., storage capacity) and permeability (i.e., injectivity); iii) a satisfactory sealing cap rock (e.g., thick, low permeability, non-fractured); and iv) stable geological environment to avoid compromising the integrity of the storage site (Solomon et al., 2008).

Studies on hydraulic integrity (i.e., permeability and capillary threshold) of cap rocks have largely considered petroleum systems techniques, and report results in petroleum industry terminology (e.g., absolute and effective permeability expressed in microdarcy, μD, or m^2). Much focus is given to assessing CO_2 storage aquifers (easier, more permeable matrix) and cap rock sealing integrity at the reservoir-seal boundary (capillary threshold). Recent studies on cap rock sealing properties (e.g., Bachaud et al., 2011; Fleury et al., 2011) show effective permeability (k_{eff}) in the microdary range ~ 10^{-19} – 10^{-18} m^2 (K_v roughly estimated at ~ 10^{-14} – 10^{-13} m/s).

2.2.2 Nuclear Waste Confinement

In many countries (e.g., Belgium, Germany, France, Japan, Switzerland and the UK) deep argillaceous formations are considered as candidate host rock for radioactive waste disposal. In other nuclear developed countries (e.g., Sweden, Finland and Canada) looking more toward granitic host rocks, clay-based materials (primarily bentonite) are proposed for use in the engineered barriers of deep geological repository (Delage et al., 2010). Australia, which has yet to develop into a nuclear power producer, has significant potential to store unwanted radioactive material in deep geological repositories (e.g., South Australian and Western Australian deserts).

Two main hydraulic properties typical of argillaceous host rocks, also referred to as mined repositories, make them interesting for nuclear waste disposal: i) a very low permeability resulting in very slow groundwater flow, or diffusive-dominated transport, through water-saturated medium, and ii) a good ability to retain radionuclides by physico-chemical adsorption on clay minerals (Bachu and McEwen, 2011; Delage et al., 2010).

Studies have reported K_v values in the Callovo-Oxfordian shale in the order of 5×10^{-14} – 5×10^{-13} m/s at depths of 422-552 m (Vinsot et al., 2011). Delage et al. (2010) include K_v values for European host clays: Opalinus (Switzerland), $(1\text{-}5)\times10^{-13}$ m/s; Callovo-Oxfordian (France), $(1\text{-}5)\times10^{-13}$ m/s; and Boom (Belgium), $(2\text{-}3)\times10^{-12}$ m/s. Similarly low K values are reported for engineered bentonite-sand barriers (e.g., 10^{-13} – 10^{-11} m/s) to limit advection transfer and to favour diffusion of radionuclides, in addition to providing high thermal conductance to enhance diffusion of heat generated by waste-containing canisters.

3. CONTAMINANT TRANSPORT AND EARLY DETECTION INDICATORS

Groundwater can show early signs of contamination from various subsurface operations when pollutant (e.g., solutes) concentrations start to fluctuate and exceed baseline values of ambient fresh groundwater. Chemical tracers can also be used in conjunction with pollutant monitoring as early detection indicators. Attention to early groundwater contamination detection indicators can prove an important contribution to the prevention of adverse environmental/hydrologic changes and to the sustainable management of minerals and energy resource operations.

Vertical reactive solute transport through non-fractured low permeability clayey confining strata plays a vital role in minimising any environmental impacts from subsurface operations. The transport of particular natural dissolved constituents (e.g., Cl^-) and isotopes (e.g., $\delta^{18}O$ and $\delta^{2}H$) found in aquitard porewater, collectively referred to as conservative tracers, by molecular diffusion (i.e., Fick’s Law) is well established for shallow groundwater systems (e.g., Hendry and Wassenaar, 2000; Desaulniers et al., 1981). These naturally-present tracers can provide early identification of potential contaminants. Further, it is now possible to measure $\delta^{18}O$ and $\delta^{2}H$ directly on drill core using vapour equilibration without having to rely on multiple nests of piezometers to study vertical connectivity (e.g., Hendry and Wassenaar, 2010).

Transport of typically non-conservative cations (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}) has also been investigated. For example, Timms & Hendy (2008, 2003) studied the long-term (2 ka) hydraulic integrity of thick clay-rich till aquitards associated with potash mines in Canada. Field and laboratory measurements used in conjunction with PHREEQC 1D reactive transport simulations showed that breakthrough of dissolved cations, in relation to a conservative Cl^- tracer, was largely retarded within the aquitard. Cation exchange properties of the aquitard resulted in further retardation effects suggesting an effective natural barrier to vertical brine migration over the long term.

Dissolved gas (e.g., CH_4, CO_2) and formation brine migration concerns potential groundwater pollution from CSG and CO_2 storage operations. Methane can migrate into shallow aquifers through leaks in production well casings and/or as a result of directional drilling and hydraulic fracturing (e.g., Osborn et al., 2011). Similarly, CO_2 can escape through leaks in injection wells and by over-pressurization of cap rock seals (e.g., Fleury et al., 2011).

Diffusion of dissolved gases through non-fractured argillaceous confining strata can retard their long-term transport to overlying aquifers (e.g., Fleury et al., 2009). Identification and monitoring of dissolved thermogenic CH_4 (CSG) and CO_2 (CO_2 storage) diffusion, in addition to displaced metal-rich formation brines, could therefore act as early detection indicators of potential contamination. Particularly related to CSG operations, for example, the $\delta^{13}C_{CH4}$ and $\delta^{13}C_{DIC}$ isotope signatures could be used as important tracers.

Understanding the behaviour of CO_2 is challenging due to its complex phase behaviour (i.e., CO_2 can exist as a liquid, gas, supercritical fluid or a solute in water depending on the physical/chemical conditions) and the wide range of possible trapping mechanisms (i.e., residual, solubility, structural and mineral). In fact, dissolved CO_2 has been found to be more effective in attacking cap rock minerals than supercritical CO_2 (Holloway et al., 1996).

Different mechanisms for CO_2 migration are possible, from small to large scales: i) molecular diffusion (at geological time scales) of dissolved CO_2 in the pore water from the reservoir zone into the cap rock formation, ii) CO_2 diphasic flow after capillary breakthrough, iii) CO_2 flow through existing open fractures. The following mechanisms can accelerate or slow down the migration: i) chemical alteration of the mineralogical assemblage of the cap rock under the influence of acid water, ii) re-opening of pre-existing fractures or micro-cracks induced by overpressure of the repository, iii) a combination of the above (chemical alteration of the mineral filling the fractures) (Fleury et al., 2011).

Chemical tracers have been used extensively worldwide at CO_2 storage sites (pilot) for monitoring subsurface movement of CO_2, quantifying trapping capacity and determining containment and leakage rates (e.g., Myers et al., 2013; Bachaud et al., 2011). For example, perdeuterated methane (CD_4), krypton (Kr) and sulphur hexafluoride (SF_6) were used as tracer gases for the CO2CRC Otway Stage 1 Project. Breakthrough of injected CO_2 was identified by the presence of tracer compounds, an increase in CO_2 concentrations over background levels and a change in the $\delta^{13}C$ of the measured CO_2 (Myers et al., 2013).

The acidic nature of aqueous CO_2 causes a decrease in pH (although pH would be a secondary indicator), an increase in alkalinity, and increase in dissolved inorganic carbon (DIC) and the mobilization of cations (e.g., Na^+, Ca^{2+}, Mg^{2+}) and possibly metals (e.g., Fe). Further, CO_2 can undergo exchange reactions with formation brines and minerals that could cause a change in the isotopic composition. Therefore, monitoring isotopic changes of formation fluids and groundwater from overlying aquifers can act as natural early warning tracers of potential contamination, provided adequate baseline studies have been conducted (Myers et al., 2013).

Despite extensive use of artificial/natural tracer compounds, studies have predominantly focused on monitoring breakthrough up-dip or at well sites within the injection reservoir. Limited data is available on tracer breakthrough and CO_2 transport through cap rocks and subsequently in overlying aquifers as early detection indicators for possible groundwater contamination.

Transport of radionuclides from nuclear waste (e.g., ^{239}Pu, ^{135}Cs, ^{129}I, ^{99}Tc) stored in thick water-saturated argillaceous mined repositories largely relies on the hydrogeological properties of the host rock. For instance, long-term production of heat due to decaying radionuclides is of concern particularly with regard to thermal conductivity of host rocks, and the likelihood of fracturing by thermally induced fluid pressures (Bachu and McEwen, 2011).

Bentonite used in the construction of vital tertiary engineered barrier systems also depend on the possible combined effect of heat, mechanical and chemical stress on hydrated bentonite to minimise radionuclides transport in hydrous environments (Delage et al., 2010). Long-term (millennia) integrity of bentonite must be maintained to ensure safe containment of radioactive particles.

Reactive transport of radionuclides through low permeability clay-rich host rocks is retarded by rock minerals-radionuclide interactions and has been extensively studied. Under such tight and saturated environment, transport is likely to be by diffusion, although colloidal transport of radionuclides has also been identified. Environmental isotopes and tracer compounds naturally found within host rock porewaters, in conjunction with radionuclides, could be studied and monitored to provide an early warning indication of groundwater contamination.

4. INNOVATIVE METHODS AND LEADING PRACTICES

Proponents of subsurface developments in areas of perceived high risk of vertical connectivity and groundwater contamination will be subject to consent conditions that require a method to be demonstrated with no adverse environmental impact.

The concept of leading practice is simply the best possible way of conducting activities for a given area. As new challenges emerge and new solutions are developed, it is important that leading practices be flexible in developing solutions that match site-specific requirements (Laurence, 2011). Leading practices is, therefore, as much about possible approaches as it is about a fixed set of practices or a particular technology. For example, new technologies such as geotechnical centrifugation can provide data on matrix permeability and transport properties of confining strata, as one part of an overall assessment approach (Timms et al., 2012).

Innovative centrifuge permeameters (Fig. 3) are being developed by a UNSW team, as part of NCGRT research, to assess the hydraulic integrity of confining strata. This new assessment technique complements and improves site assessments and numerical modelling of potential cumulative impacts (Timms, 2012).

Figure 3: New UNSW-NCGRT geotechnical centrifuge with two centrifuge permeameter modules attached to either side of the geotechnical beam (2 m diameter) for characterising hydraulic behaviour of low permeability drill core (65-100 mm diameter; 20-200 mm length).

Tests of drill core in the UNSW-NCGRT geotechnical centrifuge using ASTM D7664-10 have enabled relatively rapid measurement of K_v of clayey sediments and shale. The technical specifications of the Broadbent G-18 (875 RPM_{max}, 2 m diameter) centrifuge, including the permeameter module (550 g_{max} for 2 × 4.2 kg samples) has been established in a new UNSW facility (Timms, 2012).

The centrifuge permeameter enables large permeability datasets to be obtained in reasonable time for confining strata that would otherwise not be possible. Recent K_v data of semi-consolidated smectite varied from 10^{-10} - 10^{-9} m/s depending on stress state at depths of up to 40 m in the Gunnedah coalfields area. By contrast, shale can be 10 to 100 times less permeable with test values to date ranging from $<10^{-12}$ - 10^{-10} m/s (Fig. 4). With future development of instrumentation in the UNSW-NCGRT facility, even lower K values could be measured, along with the variation of K value with moisture or saturation.

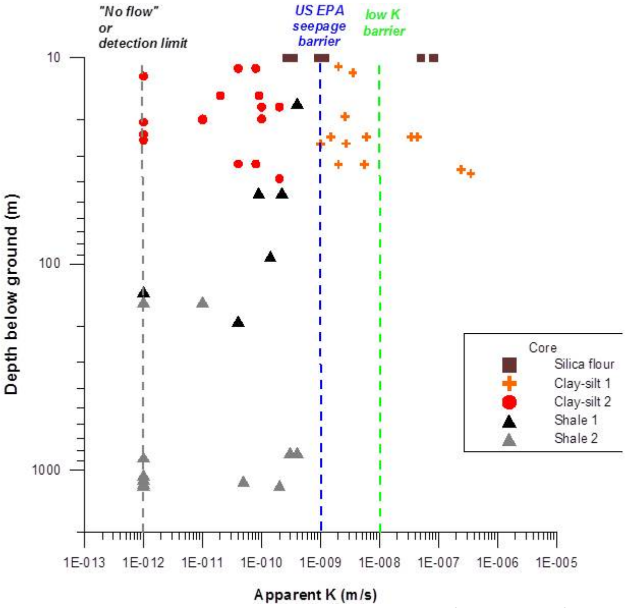

Figure 4: Hydraulic conductivity (K) as a function of depth for argillaceous core specimens tested in the NCGRT centrifuge permeameter module at high g-levels.

Table 1: Geotechnical centrifuge flow setups and types of tests (Timms et al., 2012).

Setup	Centrifuge Permeameter Tests
No flow	Compressibility, specific storage, pore water extraction
Steady flow	Permeability, reactive transport, effective porosity
Transient flow	Permeability, water retention curve

Findings have so far highlighted the sensitivity of K to moisture content and small fractures. Minimally disturbed core samples from depths greater than 100 m have been tested, although load restrictions in this centrifuge cannot match in situ lithostatic stresses at such depths. Nevertheless, the permeability values are consistent with larger permeability datasets for shales (e.g., Neuzil, 1994).

Steady state flow conditions in the centrifuge also enable reactive transport experiments to quantify the degree of contaminant retardation under in situ conditions. A range of other tests are also possible for no flow and transient flow conditions in the centrifuge permeameter module (Table 1). For example, the retardation of trace metals and analogues of radionuclides were defined for a natural glacial till seepage barrier over thousands of years during 3 months of centrifuge modelling (Timms et al., 2009). Analysis of both aqueous phase (core effluent) and solid phase (core dissection after testing) enable a very large range of retardation values to be measured for realistic flow conditions.

5. CONCLUSIONS

The Earth's crust is in increasing demand from new and prospective mineral and energy resource-related developments. Low permeability argillaceous formations (aquitards) naturally confine and minimize potential pollution of shallow groundwater resources. The flow of groundwater through confining strata is typically very slow, but could be significant over geological time scales. Due to their very tight nature, large gaps exist in the understanding of aquitard hydraulic integrity, including retardation and migration of contaminants and solutes. Newly-developed geotechnical centrifuge permeameters, testing drill core (clayey sediments and shale) under high gravity environments, can directly address questions of subsurface flow at scales that are not otherwise possible. Future research with improved instrumentation would enable experimentation at lower K values ($<10^{-12}$ m/s) and under in situ conditions (moisture content). There are only a limited number of studies on reactive contaminant transport of tight matrix via centrifugation, with significant potential to enhance best practice with regard to site evaluation and addressing early indicator signals for groundwater contamination.

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REFERENCES

Bachaud, P., Ph. Berne, F. Renard, M. Sardin and J.P. Leclrc, (2011). Use of tracers to characterize the effects of CO2-saturated brine on the petrophysical properties of low permeability carbonate cap rock. Chemical Engineering Research and Design, 89: pp. 1817-1826.

Bachu, S. and T.M. McEwen, (2011). Geological media and factors for the long-term emplacement and isolation of carbon dioxide and radioactive waste. In: Toth, F.L. (Ed), Geological Disposal of Carbon Dioxide and Radioactive Waste: A Comparative Assessment, Springer, pp.23-79.

Delage, P., Y.J. Cui and A.M. Tang, (2010). Clays in radioactive waste disposal. Journal of Rock Mechanics and Geotechnical Engineering, 2(2): pp. 111-123.

Desaulniers, D.E., J.A. Cherry and P. Fritz, (1981). Origin, age and movement of porewater ion argillaceous quaternary deposits at four sites in southwestern Ontario. Journal of Hydrology, 50: pp. 231-257.

Elliot, T.R. and M.A. Celia, (2012). Potential restrictions of CO2 sequestration sites due to shale and tight gas production. Environmental Science & Technology, 46: pp. 4223-4227.

Ferguson, G., (2013). Subsurface energy footprints. Environmental Research Letters, 8: 6pp 014037.

Fleury, M., P. Berne and P. Bachaud, (2009). Diffusion of dissolved CO2 in cap rock. Energy Procedia, 1: pp. 3461-3468.

Fleury, M., J. Pironon, Y.M. Le Nindre, O. Bildstein, P. Berne, V. Lagneau, D. Broseta, T. Pichery, S. Fillacier, M. Lescanne and O. Vidal, (2011). Evaluating sealing efficiency of cap rocks for CO2 storage: an overview of the Geocarbone Integrity Program and results. Energy Procedia, 4: pp. 5227-5234.

Hendry, M.J. and L.I. Wassenaar, (2010). Inferring heterogeneity in aquitards using high-resolution δD and δ18O profiles. Groundwater, 47(5): pp. 639-645.

Hendry, M.J. and L.I. Wassenaar, (2000). Controls on the distribution of major ions in porewaters of a thick surficial aquitard. Water Resources Research, 36(2): pp. 503-513.

Holloway, S., (1996). An overview of the Joule II Project “The Underground Disposal of Carbon Dioxide.” Energy Conservation & Management, 37(6-8): pp. 1149-1154.

International Energy Agency (IEA), (2011). World Energy Outlook 2011. Paris, France: IEA.

Intergovernmental Panel on Climate Change (IPCC), (2005). Special Report on Carbon Capture and Storage. In: Metz, B., et al. (Eds), Working Group III of the Intergovernmental Panel on Climate Change, Cambridge, UK.

Laurence, D., (2011). A Guide to Leading Practice Sustainable Development in Mining. Canberra, Australia: Australian Government, Department of Resources, Energy and Tourism.

Myers, M., L. Stalker, B. Pejcic and A. Ross, (2013). Tracers - past, present and future applications in CO2 geosequestration. Applied Geochemistry, 30: pp. 125-135.

Neuzil, C.E., (1994). How permeable are clays and shales? Water Resources Research, 30(2): 145-150.

Osborn, S.G., A. Vengosh, N.R. Warner and R.B. Jackson, (2011). Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. Proceedings of the National Academy of Sciences of the United States of America (PNAS), 108(20): pp. 8172-8176.

Queensland Water Commission (QWC), (2012). Underground Water Impact Report for the Surat Cumulative Management Area. Queensland, Australia, 224pp.

Solomon, S., M. Carpenter and T.A. Flach, (2008). Intermediate storage of carbon dioxide in geological formations: a technical perspective. International Journal of Greenhouse Gas Control, 2: pp. 502-510.

Timms, W.A., (2012). Environmental ‘time machine’ – the integrity of aquitards overlying coal seams. AusIMM Bulletin, April 2012, pp.79-81.

Timms, W., I. Acworth, A. Hartland and D. Laurence, (2012). Leading practices for assessing the integrity of confining strata: application to mining and coal seam gas extraction. In: McCollough, C.D., Lund, M.A., Wyse, L. (Eds) 2012 International Mine Water Association Symposium Proceedings, Bunbury, Westhern Australia, pp.139-148.

Timms, W., M.J. Hendry, J. Muise and R. Kerrich, (2009). Coupling centrifuge modeling and laser ablation ICP-MS to determine contaminant retardation in clays. Environmental Science & Technology, 43: 1153-1159.

Timms, W.A. and M.J. Hendry, (2008). Quantifying the impact of cation exchange on long-term solute transport in a clay-rich aquitard. Journal of Hydrology, 332: pp. 110-112.

Timms, W.A. and M.J. Hendry, (2003). Application of centrifuge modeling to assess long-term brine migration in thick clay till, Saskatchewan, Canada. AusIMM Conference "Water in Mining", Brisbane, Australia, pp.363-372.

Vinsot, A., J. Delay, R. de La Vaissiere and M. Cruchaudet, (2011). Pumping tests in a low permeability rock: results and interpretation of a four-year long monitoring of water production flow rates in the Callovo-Oxfordian argillaceous rock. Physics and Chemistry of the Earth, 36: pp. 1679-1687.