THE POTENTIAL FOR METHANE HYDRATE FORMATION IN DEEP REPOSITORIES OF SPENT NUCLEAR FUEL IN GRANITIC ROCKS

Antonin Chapoy 1, Bahman Tohidi 1*, John Smellie 2 and Ignasi Puigdomenech 3

1Hydrafact Ltd, Quantum Court, Heriot-Watt University Research Park, Edinburgh, EH14 4AP UNITED KINGDOM
2Conterra AB, Stockholm, SWEDEN
3SKB, Stockholm, SWEDEN

ABSTRACT
Underground storage is one of the options being considered in Sweden and Finland for the safe disposal of spent nuclear fuel. Two sites in Sweden and four sites in Finland have been investigated for this purpose. The selected site in Sweden by SKB (Swedish Nuclear Fuel and Waste Management Co.) is that of Forsmark, while the selected site by Posiva Oy in Finland is that of Olkiluoto. Climate modelling shows that these Fennoscandian sites will undergo significant climate changes in the next 120,000 years, including glaciations with an ice thickness of perhaps up to two thousand metres. The presence of underground water with dissolved hydrocarbon gases, combined with low temperature and high pressure conditions associated with glaciations, could result in gas hydrate formation.

An eventual build up of methane gas hydrates above a potential repository for nuclear waste may give rise to some safety concerns during the expected lifespan of the repository. The dissociation of the solid methane hydrate phase to water/ice and methane gas (e.g. during warm periods), would result in a volume change that could affect the rock, especially if large quantities are dissociated in a short period of time in a confined area. The potentially large release of gas could then lead to a reduction in the strength of the bedrock hosting the repository and associated risks.

In this work a thermodynamic model was used to investigate whether the pressure, temperature, dissolved gas and salinity of the water are conductive to gas hydrate formation. Although the results showed that the amount of dissolved gas is not enough for hydrate formation, the calculations revealed some interesting behaviour of hydrate formation from dissolved gases as compared to hydrate formation from a free gas phase.

Keywords: Gas hydrate, methane, underground storage, groundwater, permafrost.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DW</td>
<td>Distilled water</td>
</tr>
<tr>
<td>H</td>
<td>Hydrate</td>
</tr>
<tr>
<td>L</td>
<td>Liquid</td>
</tr>
<tr>
<td>P</td>
<td>Pressure [bar]</td>
</tr>
<tr>
<td>T</td>
<td>Temperature [°C]</td>
</tr>
<tr>
<td>V</td>
<td>Vapour</td>
</tr>
</tbody>
</table>

Subscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>Water</td>
</tr>
</tbody>
</table>

INTRODUCTION
Underground storage is one of the options being considered in Sweden and Finland for the safe disposal of nuclear waste. Two sites have been selected for this propose. Climate modelling shows that these sites will undergo significant climate changes in the next 120,000 years, including glaciation with an ice thickness of thousands 1000s of metres. The presence of

* Corresponding author: Phone: +44(0)1314 513 672 Fax +44(0)1314 513 797 E-mail: bahman.tohidi@pet.hw.ac.uk
underground water with dissolved hydrocarbon gases, combined with low temperature and high pressure conditions associated with glaciation could result in gas hydrate formation. The gas hydrates could be accumulated during glacial periods and could be dissociated during warm periods, resulting in pressure build up and a reduction in the rock strength. Gas hydrates are commonly present in and below the current permafrost regions and it is conceivable that if the area of permafrost expands during possible future glacial periods, methane gas hydrate formation may take place under the permafrost layer due to lower temperatures even without the waste disposal sites being buried by glaciers. Such a build-up of methane gas hydrates above a potential repository for nuclear waste may give rise to some safety concerns during the expected lifespan of the repository. These include:

1. Important hydrogeological and geochemical implications of methane hydrate formation. During permafrost periods there is the potential for sealing of porosity and fracture space, thus reducing bedrock permeability. The groundwater chemistry can be affected by the freeze-out of salts well below the extent of the permafrost, to the base of hydrate formation, because methane hydrates are stable well beneath the permafrost base.

2. The dissociation of the solid methane hydrate phase to water/ice and methane gas (e.g. during warm periods), would achieve a volume change that could affect the rock, especially if large quantities are dissociated in a short period of time in a confined area. Although the porosity of the Fennoscandian granite rocks of interest is too small for this process to be of importance, methane gas hydrates could be formed in sufficient large amounts in empty cavities within the nuclear repository constructions. The potentially large release of gas could then lead to a reduction in the strength of the bedrock hosting the repository, i.e. potentially increasing the groundwater flow in the upper part of the repository bedrock.

3. In the context of a nuclear repository engineered barrier system, the melting of permafrost ice and gas hydrates may subsequently cause a dilution in groundwaters. Very dilute groundwaters will increase the stability of colloids derived from bentonite used as a buffer material to radionuclide transport. The removal of bentonite colloids during long periods of time by flowing groundwaters of very low ionic strength may affect the future performance of the nuclear repositories.

The objective of this work is to evaluate the risks associated with gas hydrate formation and dissociation (due to possible climate change in the next 120,000 years) on nuclear waste repository in granitic rock at about 500 m depth. The project will investigate the potential for hydrate formation (and subsequent dissociation, if necessary) by simulating the pressure and temperature condition.

**THERMODYNAMIC MODELLING**

A general phase equilibrium model based on the uniformity of fugacities of each component in all phases has been used to model the phase behaviour of the methane-water system. A full description and validation of the thermodynamic model can be found elsewhere [1]. Some of the predictions for hydrate phase equilibria in presence of distilled water (Figure 1) and NaCl (Figure 2) are presented below:

Figure 1. Hydrate stability of methane in the presence distilled water (DW) – Comparisons with experimental data [2-6]
RESULTS AND DISCUSSIONS

The incipient hydrate-liquid-water-vapour (H–LW–V) curve for systems containing methane in the presence of various concentrations of salt (NaCl) is presented in Figure 2. As shown in the figure, the presence of salt shifts the hydrate stability zone to higher pressure and/or lower temperature conditions.

However, in the prevailing conditions, the gas for hydrate formation is in the form of dissolved gas. In order to evaluate the potential for hydrate formation as a result of methane gas accumulation under an impermeable layer of permafrost, the methane hydrate stability zone as a function of dissolved gas and salt concentration has been calculated. In Figure 3, the maximum methane solubility, i.e., at saturation was calculated. Typical values at hydrate forming conditions for a 5 wt% NaCl concentration are given in Table 1 and plotted in Figure 4. Figures 5 and 6 show the hydrate stability temperature as a function of gas solubility at two typical system pressure of 50 and 100 bar and over a wide range of salt concentrations (i.e., 0-25 mass%).
RELEVANCE TO FINNISH SITES
Field data available from the Olkiluoto site in Finland are shown in Figure 7 and in Figure 8 [11]. Using these data, the possibility of hydrate formation for some typical NaCl and methane concentrations was analysed.

Figure 7. Salt concentrations (total dissolved solids, TDS) in the ground-waters at Olkiluoto, Finland [11]. The maximum salinities are ~10 mass% at 900 m depth. Dark blue symbol represents present day Baltic Sea salinity at Olkiluoto.

Figure 8. Methane concentrations in the ground-waters at Olkiluoto, Finland [11]. Maximum methane concentration: ~4×10^{-2} mol/L ~7.3×10^{-4} mole fraction.

Figure 9 shows the hydrate stability pressure as a function of gas solubility at various salt concentrations. The figure shows that at the maximum CH₄ content in the ground-waters from Olkiluoto (~0.00073 mole fraction) and at the corresponding salinity of 10 mass% NaCl, the stability pressure for the hydrate is 50 bar, and therefore the ground-water pressure at the corresponding depth (~100 bar) in Olkiluoto lies outside the hydrate stability zone.

The high methane concentrations at Olkiluoto represent the worst case for hydrate formation among the sites discussed here (greatest methane concentration: ~4×10^{-2} mol/L ~7.3×10^{-4} mole fraction). At 500 m depth at Olkiluoto, Figure 8 shows that the methane concentration is ~0.35 L_CH₄/L_w, which corresponds to ~0.00025 mole fraction, and in order to be inside the hydrate stability region, Figure 5 shows that the salinity needs to be larger than 25 % and the temperature below ~10 °C at the prevailing hydrostatic pressure at that depth, i.e., 50 bar.

At greater depths at Olkiluoto, i.e., at 1,000 m where the hydrostatic pressure is 100 bar, the methane concentration and salinity increases, the methane mole fraction is up to ~0.00073 and the salinity almost up to 10%. Figure 6 shows that to be inside the hydrate stability zone, the salinity needs to be higher than 20 mass% and the temperature below ~5 °C. This is also illustrated in Figure 9. The required combination of pressure, NaCl and methane to be inside the hydrate stability zone is not encountered at the site.

CONCLUSIONS
The main aim of this work was to establish whether the pertaining pressure and temperature conditions and dissolved gas concentration in
groundwater is conducive to gas hydrate formation using a modelling investigation.

The computer simulations for determining the hydrate stability zone of dissolved methane in the presence of salt show that a decrease in the system pressure and/or an increase in salt concentration favours hydrate formation, as both factors reduce equilibrium gas solubility in the aqueous phase. This behaviour is unlike that of the system including a gas phase, where a higher gas pressure (which corresponds to an increase in gas solubility) favours hydrate formation.

The main conclusion is that at the Olkiluoto site in Finland, the methane concentrations, salinities and prevailing hydrostatic pressures are outside the zone of methane hydrate stability even for future periglacial (permafrost) conditions when temperatures at the repository depths (about 500 m) are expected to become close to 0 °C for some periods of time.

ACKNOWLEDGMENTS

The authors would like to acknowledge SKB for its financial support and permission to publish this work.

REFERENCES