



Carbon capture and storage—Solidification and storage of carbon dioxide captured on ships



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ABSTRACT

To meet the International Maritime Organization (IMO) target of 20% reduction of CO₂ emissions from marine activities by 2020, application of Carbon Capture and Storage (CCS) on ships is considered as an effective way to mitigate CO₂ emissions while other low carbon shipping technologies are being developed. Literature reviews on CCS methods for onshore applications indicate that the current CCS technologies could not be implemented on boards directly due to various limitations on ships. A novel chemical CO₂ absorption and solidification method for CO₂ storage on-board is proposed, presented and analyzed. Technical feasibility with explanation of principles and cost assessment are carried out for a case ship with a comparison to a conventional CCS method. The paper also presents results obtained from laboratory experiment including factors that affect the absorption. Theoretical study and laboratory experiment illustrate the proposed CO₂ solidification method is a promising, cost effective and feasible method for CO₂ emissions reduction on ships.

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1. Introduction

Climate change has become a popular topic simply because it leads the melting glaciers, rising sea levels and the extinction of endangered species. It is well-known that greenhouse gases (GHG) are the cause of the climate change which is mainly contributed by the carbon dioxide (Houghton, 2004). According to IPCC report, the current CO₂ concentration in the atmosphere is increased by 100 ppm which is about 34% increment compared with the pre-industrial level (Rogner et al., (2007)). Fig. 1 presents the growing of CO₂ emissions from 2000 to 2009 (Boden et al., 2010). Although the emissions are a little bit declined from 2008 to 2009, the tendency of the curve is obviously climbing.

For the global economy, international shipping have an immeasurable effect as it is the most effective way for large quantity and long distance transportation of international trade. Referring to the report of *Second IMO GHG Study 2009*, international shipping is estimated to have 870 million tones CO₂ emitted in 2007 which is about 2.7% of the global CO₂ emissions (Buhaug et al., 2009). There are numbers of methods to reduce the ship GHG emissions. EEDI, EEOI and SEEMP stipulated by IMO are focusing on increasing the energy efficiency. With high energy efficiency, the fuel

consumed will be reduced so that the CO₂ generated will be decreased. EEDI, EEOI and SEEMP regulations are proposed to be entered into force on 2013 with an aim to reduce about 180 million tons of CO₂ emissions from international shipping annually by 2020. It is about 20% of the current emissions level. Thus, so many projects emerge with a target of 20% reduction of CO₂ emissions.

CCS is an effective way to mitigate and even eliminate the effect of global warming caused by CO₂ emissions. It is now only used on shore based power plants and industrial processes (Global Carbon Capture and Storage Institute). Fig. 2 presents three general ways of CCS that are available for onshore application. The principles of pre-combustion method are to remove carbon component from the fossil fuel prior to its combustion. Oxy-fuel capture method is to burn the fossil fuel with pure oxygen rather than oxygen in air so that only CO₂ and water vapor are produced after combustion and CO₂ can be easily captured by condensing the flue gases. Post-combustion capture method is to have CO₂ captured from the flue gases after the combustion of the fossil fuel.

Although these methods could help capture carbon from fuel oil, mechanically installation of the systems on ships will bring great impacts on shipping performance. For instance, additional power consumption will increase fuel consumption, more space taken leads a reduction of cargo transported and storage of CO₂ on ships in a form of gas or liquid state is difficult and unsafe. No matter what kind of method is considered, the impacts on shipping performance should be minimized.

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Nomenclature

CCS	carbon capture and storage
CFD	computing fluid dynamic
CPCS	chemical processes for carbon Solidification
<i>D</i>	diameter
DWT	deadweight tonnage
EEDI	energy efficiency design index
EEOI	energy efficiency operational indicator
EIGA	european industrial gases association
EOR	enhanced oil recovery
GHG	greenhouse gases
<i>H</i>	height
HSFO	high sulfur fuel oil
ICP	inductively coupled plasma
IMO	international maritime organization
IPC	inductively coupled plasma
IPCC	intergovernmental panel on climate change
ITTC	international towing tank conference
LBP	length between perpendiculars
LOA	length overall
<i>M</i>	molar mass
<i>m</i>	mass
MCR	maximum continuous rating
<i>n</i>	molar number
<i>P</i>	power
<i>p</i>	profit
<i>R</i>	rate
SEEMP	ship energy efficiency management plan
SFOC	specific fuel oil consumption
<i>t</i>	time
<i>V</i>	volume
π	pi
ρ	density

$Ca(OH)_2$	calcium hydroxide
$CaCO_3$	calcium carbonate
CaO	calcium oxide
CO_2	carbon dioxide
CO_3^-	carbonate ion
H_2O	water
Na_2CO_3	sodium carbonate
$NaOH$	sodium hydroxide
NO_x	nitrous oxides
SO_x	sulfur oxides

Atomic and molar weight

Carbon (<i>C</i>)	12
Hydrogen (<i>H</i>)	1
Oxygen (<i>O</i>)	16
$Ca(OH)_2$	74
$CaCO_3$	100
Calcium (<i>Ca</i>)	40
CaO	56
CO_2	44
H_2O	18
Na_2CO_3	106
$NaOH$	40
Sodium (<i>Na</i>)	23

Units

<i>L</i>	litre
<i>L/min</i>	litre per minute
<i>mol</i>	mole number
<i>ppm</i>	parts per million

Chemical substances

A novel carbon capture method is proposed in order to reduce the power requirement, save spaces on board and avoid CO₂ storage in a gas or liquid form on ships. This method applies two chemical processes and a physical step to absorb CO₂ from exhaust gases, precipitate the CO₃⁻ ion and separate CaCO₃ from the absorption solution on ship board.

In this study, the results obtained from laboratory experiment are extended to apply on a case ship. An economical assessment is presented by comparing the chemical processes for carbon solidification (CPCS) with the CO₂ compression and liquefaction

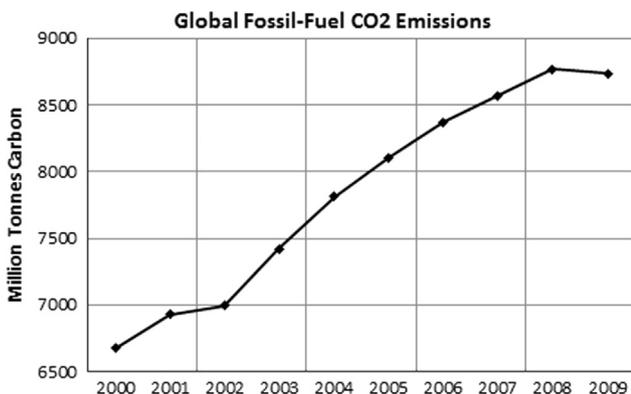


Fig. 1. Tendency of CO₂ emissions from 2000 to 2009.

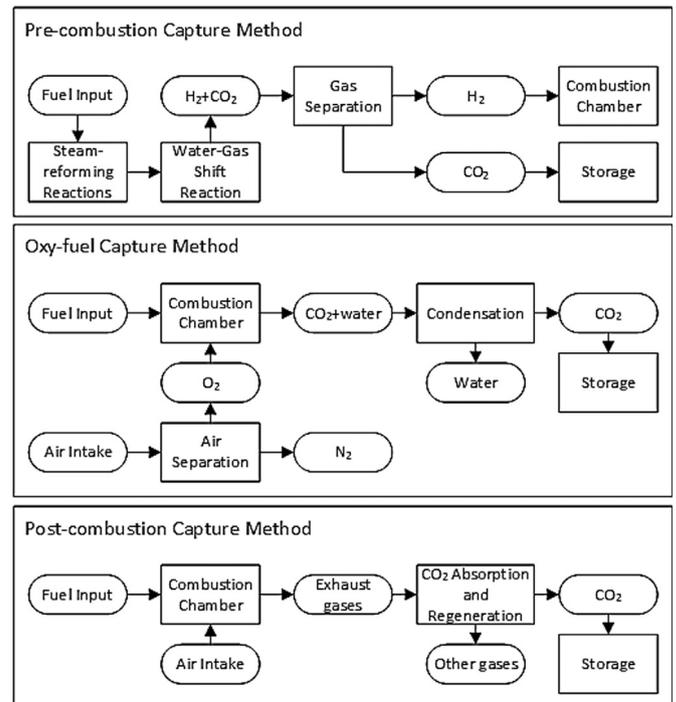
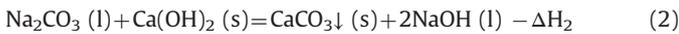
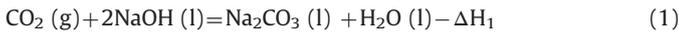


Fig. 2. General carbon capture methods.

method used commonly for the case ship, together with the results obtained from the experiment.

2. Chemical processes for carbon dioxide solidification

There are two chemical processes involved which include CO_2 absorption and CO_3^- ions precipitation. The reactions related to these two processes are shown in Eqs. (1) and (2) (Pflug et al., 1957; Mahmoudkhani and Keith, 2009):



In the first reaction, the carbon dioxide is absorbed by sodium hydroxide (NaOH, caustic soda). Sodium hydroxide reacts with acid gases, such as CO_2 , SO_x and NO_x , is a natural process. The products from this reaction are sodium carbonate (Na_2CO_3 , washing soda) and water. Na_2CO_3 is a relative stable compound so that CO_2 can be stored as CO_3^- ions in the Na_2CO_3 solution. After the absorption reaction, the Na_2CO_3 solution will react with calcium oxide (CaO, quicklime) and water. Finally, the precipitated calcium carbonate (CaCO_3 , limestone) is produced, as shown in reaction (2). The CO_3^- ions are precipitated in the form of CaCO_3 compound. After filtering, washing and drying processes, the powders of precipitated calcium carbonate will be obtained which can be stored safely on-board and unloaded at the destination of a voyage. The reaction presented in Eq. (3), generating calcium hydroxide ($\text{Ca}(\text{OH})_2$, hydrate lime), is an internal reaction of reaction (2). It is an exothermal reaction where reaction heat can be recovered and reused (Souto et al., 2008).



The heat released during three reactions is 109.4, 5.3 and 65 kJ per mol CO_2 respectively (Mahmoudkhani and Keith, 2009). While dissolving NaOH into water, there are heat released as well which is 35.82 kJ per mol NaOH (Japan Soda Industry Association, 2006).

Based on these reactions, CO_2 from the exhaust gases are eventually captured and stored in a solid form. Referring to the conservation of mass, the masses of reactants are equal to the masses of the products. As masses are related to molecule masses and molar numbers, the relationships between different substances are shown as following equation

$$m_1/m_2 = (n_1 \times M_1)/(n_2 \times M_2) \quad (4)$$

where

m_1	total mass of substance 1 (ton);
m_2	total mass of substance 2 (ton);
n_1	molar number of substance 1 (mol);
n_2	molar number of substance 2 (mol);
M_1	molar mass of substance 1 (kg/mol);
M_2	molar mass of substance 2 (kg/mol).

This relationship will be used to derive the masses of different chemical substances involved in the reactions.

As the CaCO_3 is generated from the solution, what obtained from reactions is CaCO_3 mud which is a mixture of NaOH solution and CaCO_3 (Metso, 2011). To separate the sediment from the solution, a filtration process is applied. After filtration and drying, solid sediment will be available for storing on ship.

Other than being able to retrofit on existing ships, there are many advantages when applying CPCS comparing to CO_2 compression and liquefaction for shipboard application. The final product precipitated CaCO_3 from the solidification processes can be used by many applications in industry, for instance, paper making,

construction and plastic industries. Due to a large quantity of precipitated CaCO_3 produced, profits made by selling the product could be considerable. When storing liquefied CO_2 on board, issues like ship stability, spaces occupied and high requirement for storage tank due to the instability of liquefied CO_2 are serious problems. With the application of CPCS, all these problems will be solved. These advantages will be presented in detail in the section of case ship study.

3. Experiment and results

Based on the principles of the solidification processes introduced above, two steps of experiment are designed: chemical absorption and precipitation, and physical filtration. In the chemical processes, pure CO_2 is used.

A flow chart of the experimental rig is shown in Fig. 3. Fig. 4 is a picture of the experiment rig. The flow of CO_2 gas contained in a CO_2 bottle is controlled by a regulator. The gas is piped into NaOH solution inside a measuring cylinder. A diffuser is used to increase the contact area between the gas and solution by generating gas bubbles. Inside the measuring cylinder, the gas is absorbed by the solution. After the absorption, CaO powders are added into the measuring cylinder so that the CO_3^- ions can be precipitated.

After the precipitation, the mixture of sediment and solution goes through a funnel with filter paper where the sediment and solution are separated. After the filtration, the sediment obtained will be dried for further measurement.

Table 1 presents the results of gas absorption rate, NaOH regeneration rate and CaCO_3 filtration efficiency achieved from experiment. The CO_2 absorption rate is a ratio between gases absorbed and that gas fed in. The regeneration rate of NaOH is defined as the ratio of NaOH regenerated and that initially supplied. The CaCO_3 filtration efficiency is determined by ratio of CaCO_3 separated to theoretical formatted from reaction.

From the table, the gas absorption rate is nearly 68% but it is only the rate under laboratory conditions. For an industrial application, a much better mixing process of gas and solution can be obtained by using a mechanical stirrer so that the absorption rate will be higher than that under laboratory conditions. Another factor will be considered in the industrial processes is the purity and concentration of CO_2 gas. Due to the impurities in exhaust gases in a practical application, further treatments may be required for purification so the absorption rate will be varied.

Whatman grade 589/3 qualitative filtration papers are used for the separation of NaOH solution and CaCO_3 in the experiment. This type of filter paper is suitable for high retention of fine particles and have an excellent resistance from strong alkali solution. The filter papers with a diameter of 125 mm are selected to match the funnel. The particle size of CaCO_3 ranges from 1 to 3 μm and pore size of filter papers is less than 2 μm which is the smallest one for

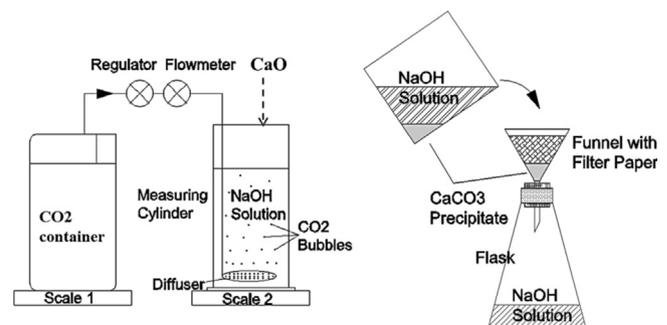


Fig. 3. Schematic of the experiment systems.



Fig. 4. Pictures of experiment rig.

Table 1
Experiment results.

Experiments Rates	Results (%)
CO ₂ Absorption rate	67.85
NaOH Regeneration rate	85.37
CaCO ₃ filtration efficiency	82.17

Table 2
Change of absorption rate with gas input flow rate.

Solution volume (ml)	Solution column height (cm)	Cylinder diameter (cm)	CO ₂ Flow Rate (L/min)	CO ₂ Absorption rate (%)
–	–	–	1	77.67
~900	30	6	2	76.27
–	–	–	3	74.96

laboratory use. The small pore size does not only lead a long period of filtration processes but also result in a small amount of CaCO₃ slipping through the filter. The CaCO₃ filtration efficiency is expected to be much higher in practical application because industrial filtration method, such as pressure disc filter or centrifugal separation. To simplify the study, the filtration efficiency used in the case ship study is taken as 100%.

In order to estimate the CO₂ absorption rate, four parameters were examined during the experiment: gas input flow rate, change of absorption cylinder diameter with fixed volume of solution, change of absorption cylinder diameter with solution column height unchanged and change of solution column height with the same diameter of cylinder.

3.1. Impact of gas flow rate on absorption rate

To find out effect of the gas flow rate on the CO₂ absorption rate, three runs of experiment with different gas flow rates are conducted. The selected gas flow rates are 1, 2 and 3 L/min. The selection of gas flow rate is restricted by the experiment equipment because higher flow rate will lead to an unstable pipe connection and even disconnected. To ensure the accuracy of reading on flow meter, only integer scales are selected for comparison. For these three sets, the same quantity solution is used with the solution column height of 30 cm. The diameter of the measuring cylinder is 6 cm. The results are presented in Table 2 and Fig. 5.

According to the experimental results, the CO₂ absorption rate increases as the input gas flow rate decreases. The reason being a small gas flow rate allows more time for contact of the gas and the solution. As the gas flow increases, the amount of CO₂ slipped from

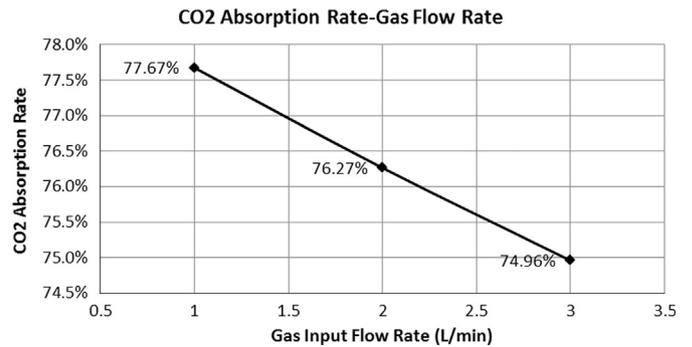


Fig. 5. CO₂ absorption rate vs. gas flow rate.

Table 3
Changing of absorption rate with container diameters (solution quantity unchanged).

Solution volume (ml)	Solution column height (cm)	Cylinder diameter (cm)	CO ₂ Flow rate (L/min)	CO ₂ Absorption rate (%)
–	30	6	–	74.96
~900	18	8	3	72.08
–	10.5	10	–	65.44

the absorption process will be increased. However, the reduction rate is only 2.7% when the gas flow rate is increased from 1 L/min to 3 L/min. Hence, it is concluded that the flow rate has no significant effect on absorption rate under the conditions used in the experiment.

3.2. Impact of cylinder diameters on absorption rate with fixed volume of solution

According to Table 3 and Fig. 6, the absorption rate is decreased while the container has a larger diameter. It is easy to find that container with a large diameter leads a short time for CO₂ gas contacting with the solution. It is because column height is reduced as the cylinder diameter is increased when the volumes of the solution are fixed. When the diameter is changed from 6 to 8 cm, less than 3% of the gas are released and wasted. The percentage grows to 6.64% when the diameter is increased from 8 to 10 cm. From the curve above, it is obviously that declining of the curve is faster along the X axis. Hence, the absorption rate will be increasingly reduced when enlarging the diameter. On the contrary, narrowing the diameter will lead a greatly increasing on absorbing gas when changing diameter of cylinder without

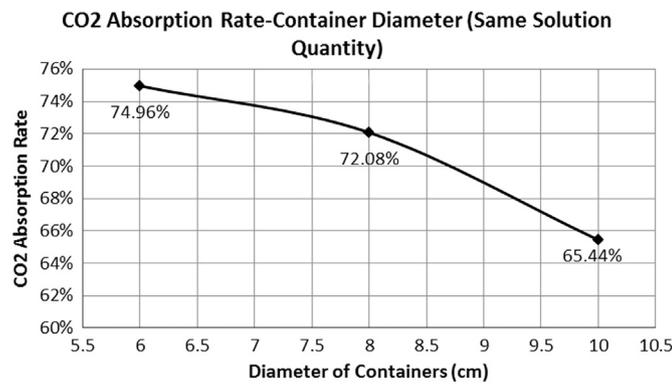


Fig. 6. Effect of container diameter on gas absorption rate with unchanged solution quantity.

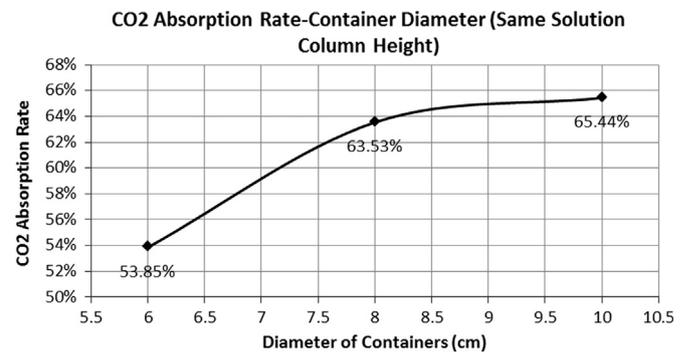


Fig. 7. Effect of container diameter on gas absorption rate with fixed solution height.

Table 4
Changing of absorption rate with container diameters (same solution column height).

Solution volume (ml)	Solution column height (cm)	Cylinder diameter (cm)	CO ₂ Flow rate (L/min)	CO ₂ Absorption rate (%)
296.88	–	6	–	53.85
527.79	10.5	8	3	63.53
824.67	–	10	–	65.44

Table 5
Change of absorption rate with solution column heights (fixed container diameter).

Solution volume (ml)	Solution column height (cm)	Cylinder diameter (cm)	CO ₂ Flow rate (L/min)	CO ₂ Absorption rate (%)
848.23	10.5	–	–	53.85
508.94	18	6	3	69.94
296.88	30	–	–	74.96

changing volume of the solution. It is a feasible and effective way of enhancing CO₂ absorption rate by increasing the contact rate between gas and solution.

3.3. Impact of cylinder diameters on absorption rate with solution column height unchanged

According to the result above, a better mixing and long contact time between gas and solution will bring a higher absorption rate of CO₂ gas. Results in Table 4 and Fig. 7 show the effect of change of the cylinder diameter (cross-section area) on absorption rate with fixed height of solution column height.

Results shows when the cylinder diameter varies from 6 to 10 cm with the same column height of 10.5 cm, the highest absorption rate takes place when the diameter is 10 cm. When the diameter is changed from 6 to 8 cm, the absorption rate is increased by 9.7%. A further increase in the diameter from 8 cm to 10 cm, the rate is increased only by 1.91%. It is understandable that the absorption rate will be increasing when the solution column cross-section area is increased. For the given test rig set up, the results indicate that a too large cross-section area does not help to increase the absorption rate much. This could be because the diffuser size is not increased as the diameter increases. Hence, when the cross-section is too large the gas bubble could not reach to the edge area of the cylinder. This means there is room for test rig optimization to achieve the best match of solution column cross-section area, diffuser size and column height.

3.4. Impact of column height on absorption rate with a fixed cylinder diameter

According to Table 5 and Fig. 8 above, the absorption rate is increased while the height of the solution column is increased. This is because as the solution height increased, the path of gas are increased, resulting in an increase in the contacting time between the gas and solution. Hence, more gas will be absorbed. When the height is increased from 10.5 to 18 cm, the absorption rate is raised by 16.09%. The rate grows only 5.02% when the solution column is

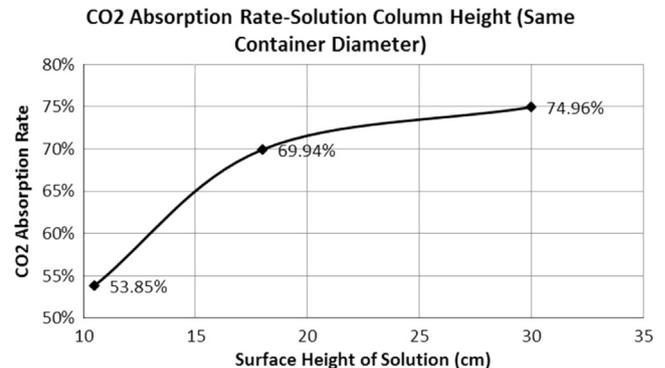


Fig. 8. Effect of solution column height on gas absorption rate with same cylinder diameter.

changed from 18 to 30 cm. It is because with small solution column height, the path of gas is too short to have a good contact with solution. When the solution height increased, the change will be significant at the beginning and then will be very slightly. This indicates that there is an optimal match between the column height and gas supply rate.

4. Case ship study

Nowadays, there are two technologies used onshore for the storage and transportation of CO₂ captured, i.e. compressed CO₂ and liquefied CO₂. For pipeline transportation, compressed CO₂ is a preferred option (Ciferno et al., 2010; Witkowski and Majkut, 2012). If captured CO₂ is transported by a ship, both compressed CO₂ and liquefied CO₂ technologies can be used, where the latter is achieved by a combination of increased pressure and reduced temperature (Metz et al., IPCC, 2005). Currently, only the liquefied CO₂ method has been used for ship transportation (Aspelund et al., 2006) due to the factor of some 580 times of volume reduction from gas form CO₂ to liquid form CO₂.

There are some technical challenges in storing and transporting CO₂ in liquid form on ships.

In addition to the requirement of low temperature and high pressure, liquefied CO₂ has a triple phase point. The triple phase point is an unstable state of CO₂ which means a phase change of CO₂ may take place from liquid state to solid or gas without a change in temperature or pressure. Storage of CO₂ liquid also has special requirements on the materials of storage tanks in order to cope with high pressure and low temperature. It is essential to make sure that there is no water or moisture contained in liquefied CO₂ to prevent corrosion of tank materials. Compared with the method of CPCS, the volume taken by liquefied CO₂ is 3% more than that of CaCO₃ (Barthelemy et al., EIGA, 2010). In addition, carrying liquefied CO₂ causes a ship stability problem – sloshing, due to its viscosity is about 1/3 of water (Wischniewski; Fresh water and seawater properties, ITTC, 2011). In summary, in comparison with the CO₂ liquid, storing solid CO₂ in the form of CaCO₃ on ships has the following advantages:

- (a) CaCO₃ can be reused or land disposal;
- (b) no particular requirements on storage tank materials;
- (c) no corrosion problems;
- (d) less volume taken; and
- (e) no impact on ship stability.

Other than the above ship operational and CO₂ storage advantages, a case study on a selected ship indicates that applying CPCS on ships will bring an economical profit by selling the by-products of CPCS. The following section presents a feasibility study of applying CPCS on the case ship.

The specifications of the case ship are listed in Table 6, along with the details of voyage of the vessel. Since the power output of auxiliary alternators is only about 8.4% of the main engine power, fuel consumption and CO₂ emissions of the auxiliary engines are not considered in the case ships study.

4.1. Cost estimation of CPCS

4.1.1. Total CO₂ generated during a voyage

According to the project guide of the selected engine and fuel type used, the gas flow rate of CO₂ emissions can be estimated as Eq. (5):

$$\begin{aligned} \dot{m}_{CO_2} &= C_{HSFO} \times P \times SFOC \\ &= 3.021 \times 18,660 \times 174 \times 1000/3600 \\ &= 2.72 \text{ kg/s} \end{aligned} \tag{5}$$

where

\dot{m}_{CO_2} mass of CO₂ in exhaust gas (ton);
SFOC specific fuel oil consumption (g/kWh);

P power output of main engine (kW);
C_{HSFO} carbon factor of HSFO (MEPC (2010)).

With this flow rate of CO₂, the total CO₂ generated during a voyage (16 days) is 3766.54 t.

4.1.2. Exhaust gas by-pass into CPCS system

Based on the IMO target of 20% CO₂ emissions reduction by 2020, the CPCS system will be designed to absorb and store 20% of CO₂ emitted from the engine of the case ship, i.e. 753.31 t of CO₂. According to the experiment results, the average CO₂ absorption rate is 67.85%. To achieve 20% reduction of CO₂ emissions, the amount of exhaust gases by-passed to the CPCS system can be derived with eq. (6):

$$\begin{aligned} R_{by-pass} &= R_{target}/R_1 \\ &= 20\%/67.85\% \\ &= 29.48\%. \end{aligned} \tag{6}$$

where

R_{by-pass} percentage of exhausted gas by-pass into the CPCS system;
R_{target} targeted CO₂ reduction required by IMO regulations;
R₁ absorption rate of CO₂.

According to the above estimation, there is about 30% of exhaust gas should be fed into the CPCS system in order to achieve the target of 20% CO₂ reductions from the main engine exhaust gas. The mass flow rate of CO₂ fed into the CPCS can be derived: 2.72 × 29.48% = 0.80 kg/s. The quantity of CO₂ bypassed per voyage is 1110 t.

4.1.3. Initial quantities of chemical substances required

The quantities of all chemical substances involved in the reaction can be derived by applying Eq. (4) in conjunction with the Eqs (1)–(3). Thus, the quantities of caustic soda (NaOH) and quicklime (CaO) required per voyage are 86 t and 959 t, respectively. The limestone CaCO₃ finally produced per voyage is 1712 t.

4.1.4. Consumption of NaOH by CPCS system

In the CPCS system, NaOH solution will be regenerated after the causticizing reaction. For the case ship, the NaOH is assumed to be replenished on a daily basis. Since its regeneration rate is 85.37% according to the experiment results, the daily consumption of NaOH can be calculated by the following equation:

$$\begin{aligned} m_{refilled} &= m_{system} \times (1-R_2) \\ &= 85.60 \times (1-85.37\%) \\ &= 12.52 \text{ ton/day} \end{aligned} \tag{7}$$

Table 6
Specifications of the case ship.

Route details		Vessel dimensions			Engine and generator specifications		
Origin	Port of Qinhuangdao	Type	Bulk carrier ^a	Main engine	MAN B&W: 6S70MC-C7 ^b		
Destination	Port of San Francisco	LOA	292 m	No. of main engine	1		
Range	5547 Nm	LBP	283.5 m	Engine speed	91	rpm	
Service speed	15.2 Knot	Breadth	45 m	MCR	18,660	kW	
Duration	16 Day	Depth	24.8 m	SFOC	174	g/kWh	
		Draught	16.5 m	Generators	HHI/Himsen: 7H17/28 ^c		
		Gross	94,360 ton	No. of generators	3 (1 stand-by)		
		DWT	157,500 ton	Engine speed	900	rpm	
		Water ballast	78,000 m ³	Output	780	kW	
		Fuel type	HSFO	SFOC	189	g/kWh	

^a Sources of data: Significant of Hyundai Trust (2011).

^b Project Guide of MAN Diesel Engine (2009).

^c HIMSSEN Engine (2012).

Table 7
Quantities of substances consumption and costs.

Chemicals	Quantities (ton)	Unit price (\$/ton)	Cost (\$)
Caustic soda (NaOH) consumed	200	83.33 ^a	16,695
Quicklime (CaO) consumed	959	11.11	10,652
Sum			27,347

^a Sources of data: Prices achieved from Alibaba.com.

where

m_{refilled} daily consumption of NaOH (ton);
 m_{system} the theoretical quantity of NaOH needed by system (ton);
 R_2 regeneration rate of NaOH.

The total NaOH consumed during a voyage can be derived as following:

$$m_{\text{total}} = m_{\text{refilled}} \times t = 12.52 \times 16 = 200.34 \text{ t} \quad (8)$$

where

m_{total} total NaOH required during a voyage (ton);
 t duration of a voyage (days);

4.1.5. Operational cost of CPCS system

Operational cost of the CPCS is made of 3 components, i.e. cost of chemicals consumed; cost of fuel operating the CPCS and cost of cargo lost penalty due to space taken by the chemical reactant and CPCS product.

4.1.5.1. *Cost estimation of chemical substances.* Table 7 presents the quantities of chemicals consumed and their unit prices.

4.1.5.2. *Energy consumption and fuel costs.* The energy consumed for CPCS process includes energy required for CO₂ separation from the engine exhaust gas; energy for CO₂ gas and chemical solutions' transfer through the CPCS system; and energy used for handling and storing solid chemicals and end product of CPCS (CaCO₃) on ships. Since the energy consumed in handling solids materials are much smaller compared with that in CO₂ gas separation and transportation, the energy consumed for solid materials handling is ignored in estimating the system energy consumption.

The power required by gas separation is due to the application of membrane device which is about 0.5 MJ/kg CO₂ separated (Barbieri et al., 2011). Thus, the energy consumption by the membrane system can be obtained as the following:

$$\begin{aligned} P_M &= \dot{p}_M \times m_{\text{CO}_2} / t \\ &= 0.5 \times 10^3 \times 3766.54 \times 10^3 \times 29.48\% / (16 \times 24 \times 3600) \\ &= 401.59 \text{ kW} \end{aligned} \quad (9)$$

Where

P_M power required by membrane device (kW);
 \dot{p}_M energy required for CO₂ separation (kJ/kg CO₂);
 m_{CO_2} mass of CO₂ separated (kg);
 t operation time of membrane device (s).

CO₂ gas pumps (blowers) are used to feed the CO₂ gas after the separation unit to pass through the CPCS. The solution height of the reaction tank designed is about 6.44 m. The blowers should provide enough pressure to feed gas into the bottom of the tank. Other than head loss due to solution height in tank, there are friction loss and

Table 8

Volumes and mass of coal losses due to storage of chemicals. (Bunker Price of Hong Kong, November 2013.)

Chemical substances	Density (kg/m ³)	Volume (m ³)
NaOH	2130	94
CaO	3355	286
CaCO ₃	2711	632
Sum		1112

fitting loss for CO₂ to go through the duct system. Assuming the diameter and the length of the duct from the outlet of membrane device to reaction tank are 1 m and 10 m respectively and there are one baffle and two 90° bends along the system. The pressure drops due to friction and fitting estimated at about 0.99 Pa (Massey and Ward-Smith, 2012). The power required for gas input can be obtained with Eq. (10):

$$\begin{aligned} P_B &= \dot{m}_{\text{CO}_2} \times \Delta P_B / \rho_{\text{CO}_2} \\ &= 0.80 \times (0.99 + 1.815 \times 9.81 \times 6.5) / 1.815 / 1000 \\ &= 0.05 \text{ kW} \end{aligned} \quad (10)$$

Where:

P_B power required by gas blower (kW);
 \dot{m}_{CO_2} mass flow rate of CO₂ (kg/s);
 ΔP_B pump pressure required to transfer fluid or gas (Pascal);
 ρ_{CO_2} density of CO₂ (kg/m³).

Thus, the total power consumption for CO₂ separation and CPCS is 401.64 kW. The fuel oil consumed due to gas blower and membrane is 29.15 t per voyage and the fuel cost is estimated to be \$18,072.66.

4.1.5.3. *Cargo penalty due to CPCS system application.* Table 8 lists the density and volume of the chemicals involved in CPCS. The total volume taken by the chemicals is 1112.49 m³. The density of coal is 929 kg/m³ so the mass of coal cargo in an equivalent volume is 1033.50 t (Bulk Density Chart, Anval Valves Ltd.). According to the current coal shipping price 15 \$/ton (ChinaCCM, 2013), the total cost of cargo freight penalty due to CPCS system application is 15 × 1033.50 = \$ 15,502.48.

4.2. Profits made by selling by the product from CPCS system

There are two parts of profits resulting from applying of the CPCS system

- Profit made from selling the final product of CPCS
- Saving from carbon credits.

The final product from CPCS is CaCO₃ (limestone) which is an industrial raw material widely used in many different industries, such as paper making, construction and plastic industries. The commercial price of limestone is 50 \$/ton. The carbon credit is 15 \$/ton based on the report of '2012 Carbon Dioxide Price Forecast' (Wilson et al., 2012). Thus, the profits made from selling CaCO₃ and saving of CO₂ credits are \$85,603.23 and \$11,299.63.

4.3. Cost comparison between CPCS and liquefaction method

Having conducted the above cost analysis, Table 9 is resulted to present costs and profits of CPCS in a comparison with the conventional liquefied CO₂ storage method.

Table 9
Costs and profits comparison.

Costs per voyage (\$)	Operation costs				Profits			Total costs
	Capture cost	Chemicals cost	Liquefaction cost	Freight reduction	Carbon credits	CaCO ₃	CO ₂	
CPCS	18,073	27,347	–	15,502	– 11,300 ^a	– 85,603	–	– 35,981
Liquefaction	18,073	–	21021 ^b	9932	– 11,300	–	– 18,833 ^c	6758

^a Negative sign means earning profits.

^b Wischnewski; The physics hyper textbook, 1998; c: Melzer, 2012.

It can be seen that if the CaCO₃ were sold at the destination of a voyage, applying CPCS can make \$ 35,981.07 profit while capturing 20% CO₂ emissions from engine exhaust.

The operation cost and profit made from liquefaction method are listed in the table above. There are no chemical substances involved in liquefaction method so there is no cost due to purchase chemical substances. However, energy cost due to CO₂ liquefaction processes is considerable referring to liquefaction cost in the table. The freight reduction is resulted from the storage of liquefied CO₂. The profits are made from saving carbon credits and selling CO₂ for enhanced oil recovery (EOR).

5. Conclusions

The laboratory experiment examined the impacts of four key factors in CPCS. The results show that the CO₂ absorption rate varies with various parameters, such as solution volume, height, cross-section area and CO₂ gas flow rate. The results provide an insight of CPCS effectiveness and offer a useful reference in onboard system design.

The comparative study between CPCS and liquefaction for CCS onboard ships has shown that the liquefaction method has a merit of low running cost. The CPCS method has a higher profit from selling the end product. The profit is sufficient to overweight the running cost and freight penalties. The study proves that, CPCS for marine CO₂ capture and storage offers advantages of fewer requirements for captured CO₂ storage and transportation; safety and stability of ship operation are not affected. It is a cost-effective method bringing profits every single voyage if the product of CaCO₃ were sold. Conclusions can be made that the proposed chemical absorption processes for carbon dioxide solidification is a feasible and cost effective method for ship CO₂ emissions reduction.

Further studies should be conducted to analyses the factors that could improve the CO₂ absorption rate. Factors that can increase NaOH regeneration rate and filtration efficiency of CaCO₃ should also be investigated and analyzed in order to increase the total efficiency of the system. To verify the results from experiment, Computing Fluid Dynamic (CFD) study is underway for system simulation and onboard system design.

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References

- Aspelund, A., Mølnevik, M.J., Koeijer, G.D., 2006. Ship Transport of CO₂—technical solutions and analysis of costs, energy utilization. *Exergy Effic. CO₂ Emiss.*
- Witkowski, A., Majkut, M., 2012. The impact of CO₂ compression systems on the compressor power required for a pulverized coal-fired power plant in post-

combustion carbon dioxide sequestration. *The Archive of Mechanical Engineering IX*, 343–360.

- Boden, T.A., G., Marland, Andres, R.J., 2010. Global, Regional, and National Fossil-Fuel CO₂ Emissions, Carbon Dioxide Information Analysis Centre, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A. http://dx.doi.org/10.3334/CDIAC/00001_V2010.
- Bunker Price of Hong Kong, November 2013. *Marine Engineers Review*, Institute of Marine Engineering, Science and Technology p. 38.
- Bulk Density Chart, Anval Valves Pvt Ltd.
- Souto, E.C.S., Damasceno, J.J.R., Hori, C.E., 2008. Study of operational conditions for the precipitated calcium carbonate production. *Materials Science Forum*, vol. 591–593, pp 526–530.
- Fresh water and seawater properties, 2011. *International Towing Tank Conference (ITTC)*, p. 8.
- Barthelemy, H., Bourdeaud'huy, D., Jolivet, J.-L., Kohl, U., Krinninger, K., Teasdale, D., Webb, A., Williams, S., 2010. IGC Doc 164/10/E: Safe Handling of Liquid Carbon Dioxide Containers that Have Lost Pressure. *European Industrial Gases Association (EIGA) Aisbl*.
- HiMSEN Engine, 2012. IMO Tier II Program, Marine & Offshore GenSets, Marine Propulsion System Stationary GenSets, Hyundai Energy and Machinery Heavy Industries CO. LTD.
- Houghton, J.T., 2004. *Global Warming: The Complete Briefing. Chapter 3, Greenhouse Gases*. Cambridge University Press, New York, USA.
- IPCC, 2005. In: Metz, B., Davidson, O., de Coninck, H.C., Loos, M., Meyer, L.A. (Eds.), *IPCC Special Report on Carbon Dioxide Capture and Storage*. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, p. 442.
- Barbieri, G., Brunetti, A., Scura, F., Drioli, E., 2011. CO₂ Separation by Membrane Technologies: Applications and Potentialities.
- Ciferoni, J., Litynski, J., Plasynski, S., Murphy, J., Vaux, G., Munson, R., Marano, J., 2010. Carbon dioxide capture and storage RD&D roadmap. Department of Energy and National Energy Technology Laboratory.
- Melzer, L.S., 2012. Carbon dioxide enhanced oil recovery (CO₂ EOR): factors involved in adding carbon capture, utilization and storage (CCUS) to enhanced oil recovery.
- Mahmoudkhani, M., Keith, D.W., 2009. *Low-Energy Sodium Hydroxide Recovery for CO₂ Capture from Atmospheric Air—Thermodynamic analysis*. Energy and Environmental System Group. Institute for Sustainable Energy, Environment, Economy, University of Calgary, Canada.
- Massey, B.S., Ward-Smith, A.J., 2012. *Mechanics of Fluids*. Spon Press, London; New York, NY.
- MEPC 60/WP.6, 2010. Prevention of Air Pollution from Ships, Communication with IPCC on CO₂ Conversion Factors, Marine Environment Protection Committee, IMO.
- Pflug, I.J., Angelini, P., Dewey, D.H., 1957. Fundamentals of Carbon Dioxide Absorption as they Apply to Controlled-Atmosphere Storage. Department of Agricultural Engineering and Horticulture.
- Project Guide of MAN Diesel Engine: MAN B&W: S70MC-C7, 2009. 4th Edition. Branch of MAN Diesel SE, Germany.
- Wilson, R., Luckow, P., Biewald, B., Ackerman, F., Hausman, E., 2012. *2012 Carbon Dioxide Price Forecast*, Synapse. Energy Economics Inc.
- Rogner, H.-H., Zhou, D., Bradley, R., Crabbé, P., Edenhofer, O., Hare, B., (Australia) Kuijpers, L., Yamaguchi, M., 2007. In: Metz, B., Davidson, O.R., Bosch, P.R., Dave, R., Meyer, L.A. (Eds.), *Introduction in Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Buhaug, Ø., Corbett, J.J., Endresen, Ø., Eyring, V., Faber, J., Hanayama, S., Lee, D.S., Lee, D., Lindstad, H., Markowska, A.Z., Mjelde, A., Nelissen, D., Nilsen, J., Pålsson, C., Winebrake, J.J., Wu, W., Yoshida, K., April 2009. Second IMO GHG Study International Maritime Organization (IMO) London, UK.
- Significant Ships of Hyundai Trust, 2011. 180,000 dwt Cape Sized Bulk Carrier From Sungdong, p. 48–49.

Web reference

- Alibaba.com: (http://www.alibaba.com/product-gs/445114514/Caustic_Soda.html); (http://www.alibaba.com/product-tp/113123860/QUICK_LIME.html); (http://www.alibaba.com/product-gs/594411302/light_calcium_CaCO3.html?sp=0) (12.12.13).

B., Wischnewski. Peace Software, (http://www.peacesoftware.de/einigewerte/co2_e.html) (12.11.13).
The Physics Hypertextbook (<http://physics.info/heat-latent/>) (12.12.13).
International ocean freight rate statistics, China Commodity Marketplace (CCM), 2013. (http://www.chinaccm.com/40/20131206/402204_1576181.shtml) (22.11.13).
Slaking and Causticising, Metso Fiber Karlstad AB, 2011, <http://www.metso.com/pulpandpaper/MPwFiber.nsf/WebWID/WTB-101115-2256F-DE839?>

OpenDocument&mid=71967A486FAB2F29C22575B00048DEBB#.
Ud0_7aXs5CA. (18.7.13).
Understanding CCS, What is CCS how does it work and why is it important, Global Carbon Capture and Storage Institute (<http://www.globalccsinstitute.com/understanding-ccs/the-climate-change-challenge>) (5.12.2012).