Gas hydrate stability in the vicinity of a deep geological repository for radioactive wastes: A scoping study.

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Gas hydrate stability in the vicinity of a deep geological repository for radioactive wastes: A scoping study.

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Foreword

This report is the published product of a scoping study by the British Geological Survey (BGS) into the likelihood of certain gas hydrates becoming stable within and around an underground repository for the storage of radioactive wastes. The preliminary investigations considered whether the temperature and pressure changes associated with glacial and permafrost conditions had the potential to stabilise CO_2 and methane hydrates within the geosphere, and if they did, to suggest areas for more detailed future investigation.

Contents

FIGURES

Summary

This report describes the results of a scoping study to assess the potential for the formation of CO_2 and methane hydrates within the geosphere of the UK during glacial and permafrost conditions. It is likely that several future glacial cycles will occur within safety assessment timescales for a UK repository for radioactive wastes. These are likely to produce lower temperatures within the geosphere and also possibly higher pressures beneath ice sheets, and the effects of these need to be considered in long term safety assessments. The purpose of this scoping study was to consider if glacial/permafrost conditions had the potential to stabilise gas hydrate phases within the geosphere beneath the UK, especially in relation to more northerly parts of the UK.

Gas hydrates are a group of crystalline, ice-like solids that are generally stable under elevated pressures and lower temperatures. Many different gases form hydrates, methane hydrate is by far the most common hydrate on Earth, being widely distributed within polar regions and along deepwater continental margins where high pressure, low temperature environments coexist with a supply of gas. Hydrate distribution has changed over the recent geologic past, and in particular as a result of waxing and waning glacial cycles. It is possible therefore, that future 'glacial' conditions within the UK geosphere might favour the formation of hydrate phases, and that they might form in the vicinity of a deep repository for radioactive wastes. Given that several glacial cycles are likely to occur within safety assessment timescales, it is important to assess whether hydrate phases could be stabilised during them. Also, if hydrates become stabilised during glacial events, what are the possible effects several cycles of hydrate formation/destabilisation might have on the repository environment. Methane and CO_2 are of particular interest to this study as they could form within packages containing radioactive wastes as a result of degradation of celulosic materials. Methane could also form in the surrounding geosphere through the degradation of organic matter in the rocks.

There are a range of factors that effect hydrate stability, and not all of these could be included within this initial scoping study. The variables that were considered were pressure, temperature and salinity, and it was assumed that sufficient amounts of gas were available in solution for hydrate to form and that pore size had no effect on hydrate stability. Thermodynamic equilibrium was assumed, and as a consequence time-dependant factors such as the rate of hydrate formation, or rate of heat input were also not taken into account.

The results of the modelling are briefly as follows:

- Neither CO_2 or methane hydrates are stable within the UK onshore geosphere under present day conditions (assumed average surface temperature of 10°C and a geothermal gradient of 25°C/km).

- For average surface temperatures below 0°C (permafrost conditions) CO_2 hydrate becomes stable in the presence of dilute groundwater about 300 m into the geosphere (with an assumed geothermal gradient of 25°C/km and pressure controlled by a hydrostatic head). Methane hydrate requires colder conditions, and an average surface temperature of -5°C would be needed to first stabilise it at about 400 m depth under similar conditions.

- Under likely permafrost conditions (average surface temperature of -10°C), both CO_2 and methane hydrates could be stable at likely repository depths (assumed to be about 400-800 m deep). This is particularly the case in the presence of dilute groundwaters, but they could also form in the presence of relatively saline groundwaters.

- A 1 km thick ice sheet having a basal temperature of 0°C would stabilise CO_2 hydrate beneath it in the presence of a range of fluid salinities. The CO_2 hydrate stability zone is limited however, and would not penetrate below the shallowest assumed likely repository depth (400 m). The situation is similar for ice sheets of 500-1500 m thickness, however it

changes if a basal ice sheet temperature of -5°C is assumed. In this case CO_2 hydrate could be stable within the shallower parts of likely repository depths.

- A 1 km thick ice sheet having a basal temperature of 0°C would also stabilise methane hydrate beneath it in the presence of a range of fluid salinities, and the more dilute of these would facilitate methane hydrate stability to within the shallower parts of likely repository depths. Thicker or thinner ice sheets would impart slightly deeper or shallower hydrate stability zones respectively. However, there are larger changes if a basal ice sheet temperature of -5°C is assumed. In this case methane hydrate could be stable throughout the all likely repository depths in the presence of relatively dilute groundwaters.

Given that there appears to be significant potential for hydrate formation within a possible repository and/or in the surrounding geosphere, there is a need to make a more quantitative assessment of the processes involved. Suggestions of areas for possible future work to provide the necessary detailed data include:

- Producing a realistic thermal model for site of interest covering several glacial cycles.

- Producing a realistic model for changing pressure gradients through the relevant parts of the geosphere due to the effects of ice loading.

- Investigate likely gas compositions and production rates within the repository and the surrounding geosphere.

- Ascertain whether hydrate formation and disassociation will impact the physical properties of repository materials or the surrounding geosphere.

- Assess the potential for, and impact of, episodic gas production as a result of hydrate breakdown.

Investigations such as those above should lead to an improved understanding of the potential for hydrate formation within a repository and the surrounding geosphere. Ultimately, this should allow an assessment of whether hydrate formation will be a problem, possible benefit, or of neutral consequence for the safety case of a repository.

1 Introduction

Gas hydrates are a group of crystalline, ice-like solids that are generally stable under elevated pressures and lower temperatures. They are a sub-group of a class of phases called 'clathrates', in which small, non-polar molecules (typically gases) are trapped within 'cages' of different molecules (hydrogen bonded water molecules in the case of hydrates). Without the presence of the trapped molecules, the lattice structure of hydrate clathrates would collapse into a conventional ice crystal structure or liquid water. Many different gases form hydrates, but by far the most common on Earth is methane hydrate. One noteworthy feature of gas hydrates is their relative ease of formation, only requiring the presence of gas and water under appropriate temperatures and pressures. Unlike the reactions of many rock-forming minerals, hydrate phases can grow relatively rapidity. Indeed, their relatively rapid growth can be a serious impediment to the functioning of natural gas pipelines, which they can block.

In terms of abundance and distribution, methane (CH_4) hydrate is by far the most common hydrate on Earth, being widely distributed within polar regions and along deepwater continental margins where high pressure, low temperature environments coexist with a supply of methane (Kvenvolden, 1998; Sloan, 1998). Methane hydrate consists of methane and water in a 1:5.75 ratio (assuming a fully occupied structure), and typically 1 dm^3 of methane hydrate would destabilise into about 0.8 dm^3 of water and 167 dm^3 of methane gas. Current estimates of global hydrate volumes suggest 2 x 10^{14} m^3 of methane could exist within these natural hydrate reserves, which is approximately 30 times the quantity available in the atmosphere at present, representing one of the largest stores of organic carbon on this planet (Soloviev, 2002; Long *et al.*, 2005), Much work is ongoing to study methane hydrates:

a) To investigate their possible use as a future energy resource if the methane within the hydrates can be successfully extracted from the surrounding sediments.

b) To ascertain if global climate change through anthropogenic releases of greenhouse gases will lead to hydrate destabilisation and release of methane (a powerful greenhouse gas), exaserbating climate change. Indeed, there is evidence to suggest these natural reserves have released considerable quantities of methane gas into the atmosphere in the geological past at times of sudden climate change, and therefore need to be considered as a possible future environmental hazard (Kvenvolden, 1998; Kennett *et al.*, 2000; Buffet and Archer, 2004; Kemp *et al.*, 2005).

c) To assess the role of hydrate destabilisation on slope stability and its link to submarine landslides. For example, enhanced continental slope failure during glacial-interglacial transitions is believed to have occurred at the same time as the release of large quantities of methane from gas hydrates during the Pleistocene (Maslin *et al.*, 2004).

Other natural hydrates are far less common on the Earth, though two that are worth mentioning are carbon dioxide (CO_2) hydrate and 'air hydrate'. CO_2 hydrate is relatively rare in nature, having only been identified at deep-water hydrothermal venting sites in the Okinawa Trough offshore Japan (Sakai *et al.*, 1990; Shitashima *et al.*, 2008). However, there is increasing interest in CO_2 hydrate as a possible storage phase for anthropogenic CO_2 – either within the water column of deep oceans (e.g. Hirai *et al.*, 1997; Wilson, 1992) or on the bed of deep oceans (e.g. Austvik and Løken, 1992) or within deep-water sediments (Camps, 2007; House *et al.*, 2006; Koide *et al.*, 1997; Rochelle *et al.*, in press). Air hydrate is probably relatively common in polar regions. It is formed within the lower parts of large ice sheets by the pressure of overlying ice compressing trapped air bubbles to a pressure where hydrate phases become stable (e.g. Shoji and Langway, 1982). Air hydrates form once ice thicknesses exceed 500-1200 m (Lipenkov *et al.*, 1996).

Methane and CO_2 are of particular interest to this study as they could form within packages containing radioactive wastes as a result of degradation of celulosic materials. Methane could

also form in the surrounding geosphere through the degradation of organic matter in the rocks. In terms of present day methane and CO_2 hydrate stability zones around western Europe, preliminary modelling work suggests that they will not be found onshore and are unlikely to be found at water depths of less than about 300 m (Camps, 2007). However, the current hydrate stability zones during the present interglacial do not reflect their stability during other parts of the glacial cycle. Indeed, for relatively high latitude locations (such as the UK), warm interglacials represent only about 10-25% of the last few 100 kyears (e.g. Heathcote and Michie, 2004; IPCC, 2001). For much of the rest of the time the land was either covered by ice sheets 100s m thick, or under deep permafrost. Increased pore pressures due to ice loading, or decreased temperatures due to permafrost, can lead to a much wider distribution of the hydrate stability zones, potentially coinciding with potential repository locations. Hydrate phases then might form within or around an underground repository for the storage of radioactive wastes if sufficient gas was present. Given the timescales considered within repository safety cases (in the order of a million years), there is potential for rocks at likely repository depths to undergo several phases of hydrate formation and destabilisation as glacial events wax and wane.

The formation (followed by breakdown) of new solid phases within the repository or within the surrounding geosphere might lead to changes in the physical and fluid flow properties of the solids in question (rocks, buffer/backfill etc). The periodic breakdown of hydrate phases at the end of a glacial event might also lead to larger, episodic releases of gas rather than slow and steady releases. This might impact fluid flow, gas transport etc.

The purpose of this report is to address the initial question of whether there is a reasonable likely-hood that gas hydrates could become stable at repository depths during glacial cycles. The approach taken is of a series of scoping calculations based around 3 different scenarios. Two of these scenarios consider glacial/permafrost conditions, and utilise reconstructions of past climates as of predictors of possible future conditions. Though some of the calculations are generic in nature, they are illustrated with reference to possible conditions in north-west England. Other, more detailed follow-on issues will have to be the focus of subsequent studies, such as whether sufficient gas might be present to form hydrates, and the impact that any hydrates might have on the physical or flow properties of rocks.

2 Requirements for hydrate stability

2.1 TEMPERATURE AND PRESSURE

Gas hydrates are generally stable at lower temperatures and pressures above atmospheric pressure (see Figure 1), though their exact stability range varies with the gas involved. Methane and CO_2 provide contrasting cases because of their differing phase behaviour. Methane is a gas over a wide range of pressures and temperatures, and as a consequence its stability profile has a relatively simple relationship with pressure and temperature (Figure 1). CO_2 on the other hand, undergoes a phase change from gas-liquid at relatively moderate conditions, and this results in a more complex stability relationship with pressure and temperature (Figure 1). Although for many pressures and temperatures both CO_2 hydrate and methane hydrate are stable, CO_2 hydrate has a slightly larger stability field at lower pressures/temperatures, whereas methane hydrate has a larger stability field at higher pressures/temperatures (Figure 1).

In this study it was assumed that the sub-surface pressure gradient is controlled by a simple hydrostatic head, and the sub-surface temperature profile is controlled by a uniform geothermal gradient. It is recognised however, that these are simplifications, and the effects of more complex situations are discussed in the Results section.

2.2 GAS SATURATION

Even if sufficiently high pressures and sufficiently low temperatures exist for hydrates to form, there still needs to be enough gas present to achieve saturation with respect to hydrate phases. In other words, hydrate phases will not form in areas of very low dissolved gas concentration. By way of an example, consider CO_2 and methane solubility in water of seawater salinity and at a pressure of 10 MPa (100 bar, or about 1000 m of hydrostatic head). Figure 2 shows that CO_2 is more soluble than methane, reaching a maximum solubility of about 1.5 mol kg^{-1} at approximately 10°C. Methane on the other hand only reaches a maximum solubility of about 0.13 mol kg^{-1} at about 14°C. The data for CO_2 presented in Figure 2 were sourced from experimental investigations (Enick and Klara, 1990; King *et al.*, 1992; Kojima *et al.*, 2003; Kuk and Montagna, 1983; Wiebe, 1941; Wiebe and Gaddy, 1939, 1940) whereas the data for methane were generated using a code (CH4_solubility.exe) reported by Duan and Mao (2006), which is available for download at http://www.geochem-model.org/programs.htm.

Outside the hydrate stability zone, gas solubility generally increases with increasing pressure and decreases with increasing temperature, and this can be predicted with various geochemical models. Once hydrate becomes stable however, CO_2 and methane solubilities rapidly decrease with decreasing temperature (Figure 2) – a trend that most geochemical models do not reproduce (due to data for hydrate phases not being present in their thermodynamic databases).

In terms of the repository environment and a cyclic geotherm caused by glacial events, it is clear that groundwaters at certain depths could experience cooling to the point where dissolved gas could crystallise out as hydrate phase, or at other times, experience warming to the point where dissolved gas can exsolve to become bubbles.

2.3 OTHER FACTORS

There are also other factors as well as those described above that can control on hydrate stability. One of the most notable is salinity, with hydrate stability being reduced in more concentrated solutions (e.g. Sloan, 1998; see Figure 1). As hydrate forms it consumes water, and in regions of restricted fluid movement (such as in fine-grained rocks) this results in an increase in salinity of the remaining porewater – this is found in regions of current rapid hydrate growth such as the Cascadia Margin (e.g. Torres *et al.*, 2004). It is possible that if the increase in salinity is sufficiently large (and if pressure/temperature conditions are moderate), then it can result in the cessation of hydrate formation until the 'excess salinity' has had time to diffuse/advect away from the region of hydrate formation. The authors know of no natural examples where salinity increase has been so large that it reached the point of halite precipitation. However, this has been observed in laboratory experiments using restricted amounts of saline water and relatively large amounts of CO_2 (Camps et *al.*, in press).

Another factor having an impact on hydrate stability is that of the size of the pores that hydrate forms in. The effect of this is more subtle than that of salinity, but previous studies (Anderson *et al.*, 2003, Llamedo *et al.*, 2004) show a clear reduction in hydrate stability as pore sizes become smaller (especially for sub-micron pore sizes). The effect of this has not been included in this study, but this might be a factor to consider in detailed studies of hydrate formation in fine-grained rocks such as clays.

There are regions of pressure/temperature conditions where one hydrate is more stable compared to another, and in such regions it is possible for one hydrate to replace another. For example, under certain conditions CO_2 hydrate can replace methane hydrate, and it has been suggested that this could be utilised for both disposing of anthropogenic CO_2 whilst at the same time producing methane for energy generation (IEA GHG, 2000a,b; Nakano, 1998).

Finally, it is also possible that small amounts of gases other than CO_2 and methane could result in a mixed (i.e. impure) hydrate having enhanced stability relative to pure CO_2 or methane

hydrates. In addition, gases such as butane and propane form 'structure II' hydrates that have wider conditions of stability than 'Structure I' (methane) hydrates, and so will form more readily. These issues will not be considered further in this scoping study, but it is useful to note that for any future detailed work it would be beneficial to have quantitative data on likely gas compositions.

3 Methodology

In this scoping study to assess whether there could be a reasonable chance that subsurface hydrates might form during glacial cycles the only variables considered were pressure, temperature and salinity. It was assumed that sufficient amounts of gas were available in solution for hydrate to form and that pore size had no effect on hydrate stability. Thermodynamic equilibrium was assumed, and as a consequence time-dependant factors such as the rate of hydrate formation, or rate of heat input were also not taken into account.

Several models have been produced to account for changes in hydrate stability as a function of salinity. These include:

- 'CSMHYD' produced by Dendy Sloan and coworkers at The Centre For Hydrate Research at the Colorado School of Mines (Sloan, 1998). This DOS programme will predict hydrate data for several gases and is available for download at http://inside.mines.edu/research/chs/software/csmhyd.html.

- 'HWHYD' produced by Bahman Tohidi and coworkers at the Centre for Gas Hydrate Research, Institute of Petroleum Engineering, Heriot-Watt University. This code predicts hydrate data for a range of gases, some of which are active in the demo version that can be downloaded at http://www.pet.hw.ac.uk/research/hydrate/download.htm.

- 'hydrate-co2-salts.exe' 'hydrate-ch4-salts.exe' produced by Zhenhao Duan and coworkers at Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing. These gas-specific codes can be downloaded at http://www.geochem-model.org/programs.htm, and are described in Duan and Mao (2006), Duan and Sun (2006), Sun and Duan (2007).

It was beyond the scope of this preliminary scoping study to conduct a detailed comparison exercise between these different codes to ascertain how their predictions compare to each other. In part this was because the codes have been built around, and tested on, very similar experimental data and they should therefore produce very similar results. However, it was mainly because significant uncertainties exist in other areas considered within this report, and it is thought that the 'uncertainties' introduced through the use of different hydrate stability models are relatively low by comparison.

This study utilised the codes 'hydrate-co2-salts.exe' and 'hydrate-ch4-salts.exe'. The choice of using these was based upon their ease of use and compatibility with the code used for methane solubility (Sun and Duan, 2007). A range of (NaCl equivalent) salinities were considered, from pure water to a brine of 150 g L^{-1} (150000 ppm). This range covers most salinities encountered during previous investigations for a potential UK repository (e.g. see data in Metcalfe *et al.*, 2007), though at the likely repository depths considered (assumed to be 400-800 m) porewater salinity is expected to be low-moderate. The data from the modelling conducted in this study are given in Appendix 1, and were used to produce the CO_2 and methane hydrate stability plots in Figure 1, which were used as a basis for the rest of this study.

The hydrate stability data were converted into plots of hydrate stability with depth using the following assumptions:
- 1 bar = 10 m of water
- water density = 1 (though this would be higher with dissolved salts)
- water density does not change with depth
- ice has density of 0.9

It is acknowledged that the assumption of uniform water density may not be truly accurate. Dissolved salts will increase the density of water, and hence the pressure at depth. The effect of not including this in the calculations will be to slightly underestimate pressures and hence hydrate stability.

Temperature/geothermal gradient has a strong control on maximum depths of hydrate stability, and so it is important to determine this accurately. In this scoping study estimates were used that were based on a limited search through pre-existing information. It is acknowledged however, that ideally, a more thorough determination of subsurface temperatures needs to be conducted in order to reduce uncertainties to a minimum (for example by modelling temperature measurements taken from boreholes).

In this study hydrate stability was not considered below 0°C (i.e. the hydrate was assumed to be in contact with liquid water that could transport dissolved gas to the region of hydrate growth).

The information described above was used to consider 3 different scenarios, and these are treated in detail in the following section:

1) *Present day conditions*

   In this study the current average surface temperature has been taken as 10°C (Heathcote and Michie, 2004) and that there is a stable geothermal gradient of 25°C/km (based upon data in Gale *et al.*, 1984). It is also assumed that the water table lies at the ground surface, and that all sub-surface pressures are controlled by a hydrostatic head (i.e. *in-situ* pressure is a straightforward function of depth).

2) *Deep permafrost*

   The base case considered is of an average surface temperature of -10°C. This is towards the lower end of the temperature range given for modern day analogues of north-west England (Heathcote and Michie, 2004) and also that of Renssen and Vandenberghe (2003) for the lowlands of Belgium and the Netherlands after the last glacial maximum (some 20-25 kyears ago). The base case also assumes that there is a stable geothermal gradient of 25°C/km. However, it is recognised that glacial cycles are transitory events compared to geologic timescales, and that a simple linear geothermal gradient of 25°C/km from a surface temperature of -10°C may not be truly realistic. It is more likely that there will be a stable 'deep' geothermal gradient, and a 'shallower' geothermal gradient that varies as glacial events wax and wane. These issues are discussed further in the Results section.

3) *An ice sheet 1 km thick*

   The base case in this scenario is of an ice sheet 1 km thick that imparts an effective hydrostatic head of 900 m to the underlying geosphere. This thickness of ice is well within some current models (e.g. Boulton and Hagdorn, 2006), though it is somewhat thicker than the 625 m suggested by Heathcote and Michie (2004). It also assumes that there is melting at the base of the ice sheet (i.e. a 'wet-bottomed' ice sheet), and that this equates to a temperature of approximately 0°C. Modifications to these assumptions are discussed further in the Results section below.

For the purpose of illustrating the potential importance of hydrate formation upon the repository environment, it was assumed that a likely repository depth could be in the region of 400-800 m

below the current land surface. This assumption is purely illustrative, and makes no suggestion as to where a repository might be sited.

4 Results

4.1 PRESENT DAY CONDITIONS

The CO_2 and methane hydrate stability data in Figure 1 were converted into plots of hydrate stability with depth in Figures 3 and 4. An average surface temperature of 10°C was assumed, together with a geothermal gradient of 25°C/km.

The current geothermal profiles in Figures 3 and 4 both lie well outside the hydrate stability zones for all water salinities considered. Thus CO_2 and methane hydrates are not currently stable at likely onshore repository depths within the UK.

4.2 DEEP PERMAFROST

One of the most straightforward ways to stabilise hydrates in these scenarios would be to cool the geosphere. Indeed, taking the above scenario and dropping the average surface temperature by only 10°C (i.e. an average surface temperature of 0°C) would be enough to just stabilise CO_2 hydrate in the presence of dilute groundwaters at approximately 300 m depth (assuming a similar geothermal gradient of 25°C/km). By comparison, methane hydrate would require a slightly cooler average surface temperature (-5°C) before it would start to stabilise at approximately 400 m depth. These temperatures are relatively mild compared to temperatures that could exist during glacial permafrost conditions, and thus there is scope for hydrates to be stable below a permafrost layer[1].

In this scenario it was assumed that sub-zero temperatures had existed for a long time, and that permafrost extended deep into the geosphere. Although there is considerable evidence for relict permafrost features in the UK (such as former ice wedges [Worsley, 1966], brecciated chalk bedrock [French, 2008], and polygonal patterned ground [Morgan, 1971; Rochelle, 2003]), less is known about the depth to which the ground was frozen. Some areas of current permafrost have frozen ground to considerable depths. For example, permafrost currently reaches depths of over 500 m at the Lupin Mine, Nunavut, Canada, and over 1000 m in parts of Siberia (e.g. French, 1996). These areas have had many hundreds of thousands of years of very cold conditions for the freezing front to reach such depths. By contrast, the UK will have experienced cold temperatures for much shorter timescales in the past, and as a consequence the permafrost layer was probably thinner. That said, it appears that it only takes a very few thousand years for >200 m of permafrost to form. Indeed, Heathcote and Michie (2004) estimate that it would take as little as 200-2000 years to freeze the ground to a depth of 200 m given an average surface temperature of -5°C. Thus there is potential for considerable thickness of frozen ground in the UK during similar, future glacial events.

It is beyond the scope of this study to produce a permafrost model for north-west England, and so an average surface temperature of -10°C was assumed as a likely limiting lower temperature case. This compares well with the lower end of the temperature range for modern day analogues of the Sellafield area (Heathcote and Michie, 2004), and also that given by Renssen and

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[1] This scenario has already been observed at Messioykah in Siberia, which is the only known example of the exploitation of methane hydrate for energy. The exploited gas is found beneath impermeable caps of gas hydrate (deeper) and permafrost (shallower). See Sloan (1998) for further information.

Vandenberghe (2003) for the lowlands of Belgium and the Netherlands after the last glacial maximum (some 20-25 kyears ago). Initial calculations assumed a stable geothermal gradient of 25°C/km once more, resulting in a permafrost thickness of 400 m. The presence of deep permafrost would effectively result in an overall shift in the geothermal profile by 20°C cooler relative to the scenario in Section 4.1 above, and the results of this are given in Figures 5 and 6.

It is recognised however, that a linear geothermal gradient of 25°C/km from a surface temperature of -10°C may not accurately represent actual conditions of the past. It is more likely that that there is a 'deep' geothermal gradient that is relatively insensitive to the transitory, glacial timescale processes, and a 'shallow' geothermal gradient that changes as glaciations wax and wane. For example, under the coldest permafrost conditions the 'shallow' geothermal gradient may be much larger/steeper that 25°C/km. Simple linear geothermal gradients are also unlikely, and in reality they are probably non linear with a complex dependence on heat input/loss, thermal conductivity, heat capacity etc. Though these complexities are recognised, it is beyond this preliminary study to investigate them fully, though this would be a useful area to quantify as temperature has such a strong control on hydrate stability.

It is noted that ice formation to a depth of 400 m could coincide with zones of hydrate formation (as is currently seen in Arctic regions of areas such as northern Canada (e.g. Majorowicz and Osadetz, 2001). The modelling in this study used the Duan group codes and did not consider in detail the effects of ice on hydrate stability (e.g. apparent hydrate 'preservation' outside its region of stability). For simplicity only hydrate stabilities above 0°C were considered in this scoping study (which would not be the case *within* the permafrost zone). However, data exist on the stability of hydrate in the presence of ice, and so it should be possible to model the potential for hydrate formation within frozen ground and ice sheets in future studies.

CO$_2$ hydrate (Figure 5)

For all the fluid salinities considered, temperatures within the geosphere between 300-500 m depth lie within the predicted CO_2 hydrate stability zone, and so CO_2 hydrate could potentially exist within and below a zone of deep permafrost. For very dilute waters the CO_2 hydrate stability zone extends further, between 100-800 m into the geosphere. In this scenario therefore, it seems likely that CO_2 hydrate could form throughout the range of likely repository depths (for all groundwaters except concentrated brines).

The effect of a non-linear geothermal gradient (see comments above) would probably be to increase temperatures at depth, and hence reduce the maximum depth of the CO_2 hydrate stability zone.

A thinner permafrost zone would result in warmer temperatures at depth, and hence a shallower CO_2 hydrate stability zone. For example, an average surface temperature of -5°C would result in approximately 200 m of permafrost (as per Heathcote and Michie, 2004) and a reduced CO_2 hydrate stability zone down to about 600 m for very dilute waters. However, CO_2 hydrate would no longer be stable for a brine equivalent to 150 g L^{-1} NaCl. Only for surface temperatures averaging 0°C and above would CO_2 hydrate not be stable for even the most dilute fluids.

Methane hydrate (Figure 6)

For all except the most saline fluids considered, temperatures within the upper geosphere lie within the predicted methane hydrate stability zone. For very dilute waters this stability zone extends between approximately 250-900 m deep (i.e. throughout the range of likely repository depths). However, for a brine equivalent to 100 g L^{-1} NaCl, methane hydrate stability would only be marginal between about 350-500 m deep.

The effect of a non-linear geothermal gradient or thinner permafrost zone would be to increase temperatures at depth, and hence reduce the maximum depth of the methane hydrate stability zone. For example, at an average surface temperature of -5°C and above, methane hydrate would not be stable for even the most dilute fluids.

4.3 THICK ICE SHEET COVERING THE LAND SURFACE

In this scenario, it was assumed that a 1 km thick ice sheet covered the land surface. This thickness of ice is well within the range given in recent studies, which suggest maximum thickness possibly up to about 1.5 km during the last glacial cycle for west Cumbria (Boulton and Hagdorn, 2006). As with the two scenarios above, a 25°C/km geothermal gradient is again assumed. It is possible that over several glacial cycles there would be some erosion at ground level, and hence a decrease in pressure at depth. The effect of this is thought to be small and so it was not included in this scoping study, though this is an area of potential future investigation.

The presence of a 1 km thick ice sheet would cause two differences relative to the scenario in Section 4.1 above:

1) That there was liquid water in contact with the bottom of the ice sheet. For simplicity, the change in melting point of ice with increasing pressure was ignored, and hence an ice sheet bottom temperature of 0°C was assumed. As a geothermal gradient of 25°C/km is also assumed, this results in an overall shift in the geothermal profile by 10°C cooler compared to present day conditions (cf. Section 4.1). However, some recent studies have noted that basal ice temperatures may have been as low as -5°C in the past (Boulton and Hagdorn, 2006), and the impact of these lower temperatures are described in the paragraphs below.

2) That pore pressures in the rock would increase, in this case by 9 MPa (90 bar). The net effect of this is to shift the hydrate stability profiles upwards by 900 m relative to those considered in Section 4.1 above. It is acknowledged that this may be an oversimplification (and possible overestimation) of pressures in sediments beneath ice sheets, but it provides a useful limiting (i.e. maximum) pressure condition for this scoping study. It might be beneficial for more detailed future studies to quantify pressure conditions beneath ice sheets.

The results of this scenario are given in Figures 7 and 8.

In the following descriptions the potential for hydrate formation within the ice sheet has been ignored, because the focus of this study lies within the geosphere, However, it is acknowledged that hydrates could exist in the lower (i.e. higher pressure) parts of large ice sheets (e.g. for air hydrates see Lipenkov *et al.* [1996] and Shoji and Langway [1982]).

CO_2 hydrate (Figure 7)

For all the fluid salinities considered, temperatures within the shallow geosphere lie within the predicted CO_2 hydrate stability zone, and so CO_2 hydrate could potentially exist below a 1 km thick ice sheet. For very dilute waters the CO_2 hydrate stability zone is predicted to extend approximately 400 m into the geosphere, but perhaps only about 100 m for a brine equivalent to 150 g L^{-1} NaCl.

Given that a 'wet-bottomed' ice sheet is assumed, and given that ice melting at the base of the ice sheet would produce very dilute water, it seems likely that the CO_2 hydrate stability zone in this scenario would lie towards the upper end of the range predicted (i.e. closer to 400 m). However, even this maximum value only just coincides with the assumed minimum likely repository depth. In this scenario therefore, it seems unlikely that CO_2 hydrate would form within the likely range of repository depths (LRD).

The situation is somewhat different if an ice sheet frozen to the base is considered, having a basal temperature of -5°C is (Boulton and Hagdorn, 2006; Heathcote and Michie, 2004). Under

these conditions and with a stable geothermal gradient of 25°C/km, then the CO_2 hydrate stability zone would extend to greater depths within the geosphere - by approximately 200 m compared to the previous case. Thus for very dilute waters the CO_2 hydrate stability zone might extend to approximately 600 m into the geosphere, but perhaps only about 300 m for a brine equivalent to 150 g L^{-1} NaCl. In this modified scenario therefore, it appears possible that CO_2 hydrate could form within the upper parts of the likely repository depth range if dilute groundwaters were present.

Given the relative insensitivity of the near vertical part of the hydrate stability curves to pressure/depth, the above conclusions would hold even for a much thicker ice sheet (possible thicknesses of up to 1.5 km having been reported by Boulton and Hagdorn, 2006). Even an ice sheet of only 500 m thickness (more akin to the 625 m estimated by Heathcote and Michie, 2004) would produce a broadly equivalent hydrate stability zone. Only for ice sheets of less than 500 m would there be a large decrease in hydrate stability zone.

The effect of a non-linear geothermal gradient has not been considered in the above calculations, but again its effect would probably be to reduce the maximum depth of the CO_2 hydrate stability zone. However, the above calculations do demonstrate the generally higher relative importance of temperatures compared to pressures in controlling CO_2 hydrate stability. This underlines the importance of having accurate thermal model for the site under study.

Methane hydrate (Figure 8)

For all the fluid salinities considered, temperatures within the shallow geosphere lie within the predicted CO_2 hydrate stability zone, and so methane hydrate could potentially exist below a 1 km thick ice sheet. Indeed, the methane hydrate stability zone is predicted to extend further into the geosphere compared to CO_2 hydrate. For very dilute waters the methane hydrate stability zone is predicted to extend approximately 650 m into the geosphere, but perhaps only about 300 m for a brine equivalent to 150 g L^{-1} NaCl.

Given that a 'wet-bottomed' ice sheet is assumed, and given that ice melting at the base of the ice sheet would produce very dilute water, it seems likely that the methane hydrate stability zone in this scenario would lie towards the upper end of the range predicted (i.e. closer to 600 m). This maximum value overlaps with the upper half of the assumed likely repository depth range. In this scenario therefore, it seems possible that methane hydrate could form within the shallower parts of the likely repository depth range.

The methane hydrate stability zone is extended if a basal ice sheet temperature of -5°C is considered (as per Boulton and Hagdorn, 2006). Under these conditions and with a stable geothermal gradient of 25°C/km, then the methane hydrate stability zone would be extended by approximately 250 m compared to the previous case. Thus for very dilute waters the methane hydrate stability zone might extend to approximately 900 m into the geosphere, but perhaps only to about 550 m for a brine equivalent to 150 g L^{-1} NaCl. In this modified scenario therefore, it appears very possible that methane hydrate could form within the upper part of the likely repository depth range, or even throughout all of it if dilute groundwaters were present.

Unlike CO_2 hydrate, the methane hydrate stability curves show a greater dependency on pressure. As a consequence, a much thicker ice sheet would lead to an expansion of the hydrate stability zones. Thus an increase in ice sheet thickness to 1.5 km (as per Boulton and Hagdorn, 2006) would result in an expansion of the hydrate stability zone. For example, compared to the base case above (i.e. a 0°C basal ice sheet temperature), this would result in an increase in hydrostatic head of about 450 m. For very dilute waters the methane hydrate stability zone is then predicted to extend to approximately 750 m into the geosphere, and perhaps about 400 m for a brine equivalent to 150 g L^{-1} NaCl. The methane hydrate stability zone would be extended a little further for a basal ice sheet temperature of -5°C. Thus for a 1.5 km thick ice sheet it seems very possible that methane hydrate could form throughout the likely repository depth range.

A reduction in ice sheet thickness would have the opposite effect to that outlined in the paragraph above. An ice sheet of only 500 m thickness having a basal temperature of 0°C would allow for a reduced hydrate stability zone down to approximately 500 m into the geosphere in the presence of very dilute fluids. In this modified scenario methane hydrate would not be stable in the presence of concentrated brines

The effect of a non-linear geothermal gradient was again not considered in the above scoping calculations, though its effect would likely be to increase temperatures at depth, and hence reduce the maximum depth of the methane hydrate stability zone.

5 Implications and recommendations

Although present day conditions within the UK geosphere are not suitable for the formation of methane and CO_2 hydrate, both of the glacial/permafrost scenarios considered in Section 4 above show there is potential for hydrate phases to form within a possible repository and/or in the surrounding geosphere. Given that safety assessments are likely to consider timescales in the order of a million years, and given that past glacial cycles are about 100-125 kyears long, there is the possibility of 8-10 future glacial cycles within a safety assessment timeframe. It would appear therefore, that safety assessments should give due consideration of the effects resulting from the possible formation of hydrate phases in and around a repository environment.

That hydrate phases only require gas and water to grow, suggests that they will form relatively readily given the appropriate conditions of pressure, temperature and fluid composition. Whether hydrates form or not will also depend on the supply of gas and the rock types present. For example, CO_2 and methane could form within LLW/ILW waste packages as a result of degradation of celulosic materials such as paper and clothing, or possibly ion-exchange resins. Gas (in particular methane) could also form in the surrounding geosphere through the degradation of organic matter. This would be especially the case if the repository was situated within organic-rich mudrocks, or if it was in relatively close proximity to sedimentary basins. Dissolved gas might also be brought close to the repository through the slow migration of groundwaters. There appears the potential therefore, for the slow and steady production/advection of gas within and around a deep radioactive waste repository.

For *in-situ* conditions outside the hydrate stability zone, dissolved or free phase gas would just migrate as a function of the local hydrogeological conditions. However, a suitable decrease in temperature would allow the formation of gas hydrates, and so the migration of gas-laden groundwater passing through this zone would result in the growth of gas hydrate crystals within pore spaces in the rock.

The formation of gas hydrates could have several implications:

- Firstly, if enough hydrate fully blocked pore spaces, then it could help reduce the permeability of the rocks. As a consequence this would reduce the potential for groundwater flow, and hence radionuclide transport. This would however, require the formation of very large amounts of hydrate. It is worth noting that as hydrate formation effectively consumes water, the remaining porewater becomes more saline (cf the formation of brines in areas of permafrost). Saline porewaters would be denser than surrounding waters and this could impact local groundwater movement.

- Secondly, samples of hydrate recovered from offshore sediments commonly occur as nodules, lenses or discrete horizons as well as pore-filling cement, and there is currently debate as to how such masses of hydrate formed. Some researchers have suggested that hydrate formation effectively pushes the surrounding mineral grains apart, especially in relatively shallow sediments (Torres *et al.*, 2004). If this were to occur at greater depths in

the rocks surrounding a repository then there is potential for it to alter the physical characteristics of the rock.

- Thirdly, if significant amounts of gas were locked up within hydrate phases during glacial/permafrost events, then this might be released at the start of warm interglacial periods when hydrate phases destabilise. A consequence of this could be a relatively short-term pulse of gas movement, which could have consequences for radionuclide transport. Gas migration might be enhanced if the hydrate growth had permanently changed the physical properties (i.e. overall permeability) of the rock.

- Finally, if hydrates did form and did have an impact on the repository environment, then several cycles of formation and destruction would be expected within safety assessment timescales as glacial events wax and wane.

The above scenarios have only considered the rocks and overlying ice in relation to ice (permafrost) and hydrate stability. However, the presence of the repository itself may influence ice and hydrate formation, either directly of indirectly. For example, the repository may change the temperatures in its vicinity:

- Its presence might change temperatures locally, for example by modifying local groundwater movement.

- Heat from radioactive decay within the waste packages (especially in the case of high level waste) will warm the surrounding geosphere. Advection of groundwater may mean that some of this heat is carried upwards to shallower parts of the geosphere.

There may be different (and possibly opposing) impacts of these changed temperatures, though they may operate over different timescales. Warmer temperatures around the repository would tend to reduce the potential for ice or hydrate formation locally. In theory this might result in, for example, a thinner permafrost (or hydrate) zone above the repository (e.g. see the sketch in Figure 9). On one hand this might be seen as advantageous if it prevented the formation of unwanted secondary phases in and around the repository. However, on the other hand, under certain circumstances it might provide a mechanism that might act to focus hydrate formation above the repository.

If sources of gas were present in the geosphere around the repository, then they might accumulate under any thinned region of permafrost (e.g. see the sketch in Figure 10). Continued reductions in temperature might then form thicker permafrost and stabilise hydrate below the permafrost (e.g. see the sketch in Figure 11). The 'reservoir' of gas trapped under the thinned region of permafrost may then act as a focus for hydrate formation. Breakdown of this hydrate at the onset of interglacial conditions might provide a source of buoyant gas directly above the repository – possibly influencing local groundwater flow. Though this example is somewhat theoretical, it serves to illustrate the possible complexities that might result as a consequence of hydrate formation.

This study shows the potential for hydrate formation within a possible repository and/or in the surrounding geosphere. However, as this was only a scoping study there is a need to make a more quantitative assessment of the processes involved. Suggestions of areas for possible future work to provide the necessary detailed data are as follows:

1) Produce a realistic climate model for site of interest. This should include an assessment of likely depths and durations of ice sheet cover and permafrost events, and also durations of warm interglacials.

2) Produce an accurate thermal model for the proposed repository site. This should include:
   a. As a starting point, an accurate assessment of current temperature profiles.
   b. A time-dependant model for ground surface temperatures through a full glacial cycle.
   c. A model of repository temperatures over time, especially if some of the waste will provide a source of heat.

    d. A time-dependant model for temperature profiles through the geosphere. This may require the generation of new data on properties such as the thermal conductivity and heat capacity of relevant rock types.

    e. Use (a)-(d) above to produce a small number of well-defined scenarios that can be used to illustrate the thermal evolution of the geosphere during future glacial cycles.

3) Produce a realistic time-dependant model for pressure gradients through the relevant parts of the geosphere, and in particular the effects of ice loading. The effects of pressure changes due to erosion of the land surface could also be investigated, though in many instances they are likely to be very small given the timescales in question.

4) Investigate likely gas compositions and production rates within the repository and the surrounding geosphere, and assess whether gas concentrations will be high enough to allow hydrates to form if pressure/temperature conditions are suitable.

5) Ascertain whether hydrate formation and disassociation will impact the physical properties of repository materials or the surrounding geosphere.

6) Assuming hydrate formation is likely to occur, assess the potential for, and impact of, episodic gas production as a result of hydrate breakdown.

7) If the results of (1)-(6) above still indicate the likelihood of hydrate formation, then a comparison exercise should be done to compare and test the different hydrate stability models available. The most appropriate one (or a new one specifically designed for modelling the repository environment) could then be used to make detailed assessments of hydrate stability within and around a possible future repository.

Investigations such as those above should lead to an improved understanding of the potential for hydrate formation within a repository and the surrounding geosphere. Ultimately, this should allow us to ascertain whether hydrate formation will be a problem, possible benefit, or of neutral consequence for the safety case of a repository.

6 Conclusions

In the future it is likely that several glacial cycles will occur within safety assessment timescales for a UK repository for radioactive wastes. These are likely to produce lower temperatures within the geosphere and also possibly higher pressures beneath ice sheets, and the effects of these need to be considered in long term safety assessments. The purpose of this scoping study was to consider if glacial/permafrost conditions had the potential to stabilise gas hydrate phases that are currently not stable within the UK onshore geosphere.

In brief, the results of the modelling are as follows:

• Neither CO_2 or methane hydrates are stable within the UK onshore geosphere under present day conditions (assumed average surface temperature of 10°C and a geothermal gradient of 25°C/km).

• For average surface temperatures below 0°C (permafrost conditions) CO_2 hydrate becomes stable in the presence of dilute groundwater about 300 m into the geosphere (with an assumed geothermal gradient of 25°C/km and pressure controlled by a hydrostatic head). Methane hydrate requires colder conditions, and an average surface temperature of -5°C would be needed to first stabilise it at about 400 m depth under similar conditions. Under likely permafrost conditions (average surface temperature of -10°C), both CO_2 and methane hydrates could be stable at likely repository depths (assumed to be about 400-800 m deep). This is particularly the case in the presence of dilute groundwaters, but they could also form in the presence of relatively saline groundwaters.

- A 1 km thick ice sheet having a basal temperature of 0°C would stabilise CO_2 hydrate beneath it in the presence of a range of fluid salinities. The CO_2 hydrate stability zone is limited however, and would not penetrate below the shallowest assumed likely repository depth (400 m). The situation is similar for ice sheets of 500-1500 m thickness. A 1 km thick ice sheet having a basal temperature of 0°C would also stabilise methane hydrate beneath it in the presence of a range of fluid salinities, and the more dilute of these would facilitate methane hydrate stability to within the shallower parts of likely repository depths. Thicker or thinner ice sheets would impart slightly deeper or shallower hydrate stability zones respectively. However, there are larger changes if a basal ice sheet temperature of -5°C is assumed. In this case CO_2 hydrate could be stable within the shallower parts of likely repository depths, and methane hydrate could be stable throughout the all likely repository depths in the presence of relatively dilute groundwaters.

Given that there appears to be significant potential for hydrate formation within a possible repository and/or in the surrounding geosphere, there is a need to make a more quantitative assessment of the processes involved. Suggestions of areas for possible future work to provide the necessary detailed data include:

- Produce a realistic thermal model for site of interest covering several glacial cycles, and produce a small number of well-defined scenarios showing changing temperature profiles through the geosphere.

- Produce a realistic model for changing pressure gradients through the relevant parts of the geosphere including the effects of ice loading (and possible land surface degradation).

- Investigate likely gas compositions and production rates within the repository and the surrounding geosphere, and assess whether gas concentrations will be high enough to allow hydrates to form if pressure/temperature conditions are suitable.

- Ascertain whether hydrate formation and disassociation will impact the physical properties of repository materials or the surrounding geosphere.

- Assuming hydrate formation is likely to occur, assess the potential for, and impact of, episodic gas production as a result of hydrate breakdown.

Investigations such as those above should lead to an improved understanding of the potential for hydrate formation within a repository and the surrounding geosphere. Ultimately, this should allow an assessment of whether hydrate formation will be a problem, possible benefit, or of neutral consequence for the safety case of a repository.

7 References

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Figure 1 CO_2 and methane hydrate stability over a range of temperatures and pressures. Constructed using data from a model by Duan and Sun (2006) – see Appendix 1. Note the curves for pure water and for a brine, and also the approximate position of part of the phase boundary between gaseous and liquid CO_2.
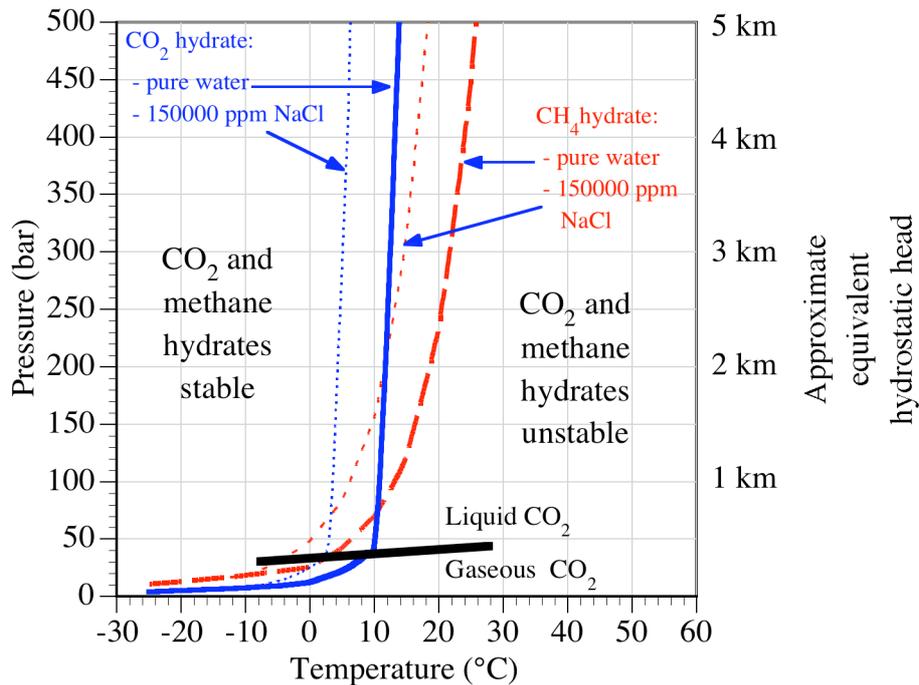
Figure 2 CO_2 and methane solubility in a seawater salinity fluid in the presence and absence of hydrate phases. CO_2 data based on Enick and Klara (1990), King *et al.* (1992), Kojima *et al.* (2003), Kuk and Montagna (1983), Wiebe (1941), Wiebe and Gaddy (1939, 1940); methane data generated using the code of Duan and Mao (2006).
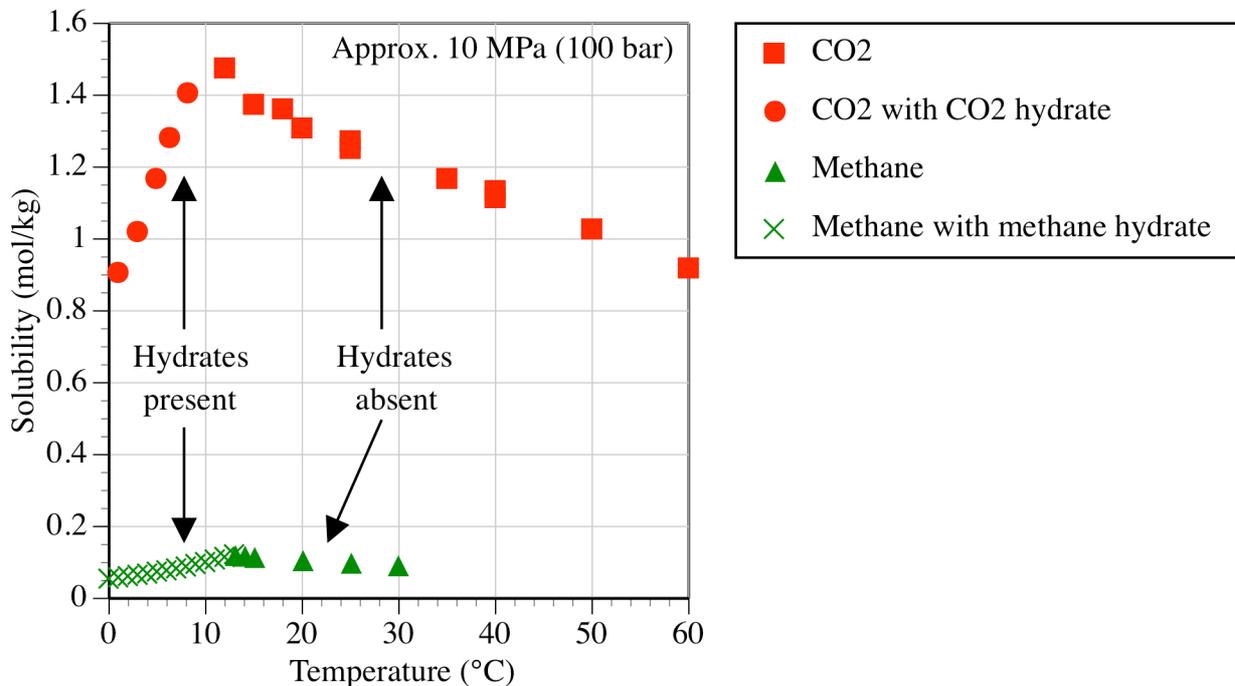
Figure 3   Present day conditions: CO₂ hydrate stability curves for range of salinities. LRD
represents the range of 'likely repository depths'.
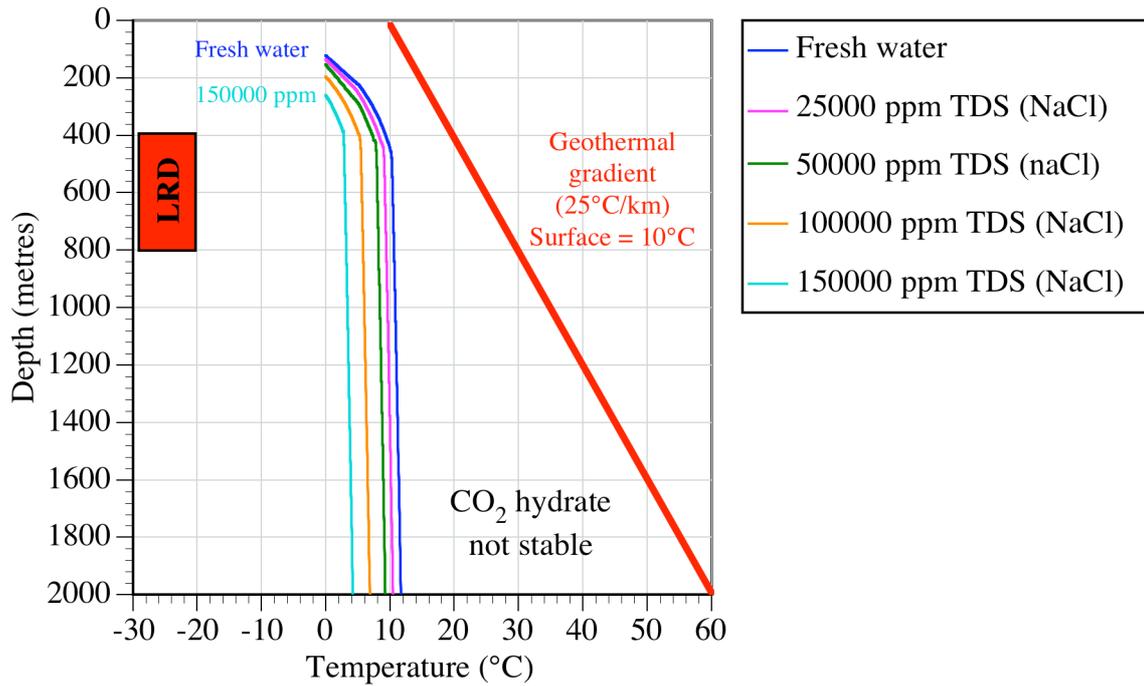
Figure 4   Present day conditions: Methane hydrate stability curves for range of salinities.
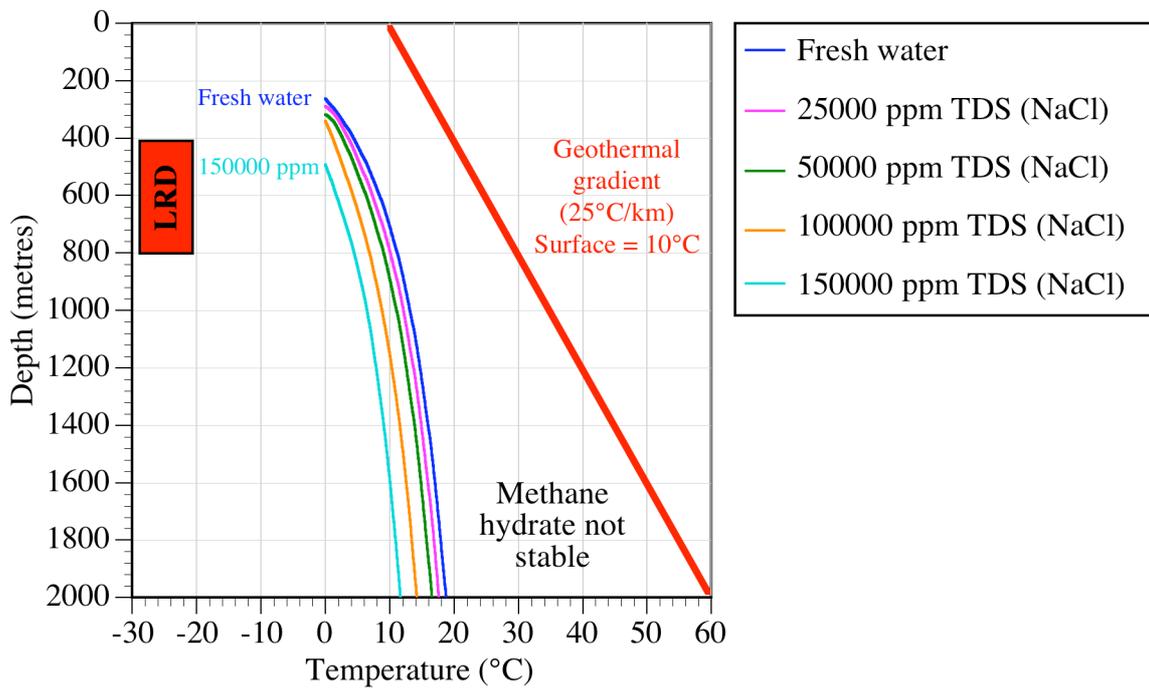
Figure 5   Permafrost conditions: CO_2 hydrate stability curves for range of salinities. The dashed line shows that CO_2 hydrate just becomes stable at a maximum surface temperature of 0°C.
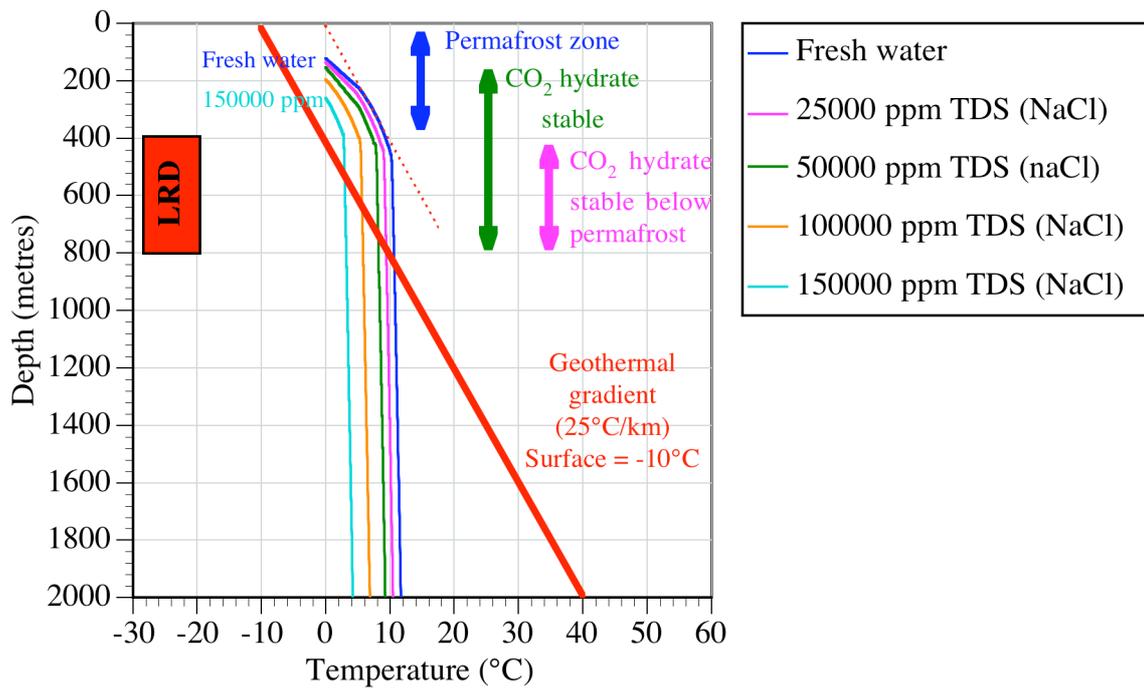
Figure 6   Permafrost conditions: Methane hydrate stability curves for range of salinities. The dashed line shows that methane hydrate just becomes stable at a maximum surface temperature of -5°C.
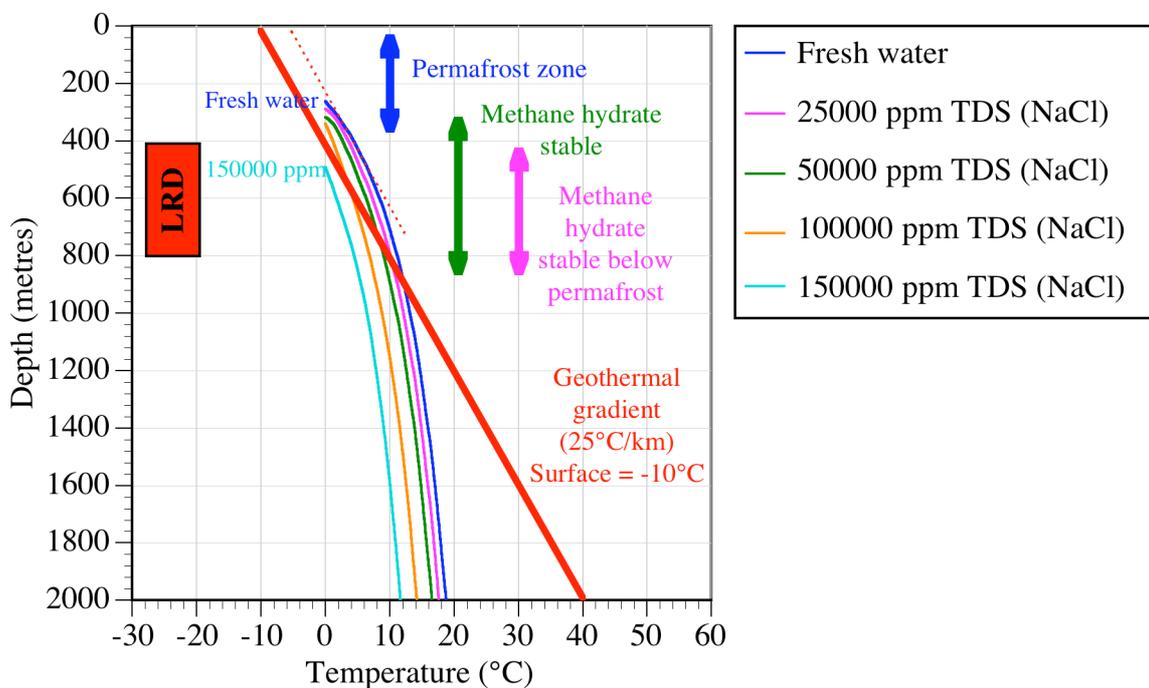
Figure 7   Ice sheet conditions: CO_2 hydrate stability curves for range of salinities. Dashed line represents a basal ice sheet temperature of -5°C.
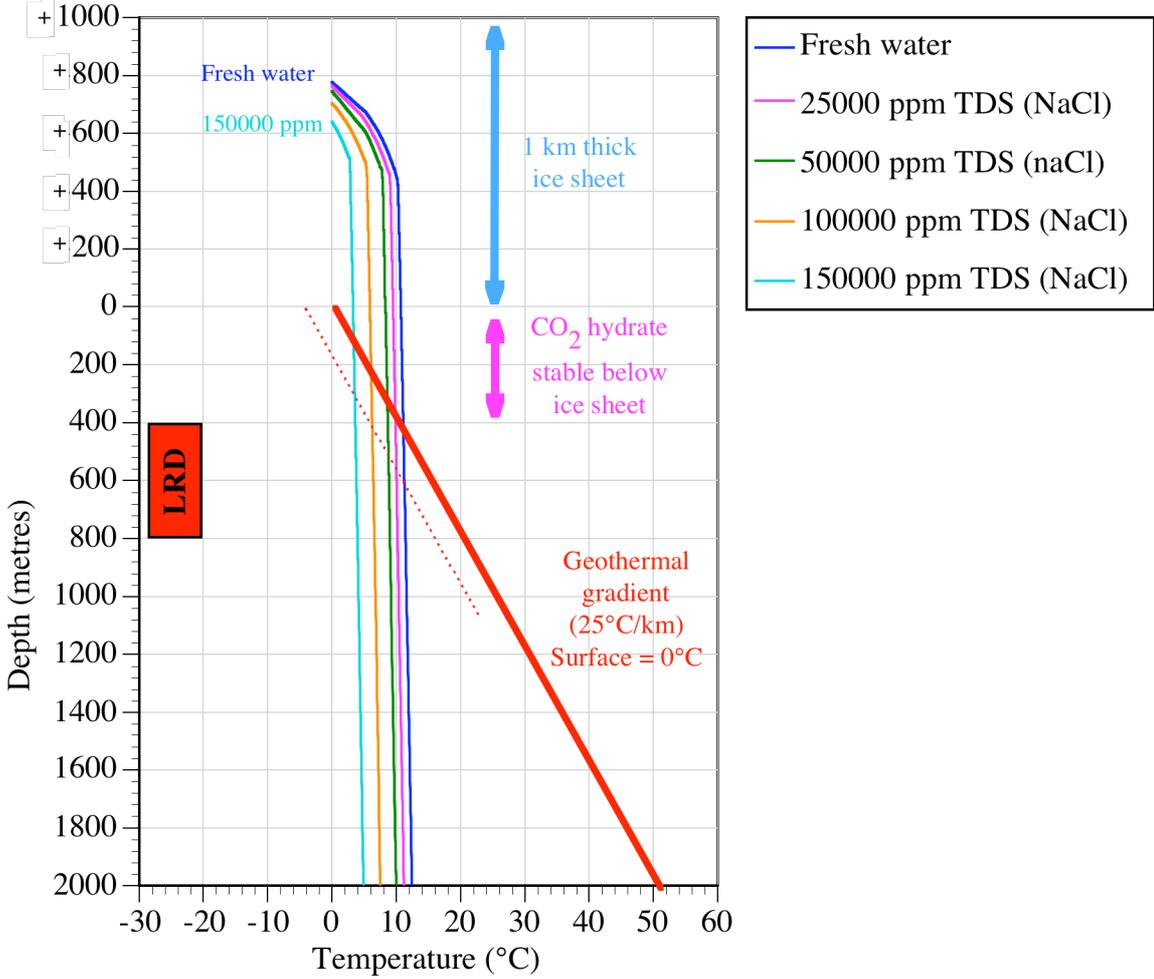
Figure 8   Ice sheet conditions: Methane hydrate stability curves for range of salinities. Dashed line represents a basal ice sheet temperature of -5°C.
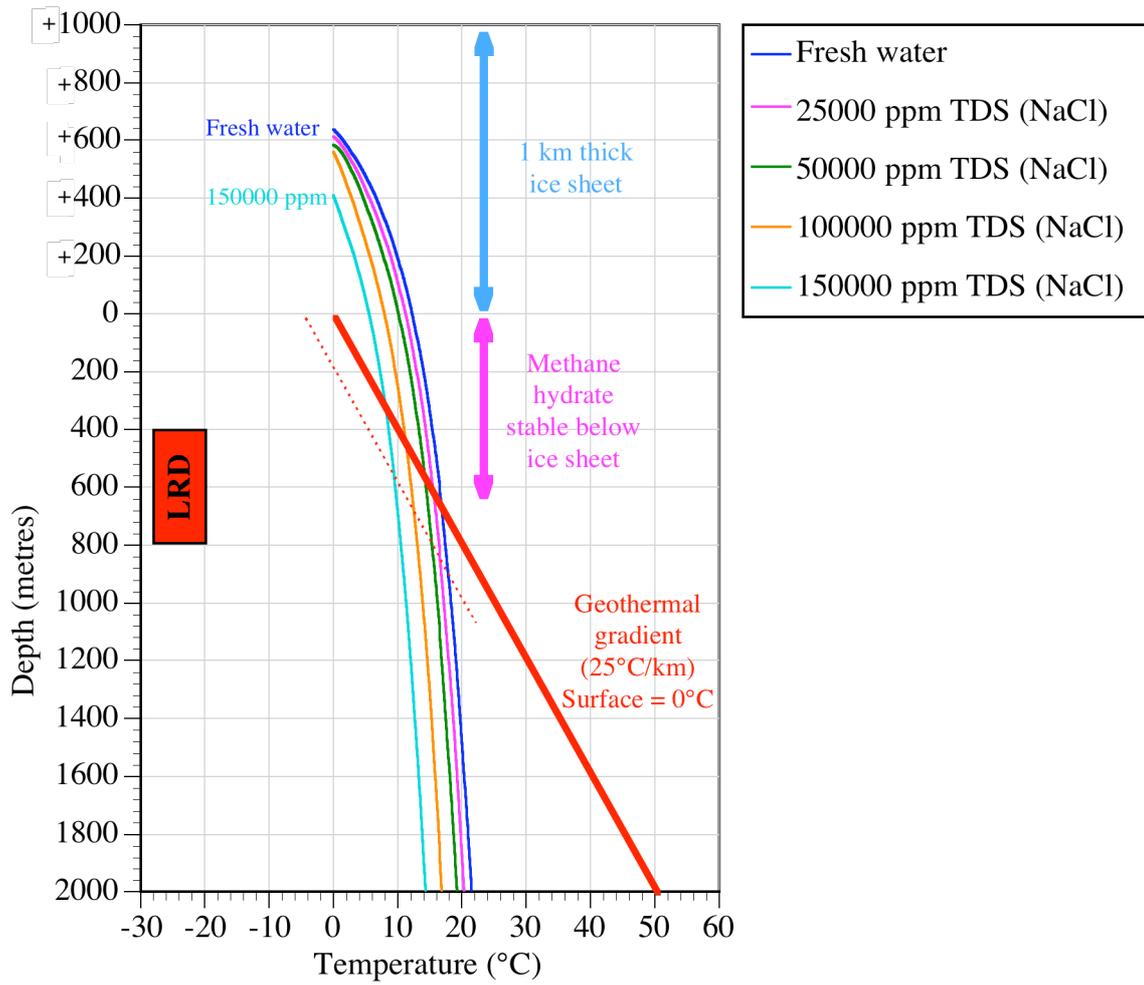
Figure 9   Schematic representation of heat from a repository warming the surrounding geosphere. This produces a region of thinned permafrost directly above the repository.
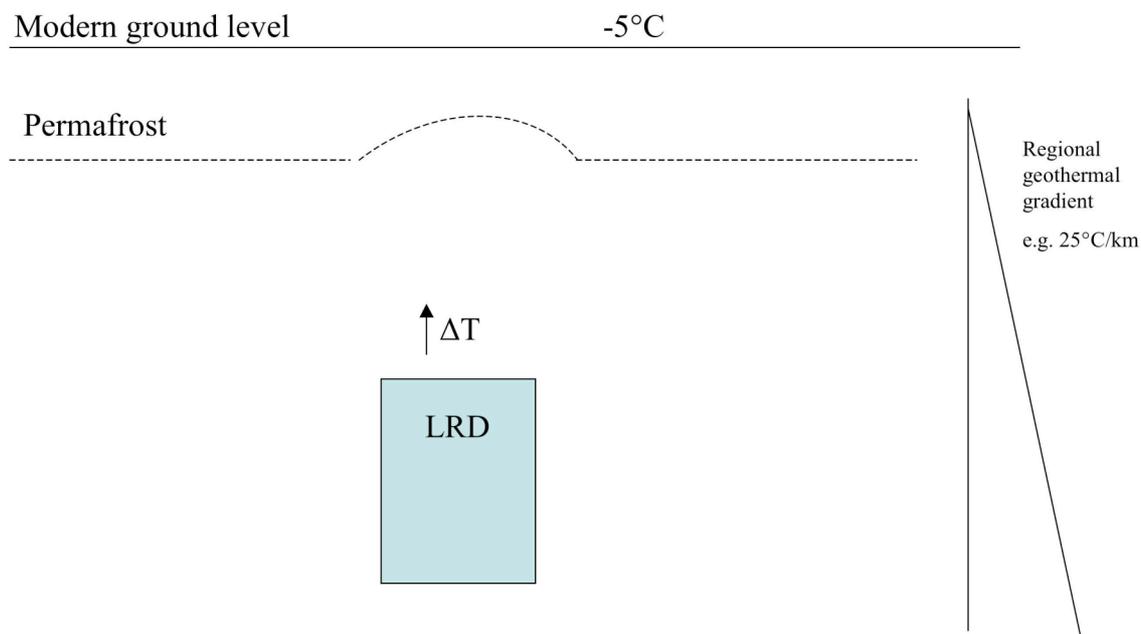
Figure 10   Schematic representation of gas accumulation under a region of thinned permafrost directly above a repository - under initial (shallower) permafrost conditions.
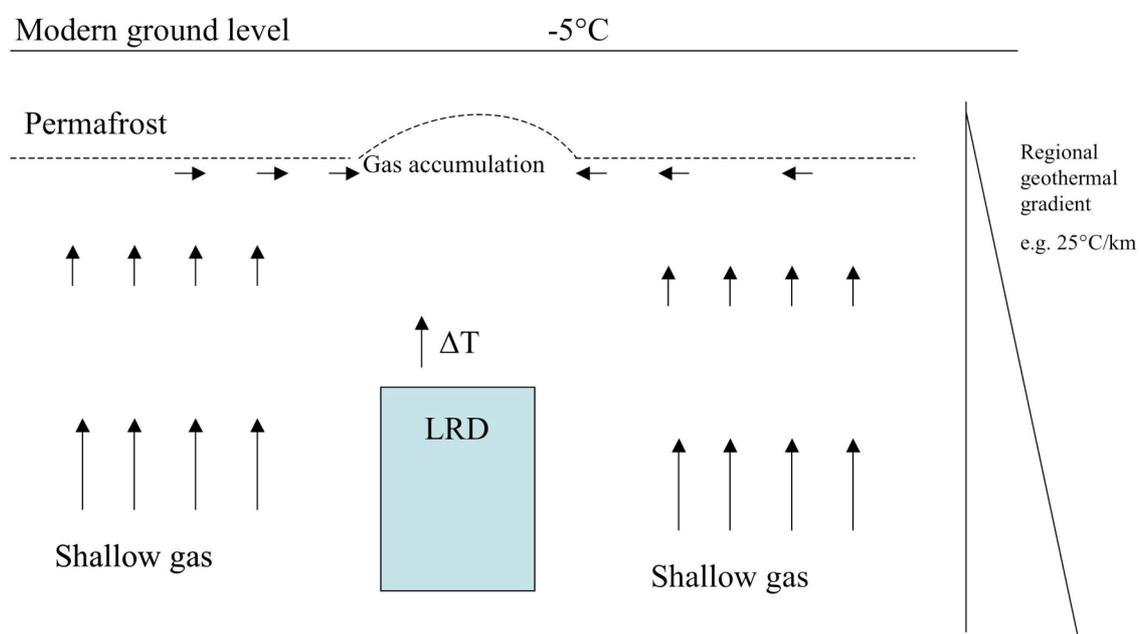
Figure 11   Schematic representation of hydrate accumulation directly above a repository under deep permafrost conditions.

Modern ground level   -10°C
_____

Regional
geothermal
gradient
e.g. 25°C/km

Permafrost
- - - - - - - - - - - - - - - - - -   Hydrate -
                                            accumulation
Methane
hydrate zone
-    ↑ ΔT - - - - - - - - - - - - - - - -

                            ┌──────────┐
↑ ↑ ↑ ↑   │   LRD   │   ↑ ↑ ↑ ↑
                            └──────────┘
Shallow gas   Shallow gas
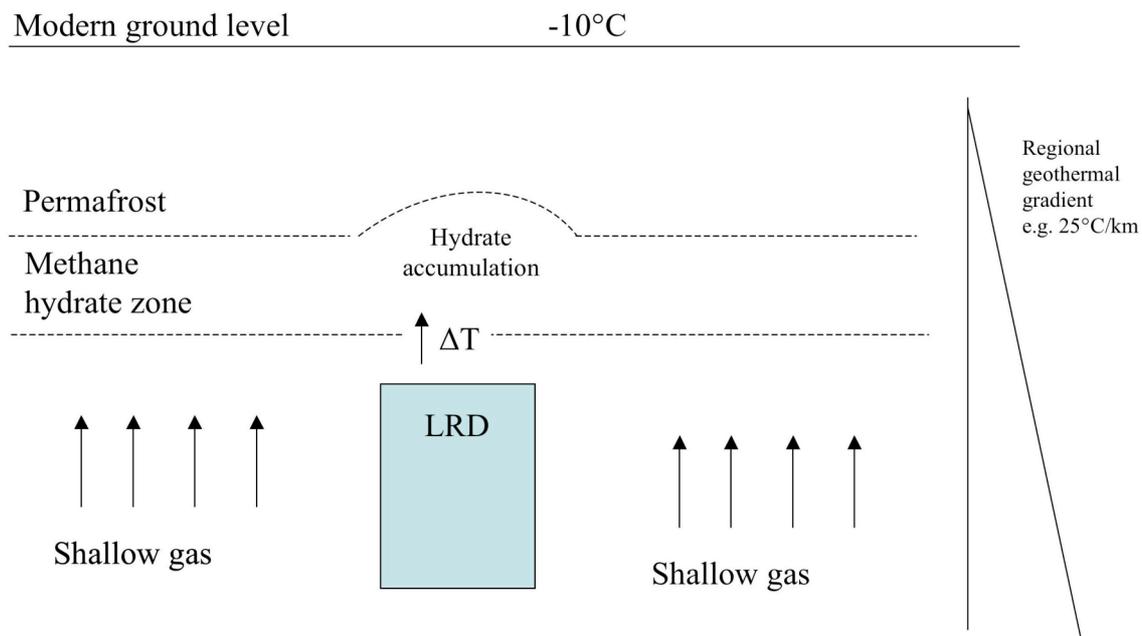
Appendix 1   Hydrate stability data

The following pages contain the data for CO_2 and methane hydrates that were used to construct the figures used in this report.

Note that more data were calculated and used for CO_2 hydrate compared to methane hydrate. This was to minimise curve-fitting artefacts produced by the software used (DeltaGraph) as a consequence of the pronounced inflection in the CO_2 hydrate stability curves.

Equilibrium pressure (bar) for CO$_2$ hydrate stability (based on a model by Duan and Sun, 2006)

Temp (°C)	Fresh water (0)	25000 ppm (0.43)	50000 ppm (0.86)	100000 ppm (1.71)	150000 ppm (2.57)
0.0	12.2	13.7	15.3	19.5	25.9
1.0				22.1	29.8
2.0				25.2	34.6
2.5					37.4
2.75					39.0
2.8					39.3
2.9					48.9
3.0				28.9	58.9
3.1					69.2
3.2					79.7
3.3					90.5
3.4					101.5
3.5					112.8
4.0				33.4	171.9
4.5		23.6		36.0	
5.0	22.1	25.1	28.7	39.0	305.0
5.25				40.6	
5.5		26.9		48.6	
5.6				58.4	
5.7				68.4	
5.8				78.7	
5.9				89.2	
6.0	25.1	28.7	33.1	100.0	457.1
7.0	28.7	33.0	38.5	218.5	723.9
7.25			40.0		
7.5			41.7		
7.75			43.5		
8.0	32.9	38.3	57.9	355.7	823.6
8.1			67.7		
8.2			77.7		
8.25			88.0		
8.3			88.0		
8.4			98.4		
8.5	35.3	41.5	109.1		
8.6			120.1		
8.7			131.2		
8.75		43.3			
8.8			142.5		
8.9			154.0		
9.0	38.1	45.2	165.7	511.5	1043.5
9.1		50.0			
9.2		59.4			
9.3		69.1			
9.4		79.1			
9.5	41.2	89.3			
9.6		99.7			
9.7		110.3			
9.75	42.9				
9.80		121.1			
9.9		132.1			
10.0	44.8	143.3	292.9	686.8	
10.1	45.6				
10.2	46.4				
10.3	50.4				
10.4	59.7				
10.5	69.2				
10.6	79.0				
10.7	89.0				
10.8	99.3				
10.9	109.8				
11.0	120.4	265.8	437.9	884.2	
12.0	236.6	406.1	601.2	1107.2	
13.0	373.1	564.3	784.4		
14.0	525.9	741.5			
15.0	697.1				

Equivalent depth (metres) for CO$_2$ hydrate stability (for an assumed hydrostatic head)

Temp (°C)	Fresh water (0)	Salinity of NaCl solution in ppm (molality in brackets) 25000 ppm (0.43)	50000 ppm (0.86)	100000 ppm (1.71)	150000 ppm (2.57)
0.0	122.1	136.6	153.1	195.0	259.0
1.0				221.3	297.9
2.0				252.3	345.7
2.5					374.3
2.75					390.1
2.80					393.4
2.90					489.3
3.0				289.0	589.4
3.1					692.2
3.2					797.4
3.3					905.1
3.4					1014.6
3.5					1127.6
4.0				333.7	1719.2
4.5		235.7		360.0	
5.0	221.2	251.4	287.3	389.8	3049.6
5.3				406.3	
5.5		268.5		486.0	
5.6				583.8	
5.7				684.2	
5.8				787.0	
5.9				892.1	
6.0	251.2	287.1	330.7	999.5	4571.3
7.0	286.5	330.1	384.6	2185.0	7238.9
7.3			400.3		
7.5			417.1		
7.8			435.3		
8.0	328.9	383.1	578.7	3557.2	8235.9
8.1			676.7		
8.2			776.9		
8.25			879.7		
8.30			879.7		
8.40			984.5		
8.5	353.5	414.9	1091.5		
8.6			1200.5		
8.7			1311.8		
8.8		432.7			
8.8			1424.8		
8.9			1540.3		
9.0	381.0	451.9	1657.2	5114.6	10434.9
9.1		500.0			
9.2		594.5			
9.3		691.5			
9.4		790.9			
9.5	412.1	892.6			
9.6		996.5			
9.7		1102.6			
9.75	429.3				
9.80		1210.7			
9.90		1320.7			
10.0	447.9	1432.9	2928.7	6868.1	
10.1	455.7				
10.2	463.9				
10.3	504.0				
10.4	596.9				
10.5	692.3				
10.6	790.2				
10.7	890.5				
10.8	992.9				
10.9	1098.0				
11.0	1204.5	2658.2	4379.1	8841.6	
12.0	2365.5	4061.2	6012.3	11072.1	
13.0	3731.1	5642.5	7844.0		
14.0	5259.4	7414.7			
15.0	6970.9				

Equivalent depth (metres) for CO_2 hydrate stability - BELOW A 1 km ICE SHEET

Salinity of NaCl solution in ppm (molality in brackets)

Temp (°C)	Fresh water (0)	25000 ppm (0.43)	50000 ppm (0.86)	100000 ppm (1.71)	150000 ppm (2.57)
0.0	-777.9	-763.4	-746.9	-705.0	-641.0
1.0				-678.7	-602.1
2.0				-647.8	-554.3
2.5					-525.7
2.75					-509.9
2.80					-506.6
2.90					-410.7
3.0				-611.0	-310.6
3.1					-207.8
3.2					-102.6
3.3					5.1
3.4					114.6
3.5					227.6
4.0				-566.3	819.2
4.5		-664.3		-540.0	
5.0	-678.8	-648.6	-612.7	-510.2	2149.6
5.3				-493.7	
5.5		-631.5		-414.0	
5.6				-316.2	
5.7				-215.8	
5.8				-113.0	
5.9				-7.9	
6.0	-648.8	-612.9	-569.3	99.5	3671.3
7.0	-613.5	-569.9	-515.4	1285.0	6338.9
7.3			-499.7		
7.5			-482.9		
7.8			-464.7		
8.0	-571.1	-516.9	-321.3	2657.2	7335.9
8.1			-223.4		
8.2			-123.1		
8.25			-20.3		
8.30			-20.3		
8.40			84.5		
8.5	-546.5	-485.1	191.5		
8.6			300.5		
8.7			411.8		
8.8		-467.3			
8.8			524.8		
8.9			640.3		
9.0	-519.0	-448.1	757.2	4214.6	9534.9
9.1		-400.0			
9.2		-305.6			
9.3		-208.5			
9.4		-109.1			
9.5	-487.9	-7.4			
9.6		96.5			
9.7		202.6			
9.8	-470.7				
9.8		310.7			
9.9		420.7			
10.0	-452.1	532.9	2028.7	5968.1	
10.1	-444.3				
10.2	-436.1				
10.3	-396.0				
10.4	-303.1				
10.5	-207.7				
10.6	-109.8				
10.7	-9.5				
10.8	92.9				
10.9	198.0				
11.0	304.5	1758.2	3479.1	7941.6	
12.0	1465.5	3161.2	5112.3	10172.1	
13.0	2831.1	4742.5	6944.0		
14.0	4359.4	6514.7			
15.0	6070.9				

Note: Negative values above represent the predicted position of hydrate stability above the base of the ice sheet.

Equilibrium pressure (bar) for methane hydrate stability (based on a model by Duan and Sun, 2006)

Temp (°C)	Fresh water (0)	25000 ppm (0.43)	50000 ppm (0.86)	100000 ppm (1.71)	150000 ppm (2.57)
	Salinity of NaCl solution in ppm (molality in brackets)				
0.0	26.2	28.8	31.7	34.1	49.1
5.0	42.5	47.1	52.2	65.2	84.8
10.0	70.9	79.2	89.0	115.3	158.8
15.0	124.5	142.0	163.4	223.2	321.0
20.0	237.0	275.3	320.8	439.6	611.5
25.0	454.8	522.7	599.6	788.6	1048.2
30.0	800.4	902.7	1017.0		

Equivalent depth (metres) for methane hydrate stability (for an assumed hydrostatic head)

Temp (°C)	Fresh water (0)	25000 ppm (0.43)	50000 ppm (0.86)	100000 ppm (1.71)	150000 ppm (2.57)
	Salinity of NaCl solution in ppm (molality in brackets)				
0.0	261.7	287.9	317.0	340.7	490.8
5.0	425.5	470.5	521.7	651.5	847.7
10.0	708.7	792.1	889.9	1152.9	1587.9
15.0	1244.8	1420.3	1633.9	2232.3	3209.6
20.0	2369.9	2752.9	3208.1	4396.2	6115.3
25.0	4547.7	5226.7	5996.1	7886.2	10481.9
30.0	8004.2	9027.4	10170.0		

Equivalent depth (metres) for methane hydrate stability - BELOW A 1 km ICE SHEET

Temp (°C)	Fresh water (0)	25000 ppm (0.43)	50000 ppm (0.86)	100000 ppm (1.71)	150000 ppm (2.57)
	Salinity of NaCl solution in ppm (molality in brackets)				
0.0	-638.3	-612.1	-583.0	-559.4	-409.2
5.0	-474.5	-429.5	-378.3	-248.5	-52.3
10.0	-191.3	-107.9	-10.2	252.9	687.9
15.0	344.8	520.3	733.9	1332.3	2309.6
20.0	1469.9	1852.9	2308.1	3496.2	5215.3
25.0	3647.7	4326.7	5096.1	6986.2	9581.9
30.0	7104.2	8127.4	9270.0		

Note: Negative values above represent the predicted position of hydrate stability above the base of the ice sheet.