HYDRATES FOR DEEP OCEAN STORAGE OF CO_2

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ABSTRACT
A study has been performed to evaluate how hydrates can be utilised as the basis for deep ocean CO_2 disposal processes. By converting CO_2 gas to solid hydrates, a cost-efficient way of transporting CO_2 may be achieved. The paper describes the proposed production and transportation method for sequestration of 20,000 tonne CO_2/day and gives a preliminary estimate of the CO_2 abatement cost of about 36 US$/tonne CO_2 for a 1000 km disposal distance.

Keywords: CO_2 hydrates, novel hydrate technology, CO_2 disposal

INTRODUCTION AND BACKGROUND

One suggested alternative for CO_2 sequestration is direct deep ocean storage of CO_2, which is the likely long-term destination of the large atmospheric release of CO_2 that occur in the modern world. Background information on disposal of CO_2 in the ocean can be found in the open literature, e.g. [1], [2].

Direct injection of *liquid* CO_2 is one scenario for deep ocean storage of CO_2. Under the conditions that prevail in the deep ocean, liquid CO_2 in contact with seawater will tend to form CO_2 hydrates. It is known that CO_2 hydrates are denser than both seawater and CO_2 and should sink to the bottom of a liquid CO_2 pool at the sea floor. This predicted behaviour has led to the scenario that CO_2 hydrates could be used for long term storage of CO_2 on the deep ocean floor.

An attribute of hydrates is that the substance is meta-stable at atmospheric pressures and moderate sub-zero temperatures. This, together with the potential high gas content of hydrate, forms the basis for the idea that hydrates can be used for gas transport. Hydrate technology has been evaluated by Aker Kvaerner and the Norwegian University of Science and Technology (NTNU) since early 1990's as an alternative way to capture and transport natural gas. Cost estimates have indicated that capital cost of hydrate technology may for some developments be considerable lower than e.g. LNG (liquefied natural gas) and pipeline transport. See e.g. Gudmundsson et al. [3], [4] for summaries of the hydrate technology and different possible applications.

With this background, Aker Kvaerner on commission from IEA (International Energy Agency) has performed an engineering study

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evaluating how hydrates possibly can be utilised as the basis for deep ocean CO_2 disposal processes. This paper contains an excerpt of the study and presents the following topics:

1. By converting CO_2 gas to solid hydrates, a cost-efficient way of transporting CO_2 may be achieved. The paper describes the proposed production and transportation method and gives a preliminary estimate of the CO_2 abatement cost.

2. A method of sinking CO_2 to the bottom of the deep ocean by virtue of the relatively high density of the hydrate. The paper presents a rough analysis of the sinking of the hydrates.

The solid lumps of hydrates are expected to form a temporary accumulation of hydrate before decomposing as a result of which the CO_2 content will dissolve in the surrounding seawater. No evaluations have been performed of the environmental effects of high local CO_2 concentration of the sea water.

In this work the environmental issues of Deep Ocean disposal of CO_2 have not been assessed. Of course, all environmental impacts related to ocean disposal must be evaluated in great detail prior to utilizing the ocean as a sink for CO_2.

CO_2 HYDRATE PRODUCTION AND TRANSPORTATION PROCESS

Concept Summary

CO_2 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_2 is released before reaching the deep ocean. Figure 1 shows a schematic of the concept, which is further described below.

The basis for the concept evaluation and cost estimate is 20,000 tonnes/d CO_2 arriving at the hydrate production plant at 10 bara and 30 °C. The following key data are presented:

<u>Production</u>
Design rate: 20,000 tonne/d CO_2
⇒ Hydrate production rate: 3000 m^3/hr
⇒ Transportation rate: 3577 tonnes/hr
Hydrate heat of formation: 313,000 kW
Heat removal: 43,000 kW (seawater cooling) + 360,000 kW (cooling media)
Power demand: 78,000 kW (electrical) + 61,000 kW (turbine)

<u>Transport</u>
Transport distance: 1,000 km
Carrier type and cargo capacity: Bulk vessel; 169,400 dwt, 120,000 tonnes capacity
Number of carriers: 4

<u>Emission</u>
Estimated CO_2 emission: 2700 tonnes/d
CO_2 capture efficiency: 87%

CO_2 Hydrate Production

The suggested scheme for the hydrate production process where CO_2 gas is converted to hydrates is based on in-house experience and knowledge of similar processes.

Gas hydrates form readily when gas is contacted with water at pressure/temperature conditions within the hydrate-forming region for the given gas. For efficient mixing, it is suggested that the hydrate production process should occur with CO_2 in the vapour phase. For the purpose of this study, the reactor conditions are chosen to:

Pressure: 36 bara
Temperature: 2 → 8 °C
(increasing, as the reaction is exothermic)

The CO_2 is hence pressurised and cooled, and contacted with fresh water at 36 bara and 2 °C. Conversion of the CO_2 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 suggested 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.

An analysis was performed to attempt to investigate the necessary particle size of the hydrates (see below). The necessary size of the hydrate particles is highly dependent on the dissociation rate of frozen hydrates in seawater. In the study, however, only high-level estimates of the processes and the associated costs were made. The total cost is not expected to be significantly dependent on the hydrate-block-producing equipment.

CO_2 Hydrate Transportation

Two potential systems were identified for shipping and offshore discharge of CO_2 hydrates. One method is based on the methods used for offshore rock dumping (bulk vessel), while the other utilises container transport methods.

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.

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. The round-trip was estimated as shown in the following table:

	169,400 dwt	**74,300 dwt**
Onloading (producing full cargo):	1.6 d	0.7 d
Transit	1.5 d	1.6 d
Offloading (assumed)	1.0 d	0.9 d
Return	1.5 d	1.6 d
ROUND TRIP	5.6 d	4.8 d

For the study, no docking time was taken into account and no storage onshore was assumed. The estimate resulted in the following numbers of carriers:
169,400 dwt: 4 carriers required
74,300 dwt: 8 carriers required

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 was recommended and used for further evaluations.

The size and the shape of the hydrate blocks will have an effect on the transport system and the efficiency and rate of loading.

Cost

A rough cost estimate for the production and transportation of CO_2 hydrates was performed, reflecting the technical concepts presented above. The CAPEX estimates are 50/50 estimates with overall accuracy of +/- 50 % and 80 % confidence interval. OPEX estimates and cost per tonne of hydrates are included, covering the same elements as the CAPEX estimate.

The estimates are high level estimates based on knowledge of costing of similar plants and systems. 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 cost estimate for the carrier is based on international new-build prices.

The OPEX cost is scaled from similar onshore gas/oil processing plants, though such that the energy and fresh water requirements have been addressed separately. The energy unit prices are based on current market prices.

95% production regularities have been assumed and the capture efficiency is estimated to 87%. No CO_2 purchase cost has been included. The numbers are given in 2003-currency.

COST ITEM	**Cost (mill USD)**
Onshore production facilities	756
Hydrate bulk carriers, 4 off	200
Contingency, 20%	191
SUM CAPEX	**1147 mill USD**

COST ITEM	**Cost (mill USD)**
Annual OPEX in % of CAPEX, 3%	**34**
Electrical consumption	**26**
Water purchase	**5**
SUM OPEX	**77 mill USD**

Assuming an operational period of 25 years after completion of construction and a discount rate of 10%, an abatement cost of 36.2 US$/tonne CO_2 resulted.

Challenges

Aker Kvaerner has through the years been involved in several studies and technical development work where hydrates have been evaluated as a means for natural gas transport. Aker Kvaerner 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_2.

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. In general, conservative methods, equipment and solutions have been chosen, leaving room for possible optimisation of the process. Technology and know-how gaps have been identified and are outlined in the study.

The major challenges related to CO_2 hydrate production and transportation are considered the following:

- Verification of CO_2 hydrate properties and behaviour.
- Effective heat removal in the production process.
- Effective hydrate/water separation.
- Effective hydrate freezing and hydrate block production.
- Effective loading: the loading rates must exceed the production capacity.
- Minimise melting of the hydrates during transport and handling.
- 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.

The hydrate blocks have a minimum size requirement. More detailed information is needed on this dissociation rate, in order to accurately determine the necessary block size of the discharged hydrates.

HYDRATE SINKING AND DISSOCIATION PROCESS

The aim of this analysis was to calculate the necessary hydrate particle size for sinking hydrates into the deep ocean. The criterion was that only a few percentage of the hydrate dissociated during the sinking to 3000 m, being strongly dependent on the dissociation rates of hydrate in water.

By comparing the assumed pressure and temperature profiles with the equilibrium curve for CO_2 hydrates, it is found that above approximate 200 m water depth (WD), with pressure $P < 21$ bara and temperature $T > 5$ °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_2 “concentration” between seawater and hydrate.

Very little data on the dissociation rate of frozen hydrates in water was found in the open literature, and there were large discrepancies in the reported values. Based on different considerations and evaluations, dissociation rates of $5 \cdot 10^{-5}$ m/s was used for dissociation down to 200 m WD, and $5 \cdot 10^{-7}$ m/s was used for WD above 200 m.

The necessary hydrate particle sizes were estimated by setting a particle diameter and calculating the time to reach 3000 m through terminal velocity calculations (spherical particles assumed). 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.

By employing these considerations, a necessary hydrate block of r = 0.4 m, V = 0.3 m^3, resulted. It should however be stressed that there are large uncertainties in the calculations.

CONCLUDING REMARKS
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 still required to confirm the feasibility for the gas hydrate transport chain.

This work is however performed as part of a larger evaluation of alternative transport methods for deep ocean CO_2 sequestration. The work presented within this paper indicate that CO_2 transported as hydrate might be a feasible alternative for transporting CO_2 to the final destination of deep ocean CO_2 sequestration. Technology and know-how gaps were defined. However, substantial cost-savings compared to the cost estimate presented here might be obtained with further development of the processes.

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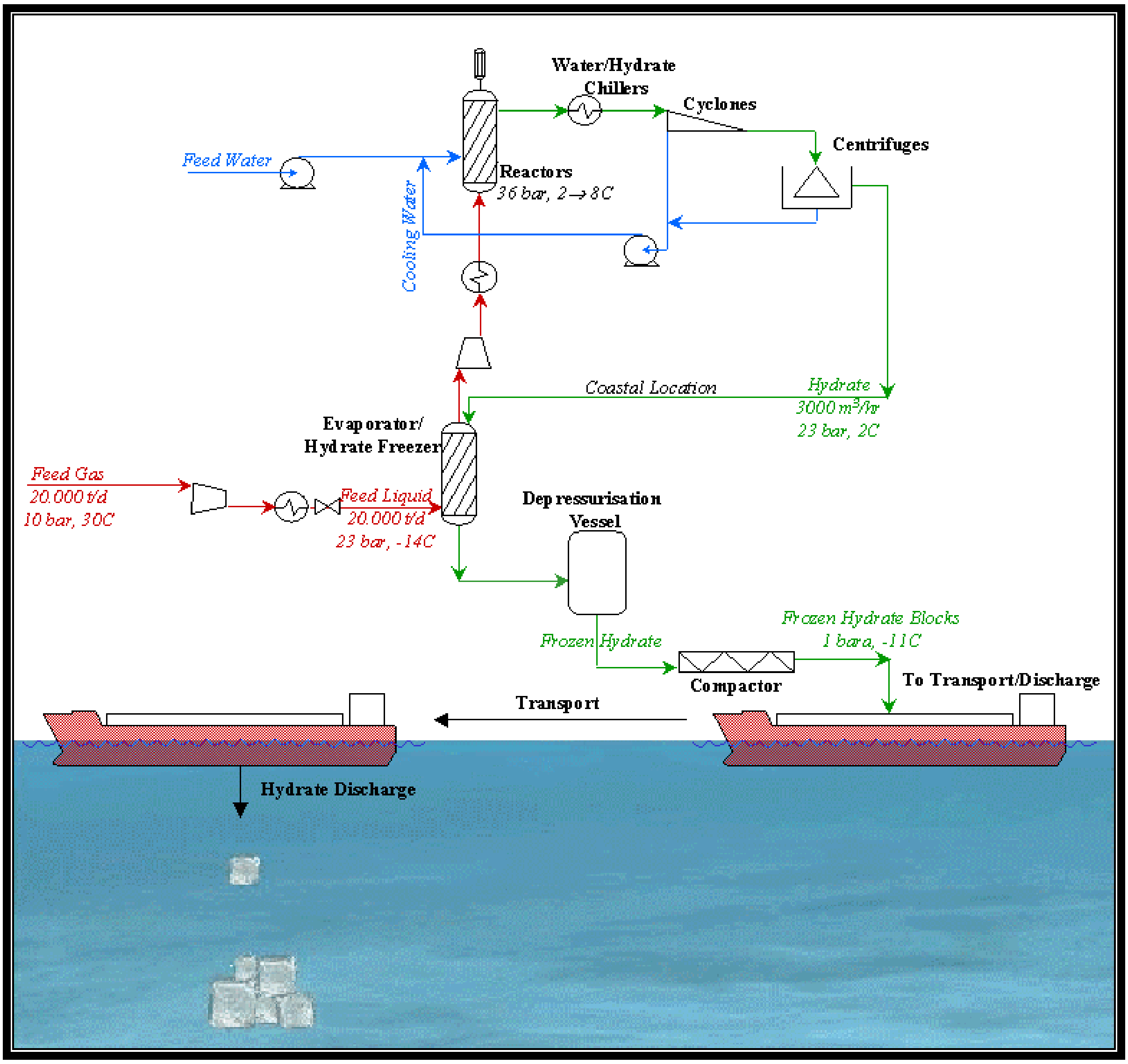

Figure 1: Gas Hydrates for Deep Ocean Storage of CO_2. Overall Concept Schematic.