Compliance & Regulation | Calcium Hydroxide Technology | Latest R&D news

Road to 2050

The Carbon Capture Technical Journal

Unveiling the decarbonization solutions for the shipping industry to approach the challenges of 2030 and 2050.

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ECOSPRAY
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MEPC 78 Discussions On Onboard Carbon Capture – Follow Up

Proposal by Liberia for discussion at MEPC 79 Meetings

Background

During the MEPC 78 meetings, a discussion looked at the implementing criteria for considering the onboard CO_2 capture within the measures for reducing the carbon intensity of international shipping as introduced by Resolution MEPC.328(76) adopted by MEPC 76.

Proposal for including carbon capture technologies in the IMO regulatory framework to reduce GHG emissions from ships.

In September 2022, Liberia and the International Chamber of Shipping sponsored a submission to IMO to take the discussion further and for the recognition of Onboard CO_2 Capture technologies within the strategies available for the shipping industry.

The assessment originates from the challenge imposed on the shipping industry by the IMO 2050 targets.

It has been evaluated that before new sustainable fuels and energy sources, as well as new technologies, are consolidated and available worldwide, and before infrastructures are adapted, there will be a transition period which will see the testing, adoption and operation of a wide variety of technologies.

The two sponsors have therefore concluded that the Rules should consider every technology that can ease the transition period and help achieve the 2050 target. Both carbon capture and storage (CCS) and carbon capture use and storage (CCUS) have an enormous potential to meet the decarbonisation targets in the marine industry.

It has been recognised that the effect of the onboard CCS or CCUS on a ship's CO_2 emissions corresponds to the CO_2 produced by fuel consumption as documented by the bunker delivery notes, minus the quantities of CO_2 captured and delivered ashore.

These quantities are all measurable and recordable.

Based on the above, the two sponsors agree that the reduction in CO_2 emissions through CCS or CCUS technologies is to be accounted for in the EEDI and EEXI indexes calculation and in the CII calculation.

It would be implemented in the current formulae by subtracting the captured CO_2 quantity.

The above assessment led the two sponsors to the following proposals:

- Amendment of the EEDI formula in the 2018 Guidelines on the method of calculating the Attained Energy Efficiency Design Index (EEDI) for new ships
- Amendment of CII formula in 2022 Guidelines on operational Carbon Intensity Indicators and the calculation methods (CII Guidelines, G1)
- Introduction of a document for the recording the CO_2 captured and delivered ashore as a CO_2 Receipt Note.
- Establishment of a working group whose task is to:
  - Identify the technologies best suited for onboard use
  - Define and complete amendments of the EEDI/EEXI formula (figure 1) and mass of CO_2 in CII formula (figure 2)
  - Identify the right methods for CO_2 disposal
  - Define means for verifying and recording the quantities of CO_2 disposed
  - Prepare a comprehensive report for MEPC 80.

EEDI Formula is amended as follows

$$\frac{\left[\begin{array}{l} (\prod_{j=1}^{n} f_j) * (\sum_{i=1}^{nME} P_{ME(i)} * C_{FME(i)} * SFC_{ME(i)}) + (P_{AE} * C_{FAE} * SFC_{AE}) + \\ ((\prod_{j=1}^{n} f_j * \sum_{i=1}^{nPTI} P_{PTI(i)} - \sum_{i=1}^{neff} f_{eff(i)} * P_{AEeff(i)}) * C_{FAE} * SFC_{AE}) - \\ (\sum_{i=1}^{neff} f_{eff(i)} * P_{eff(i)} * C_{FME} * SFC_{ME}) - (\sum_{i=1}^{nCCS} f_{capture(i)} * Q_{CCS(i)}) \end{array}\right]}{f_c * f_i * f_l * \text{Capacity} * f_w * f_m * V_{ref}}$$

Figure 1

where:

- Q_{CCS} is the quantity of CO_2 in ton captured and stored on board per hour of operation at the shaft power of the engine as defined in 2.2.5.

$$f_{capture} = \left(\frac{CO_{2capacity}}{\sum_{i=1}^{n} C_{F(i)} * Fuel_{onboard\,(i)}} \right)$$

where:

- $CO_{2capacity}$ is the total quantity of CO_2 in ton able to be stored on board;

and

- $Fuel_{onboard}$ is the 50% of the total quantity of fuel(s) in ton which can be carried in the ship's storage tanks.

However, the Administration can consider higher $f_{capture}$ up to $f_{capture}=1$, taking into account the intended voyages and the possibility to discharge ashore the captured CO_2 more frequently than the intervals corresponding to the ship's range.

Mass of CO_2 emissions (M) in CII formula is replaced as follows

The total mass of CO_2 is the sum of CO_2 emissions (in grams) from all the fuel oil consumed on board a ship in a given calendar year, as follows:

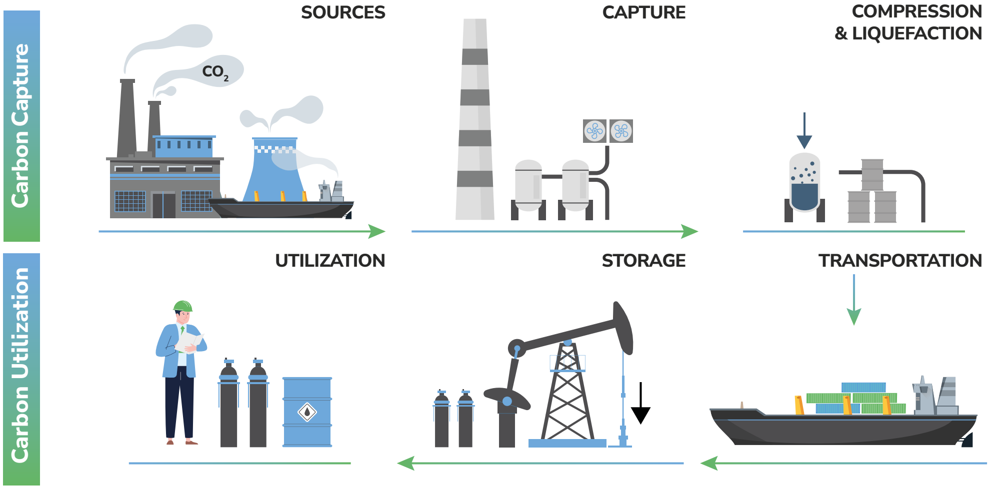
$$M = FC_j x C_{Fj} - M_{CO2captured}$$

Figure 2

where:

- j is the fuel oil type;
- FC_j is the total mass (in grams) of consumed fuel oil of type in the calendar year, as reported under IMO DCS;
- C_{Fj} represents the fuel oil mass to CO_2 mass conversion factor for fuel oil type j, in line with those specified in the 2018 Guidelines on the method of calculation of the attained Energy Efficiency Design Index (EEDI) for new ships (resolution MEPC.308(73)), as may be further amended. In case the type of the fuel oil is not covered by the guidelines, the conversion factor should be obtained from the fuel oil supplier supported by documentary evidence; and
- $M_{CO2captured}$ is the total mass of CO_2 delivered ashore whose quantity is certified by the CO_2 Receipt Note.

CARBON CAPTURE, UTILIZATION & STORAGE (CCUS)



Source: Bureau Veritas

According to BV, the interest of the marine industry in CCUS is growing up due to the benefits this technology offers in terms of: availability, sustainability, efficiency.

Calcium Hydroxide-based carbon capture

Ocean Liming

Carbon ocean chemistry

Ocean liming is a technology that aims to remove carbon dioxide from the atmosphere, storing it as bicarbonate ions in the ocean. The technique was proposed for the first time in the 1990s (Kheshgi, 1995) as a potential geoengineering option to decrease the atmospheric concentration of CO_2.

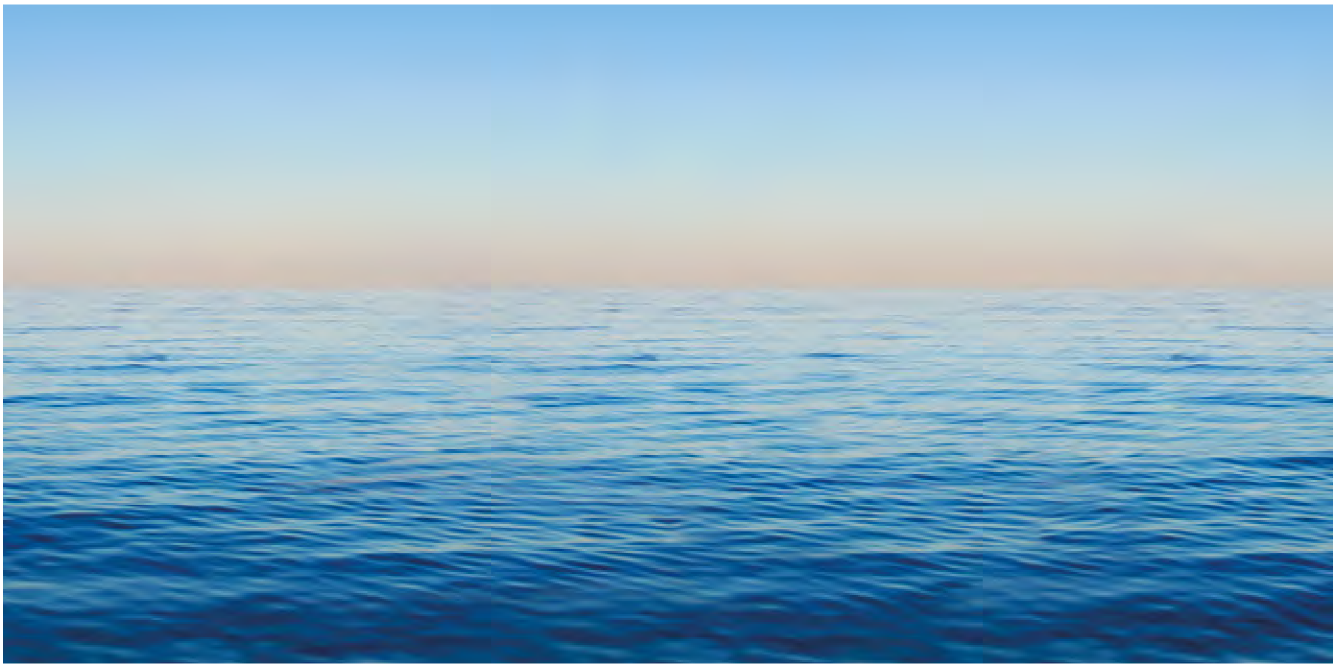
From the geological perspective, the mechanisms involved in the carbon cycle are the 'deep carbon cycle' (Myr) and the 'carbon compensation cycle' (kyr). On a shorter timescale, the fundamental natural mechanisms controlling CO_2 concentration in the oceans are the 'solubility pump' and the 'biological pump'. The first is roughly related to ocean water circulation, and the second to the planktonic life cycle and biogenic calcareous material production (PIC=particulate inorganic carbon). The average carbon dioxide concentration on the seawater surface is 15%, and its residence time is ~200 kyr. The ocean can trap an average of 50 times the carbon dioxide concentration in the atmosphere and 19 times in the biosphere. CO_2 diffuses into the upper layer of the oceans by the difference in partial pressure. Ocean water acts as a buffer for pH oscillations: CO_2 from the atmosphere readily converts into carbonate and bicarbonate ions in ocean water, reducing the partial pressure of CO_2 dissolved so CO_2 can dissolve further. The exchange of CO_2 between the atmosphere and the surface mixed layer (roughly the top 100 m) of the ocean is rapid (1 year) compared with the exchange between the mixed layer and deeper layers of the ocean (100 years) (Kheshgi, 1995).

To summarise, the ocean is the largest inorganic carbon reservoir, participating in the global ocean-atmosphere-crustal system in exchange with atmospheric CO_2.

As a result, it exerts a significant control on atmospheric CO_2 levels.

Precipitated (biogenic) Inorganic Carbon (PIC)

Most carbonate in sediments has a biogenic origin (pelagic and benthic organisms). The primary calcifying organisms are planktonic and produce both calcite and aragonite. The contribution of organisms to the total calcium and carbonate content in oceans is calculated as four times that of rivers. After death, biogenic calcium carbonate sinks, undergoing both dissolution and burying. It has been estimated that around 25% of biogenic carbonate is buried in sediments, contributing to the 'inorganic carbon pump' that removes carbon dioxide from the atmosphere and ocean, relegating it to the crustal reservoir.



Basics about the chemistry of the ocean liming process

'Traditional' Ocean Liming

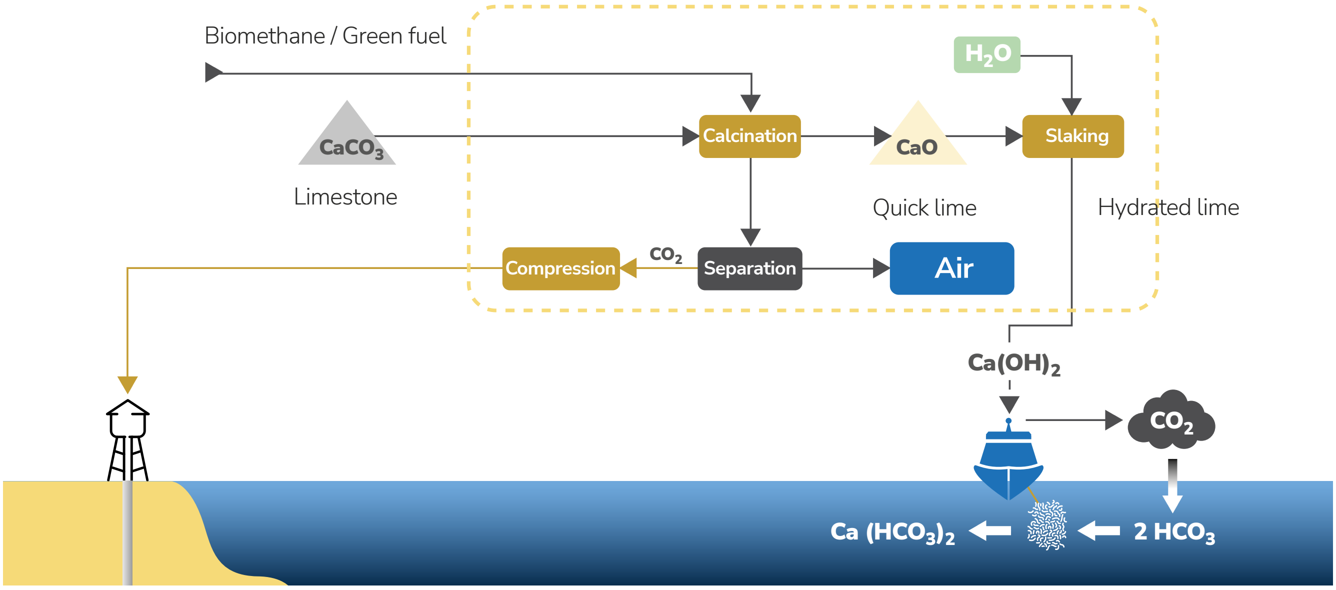
'Traditional' methods for ocean liming involve applying sodium carbonate to seawater to enhance the carbon capture ability of oceans by increasing the pH of seawater, counteracting the acidification induced by increased atmospheric CO_2 concentration.
Because of the solubility of sodium carbonate in seawater, this reaction will ensure the availability of carbonate ions and the local increase in the pH value boosting the carbon dioxide solubility, drawn from the atmosphere, and converted into carbonate ions. Carbonate ions will react with cations already available in seawater and precipitate as inorganic carbonate phases. The alternative reaction proposed involved using $CaCO_3$ (calcium carbonate) instead of Na_2CO_3. Due to the low solubility of calcium carbonate, this reaction will not ensure the same kinetics and pH increase as the previous one. A third alternative proposed was the direct application of CaO in seawater. CaO is immediately hydrated into $Ca(OH)_2$, with low solubility but higher compared to calcium carbonate. This will lead to immediate carbon capture by the alkalinised seawater, calcium carbonate precipitation and sedimentation.

Ocean Liming Using Nanosized Calcium Carbonate

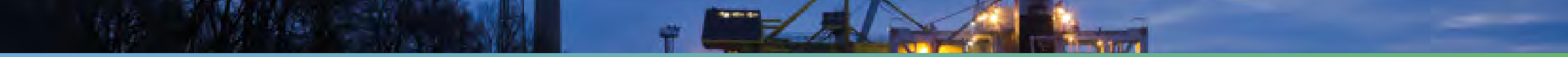
We need to consider that, even if the volumes involved in ocean liming are small compared to the entire ocean, locally, the natural buffering ability of oceans will be altered by adding strong bases. Although, no records are available to evaluate the effects of a massive and long-term application of ocean liming.
However, the principle of ocean liming can be applied directly to carbon dioxide produced during the fuel's combustion, moving the attention from the whole ocean-atmosphere-crustal system to the anthropic input at its source, preventing carbon dioxide emissions instead of remediating at them. Carbon dioxide can be mineralised onboard ships using $Ca(OH)_2$ (calcium hydroxide) to precipitate calcium carbonate, exploiting the same basic principles of ocean liming, which will occur ex-situ. Alkalinisation will take place in onboard reactors and will not change the ocean buffer's performance. Carbon dioxide from exhaust gas bubbling into a suspension of $Ca(OH)_2$ produces calcium carbonate following the reaction as per figure 3. The reaction is the same as in ocean liming using CaO but occurs in a reactor with flowing combustion fumes. The product (calcium carbonate) is precipitated in nano-size calcite crystals. It can be disposed of in seawater as one of the phases naturally occurring in oceans. This approach will potentially lead to negative CO_2 emissions by ships' engines without adding new components to the seawater system.

$$Ca(OH)_2 + CO_2 \leftrightarrow Ca^{2+} + OH^- + HCO_3^- \leftrightarrow Ca^{2+} + OH^- + H^+ + CO_3^{2-} \leftrightarrow CaCO_3 + H_2O$$

Figure 3



Source: Ecospray

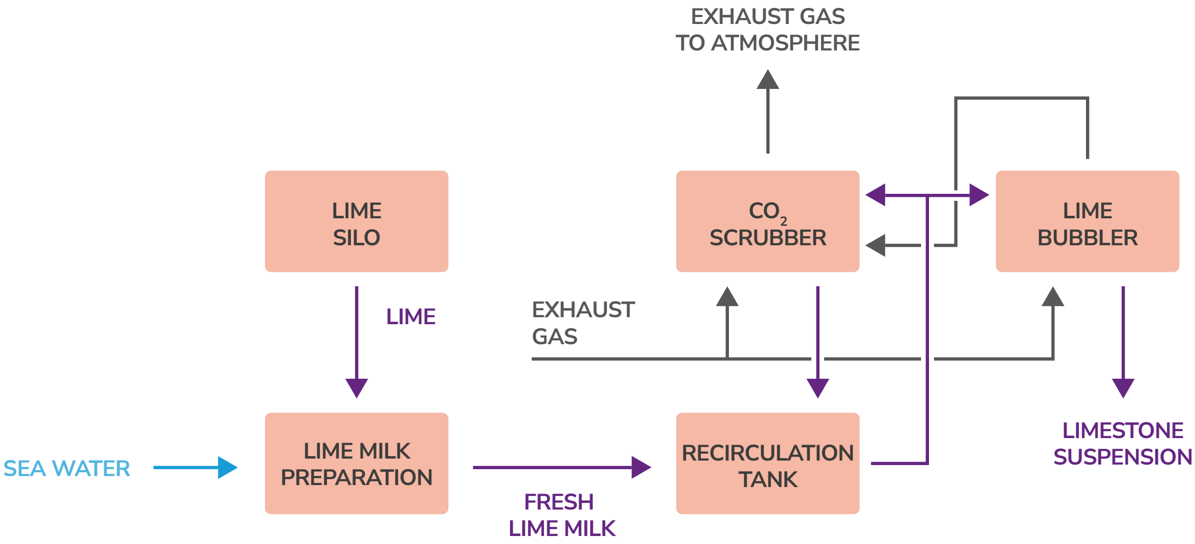


Eco-compatibility and stability of mineralisation products in seawaters

Calcium carbonate precipitate by ocean liming modified for the onboard reactor application as described above, will be chemically ($CaCO_3$) and structurally (mineral calcite or aragonite) comparable to planktonic (foraminifera, coccolithophorid and pteropods) mineralised products. For this reason, it can be compared to naturally occurring carbonates. The major difference will be the size of particles. They are larger in the ocean liming -obtained carbonates. Since the sinking rate is related to many factors and among them the size and shape of particles, larger particles will sink at a higher rate concerning proper Precipitated (biogenic) Inorganic Carbon, increasing the particles chance of surviving as mineralised carbon dioxide and being buried. If not buried, they will dissolve, entering the carbon compensation cycle as PIC.

Technology Explained

Scrubbing the exhaust gas with calcium hydroxide suspension with a solid content ranging from 10% to 30% (lime milk) is a viable alternative to other carbon capture technologies (i.e. with amines) to capture carbon dioxide onboard ships. Calcium hydroxide reacts with CO_2 forming calcium carbonate that can be discharged overboard in a stable form of mineralised CO_2.



Source: Ecospray

Design

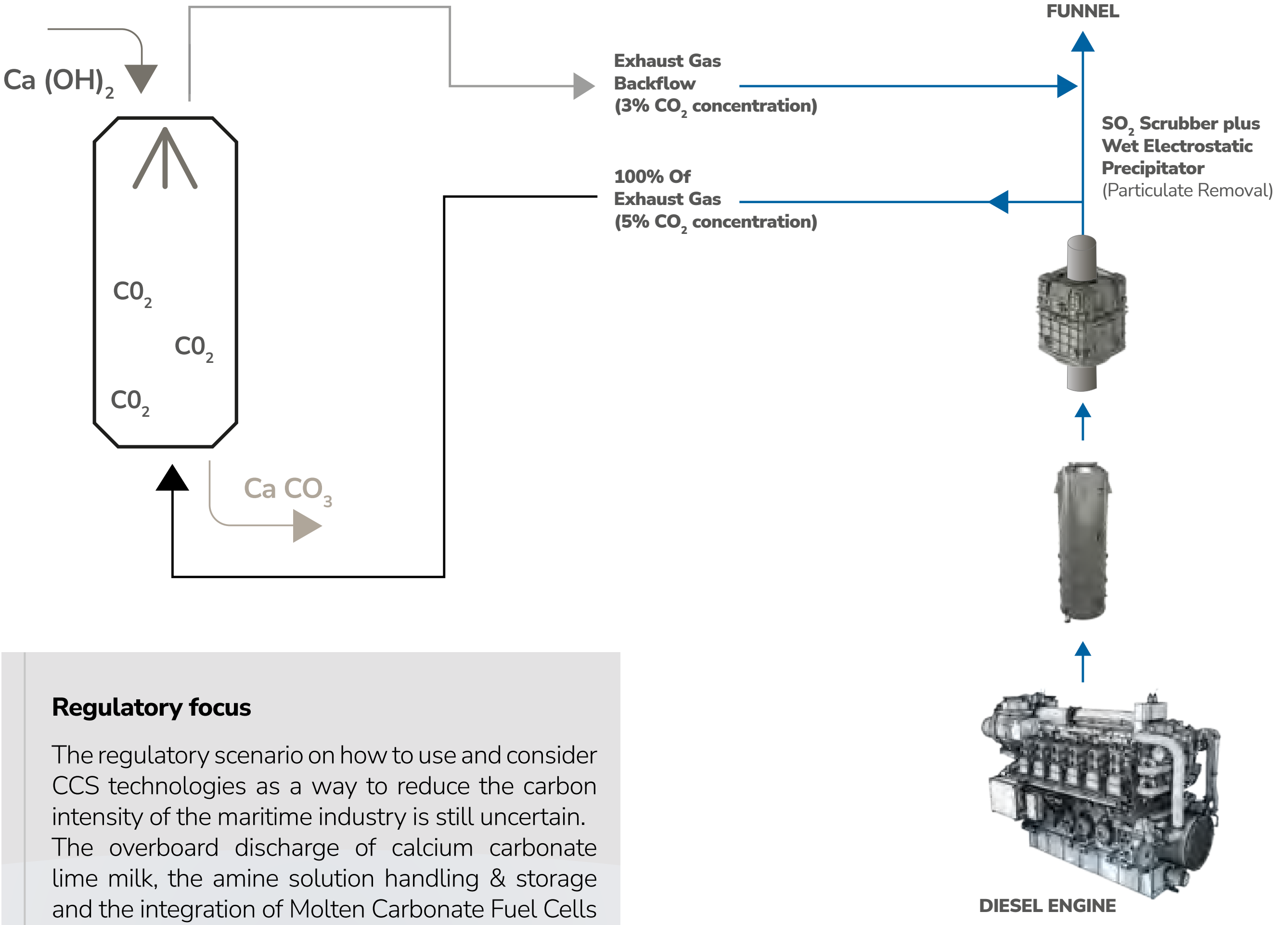
Compared to the amines-based technology, the two technologies have significant differences:

- **Footprint**
  Carbon capture with amine system implies installing three reactors (absorption tower, stripping tower, condensing tower) and two tanks. The lime milk solution is smaller, having only one tower (absorption tower) and a tank, because of the peculiarity of this solution to bind CO_2 permanently in calcium carbonate and bicarbonate, very stable compounds that can be discharged into the sea. However, the calcium hydroxide-based technology implies the storage of a large quantity of lime for the CO_2 absorption reaction while, looking at the amine-based process, it involves the necessity for a CO_2 liquefaction system and the relevant onboard storage (cryogenic pressurised tanks), dimensioned according to the specific needs.

- **Power consumption**
  Lime milk plant doesn't need to regenerate the reagent, hence has lower energy consumption than the amine plant.

- **Toxicity**
  Lime milk is not toxic to humans; amines can be dangerous but only if inhaled or ingested.

- **Reagent storage**
  Lime cannot be regenerated, so a fresh solution is always required. Hence for the lime storage (for the lime milk production), storage space is needed. In the amines-based solution, the reagent is regenerated; therefore, minimal storage (only for make-up means) is foreseen.



Typical onboard configuration

Source: Ecospray

Regulatory focus

The regulatory scenario on how to use and consider CCS technologies as a way to reduce the carbon intensity of the maritime industry is still uncertain. The overboard discharge of calcium carbonate lime milk, the amine solution handling & storage and the integration of Molten Carbonate Fuel Cells in the ship's environment are only some of the topics under discussion with administrations and authorities, to let no stones unturned.

On Board Application

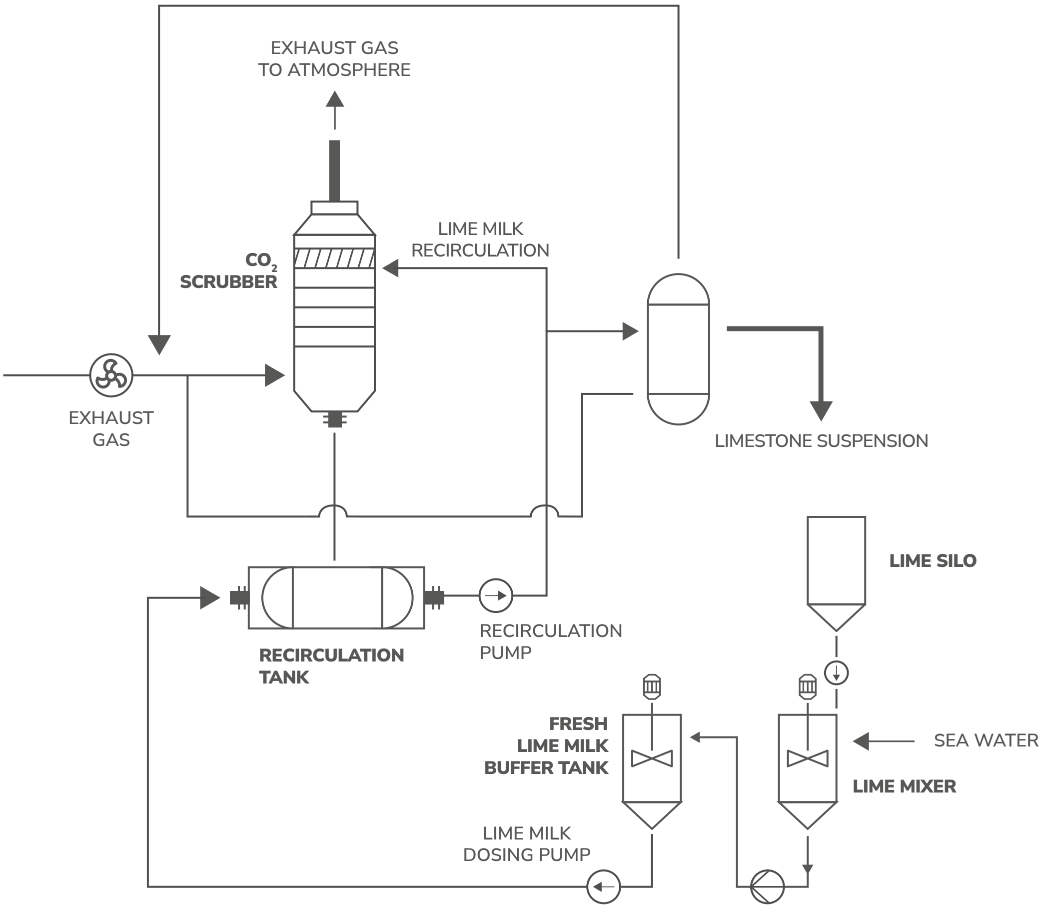
Exhaust gas from the DeSOx scrubber is fed to the lime scrubber by the exhaust gas fan during system operation. The gas is withdrawn downstream of the DeSOx scrubber. Hence its SOx content is usually below 20 mg/Nm^3, and the temperature is in the range 25÷50°C.

The lime scrubber is a plate tower whose design enhances contact between the flue gas and the reagent (lime milk) thanks to transversely mounted perforated trays.
Exhaust gas enters the scrubber below the lowest tray and flows counter-current to the lime milk suspension.

Calcium hydroxide (lime), used to produce the lime milk (suspension of calcium hydroxide particles in water), is stored on board as powder. Lime is mixed with seawater on board in the lime mixer and is continuously kept under agitation by a mixer in the fresh lime milk buffer tank to avoid sedimentation of the solids.

The lime suspension from the recirculation tank is sprayed onto the top tray.
Exhaust gas leaves the scrubber from the top after passing through a demister.

After a few absorption cycles, a side stream of the calcium hydroxide solution/lime milk is withdrawn from the recirculation line. It goes to a dedicate tank (lime milk tank/ bubbler) where a small flow of exhaust gas is injected and bubbled in the tank by a sparger. Here, a second absorption stage occurs, increasing the contact time between the lime milk and exhaust gas to complete the conversion of lime into limestone. Spent lime milk leaves the tank/bubbler and is discharged overboard. The exhaust gas leaves the bubbler/lime milk tank from the top and is recycled back to the scrubber.



Source: Ecospray

Road to 2050: where are we?

Q1-2021
MCFC: process definition for marine applications

Q2-2021
MCFC: feasibility study for different types of ships

Q3-2021
AMINE: feasibility study for amine technology and lime milk technology

Q4-2021
MCFC: electrode chemical mix, production methodologies and quality control

Q1-2022
MCFC: stack geometry, thermofluid dynamics and selection of materials

Q2-2022
AMINE: class approval for onboard installation and tests - LAB 1 Alzano

Q2-2022
MCFC: new lab for fuel cell development and testing (Genoa, Italy)

Q3-2022
AMINE: pre-assembled skid for ashore and onboard testing, ready at Ecospray facility

Q4-2022
AMINE + LIME MILK: testing completed at Ecospray facility

Q4-2022
MCFC: CO_2 liquefaction system and treatment for onboard storage

Q4-2022
MCFC: marine engine exhaust gas pollution check for fuel cell compatibility (ULEV) – LAB 1 Alzano

Q1-2023
AMINE + LIME MILK: testing completed at Ecospray facility

Q1-2023
MCFC: Ultra-compact catalytic steam reforming reactor and ultra-compact heat exchangers for high temperature applications

Q1-2023
AMINE + LIME MILK: completion of onboard testing

Q2-2023
MCFC: pilot system installed in LAB 1 (power: 20 kW) – lab & testing

Q2-2023
AMINE + LIME MILK: industrialization

Q1-2024
MCFC: industrial pilot system installed on board (power 400 kW) – lab & testing

Amine & Lime Milk Pilot Results

Test Purpose

As explained in Technical Journal No. 2, the amine liquid solution is used as a reagent in the CO_2 scrubber to absorb carbon dioxide from the exhaust gas reversibly. CO_2-rich amine solution is subsequently regenerated using the combined action of vacuum and heat at a dedicated point in the plant and then re-used in the primary scrubber. The pilot plant underwent several tests to demonstrate the efficiency of the CO_2 absorption/desorption process. The pilot plant's target was to remove 40% of the CO_2 content from the exhaust gas.

Test Procedure

The test campaign, completed in January 2023, aimed to assess the operation of the pilot plant in different operating conditions to identify the most efficient ones in terms of CO_2 capture and amine solution regeneration capabilities.

The goal was to reach and record the higher CO_2 capture rate within the limits of process conditions and maximise the regeneration rate of the amine blend. Data collected during the first phase of tests (tests in Ecospray) allowed us to define the maximum CO_2 capture rate and the optimal operating condition.

A second phase of trials (onboard testing) is planned. The aim is to operate the system in a steady condition for more extended periods to re-confirm the results obtained during the testing campaign in ES and to retrieve important information about the amine degradation on the mid-long-term operation.

The onboard tests will also allow the fine-tuning of the control system and enable further investigation on amine and water mass balance and of the system's energy consumption. The best sets of values will be replicated onboard to confirm the results obtained in Ecospray (see below) and new operating conditions will be tested (different pressure, gas flow, regeneration amine flow, temperature...). At the end of the trials, we will define the best operating working conditions for the full-scale plant design.

Amine and lime milk pilot plant

Lime milk preparation

Findings Of The Pilot Plant Operation

The system's carbon capture performance was better than expected.

The best CO_2 absorption results (69%) intended as the higher CO_2 concentration reduction in the exhaust gas, has been achieved with half of the total possible exhaust gas flow rate and 60% of the amine flow rate to the regenerating section of the system – see figure 4.

However, the most efficient system set-up, which resulted in the best overall CO_2 capture (40%) - intended as the higher stripped CO_2 mass flow rate - and the highest amine regeneration efficiency, has been achieved with the maximum exhaust gas flowrate and the maximum amine flowrate at the regeneration stage - see figure 5.

Figure 4

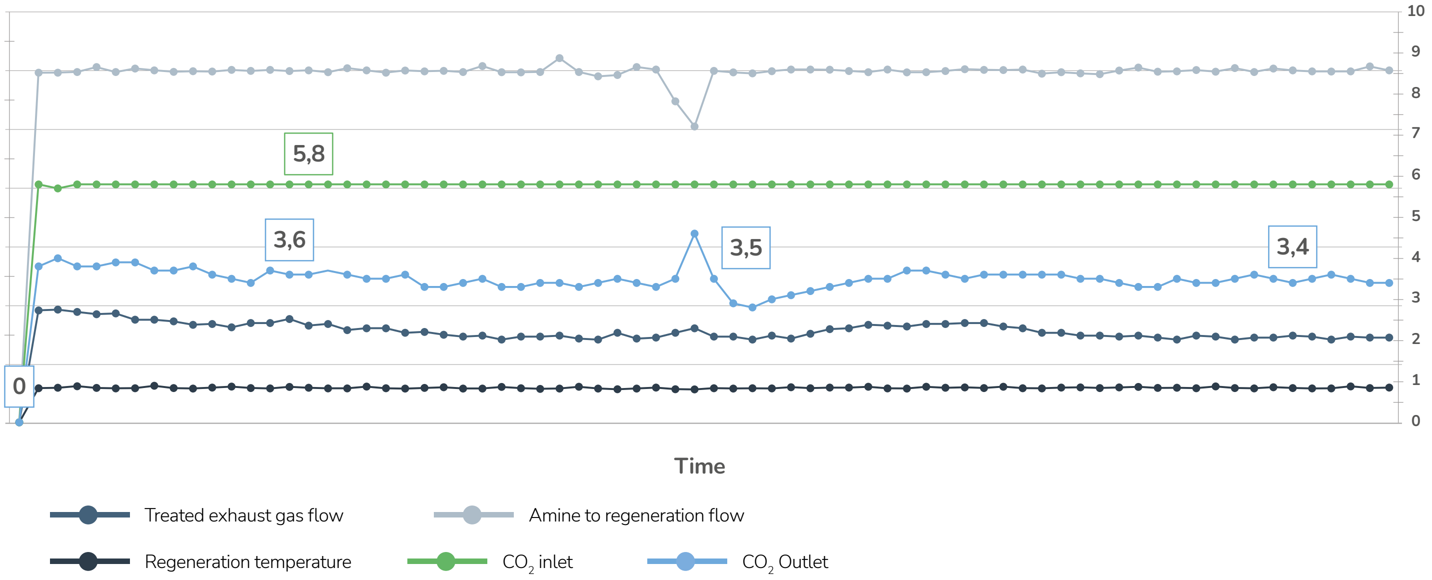
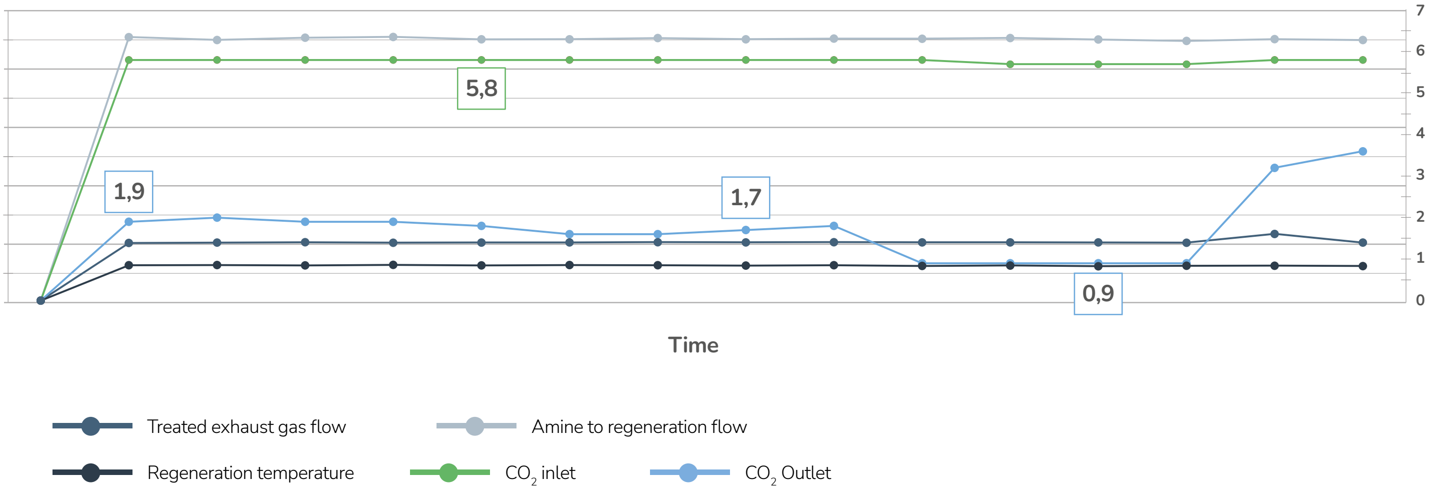


Figure 5



In the next issue:

"Results on calcium hydroxide technology
and updates on the onboard tests"

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