



# **Gas Hydrates for Deep Ocean Storage of CO<sub>2</sub>**

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## **CO<sub>2</sub>-HYDRATES FOR TRANSPORTATION AND DEEP OCEAN STORAGE OF CO<sub>2</sub>**

### **Background to the Study**

The IEA GHG R&D programme has issued reports on a range of technologies which reduce or eliminate CO<sub>2</sub> emissions from large power plants and major industrial processes by capturing the CO<sub>2</sub> for geological sequestration. Other reports have investigated the potential for geological sequestration of CO<sub>2</sub> and the associated costs. A controversial alternative to geological sequestration is injection of CO<sub>2</sub> for storage in the deep ocean, which is the likely long term destination of the large atmospheric releases of CO<sub>2</sub> which occur in the modern world.

Under the conditions which prevail in the deep ocean, liquid CO<sub>2</sub> is denser than seawater and would initially exist as pools, filling any low points on the ocean floor. However the liquid CO<sub>2</sub> pool would be in contact with seawater and, because of the high effective concentration of CO<sub>2</sub> and the low temperature, it would tend to form CO<sub>2</sub> hydrates. This phenomenon has been observed on a very small scale and is also predictable from chemical and physical properties of CO<sub>2</sub> hydrates. Furthermore it is known that CO<sub>2</sub> hydrates are denser than both seawater and CO<sub>2</sub> and should sink to the bottom of a liquid CO<sub>2</sub> pool. This predicted behaviour has lead some to conjecture that CO<sub>2</sub> hydrates could be used for long term storage of CO<sub>2</sub> on the deep ocean floor. In 1997 the IEA GHG R&D programme issued a report which reviewed Oceanic and CO<sub>2</sub> hydrate chemistry<sup>1</sup>.

This study has the aim of understanding what role, if any, CO<sub>2</sub> hydrates might play in long term storage of CO<sub>2</sub> in the deep ocean. During formulation of the study scope it became apparent that CO<sub>2</sub> hydrate deposits on the sea floor could not be stable in the long term since a necessary condition for this would be maintenance of sufficient partial pressure of CO<sub>2</sub>. As the prevailing concentration of CO<sub>2</sub> in the surrounding seawater is very low, any hydrate deposit would slowly decompose. Observed dissolution rates for small portions of hydrate indicated that dissolution could be several centimetres per day and, even if this could be reduced by a few orders of magnitude, for example by burying or otherwise sealing the hydrate from the surrounding seawater, inevitably the hydrate deposit would decompose. It could not survive for the tens of thousands of years expected of long term storage.

One attribute of CO<sub>2</sub> hydrates which is worth noting in this context is that the density of CO<sub>2</sub>-hydrate is greater than that of seawater at all depths, which means the hydrate would sink. Solid CO<sub>2</sub> also enjoys this advantage. Other means of transporting CO<sub>2</sub> to the deep ocean as liquid or gas require the CO<sub>2</sub> to be physically routed to the release point at several thousands of meters depth. This is not a trivial thing to do either from cost or logistical viewpoints.

A further attribute of CO<sub>2</sub>-hydrate as compared to pure CO<sub>2</sub> is the comparative ease of transport. The substance is meta-stable and can, in principle, be moved by bulk carrier without refrigeration. Liquid CO<sub>2</sub>, on the other hand, has to be moved in pressurised tankers which are expensive and limited in size. Solid CO<sub>2</sub> might be more amenable to cheap bulk transport but would probably require some refrigeration and is rather expensive and energy intensive to produce.

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<sup>1</sup> Ocean storage of CO<sub>2</sub>. A review of oceanic carbonate and CO<sub>2</sub> hydrate chemistry. IEA GHG September 1997



A study was thus commissioned to establish the costs and feasibility of using CO<sub>2</sub> hydrates for transport from an onshore capture site to a deep ocean location. Other aspects of a possible role for CO<sub>2</sub>-hydrates in deep ocean CO<sub>2</sub> storage are also considered.

## **Approach adopted**

No work has been done on large scale production and transport of CO<sub>2</sub>-hydrates. A few organisations have studied production and transport of methane hydrates primarily as an alternative to LNG<sup>2</sup> schemes. A limited amount of work has been done on use of CO<sub>2</sub> hydrates as the basis for a CO<sub>2</sub> capture process<sup>3</sup>. Thus, in order to assess the option of using CO<sub>2</sub>-hydrates, it was necessary to draw heavily on experiences in the development of the methane hydrate transport process. Even the production of methane hydrates on a large scale is poorly understood and no pilot scale facilities have ever been built and operated for a complete production process. Estimating the costs and feasibility would thus have to be undertaken on a rather broad basis, utilising overall heat and material flow requirements, the general properties of the materials to be handled and the generic chemical engineering unit operations most likely to be applicable. It is on this basis that the selected contractor, Aker Kvaerner Technology (Norway) was asked to proceed with this part of the study.

Consideration of the other roles of CO<sub>2</sub> hydrates in ocean storage schemes was done in house and is summarised in this overview. Some supporting calculations are attached in an appendix to this overview.

## **Results and Discussion**

### **Roles of CO<sub>2</sub> hydrates in deep ocean storage**

The main potential roles identified for CO<sub>2</sub> hydrates are:-

- 1) As a transient intermediate which can affect the way CO<sub>2</sub> disperses in the deep ocean
- 2) As long term storage, when buried beneath a sufficiently thick layer of sediments
- 3) As means of transporting CO<sub>2</sub> by ship from a coastal location – transportation to a deep sea storage site is examined in this report but in principle the technology might also be useful for long distance shipment of CO<sub>2</sub> for geological storage.

Each of these is discussed separately below.

#### **1) Transient intermediate**

One of the main roles of CO<sub>2</sub> hydrates in deep ocean storage is as an intermediate which will form whenever CO<sub>2</sub> is introduced into cold seawater in such a way that there is a significant CO<sub>2</sub> partial pressure. CO<sub>2</sub> hydrates are the stable species when water and sufficient CO<sub>2</sub> are in contact at temperatures below 11°C. Because the deep seabed temperature is just a few degrees above zero Celsius, the conditions are right for hydrates to form if CO<sub>2</sub> is injected in quantity. For example between 2 and 4°C, a typical seafloor temperature at depths of >3000m, a CO<sub>2</sub> partial pressure of 18 to 20 bars results in hydrate formation. Liquid CO<sub>2</sub> at this temperature has a somewhat higher effective partial pressure (around 35-40 bar), so that hydrate formation will occur immediately at the liquid-CO<sub>2</sub>/water interface. When the solid hydrate forms, the main effect is one of greatly slowing the dissolution process. Above large open pools of CO<sub>2</sub>, any hydrate which forms is likely to sink, thus re-exposing the water/liquid CO<sub>2</sub> interface. It should be noted that liquid CO<sub>2</sub> is lighter than seawater down to a depth of

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<sup>2</sup> Liquefied Natural Gas

<sup>3</sup> For example see report Ph3/26 Capture of CO<sub>2</sub> using water scrubbing

about 2750 meters below which compressibility effects result in it being heavier, with the tendency to lie in pools on the ocean floor.

In the case of small droplets of gas or liquid a more stable solid film can form. However this has only a short lived effect on slowing the dissolution of CO<sub>2</sub> in water; these are probably only of relevance in determining the local concentrations of CO<sub>2</sub>, and hence acidity, which occur when a stream of pure CO<sub>2</sub> is released in the hydrate forming zone.

## 2) Storage under sediments

As mentioned above, a partial pressure of about 20 bar is required to stabilise CO<sub>2</sub> hydrates in the deep ocean. The solubility of CO<sub>2</sub> in water is such that this equates to an equilibrium concentration of about 4%wt.

The pressure solubility curve for CO<sub>2</sub> in water is shown in figure 1 (based on data from Crawford and others, 1963; Holm, 1963, Jarrell and others, 2002). Note the rather nonlinear behaviour above about 70 bars (1000psi) partial pressure. General circulation of seawater can be expected to cause rapid dilution and reduction in local CO<sub>2</sub> levels. It is thus evident that CO<sub>2</sub> hydrates could only be stored for the long term in the deep ocean, if they are buried under sufficient sediment to prevent the ready migration of CO<sub>2</sub> released by decomposition.

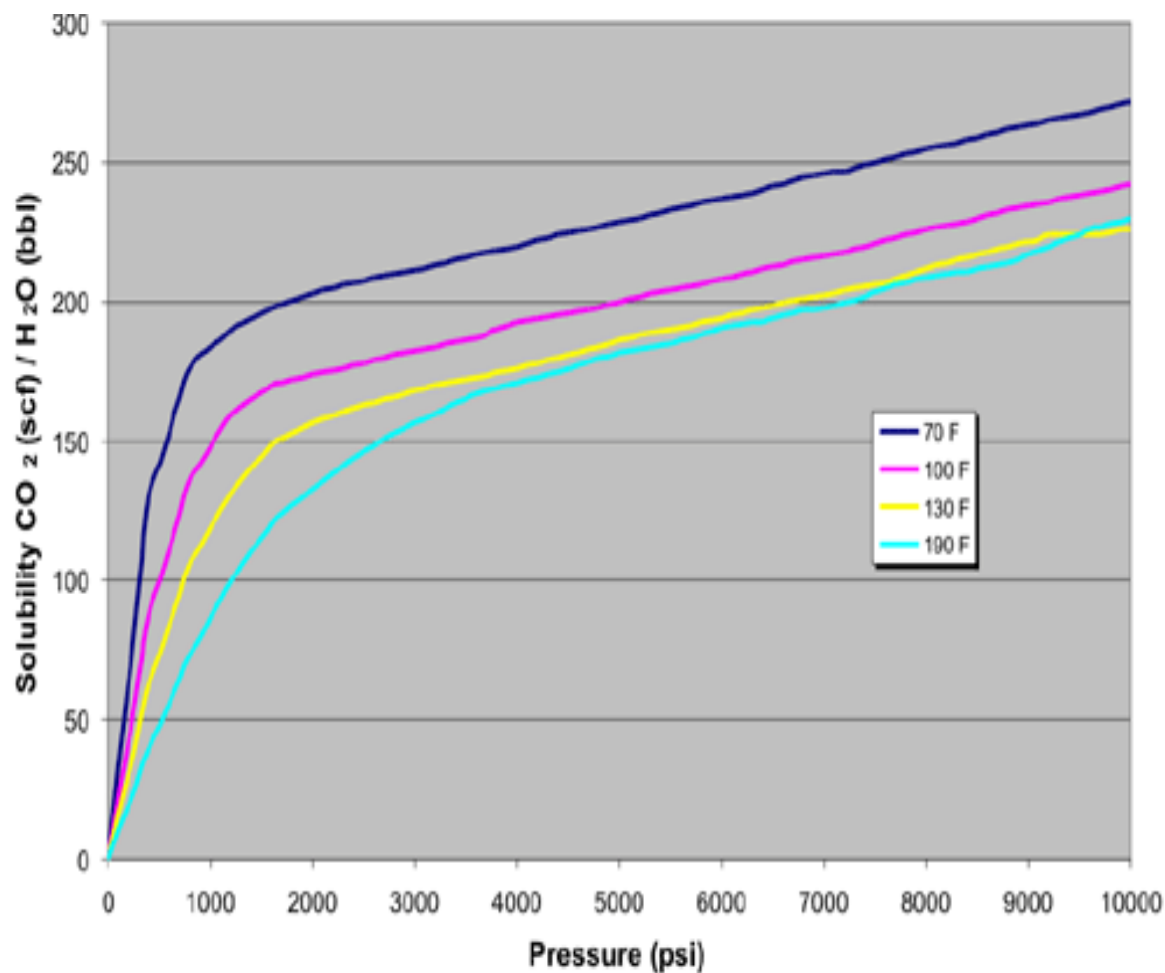


Figure 1. Variation of CO<sub>2</sub> solubility in pure water with pressure

Methane hydrate deposits are found below the sea floor. Because of the geothermal gradient they are only stable to limited depth (a few hundred meters) in the sediments. Also, because in the open ocean there is no concentration of methane to stabilise the hydrates, they are not found unless there is a layer of 100m or so of sediment above them. (An exception to this is isolated deposits around natural gas seepages on the sea floor where there is sufficient methane concentration to stabilise the hydrate.) The layer of sediment is sufficient to effectively seal in the methane on geological time scales. Methane hydrates, unlike CO<sub>2</sub>-hydrates, are lighter than water and so, without some overburden, would float upwards.

The phase equilibrium for CO<sub>2</sub>-hydrates is similar to that for methane although methane hydrates are stable up to slightly higher temperatures. It would thus appear that CO<sub>2</sub> could, in principle, be stored as hydrate on the sea floor, if a substantial overburden was placed on top. This is illustrated by the small triangular region at the bottom of the overall hydrate stability zone shown for methane in figure 2 (based on a diagram produced by Herriot-Watt University). However, placing such a thick layer of overburden is considered to be a rather impractical proposition and this storage possibility is not considered further here.

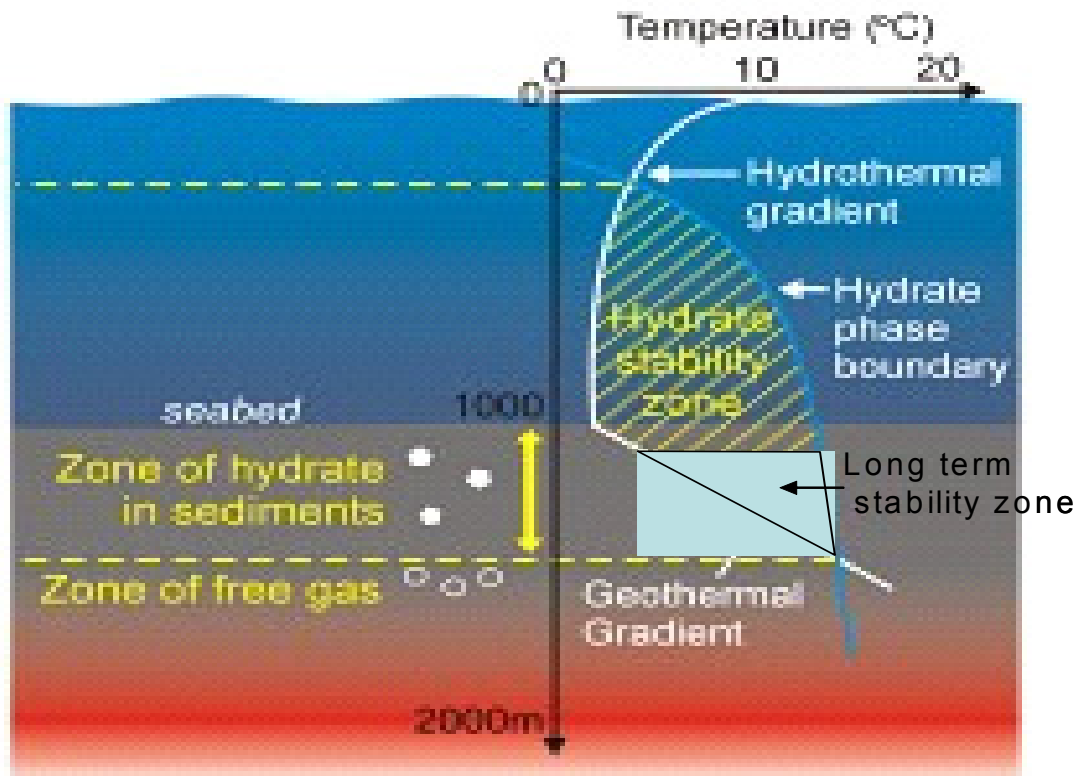


Figure 2 Methane hydrate stability zone

### 3) Transport and dispersal of CO<sub>2</sub>-hydrates

Theoretically pure CO<sub>2</sub> hydrates can contain almost 30% weight of CO<sub>2</sub> with the balance being water. Such hydrates are meta-stable at atmospheric pressure and slightly sub-zero temperature. This means that they could be transported in bulk without pressurisation or active refrigeration. The relatively high weight content might make this economically attractive in comparison with the alternatives for shipping CO<sub>2</sub> which are either as a refrigerated liquid under a pressure of at least 6 bar or as a solid below the sublimation temperature of -55°C.

Similar comparisons have been made for transport of natural gas as hydrates with the conclusion that transport as a liquid in atmospheric refrigerated tankers is somewhat more economic. In the case of methane the hydrate transport route suffers from a much lower theoretical weight content (little more than 10%), and from the fact that methane (unlike CO<sub>2</sub>) can be liquefied at atmospheric pressure. This means that ships for transporting methane hydrate would have much smaller effective capacity than those for CO<sub>2</sub>-hydrate transport leading to higher unit costs. A complementary study, on the cost of bulk liquid CO<sub>2</sub> transport, is in hand and will enable a comparison to be made of these 2 shipping options.

This report, prepared by Aker Kvaerner Technology (AKT), considers the prospects for designing and operating a CO<sub>2</sub> hydrate production and transport process along these lines and gives a rough estimate of the unit costs. Production equipment and vessels for containing hydrates have never been constructed or tested so the designs on which this study is founded are assessments of the general sort of equipment which would be required. The main features of this report are described below.

A brief assessment of the likely fate of CO<sub>2</sub>-hydrates when released to sink into the deep ocean has also been made and is presented in an appendix to this overview.

### **CO<sub>2</sub>-hydrate production process**

The AKT report proposes a hydrate formation process in which hydrate crystals are grown in large, continuously-stirred tank reactors to form a hydrate/water slurry. This slurry is then dried to less than 10% free water in two steps using hydro-clones followed by mechanical centrifuges. The wet crystals are then contacted with cold liquid CO<sub>2</sub> to cool them down to be stable enough for transport and to convert some more of the residual water to CO<sub>2</sub>-hydrate. In order to produce large dense blocks with very low porosity a conventional rolling mill is proposed. The overall process is plausible but, apart from elements of the first reaction stage, is unproven. It does however indicate the main material and heat flows as well as equipment requirements and sizes so that an estimate of the capital and operating costs can be made.

Key assumptions are:

1. the ability to grow crystals with high CO<sub>2</sub>/water stoichiometry
2. the ability to compact the material to a very low voidage.
3. the ability to agglomerate and handle the material as large lumps

Only if these three are possible will the hydrate product be in a form which will sink without significant decomposition.

The process is amenable for both land based and deep ocean operation. However the deep ocean case requires the largest size of floating structure yet deployed.

### **Transportation**

The preferred method of shipping is in bulk atmospheric carriers, typically of about 150 000 tonnes deadweight. Special, insulated holds would be required but, more significantly, would have to be designed for bottom withdrawal of the material with a mechanical handling system. This would bring the material to moon pools from which it would be allowed to sink in the ocean. A more reliable but also more expensive alternative might be discharge doors in the bottom of the hold, allowing discharge directly to the sea. In all cases the discharge system occupies significant space which reduces the effective capacity of the ships.

Such ships could also be used for transporting CO<sub>2</sub>-hydrate on the way to onshore geological storage sites, although this application has not been assessed here.

## **Sinking process**

Calculations were performed to determine how large the lumps of hydrate would have to be to allow them to sink without significant dissolution on the way down. It proved difficult to quantify this accurately as there is much uncertainty about the sink rate and the dissolution rate. However it is concluded that lumps in the order of 20 cm to 1 meter would be required.

## **Costs**

The most important conclusions of this work are the predicted costs. If these are excessive, then this process of bringing about deep ocean storage will not be competitive. For the case of onshore manufacture, with a typical sailing distance of 1000km, the overall cost is calculated to be \$20/tonne of CO<sub>2</sub> stored. The efficiency of capturing the CO<sub>2</sub> in the hydrate is about 87%. The offshore case, in which cold liquid CO<sub>2</sub> is delivered to the offshore site, costs \$22/tonne with an efficiency of 85% and includes a notional \$8/tonne for pressurised shipping of liquefied CO<sub>2</sub>.

## **Health, Safety and Environmental considerations**

There are some risks associated with transport of CO<sub>2</sub>-hydrate as it slowly decomposes with release of an asphyxiating, mildly toxic gas. However these risks do not appear to be insurmountable. The main environmental effects are associated with the presence of the hydrate on the sea bed for a number decades and the altered pH and CO<sub>2</sub> concentration near the storage site. The extent of these effects is outside the scope of this report. There is a minor environmental effect resulting from the consumption of significant quantities of potable water. This might be alleviated if non-potable water was suitable for hydrate formation and a suitable source could be found.

## **Fate of the hydrate deposit**

Rough calculations indicate that a hydrate pile of 1 or 2 km diameter might be expected to form. There would be some dispersion of the material as it sank due to ocean currents and the asymmetric shapes of the lumps. This dispersion might be no more than a few hundred meters and may not have much effect on the size of the hydrate pile. It would take about a decade for the pile to build up to a size at which the supply rate equalled the dissolution rate; on cessation of the project the pile could take 5-10 years to disappear.

## **Expert Reviewers' Comments**

Expert reviewers expressed concerns about the practicality of the proposed hydrate production process, the assumed capacity of the ships and the possibility that the material might be difficult to unload after a period in the cargo holds. These concerns are very real and the authors of the report do stress the considerable uncertainties which exist. Nevertheless the report is able to give an indication of the likely costs on the basis that favourable solutions are found for all of the required steps. The capital costs are considered to be with -50 to + 80% which is felt adequately reflect these uncertainties. Even so it has to be accepted that "showstoppers" might exist which would make practical deployment of the system impossible.

## Major Conclusions

A main conclusion of this work is that CO<sub>2</sub> cannot be stored in the deep ocean in the form of hydrates for any significant period because the material is not stable. A second conclusion is that ocean transport of CO<sub>2</sub> in the form of hydrates is expensive but not excessively so. Until there is a better understanding of the cost of alternative shipping options it cannot be entirely disregarded.

Finally CO<sub>2</sub> hydrates could offer a way of bringing CO<sub>2</sub> into the deep ocean in a relatively benign form.

## Recommendations

The costs of CO<sub>2</sub> hydrate shipping need to be compared to the options of solid CO<sub>2</sub> and liquid CO<sub>2</sub> shipping to determine whether there is any chance that it could be competitive.

If it is found that there is a chance that it is competitive, further work might be undertaken to establish whether there are any significant environmental advantages of delivering CO<sub>2</sub> in the dilute form of hydrates rather than as pure liquid or solid CO<sub>2</sub> for storage in the deep ocean. Its usefulness for delivering CO<sub>2</sub> for geological storage should also be explored at that time.

In order to develop a practical process a great deal of experimental work would be required. All the relevant material and stream properties and kinetics of hydrate formation/dissociation would need detailed measurement as little data is currently available. Pilot scale tests of the various process steps would be required. A more thorough examination of the types of process equipment which could be employed for the various unit operations should also be made. There are alternative devices to those suggested in this report which might be more effective, such as pressurised rotary filters instead of centrifuges, and extruders instead of double rollers. The environmental impact of CO<sub>2</sub>-hydrate pile in the deep ocean would have to be established.

Further significant investment in research on CO<sub>2</sub>-hydrate manufacture would be unwise until there is a reasonable consensus as to the acceptability of deep ocean storage of CO<sub>2</sub>, or until the value of this method of transportation for geological storage is demonstrated.



## **Appendix**

### **Build up and dissolution of CO<sub>2</sub>-hydrates deposited at surface for deep ocean storage**

#### **Background**

The study of the manufacture and transport of CO<sub>2</sub>-hydrates did not estimate the size and lifetime of the temporary accumulation on the ocean floor, nor did it estimate what the local effect might be on CO<sub>2</sub> concentration and pH. This note gives a rough estimation of these factors.

The CO<sub>2</sub>-hydrate is formed into large lumps and, it is assumed, allowed to sink to the bottom of the deep ocean for long term storage. The lumps are expected to form a temporary accumulation of hydrate before decomposing; as a result of this, the CO<sub>2</sub> content will dissolve in the surrounding seawater with consequent effects on CO<sub>2</sub> concentration and pH.

#### **Approach**

In order to make order of magnitude estimates, very simple geometric models are proposed for the sinking, accumulation and dissolution processes. In view of even greater uncertainties as to prevailing currents and dissolution rates, these models are considered adequate to give an indication of the size and lifetime which is what is required for this study. Much background information on disposal of CO<sub>2</sub> in the ocean can be found in the following publications:

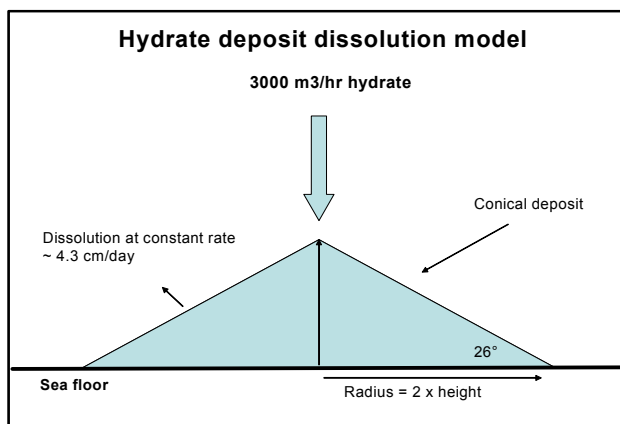
- Direct Ocean Disposal of Carbon Dioxide. Edited by N Handa and T Oshumi. Terrapub, Tokyo, 1995. ISBN 4-88704-1115-2
- Ocean Storage of CO<sub>2</sub> – A review of Oceanic Carbonate and CO<sub>2</sub> Hydrate Chemistry. Sept 1997 report by IEA Greenhouse Gas R&D programme ISBN1 898373 09 4

Useful general information is available at the following URLs

- National Energy Technology Laboratory.  
<http://www.netl.doe.gov/scng/hydrate/about-hydrates/conditions.htm>
- Herriot Watt University  
[http://www.pet.hw.ac.uk/research/hydrate/hydrates\\_where.html](http://www.pet.hw.ac.uk/research/hydrate/hydrates_where.html)

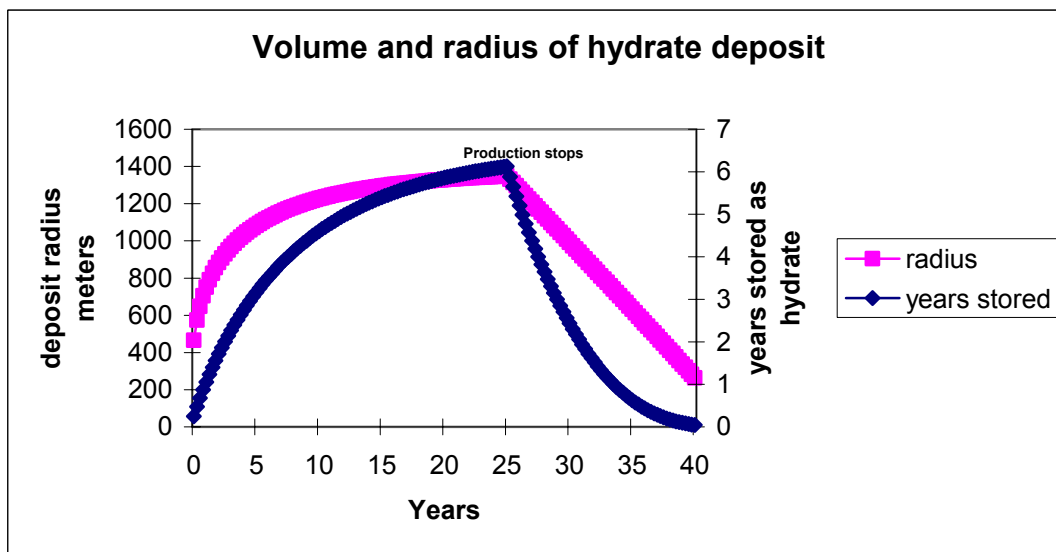
## Estimation of dimensions of the deposit

Rough calculations have been made of the size of hydrate deposit which would form and its lifetime once continuous addition of hydrate was stopped. This has been based on a simple model in which the falling hydrate spreads out with a constant angle of repose to form a conical deposit (see fig A1). The dissolution is presumed to occur at constant rate over the surface of the cone. The rate of dissolution is taken as the same as used in the calculations on dissolution during sinking in the AKT report which is about 4.3 cm per day. The cone is taken as having radius equal to twice the height (equivalent to an angle of repose of 26 degrees). A 3000 m<sup>3</sup>/hr deposition rate storing 20, 000 tons per day of CO<sub>2</sub> (the basis for the AKT study) would result in a cone approximately 1.4 km in diameter and 350 meters high which would take 5-10 years to build up to equilibrium size. On cessation of the operation the deposit would substantially disappear after about 10 years. Times and sizes are greatly affected by the assumed dissolution rate but not by the shape of the deposit. The conical deposit, which it is presumed would build up on the sea floor in this simple model, represents only about 6 years of deposition, so most of the material placed during a long term project would dissolve.



**Fig A1 Simplified geometry of hydrate deposit**

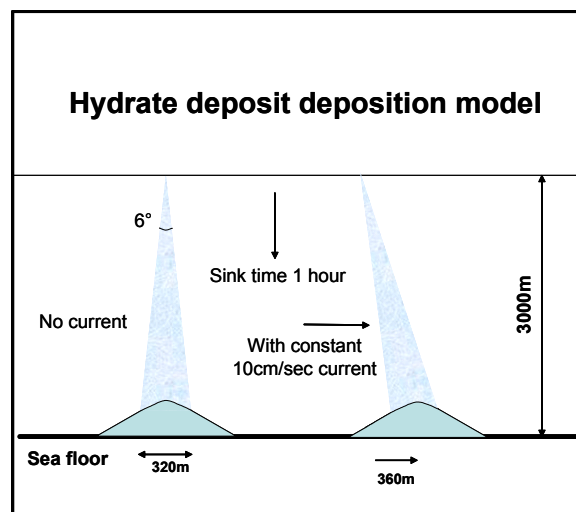
Figure A2 (below) illustrates these predictions. It is concluded that it would be impractical to consider covering any hydrate deposit formed because most of the hydrate would have dissolved by the time the covering operation was started and most of the remnants would dissolve before an adequate covering could be put in place.



**Fig A2 Build up and decay of hydrate deposit with time**

In practice lumps of hydrate sinking over a trajectory of 3000 m will land on the sea floor distributed over a considerable area. The extent of this distribution will depend on the extent and variability of ocean currents and on the aerodynamic shape of the lumps. Only limited data could be found on the shape of such a distribution.

Practical experience from ocean disposal of mine tailings, drill cuttings and civil engineering rock dumping operations might provide further insight into these dispersal processes. In the absence of currents, irregularly shaped lumps will fall in an erratic way so that they can be visualised as falling into the base of a cone which has its top as the discharge point. If the deviation from vertical fall is, say, up to 3 degrees of arc the bulk of the material will fall within a radius of 160 meters after descending 3000 meters. This is smaller than the size of the temporary hydrate mountain (radius ca. 700 meters).



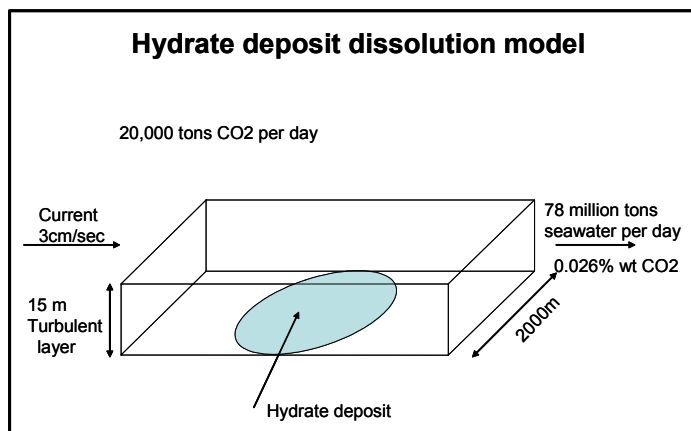
**Fig A3 Dispersion of hydrate whilst sinking**

Deep ocean locations will not be subject to strong currents and most of the sinking trajectory will be affected predominantly by weaker, less variable flows which might typically be of the order of several cm/sec. A 10cm/sec general current acting over a 1 hour sinking time will result in material moving about 360 meters from the release point. The combination of random fall and current effects will be to increase the area covered by the hydrate deposit but not greatly. Also the increased area exposed for dissolution will limit the effect and it is likely that the area covered by the temporary deposit will no more than a few square kilometres. This simple model is illustrated in fig. A3.

### Estimation of local pH changes

Very rough estimates of local pH can be made. The equilibrium concentration of CO<sub>2</sub> at the surface of pure hydrate at deep sea bed temperature conditions will be about 4% wt. This corresponds to a local pH of about 3.5.

To estimate pH in the general vicinity of the deposit it is assumed (see fig A4) that there is a small current of 3 cm/sec and that the turbulent boundary layer is 15 meters thick. The width of the deposit is taken as 2000 meters. The average concentration which would build up in this stream due to release of 20,000 ton/day of CO<sub>2</sub> is then about 0.025% wt CO<sub>2</sub> corresponding to a pH of about 5.7. Thus in the near field, local acidity would be quite high



**Fig A4 Model of released CO<sub>2</sub> initial dilution**



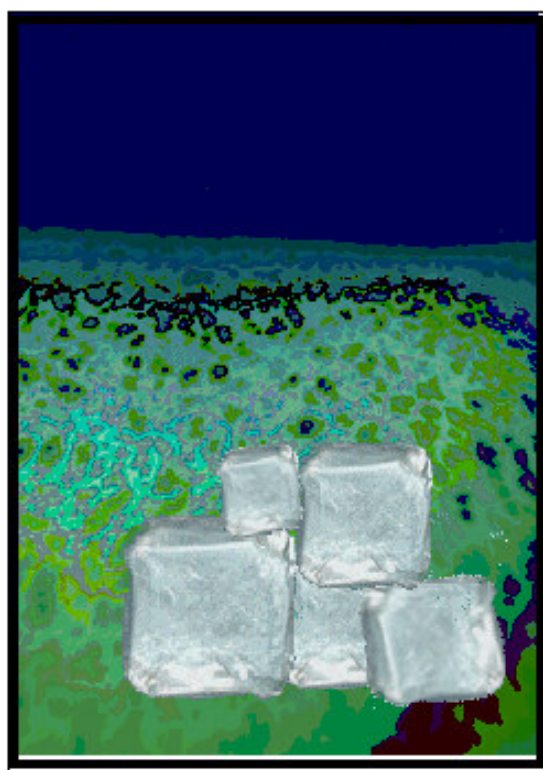
compared to the typical normal level in the sea of 8.1. To increase pH to an acceptable value, say within 0.5 units of the ambient level, a further dilution of about 75 times would be required.



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# Gas Hydrates for Deep Ocean Storage of CO<sub>2</sub>

October, 2003



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# TECHNICAL DOCUMENTATION FRONT SHEET



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## EXECUTIVE SUMMARY

The objective of this study was to determine the cost and feasibility of using carbon dioxide hydrates in the transport chain for Deep Ocean disposal of CO<sub>2</sub>.

The report addresses a novel concept for using hydrates for Deep Ocean disposal of CO<sub>2</sub>. The CO<sub>2</sub> rate investigated was 20,000 tonnes/d. Two cases were evaluated:

- Coastal Location

CO<sub>2</sub> is converted to hydrates in a land-based production plant under pressure. The resulting CO<sub>2</sub> hydrates are brought to sub-zero temperatures and depressurised, prior to being compacted to hydrate blocks. The hydrate blocks are shipped to an offshore location in bulk-type carriers. The fundamental basis for the transport scheme is that hydrates are metastable at atmospheric pressure and below-zero temperatures. 1000 km offshore, the hydrates are discharged overboard. By virtue of the relative higher density of CO<sub>2</sub> hydrates compared to seawater, the hydrates will sink to the bottom of the Deep Ocean, which will absorb the released CO<sub>2</sub> upon dissociation of the hydrates. The total CO<sub>2</sub> capture efficiency has been estimated to 87%.

- Offshore Location

CO<sub>2</sub> is converted to hydrates on a deck-based production plant under pressure. The resulting CO<sub>2</sub> hydrates are compacted to hydrate blocks and depressurised, prior to discharging overboard. By virtue of the relative higher density of CO<sub>2</sub> hydrates compared to seawater, the hydrates will sink to the bottom of the Deep Ocean, which will absorb the released CO<sub>2</sub> upon dissociation of the hydrates. The total CO<sub>2</sub> capture efficiency has been estimated to 84%.

The analysis is not a full life cycle analysis and only considers emissions directly related to the operation of the production and transport system. The full environmental impact of a hydrate process is not covered in this feasibility study and must be evaluated separately.

Large volumes of fresh water are consumed by the process and could be a significant resource constraint.

Large-scale production and transportation of hydrates is a novel technology that has not been proven. As such, there exist several uncertainty elements in the technical feasibility evaluation. Substantial research & development as well as detailed engineering and cost estimates are required prior to constructing a hydrate transport chain.

The CAPEX estimates are 50/50 estimates with overall accuracy of  $\pm 50\%$  and 80% confidence interval. The following abatement costs, exclusive capture, have been estimated:

- Coastal Location Case: 23 US\$/tonne CO<sub>2</sub>
- Offshore Location Case: 25 US\$/tonne CO<sub>2</sub>

The onshore plant estimates is based on estimates of the equipment cost and developed by equipment cost factoring representative for gas processing plants in the Far East.

These numbers are not directly comparable, as the CO<sub>2</sub> is assumed available at the offshore location. Hence, a CO<sub>2</sub> transportation cost needs to be added to the Offshore Location Case in order to compare the options.

In the presented concept, focus has been placed on utilisation of “proven” equipment components to reach a concept that in itself is not yet commercialised. Investment and operating cost savings may potentially be realised if new technology components are incorporated.

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Aker Kværner Technology has through the years been involved in several studies where hydrates have been evaluated as a means for gas transport. However, all of the work performed has been related to the production and transport of natural gas – not CO<sub>2</sub> – hydrates. AKT has in this study drawn on experience from earlier studies related to natural gas hydrates, but have modified solutions to correspond with capture and transport of CO<sub>2</sub>. Where no literature data on CO<sub>2</sub> hydrates was found, natural gas hydrate properties have been assumed valid.

Technology and know-how gaps have been identified and include separation equipment, hydrate block production and offloading techniques, in addition to fundamental knowledge of the resulting CO<sub>2</sub> hydrates' properties, e.g. dissociation rates in water, effective density and behaviour under transportation. In particular, the effective density of the hydrate blocks is crucial for the feasibility of hydrates for Deep Ocean Storage of CO<sub>2</sub>. It is essential that the effective density of hydrate blocks as a function of possible gas content, free water content, gas entrapment, etc. is studied in more detail.

In addition, the data transfer from natural gas systems has to be verified. Recommendations for further work focus on investigation of these fundamental properties.

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## 1. INTRODUCTION AND SUMMARY

### 1.1. BACKGROUND

Greenhouse gases have been accumulating in the atmosphere since the industrial revolution and carbon dioxide is the main greenhouse gas emitted by human activities. The concentration of CO<sub>2</sub> in the atmosphere has increased from about 280 ppm, before the industrial revolution, to the present day value of 370 ppm (IEA GHG 2002). The main source of CO<sub>2</sub> emission from human activities is fossil fuel combustion and the largest single contributor to emissions from fossil fuels is power generation. Transport is another major contributor. CO<sub>2</sub> sinks include storage in the atmosphere and ocean uptake.

The International Energy Agency Greenhouse Gas R&D Programme (IEA GHG) was established in 1991 to evaluate technologies that could be used to avoid emissions of greenhouse gases, particularly from the use of fossil fuels and to identify targets for useful R&D. IEA GHG is an international organisation, supported by sixteen countries world-wide, the European Commission and several industrial organisations.

The Programme managers have been asked to commission a study to establish the costs and feasibility of using CO<sub>2</sub> hydrates for ocean disposal of carbon dioxide as a means to abate CO<sub>2</sub> emissions. Aker Kværner Technology (AKT) was awarded the study "Gas Hydrates for Deep Ocean Disposal of CO<sub>2</sub>" and has performed the study in accordance with Scope of Work described in latest revision of document "IEA/CON/02/83 Gas Hydrates for Deep Ocean Disposal of CO<sub>2</sub>" (June 12, '03).

It is known that CO<sub>2</sub> readily forms gas hydrates when contacted with water at elevated partial pressure and temperatures below 11 °C. It has been envisaged that CO<sub>2</sub> hydrates can be utilised as the basis for Deep Ocean disposal processes in two ways:

1. Bulk transport of CO<sub>2</sub> to the disposal site. Hydrates may contain a large amount of captured CO<sub>2</sub>; up to a theoretical maximum of 184 Sm<sup>3</sup> CO<sub>2</sub> per m<sup>3</sup> hydrate. By converting CO<sub>2</sub> gas to solid hydrates, a cost-efficient way of transporting the gas may be achieved.
2. A method of sinking CO<sub>2</sub> to the bottom of the Deep Ocean by virtue of the relatively high density of the hydrate. The underlying principle is that the density of the pure hydrate is greater than that of seawater so that CO<sub>2</sub> hydrates discharged into the ocean will sink. In the absence of sufficient CO<sub>2</sub> partial pressure, CO<sub>2</sub> hydrates exposed to seawater will decompose. Hydrate particles discharged into the ocean should be of a sufficient size so that only a small percentage of the captured CO<sub>2</sub> is released before reaching the Deep Ocean.

In this study, bulk production, transport and sinking of solid hydrates have been evaluated.

AKT has through the years been involved in several studies where hydrates have been evaluated as a means for gas transport. However, all of the work performed has been related to the production and transport of natural gas. AKT has in this study drawn on experience from earlier studies related to natural gas hydrates, but have modified solutions to correspond with capture and transport of CO<sub>2</sub>.

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## 1.2. CONCEPT SUMMARY

Two cases for utilising hydrates in the transport chain for Deep Ocean disposal of CO<sub>2</sub> were evaluated:

- Coastal Location  
CO<sub>2</sub> is to be converted to hydrates in a land-based production plant. The hydrates shall be shipped to a location 1000 km offshore, where the hydrates are discharged overboard. The hydrate blocks discharged into the ocean should be of a sufficient size so that only a small percentage of the captured CO<sub>2</sub> is released before reaching the Deep Ocean.
- Offshore Location  
CO<sub>2</sub> is to be converted to hydrates on a deck-based production plant. The hydrates are to be discharged overboard directly from the offshore structure. The hydrate blocks discharged into the ocean should be of a sufficient size so that only a small percentage of the captured CO<sub>2</sub> is released before reaching the Deep Ocean.

A critical issue for both cases is the ability to create adequately dense hydrate blocks. This requires compaction to achieve low porosity as well as a high CO<sub>2</sub> content in the crystal structure and low free water content.

The concepts for the two options are summarised below.

### Coastal Location

20.000 tonnes/d CO<sub>2</sub> arrives at the hydrate production plant at 10 bara and 30 °C. The gas is pressurised and cooled, and contacted with fresh water at 36 bara and 2 °C. Conversion of the gas to hydrates takes place in stirred tank reactors, a total of 8 off, divided on 4 trains. The system is excess water-continuous due to the need for efficient heat removal. The hydrates are separated from the water phase by cyclonic separation equipment.

Long-distance transportation of hydrates is only considered feasible for atmospheric, sub-zero conditions, where hydrates are in a meta-stable state. Hence, the hydrates are frozen (approx.-11 °C) and depressurised. The resulting hydrate particles are compacted to hydrate blocks and loaded onto a specially designed bulk-type carrier vessel. Four carriers are recommended, eliminating the need for large capacity onshore hydrate storage and excess handling. Discharge of the hydrates offshore is performed through a moonpool in the vessel.

The following key data are presented:

Design Rate	20000	tonne/d CO <sub>2</sub>
Hydrate Production Rate	3000	m <sup>3</sup> /hr
Transportation Rate	3577	tonnes/hr
Hydrate Heat of Formation	313000	kW
Heat Removal	42952	kW (Seawater Cooling)
	360000	kW (Cooling Media)
Power Demand	78193	kW (Electrical)
	60480	kW (Turbine)
Equipment Dry Weight	8090	tonnes
Transport Distance	1000	km
Carrier Cargo Capacity	120,000	tonnes
Number of Carriers	4	
Estimated CO <sub>2</sub> Emission	2698	tonnes/d
CO <sub>2</sub> Capture Efficiency	87%	

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### Offshore Location

20.000 tonnes/d CO<sub>2</sub> arrives at the hydrate production plant at 10 bara and -50 °C. The gas is pressurised and contacted with fresh water at 36 bara and 2 °C. Conversion of the gas to hydrates takes place in stirred tank reactors, a total of 8 off, divided on 4 trains. The system is excess water-continuous due to the need for efficient heat removal. The hydrates are separated from the water phase by cyclonic separation equipment.

The hydrates are compacted to hydrate blocks in high-pressure compactors prior to depressurisation and directly discharged overboard.

The following key data are presented:

Design Rate	20000	tonne/d CO <sub>2</sub>
Hydrate Production Rate	3000	m <sup>3</sup> /hr
Hydrate Heat of Formation	313000	kW
Heat Removal	3400	kW (Seawater Cooling)
	355000	kW (Cooling Media)
Power Demand	47195	kW (Electrical)
	56000	kW (Turbine)
Equipment Dry Weight	6492	tonnes
Fresh Water Requirements	2740	m <sup>3</sup> /hr
Offshore Structure	modified, newbuilt VLCC	
Water Supply	VLCC, 1 off	
Estimated CO <sub>2</sub> Emission	3154	tonnes/d
CO <sub>2</sub> Capture Efficiency	84%	

### 1.3. COST SUMMARY

The following abatement costs have been estimated for the two concept options:

- Coastal Location Case: 23US\$/tonne CO<sub>2</sub>
- Offshore Location Case: 25US\$/tonne CO<sub>2</sub>

The onshore plant estimate is based on estimates of the equipment cost and developed by equipment cost factoring representative for gas processing plants in the Far East. The offshore plant estimate is based on equipment cost factoring for offshore FPSO for oil and gas processing, adjusted for the requirements of a hydrate formation plant. The cost estimates for the hydrate bulk carriers and VLCC tanker for water transport are based on international new-build prices. The hull for the offshore plant is likewise based on a VLCC tanker hull adjusted for the requirements of a topside hydrate plant.

These numbers are not directly comparable, as the CO<sub>2</sub> is assumed available at the offshore location. Hence, a CO<sub>2</sub> transportation cost needs to be added to the Offshore Location Case in order to compare the options.

### 1.4. COMPARISON OF OPTIONS

The feasibility of both the Coastal Location and the Offshore Location options are dependent on technology development and proper design, and on the mapping of fundamental properties of the hydrates and their behaviour. It is at this stage not possible to differ between the options based on feasibility as both options are subjected to significant uncertainties.

Using cost evaluations, the CO<sub>2</sub> abatement cost for the Coastal Location Case seems to be significantly lower than for the Offshore Location Case when the liquid CO<sub>2</sub> transport to the offshore site is included.

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### 1.5. RECOMMENDATION FOR FURTHER WORK

Large-scale production and transportation of gas hydrates has been investigated since the early 90's. Several companies are still exploring the hydrate technology as an alternative transport alternative for moderate and smaller gas volumes to the market. However, production and transportation of gas hydrates is a novel technology that has not been proven. As such, there still exist some uncertain technical elements in the conceptual design. Substantial research & development are still required to confirm the feasibility for the gas hydrate transport chain.

Most important are the know-how gaps related to fundamental knowledge of the resulting CO<sub>2</sub> hydrates' properties, e.g. effective density, dissociation rates in water and behaviour under transportation. In addition, the data transfer from natural gas systems has to be verified. It is strongly recommended to focus on these fundamental variables, as they are decisive for the technical feasibility of utilising gas hydrates for Deep Ocean disposal of CO<sub>2</sub>.

If utilising hydrates in the transport chain for Deep Ocean storage of CO<sub>2</sub> is to be evaluated further, it is suggested to carry out a development program in two phases.

1. Firstly, the fundamental properties of CO<sub>2</sub> hydrates should be investigated. This stage should include, but is not limited to, the following experimental investigation:
  - Production of CO<sub>2</sub> hydrates with low free-water content.
  - Measuring the CO<sub>2</sub> content of the above hydrates.
  - Measuring the density of the above hydrates.
  - Testing the feasibility of hydrate compacting.
  - Measuring the dissociation rates of hydrates in seawater.
  - Measuring the stability of the compacted hydrates at negative temperatures.
  - Measuring the stability of the compacted hydrates under stress.

The sequence indicates the criticality of the parameters and investigations should be carried out in this order. Detailed knowledge of these fundamental values should form the basis for any further evaluation of the hydrate process.

2. Secondly, if the fundamental values above are considered suitable for the hydrate process, engineering parameters and large-scale equipment should be evaluated. This phase is believed to be more extensive than the first phase, and should among other factors include:
  - Reaction rate studies to determine hydrate reactors.
  - Hydrate/water separation equipment.
  - Continuous hydrate freezing.
  - Large-scale hydrate depressurisation.
  - Large-scale hydrate block production.
  - Ship loading and offloading techniques/equipment.

We strongly recommend to carry out the experiments that are outlined in phase 1, if the hydrate production and transportation chain for Deep Ocean storage of CO<sub>2</sub> looks commercial attractive.

There are several good reasons for this approach:

- ❑ The experiments are of fundamental nature
- ❑ The results of these experiments give two options: go or no go
- ❑ The experiments are relatively easy to carry out
- ❑ Existing laboratory at NTNU (Norwegian University of Science and Technology) in Trondheim is available for such experiments, at moderate cost. Small-scale pilot and apparatus are available.

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## 2. STUDY DESIGN PREMISES AND ASSUMPTIONS

### 2.1. GENERAL

AKT has not in any way in this report assessed Deep Ocean disposal of CO<sub>2</sub>. It is in AKT considered opinion that all environmental impacts related to ocean disposal must be evaluated in great detail prior to utilising the ocean as a sink for CO<sub>2</sub>.

Bulk production and transport of gas hydrates have never been done on an industrial scale and the hydrate technology is as such not proven. Some of the equipment has not even been demonstrated on a laboratory scale. AKT has in this study drawn on experience from earlier studies related to natural gas hydrates, but has modified solutions to correspond with capture and transport of CO<sub>2</sub> instead of natural gas. Available in-house database for technologies and cost for relevant processes/equipment has been used. Where new technology is needed, this is specified, and solutions are outlined. Development and engineering of novel technologies have however not been performed. Substantial research & development as well as detailed engineering and cost are required prior to constructing a hydrate transport chain.

### 2.2. OBJECTIVE

The objective of this study was to determine the cost and the feasibility of using gas hydrates in the transport chain for Deep Ocean disposal of CO<sub>2</sub>.

### 2.3. SCOPE OF WORK

The Scope of Work for the present study is described in latest revision of document "IEA/CON/02/83 Gas Hydrates for Deep Ocean Disposal of CO<sub>2</sub>" (June 12, '03).

The following cases were studied:

#### **Coastal Location**

Bulk production of CO<sub>2</sub> hydrates is to be designed for a land-based production plant. The hydrates shall be stored at the plant if necessary – prior to shipping to an offshore location. The hydrates shall be discharged offshore and allowed to sink to 3000 m. The hydrate production process shall be capable of producing hydrate material which will sink without more than a few percent dissolving during the journey to 3000 m water depth.

#### **Offshore Location**

Bulk production of CO<sub>2</sub> hydrates is to be designed for a deck-based production plant. The offshore hydrate production process shall be similar to the land based process. The hydrates shall be discharged overboard and allowed to sink in at 3000 m. The hydrate production process shall be capable of producing hydrate material which will sink without more than a few percent dissolving during the journey to 3000 m WD. The Offshore Location Case will hence be very similar to the Coastal Location Case, but without storage and transportation.

In addition, a brief analysis of the challenges related to production of hydrates in a subsea facility was to be undertaken.



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## 2.4. DESIGN BASIS AND ASSUMPTIONS

The main underlying assumptions for this study are summarised in Appendix B – Basis of Design. This document was agreed with the Client prior to conducting the study.

The main production and design data are as follows:

Gas rate: 20,000 tons per day of CO<sub>2</sub>. This corresponds to  $10.8 \cdot 10^6$  Sm<sup>3</sup> CO<sub>2</sub>.  
 Gas inlet conditions: 10 bar, 30 °C for Coastal Location Case  
 10 bar, -50 °C for Offshore Location Case  
 Seawater conditions: 10 °C  
 Transport distance: 1000 km

For the Offshore Location Case, the supplied CO<sub>2</sub> is in liquid state for efficient transportation to the offshore site. The CO<sub>2</sub> is assumed pressurized and refrigerated to minimize design pressure and hence cost.

A hydrate gas content of 150 Sm<sup>3</sup> CO<sub>2</sub> pr. m<sup>3</sup> hydrate, excluding voids, is assumed. The hydrate plant shall hence be designed for a production of approximate 3000 m<sup>3</sup> pure hydrate.

In the case of separation of hydrates from water, a separation efficiency of 90% is assumed, i.e. 10% of the separation product is water.

The assumption of hydrate gas content in connection with the assumed separation efficiency results in a bulk gas content of 133 Sm<sup>3</sup> CO<sub>2</sub> pr. m<sup>3</sup> final product.

No evaluation of the CO<sub>2</sub> chain upstream the hydrate production facility has been performed (capture and/or transportation), i.e. it is assumed that CO<sub>2</sub> is “available” at the production facilities at the above-stated conditions.

Necessary electrical power is assumed imported for the Coastal Location Case, whereas it is generated on-site for the Offshore Location Case (diesel turbines). CO<sub>2</sub> emission from electrical power generation has been included in the CO<sub>2</sub> balance both for the Coastal and the Offshore Location Cases.

Assumptions made in connection with cost estimates are given in Chapter 9.

## 2.5. HYDRATE PROPERTIES USED IN THE STUDY

Assumption		Results	
Hydrate Gas Content:	150 Sm <sup>3</sup> CO <sub>2</sub> pr. m <sup>3</sup> pure hydrates	} Bulk gas content:	133 Sm <sup>3</sup> CO <sub>2</sub> pr. m <sup>3</sup> cargo
Separation Efficiency:	90 %		Bulk hydrate density: 1052 kg/m <sup>3</sup>
Heat of formation	350 kJ/kg		
Heat capacity	2.2 kJ/kgK		



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### 3. GENERAL SYSTEM DESCRIPTION

#### 3.1. INTRODUCTION

The CO<sub>2</sub> hydrate chain is split into three major components:

- Production facilities
- Transportation
- Sinking

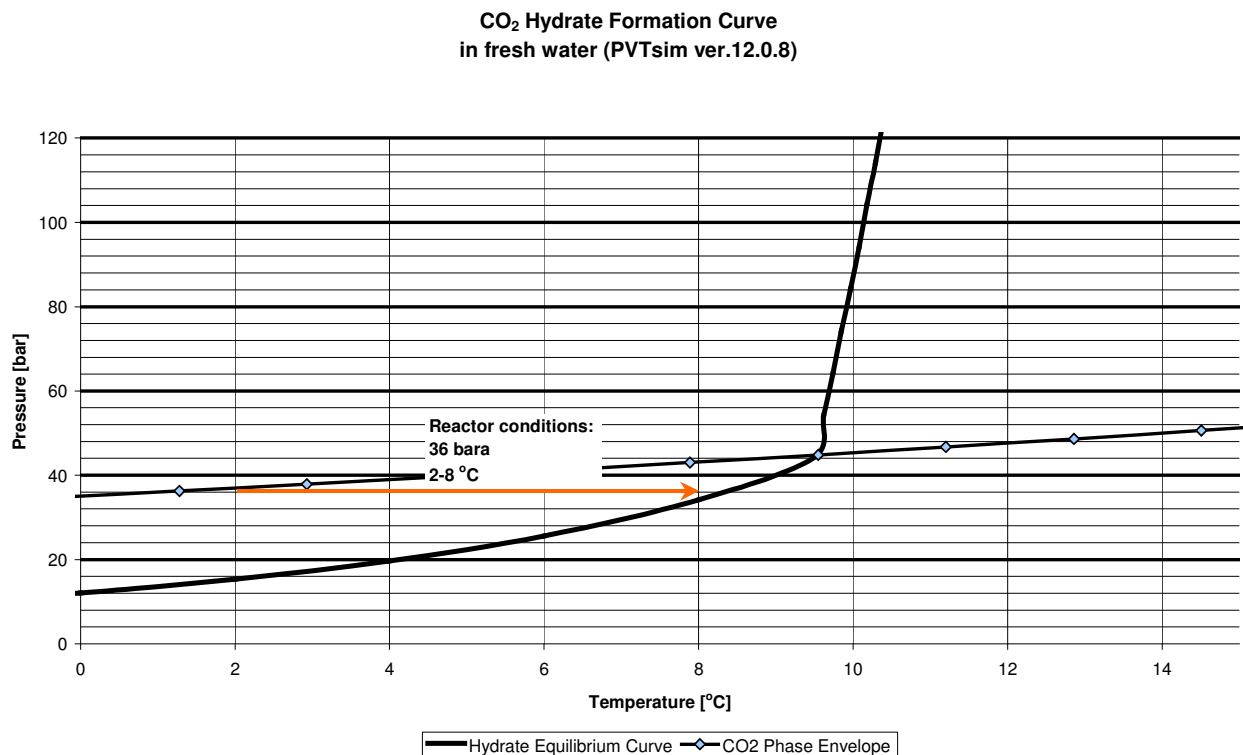
For the Offshore Location Case, only production and sinking is included.

The production and transportation designs are to a large degree based on in-house data from relevant studies. All sizes and cost are however scaled to correspond with the present process details.

CO<sub>2</sub> rate investigated is 20,000 tonne per day, corresponding to approximate  $10.8 \cdot 10^6$  Sm<sup>3</sup>/d. Assuming a gas content of 150 Sm<sup>3</sup>/m<sup>3</sup> in the hydrates, a hydrate production rate of approximate 3000 m<sup>3</sup>/hr results. The production facility will have four 25% (5,000 tonnes CO<sub>2</sub> /d) production trains.

#### 3.2. FORMATION CONDITIONS

Gas hydrates form readily when gas is contacted with water at pressure/temperature conditions within the hydrate-forming region for the given gas. Figure 3-1 shows the hydrate formation curve for CO<sub>2</sub> in fresh water. Appendix C presents a discussion around the hydrate formation curve determination.



**Figure 3-1: CO<sub>2</sub> Hydrate Formation Curve and Formation Conditions.**

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Superimposed on the hydrate equilibrium curve is the phase envelope of CO<sub>2</sub>. For efficient mixing, the hydrate production process should occur with CO<sub>2</sub> in the vapour phase. For the purpose of this study, the reactor conditions are chosen to:

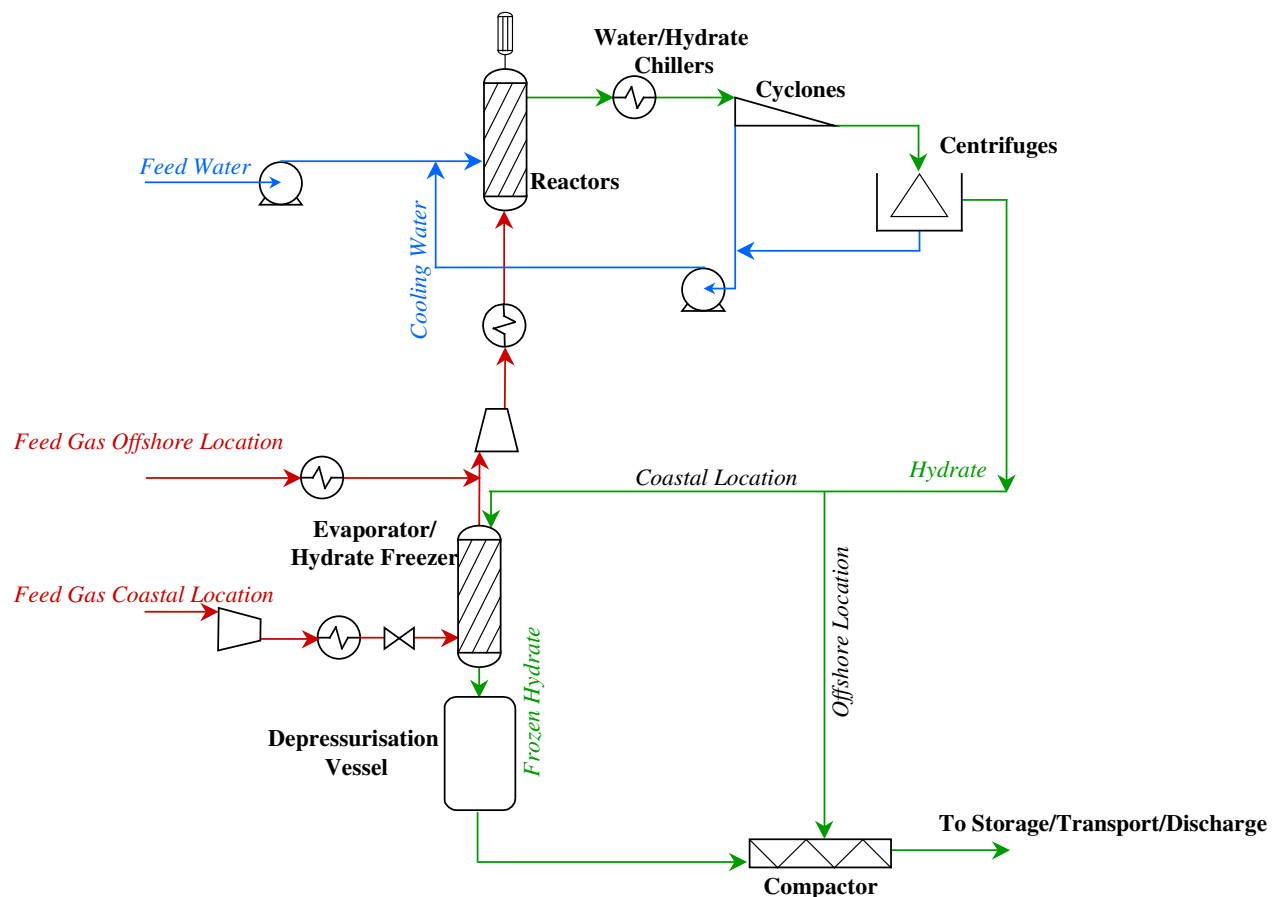
Pressure: 36 bara  
Temperature: 2-8 °C

for both the Coastal and the Offshore Location Cases.

### 3.3. HYDRATE PRODUCTION

Appendix E presents a brief discussion around the industrial production of gas hydrates. Figure 3-2 below shows a simplified diagram of the proposed hydrate production process.

Due to large heat of formation when gas hydrates are formed, it is strongly believed that the production system has to be water-continuous for efficient heat removal. Circulation of excess, cold water is used for heat removal, and the temperature is allowed to rise to close-equilibrium condition within the reactor.



**Figure 3-2: Simplified diagram of the hydrate production process.**

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For the Coastal Location Case, the Feed Gas is compressed and cooled (liquefied) and sent into an Evaporation Tower. In this tower, the gas is re-evaporated while the counter-current flowing hydrate product (see below) is brought to sub-zero degrees.

In the Offshore Location Case, the Feed entering at low temperature conditions is utilised for removal of the heat of formation.

Further, the gas is re-compressed and cooled to reactor conditions. The reactor conditions are in this study set to 2 °C and 36 bara. Fresh Water for hydrate conversion is injected into the Reactor.

The water and gas is converted into hydrates in the Reactors, where the temperature is assumed to increase to 8 °C. The Hydrate/Water slurry leaving the Reactors is first cooled, then dried in two sets of Separation Equipment. Removal of hydrate heat of formation in the Reactor is provided by cold water. The cooled water from the Separation Equipment is re-injected into the Reactor. The large amount of cooling water required determines the size of the reactors. There are two reactors in series per train with cooling in-between.

Long-distance transportation of hydrates is only considered feasible for atmospheric, sub-zero conditions, where hydrates are in a metastable state. Hence, for the Coastal Location Case, the hydrates leaving the Separation Equipment are led to the Hydrate Freezer (evaporation tower) where the temperature of the hydrate is decreased to below-zero conditions. The pressure is subsequently released in Depressurisation Vessels and the hydrate is in its metastable state at ambient pressure. In this condition, the hydrate is brought through a mechanical Compactor for creating hydrate blocks of sufficient size. The (metastable) hydrate blocks are transported to storage and/or transportation carrier.

For the Offshore Location Case, the hydrates leaving the separation equipment are brought through a mechanical Compactor for creating hydrate blocks of sufficient size, whilst being depressurised. From the petroleum industry it is known that hydrates exposed to ambient temperature and atmospheric pressure take long time to dissociate. These hydrates are not frozen, but have been compacted in the pipe system. It is therefore assumed that compacted, unstable (non-frozen) hydrates dissociate at a rate sufficiently slow for the Offshore Location Case, where the time exposed to atmospheric conditions is small.

The hydrate blocks are therefore directly discharged overboard.

### 3.4. HYDRATE TRANSPORTATION

Basis for the transport vessel is a standard bulk carrier, but with specially designed cargo holds.

The loading of the hydrate blocks from the production/storage facility to the transportation vessel is assumed to be performed as for ore carriers, by conveyor belts dropping the hydrate directly into the cargo holds.

Discharge of the hydrate offshore will be performed in a similar way as rock dumping is performed, i.e. through a moonpool in the vessel, potentially with a fall pipe installed. To get the hydrate to the discharge moonpool, vertical bucket conveyors are used to lift the hydrates from the cargo holds. Sloping tank bottoms ensure gravity feed of hydrate to the conveyors.

### 3.5. HYDRATE SINKING PROCESS

In Appendix D an analysis of the hydrate sinking process is presented. Figure 3-3 shows a schematic of the sinking process. A criterion of maximum 5% dissolving during sinking to 3000 m is applied for the sinking analysis.

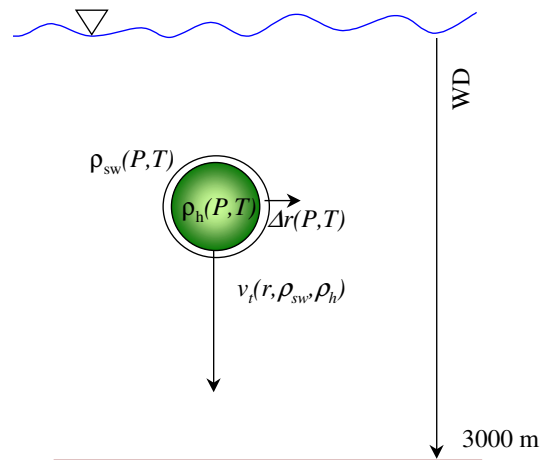
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**Figure 3-3: Schematic of the Hydrate Sinking Process.**

The necessary hydrate particle size that only results in a few percentages dissociation during the sinking process to 3000 m is strongly dependent on the dissociation rates. By using experimental values for the dissociation rates as found in the open literature, a diameter range from 2 cm to more than 2 m results. By employing “most likely” values, a diameter of less than 1 m results.

The size and shape of the hydrate blocks will have an effect on the transport system and the efficiency and rate of loading. Development work is anticipated to ensure that the system is working effectively, but in general no special requirements are expected for hydrate sizes/shapes within the estimated ranges, as the basic mechanisms will be the same.

In this study, only high-level estimates of the processes and the associating costs are made. The total cost is not expected to be significant dependent on the cost of the equipment producing the hydrate blocks.

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## 4. PROCESS DESIGN

This chapter summarises the process design for the main process systems and results in equipment lists for the two options.

### 4.1. COASTAL LOCATION CASE

#### 4.1.1. Inlet Gas Treatment

Reference is made to PFD IEA-AKT-1001.

The Feed Gas, (20.000 tonne/d CO<sub>2</sub>) arrives at the site at 10 bar and 30 °C. The gas consists of 100% CO<sub>2</sub> hence there is no need for purification. The gas is compressed and cooled (liquefied) to enable re-evaporation for freezing of the hydrate product. Evaporation takes place in an evaporation tower at approximate -14 °C and 23 bar.

The gas leaving the evaporation tower needs to be further compressed and cooled in order to reach Reactor conditions. Direct seawater coolers are chosen for this last cooling stage, and the temperature is assumed to reach 17 °C. Due to the relatively low heat capacity of the Feed Gas compared to the water, this is tolerated for reactor gas feed conditions.

The potential for heat uptake in the gas in the evaporation tower depends on the pressure and temperature conditions. At ~ -14 °C and 23 bar, the total isothermal evaporation requires approximate 64 MW.

#### 4.1.2. Fresh Water

Reference is made to PFD IEA-AKT-1002.

2740 m<sup>3</sup>/hr of fresh water (make-up water corresponding to the amount of water leaving with the hydrate product), is injected into the 1<sup>st</sup> stage reactor. Fresh water condition of 15 °C and 1 bar is assumed and the fresh water is pressurised to reactor operating conditions prior to entering the reactor. The fresh water is not cooled, as the amount of fresh water is relatively small compared to the amount of cold re-circulation water.

There is no requirement for high purity water supply for the hydrate process. Salt in large amounts will however depress the hydrate formation and should be avoided. The use of seawater may be possible, but leads to increased cost and energy consumption, see discussion under "alternative process" in Sect. 8.3.

Deaeration of the feed water has not been included in the study, but the need should be evaluated in a more detailed study.

#### 4.1.3. Reactor

Reference is made to PFD IEA-AKT-1002.

##### Overall Reactor Arrangement

A total of 313 MW is released during hydrate formation, and water is used for direct cooling of the reactors. The reactor feed temperature is 2 °C and the temperature in the reactor is assumed to increase to 8 °C. In order to decrease the amount of water circulating and thereby the size of the reactors, two reactors pr. train is chosen, with intercooling between. Same reactor size is chosen for both the 1<sup>st</sup> stage and the 2<sup>nd</sup> stage reactors, and 50% of the total gas is assumed to be converted in each reactor.

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Degassers (gas separators) are included downstream each reactor to prevent hydrates forming in the subsequent coolers and also to ensure adequate mixing of gas and water in the second reactor. Any unconverted gas from degasser downstream the second reactor may be routed to upstream the inlet gas compressor. A conversion of 100% is used as an assumption for the mass and energy calculations in this study.

#### Continuous Stirred Tank Reactor (CSTR)

A conventional CSTR reactor has been chosen for the design of the hydrate plant. The residence time per hydrate reactor is assumed to be 30 seconds. The reactor operating pressure is in the order of 36 bara with a design pressure set to 50 bara. The vessel inside diameter is 3.8 m with a height (tan/tan) of 8.8 m.

A CSTR with a continuous outflow from the reactor equal to the total feed stream can be used in the hydrate process. Because of the mixing, the concentration inside the reactor will equal the outflow. Agitation will enhance the mass transfer area for the hydrate reaction. The hydrate reaction is also dependent of the heat transfer and heat removal. A CSTR will give a steady state temperature where the heat of reaction is removed by the outlet streams.

CSTR reactors have been proven for hydrate conversion in laboratory scales and up-scaling of these reactors is often considered straightforward. There may be room for optimisation by possible employing other types of reactors.

#### **4.1.4. Heat Removal**

Heat removal is split in two: cooling of the process water (removal of heat of formation) and cooling of the inlet gas. The latter include the freezing of the hydrate product.

##### Inlet Gas Cooling

Reference is made to PFD IEA-AKT-1001.

A total of 43.3 MW is necessary for the liquefaction of the process inlet gas. Of this, approximate 39.6 MW is removed by direct seawater cooling. It is assumed that the gas reaches a temperature of 17 °C through direct seawater cooling. The temperature is brought down to 5 °C in a cooling media cooled heat exchanger and the temperature is taken down further to -14 °C through Joule-Thomson expansion cooling.

Isobaric evaporation of the liquid CO<sub>2</sub> at these conditions demands approximate 64 MW, which is taken from the counter-flowing hydrate particles and free water. Removing 64 MW leads to an outlet hydrate temperature of -11 °. The transport temperature for the frozen hydrate needs to be optimised, but for the purpose of this study, -11 °C is considered.

Re-compression of the gas to reactor conditions increases the temperature, and direct seawater cooling is used for after-compression cooling (3.4 MW).

##### Process Water Cooling

Reference is made to PFD IEA-AKT-1002.

The heat of formation is removed in cooling media exchangers after each reactor. The excess water from separation is recycled into the 1<sup>st</sup> stage reactor.

The water is cooled prior to the separation equipment to reactor inlet conditions (2 °C). Due to the relatively small amounts of fresh water compared to re-cycled water injected into the reactor, the fresh water is not cooled. Assuming a fresh water inlet temperature of 15 °C, the total water phase entering the hydrate reactor holds approximate 3.5 °C. Higher fresh water temperature can be met with higher water re-circulation rate.

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The total cooling requirement of 355 MW is the sum of removal of hydrate heat of formation, hydrate cooling, and fresh water cooling.

#### 4.1.5. Hydrate/Water Separation

Reference is made to PFD IEA-AKT-1002.

The hydrate/water slurry leaving the reactor system enters a hydrate/water separation system. Separation calculations are based on an efficiency of 90%. I.e. 10% on weight basis of the resulting product is water.

In this study, cyclonic separation of hydrates and water has been chosen. Due to the relatively similar densities of the two fluids, high G-forces are required. Hydrocyclones are selected for the bulk water separation. Hydrocyclones have no moving parts hence no energy is consumed other than the pressure loss in the process stream itself. It is assumed a water content of 50% in the hydrocyclone discharge.

For final dehydration to 10% water content, centrifuges are required. The energy consumption for centrifuges is reported from the supplier to 1 kW per m<sup>3</sup>/hr feed. Neither hydrocyclones nor centrifuges have been proven for this service and equipment development will be required.

All the water removed in the separation processes is returned to the 1<sup>st</sup> stage hydrate reactor. Any small hydrate particles escaping the separation process will act as nucleation sites in the reactor and enhance hydrate formation. In addition, the water's "freezing memory" may act to enhance hydrate formation rate (Takeya et al. 2000).

Continuous hydrate/water separation has not been proven and equipment/system/procedure development will be required

#### 4.1.6. Hydrate Freezing

The hydrate and 10% free water leaving the separation equipment at 23 bar and 2 °C shall be brought to sub-zero conditions. Removing 64 MW leads to an outlet temperature of -11 °C. The transport temperatures for the frozen hydrate needs to be optimised, but for the purpose of this study, -11 °C is considered.

The Freezing Tower is assumed as a tank vessel where the hydrates enter at the top. A residence time of 120 seconds is assumed. The design pressure is set to 35 bara. The vessel inside diameter is 3 m with a height (tan/tan) of 8.8 m.

At the top, the hydrate is forced through a mesh in order to create small particles with large surface area. The liquefied gas is entering the bottom end of the chiller and counterflows the hydrate particles whilst being evaporated. The main purpose of this is to freeze the hydrate, however two positive side effects should be noted.

- Some of the remaining water in the hydrate is likely to be converted to hydrates. This effect has however not been realised in the transport volumes or in the production process.
- Manageable hydrate particles of uneven sizes are created

Continuous hydrate freezing has not been proven and equipment/system/procedure development will be required.

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#### **4.1.7. Hydrate Depressurisation**

The frozen hydrate product and small amounts of gas continue into one of three batch depressurisation tanks. Product enters the first tank at the same time as the second tank is depressurised and the product is removed from the third tank (at 1 bara). One tank is depressurised per 20 min. Approximate 80 vol. % of each tank is filled with hydrate product. Transport to and from these tanks occurs by gravity flow.

Released gas from the depressurisation tanks should be re-routed back to the process.

Large-scale hydrate depressurisation has not been proven and system/procedure development will be required. It may also be room for optimisation and cost reduction for the depressurisation step.

#### **4.1.8. Hydrate Block Production**

The depressurised, frozen hydrate particles are routed to the hydrate block production facility. Hydrate blocks are produced using double roll compactors. Hydraulic pressure is applied to the particles via the upper roller as they pass through the rollers compacting them into a continuous sheet of hydrate. The compacted hydrate is then cut into blocks of the required size. It is estimated that two compactors are required for each production train. Each compactor has a roller width of 70 cm.

The blocks are then transported directly by conveyor to the cargo ship.

Double roll compactors have not been proven for this service and equipment development will be required.



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#### 4.1.9. Equipment List

##### Main Equipment List - Hydrate Generation Onshore

Tag no	Service	Weight (tonnes)	No off	Total weight (tonnes)	Power Consumed Gas Turbine (kW)	Power Consumed Electrical (kW)
08CJ-001-2 A/B/C/D	Reactor Agitator with sealing	1	8	8		2000
08VF-001-2 A/B/C/D	Reactors	55	8	440		
08VA-001-2 A/B/C/D	Degassers	12	8	96		
08HX-001 A/B/C/D/E/F	Reactor Interstage Cooler	120	6	720		
08HX-002 A/B/C/D/E/F	Reactor After Cooler	120	6	720		
08VZ-001 A/B/C/D/E/F/G	Hydrocyclone pre-separation	8	28	224		
08XX-001 A/B/C/D/E/F	Sentrifuge skids	15	24	360		6000
08PA-001 A/B/C/D	Fresh Water Feed Pump	11	4	42		3880
08PA-002 A/B/C/D	Re-circ pump (from cyclones)	24	4	96		8188
08PA-003 A/B/C/D	Re-circ pump (from centrifuges)	8	4	31		1240
27JI-001 A/B/C/D	Gas Metering	57	1	57		
23KA-001 A/B/C/D	Gas Inlet Compressors	64	4	256		27460
23KA-002 A/B/C/D	Reactor Gas Compressors	38	4	152		6646
23HX-001 A/B/C/D	Pre-Coolers (direct seawater)	16	4	66		
23HX-002 A/B/C/D	Coolers	11	4	45		
23HX-003 A/B/C/D	Reactor Inlet Gas SW Cooler	11	4	45		
23XX-001 A/B/C/D	Evaporation Tower/Freezers	20	4	80		
23VA-001 A/B/C/D	Scrubbers	11	4	44		
40KA-001 A/B/C	Compressor	120	3	360	60480	
40HX-001 A/B/C/D....	Condensers	50	15	750		
40 VA-001 A/B/C/D	Buffer Tank	1	4	4		
50PA-001 A/B/C/D	Seawater Pumps	18	6	108		8580
08VX-001-2-3 A/B/C/D	Hydrate Depressurization Tanks	125	12	1500		
08XX-002 A/B/C/D/E/F/G/H	Hydrate Compactors	100	8	800		4000
TOTAL MAIN EQUIPMENT (+10%)				7704		
The equipment below has been identified, but not quantified technically. To complete the estimate, an allowance of 5 % on a weight basis has been made						
53	Water Treatment Package					
53	Fresh Water Storage					
62	Fuel Oil ( Turbine Dual Fuel )					
56	Open Drain					
57	Closed Drain					
64	Inert Gas					
63	Compressed Air					
65	Hydraulic Power					
41	Cooling Medium					
66	Sewage					
71	Fire water					
82	Power Distribution					
86/87	Instrumentation / Controls					
Total weight including allowance				8090		
					<b>Turbine</b>	<b>Electrical</b>
					60480	67994

#### 4.2. OFFSHORE LOCATION CASE

The premise of the Offshore Location Case was to design a production process similar to the Coastal Location Case. However, some significant optimisation from the Coastal Location Case is possible, including no freezing of the hydrate product, and utilisation of the cold feed conditions.

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#### **4.2.1. Inlet Gas Treatment**

Reference is made to PFD IEA-AKT-1003.

The Feed (20.000 tonne/d CO<sub>2</sub>) arrives at the site at 10 bar and -50 °C (liquid state). The liquid is pumped to 24 bar and further led into a heat exchanger where the feed is evaporated. The cold conditions of the feed are utilised for cooling the cooling media.

Further treatment is identical to the Coastal Location Case: The gas leaving the heat exchanger needs to be compressed and cooled in order to reach Reactor conditions. Direct seawater coolers are chosen for this last cooling stage, and the temperature is assumed to reach 17 °C. Due to the relatively low heat capacity of the Feed Gas compared to the Feed Water, this is tolerated for reactor gas feed conditions.

#### **4.2.2. Fresh Water**

Reference is made to PFD IEA-AKT-1002 and Sect. 4.1.2. Fresh water supply is identical to Coastal Location Case.

#### **4.2.3. Reactor**

Reference is made to PFD IEA-AKT-1002 and Sect. 4.1.3. The reactor arrangement is identical to the Coastal Location Case.

#### **4.2.4. Process Water Cooling**

Reference is made to PFD IEA-AKT-1002. The process water cooling is identical to the Coastal Location Case.

The heat of formation is removed in cooling media exchangers after each reactor. The excess water from separation is recycled into the 1<sup>st</sup> stage reactor.

The water is chilled prior to the separation equipment to reactor inlet conditions (2 °C). Due to the relatively small amounts of fresh water compared to re-cycled water injected into the reactor, the fresh water is not cooled. Assuming a fresh water inlet temperature of 15 °C, the total water phase entering the hydrate reactor holds approximate 3.5 °C. Higher fresh water temperature can be met with higher water re-circulation rate.

The total cooling requirement of 355 MW is the sum of removal of hydrate heat of formation, hydrate cooling, and fresh water cooling.

#### **4.2.5. Hydrate/Water Separation**

Reference is made to PFD IEA-AKT-1002 and Sect. 4.1.5. Hydrate/water separation is identical to Coastal Location Case.

#### **4.2.6. Hydrate Block Production and Depressurisation**

The hydrate + 10% water leaving the separation equipment is routed to the hydrate block production facility. Hydrate blocks are produced using a double roll compactors. Hydraulic pressure is applied to the pellets via the upper roller as they pass through the rollers compacting them into a continuous sheet of hydrate whilst being depressurised. The compacted hydrate is then cut into blocks of the required size. It is estimated that two compactors are required for each production train. Each compactor has a roller width of 70 cm.

The blocks are then transported directly by conveyor to overboard discharge.

Double roll compactors have not been proven for this service and equipment development will be required.

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#### 4.2.7. Equipment List

##### Main Equipment List - Hydrate Generation Offshore (No freezing)

Tag no	Service	Weight (tonnes)	No off	Total weight (tonnes)	Power Consumed Gas Turbine (kW)	Power Consumed Electrical (kW)
08CJ-001-2 A/B/C/D	Reactor Agitator with sealing	1	8	8		2000
08VF-001-2 A/B/C/D	Reactors	55	8	440		
08VA-001-2 A/B/C/D	Degassers	12	8	96		
08HX-002 A/B/C/D	Reactor Interstage Cooler	120	6	720		
08HX-003 A/B/C/D	Reactor After Cooler	120	6	720		
08VZ-001 A/B/C/D/E/F/G	Hydrocyclone pre-separation	8	28	224		
08XX-001 A/B/C/D/E/F	Sentrifuge skids	15	24	360		6000
08PA-001 A/B/C/D	Fresh Water Feed Pump	11	4	42		3880
08PA-002 A/B/C/D	Re-circ pump (from cyclones)	24	4	96		8188
08PA-003 A/B/C/D	Re-circ pump (from centrifuges)	8	4	31		1240
27JI-001 A/B/C/D	Gas Metering	57	1	57		
23PA-001 A/B/C/D	Pre-Feed Pumps	5	4	20		375
23HX-001 A/B/C/D	"Gas Heater"	50	4	200		
23KA-001 A/B/C/D	Reactor Gas Compressors	38	4	152		6646
23HX-002 A/B/C/D	Reactor Inlet Gas SW Cooler	11	4	45		
23VA-001 A/B/C/D	Scrubbers	11	4	44		
40KA-001 A/B/C/D	Compressor	120	2	240	56000	
40HX-001 A/B/C/D....	Condensers	50	11	550		
40 VA-001 A/B/C/D	Buffer Tank	1	4	4		
50PA-001 A/B/C/D	Seawater Pumps	18	5	90		7000
08XX-002 A/B/C/D/E/F/G/H	Hydrate Compactors	140	8	1120		4000
80 EG001 A/B	Power Generator	181	2	362		
TOTAL MAIN EQUIPMENT (+10%)				6183		
The equipment below has been identified, but not quantified technically. To complete the estimate, an allowance of 5 % on a weight basis has been made						
52	Ballast Water					
53	Water Treatment Package					
53	Fresh Water Storage					
62	Fuel Oil					
56	Open Drain					
57	Closed Drain					
61	Jet Fuel					
62	Diesel Oil					
64	Inert Gas					
63	Compressed Air					
65	Hydraulic Power					
41	Cooling Medium					
66	Sewage					
69	Lube Oil					
71	Fire water					
84	Emergency Power					
86/87	Instrumentation / Controls					
Total weight including allowance				6492		
					<b>Turbine</b>	<b>Electrical</b>
					56000	39329

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## 5. LOGISTICS

### 5.1. TRANSPORTATION, INCLUDING ON AND OFFLOADING

#### 5.1.1. General

Two potential systems are identified for shipping and offshore discharge of CO<sub>2</sub> hydrates. One method is based on the methods used for offshore rock dumping, while the other utilises container transport methods.

The major challenges related to both methods are given below:

- Effective loading: The loading rates must exceed the production capacity, i.e. 72470 m<sup>3</sup>/d (76238 tonnes/d)
- Minimise melting of the hydrates during transport and handling: At atmospheric pressure the hydrate are stable at temperatures below –10°C to –15°C.
- Effective offshore offloading/discharge: In addition to limiting the actual time the offloading/discharge takes, the offloading operation should be as independent of the weather as possible.
- No existing systems for handling hydrate in such quantities are currently in operation and development of new technology or modification of existing technology is required.
- The hydrate blocks have a minimum size requirement.

#### 5.1.2. Transport by Bulk Type Vessel

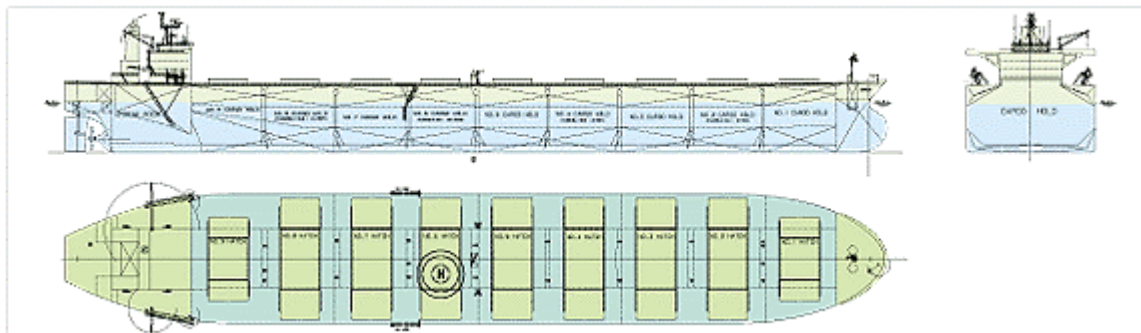
##### Vessel description

Basis for the vessel is a standard bulk carrier, in this case the Samsung standard Bulk carrier series. Hull shape, propulsion and machinery systems are assumed to be as described for these ships, however the cargo holds need to be modified to allow for insulation and offshore offloading. This will result in a reduced cargo capacity. This reduction is assumed to be approximately 25%.

The major modifications are summarised below:

- All Cargo holds to be insulated to minimise melting of the hydrates during transport
- Sloping tank bottoms in all tanks to enable the hydrate lumps to slide by gravity to the offloading systems
- Moonpools for discharge of hydrate through hull to be included in design
- Offloading systems to be included.
- Boil-off gas will be vented to atmosphere to prevent pressure build-up in the cargo and to ensure that the crew will not be exposed to toxic levels of CO<sub>2</sub>.

##### Samsung standard bulk carrier data



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#### Principal particulars

##### **169,400 dwt**

###### Principal dimensions

Length o.a.	292.0m
Length b.p.	281.0m
Breadth, mld.	46.0m
Depth, mld.	23.5m
Design draught, mld.	16.5m
Scantling draught, mld.	17.3m

###### Dead weight

At design draught	159,600mt
At scantling draught	169,400mt
Cargo holds (100% full)	185,000 m <sup>3</sup>

Main engine	HSD – B&W 6S70MC
Max continuous rating (MCR)	22,000 bhp x 87,4rpm
NCR (85% MCR)	18,700 bhp
Speed	15.0 knots
Daily fuel consumption	55.4 mt/d

##### **74,300 dwt**

###### Principal dimensions

Length o.a.	224.8m
Length b.p.	217.0m
Breadth, mld.	32.2m
Depth, mld.	19.2m
Design draught, mld.	12.2m
Scantling draught, mld.	14.0m

###### Dead weight

At design draught	62,600mt
At scantling draught	74,300mt
Cargo holds (100% full)	88,400 m <sup>3</sup>

Main engine	HSD – Sulzer 7RTA48T
Max continuous rating (MCR)	12,220 bhp x 117rpm
NCR (85% MCR)	11,000 bhp
Speed	14.5 knots
Daily fuel consumption	32.6 mt/d

Rough estimates then give a cargo capacity of the largest vessel of some 120,000 tonnes while the smaller vessel will have a capacity of approximately 50,000 tonnes.

#### Loading of vessel

Loading is assumed to be performed as for ore carriers, i.e. by conveyor belts dropping the hydrate directly into the cargo holds. The effect of hydrate blocks being crushed when dumped into the cargo hold need to be evaluated, as the hydrate blocks have a minimum dimension to avoid the blocks from vaporising in the water.

Potentially the loading arms should be insulated to reduce the melting of hydrate during loading.

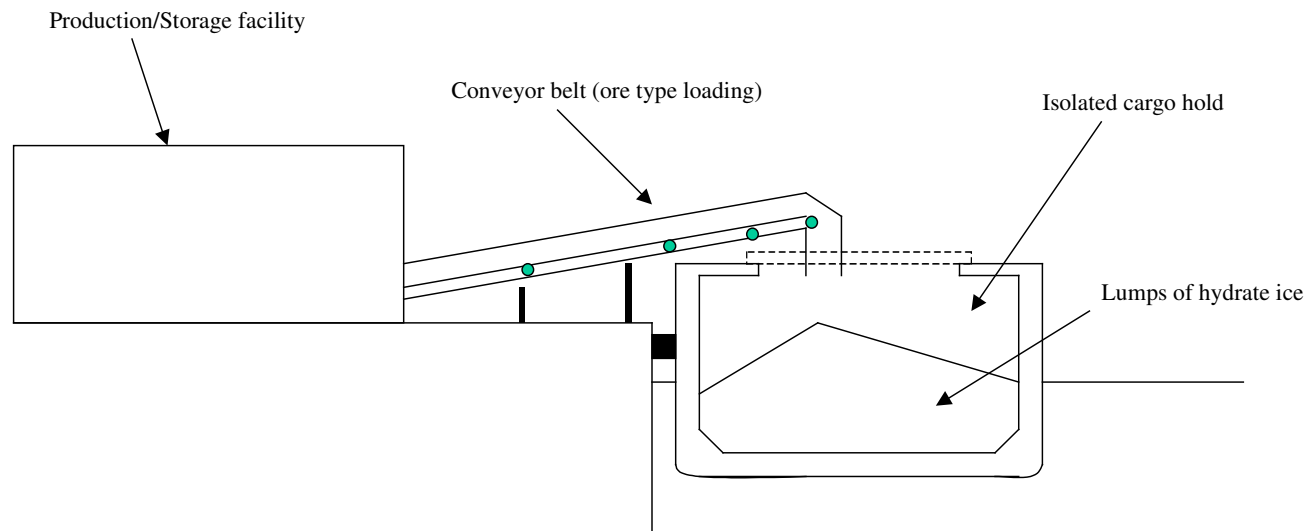
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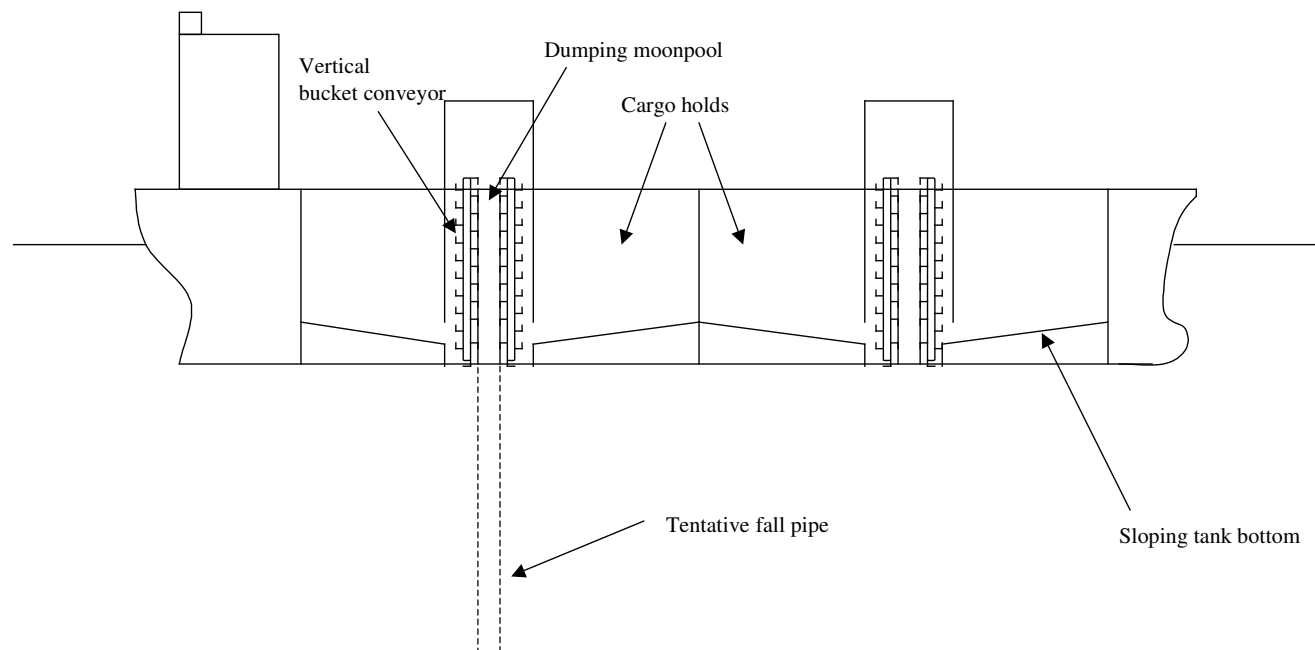
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**Figure 5-1: Loading of Hydrate to Bulk Type Vessel**

#### Offshore offloading/discharge

Discharge of the hydrate offshore will be performed in a similar way as rock dumping is performed, i.e. through a moonpool in the vessel potentially with a fall pipe installed if found to be required. To get the hydrate to the discharge moonpool vertical bucket conveyors are used to lift the hydrates from the cargo holds. Sloping tank bottoms ensure gravity feed of hydrate to the conveyors.



**Figure 5-3: Discharge of Hydrate from Bulk Type Vessel**

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### 5.1.3. Transport by Container Type Vessel

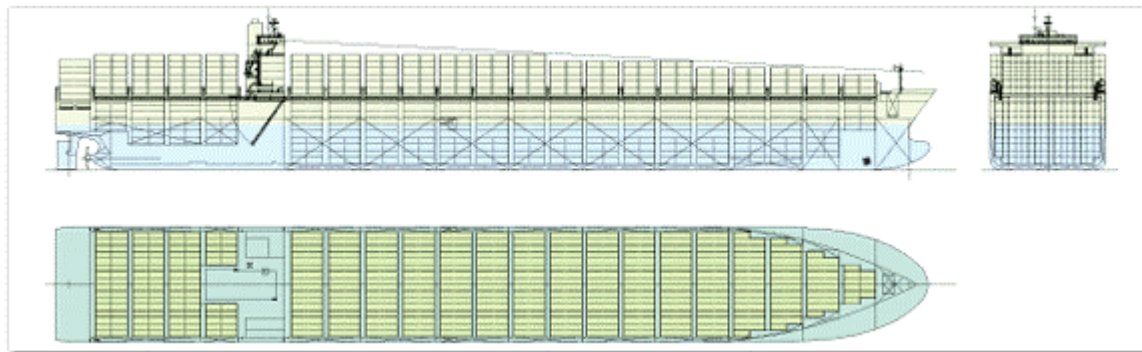
#### Vessel description

Basis for the vessel is a standard container vessel, in this case the Samsung standard container vessel series. Hull shape, propulsion and machinery systems are assumed to be as described for these ships, however the container capacity will be governed by the deadweight and not the available container capacity as the hydrate containers will be significantly heavier than a typical container handled by this type of vessel. In addition space for the emptied containers need to be available after offloading hence the logistics need to be carefully planned for this solution.

The major modifications may be summarised as below:

- Onboard container crane(s) for offloading at sea to be included on vessel.
- Boil-off gas must be vented to atmosphere to prevent pressure build-up in the containers and to ensure that the crew will not be exposed to toxic levels of CO<sub>2</sub>.

#### Samsung standard container vessel data



Principal particulars:

#### **5,800 TEU**

Principal dimensions

Length o.a.	277.0m
Length b.p.	263.0m
Breadth, mld.	40.0m
Depth, mld.	24.3m
Design draught, mld.	12.0m
Scantling draught, mld.	14.0m

Dead weight

At design draught	50,100mt
At scantling draught	67,700mt
Container capacity on deck/in hold	3,184 TEU/ 2,668 TEU

Main engine

Max continuous rating (MCR)	HSD – B&W 10K98MC-C
NCR (85% MCR)	77,600 bhp x 104rpm
Speed	69,800 bhp
Daily fuel consumption	26,4 knots
	204,8 mt/d



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**4,800 TEU**

## Principal dimensions

Length o.a.	293,6m
Length b.p.	281.0m
Breadth, mld.	32.25m
Depth, mld.	21.3m
Design draught, mld.	12.0m
Scantling draught, mld.	13.5m

## Dead weight

At design draught	54,600mt
At scantling draught	66,600mt
Container capacity on deck/in hold	2,546 TEU/ 2,295 TEU

Main engine	HSD – B&W 9K90MC
Max continuous rating (MCR)	55,890 bhp x 104rpm
NCR (85% MCR)	50,300 bhp
Speed	24.5 knots
Daily fuel consumption	150.1 mt/d

**4,300 TEU**

## Principal dimensions

Length o.a.	259.8m
Length b.p.	244.8m
Breadth, mld.	32.25m
Depth, mld.	19.3m
Design draught, mld.	11.0m
Scantling draught, mld.	12.6m

## Dead weight

At design draught	39,600mt
At scantling draught	50,500mt
Container capacity on deck/in hold	2,727 TEU/ 1,584 TEU

Main engine	HSD – B&W 8K90MC
Max continuous rating (MCR)	49,680 bhp x 104rpm
NCR (85% MCR)	44,710 bhp
Speed	24.6 knots
Daily fuel consumption	133.4 mt/d

The cargo capacity for these vessels as hydrate carriers are assumed to be given by the deadweight capacity as presented above.

Loading of vessel

A system for placing the hydrate into the container should be developed. This may be a system with a conveyor belt placing the hydrate directly into the container. The container is kept in the correct position by a vertical and horizontal moving lifting table.

The containers are then loaded onto the ship as standard container loading, potentially by using the onboard container cranes.



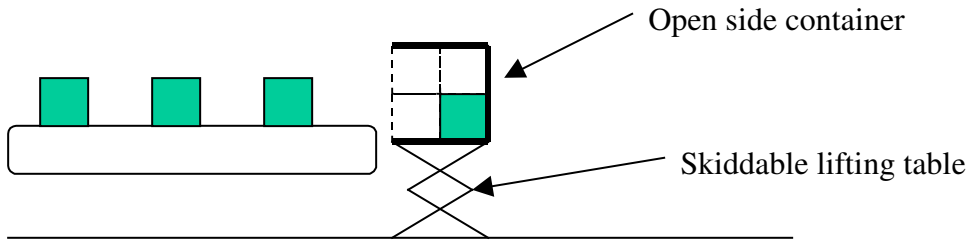
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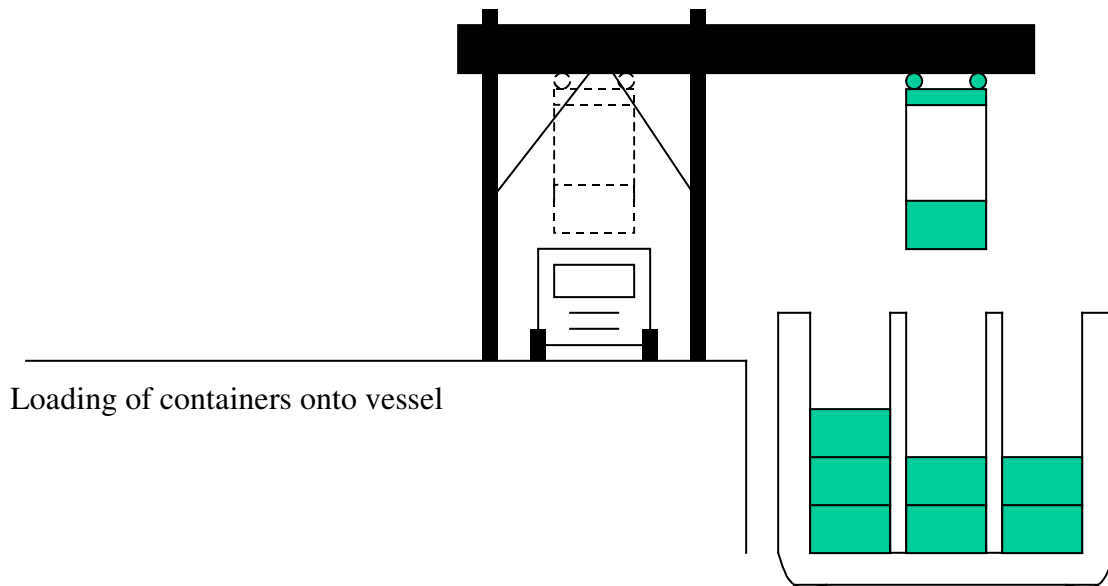
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Loading of Hydrate into containers



**Figure 5-5: Loading of Containers and Container Vessel**

Offshore offloading/discharge

Offloading/discharge of the hydrates will be performed by the onboard container cranes. The containers are lifted over the shipside and tilted to let the hydrates fall out of the open side of the container. The empty container is then placed back on the vessel and the operation is repeated.

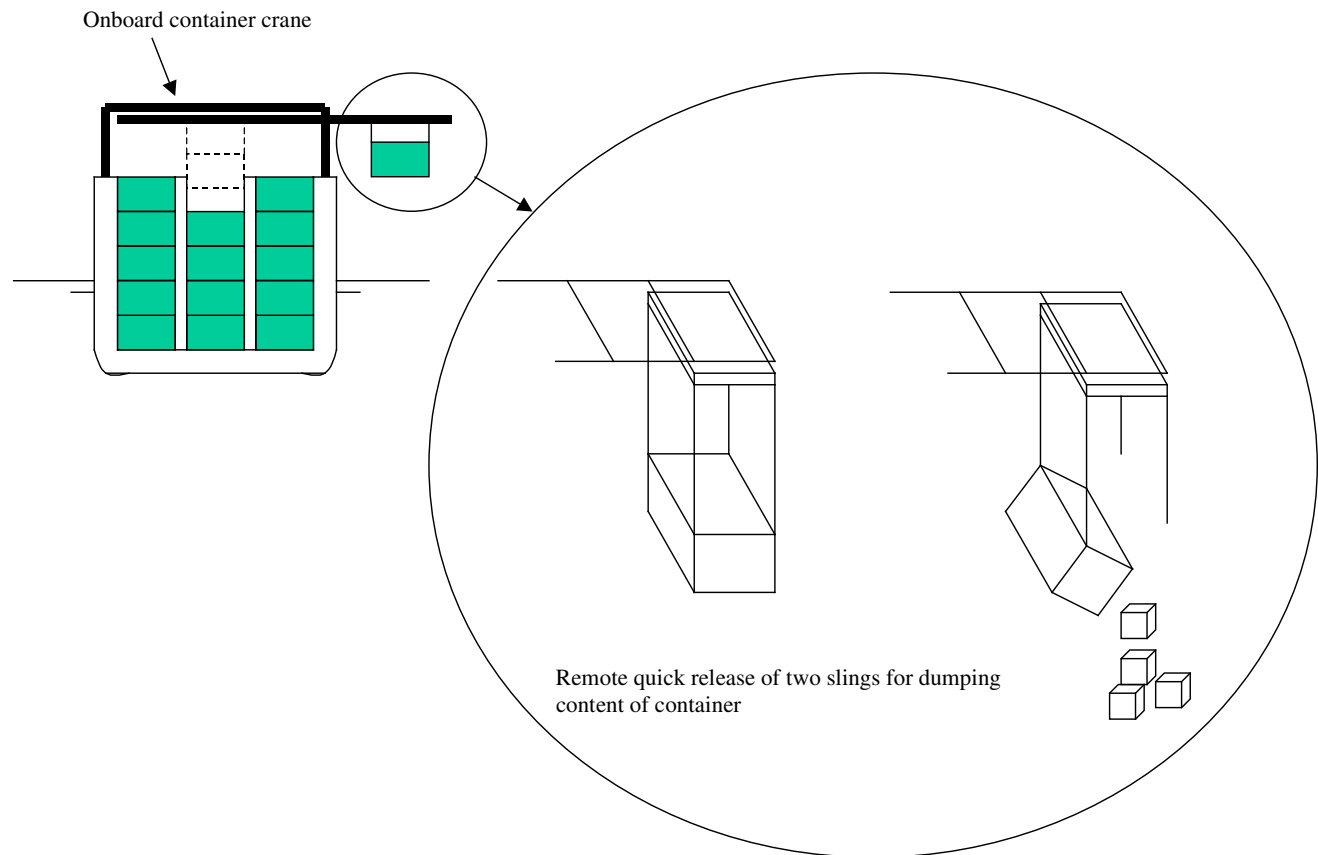
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**Figure 5-7: Offloading/Discharge from Container Vessel**

#### 5.1.4. Pros and Cons

Both the concepts for transport and discharge of the hydrate at sea described above have strengths and weaknesses. In the following evaluation of the concepts these pros and cons are seen in relation to the project requirements.

##### Project requirements

The transport and discharge solution shall handle a daily production of 72,470 tonnes of CO<sub>2</sub> hydrates. To enable this, high regularity are needed. If a high regularity is not achieved the hydrate production must be stopped or an over-capacity in the transport system in addition to storage space is required.

##### Bulk vessel transport

The insulated cargo holds, the moonpools for discharge of the hydrate and the hydrate offloading system all contribute to make the vessel a specially designed vessel. This will again lead to an increased price and risk for the fabrication of the vessel. Conversion of existing vessels may be an option, but this would be a major conversion job, with the risks related to such projects.

The loading system is assumed to be similar to ore and rock loading systems. Some modifications are expected to be required, but in general no special problems are expected. The size and shape of the hydrate blocks will have an effect on the system and the efficiency and rate of loading.

Shape and size of the hydrate blocks will also have an effect on the sloped tank bottoms and the bucket conveyors, and development work is required to ensure that the system is working effectively. It is however expected to be a relatively effective system enabling an acceptable offloading time offshore. The effect of

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weather on the offloading needs to be investigated, but as long as no lifting is required the system is assumed to be less weather sensitive than the container based system.

If a fall pipe is found to be required to ensure deposit of the hydrate on an acceptable depth systems identical to the fall pipe systems on rock dumping vessels may be utilised.

#### Container vessel transport

Transport by container vessel requires a limited amount of modifications to standard vessels. The only required modification is the inclusion of onboard container cranes. However the loading capacity of the container vessels are limited compared to the bulk carriers. Also the offloading by use of cranes are more weather sensitive and may significantly affect the regularity of this option. In addition the offloading rate will be limited by the container handling which involves many operations, hence both offloading rate and regularity will be dependent on the crane operations.

Vent systems must be included for both vessels, but the vent system for the container type vessel will be more complicated than for the bulk type vessel.

Also a special system for loading the hydrate blocks into the containers need to be developed. Some development work is also required for the onboard container cranes.

### **5.1.5. Conclusion**

In general, the loading and offloading is assumed to be quicker for the bulk vessel system. The offloading system is expected to be less weather sensitive as use of cranes are avoided and the loading capacity per vessel is higher for the bulk vessel solution. In addition, the shore based loading system is considered to be relatively straightforward. Based on this the bulk vessel solution is recommended even though it requires a specially designed vessel, most likely being a newbuild.

## **5.2. NUMBER OF CARRIERS REQUIRED**

Based on the above discussion on the transportation vessels, a bulk-type vessel is used as basis for both the logistic evaluation and the cost estimation.

### **5.2.1. General**

General data of the relevant vessels are:

#### **169,400 dwt**

Cargo holds (100% full)	185,000 m <sup>3</sup>
Cargo capacity:	120,000 tonnes
Speed	15.0 knots
Daily fuel consumption	55.4 t/d

#### **74,300 dwt**

Cargo holds (100% full)	88,400 m <sup>3</sup>
Cargo capacity	50,000 tonnes
Speed	14.5 knots
Daily fuel consumption	32.6 t/d

Even with 30% porosity in the bulk cargo, it will be the vessel tonnage capacity that is limiting the transportation volume. This leads then to volume capacities of:

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- 114068 m<sup>3</sup> hydrates for the 169,400 dwt vessel
- 47529 m<sup>3</sup> hydrates for the 74,300 dwt vessel

### 5.2.2. Round-Trip Calculations

Hydrate Production (20,000 tonne CO<sub>2</sub>/d): 72072 m<sup>3</sup>/d

Transport distance: 1000 km

#### 169,400 dwt

Onloading (producing full cargo):	1,6 d
Transit:	1.5 d
Offloading (assumed):	1.0 d
Return:	1.5 d
<b>ROUND TRIP</b>	<b>5.6 d</b>

#### 74,300 dwt

Onloading (producing full cargo):	0.7 d
Transit:	1.6 d
Offloading (assumed):	0.9 d
Return:	1.6 d
<b>ROUND TRIP</b>	<b>4,8 d</b>

No docking time is taken into account.

### 5.2.3. Number of Carriers Required

Assuming no storage onshore.

#### 169,400 dwt: 4 Carriers Required

Storage Capacity Sensitivity towards Numbers of Carriers (169,400 dwt):

Numbers of Carriers	Necessary Storage Capacity
4	0 m <sup>3</sup>
3	60134 m <sup>3</sup>
2	174203 m <sup>3</sup>
1	288271 m <sup>3</sup>

Number of Carriers Sensitivity towards transport distance (no storage assumed) (169,400 dwt):

Transport Distance	Numbers of Carriers Required
100 km	2
500 km	3
1000 km	4
2000 km	6
3000 km	8
4000 km	10

Number of Carriers Sensitivity towards hydrate gas content (no storage assumed) (169,400 dwt):

Gas Content	Numbers of Carriers Required
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150 Sm <sup>3</sup> /m <sup>3</sup> (Base Case)	4
184 Sm <sup>3</sup> /m <sup>3</sup> (maximum)	4

**74,300 dwt: 8 Carriers Required**

Storage Capacity Sensitivity towards Numbers of Carriers (74,300 dwt):

Numbers of Carriers	Necessary Storage Capacity
8	0 m <sup>3</sup>
7	3348 m <sup>3</sup>
6	50876 m <sup>3</sup>
5	98405 m <sup>3</sup>

Number of Carriers Sensitivity towards transport distance (no storage assumed) (74,300 dwt):

Transport Distance	Numbers of Carriers Required
1000 km	8
2000 km	12
3000 km	17
4000 km	22

Based on the high number of carrier vessels required for the 74,300 dwt vessel contra the 169,400 dwt vessel, as well as the high sensitivity of number of carriers versus transport distance for the 74,300 dwt vessel, the 169,400 dwt vessel-type is recommended and used for further studies.

With 4 carriers, there is no need for hydrate storage at the plant location. Decreasing the numbers of carriers to 3, a storage capacity of 60134 m<sup>3</sup> is required. With intermediate storage between production and shipping, the handling operations are tripled. Although no technical objections, it is recommended to design for production directly into transportation vessel (no intermediate storage) in order to reduce handling operations and the large required storage volumes.

### 5.3. CONCLUSION

169,400 dwt vessels are recommended for the hydrate carriers. 4 carriers are required for transport of the design hydrate production rate to a location 1000 km off shore. With 4 carriers, no onshore location hydrate storage is required.

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## 6. SELECTION OF OFFSHORE STRUCTURE

Basis for the selection of the offshore substructure for support of the hydrate production facility is given in the functional requirements listed below:

- Water depth on location ~3000m
- Topside equipment weight estimate ~6500 tonnes (total topside ~4x6500 = 26000 tonnes)
- Large fresh water storage
- Potential harsh environment deployment

The water depth, in addition to requiring a floating structure, mainly affects the station keeping solution. Typically floating offshore structures on permanent location is moored by a system of anchor lines. For ultra deep water, i.e. 1500+ meters traditional steel chain/wire systems becomes too heavy and taut leg synthetic fibre rope solutions are used. Currently the deepest application for such a system is the "Deepwater Nautilus", a exploration drilling unit, moored in 2657m in the Gulf of Mexico.

As the hydrate processing facility is not connected to any seabed systems it is not necessary to keep an exact location at all times. This would allow for using dynamic positioning (DP) also for a permanently located facility. DP systems are positioning systems utilising computer controlled thrusters to stay in a given position. Such systems are frequently used on offshore construction vessels, deep water drilling rigs and also one oil producing FPSO (Seillean) located offshore Brazil. The weakness with this system are that a power black out or loss of position reference system (mainly DGPS and hydroacoustics) will result in a loss of position. For the hydrate processing facility this is not considered critical.

The large topside weight affects the size of the structure, i.e. the heavier topside the larger floater. If a column stabilised unit, i.e. semi submersible should be selected it is assumed to be among the biggest units in the world. FPSOs of similar topside weight are deployed in West Africa. If a mooring system is selected this will additionally increase the required load carrying capacity.

As large amount of freshwater is required for the hydrate production some means for storage is required. For a FPSO this storage capacity will be available in hull tanks, while a column stabilised unit would require a floating storage unit (FSU) to be connected while producing.

The environment the unit is to be deployed in will affect the structural loading and in specific the fatigue loading on the unit. In case of harsh environment deployment, as assumed in this study, the fatigue loading will be significant. This is expected to disqualify the use of old tankers as the remaining fatigue life will be very short in harsh environment, while it will allow for 15-20 years in benign waters like West Africa or similar.

Based on the above a newbuilt FPSO based on an VLCC (Very Large Crude Carrier) with DP station keeping is selected for the hydrate production facility. As only water is to be stored in the tanks it is assumed that a single hull design is acceptable. Special considerations need to be taken with respect to potential storage of cold CO<sub>2</sub>, support of the topside etc.

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## 7. ENERGY CONSUMPTION AND CAPTURE EFFICIENCY

It should be noted that the analysis presented here is not a full life cycle analysis and only considers emissions directly related to the operation of the production and transport system.

### 7.1. COASTAL LOCATION CASE

The following list of energy consumers has been worked out for the Coastal Location Case.

<b>Consumer - Coastal Location</b>	<b>Electrical [kW]</b>	<b>Turbine [kW]</b>
08CJ-001/2 A/B/C/D Reactor Agitator	2000	
08XX-001 A/B/C/D/E/F Centrifuges	6000	
08PA-001 A/B/C/D Fresh Water Feed Pump	3880	
08PA-002 A/B/C/D Cyclone Re-Circ. Pump	8188	
08PA-003 A/B/C/D Centrifuge Re-Circ. Pump	1240	
23KA-001 A/B/C/D Gas Inlet Compressor	27460	
23KA-002 A/B/C/D Reactor Gas Compressor	6646	
40KA-001 A/B/C Compressor		60480
50PA-001 A/B/C/D Seawater Pump	8580	
08XX-002 A/B/C/D/E/F/G/H Compactors	4000	
Defined Electrical Power Demand [kW]	67994	
+15% Additional Consumers [kW]	10199	
<b>Total Electrical Power Demand [kW]</b>	<b>78193</b>	
<b>Total Turbine Power Demand [kW]</b>		<b>60480</b>

The generation of electrical energy emits 396 g CO<sub>2</sub> per kWh electrical energy produced (IEA/CON/02/83).

The turbine power is generated from gas turbines (CCGT) with an assumed CO<sub>2</sub> emission of 400 g CO<sub>2</sub> per kWh.

Direct loss of CO<sub>2</sub> during production and onloading due to leakage, CO<sub>2</sub> dissolved in wastewater etc. is assumed to 1% of total CO<sub>2</sub> volume.

According to available information, the carrier consume 55.4 tonne fuel per day. Heavy fuel is assumed. An emission of 3.15 kg CO<sub>2</sub> per kg heavy fuel is assumed ([www.windpower.dk](http://www.windpower.dk)). Four ships of 169,300 dwt vessel-type are assumed. Total fuel consumption for all four ships is based on ships being in motion 3 days of the total round trip of 5.6 days (54%).

Some loss of CO<sub>2</sub> during transport and offloading, including loss of CO<sub>2</sub> due to hydrate dissociation at low water depths during sinking, is anticipated. This loss is assumed to 4% of total CO<sub>2</sub> volume.

The calculated CO<sub>2</sub> balance is as follows:

<b>Plant Capacity [tonne CO<sub>2</sub>/d]</b>	<b>20000</b>	
Emission [tonne CO <sub>2</sub> /d]	743	<b>Electrical Power Generation</b>
	581	Turbine Power Generation
	200	Loss during Production and Onloading
	374	Transportation – Fuel Consumption
	800	Loss during Transport and Offloading
<b>Total CO<sub>2</sub> Emission [tonne/d]</b>	<b>2698</b>	
<b>CO<sub>2</sub> Capture Efficiency</b>	<b>87%</b>	

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## 7.2. OFFSHORE LOCATION CASE

The following list of energy consumers has been worked out for the Offshore Location Case.

Consumer - Offshore Location	Electrical [kW]	Turbine [kW]
08CJ-001/2 A/B/C/D Reactor Agitator	2000	
08XX-001 A/B/C/D/E/F Centrifuges	6000	
08PA-001 A/B/C/D Fresh Water Feed Pump	3880	
08PA-002 A/B/C/D Cyclone Re-Circ. Pump	8188	
08PA-003 A/B/C/D Centrifuge Re-Circ. Pump	1240	
23PA-001 A/B/C/D Pre-Feed Pump	375	
23KA-002 A/B/C/D Reactor Gas Compressor	6646	
40KA-001 A/B/C Compressor		56000
50PA-001 A/B/C/D Seawater Pump	7000	
08XX-002 A/B/C/D/E/F/G/H Compactors	4000	
Defined Electrical Power Demand [kW]	39329	
+20% Additional Consumers [kW]	7866	
<b>Total Electrical Power</b>	<b>47195</b>	
<b>Total Turbine Power</b>		<b>56000</b>

The generation of electrical energy is based on the use of liquid fuel and emission of 832 g CO<sub>2</sub> per kWh electrical energy produced (IEA/CON/02/83).

The turbine power is generated from diesel turbines with an assumed CO<sub>2</sub> emission of 700 g CO<sub>2</sub> per kWh.

Direct loss of CO<sub>2</sub> during production, depressurisation and offloading, due to leakage, CO<sub>2</sub> dissolved in wastewater, hydrate dissociation at low water depths during sinking, etc. is assumed to 5% of total CO<sub>2</sub> volume.

A VLCC is assumed for fresh water supply to the offshore location. According to available information, the carrier consumes 86 tonne fuel per day. Heavy fuel is assumed. An emission of 3.15 kg CO<sub>2</sub> per kg heavy fuel is assumed ([www.windpower.dk](http://www.windpower.dk)). Total fuel consumption for the water supply ship assumes 100% of the time in motion.

The calculated CO<sub>2</sub> balance is as follows:

<b>Plant Capacity [tonne CO<sub>2</sub>/d]</b>	<b>20000</b>	
Emission [tonne CO <sub>2</sub> /d]	942	<b>Electrical Power Generation</b>
	941	Turbine Power Generation
	1000	Loss during Production, Depressurisation and Offloading
	271	Transportation, Fresh Water Supply
<b>Total CO<sub>2</sub> Emission [tonne/d]</b>	<b>3154</b>	
<b>CO<sub>2</sub> Capture Efficiency</b>	<b>84%</b>	



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## 8. CRITICAL COMMENTARY ON TECHNICAL FEASIBILITY

The objective of this study was to determine the cost and the feasibility of using gas hydrates in the transport chain for Deep Ocean disposal of CO<sub>2</sub>. No assessment has been performed regarding the feasibility of Deep Ocean storage of CO<sub>2</sub>, with its potential environmental impact.

Using gas hydrates in the transport chain for gas is not a proven technology and hence significant room for improvement in the technical concept is anticipated. However, these improvements are related to economics. In this section, no analysis or optimisation of the economics of the chain is attempted, rather an evaluation of the *technical* feasibility of the sub-processes.

### 8.1. LARGE SCALE CO<sub>2</sub> HYDRATE PRODUCTION PROCESS, INCLUDING STORAGE

#### Hydrates of CO<sub>2</sub> versus natural gas

The present study is based on in-house experience on hydrate behaviour and earlier feasibility studies. However, all previous work is related to hydrates of natural gas. Where literature information was not found, transferring natural gas hydrate behaviour to CO<sub>2</sub> hydrate behaviour was done. Discrepancies are not anticipated, but verification of CO<sub>2</sub> properties/behaviour should be performed. This includes e.g.:

- CO<sub>2</sub> hydrate formation in a continuous production process
- Stability of CO<sub>2</sub> hydrates at sub-zero, atmospheric conditions

#### Reactors

Experimental experience has shown that production of hydrates in a water-continuous CSTR is straightforward. It is not anticipated any challenges in up-scaling. It might however be room for optimising the operational conditions versus number of reactors.

#### Heat removal

Heat removal in high-pressure production systems is a proven technology and the present hydrate design is based on well-known principles and equipment. A possible technical challenge with heat removal in the hydrate production process is the possibility of hydrate formation within the hydrate/water heat exchanger. This is believed to be eliminated through degassers prior to the heat exchangers, thereby removing the reactant upstream the heat exchangers. Also, laboratory experiments have shown that hydrates, being hydrophilic, do not have a strong tendency for adhering on cold metal surfaces in a *water-continuous* system.

The amount of heat needing to be removed is not considered a *technical* challenge.

#### Hydrate/water separation

Separation of hydrates from the water phase is rendered necessary, as the system is dependent on excess water for heat removal purposes. Experimental experience has shown that production of large hydrate crystals is not feasible in the reactor in a continuous production process, the hydrates are typically only 100 µm. However, based on input from other industries, it is not envisaged that the separation stage will be a showstopper, but no equipment has been proven for this service and equipment development will be required.

It is in this study assumed a separation efficiency of 90%, rendering 356 m<sup>3</sup>/hr of water leaving with the hydrate. If this separation efficiency is not achievable, the technical feasibility of the hydrate production (and transportation) process is not believed altered, although the economics is affected. However, the separation efficiency may influence the technical feasibility of hydrates for Deep Ocean CO<sub>2</sub> disposal through the density of the hydrate product, see Sect. 8.4. It should be noted that no benefits are incorporated from possible reducing the free-water content by hydrate conversion in the freezing tower.

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#### Hydrate freezing and depressurisation

In this study, hydrate freezing is envisaged by counter-flowing the hydrate with evaporating CO<sub>2</sub>, which is not a proven technology for this service. However – although the size of the equipment might be altered based on resident time, the concept itself is considered feasible.

It is considered that enough conservatism is incorporated into the depressurisation tanks to ensure sufficient time for pressure relief. One challenge might be the transfer of the hydrate to and from the depressurisation tanks, which is assumed taking place by gravity flow in this study. It may be argued that it can be prudent to include a device for transporting the hydrates, e.g. screw-type pumps. It is not envisaged any major technical challenges with such a device, although technologies have not been proven for this service.

#### Block production

In this study, it is envisaged that hydrate blocks shall be produced from particles created in the freezing stage using compactors. This industrial process of creating larger blocks is well-known from several industries, although special development may be required to increase the efficiency in order to reduce the number of compactor units.

One large unknown is the behaviour of hydrates under mechanical stress. The size of the proposed compactors is therefore inevitable uncertain. More important, it is simply not known whether the compaction of dry hydrate particles will create blocks of sufficient size and low enough porosity with sufficient strength for handling and transport<sup>1</sup>. Producing the hydrate blocks prior to freezing is not considered an option since it is expected that the necessary residence time for freezing large hydrate blocks will render large scale production impossible.

The block-production stage is technically considered the weakest process stage due to the unknown behaviour of dry hydrate particles under stress in addition to the need for technology to be proven for service.

#### Storage

In this study, onshore storage is not included in the design. Instead, it is incorporated enough ship to eliminate storage. This is based on a wish for decreasing the total handling time, and that the necessary storage if decreasing the number of ships by one is very large (see Sect. 5.2.3). It can be argued that some storage capacity shall be included.

No technical challenges are envisaged with storage of frozen hydrate blocks. From laboratory experiments it is known that frozen hydrates are stable in air provided that the temperature is at least –10 °C. Large scale storage should only improve the picture. Hence, any storage must simply be an insulated room of sufficient size, with active cooling (cold storage).

## **8.2. LARGE SCALE CO<sub>2</sub> HYDRATE TRANSPORTATION, INCLUDING ON AND OFFLOADING**

#### Onloading

The onloading is outlined in Sect. 5.1.2. As stated, the effect of crushing when loading the hydrate blocks, i.e. the mechanical properties of the hydrate blocks, need to be evaluated. Care has to be put into the onloading design to ensure sufficient capacity. Although background data and detailed engineering is necessary, it is not believed that ship loading of the hydrate blocks will be a showstopper.

#### Transportation

Pros and cons on the vessel requirements are outlined in Sect. 5.1.4. Although using standard Bulk Type Vessels as basis, it is clear that the shipping requires specially designed carriers. The special design for the

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<sup>1</sup> As an analog, the difficulties of making a hard, compact snowball out of dry, fresh snow can be used.

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solution envisaged in this study includes insulation, sloping tank bottoms and moonpools with bucket-type conveyors for offloading. The increased cost due to special design is included in the cost estimates. The technical feasibility of long-distance ship transportation of frozen CO<sub>2</sub> hydrates depends on the properties of hydrate under bulk transportation conditions, which are not known to a large degree. This includes:

◆ Stability of frozen CO<sub>2</sub> hydrates

The meta-stability of frozen natural gas hydrates at atmospheric pressure sub-zero degrees is relatively commonly accepted and well documented. However, the data transfer from natural gas system to CO<sub>2</sub> system must be verified.

The meta-stability of hydrates must also be seen in connection with the free water content in the hydrate sample. It is proposed by many researchers that it is free water, converted to ice, that is creating a preserving barrier, preventing hydrate dissociation even at conditions outside the stability region. The connection between the amount of free water (ice barrier) and the stability of the hydrate samples should be investigated in more detail. In addition, more detailed investigations should be performed on the stability of hydrates under voyage (movement).

◆ Influence of mechanical stress on the behaviour of frozen CO<sub>2</sub> hydrates

Large-scale transportation of frozen hydrates have not been verified. The behaviour/appearance of hydrates may be altered under the mechanical stress experienced by the hydrates during transport. One area of concern is the possibility of the hydrate blocks transferring into large, not handable lumps. If this is the case, the mechanical strength of such lumps must be investigated in order to evaluate the possibility of breaking the lumps into smaller pieces prior to offloading. The effect will in any instance be increased complexity for the offloading system.

The risk associated with these uncertainties include:

1. Large boil-off of CO<sub>2</sub> during transport.
2. Prevention of efficient offloading.

Offloading

The need for special vessel design including the moonpool and vertical bucket-conveyor for offloading has been stressed above.

In addition, it is essential that the hydrates will sink rapidly without too much gas released in shallow waters. Beyond CO<sub>2</sub> emission, safety is an area of concern:

- Will the ship buoyancy decrease due to the release of gas from the hydrates directly below the boat? This might be bypassed with the ship moving during discharge.
- CO<sub>2</sub> is not a toxic gas in itself, but if released in large quanta upon discharge, it might displace oxygen to a harmful degree.

In summary, the dissociation of hydrates in water needs to be studied in more detail.

### 8.3. LARGE SCALE DECK-BASED HYDRATE PRODUCTION PROCESS

General

The basic assumption was to use same production process for the Offshore Location Case as for the Coastal Location Case. There are no movement-sensitive processes in the production process so a deck-based production process is as feasible as a land-based process, ignoring restrictions on weight and space. See Sect. 8.1 for details.

Block production and depressurisation

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The only significant difference between the Coastal and Offshore Cases is that the hydrate product is not frozen for the Offshore Location Case. Hydrate block production is envisaged to take place with pressurised hydrate feed, and depressurisation is taking place “within” the block production process. This process will have to be developed and verified for these services, but it is believed to be feasible.

This depressurisation will lead to a large CO<sub>2</sub> emission compared to the depressurisation process for the Coastal Location Case. However, the very large depressurisation vessels are omitted.

Compacting the hydrates at high pressure means that the temperature is above freezing. Hence, there will be 10 % water present, and it is envisaged that this water will act as “glue” in the compactor process. Hence, on one side, it is believed that the hydrate blocks produced offshore will have higher mechanical strength than the blocks produced onshore, eliminating the high technical uncertainties for the block-production stage. On the other side, these hydrates will not be in the meta-stable condition that frozen hydrates are. Whether compacting hydrates to large blocks will delay the dissociation enough to achieve acceptable CO<sub>2</sub> emission prior to reaching the Deep Ocean will have to be investigated and is considered a large technical uncertainty (see Sect. 8.4 and Appendix D).

#### Alternative process

It is stated in the Scope of Work that the deck-based CO<sub>2</sub> hydrate production process shall be similar to the land-based process, but there is an obvious possibility of altering the production process by producing hydrate from seawater offshore. However, two important drawbacks arise when exchanging fresh water with seawater:

- ◆ Salt is a very good hydrate inhibitor, i.e. the salinity of the water shifts the equilibrium curve towards lower temperatures. For the present process, this means that the operation window will decrease significantly and the operation temperature will be shifted to approximate 1- 4 °C at 36 bara. This will in turn lead to the need for (at least) one more reactor set in series per train since the allowable reactor temperature increase decreases.
- ◆ The salt in seawater is excluded when producing hydrates. Hence, a re-circulation scheme as pictured for the hydrate process is not feasible, as the salt will accumulate, rapidly increasing salinity until hydrate formation is totally inhibited. Therefore, using seawater as the water supply for hydrate formation means a “once-through” operation. This will in turn lead to increased cooling demand since the Feed Water has to be continuously cooled, and the Feed Water will add up to 26800 m<sup>3</sup>/hr. The incoming feed could be exchanged with cold effluent water and some of the extra cooling duty could be avoided. This will however add very large exchanger.

The increase in dry equipment weight for the hydrate process only due to exchanging fresh water with seawater is roughly estimated to 2000 tonnes. The material will also have to be changed, withstanding the increased danger of corrosion and increasing the cost. In addition, there will be environmental impacts due to overboard dumping of 23666 m<sup>3</sup> cold water (4-6 °C) pr. hour and an increased energy consumption of 30 MW (= approximate 600 t/d additional CO<sub>2</sub> emission). Using seawater has not been evaluated further.

Hence continuous fresh water feed of approximate 2700 m<sup>3</sup>/hr is needed, as this corresponds to the water volume leaving as hydrates. These amounts necessitate a very large storage volume, as well as frequent supply of fresh water.

#### Feed arrival

The design basis states arrival conditions of 10 bar and -50 °C. Means of arrival of the Feed CO<sub>2</sub> may have impact on complexity of the offshore structure. As an example, pipeline arrival of the liquid CO<sub>2</sub> will require the development of low-temperature risers since the present state-of-the-art is around -20 °C. It is assumed that CO<sub>2</sub> is “available” at the production facilities (Reactor Inlet) and neither technical nor economical aspects of the arrival of Feed CO<sub>2</sub> have been evaluated.

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#### 8.4. SINKING OF BULK CO<sub>2</sub> HYDRATE

The analysis of the CO<sub>2</sub> hydrate sinking process is presented in Appendix D. As discussed there, the discrepancies in the dissociation rate values contribute the most to the uncertainties in the calculations. However, the degree of dissociation only influences the final necessary particle size and –within the estimated size-range– has no impact on the *feasibility* of the actual sinking process.

##### Density considerations

As outlined in Appendix D, several assumptions are integrated into the analysis, which may have influence on the particle size through sinking rate. However, only “density-related” assumptions are viewed as relevant to the actual feasibility of the sinking process.

A prerequisite for the sinking process of CO<sub>2</sub> hydrates into the Deep Ocean is that the effective density of the hydrate samples is relatively larger than the surrounding seawater through the whole water column. In the present study, a constant frozen hydrate density of 1052 kg/m<sup>3</sup> (including ice) and a constant seawater density of 1030 kg/m<sup>3</sup> are assumed. This gives a relative density difference between the CO<sub>2</sub> hydrate and the seawater of 2%. For the Offshore Location Case, the free water is not converted to ice, rendering the relative density difference between the (compacted) CO<sub>2</sub> hydrate and the seawater of 3%.

According to Pickard and Emery (1990), the surface seawater density at high latitudes is approximate 1027 kg/m<sup>3</sup>. For lower latitudes, the surface seawater density is as low as 1023.5 kg/m<sup>3</sup> (at equator). The seawater density increases with water depth, up to ca. 1027.9 kg/m<sup>3</sup>. There is little variation with latitude for the deep waters. Hence, the assumed density of the seawater is on the conservative side and any error will not lead to less feasibility of the sinking process.

As described in Appendix C, the maximum density of the pure CO<sub>2</sub> hydrate is 1134 kg/m<sup>3</sup>. This value corresponds to an ideal hydrate structure (184 Sm<sup>3</sup>/m<sup>3</sup>, all cavities filled with gas). For the present study, a value of 1072 kg/m<sup>3</sup> is chosen, corresponding to a gas content of 150 Sm<sup>3</sup>/m<sup>3</sup>. It is believed that this is a conservative value (ref. Figure B2), since less gas in the hydrate will most likely not lead to sufficient stability of the structure.

However, the hydrate production process is water-continuous, with the need for separating the hydrate product from the water phase. The more residual water after the separation, the less the density of the hydrate product. In this study, residual water content of 10wt% is assumed. The high-pressure separation of hydrates from water is novel, not proven technology. AKT has been in close communication with a separation supplier about development of hydrate-water separation equipment. Although pressurised conditions are judged as a technological threshold, obtaining 90% separation efficiency is considered achievable.

Hence, development of separation equipment specially designed for the hydrate production process will be necessary, but the technology is judged as feasible and not a technical-critical step in the process.

The hydrate gas content and the separation efficiency determine together the bulk gas content and the density of the final hydrate product.

The table below illustrates the effect on the hydrate density versus gas content and free water content, for both the Coastal (ice) and the Offshore Location (water) Cases.

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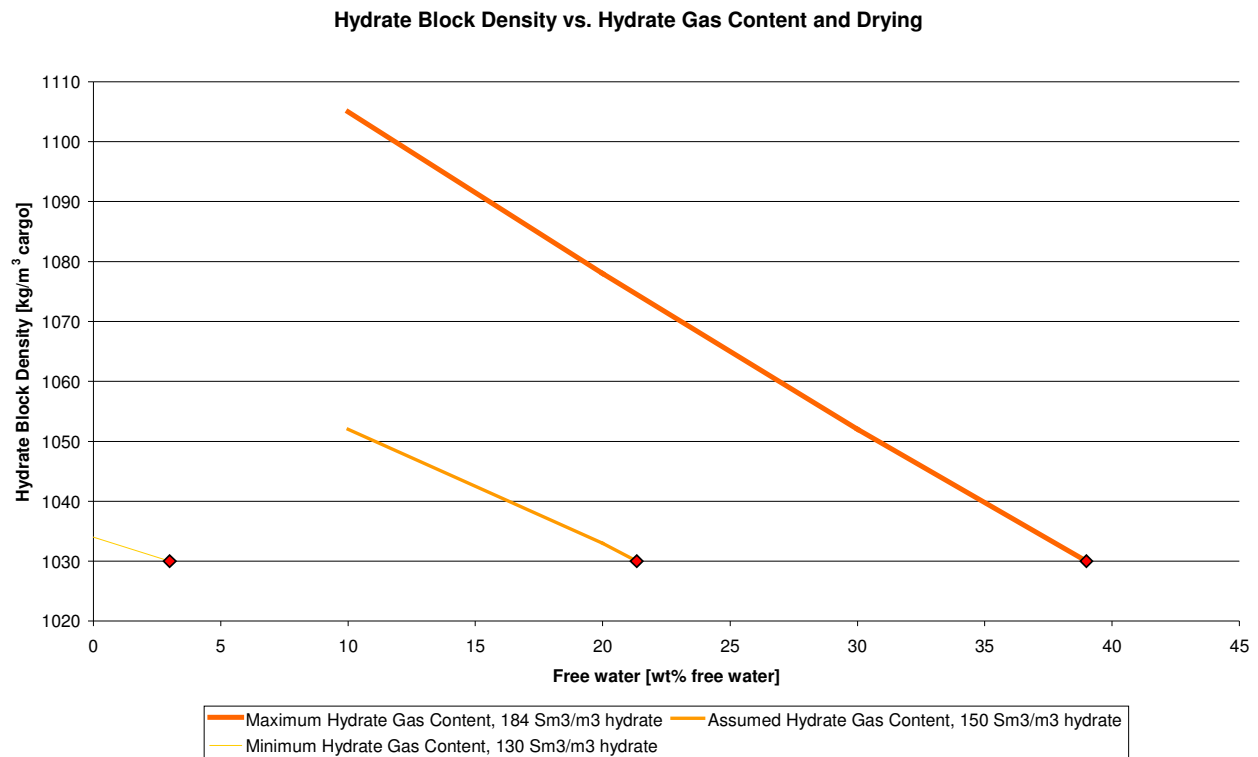
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Gas Content [Sm <sup>3</sup> /m <sup>3</sup> ]	Wt% Free Water	Hydrate Block Density [kg/m <sup>3</sup> ]
150	10	Coastal: 1052
		Offshore: 1064
150	20	Coastal: 1032
		Offshore: 1056
184	10	Coastal: 1106
		Offshore: 1120
184	20	Coastal: 1079
		Offshore: 1105

A prerequisite for the feasibility for utilisation of hydrates for Deep Ocean storage of CO<sub>2</sub> is that the hydrate block density is higher than the seawater density. In the figure below, the hydrate block density vs. the hydrate gas content and amount of free water is shown. It is seen that depending on the gas content in the pure hydrate, the separation efficiency must be between 61% and 97% in order to match seawater density.



**Figure 8-1: Hydrate block density vs. hydrate gas content and amount of free water (separation efficiency).**

It is realised that during the sinking process, the CO<sub>2</sub> hydrate will dissociate. In this work, homogeneous samples are assumed, something that seems likely in view of the production process. An area of concern is whether or not the gas will "let go" of the hydrate sample as the hydrate dissociate. Attached gas on the hydrate surface will lead to a smaller effective density of the hydrate sample. Approximate 2 vol% of the released gas entrapped on the hydrate surface will lead to a buoyant hydrate sample.



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In addition, hydrate samples are envisaged produced by compaction and is assumed to have a constant density throughout, i.e. homogeneous samples. However, if e.g. any gas is entrapped within the sample, the effective density of the hydrate will decrease. The two last effects combined could in theory lead to the hydrate samples in worst case not sinking into deep waters, but stay buoyant and release all CO<sub>2</sub> in shallow waters.

The effective density of the hydrate blocks is crucial for the feasibility of hydrates for Deep Ocean Storage of CO<sub>2</sub>. It is essential that the effective density of hydrate blocks as a function of possible gas content, free water content, gas entrapment, etc. is studied in more detail.

#### Mechanical strength considerations

The proposed process of hydrates for Deep Ocean Disposal of CO<sub>2</sub> assumes that the mechanical strength of the hydrate blocks discharged overboard is high enough so that the blocks will stay intact on the journey down to deep waters. Breaking of the blocks into smaller pieces will not ensure that the hydrate only dissociate a certain degree before reaching the Deep Ocean.

As stressed in Sect. 4.1.8 and Sect. 4.2.6, the mechanical strength of the produced hydrate blocks is not known, neither for the Coastal or for the Offshore Location Case. It is therefore considered necessary with investigation of the mechanical strength of hydrate blocks in order to assess the feasibility of utilising hydrates for Deep Ocean storage of CO<sub>2</sub>.

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## 9. COST ESTIMATE

### 9.1. INTRODUCTION

The objectives of this section is to present an order of magnitude cost estimates for the two alternative concepts for production and subsea storage of CO<sub>2</sub> hydrates. The CAPEX estimates are intended to be 50/50 estimates with overall accuracy of +/- 50 % and 80 % confidence interval. OPEX estimates and cost per metric ton of hydrates are included. The estimates reflect the technical concepts presented in this report.

Section 9.2 presents the estimating methodology. Sections 9.3 and 9.4 present cost comparisons for the concepts and the individual estimates.

The cost estimates cover the following elements for the Coastal Location Case:

1. The hydrate production plant including hydrate load-out facilities.
2. Hydrate bulk carriers (4 off) including hydrate offloading facilities.

The cost estimates cover the following elements for the Offshore Location Case:

1. The hydrate production plant including hydrate offloading facilities.
2. Substructure/hull for the offshore production plant.
3. Fresh water VLCC shuttle tanker (1 off) for the hydrate formation process.

The cost estimates do not include cost for purchase of land or land right of ways, offsite infrastructure investments, company cost and local taxes.

Note that for the onshore hydrate plant concept it is assumed that the CO<sub>2</sub> is available at the plant, thus no cost for this has been calculated. For the offshore hydrate plant concept no cost has been included for making the CO<sub>2</sub> available offshore at the plant (outside scope of work). Thus on this account the two estimates are principally unequal.

The OPEX estimates and cost per metric ton of hydrates cover the same elements as the CAPEX estimates. No cost has been included for the turbine power for the onshore concept as this is assumed supplied by the CO<sub>2</sub> producing plant.

### 9.2. ESTIMATING METHODOLOGY

The estimates are high level estimates based on knowledge of costing of similar plants and systems. The onshore plant estimates is based on estimates of the equipment cost and developed by equipment cost factoring representative for gas processing plants in the Far East. The offshore plant estimate is based on equipment cost factoring for offshore FPSO for oil and gas processing, adjusted for the requirements of a hydrate formation plant. The cost estimates for the hydrate bulk carriers and VLCC tanker for water transport are based on international new-build prices. The hull for the offshore plant is likewise based on a VLCC tanker hull adjusted for the requirements of a topside hydrate plant.

The OPEX cost is scaled from similar onshore and offshore gas/oil processing plants, though such that the energy requirements have been addressed separately. The energy unit prices, for diesel and electricity, are based on current market prices. An allowance of 0.2 US\$ per m<sup>3</sup> fresh water purchased has been made in the OPEX estimation.

95% and 85% production regularities have been assumed for the onshore and offshore alternatives.



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The main arguments for choosing 20 % contingency to reach the 50/50 estimates have been:

1. New technology and low level of detailing of the technical solutions call for a high contingency.
2. The use of as-built experience production plant cost and current international unit prices for bulk carriers and VLCC tankers decrease the requirements for contingency.

### 9.3. COST COMPARISONS

Table 9-1 and Table 9-2 below compare CAPEX and OPEX for the two options. Do note that the lack of cost for supplying CO<sub>2</sub> at the offshore plant is a principal inequality when comparing cost for the two concepts.

**Table 9-1: CAPEX Cost Comparisons**

Cost Item		Cost (mill USD)
<b>Onshore Hydrate Production Alternative</b>		
Onshore Production Facilities		756
Hydrate Transport Bulk Carriers	4 off	200
Contingency	20 %	191
<b>Sum Onshore CAPEX</b>		<b>1 147</b>
<b>Offshore Hydrate Production Alternative</b>		
Offshore Topsides Production Facilities		730
Offshore Hull for Production Facilities		80
Water Transport VLCC Tanker	1 off	68
Contingency	20 %	162
<b>Sum Offshore CAPEX</b>		<b>1 040</b>

CAPEX cost is not included for CO<sub>2</sub> transport and loading systems for the offshore hydrate plant.

The onshore hydrate plant is assumed next to the CO<sub>2</sub> producing plant.

**Table 9-2: OPEX Cost Comparison**

Cost Item		Cost (mill USD/yr)
<b>Onshore Hydrate Production</b>		
Annual OPEX in % of CA	3 %	34
Electrical consumption		26
Water purchase		5
Hydrate transport bulk ca	4 off	12
<b>Sum Onshore OPEX</b>		<b>77</b>
<b>Offshore Hydrate Production</b>		
Annual OPEX in % of CA	4 %	42
Diesel for turbine power consumption		25
Water purchase		4
Water transport VLCC ta	1 off	6
<b>Sum Offshore OPEX</b>		<b>77</b>

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#### 9.4. COST ESTIMATES

Table 9-3 to Table 9-5 show the cost estimates for the onshore hydrate plant, the hydrate transport carriers and the electrical power cost for the onshore plant. Table 9-6 to Table 9-8 show the cost estimates for the offshore hydrate plant, the offshore hull and the VLCC water transport tankers and the diesel cost for the offshore plant. A modified newbuilt VLCC tanker has been assumed used for the offshore hull. Table 9-9 shows the cost estimates for water purchase, both for the onshore and the offshore hydrate plant.

**Table 9-3: Onshore Hydrate Production Plant Cost Estimate**

<b>Cost Items</b>	<b>Cost (million USD)</b>	<b>% of Equip cost</b>
<b>Procurement</b>		
Mchanical Equipment	245	100 %
Piping	98	40 %
Electrical	49	20 %
Instrumentation	49	20 %
Spares	42	17 %
<b>Sub-total Procurement</b>	<b>484</b>	<b>197 %</b>
<b>Installation</b>		
Mechanical & Piping	74	30 %
Electrical	25	10 %
Instrumentation	25	10 %
Insulation & Painting	12	5 %
Civil	49	20 %
Fire Fighting Systems	10	4 %
Miscellaneous contracts	2	1 %
<b>Sub-total Installation</b>	<b>196</b>	<b>80 %</b>
<b>Mgmt, Eng, Construction Supervision</b>	<b>49</b>	<b>20 %</b>
<b>Other Cost</b>	<b>27</b>	<b>11 %</b>
<b>TOTAL</b>	<b>756</b>	<b>308 %</b>

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**Table 9-4: Hydrate Transport Carrier Cost Estimate for the Onshore Plant Concept**

<b>Bulk Carriers:</b>		
Scantling draught	169 400 dwt	
Storage	185 000 m3	
Cost, CAPEX		38 mill USD
Necessary ship upgrades:		
	unloading facilities (vertical bucket conveyor)	
	moonpools for unloading	
	gravity feed tank bottoms	
	Insulation	
	Steel grade for low temperatures	
	various other items	
Adjusted CAPEX		50 mill USD
No off carriers		4
<b>Total CAPEX, 4 off</b>		<b>200 mill USD</b>
Cost, operation	4 250 USD/d (crew, lubr.oil, insur)	
	8 000 USD/d (fuel)	
	4 000 USD/d (fuel, 50% operation)	
	3,0 mill USD/yr (total, 50% operation)	
<b>Cost operation, 4 off</b>	<b>12,0 mill USD/yr (total, 50% operation)</b>	

**Table 9-5: Electrical Power Cost Estimate for the Onshore Plant Cost Concept**

Defined electrical power consumption		67 994 kW
Allowance for additional power consumption	15 %	10 199 kW
Calculated electrical power consumption		78 193 kW
Assumed kWh rate:	0,04 USD/kWh	
Regularity assumed	95 %	
Real electrical power consumption		74 283 kW
<b>Annual cost of electrical power consumption</b>		<b>26,0 mill USD/yr</b>
Cost of gas for gas powered turbine is not included, assumed available from the CO <sub>2</sub> producing plant.		

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**Table 9-6: Offshore Hydrate Production Plant Cost Estimate**

<b>Cost Items</b>	<b>Cost (million USD)</b>	<b>% of Equip cost</b>
<b>Procurement</b>		
Mechanical Equipment	217	100 %
Piping	52	24 %
Electrical	11	5 %
Instrumentation	22	10 %
Structural	24	11 %
Other disc	17	8 %
<b>Sub-total Procurement</b>	<b>342</b>	<b>158 %</b>
<b>Installation</b>		
Mechanical & Piping	54	25 %
Electrical	11	5 %
Instrumentation	11	5 %
Insulation & Painting	20	9 %
Fire Fighting Systems	2	1 %
Structural	46	21 %
Other disc	9	4 %
<b>Sub-total Installation</b>	<b>152</b>	<b>70 %</b>
<b>Mgmt, Eng, Construction Supervision</b>	<b>165</b>	<b>76 %</b>
<b>Project Completion</b>	<b>72</b>	<b>33 %</b>
<b>TOTAL</b>	<b>730</b>	<b>337 %</b>

**Table 9-7: Offshore Hull and Water Transport Tanker Cost Estimates for the Offshore Plant Concept**

**VLCC tanker (newbuild):**

Conversion of old hull is considered feasible for benign waters only

Storage volume 340 000 m3

Cost, CAPEX 68 mill USD

CAPEX needs to be adjusted for:

structural reinforcement to carry topsides weight

Design life (20/25 years ?)

Dynamic positioning equipment/instrumentation and machinery

Locational factors

Minimum of production stops for maintenance

Single hull construction (water storage only)

Adjusted CAPEX	1 off	80 mill USD
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Cost, operation 6 500 USD/d (crew, lubr.oil, insur)

2,4 mill USD/yr (crew, lubr.oil, insur)

12 000 USD/d (fuel)

9 000 USD/d (fuel, 75% operation)

Cost, operation	1 off (total, 75% operation)	5,7 mill USD/yr
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**Table 9-8: Diesel Power Cost Estimate for the Offshore Plant Cost Concept**

**Power Consumption:**

*Electrical*

Defined		39 329 kW	
Allowance for add. el. power	20 %	7 866 kW	
<i>Sum Electrical Power consumption</i>		47 195 kW	1 488 335 GJ/yr

<i>Turbine</i>		56 000 kW	1 766 016 GJ/yr
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**Diesel Consumption:**

Energy Content Diesel:		42,7 GJ/tonne	
Generation of electrical energy	30 % specified efficiency		116 185 tonne/yr
Diesel turbines:	60 % assumed efficiency		68 931 tonne/yr
Regularity	85 % assumed		

<b>total diesel consumption</b>		<b>157 349 tonne /yr</b>
		185 117 m3/yr

Annual Cost of Diesel	160 US\$/tonne	25 mill US\$/yr
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**Table 9-9: Water Purchase Cost**

<b>Water Consumption:</b>	24 mill m3/yr
Regularity:	95 % Onshore Location
	85 % Offshore Location
Purchase Price assumed:	0.2 US\$/m3

Annual Cost of Water:	4.6 mill US\$/yr. Onshore Location
	4.1 mill US\$/yr. Offshore Location

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## 10. ECONOMIC ANALYSIS

### 10.1. COST PER TONNE CO<sub>2</sub> ABATED

Based on the above cost estimates, the following abatement costs have been estimated:

- Coastal Location Case: 22.3 US\$/tonne CO<sub>2</sub>
- Offshore Location Case: 24.7 US\$/tonne CO<sub>2</sub>

These numbers are however not directly comparable, as the transport of the CO<sub>2</sub> to the offshore location is not included in the Offshore Location Case.

In the estimation of cost per tonne CO<sub>2</sub> abated, the CAPEX has been spread over a 20-year production span for both options. Production regularities of 95% and 85% have been assumed for the Coastal Location and the Offshore Location Cases, respectively. The capture efficiencies estimated in Chapter 7 are allowed for. Table 10-1 below summarises the calculations.

**Table 10-1: Comparison of Cost per Tonne CO<sub>2</sub> Converted to Hydrate**

#### Cost pr. MT CO<sub>2</sub> Converted to Hydrate

Cost Item	Cost (mill USD/yr)
<b>Onshore Hydrate Production</b>	
20000 MT/day =	6033450 MT/yr at 87% capture efficiency and 95% regularity
CAPEX pr. MT, over	20 years 9.5
OPEX	12.8
<b>Sum Cost pr. MT CO<sub>2</sub></b>	<b>22.3</b>
<b>Offshore Hydrate Production</b>	
20000 MT/day =	5212200 MT/yr at 84% capture efficiency and 85% regularity
CAPEX pr. MT, over	20 years 10.0
OPEX	14.7
<b>Sum Cost pr. MT CO<sub>2</sub></b>	<b>24.7</b>

### 10.2. SENSITIVITY TOWARDS COASTAL PLANT LOCATION

As outlined in Sect. 9.2, the onshore plant cost estimates is based on estimates of the equipment cost and developed by equipment cost factoring representative for gas processing plants in the Far East.

The estimate of equipment cost is based on total equipment weight from the equipment list (see Sect. 4.1.9).

The equipment / plant cost factor used is 3.08 (see Table 9-3).

In AKT's in-house cost databases, the equipment / plant cost factor is typically 3 for Far East location, 4-5 for Continental European conditions and up to 6 for North European (Norwegian) conditions.

The CO<sub>2</sub> abatement cost versus plant location is illustrated in Figure 10-1.

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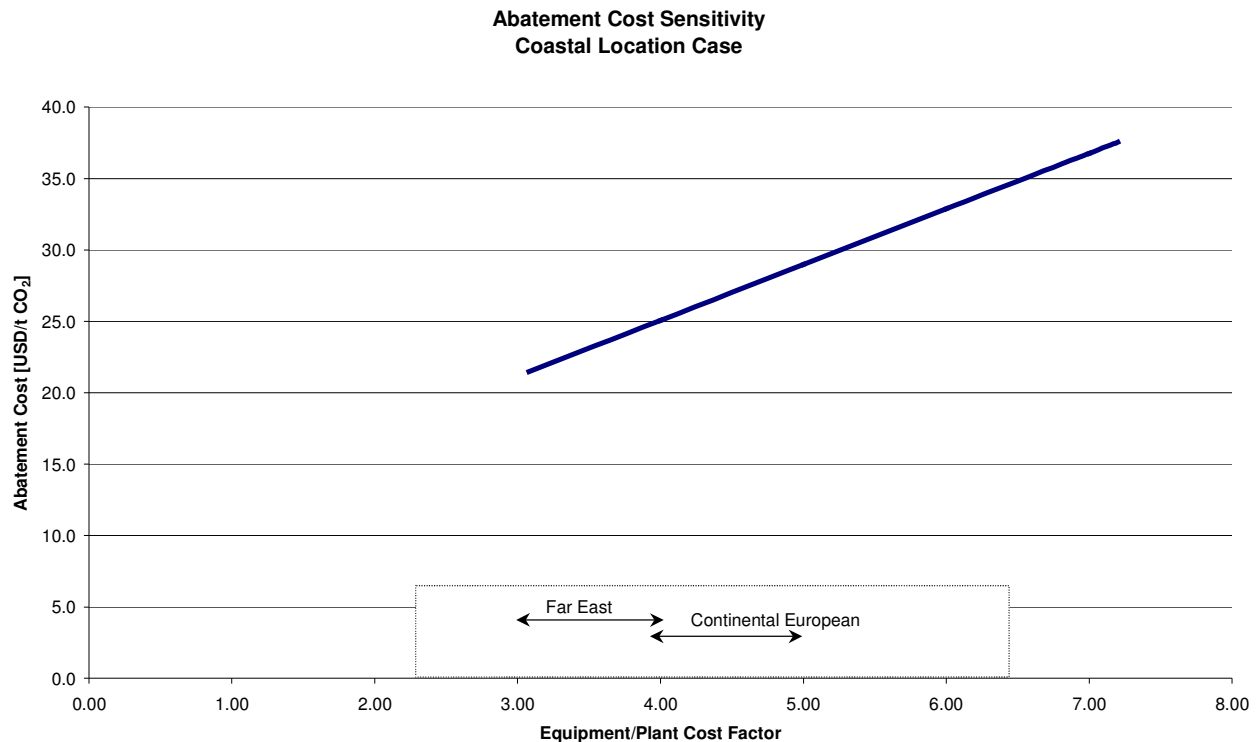
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**Figure 10-1: Abatement cost sensitivity versus plant location.**



### 10.3. SENSITIVITY TOWARDS TRANSPORT DISTANCE

#### Coastal Location Case

The number of hydrate carriers required versus transport distance is given in Sect. 5.2.3. Keeping production related cost constant, the cost per tonne CO<sub>2</sub> abated versus hydrate transport distance was calculated and is presented in Table 10-2 and illustrated in Figure 10-3.

**Table 10-2: Cost per tonne CO<sub>2</sub> abated versus hydrate transport distance (Coastal Location Case)**

#### ONSHORE

**Production Plant:** 756 mill USD  
**Electrical cons.:** 26 mill USD/yr  
**Water purchase:** 5 mill USD/yr  
**Lifespan:** 20 yrs  
**Capture:** 6033450 tonne CO<sub>2</sub>/yr

Distance	No.s Ship	CAPEX ship	SUM CAPEX	TOTAL OPEX	Cost/t CO <sub>2</sub>
100	2	100	1027	68	19.8
500	3	150	1087	73	21.0
1000	4	200	1147	77	22.3
2000	6	300	1267	87	24.9
3000	8	400	1387	97	27.5
4000	10	500	1507	106	30.1

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### Offshore Location Case

Only fresh water supply will influence the cost per tonne CO<sub>2</sub> abated versus distance. VLCC are assumed, resulting in a cost “step function” versus distance. Keeping production related cost constant, the cost per tonne CO<sub>2</sub> abated versus fresh water transport distance was calculated and is presented in Table 10-3 and illustrated in Figure 10-3.

**Table 10-3: Cost per tonne CO<sub>2</sub> abated versus water transport distance (Offshore Location Case)**

#### OFFSHORE

<b>Production plant:</b>	730 mill USD
<b>Offshore hull:</b>	80 mill USD
<b>SUM:</b>	810 mill USD
<b>Diesel:</b>	25 mill USD/yr
<b>Water purchase:</b>	4 mill USD/yr
<b>Lifespan:</b>	20 yrs
<b>Capture:</b>	5212200 tonne CO <sub>2</sub> /yr

Distance	No.s Ship	CAPEX ship	SUM CAPEX	TOTAL OPEX	Cost/t CO <sub>2</sub>
100	1	50	1032	76	24.5
1200	1	50	1032	76	24.5
1300	2	100	1092	85	26.7
3100	2	100	1092	85	26.7
3200	3	150	1152	93	28.9
4000	3	150	1152	93	28.9

As stated in the cost estimate section, the lack of cost for supplying CO<sub>2</sub> at the offshore plant is a principal inequality when comparing cost for the two concepts. By assuming a transport cost of the liquid CO<sub>2</sub> to the Offshore Location facilities, a rough comparison might be made. A transportation cost of 8 USD/tonne CO<sub>2</sub> (assuming LPG-type of tankers) was added to offshore location transportation cost and is included in Figure 10-3.



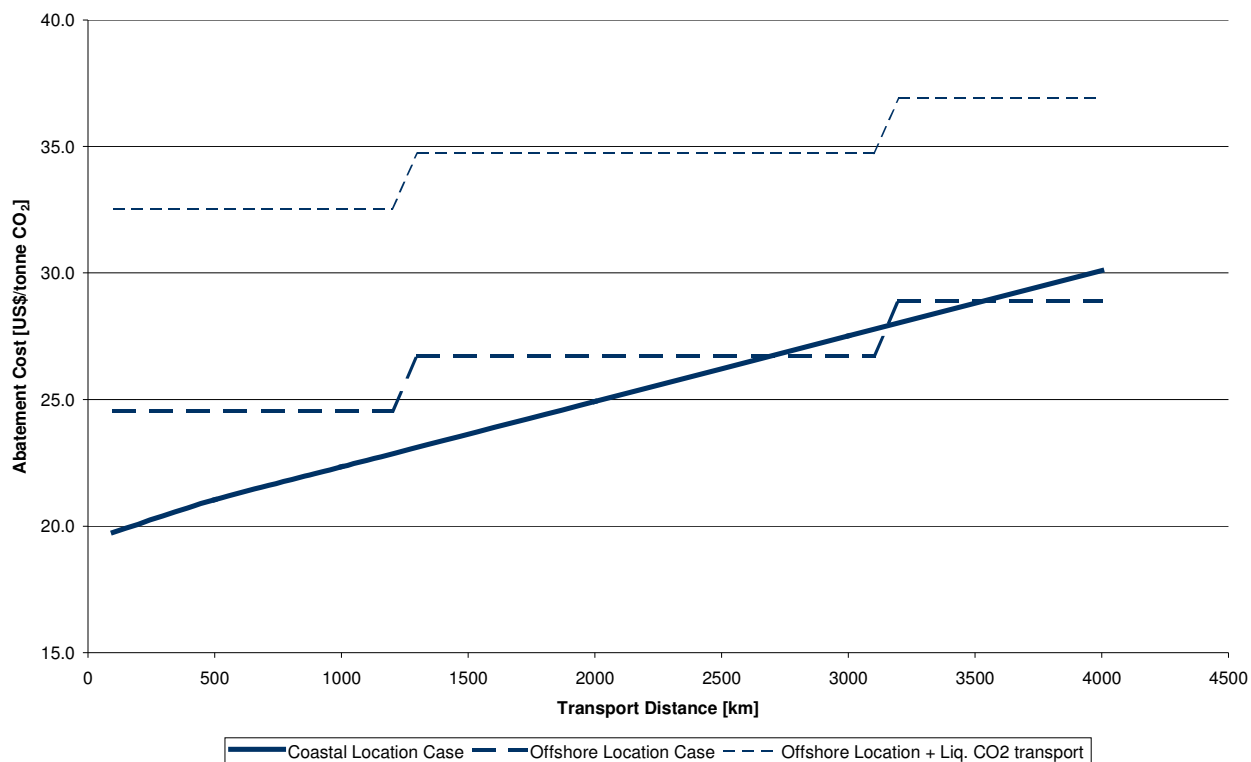
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**Figure 10-3: Cost per tonne CO<sub>2</sub> abated versus transport distance.**

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## 11. SUBMERGED PRODUCTION OF CO<sub>2</sub> HYDRATE

It has been envisaged that it may be possible to make use of favourable sub-sea pressure and temperature conditions to form hydrates more easily than with a process located on the surface. Such a process will have to be located in at least 200 m water depth in order to be within the hydrate forming pressure and temperature conditions.

A few patents and papers present possible solutions for submerged hydrate production. Spencer (1995) presents a system that might be submerged for formation of hydrates from CO<sub>2</sub> and seawater. Iijima et al. (1994) present several methods for the same. In a paper, Yamasaki (2000) presents laboratory experiments related to such production of hydrates (possibly based on Japanese Patents No. JP2001348584 and JP10265210 (in Japanese)). No detailed investigations on the technical and economical feasibility of any of the formation schemes are found.

The hydrate formation scheme presented in this study is based on the following terms:

- The formation must take place under turbulent conditions in order to achieve a large CO<sub>2</sub>-water interface and thereby a large hydrate conversion rate.
- The formation takes place in an environment with excess water in order to enable efficient heat removal. The produced hydrates are separated from the excess water phase prior to being compacted to hydrate blocks, large enough not to dissociate more than a few percentage before reaching 3000 m water depth.

From our point of view, the same terms must be fulfilled also for a potential submerged production scheme.

Turbulence must be supplied either through stirring, through possible spraying the reactant into the reactor, or possible a clever design of the reactor unit. Our experimental experience is that only stirring will create enough turbulence for efficient hydrate formation, considering that the reactor has to be excess water filled. Generally it is not proven with rotating equipment subsea.

Based on the hydrate sinking analysis, significant hydrate dissociation will also occur at 200 m water depth and below. Hence, there will be a need for larger hydrate particles. Based on AKT's experimental experience, it is not possible to continuous produce large hydrate particles within the hydrate reactor. Therefore, separation equipment and also a compacting device will have to be included in a submerged production facility.

As stated in Appendix D, the necessary hydrate block sizes is highly dependent on the dissociation rate in water. It is likely that a hydrate compactor is more crucial for submerged production than for land based production. Hence, it is believed that the feasibility of submerged production of hydrates will be highly dependent on the dissociation rate in seawater.

Hence a submerged production of CO<sub>2</sub> hydrates for Deep Ocean disposal of CO<sub>2</sub> is subjected to some of the unknown outlined for both the land and the offshore based production plants evaluated in this study. This include dissociation rates in water and hydrate compacting feasibility. In addition, there will be a need for novel technology and rotary equipment with power supply, none of which is proven technology.

Generally, the technical uncertainties related to submerged production of CO<sub>2</sub> hydrates are at this stage so large that this production scheme is not viewed viable.

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## 12. COMPARISON OF OPTIONS

### 12.1. FEASIBILITY

Production of hydrates will take place by identical processes for the Coastal and the Offshore Location Cases, hence the feasibility of the isolated production process does not alter between the two options.

Both options require the production of large hydrate blocks. The compacting rolls will need to be developed for the specific service, but the basic mechanisms will approximate be the same for the two options and the feasibility of the block production process itself does not alter between the two options.

However, for the Coastal Location Case, the hydrate blocks must be frozen for long-distance transporting purposes. The compacting is proposed *after* freezing the hydrate and free water due to unrealistic long freezing times if the freezing is to take place after compacting. An open question is whether the compacting of dry hydrates will create hydrate blocks of sufficient strength. For the Offshore Location Case, the compacting takes place from hydrates containing 10% free water. Intuitively, the compacting of “wet hydrates” is more feasible than the compacting of “dry hydrates”. The properties of compacted hydrates, whether compacted from “wet” or “dry” conditions are however not known, and will have to be looked into in more details.

Although the proposed solutions of the two options differ with regard to the hydrate product that is sunk in (frozen vs. non-frozen), and that this difference may influence the dissociation rate, it is not on this stage possible to rank the feasibility of the two options with regard to dissociation rate. The properties of the hydrates, whether frozen or non-frozen are not known in sufficient detail. It is however believed that a difference in dissociation rates will be possible to handle through the size of the produced hydrate blocks.

The Coastal Location scheme does in addition to production consist of a transportation segment, which the Offshore option does not. It is inherent that this segment adds to the complexity of the Coastal Location option, in particular since the technology is not proven. For the Offshore Location Case, the transport is carried out by other means, not evaluated as part of this study.

The design rate of 20,000 tonnes CO<sub>2</sub>/d results in large production facilities. Generally, large production facilities are more challenging on an offshore structure than a land-based plant, due to weight and space limitations. In addition, the disposal of the hydrate blocks into the Deep Ocean is considered more challenging for the Offshore option than the Coastal option. Batch offloading from a ship will be less time-sensitive than continuous offloading from the platform structure. Also from a safety point-of-view, thorough investigation and modelling of the sinking process must be performed in order to understand the behaviour of the hydrates when disposed overboard. E.g. significant release of gas immediately after discharging the hydrate blocks will be more critical for a stagnant offshore structure than for a ship that may be under movement during offloading.

### 12.2. CAPTURE EFFICIENCY

The capture efficiencies for the two options are estimated to 87% and 84% for the Coastal Location and the Offshore Location Cases, respectively. No differentiation between the options can hence be made based on capture efficiency.

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### 12.3. COST

The following abatement costs have been estimated (Sect. 10.1):

Coastal Location Case: 22.3 US\$/tonne CO<sub>2</sub>

Offshore Location Case: 24.7 US\$/tonne CO<sub>2</sub>

These numbers are however not directly comparable, as the transport of the CO<sub>2</sub> to the offshore location is not included in the Offshore Location Case. Hence, this transportation cost needs to be added to the Offshore Location Case in order to compare the options.

No work has been performed as part of this study to evaluate the transportation of CO<sub>2</sub> to the offshore location. However, the abatement cost for the Offshore Location Case is anyway higher than for the Coastal Location case, and CO<sub>2</sub> transportation costs will only add to the difference.

An “optimisation” of the Offshore Location process may be possible through the use of seawater, eliminating the need for fresh water supply and large storage capacity. However, a rough estimation of the added costs of increased equipment weight and increased power consumption neutralises the saving in no water supply and smaller hull.

It is believed that further “optimisation” and testing of the novel hydrate concept will gain both options to the same degree.

### 12.4. CONCLUSION

The feasibility of both the Coastal Location and the Offshore Location options are dependent on technology development and proper design, but mostly on the mapping of fundamental properties of the hydrates and their behaviour. It is at this stage not possible to differ between the options based on feasibility as both options are subjected to different uncertainties.

Using cost evaluations, the CO<sub>2</sub> abatement cost for the Coastal Location Case seems to be significantly lower than for the Offshore Location Case when the liquid CO<sub>2</sub> transport to the offshore site is included.

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## **APPENDIX A – PROCESS FLOW DIAGRAMS**



## Final Report

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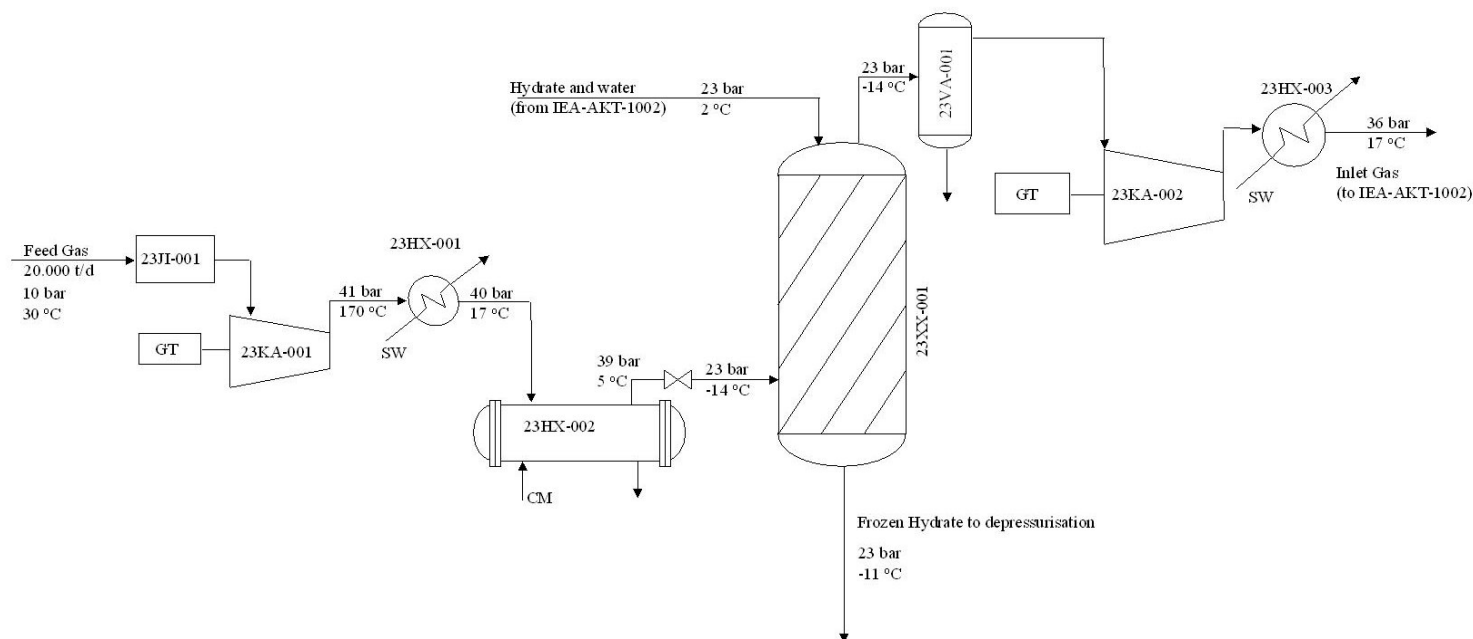
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Tag Number	23JI-001	Tag Number	23KA-001	Tag Number	23HX-001	Tag Number	23HX-002
Description	Gas Metering	Description	Gas Inlet Compressor	Description	Gas Inlet SW Cooler	Description	Gas Inlet Cooler (liquefier)
Duty (kW)		Duty (kW)	27460	Duty (kW)	39550	Duty (kW)	3722
Tag Number	23XX-001	Tag Number	23VA-001	Tag Number	23KA-002	Tag Number	23HX-003
Description	Evap. Tower / Freezer	Description	Scrubber	Description	Reactor Gas Compressor	Description	Reactor Inlet Gas SW Cooler
Duty (kW)	64000	Duty (kW)		Duty (kW)	6646	Duty (kW)	3402

IEA-AKT-1001  
Inlet Gas Treatment - Onshore

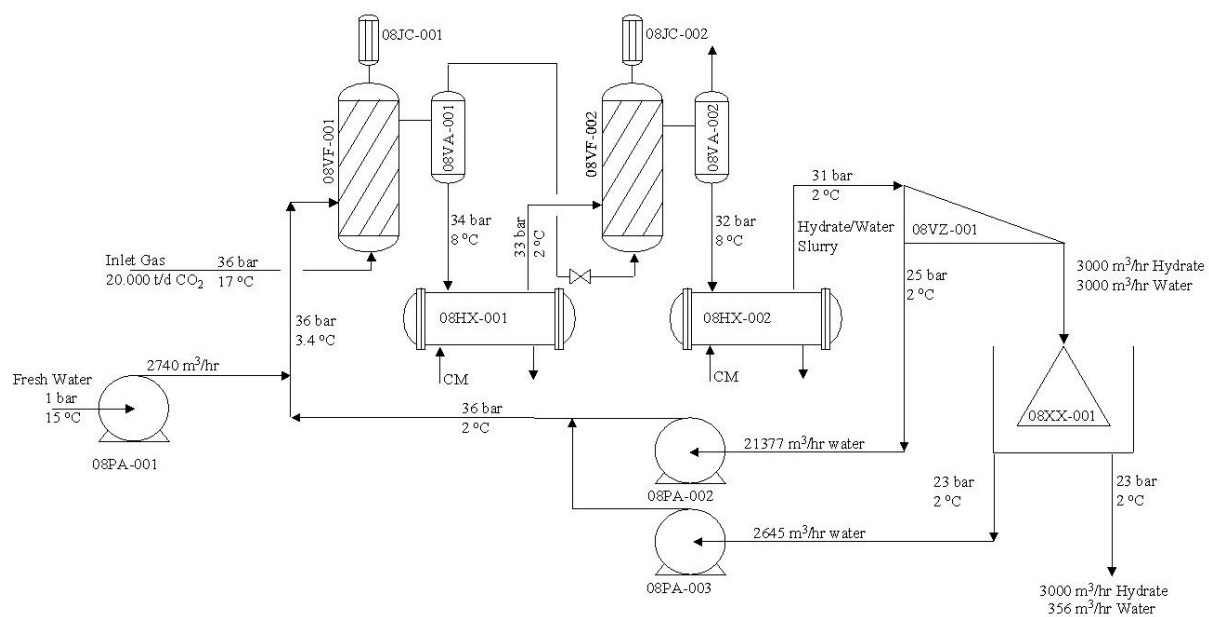
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Tag Number	08PA-001	Tag Number	08CJ-001	Tag Number	08VF-001	Tag Number	08VA-001	Tag Number	08PA-003
Description	Fresh Water Pump	Description	Reactor Agitator	Description	Reactor	Description	Degasser	Description	Centrifuge Re-Circ Pump
Duty (kW)	3603	Duty (kW)		Duty (kW)		Duty (kW)		Duty (kW)	1242
Tag Number	08HX-001	Tag Number	08CJ-002	Tag Number	08VF-002	Tag Number	08VA-002	Tag Number	08HX-002
Description	Reac. Interst. Cooler	Description	Reactor Agitator	Description	Reactor	Description	Degasser	Description	Reactor After Cooler
Duty (kW)	180000	Duty (kW)		Duty (kW)		Duty (kW)		Duty (kW)	175000
Tag Number	08VZ-001	Tag Number	08PA-002	Tag Number	08XX-001				
Description	Hydrocyclones	Description	Cyclone Re-circ. Pump	Description	Centrifuges				
Duty (kW)		Duty (kW)	8500	Duty (kW)	6000				



IEA-AKT-1002  
Main Production Process

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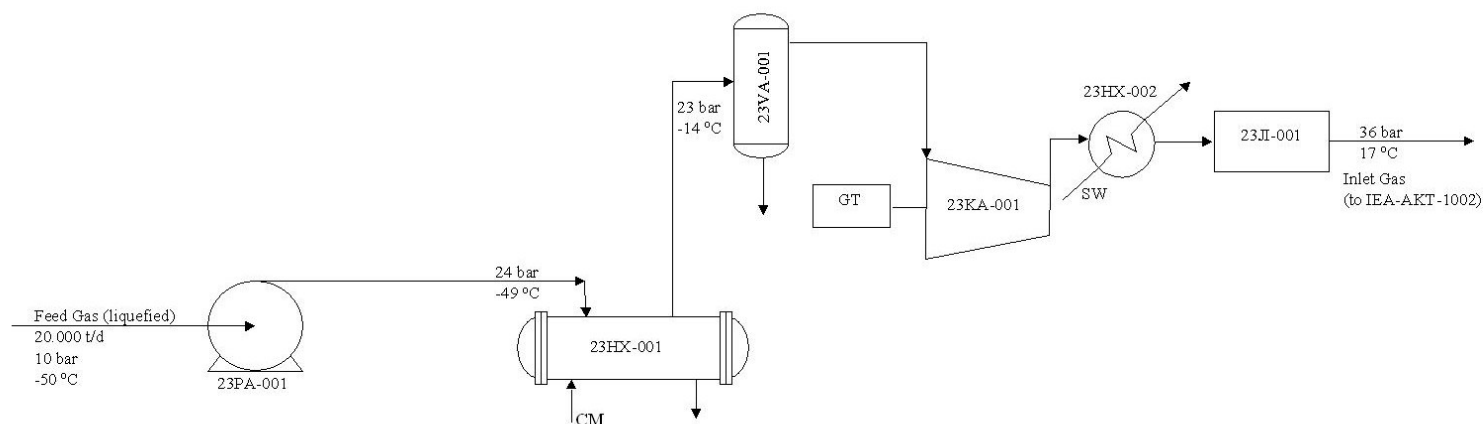
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Tag Number	23PA-001	Tag Number	23JI-001	Tag Number	23HX-001	Tag Number	23VA-001
Description	Liquid Inlet Pump	Description	Gas Metering	Description	"Gas Heater"	Description	Scrubber
Duty (kW)	375	Duty (kW)		Duty (kW)	-64000	Duty (kW)	

Tag Number	23KA-001	Tag Number	23HX-002
Description	Reactor Gas Compressor	Description	Reactor Inlet Gas SW Cooler
Duty (kW)	6646	Duty (kW)	3402



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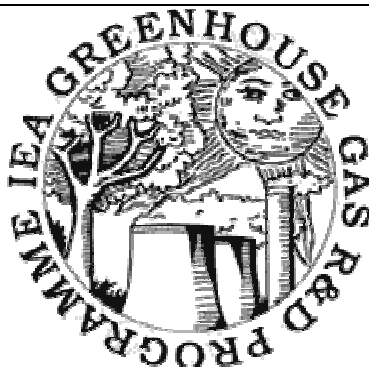
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## **APPENDIX B – BASIS OF DESIGN**

GAS HYDRATES FOR DEEP OCEAN DISPOSAL OF CO<sub>2</sub>

**Type of Report :**  
Basis of Design.

Pages : 1 of 4

**Classification:**  
Confidential

The present Basis of Design is intended to summarise the necessary background information needed to perform the study "Gas Hydrates for Deep Ocean Disposal of CO<sub>2</sub>" and to create a common understanding of the study premises and the assumptions made.

The Basis of Design should be agreed between IEA and AKT before the detailed concept work is undertaken.

Issued for Approval	C	21.07.03			ViA
Draft	0	20.06.03	ViA	SWW	ViA
Reason for issue	Rev.	Issue Date	Made by	Chk'd by	Proj. Appr.
Contract/PO no.:	Document no.:	Responsible party: <b>AKER KVÆRNER™</b> Aker Kværner Technology AS			

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## B1 INTRODUCTION

The International Energy Agency Greenhouse Gas R&D Programme (IEA GHG) was established in 1991 to evaluate technologies that could be used to avoid emissions of greenhouse gases, particularly from the use of fossil fuels and to identify targets for useful R&D. IEA GHG is an international organisation, supported by sixteen countries worldwide, the European Commission and several industrial organisations.

The Programme managers have been asked to commission a study to establish the costs and feasibility of using CO<sub>2</sub> hydrates for ocean disposal of carbon dioxide as a means to abate CO<sub>2</sub> emissions.

Aker Kværner Technology (AKT) have been awarded the study “Gas Hydrates for Deep Ocean Disposal of CO<sub>2</sub>” and will perform the study in accordance with Scope of Work described in latest revision of document IEA/CON/02/83 GAS HYDRATES FOR DEEP OCEAN DISPOSAL OF CO<sub>2</sub> (received by E-mail June 12, '03).

The present Basis of Design is intended to summarise the necessary background information needed to perform the study and to create a common understanding of the study premises and the assumptions made.

The Basis of Design should be agreed between IEA and AKT before the detailed concept work is undertaken.

## B2 STUDY DESIGN PREMISES

### **B2.1 OBJECTIVE**

The objective of this study is to determine the cost and the feasibility of using gas hydrates in the transport chain for Deep Ocean disposal of CO<sub>2</sub>. Production on both a land-based facility and on an offshore-based facility will be evaluated. In the case of a land-based facility, the transportation with on- and offloading of the

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hydrate product will be included. In the case of the offshore-base facility, overboard discharge facility shall be included. The sinking process and dissociation rates of CO<sub>2</sub> hydrates into the Deep Ocean shall be evaluated.

## **B2.2** *HYDRATE PRODUCTION PROCESS*

A literature survey will be performed to assess different, existing bulk hydrate production processes and evaluate the maturity/availability of the different processes.

Based on the outcome of the literature study, a production process will be chosen based on concept, proven technology and cost-effectiveness. AKT will use its extensive experience from laboratory studies to rule out any processes not believed to be effective, unless proven otherwise in the open literature.

## **B2.3** *HYDRATE TRANSPORTATION PROCESS*

A literature survey will be performed to assess different available hydrate transportation processes and evaluate the maturity/availability of the different processes.

Based on the outcome of the literature study, a transport process will be chosen based on concept, proven technology and cost-effectiveness.

## **B2.4** *HYDRATE SINKING PROCESS*

The sinking process of hydrates in seawater will be addressed. A literature survey will be performed to find necessary hydrate properties. The necessary size for hydrate particles from the production process shall be estimated, based on only a few percentage of dissociation during the sinking to 3000 m water depth.

# **B3 SOFTWARE**

PVTsim ver. 12 from Calsep AS will be used as the primary PVT calculation and hydrate prediction software. Hydrate prediction will be double-checked against results from CSMhyd software, from Colorado School of Mines. CSMhyd also supply information regarding fractional occupancy of hydrate cavities at equilibrium conditions.

HYSYS ver. 2.4.1 from Hyprotech AS will be used for process simulations.

# **B4 ASSUMPTIONS**

## **B4.1** *FEED GAS RATE*

Simultaneous studies are being performed on CO<sub>2</sub> transport in a liquid state with typical quantity of 20.000 tons per day of CO<sub>2</sub>. This corresponds to approx. 382 mill. SCFD of CO<sub>2</sub>. The present study shall deal with a corresponding gas rate to get a common basis of comparison.

Hence, the CO<sub>2</sub> rate for the present study shall be assumed to 400 mill. SCFD.

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#### **B4.2** *FEED GAS COMPOSITION*

Generally, any feed gas pollutants such as NO<sub>x</sub>, H<sub>2</sub>S, HydroCarbons, etc. will shift the equilibrium curve for hydrate formation to the right, rendering a more positive situation for the hydrate formation process (larger operational window possible. As an approximate rule of thumb, the hydrate curve will shift 1 degree to the right with every mol% H<sub>2</sub>S in the gas.) Including such pollutants with the CO<sub>2</sub> may raise other issues with respect to storage in the Deep Ocean.

The feed gas composition for the present study shall be assumed to 100% CO<sub>2</sub>.

#### **B4.3** *FEED GAS PRESSURE AND TEMPERATURE CONDITIONS*

The following hydrate plant inlet conditions shall be assumed

Onshore:

- Pressure: 10 bara
- Temperature: 30 °C

Offshore

- Pressure: 10 bara
- Temperature: -50 °C (liquid)

#### **B4.4** *HYDRATE GAS CONTENT*

Theoretic maximum gas content in CO<sub>2</sub> hydrates is approximate 184 Sm<sup>3</sup> CO<sub>2</sub> per m<sup>3</sup> hydrate (Sm<sup>3</sup>/m<sup>3</sup>). According to CSMhyd, the fractional occupancies of the hydrate cavities at equilibrium (11 – 76 bar) vary between 0.7 – 0.85 for the small cavities and between 0.98 – 0.99 for the large cavities. This corresponds to a gas content of 168 – 176 Sm<sup>3</sup>/m<sup>3</sup>.

As a somewhat conservative approach, the gas content of CO<sub>2</sub> hydrates shall be assumed to be 150 Sm<sup>3</sup>/m<sup>3</sup>.

#### **B4.5** *FREE WATER CONTENT*

In case when a water-continuous production process is chosen for the design, there is a need for separating the produced hydrate particles from the excess water phase. It is assumed that a separation process will not be able to separate out all the free water, which will be converted to ice upon freezing. This water is referred to as “free water”.

A free water content of 10wt% after the separation shall be assumed.

#### **B4.6** *SEA WATER CONDITIONS*

Seawater is important for cooling purposes in the hydrate formation process.

A sea water temperature of 10 °C shall be assumed for the purpose of this study. This will apply both for the land-based and for the offshore-based production facilities.



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#### ***B4.7*** ***TRANSPORT DISTANCES***

The CO<sub>2</sub> hydrates are to be sunk into approximate 3000 m water depths. 1000 km transport distance is assumed to be more than adequate to find ocean depths of 3000 m+ from main greenhouse gas emitting countries. The transport distance to be considered shall therefore be 1000 km.

#### ***B4.8*** ***GENERAL***

It is assumed that CO<sub>2</sub> is “available” at the production facilities, both onshore and offshore location. The technology, process and/or cost of capturing and/or transporting CO<sub>2</sub> to bulk hydrate production facilities shall not be included in the present study.

It is assumed that all facilities include all required utilities.

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## **APPENDIX C – DATA PRESENTATION**

**Physico/chemical data on main properties  
related to hydrate formation and dissociation**

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## Physico/chemical data on main properties related to hydrate formation and dissociation

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### C1 EQUILIBRIUM CURVES

There exist three basic techniques for predicting the conditions for the three-phase (L<sub>w</sub>-H-V) equilibrium, or the hydrate equilibrium curve for a hydrate forming component in water.

1. The gas gravity method is the simplest method for determining the three-phase equilibrium, and makes use of the gas gravity charts of Katz (1945). These charts were generated from a limited amount of experimental data, and while it is very simple, it can only be considered as approximate.
2. The distribution coefficient method (K<sub>i</sub>-value method) was developed in the beginning of the 1940's. The method makes use of K<sub>vs</sub> charts (vapour-solid distribution) for each component. The calculation scheme is iterative.
3. The statistical thermodynamic approach generates theories for equilibria of macroscopic properties based on microscopic properties. Although limited in accuracy by the available experimental data, the statistical thermodynamics approach provides the best approximation to hydrate phase equilibria predictions. Reference is made to Sloan (1998) for a thorough description of this method.

Figure C-1 shows the hydrate equilibrium curves for CO<sub>2</sub> hydrates in fresh water. Three different hydrate prediction programs, all using the statistical thermodynamic approach, are used. From the figure it is seen a considerable discrepancy in the prediction of the hydrate formation temperature for pressures above approximate 30 bar. PVTsim from Calsep AS is well known within Aker Kværner and is the preferred hydrate prediction simulation software within the company. Calsep have an extensive experimental program for continuously improving the empirical parameters in their prediction software. The hydrate equilibrium curve predicted with PVTsim will be used for the present work.

The tabulated results from PVTsim are given in Table C2.

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## C2 GAS CONTENT

The hydrate structure consists of a crystal lattice of hydrogen bonded water molecules encasing gas molecules in cavities (see Sloan (1998) for a thorough description of hydrates and their structure). The theoretical gas content maximum corresponds to all the cavities being filled with one gas molecule each. The actual gas content in hydrates is dependent on the fraction of the cavities filled with a gas molecule, referred to as the “fractional occupancy”. This fractional occupancy of the cavities can be obtained through the statistical thermodynamic method described above and can be predicted by commercial available software.

For a given temperature, the driving forces for hydrate formation increase with increasing pressure. This results in more gas being captured in the hydrate structure and hence increased gas content. In Figure C-2, the gas content in terms of mol% CO<sub>2</sub> within the hydrate structure is shown versus pressure and temperature. It is seen that the gas content tends towards the maximum of 14.81 mol% (184 Sm<sup>3</sup> CO<sub>2</sub> per m<sup>3</sup> hydrate, n = 5.75 moles of water per mole of hydrate) with decreasing temperature, corresponding to all the cavities of the hydrate structure being filled with one gas molecule each. According to the simulation program, the pressure is only significant for T > ~ -5 °C, below which the gas content of the hydrate is not dependent on the pressure. For these low temperatures, the equilibrium curve itself is not strongly dependent on pressure (see Figure C-1).

It should be noted that the gas content of Figure C-2 is based on *equilibrium conditions*, i.e. the theoretical amount of gas trapped within the hydrate structure for the given pressure/temperature conditions. Being non-stoichiometric compounds, the gas content in hydrates can be lower than the predicted equilibrium content, and it is assumed that in an industrial process it will be significantly lower. As a basis of design for this study, a gas content of 150 Sm<sup>3</sup> per m<sup>3</sup> hydrate is assumed. This corresponds to a concentration of 12.41 mol% CO<sub>2</sub> in the hydrate (n = 7.06 mole of water per mole of hydrate). The assumed gas content is indicated in Figure C-2. It is seen that the assumed gas content of 150 Sm<sup>3</sup>/m<sup>3</sup> is significantly lower than the equilibrium values and this assumption is therefore viewed as a rather conservative approach.

## C3 HYDRATE DENSITY

The density of hydrates is directly dependent on the fractional occupancy of the hydrate cavity. With values for this fractional occupancy, and detailed information on the hydrate unit cell, the hydrate density can be calculated.

In Figure C-3, the CO<sub>2</sub> hydrate density for constant pressures are given versus temperature (PVTsim). The hydrate equilibrium curve is superimposed on the graph (secondary Y-axis). However, as stressed above, the gas content in hydrates can be lower than the predicted equilibrium content and the hydrate density in an industrial process is expected to be different from what predicted with statistical thermodynamics. In Figure C-4, the hydrate density versus gas content is given (calculated based on necessary fractional occupancy according to the method described by Sloan (1998)).

Uchida et al. (1995) summarise experimental results on the composition and density of CO<sub>2</sub> hydrates. Here, the density ranges from 1054 to 1150 kg/m<sup>3</sup>, with a recommended value of 1112 kg/m<sup>3</sup>. The gas content in the hydrates produced in an industrial process is assumed to 150 Sm<sup>3</sup>/m<sup>3</sup>, corresponding to a gas concentration of 12.41 mol% CO<sub>2</sub> in the hydrate. When converting a gas concentration of 12.41 mol% into density, a “pure hydrate density” of 1072 kg/m<sup>3</sup> results. This is somewhat lower than the recommended value by Uchida et al., which is considered natural for a continuous industrial process.

However, when produced from a water-based system, the hydrates need to be separated from the water phase prior to freezing. Based on experience, it is known that this is a challenging step in the process, and it must be assumed a non-ideal separation process, i.e. that free water is present after the separation.

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As a basis for design for this study, a free-water content of 10wt% is assumed.

It should be stressed that the separation process of hydrates from water is not yet a developed technology and the 10 wt% free-water content is based on experimental observations and assumptions only.

Based on the assumption of gas content and free water content, the density of the final hydrate product can be calculated. The free water will convert to ice upon freezing, and the density of ice is taken to 900 kg/m<sup>3</sup>. The hydrate density will then be:

$$\begin{aligned} \text{Gas content in pure hydrate:} & 150 \text{ Sm}^3/\text{m}^3 \\ \text{Pure hydrate density:} & 1072 \text{ kg/m}^3 \\ \text{TOTAL DENSITY: } \frac{m_{ice} + m_{hyd}}{V_{ice} + V_{hyd}} &= \mathbf{1052 \text{ kg/m}^3} \end{aligned}$$

$V_{hyd}$  = Hydrate volume pr. volume unit gas converted:  $1/150 \text{ m}^3/\text{Sm}^3$

$m_{hyd}$  = Hydrate mass pr. volume unit gas converted:  $1/150 \cdot 1072 = 7.146 \text{ kg/Sm}^3$

$m_{ice}$  = Free water pr. volume unit gas converted (10wt%):  $0.794 \text{ kg/Sm}^3$

$V_{ice}$  = Ice volume pr. volume unit gas converted:  $0.794/900 = 0.0008822 \text{ m}^3/\text{Sm}^3$

The change in both ice and hydrate density with temperature and pressure is neglected in this study.

## C4 HYDRATE HEAT OF FORMATION

Hydrate heat of formation (or rather, heat of dissociation) is difficult to determine experimentally due to difficulties related to experimental conditions (high pressures) and in obtaining pure samples. There are quite large discrepancies in the reported literature values, in addition to not available experimental details (e.g. experimental conditions). There also exist correlations for predicting the heat of dissociation, but with disputed accuracy.

Levik (2000) gives a substantial review of available literature data and also theoretical correlations for the heat of dissociation of hydrates. Focus is on methane and natural gas hydrates. Sloan (1998) summarises work performed in the area. Available data on the heat of dissociation for CO<sub>2</sub> hydrates found in these reviews varies between 58 kJ/mol (Nagayev et al., 1975), 63 kJ/mol (Holder et al. 1988), and 80 kJ/mol (Kamath 1984).

The unit “J/mol” refers to one mol of hydrate. In order to obtain the heat of dissociation in units of Joule per kg hydrate produced, assumptions regarding the gas content of the hydrates must be made. In Table C, various data for the heat of dissociation of CO<sub>2</sub> hydrates are given (J/mol). In addition, the converted heat of dissociation assuming an ideal hydrate structure with all cavities filled, i.e.  $184 \text{ Sm}^3/\text{m}^3$  ( $\Delta H_{diss}$  “ideal”), and “our” hydrates with an assumed gas content of  $150 \text{ Sm}^3/\text{m}^3$  ( $\Delta H_{diss}$  “real”) are given.

**Table C1: Literature reported heat of dissociation for CO<sub>2</sub> hydrate.**

$\Delta H_{diss}$ [kJ/mol]	$\Delta H_{diss}$ “ideal” [kJ/kg]	$\Delta H_{diss}$ “real” [kJ/kg]	Reference
58	393	341	281 K. Nagayev et al. 1979 / Levik 2000
60	407	353	277 K. Assumed ideal structure. Saji et al. 1992
63	425	368	Holder et al. 1988 / Levik 2000
80	545	472	Kamath 1984 / Sloan 1998

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Bozzo et al. (1975) report heat of formation values of 60 kJ/mole for hydrates with 145 Sm<sup>3</sup> gas/m<sup>3</sup> hydrate (n = 7.3 mole water/mole hydrate).

Sloan (1998) argues that guest size, i.e. the size of the gas molecule entrapped in the hydrate structure, determines the approximate heat of dissociation by determining the cavities occupied. Assuming that CO<sub>2</sub> enters both cavities in sI hydrates, the heat of dissociation will then be equal to methane, reported to 57 kJ/mol. Assuming that CO<sub>2</sub> only enters the large cavities, the heat of dissociation will then be equal to ethane, reported to 71 kJ/mol.

If CO<sub>2</sub> enters the large cavities only, the maximum density of the CO<sub>2</sub> hydrate is approximate 1050 kg/m<sup>3</sup>, and the maximum gas content is 138 Sm<sup>3</sup>/m<sup>3</sup>. An assumption in this work is a gas content of 150 Sm<sup>3</sup>/m<sup>3</sup>, indicating that both cavities need to be partly occupied. This assumption is supported by frequently reported densities of CO<sub>2</sub> hydrates of more than 1100 kg/m<sup>3</sup> and outcome from hydrate simulation software (CSMhyd, PVTsim).

Based on this, the heat of dissociation for CO<sub>2</sub> hydrates is approximate 57 kJ/mol. However, based on the large discrepancies in the reported experimental values, and the fact that they all are large than this, the heat of dissociation is assumed to 60 kJ/mol for the purpose of this study, converting to **350 kJ/kg** for hydrates containing 150 Sm<sup>3</sup>/m<sup>3</sup>.

## C5 HYDRATE HEAT CAPACITY

The CO<sub>2</sub> hydrate heat capacity for the intervals P = [20,80], and T = [2,10] were simulated to be 2.19 ± 0.03 kJ/kgK using PVTsim. As no experimental values for the heat capacity was found in the literature, this value shall be used in the present study.

## C6 HYDRATE RATE OF FORMATION

Several articles are published regarding rate of CO<sub>2</sub> hydrate formation related to Deep Ocean sequestration of CO<sub>2</sub>. However, hydrate formation when injecting liquid CO<sub>2</sub> in the Deep Ocean is not relevant for the current process, where the formation rate can be enhanced by varying parameters such as injection rate, subcooling, stirring rate etc.

A few papers have been presented on the growth rate of hydrates (e.g. Ma et al. 2002) and on crystal sizes (Shoji et al. 2002), but these are very often evaluated in stagnant system (no external stirring). It is known that turbulence in the system enhances hydrate formation rate, and as such, these experimental results cannot be used for an industrial process of hydrate formation.

Mork (2002), Mork and Gudmundsson (2002) presented a mass transfer model relating the hydrate rate of formation in a continuous stirred tank reactor to the concentration driving force and an overall mass transfer coefficient. In the thesis, Mork points out that heat transfer in the reactor limits the production rates. Significant effects on the reaction rate included superficial gas velocity, pressure and power consumption. Mork developed a bubble-to-crystal model. For methane gas experiments, the model with empirical parameters became:

$$R_{tot} = 363.3 \left( \frac{P_g}{V} \right)^{0.1801} (v_{sg})^{1.124} (C_{sol} - C_{eq}) \cdot 9.5$$

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where

$R_{tot}$  = overall mass transfer rate (mol/s)

$P_g$  = power consumption in gas-liquid reactor (W)

$V$  = reactor volume (m<sup>3</sup>)

$v_{sg}$  = superficial gas velocity (m/s)

$C_{sol}$  = gas concentration at gas-liquid interface given by gas solubility at exp. conditions (mol/m<sup>3</sup>)

$C_{eq}$  = gas concentration at hydrate crystal surface given by gas solubility at exp. conditions (mol/m<sup>3</sup>)

## C7 DISSOCIATION RATE OF HYDRATES IN WATER

In connection with Deep Ocean Sequestration of CO<sub>2</sub>, the stability of hydrates forming upon injection of liquid CO<sub>2</sub> into the deep ocean has been investigated by many researchers. Generally when evaluating experimental data, it is assumed that the shrinkage of a hydrate-covered CO<sub>2</sub> droplet is due to dissociation of the hydrate.

Evaluation of the Monterey Bay field experiment in 1998 led to an approximate release of CO<sub>2</sub> from the hydrate surface of less than  $3.4 \cdot 10^{-10}$  mol/cm<sup>2</sup> s (=  $1.5 \cdot 10^{-8}$  g CO<sub>2</sub> /cm<sup>2</sup> s) (T = 4.7 °C, WD = 620 m) (Brewer et al. 2000). By assuming a gas content of 150 Sm<sup>3</sup>/m<sup>3</sup>, this corresponds to a shrinking rate/movement of the hydrate surface of  $5.4 \cdot 10^{-10}$  m/s. The authors recognised that the estimation of the dissolution rate through the hydrate film was lower than previously reported in the literature. Sloan (2000) summarises results from experiments performed between 1992 and 1997 by several researchers. The shrinking rates of CO<sub>2</sub> droplets with hydrate shells vary here from  $1.2 \cdot 10^{-8}$  m/s to  $8.0 \cdot 10^{-6}$  m/s. Akihiro et al. present values in the range  $7 \cdot 10^{-7}$  to  $2 \cdot 10^{-6}$  m/s.

However, at least the coastal location case of the present study deals with *frozen* hydrates. Here, an ice layer will create barrier for hydrate dissociation also outside the “stable” hydrate pressure/temperature region. In theory, this will slow down the dissolution rate (at least when the hydrates are outside the stable hydrate region). No data were found on the dissociation of frozen CO<sub>2</sub> hydrates in water. However, Kawamura et al. (2002) presented experimental results on the dissociation behaviour of frozen methane and natural gas hydrates in water. Hydrate pellets of 12 mm diameter and 6 mm height were produced from methane and ice. Prepared samples were stored under atmospheric pressure and 139 K. The time taken for totally dissolving the hydrate pellets as a function of pressure and temperature were found.

Kawamura et al. (2002) showed that the following model for the movement of the hydrate-water interface  $X$  with time  $t$  describes the experimental results satisfactory:

$$X = \xi \sqrt{4\alpha_w \cdot t}$$

$$\frac{e^{-\xi^2}}{\operatorname{erf} \xi} = (1 - \varepsilon) \sqrt{\pi} \frac{\rho_H}{\rho_w} \frac{\lambda_H}{C_{p,w} (T_0 - T_D)} \xi$$

where

$\alpha_w$  = thermal diffusivity of water

$\rho_H$  = hydrate density

$\rho_w$  = water density

$\lambda_H$  = hydrate heat of dissociation

$C_{p,w}$  = heat capacity of water

$\varepsilon$  = hydrate porosity

$T_0$  = experimental temperature

$T_D$  = hydrate dissociation temperature

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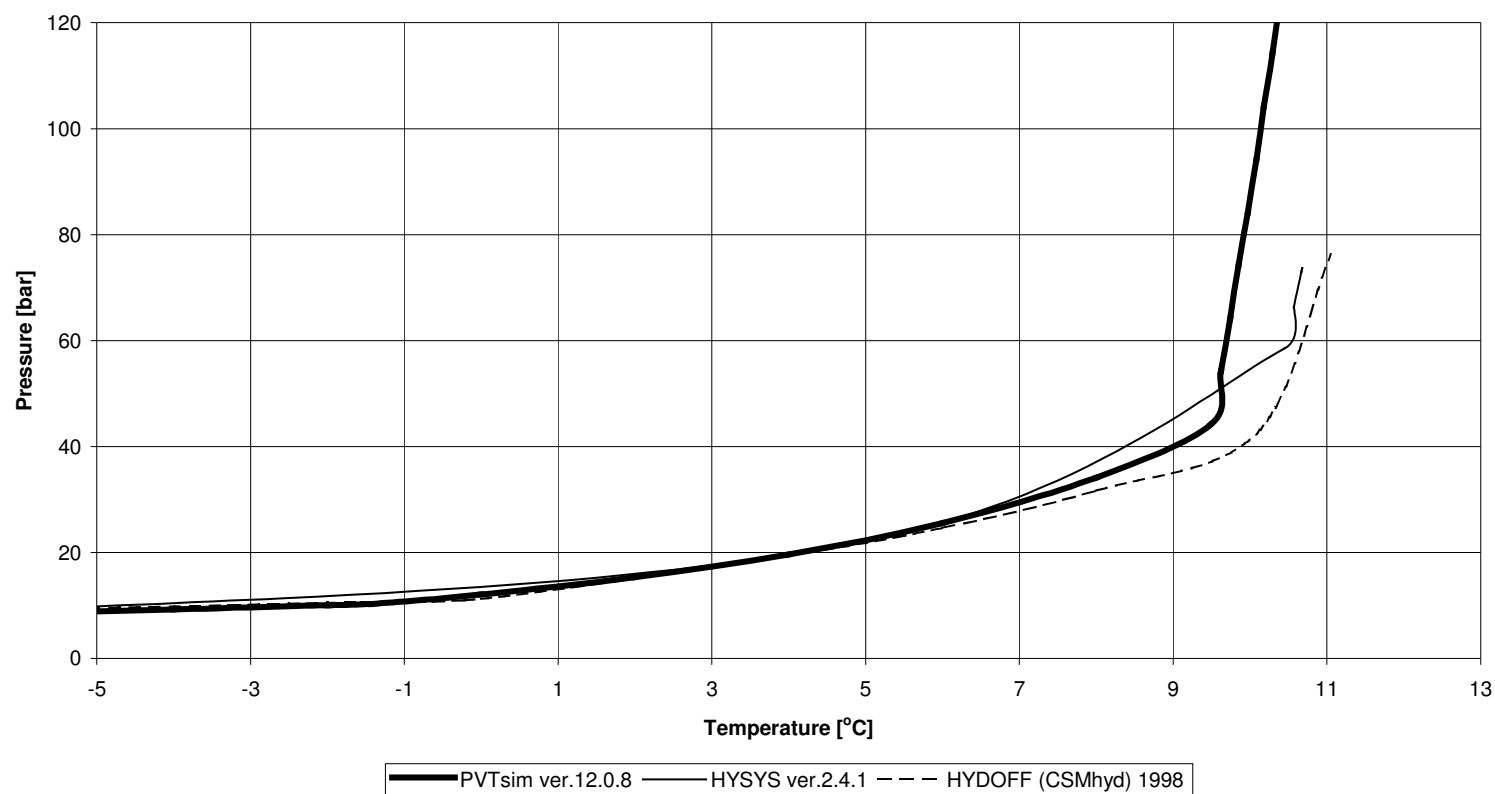
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**CO<sub>2</sub> Hydrate Formation Curves.  
Different Prediction Programs**



**Figure C-1: CO<sub>2</sub> Hydrate Equilibrium Curves in fresh water predicted with different programs.**



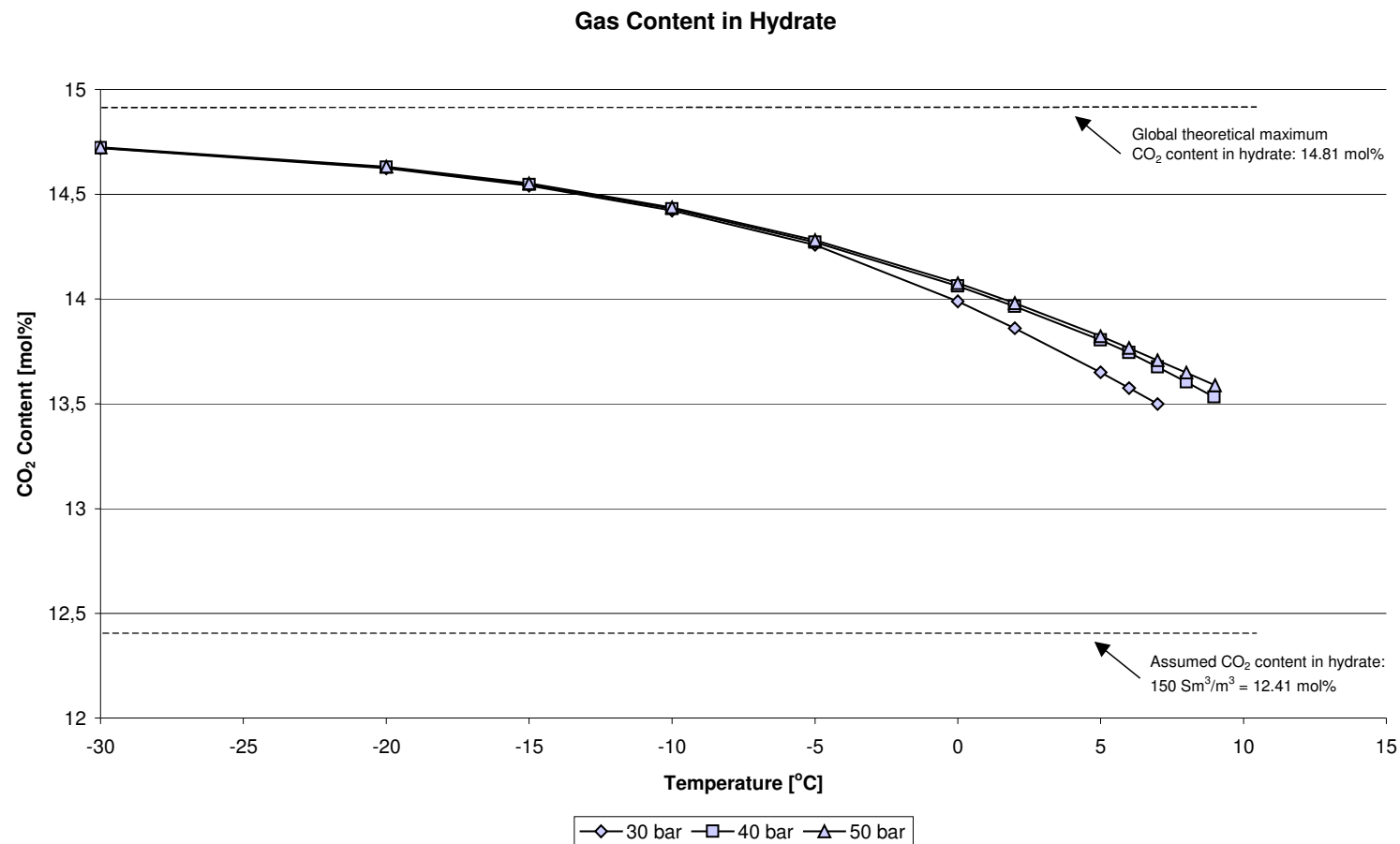
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**Figure C-2: CO<sub>2</sub> content in hydrate versus temperature and pressure. Simulated in PVTsim ver. 12.0.8.**

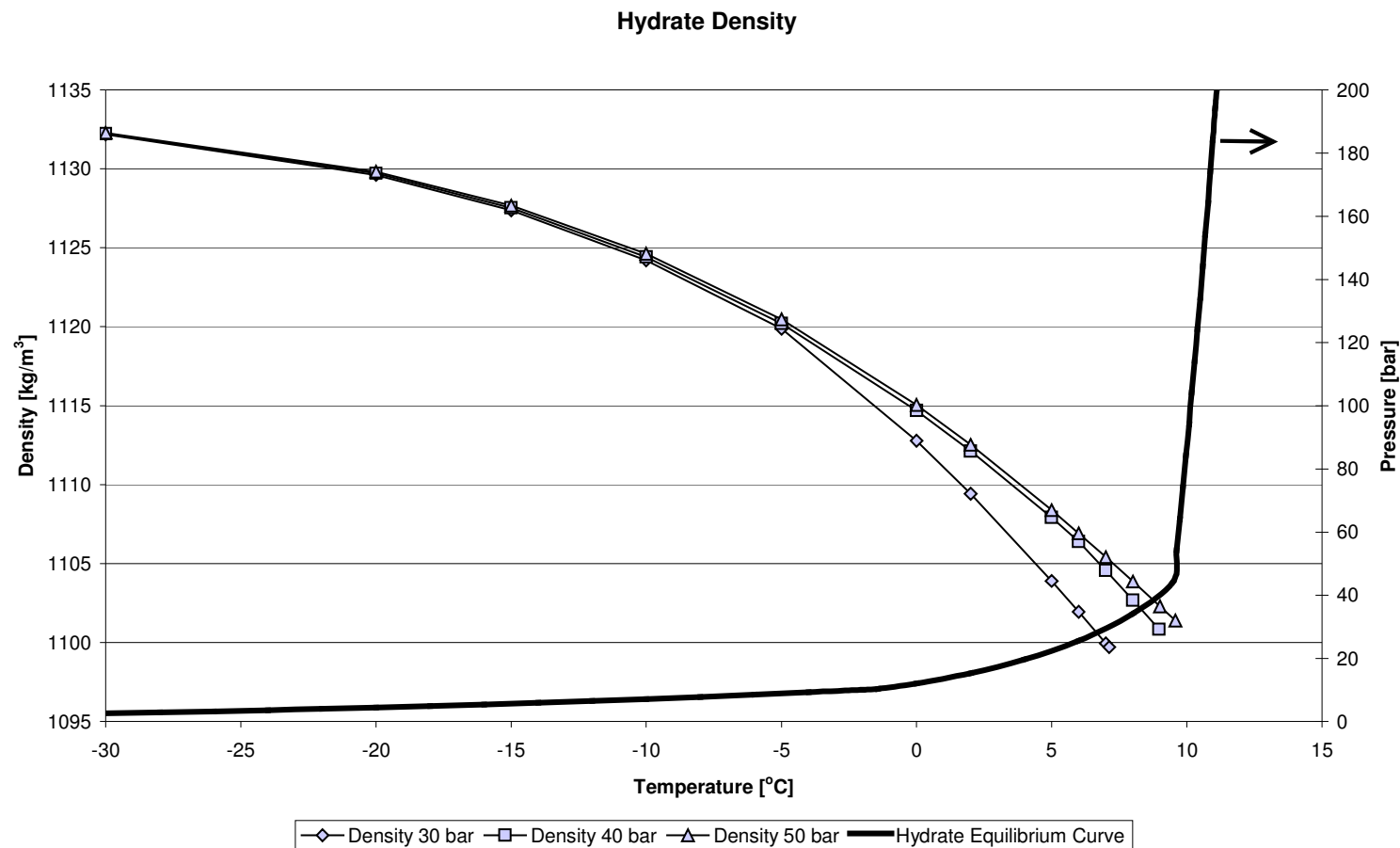
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**Figure C-3: CO<sub>2</sub> hydrate density versus temperature and pressure. Simulated in PVTsim ver. 12.0.8.**

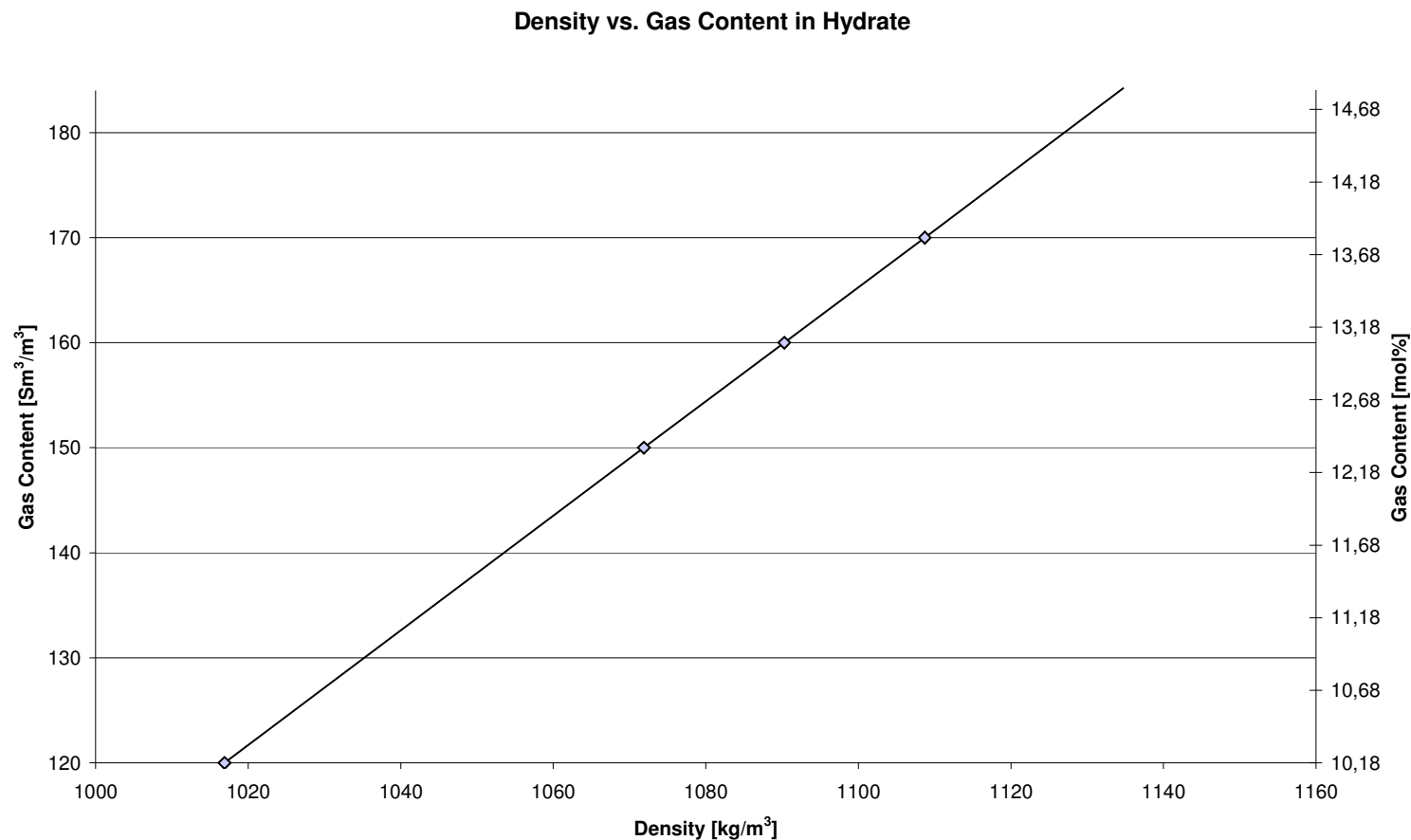
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**Figure C-4: Hydrate Density versus Gas Content**

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**Table C2: CO<sub>2</sub> hydrate equilibrium curve in fresh water. Simulated with PVTsim ver. 12.0.8**

Temperature [°C]	Pressure [bara]
-6	8.54
-4	9.29
-2	10.09
-1.43	10.33
0	12.08
2	15.34
4	19.67
6	25.59
8	34.17
9.49	44.17
9.62	54.17
9.74	64.17
9.85	74.17
9.97	84.17
10.08	94.17
10.18	104.17
10.29	114.17
10.39	124.17
10.49	134.17
10.59	144.17
10.68	154.17
10.78	164.17
10.87	174.17
10.96	184.17
11.05	194.17
11.11	200

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## **APPENDIX D – HYDRATE SINKING PROCESS**

### **Analysis of the Hydrate Sinking and Dissociation Process**

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### D1 SUMMARY

The aim of this analysis is to calculate the necessary hydrate particle size for sinking hydrates into the ocean for Deep Ocean storage of CO<sub>2</sub>.

The necessary hydrate particle size that only results in a few percentages dissociation during the sinking process to 3000 m is strongly dependent on the dissociation rates. By using experimental values for the dissociation rates as found in the open literature, a diameter range from 2 cm to more than 2 m results (spherical particles assumed). By employing “most likely” values, a diameter of less than 1 m results (volume = 0.3 m<sup>3</sup>).

The size and shape of the hydrate blocks will have an effect on the transport system and the efficiency and rate of loading. Development work is anticipated to ensure that the system is working effectively, but in general no special requirements are expected for hydrate sizes/shapes within the estimated ranges, as the basic mechanisms will be the same.

In this study, only high-level estimates of the processes and the associating costs are made. The total cost is not expected to be significant dependent on the cost of the equipment producing the hydrate blocks.

It is necessary with more detailed information on the dissociation rate of compacted CO<sub>2</sub> hydrates in water as a function of pressure and temperature.

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**D2 INTRODUCTION AND GENERAL SYSTEM DESCRIPTION**

In the Scope of Work, it is stated that the hydrate production process shall be capable of producing hydrate particles which will sink without more than a few percent dissolving. The target is to sink in at least 3000 m of water. In this study, a criterion of maximum 5% dissolving during sinking to 3000 m is applied for the sinking analysis.

When CO<sub>2</sub> hydrates are discharged into the ocean, there will be a period of time before the hydrates sink to pressure/temperature conditions that are within the stable hydrate zone. It is conceptualised that the dissociation of the submerged hydrate particles will occur due to different mechanisms for these two different zones:

1. Outside the “stable” pressure/temperature regime, the hydrates will dissociate readily with a rate that is dependent on the available heat transfer from the surroundings.
2. Within the “stable” pressure/temperature region, the hydrates will dissociate due to the CO<sub>2</sub> concentration difference between the hydrate and the surrounding water.

It is taken as a prerequisite that hydrates in their frozen, meta-stable condition (atmospheric condition) is the only feasible state for hydrate transportation over long distances. Hence, for the Coastal Location Case of this study, the hydrates discharged overboard are assumed to be at sub-zero temperatures.

Further, it is envisaged that the hydrates discharged overboard for the Offshore Location Case of this study are compacted, unstable blocks. From the petroleum industry it is known that hydrates pushed in front of cleaning pigs takes long time to dissociate when arriving at the platform (ambient temperature, atmospheric pressure). These hydrates are not frozen, but have been compacted in the pipe system. It is therefore assumed that compacted, unstable (non-frozen) hydrates dissociate at a rate sufficiently slow for the Offshore Location Case, where the time exposed to atmospheric conditions is small.

Hence, the same analysis for the hydrate sinking process applies for both the Coastal Location and the Offshore Location Cases.

Very little information is available on the kinetics of CO<sub>2</sub> hydrate dissociation for systems relevant to hydrates for Deep Ocean storage of CO<sub>2</sub>. For this analysis, literature reported values on the dissociation rate for different pressure/temperature encountered in the sinking scheme are used.

**D3 PRESSURE AND TEMPERATURE PROFILES**

The following temperature and pressure profiles versus water depth (WD) are assumed:

- Pressure. A linear relation 1 bara at sea level (WD = 0) to 300 bara at a water depth of 3000 m (WD = 3000 m).  $P = 0.0997 \cdot WD + 1$  (bara)
- Temperature. An exponentially decreasing temperature profile from 10 °C at sea level (WD = 0) to 4 °C at 500 m WD is used, with constant 4 °C below 500 m. Figure D-1 illustrates the approximate temperature development with water depth.

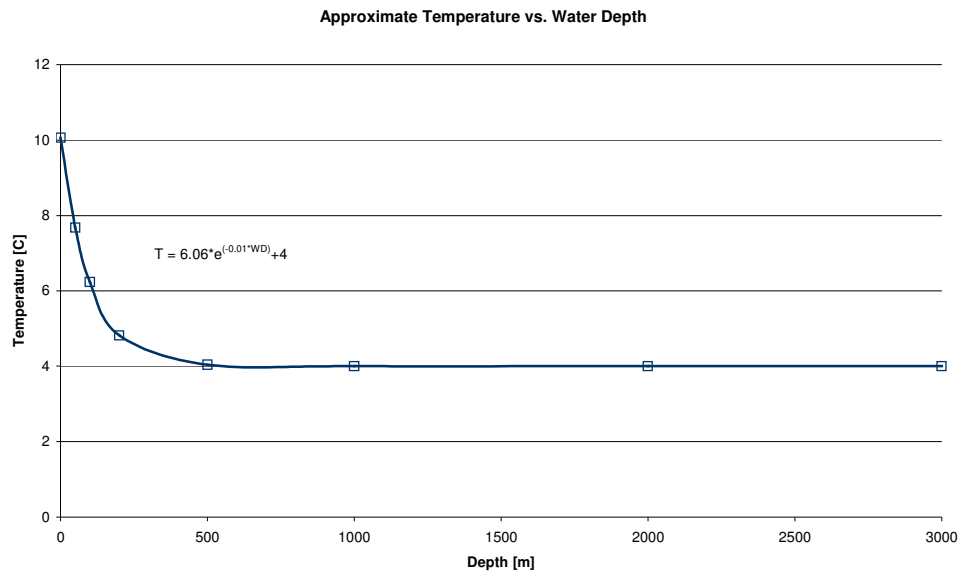
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**Figure D-1: Assumed Temperature Profile vs. WD.**

## D4 HYDRATE DISSOCIATION RATES

By comparing the assumed pressure and temperature profiles with the equilibrium curve for CO<sub>2</sub> hydrates, it is seen that above approximate 200 m WD ( $P < 21$  bara,  $T > 5$  °C), hydrates are outside their stable pressure/temperature region. Dissociation down to this water depth will then occur rapidly, given rapid enough heat transfer to the hydrate. For WD greater than approximate 200 m, the hydrate will dissociate due to difference in the CO<sub>2</sub> “concentration” between seawater and hydrate.

### Pressure below Equilibrium Pressure

Dealing with *frozen* hydrates, dissociation in water is not a common system. However, Kawamura et al. (2002) describe exactly this system for methane hydrates. In Figure D-2, the experimental results from Kawamura et al. are reproduced. The figure shows the time taken for totally dissolving methane hydrate pellets (OD = 12 mm, h = 6 mm) in water at two different temperatures versus pressure. It should be noted that all of the experimental data are for pressure/temperature conditions outside the “stable hydrate” area.



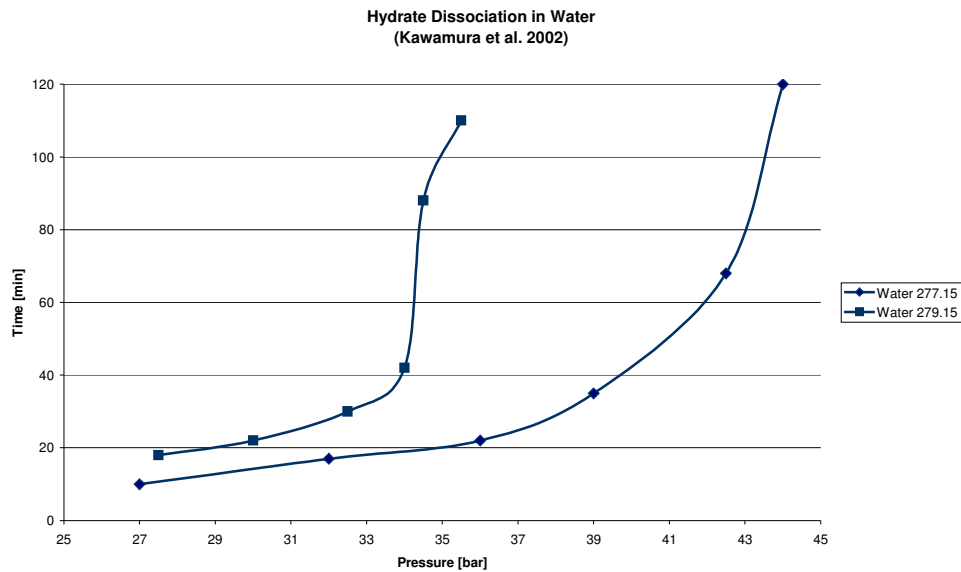
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**Figure D-2: Reproduction of Results from Dissociation Experiments.**

In the experiments, Kawamura et al. achieved good agreement with the following theoretical expression for dissociation, based on simple one-dimensional thermal condition (see Appendix B for more detailed description):

$$X = \xi \sqrt{4\alpha_w \cdot t}$$

$$\frac{e^{-\xi^2}}{\operatorname{erf} \xi} = (1 - \varepsilon) \sqrt{\pi} \frac{\rho_H}{\rho_w} \frac{\lambda_H}{C_{p,w} (T_0 - T_D)} \xi$$

Assuming that the expression is valid also for CO<sub>2</sub> hydrates (using physical data for CO<sub>2</sub> hydrate in the expression) the following dissociation rates results:

Water depth [m]	Pressure [bara]	Temp. [°C]	Diss. temp [°C]	Diss. rate [mm/s]	"Initial" diss. rate [m/s]	"Final" diss. rate [m/s]
30	4	8.5	-22	DR = 0.0537t <sup>-0.5</sup>	5.37E-05	5.00E-07
91	10	6.4	-13.8	DR = 0.0236t <sup>-0.5</sup>	2.36E-05	2.00E-07
191	20	4.9	4.5	DR = 0.0072t <sup>-0.5</sup>	7.20E-06	7.00E-08

It should be noted that two solutions were found for  $\xi$  for each pressure, but the match to the experimental data of Kawamura et al. was found by employing the lower value. Hence, the lower value is used also for this work.

It should also be noted that the dissociation rate is given as a function of time. In a one-dimensional system, it is not expected a time-dependent dissociation rate, and it is believed that this is due to experimental boundaries/limitations. Two "border values" are listed:

- "Initial dissociation rate" is taken for t=1 s, and corresponds to a high limit.
- "Final dissociation rate" is taken for high t, and corresponds to a low limit.

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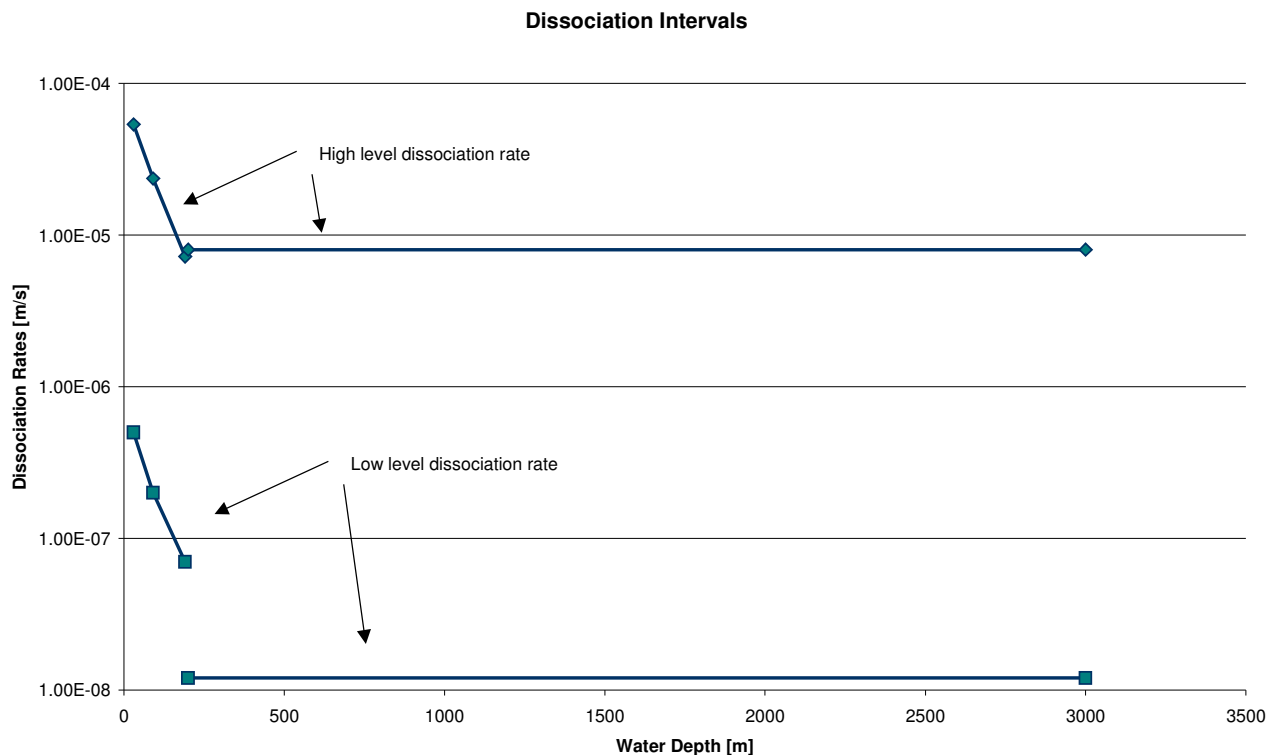
#### Pressure above Equilibrium Pressure

Experiments performed by several researchers on the shrinking rate of hydrate-covered CO<sub>2</sub> droplets in water report a hydrate dissociation rate from  $1.2 \cdot 10^{-8}$  m/s to  $8.0 \cdot 10^{-6}$  m/s. No consistency was found between the reported value and the experimental conditions. For this study, a constant dissociation rate from 200 m to 3000 m is assumed. The following maximum and minimum dissociation rates are used:

Water depth [m]	Pressure [bara]	Temp. [°C]	High diss. rate [m/s]	Low diss. rate [m/s]
200 - 3000	~20-300	~ 4	8.00E-06	1.20E-08

#### Summary Hydrate Dissociation Rate

By utilising the above maximum and minimum dissociation rate, the following high and low limit dissociation rates vs. water depth result:



**Figure D-3: High and Low Levels for Hydrate Dissociation Rates vs. Water Depth**

These upper and lower limits are used for calculating the maximum and minimum necessary hydrate particle sizes (see below).

Due to the very large dissociation rate intervals and the very large uncertainties in the absolute numbers, no differences in the analysis for the Coastal and the Offshore Location Cases are made.

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## D5 HYDRATE SINKING RATE

The velocity of a particle moving through a liquid under gravity is given by (McCabe et al. 1993):

$$\frac{du}{dt} = g \frac{(\rho_p - \rho)}{\rho_p} - \frac{C_D u^2 \rho A_p}{2m}$$

where

$du/dt$  = the acceleration of the particle p [m/s<sup>2</sup>]

$g$  = acceleration of gravity [m<sup>2</sup>/s<sup>2</sup>]

$\rho_p$  = particle density [kg/m<sup>3</sup>]

$\rho$  = liquid density [kg/m<sup>3</sup>]

$C_D$  = dimensionless drag coefficient [-]

$u$  = velocity [m/s]

$A_p$  = projected area of particle in plane perpendicular to direction of motion of particle

$m$  = mass of particle

The terminal velocity,  $u_t$ , is found by setting  $du/dt = 0$  (no acceleration). Assuming a spherical particle, the terminal velocity is

$$u_t = \sqrt{\frac{3gD_p(\rho_p - \rho)}{\rho}}$$

for high Reynolds numbers, where  $C_D = \text{constant} = 0.445$ .

## D6 NECESSARY HYDRATE PARTICLE SIZE

The necessary hydrate particle sizes were estimated by setting a particle diameter and calculating the time to reach 3000 m through terminal velocity calculations. Further, the dissociation during this time was estimated and the final volume calculated. Iterations were performed until 5% volume loss during the sinking process to 3000 m was achieved.

Two dissociation rate scenarios were applied: the lower limit and the higher limit dissociation, vs. water depth, as illustrated in Figure D-3. The calculation schemes are illustrated in the worksheet in Figure D1-5. The resulting hydrate particle sizes were (assuming spherical particles):

- $r = 1.24$  m, high limit dissociation rate
- $r = 0.02$  m, low limit dissociation rate

Note that hydrate density of frozen hydrate have been used where the free water content is ice, not water. However, this discrepancy is not significant compared to the large discrepancies in the dissociation rates.

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## MAXIMUM DISSOCIATION RATE

WD start:	0.00 m	WD start:	31.00 m	WD start:	91.00 m	WD start:	191.00 m
WD end:	30.00 m	WD end:	90.00 m	WD end:	190.00 m	WD end:	3000.00 m
Dissociation Rate	5.37E-05 m/s	Dissociation Rate	2.36E-05 m/s	Dissociation Rate	7.20E-06 m/s	Dissociation Rate	8.00E-06 m/s
Hydrate Properties		Hydrate Properties		Hydrate Properties		Hydrate Properties	
Density	1052.00 kg/m3 (incl. ice)	Density	1052.00 kg/m3 (incl. ice)	Density	1052.00 kg/m3 (incl. ice)	Density	1052.00 kg/m3 (incl. ice)
Sink rate calculation		Sink rate calculation		Sink rate calculation		Sink rate calculation	
Radius of sphere	1.2396 m	Radius of sphere	1.2383 m	Radius of sphere	1.2372 m	Radius of sphere	1.2366 m
Density seawater	1030.00 kg/m3	Density seawater	1030.00 kg/m3	Density seawater	1030.00 kg/m3	Density seawater	1030.00 kg/m3
Area sphere	19.31 m2	Area sphere	19.27 m2	Area sphere	19.23 m2	Area sphere	19.22 m2
Vol of sphere	7.98 m3	Vol of sphere	7.95 m3	Vol of sphere	7.93 m3	Vol of sphere	7.92 m3
Sinking force	175.53 Kg	Sinking force	174.98 Kg	Sinking force	174.50 Kg	Sinking force	174.26 Kg
g	9.81 m/s2	g	9.81 m/s2	g	9.81 m/s2	g	9.81 m/s2
Cd	0.45	Cd	0.45	Cd	0.45	Cd	0.45
Ut	1.25 m/s	Ut	1.25 m/s	Ut	1.25 m/s	Ut	1.25 m/s
Depth	30.00 m	Depth	59.00 m	Depth	99.00 m	Depth	2809.00 m
Sink time	24.05 s	Sink time	47.32 s	Sink time	79.43 s	Sink time	2254.26 s
Volume calculation		Volume calculation		Volume calculation		Volume calculation	
End radius	1.2383 m	End radius	1.2372 m	End radius	1.2366 m	End radius	1.2186 m
End volume	7.95 m3	End volume	7.93 m3	End volume	7.92 m3	End volume	7.58 m3
Volume loss	0.02 m3	Volume loss	0.02 m3	Volume loss	0.01 m3	Volume loss	0.34 m3
% loss	0.31 %	% loss, segment	0.27 %	% loss, segment	0.14 %	% loss, segment	4.31 %
% loss, total	0.31 %	% loss, total	0.58 %	% loss, total	0.72 %	% loss, total	5.00 %

## MINIMUM DISSOCIATION RATE

WD start:	0.00 m	WD start:	31.00 m	WD start:	91.00 m	WD start:	191.00 m
WD end:	30.00 m	WD end:	90.00 m	WD end:	190.00 m	WD end:	3000.00 m
Dissociation Rate	5.00E-07 m/s	Dissociation Rate	2.00E-07 m/s	Dissociation Rate	7.00E-08 m/s	Dissociation Rate	1.20E-08 m/s
Hydrate Properties		Hydrate Properties		Hydrate Properties		Hydrate Properties	
Density	1052.00 kg/m3 (incl. ice)	Density	1052.00 kg/m3 (incl. ice)	Density	1052.00 kg/m3 (incl. ice)	Density	1052.00 kg/m3 (incl. ice)
Sink rate calculation		Sink rate calculation		Sink rate calculation		Sink rate calculation	
Radius of sphere	0.0233 m	Radius of sphere	0.0232 m	Radius of sphere	0.0232 m	Radius of sphere	0.0231 m
Density seawater	1030.00 kg/m3	Density seawater	1030.00 kg/m3	Density seawater	1030.00 kg/m3	Density seawater	1030.00 kg/m3
Area sphere	0.01 m2	Area sphere	0.01 m2	Area sphere	0.01 m2	Area sphere	0.01 m2
Vol of sphere	0.00 m3	Vol of sphere	0.00 m3	Vol of sphere	0.00 m3	Vol of sphere	0.00 m3
Sinking force	0.00 Kg	Sinking force	0.00 Kg	Sinking force	0.00 Kg	Sinking force	0.00 Kg
g	9.81 m/s2	g	9.81 m/s2	g	9.81 m/s2	g	9.81 m/s2
Cd	0.45	Cd	0.45	Cd	0.45	Cd	0.45
Ut	0.17 m/s	Ut	0.17 m/s	Ut	0.17 m/s	Ut	0.17 m/s
Depth	30.00 m	Depth	59.00 m	Depth	99.00 m	Depth	2809.00 m
Sink time	175.34 s	Sink time	345.48 s	Sink time	580.56 s	Sink time	16487.20 s
Volume calculation		Volume calculation		Volume calculation		Volume calculation	
End radius	0.0232 m	End radius	0.0232 m	End radius	0.0231 m	End radius	0.0229 m
End volume	0.00 m3	End volume	0.00 m3	End volume	0.00 m3	End volume	0.00 m3
Volume loss	0.00 m3	Volume loss	0.00 m3	Volume loss	0.00 m3	Volume loss	0.00 m3
% loss	1.12 %	% loss, segment	0.89 %	% loss, segment	0.53 %	% loss, segment	2.55 %
% loss, total	1.12 %	% loss, total	2.00 %	% loss, total	2.52 %	% loss, total	5.00 %

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As discussed above, the expression for the dissociation rate for WD above 200 m yields a time-dependent solution. The dissociation-range for this segment is a result from solutions for low  $t$  in one end and high  $t$  in the other. The decrease in dissociation rate with time is believed to be due to experimental boundary conditions. The “initial rate” is believed to be higher than the “final rate” since the hydrate surface is moving away from the system boundary where the temperature is held constant. In a system where hydrate particles are falling with their terminal velocity through the ocean, the system can be viewed as having a “constant” surrounding temperature in the near vicinity of the hydrate/water interface. Hence, it is assumed that the initial, high dissociation rate from the experiments of Kawamura et al. is the most correct rate to use in this analysis for WD less than 200 m.

For WD larger than 200 m, the reported dissociation rate varies between  $8\text{E-}6$  and  $1.2\text{E-}8$  m/s. Sloan, being the word-leading expert on hydrates, and also experienced within the area of CO<sub>2</sub> hydrate dissociation in the Deep Ocean, has been using the value  $5\text{E-}7$  m/s.

By employing these considerations, a necessary hydrate particle of  $r = 0.4$  m,  $V = 0.3$  m<sup>3</sup>, results.

## D7 DISCUSSION ON THE VALIDITY OF THE ANALYSIS

Generally, the hydrate dissociation data is very scarce, and it is obvious from the large discrepancy in the necessary particle sizes that the quality of the available data on the hydrate dissociation rate in water is not good enough. Clearly, more exact work needs to be performed in order to get a satisfactory dissociation rate of frozen CO<sub>2</sub> hydrates in water as a function of pressure and temperature.

Several assumptions have been integrated in the sinking calculations in order to simplify the analysis. These assumptions include:

- For WD<200m, data from methane hydrate experiments have been used. CO<sub>2</sub> forms the same hydrate structure as methane, but the higher solubility of CO<sub>2</sub> in water may give a higher dissociation rate of CO<sub>2</sub> hydrates than of methane hydrates. If the dissociation rate in this segment is doubled, this will lead to an increase in the particle size of 5% for the higher limit and 40% for the lower limit.
- Homogeneous hydrate samples assumed, i.e. constant dissociation rate.
- Constant seawater density assumed.
- Hydrate density assumed (through gas content). Assuming maximum gas content leads to a decrease in the necessary particle size of approx. 10%.
- Hydrate dissociation rate independent on the surface area, i.e. constant rate. This is based on the small allowable decrease in the particle volume.
- Not taken into account any attachment of released gas onto the hydrate surface. This would give a higher bouancy of the hydrate particle, the sinking rate would be smaller and the necessary particle size larger.
- Spherical particles are assumed in the analysis, while hydrate blocks are suggested for the hydrate process.
- Terminal velocity assumed and acceleration period neglected.

However, the range in the hydrate dissociation is so large and is assumed to be the one important factor for the uncertainties of the necessary hydrate particle sizes.

Generally, the whole exercise is viewed as rather uncertain. However, from the analysis and general knowledge, it is clear that the particles have to be of a considerable size (larger than 5 cm diameter). From a practical point of view however, it is not envisaged that producing larger hydrate blocks is more challenging

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than producing medium-sized hydrate spheres as the basic mechanisms will be the same. Also, larger blocks are believed to be easier to handle from a logistical point of view.

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## **APPENDIX E – INDUSTRIAL PRODUCTION AND TRANSPORTATION**

### **Literature Review on Industrial Production and Transportation of Gas Hydrates**

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## Industrial Production and Transportation of Gas Hydrates

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### E1 INTRODUCTION

To our knowledge, industrial large-scale production and transportation of CO<sub>2</sub> hydrates have not been investigated in details. However, by assuming similar behaviour of CO<sub>2</sub> hydrates to natural gas hydrates, it is possible to take advantage of the work that has been performed on hydrates as a storage and transportation media for *natural gas*.

Investigations (patented solutions) of gas transport using hydrates include those of Benesh (1942, slightly pressurised, low temperature), Chersky (1975, pressurised, ambient temperature), Nierman (1976, pressurised, submerged vessels), Gudmundsson (1996, atmospheric, sub-zero), Gudmundsson (1999, atmospheric, sub-zero, co-transportation of oil&gas). In addition, there exist numerous patents on the production method specifically.

Recent advances have all been concentrated around pressurised production and atmospheric/low pressure, sub-zero transportation in ships. Papers describing technical and economical evaluations include Gudmundsson & Børrehaug (1996), Shiota et al. (2002), Iwasaki et al. (2002), Takaoki et al. (2002), Nakajima et al. (2002), Ota et al. (2002), Taylor et al. (2003). Although some of these solutions differ somewhat on the detail level, the basic concept is pressurised production and sub-zero, atmospheric/low pressure transportation.

### E2 INDUSTRIAL HYDRATE PRODUCTION

Spencer (1995), Spencer & Wheeler (1996) and Yamasaki (2000) present solutions using hydrates for CO<sub>2</sub> sequestration in the Deep Ocean. All systems are characterised by contacting carbon dioxide with water, fresh or seawater. However, no detailed investigations on industrial, large-scale feasibility or economics have been found.

From experimental experience it is known that gas hydrates form readily when gas is contacted with water at pressure/temperature conditions within the hydrate-forming region for the given gas, under turbulent



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conditions. Taylor et al. (2003) argue that hydrates form slowly in pressure vessels, but using continuous stirred tank reactors, it is well documented that a considerable reaction rate is achieved (Mork 2002, Mork & Gudmundsson 2002).

As far as we can see, the use of a continuous stirred tank reactor (CSTR) is the most used means of producing hydrates on a laboratory/small pilot scale. Also, CSTRs are well-know technology from several different industries and are therefore straightforward to cost. Emerging technologies with more effective reactors may be developed, e.g. Takahashi et al (2002) report a micro-bubble technology whereas Miyata et al. (2002), Ohmura et al. (2002) and Iwasaki et al. (2002) propose a hydrate formation process with super-cooled water sprayed into the gas phase. However, these technologies are not considered mature enough to be evaluated in this study. With the emergence of optimised production schemes however, it is believed that the efficiency and thereby cost can be improved compared to a “standardised” CSTR. This includes e.g. chemicals for enhancing the production rate (Han et al. 2002, Karaaslan and Parlaktuna 1999).

The effect of turbulence is recognised, but it is not unambiguously stated anywhere what the stirring rate has to be in order to efficiently produce hydrates in a continuous process.

Shirota et al. (2002) propose a basic concept for natural gas hydrate production (and shipping) and envisage the use of ice particles in contact with the gas in the production scheme. The advantages with an ice-gas system is very large conversion of ice to hydrate (almost 100% reported), and no need for dewatering of a hydrate slurry. Conversion rate numbers are not found in the open literature, and we believe that the necessary retention/contact time in present-state ice-gas system will be too long for a large-scale industrial process.

A disadvantage with producing hydrates in a water-continuous system is the excess water that needs to be separated from the hydrate. Kimura et al. (2002) evaluated several types of dehydrators and envisage the possibility of achieving 10% free water in the resulting product by using a screw press dehydrator. This is also the number assumed by others (Gudmundsson and Børrehaug 1996). Taylor et al. (2003) state that “virtually all the water can be removed”.

Several small pilot plants/ large-scale laboratory plants have been built by the above-mentioned researchers and their team. The main challenges seem to be related to the separation of hydrates from the water phase. It should be noted, however, that continuously production of hydrates on an industrial scale has not been performed and the technology is not yet proven.

### E3 HYDRATE TRANSPORTATION

Early investigations suggest transporting gas hydrates pressurised in pipelines (Chersky 1975), but due to the metastability/self preserving effect experienced by hydrates at sub-zero temperatures and atmospheric pressure, recent research concentrate on transportation at these conditions.

Gudmundsson and Børrehaug (1996) envisage hydrate transport in bulk oil carrier-type ships, slightly insulated mainly to prevent ice formation on the outside.

Takaoki et al. (2002) concluded that the hydrate should be transported in spherical pellets form due to improved self-preservation and quality assurance of the cargo. Ota et al. (2002) present the results from the investigation on the safety measures and the conceptual design of a “pellet-transporting” ship.

Taylor et al. (2003) state that the best way of transporting the hydrate is by insulated bulk carriers, barges or floating containers towed by tugboats, depending on distance.

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The main challenge seems to be related to transportation temperature and means of unloading the hydrates, in addition to the behaviour of the hydrates during transport. It should be noted, however, that transport of hydrates on an industrial scale has not been performed and the technology is not yet proven.