RECAST - A system to decarbonise long-distance shipping

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Synopsis

RECAST could deliver decarbonisation of shipping with conventional engines, using lime as a sorbent and as part of the fuel for the ship. The system involves (i) on-land processing of limestone (CaCO₃) to low-emissions lime (CaO) in a Calix LEILAC calciner, which can capture the process and heating CO₂ emissions for minimal energy or operating penalty (www.project-leilac.eu), and will be fuel agnostic, (ii) Sequestering the captured CO₂ (CCS/CCU), (iii) Using the low-emissions lime to capture the CO₂ from ship stacks (bunker fuel, marine diesel or LNG) using Calix’s Direct Capture Technology. NOx and SOx reductions are also being targeted with additives, (iv) Using the heat released by CaO recarbonation and fuel slip oxidation in the scrubber and engine waste heat to generate further motive power. Initial estimates suggest over a 1/4 increase in range per tonne of bunker fuel / LNG. Initial estimates indicate the cost of CO₂ avoided could be as low as US$70/t, depending mainly on lime costs. The innovation is to bring these technologies together in RECAST at a commercial scale on a ship, in combination with zero emissions lime production on land. This paper describes the system, and the development steps by which it will be fully demonstrated.

Keywords: Decarbonisation of shipping, Lime as sorbent, Lime as additional energy, Exothermal reaction heat recovery, Net zero CO₂, Pollutant reduction, Reduce ocean acidity, Calcium looping, Carbon Capture & Storage

1. Introduction, CO₂ reduction by calcium looping

RECAST is an innovative system which could provide a solution to the International Maritime Organisation (IMO) declaration that the shipping industry shall reduce its CO₂ emissions footprint of 900 million tonnes p.a. of CO₂ in 2012 by 50% by 2050. This declaration is already putting pressure on the industry that is struggling to reduce SOx emissions by 2020, and the need to maintain low NOx emissions. RECAST could reduce shipping emissions in steps eventually to zero by a combination of activities on land and on-board ship. The avoidance cost is estimated to be €40 - 70/t of CO₂. The novelty of RECAST, compared to other solutions, is that it is retrofittable and the industry does not have to adapt immediately to new, expensive, fuels.

2. The System – calcium looping between land and ship

2.1 On board ship lime carbonator

The essence of the system is that low-emissions lime is used on board ship to capture the CO₂ in, for example, a circulating fluidised bed (CFB) carbonator. The on-board Lime Carbonator/Scrubber performs two functions: -

1. It scrubs several emissions: CO₂, SOx, VOCs (volatile organic compounds) and Carbon in a single reactor. This is critical given the limitations of space on a ship. The CO₂ capture for this step could be set initially at 50% per nautical mile to meet the IMO targets and this could be increased later.
2. It generates energy because lime CaO is a well-established Thermo-Chemical Energy Storage (TCES) material, and energy is liberated during carbonation. This energy is extracted in the Lime Carbonator/scrubber and can be used to generate motive power on the ship with a Waste Heat Recovery, WHR, system. Simply put, lime is an extra source of high-quality energy, so that the ship has two energy sources, low cost bunker fuel and lime, which reduces the use of fossil fuels. The CO$_2$ reduction from WHR alone could be ~15% and with only 39% capture from the exhaust the system would deliver CO$_2$ reduction of 50% per nautical mile (nm). The increase in WHR capacity, and hence efficiency, makes this equipment much more justifiable.

The key components of the RECAST system on board are (i) sorbent storage sufficient for the level of capture required which will also store used sorbent for return to port (ii) the exhaust gas lime carbonators/scrubbers and (iii) the waste heat recovery system. These are indicated in Figure 2 to give an illustration of the relative sizes of the equipment. Preliminary estimates suggest that the storage of lime, the scrubbers and the waste heat system will displace some 5-9% of cargo space. This is a burden on the ship economics.

![Figure 2: The system configuration on a ship showing relative equipment sizes](image)

The waste heat recovery (WHR) system will have (i) a feed water heat exchanger connected to the engine block cooling jacket at around 80 °C (ii) a feed heat exchanger connected to the scavenge air intake as around 200 °C and (iii) a steam superheater in the exhaust gas carbonator (the scrubber) at about 600 °C. The additional motive power would depend on the level of CO$_2$ capture required. The degree of carbon capture is controlled by the feed of fresh sorbent into the scrubber circuit, the concentration of CO$_2$, and the temperature of the reaction which is controlled by the waste heat recovery system. Preliminary analysis results are shown in Table 1.

<table>
<thead>
<tr>
<th>% capture of exhaust CO$_2$</th>
<th>Bunkers for equivalent nm to 1 tonne without WHR</th>
<th>Lime per tonne of bunkers for same nm at 75% lime conversion</th>
<th>Emissions per nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>87%</td>
<td>0</td>
<td>87%</td>
</tr>
<tr>
<td>39%</td>
<td>82%</td>
<td>2.1 tonnes</td>
<td>50%</td>
</tr>
<tr>
<td>70%</td>
<td>78%</td>
<td>3.7 tonnes</td>
<td>23%</td>
</tr>
</tbody>
</table>

In the examples in Table 1 the WHR system alone saves 13% of bunkers, broadly in line with the Mirko Grljusic analysis. The capture rate in the scrubber is controlled by the lime feed rate to the CFB and the reaction temperature in the bed which is controlled by the rate of waste heat extraction. When 39% of the CO$_2$ is captured on lime reacted at 2.6 tonnes per tonne of bunkers the CO$_2$ emissions reduce to 50% per nautical mile. This delivers the IMO target for 2050. In due course as the target emissions changes increasing capture up to 70% by feeding lime at 3.7 tonnes per tonne of bunkers will reduce emissions down to only 23% per nm. The final 23% will be addressed in Section 4 below.

Lime is a well-established CO$_2$ sorbent which is proven in numerous Calcium Looping projects. It has been demonstrated at pilot scale on land for CO$_2$ reduction from power plants and other point sources, such as lime and cement. RECAST adapts the elements of Calcium Looping to the marine situation. Lime is proven at industrial scale also to capture SOx, and the process is carried out at a sufficiently high temperature that unburnt fuel and VOCs from the engine are completely burnt, and the exhaust is scrubbed to remove all the particulates, including any black carbon. With the addition of a small amount of ferrous oxide, Fe$_3$O$_4$, the scrubber will reduce the NOx in the exhaust. This is an old established industrial process. Thus, the Lime Carbonator will deal with a wide range of ship emissions in the one process. It will replace the SOx scrubbers.
Initial estimates indicate the cost of CO₂ avoided could be as low as €40/t, depending mainly on lime costs. This is very much lower than the $150-300/tonne CO₂ figures quoted in the Mission Possible report from the Energy Transitions Commission⁷. Figure 3 shows the calculated relationship. It would require very considerably less renewable energy than the solutions proposed in the Transport and Environment Report on Decarbonising EU Shipping⁸.

2.2 RECAST Lime production and recycling on land
The manufacturing of low emissions lime on land is a process being developed for the lime industry using the Calix LEILAC Technology⁹. The EU pilot projects LEILAC shown in Figure 2, and its scale up in the LEILAC2 project now underway will deliver lime for all applications. In a RECAST application this reactor will produce low emissions lime and the CO₂ produced will be sequestered in the deep subsurface. The LEILAC2 project will also demonstrate low emissions heating technologies, including electricity, so that the lime is genuinely emissions free. The limestone feedstock will be (i) used sorbent returned from ships together with (ii) a proportion of new limestone, quarried and ground to a fine powder.

The introduction of RECAST on ships would require a supply of low emissions lime at bunkering ports. Ships pick up bunkers from a small number of major ports, indeed 75% of bunkers are lifted at ~10 ports worldwide shown in Table 2. Ships would load bunkers and load lime at the same time. The facility to load lime would also have the capability of taking off the ship the used sorbent from the previous voyage and recycling it to a LEILAC Calciner plant for reprocessing. Transporting lime (and ground limestone) by truck is a well-established technology.

Lime reduces in its ability to absorb CO₂ with the number of cycles it makes. Hence the continuous requirement for a supply of new limestone. It is anticipated that lime will make between 10 and 20 cycles before its capture capacity becomes too low⁸⁹. Hence a stream of at least 10% of fresh ground limestone would be added to the returned sorbent. Ideally the major ports, or nearby refineries producing bunkers, would be equipped with LEILAC calciners to produce or recycle the lime.

<table>
<thead>
<tr>
<th>Table 2 – The world’s major bunkering ports / countries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Singapore</td>
</tr>
<tr>
<td>Rotterdam, Netherlands</td>
</tr>
<tr>
<td>Antwerp, Belgium</td>
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</table>

Figure 2: The LEILAC1 Pilot Plant for low emissions Lime

Figure 3 - $/tCO₂ avoided
31.5kT DWT Ship
3 Lime Reactions in the Scrubber and the LEILAC Calciner

When lime is carbonated in the ships scrubber there will be a series of reactions taking place. The temperature, at about 600 °C, will be sufficiently high that any hydrocarbons or carbon compounds will burn and add to the heat in the reactor available for the WHR system and add to the CO\textsubscript{2} to be captured. Sulphur compounds will react with the lime, CaO, to become gypsum, CaSO\textsubscript{4}. NO\textsubscript{x} will be reduced to N\textsubscript{2}.

Two and four stroke marine diesel engines are very well established. Two stroke engines run on an excess air ratio, lambda, of over 2. This means that the exhaust has a high excess air contact and that the concentration of CO\textsubscript{2} is low, at around 6%. Coal fired power station flue gases have 2.5-3 times the concentration so a key part of the scrubber design will be handling the high volumes of exhaust gas at low CO\textsubscript{2} concentration. A typical gas composition is shown in Table 3

<table>
<thead>
<tr>
<th>Table 3 – Main components of marine engine exhaust</th>
<th>Scrubber reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>76%</td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>0.15%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>13%</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>5-6%</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>5-6%</td>
</tr>
<tr>
<td>SO\textsubscript{2}, SO\textsubscript{3} S</td>
<td>0.2-0.33%</td>
</tr>
<tr>
<td>Other Hydrocarbons &amp; particulates</td>
<td>0.1-2%</td>
</tr>
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<td></td>
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</tbody>
</table>

On board ship the carbonation reaction occurs very quickly in the surface of the lime particles pore network and once the surface layer of perhaps 50 nm is converted the reaction slows down because the CO\textsubscript{2} has to diffuse through the solid into the core CaO. Hence the lime supplied to the scrubber will be greater than the lime which reacts capturing CO\textsubscript{2}, and some lime will be unreacted in the core of the particles.

On land in the LEILAC calciner the reaction temperature will be above 900 °C, which is the equilibrium temperature at 100% CO\textsubscript{2}. The powdered limestone and used sorbent fall from the top of the calciner down an externally heated reactor tube. The atmosphere is 100% CO\textsubscript{2} at atmospheric pressure. When the particles reach >900 °C they “explode” into lime and CO\textsubscript{2}. The CO\textsubscript{2} rises up the reactor, heating the incoming powder, and the lime falls to a hopper at the base. The source of heating in LEILAC2 will include electricity, and a variety of low-cost recycled fuels.

The limestone to lime reaction will probably be further extended in the product hopper at the bottom of the reactor. Some steam is introduced which reduces the partial pressure of CO\textsubscript{2}. This encourages further calcination, which is endothermic. This calcination absorbs some energy thus cooling the product from the peak temperature. The fresh lime, and the hot CO\textsubscript{2} together with the hot flue gases have considerable enthalpy which is recaptured in heat exchangers to maximise heat integration.

On land capture processes have the advantage that industrial emissions are regulated, benefit from economies of scale and CCS and CCUS facilities are being developed worldwide. Large scale on-land production of low emissions lime with CCS is required to deliver net shipping emissions reduction. From a shipping company’s perspective, the emissions from the Lime Carbonator, with WHR, will more than meet the IMO target at only 39% exhaust CO\textsubscript{2} capture.
The potential of ocean liming

As the world’s environmental regulations tighten it will be necessary to deliver shipping without emissions. RECAST ships have the potential to do that (i) by increasing the feed of lime to increase CO₂ capture and (ii) by discharging some used sorbent into the ocean if ocean liming is permitted far offshore. In the surface of the ocean the unreacted lime reacts with the dissolved CO₂ to produce calcium bicarbonate for which the ocean has a very large capacity. Each mol of CaO in the ocean draws in 1.7 mols of CO₂ from the atmosphere which can offset the residual CO₂ emissions. In addition this reduces ocean acidification. Any limestone or gypsum would simply sink to the bottom as they are both effectively insoluble in sea water.

The impact of ocean liming, should it be approved under the London Protocol, is that net zero emissions can be achieved. Ocean liming has a powerful impact on the net emissions performance, but it demands that a greater proportion of the lime is mined and calcined afresh, which is clearly a cost addition.

In Table 4 the impact of a proportion of the used sorbent being used to lime the ocean is shown at different levels of CO₂ capture from the exhaust. This is for an example with 75% lime conversion in the CFB and a pre-RECAST bunkers consumption of 1.44 tph. Taking 70% capture it can be seen that with 50% of the used sorbent scattered in the ocean the emissions from the ship are down to a residual 8%. This requires a lime feed of 3.7 tph of which only 1.65 tph will be returned to port. The demand for fresh limestone on the port recalcination facility for this ship would be thus increased from 10% limestone feed to 60%.

It should be stressed that ships operating inshore and in environmentally sensitive waters will keep used sorbent on board and commence the offsetting ocean liming process only when suitably distanced offshore.

<table>
<thead>
<tr>
<th>CO₂ capture from exhaust</th>
<th>CO₂ emissions percentage of original per nm</th>
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<tbody>
<tr>
<td></td>
<td>50%</td>
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<tr>
<td>Lime feed tph</td>
<td></td>
</tr>
<tr>
<td>Zero ocean liming</td>
<td>40%</td>
</tr>
<tr>
<td>25% ocean liming</td>
<td>34%</td>
</tr>
<tr>
<td>50% ocean liming</td>
<td>29%</td>
</tr>
<tr>
<td>For initial bunker consumption 1.44 tph, 75% lime conversion</td>
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5 The demonstration steps required for commercialisation

Whilst each of the elements of the RECAST system are well established, they have not been proven in this configuration. The development risk is largely associated with combining the required technologies effectively, because each of the steps have been developed to varying extents by research groups worldwide. The system’s innovation is to bring these technologies together in a RECAST ship.

Clearly the economics of the system are crucial. Preliminary studies suggest a carbon capture cost of $40-70/tCO₂ but this needs to be checked and reconfirmed at each stage of the development. It will thus be important to follow a development programme along the following lines.

- Demonstrate delivery of low-emissions lime with the necessary surface area and particle size distribution from a LEILAC Calciner and show that this can be scaled up to industrial quantities. This step is happening within the H2020 projects LEILAC and LEILAC2 as they apply to the lime industry.
- Establish the kinetics of the capture reaction at about 600°C with this sorbent to support the design of a CFB scrubber reactor with WHR steam generation.
• Demonstrate the capture of CO₂ from exhaust gases at the concentrations of marine engines, this requires an existing calcium looping demonstration to undertake a specific experiment to achieve TRL4
• Design and build a carbonator scrubber at 1-2MW scale which can be tested with a marine engine on land. This demonstration could then include storage for fresh and used lime sorbent, which is filled from a truck, and then with used sorbent from the carbonator. Used sorbent is then trucked back to the calciner for regeneration so that the whole cycle is at TRL6
• Transfer this demonstration in total to a ship so that its operation can be demonstrated on a 1-2MW slip stream of the ship’s exhaust in practical ship operating conditions which would achieve TRL7
• Design, build and operate a full-size system for a ship to show the total operation and economics. Optimise the proportion of new limestone needing to be added to the returned sorbent. The system would be TRL9. Its capital and operating costs would be established, its competitive position would be clear, and it would be ready for investment by ship owners/operators.
• Investigate the composition of used sorbent, in particular the impurities from the non-hydrocarbon components of the fuel, and its impact on the ocean. The ocean activity will be modelled taking account of the particle size, the percentage conversion to limestone and the surface area to determine the CO₂ take up. Work with the IMO to develop ocean liming offset approvals for RECAST.

It is anticipated that the totality of this programme could take 3-5 years. Work on the sorbent and its application to carbon looping is underway for a number of different industries and this fundamental learning will assist the RECAST development.

6 Conclusion

With RECAST developed and demonstrated the marine world will have available a system for decarbonising long-distance shipping emissions by >50% by scrubbing the exhaust of fossil fuelled marine engines with lime. The further steps would have been established which could take emissions to zero with some ocean liming. In sum, the impact of RECAST will be to demonstrate that the IMO’s objective can be exceeded.

There is no comparable CO₂ emissions reduction system. Alternative approaches include battery power and converting the engine to burn ammonia or hydrogen as fuels. The low energy density of these fuels would displace cargo space for tankage similar to RECAST. It has been demonstrated that the methane slip from LNG is such that LNG yields little net GHG emissions reduction⁴⁳.

The Transport and Environment report on decarbonising European shipping developed the renewable energy requirement to decarbonise shipping by 2050. Comparing the T&E optimum Technical Mix scenario with an optimum RECAST mix scenario suggests that RECAST would need considerably less renewable energy. RECAST would reduce ocean acidity, and it will be cheaper overall despite some cargo reduction constraints from shipboard equipment. The Renewable energy need of the leading strategies to deliver the EU requirement of 284TWh p.a. of shaft motive power is shown in the Table 5.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>All battery power, suitable inshore</th>
<th>“RECAST mix” - Domestic = battery/ Coastal = 50% H₂ 50% RECAST/Ocean = 100% RECAST</th>
<th>T&amp;E “Technology mix” - Domestic = battery/ Coastal = 50% battery 50% H₂/Ocean = 50% H₂ 50% NH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Renewables need</td>
<td>350 TWh</td>
<td>450 TWh</td>
<td>800 TWh</td>
</tr>
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</table>

The lime industry would need to build emissions free lime capacity in parallel with ship conversions, starting near major bunkering ports. Ports could make emissions free lime available with their bunkering operations. Delivery of lime, and used sorbent, largely limestone, is well established. The RECAST process of Figure 1 would allow environmentally responsible use of fossil fuels in existing engines for many years to come. It could achieve net zero at lower cost than the T&E options.

RECAST would apply to all major ship types using fossil fuels in 2 and 4 stroke marine diesel engines: bulk carriers, tankers, container ships, cruise ships and passenger liners. Under the long-term ambition, RECAST would enable the ship to deliver net zero emissions by some ocean liming with used sorbent. It would be scalable from a few ships to the whole ocean fleet.
Monitoring RECAST would be straightforward. Ships fitted with RECAST will be commercially motivated to use lime because it reduces their fossil fuel consumption. Ports selling bunker fuels can monitor the lime sales. The measure of low emissions lime sales versus fuel sales to the ship will give confidence that CO$_2$ is being captured, enabling the process to be rolled out worldwide.

Preliminary estimates suggest that RECAST can reduce GHG emissions at a cost of €40-70/tonne. This compares very favourably with other estimates of the cost of shipping decarbonisation. The “Mission Possible” report estimates shipping decarbonisation to cost between €150 and €350/tonne. This would give RECAST ships environmental performance of the highest level at a reasonable cost. The combination of inshore and long-distance European shipping fitted with RECAST would improve the financial competitiveness of European maritime industries and shipping companies and place them in a leading position in the field of green shipping.

Retrofitting RECAST could also be attractive to inshore shipping because the emissions would probably meet Mediterranean and inshore regulations for Sulphur and particulates without shifting to expensive marine diesel fuels. Engine manufacturers will have the confidence and design data to retrofit zero carbon emissions RECAST systems to ships using their engines.

In summary, RECAST will enable the retrofitting of the current international maritime fleet to deliver >50% per nm reduction of emissions of CO$_2$ and SOx from fossil fuels on all major emitting ship types. Cost could be €40 - 70/t of CO$_2$.

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