Engineering challenges of ocean liming

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Abstract

The relationship between the level of atmospheric CO_2 and the impacts of climate change are uncertain, but a safe concentration may be surpassed this century. Therefore, it is necessary to develop technologies that can accelerate CO_2 removal from the atmosphere. This paper explores the engineering challenges of a technology that manipulates the carbonate system in seawater by the addition of calcium oxide powder (CaO; lime), resulting in a net sequestration of atmospheric CO_2 into the ocean (ocean liming; OL). Every tonne of CO_2 sequestered requires between 1.4 and 1.7 tonnes of limestone to be crushed, calcined, and distributed. Approximately 1 tonne of CO_2 would be created from this activity, of which >80% is a high purity gas (pCO_2 >98%) amenable to geological storage. It is estimated that the thermal and electrical energy requirements for OL would be 0.6 to 5.6 GJ and 0.1 to 1.2 GJ per net tonne of CO_2 captured respectively. A preliminary economic assessment suggests that OL could cost approximately US$72-159 per tonne of CO_2. The additional CO_2 burden of OL makes it a poor alternative to point source mitigation. However, it may provide a means to mitigate some diffuse emissions and reduce atmospheric concentrations.

1. Introduction

1.1 Context

Although substantial scientific research and political negotiation has been undertaken over the last 30 years, a widely agreed solution to anthropogenic climate change has yet to be established. While it is unknown exactly what level of carbon dioxide (CO_2) in the atmosphere can be sustained without causing 'dangerous' or 'extremely dangerous' climate change, generally a maximum of 450 ppmv CO_2 (-eqv) is quoted [1], which will be realised in the next 30 years if the current rate of emissions remain unchanged. Therefore, it is unsurprising that a number of schemes have been proposed to counteract climate change through direct manipulation of the Earth's climate system, which are referred to as 'geoengineering' [2-3]. While 'conventional' mitigation (decarbonisation of energy supplies, lower carbon intensive consumption, land use management to preserve terrestrial carbon pools) is the only sustainable solution, it could take a whole century to be fully implemented. Until then, geoengineering technologies may mitigate some of the more harmful effects of climate change.

Geoengineering is broadly categorised into technologies that mitigate incoming solar radiation (stratospheric aerolsols, cloud brightening, increased surface albedeo) and those that remove carbon dioxide from the atmosphere (afforestation, biochar, direct air capture, enhanced weathering). Prior to the implementation of such technologies, a thorough understanding of effectiveness and environmental impact is required. Therefore, substantially more research is required for most of these technologies. For instance, uncertainly surrounding the effectiveness of direct air capture has produced cost estimates that range between US$100 and US$1000 tCO_2^{-1} [4-5], and the potential of biochar, afforestation, and soil carbon management is promising albeit uncertain given the resource conflict with food production. It is unlikely that these technologies will have the capacity or cost competitiveness to mitigate point source emissions [6] but may be used to mitigate some of the more diffuse carbon emissions (e.g. land use change and aviation[5]), or may form part of an enhanced recovery process if a dangerous level of climate change is surpassed (e.g.[7]). This paper presents a technoeconomic assessment of ocean liming (OL), which is a technology that removes carbon dioxide from the atmosphere for storage as bicarbonate ions in the ocean[8]. This paper is timely in light of recent national and international discussions on geoengineering [9-10], and covers a specific technology that has been sparsely reported on.

The increase in atmospheric CO_2 concentration from pre-industrial levels is responsible for a 0.1 decrease in surface water pH. Over the coming 100 years, this is predicted to decrease further by up to 0.4 units [11]. Ocean acidification is a substantial existential threat for carbonate forming organisms (e.g. some algae and coral) which are vitally important basal components of marine ecosystems. A potential considerable secondary effect of ocean liming is the increase in localised and distributed surface water pH, and if implemented globally together with conventional mitigation measures could raise surface ocean pH back to pre industrial levels.

1.2 Ocean Alkalinity Enhancement

Intentional manipulation of ocean alkalinity was first proposed by Kheshgi [8], in which particulate hydroxide minerals are added to the surface ocean. Dissolution of the particles promotes a number of reactions in the carbonate system which ultimately results in a drawdown of atmospheric CO_2 (Equation 1). To effect change in the CO_2 concentration of the atmosphere, alkalinity modification would need to be limited to the surface ocean (<100 m), which is relatively well equilibrated with the atmosphere. Modifying the alkalinity in the deep ocean would have little immediate effect until deep waters were brought into contact with the atmosphere via thermohaline circulation. The assessment by Kheshgi [8] presents a carbon balance for a number of ocean liming schemes, but omits a comprehensive energy assessment. Other researchers have described similar schemes such as CO_2 stripping of flue gas using limestone [12-13], and direct application of limestone into upwelling regions [14]. Generally, the aim of these techniques is to promote the reaction in Equation 2

$$CaO + 2CO_2 + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^-$$

Equation 1

$$CaCO_3 + CO_2 + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^-$$

Equation 2

Alternatively, House et al, [15], and Rau [16] have suggested promoting alkalinity creation through the electrochemical splitting of carbonate or seawater, where the created acidity is neutralised through dissolution of carbonate or silicate minerals.

The basic concept of OL is to increase ocean pH (and increase CO_2 uptake) by adding alkalinity in the form of calcium or magnesium oxide/hydroxide (see [17]). 1 mole of added calcium or magnesium oxide (i.e. 2 moles of alkalinity) neutralises 2 moles of carbonic acid. In order to re-establish equilibrium, 2 moles of atmospheric carbon dioxide dissolve into the ocean. However, this theoretical level of CO_2 uptake is not reached. In reality, between 1.6-1.8 moles of carbon dioxide are absorbed (depending on temperature and atmospheric CO_2 concentration; Figure 1) due to the reaction between a small proportion of the hydroxyl and bicarbonate ions to form carbonate and water (see supporting information for details; and [18]).

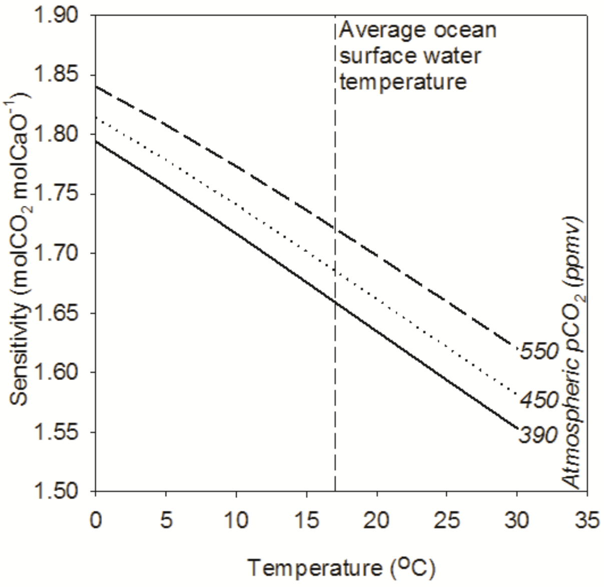

Figure 1: Sensitivity (in moles of atmospheric CO_2 uptake for every mole of $Ca(OH)_2$ addition) of ocean alkalinity enhancement over a range of temperatures. Calculated using CO_2Sys [19], with equilibrium coefficients from Dickson and Millero [20].

The surface ocean is already 4-5 times supersaturated with respect to calcium carbonate. Therefore, it may be intuitive to expect carbonate minerals to precipitate if dissolved Ca^{2+} and CO_3^{2-} concentrations were to increase, which would reverse the effect of ocean liming (effectively the reverse of Equation 2). However, the presence of magnesium, sulphate and phosphate in the surface ocean inhibits the precipitation of calcite (calcium carbonate; [21]), and below approximately 19-25 times supersaturated spontaneous nucleation is inhibited considerably [22]. Given that carbon in the surface ocean is transported to the deep ocean (via the thermohaline circulation), and that surface oceans may be seeded with calcium carbonate minerals (as particulate inorganic carbon, which will overcome the energy barrier associated with spontaneous nucleation), the feasibility of OL is likely to be a function of application rate, precipitation rate, and surface ocean turnover. A full analysis of the geochemical response to adding alkalinity into the ocean is beyond the scope of this paper, which is discussed in more detail in [13, 14]. An efficiency factor has been incorporated into the base case technoeconomic analysis in this paper to account for 5% carbonate precipitation, but given the lack of data on aboitic and biotic carbonate precipitation rates at elevated alkalinity (including localised effects at the point of addition), the efficiency factor used here is largely speculative.

1.3 Scope of the paper

This paper examines the energy requirements and carbon emissions from a complete process cycle of lime addition to the surface ocean from quarrying, through calcination and hydration to dispersion into the ocean (Figure 2), substantially expanding upon the preliminary assessment by Kheshgi [8] by providing full life cycle energy requirements, carbon emissions and economic costs for a range of calcination equipment and feedstock minerals. To generate the calcium or magnesium oxide for this process, limestone (primarily calcium carbonate; $CaCO_3$) or dolomite (calcium and magnesium carbonate; $CaMg(CO_3)_2$) must be calcined. Calcination produces CO_2, which at first may seem counterproductive. Indeed, OL is only notionally feasible if this high purity CO_2 from calcination in captured and sequestered. This work focuses on the key energy consuming activities associated with OL (limestone extraction, comminution, calcination, CO_2 capture and storage, and ocean transport) and their associated carbon dioxide emissions, although the long term fate of geological CO_2 has not been included. Complete carbon (as CO_2) balances, and energy requirements are developed for all the options, as well as both capital and operating costs. The environmental impact of OL has not been quantified in this assessment, but has been qualitatively described in Section 7. A sensitivity analysis is also carried out on a number of the most important variables, and a final assessment is given for the technological gaps identified and proposed additional work to bridge those gaps. Although enough is understood to make this assessment, additional work is required to understand both the biological and geochemical consequences of adding alkalinity to the surface ocean.

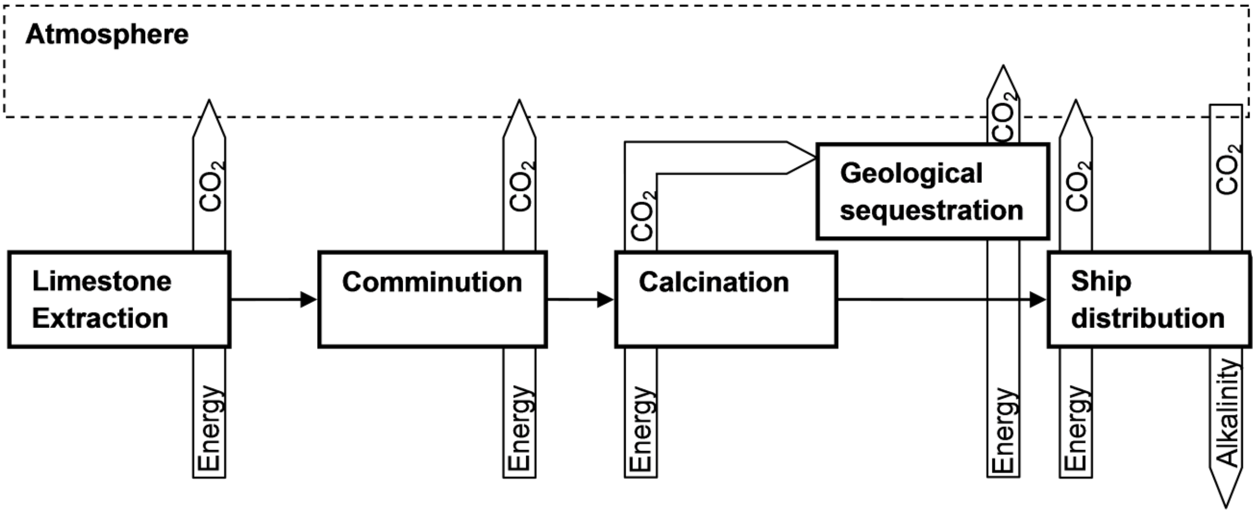

Figure 2: Simplified schematic of Ocean Liming

2. Limestone Extraction

The first step in the production of lime is to identify a suitable deposit of raw material and extract it. Limestone deposits cover about 10% of the Earth's land surfaces [23-24], and are distributed widely over most of the world [25]. Thus, availability of limestone is not a limiting factor in this proposal (see discussion in [13] and supporting information).

2.1 Process description

The capital, operating and maintenance costs of primary fragmentation of the rock are low in relation to those of the subsequent operations to produce saleable limestone or calcined products [25-26], The cost of crushed limestone is approximately US$ 8 t^{-1} [16], half of which is typically attributed to crushing energy [27]. Therefore, a ~US$4 material cost has been used in this study, and the energy requirements for comminution have been dealt with separately. A sensitivity analysis of material cost is included in Section 7.1.

2.2 Energy and carbon cost

A brief overview of carbon and energy balances for extraction processes are summarised in Table 1. A number of studies [27-29] suggest that excavation, drilling, blasting, and short range hauling of a range of ores and rock to be between 12.5 and 96.7 MJ t^{-1}. While these values are based on extraction of material substantially harder than limestone, they are sufficient to conservatively describe extraction processes for OL (approximately 20 MJ t^{-1} has been used this study). Carbon emissions associated with land use change are negligible when compared with the overall carbon budget of OL (see supporting information).

Table 1: Energy requirements and carbon dioxide emissions from extraction processes

Source	[27]		[28]		[29]	
Material	Gold and iron ore		Iron ore and bauxite		Marble*	
	Energy (MJ t^{-1})	Emission ($kgCO_2$ t^{-1})	Energy (MJ t^{-1})	Emission ($kgCO_2$ t^{-1})	Energy (MJ t^{-1})	Emission ($kgCO_2$ t^{-1})
Drilling	1.0	0.1	1.2-1.3	0.1	2.2 (electric)	0.3
Blasting	1.6	0.1	2.0-3.3	0.4-0.7		
Loading and Hauling	14.3	1.1	36.1-92.1	2.6-6.0	10.3	0.8
Total	16.9$^+$	1.3	39.3-96.7	3.1-6.8	12.5	1.1
Total $tCaO^{-1}$†	30.2	2.3	70.2-172.7	5.5-12.1	22.3	2.0

*assuming a density of marble of 2.56 t m^{-3}
$^+$Lowest may be 12.2 MJ t^{-1}
† Assuming 1 tonne of limestone produces 0.56 tonnes of CaO

3. Comminution

The dissolution dynamics (particle settling rate, dissolution time/rate) of lime in the surface ocean will be controlled primarily by size reduction processes. Applying a shrinking core relationship coupled to stoakes sinking velocity, the initial particle size can be estimated (see supporting information). The optimal particle diameter for lime powder is >80 µm assuming a surface ocean depth of 100 m and an approximate dissolution rate of 10^{-6} kg m^{-2} s^{-1} ([30]; based on dissolution in fresh water, no such data exists for saline water). A particle of this size will completely dissolve by the time it reaches the bottom of the mixed layer. Given the uncertainty of the dissolution rate the required particle size may be between 50-100s µm. Therefore, comminution of limestone or lime to approximately 100s µm would require primary, secondary, and tertiary crushing together with limited grinding.

3.1 Crushing and Grinding

The particles must be 'ground' for diameter reduction below 1mm, using a range of mature grinding technologies [31]. The energy requirements for grinding depend on the quantity of new surface area that is created, increasing by around 8-10% for every 1 m^2 g^{-1} of surface area (Figure 3) [32-35]. It is convenient to express comminution in terms of surface area as it can be directly related to dissolution rates, which are similarly expressed as a function of surface area (see discussion in [36]).

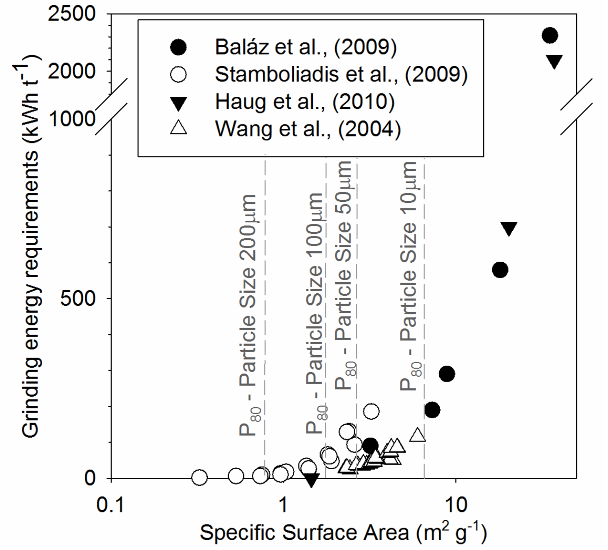

Figure 3: Relationship between surface area created and electrical energy used in grinding. The approximate P_{80} (this is the size of which 80% of the product passes) is presented.

3.2 Energy requirements and CO_2 production

Here we assume a total of 90 MJ or electricity and 18 MJ of fuel per tonne of feedstock is required for extraction and comminution. This approximately equates to 15 $kgCO_2$ t^{-1}, which is three times greater than the industry average of 4.5 kg CO_2 per tonne of limestone [37] as it includes limited grinding (~100 µm).

4. Calcination

Humankind has been making lime for thousands of years, and together with charcoal burning it is probably the first 'industrial' process to be developed by society. The development of lime production equipment is mature, but the emphasis is on the local manufacture of lime in relatively small quantities (a few hundred tonne day^{-1}) to produce material for local markets. In order to achieve significant reductions of atmospheric CO_2 by liming the oceans, total production would be on the order of millions of tonnes per day. Whist the knowledge available on lime making can be used to assess the process feasibility, there are substantial challenges of scaling up production. The product requirements for the process are a lime of appropriate quality while all, or almost all, of the CO_2 produced (from chemical decomposition and fossil fuel combustion) from the calcination process is captured. The feasibility of adding lime to the ocean requires that this CO_2 is captured and stored.

Calcination is a highly endothermic reaction that requires approximately 3100 MJ $tonne^{-1}$ of CaO (note: this value is quoted between 2910 and 3492 MJ $tonne^{-1}$ of CaO [38]). The degree of calcium carbonate dissociation is temperature and pCO_2 dependent. Lime quality is specifically tailored to its markets with respect to reactivity, impurities, and flue gas CO_2 content. Occasionally associated with limestone deposits is magnesium carbonate (<4%) usually considered an 'impurity'. This also dissociates in a similar manner to calcium carbonate, but in a lower temperature range, typically 250°C to 550°C. Dolomitic carbonate minerals, containing 50-58% $CaCO_3$ and 40-48% $MgCO_3$, are also calcined for steelmaking and refractories. This is also a highly endothermic reaction, reported by Boynton [39] to require 3027 MJ $tonne^{-1}$ of CaO + MgO. This is lower than the weighted average of the heats of dissociation of the components (~3140 MJ $tonne^{-1}$), reflecting the differences in the formation of dolomitic deposits.

From a broad analysis of the available technologies, two variations of flash calciners have been incorporated into the technoeconomic assessment (a standard oxy-fuel flash calciner, and an Endex Catalytic Flash Calciner (CFC) system developed by Calix Ltd.). Jenkins [40] summarises the energy requirements for common kiln designs (see supporting information).

4.1 Calcination Processes

4.1.1 Flash calcination (with oxy-fuel)

They are so-called because of the short residence time of the product within the furnace [41], and can only be used for pulverised material up to a few hundred micron particle size. Upward flow calciners are used in the alumina, cement, and lime industries, in which hot air is introduced at the bottom and fuel is added part of the way up. These furnaces are all used to undertake highly endothermic chemical reactions driving off CO_2 or water of crystallisation and operate under pseudo isothermal conditions. These reactions involve particle weight loss so upward flow is ideal since the heavier particles tend to remain in the furnace until the volatile component has been evolved. Given that new hardware would be required for OL, and CO_2 gas purity would be a prerequisite, an oxy-fuel system is suggested to be the most appropriate. Additional electrical energy is required for air separation (MJ 255-332 $tCaO^{-1}$; calculated from [42]) Oxy-fuel systems are not routinely used by the current lime production industry given that there is few economic drivers for creating high purity CO_2 gas. However, oxy-fuel calcination equipment is being developed as part of chemical looping technology [43].

4.1.2 Endex Catalytic Flash Calciner

A novel contemporary calcining technology, based on a pressurised steam flash calciner design, has been developed by Calix Ltd [44-45] (http://www.calix.com.au), and could be used for OL. In the Endex CFC system, dolomite is first crushed and ground to produce particles of the desired size, typically 125 µm or less. The limestone particles are injected into a flash calciner in which natural gas (or any other gaseous fuel source) is combusted with air. The hydration process is incorporated into the calciner so that the liberated low-grade is used to generate steam and preheat the limestone input, thereby reducing fuel consumption. Calix Ltd. have shown that there is sufficient energy in the hot flue gas of the calciner to produce sufficient electricity for the plant [46]. The cost of the Endex CFC process is presented in the economic analysis spreadsheet in the supporting information.

4.2 CO_2 storage from lime making

The quantity of CO_2 produced from the calcination process is a function of the stone purity and its calcination temperature. From the stoichiometric chemistry of the reaction a tonne of 100% pure (as $CaCO_3$) limestone will generate 440 kg of CO_2 when fully calcined. The fuel used to calcine the limestone will contribute to the total CO_2. This produced CO_2 must be isolated from the atmosphere for OL to be notionally feasible.

It may be possible to directly inject a flue gas from an oxy-fuel system (95% dry mass CO_2) into a geological storage reservoir, although some additional purification (to >98%) has been included in this study [42, 47]. Li et al., [48] suggests a two stage low temperature flash or distillation process would be sufficient to purify the gas stream (requiring ~300 MJ tCO_2^{-1}). Therefore, the additional electricity demand (oxy-fuel and distillation) is approximately 562 MJ $t(CaO)^{-1}$, to produce >98% CO_2 gas stream. Endex CFC has a reported effluent gas composition of ~100% CO_2 [46]. This study assumes that the material cost of transporting and injecting high purity CO_2 into a geological formation is US$ 5 tCO_2^{-1}, the energy for compression and injection is included separately (see Section 6.1.3 and [49]).

The use of solar power calcining technology would reduce CO_2 production from fossil fuel combustion [50-51], and the uncertainties surrounding geological storage of CO_2 (although storage is still required for the CO_2 produced from chemical decomposition). While, current estimates for additional capital and operational costs are potentially prohibitive, further development in this technology may have important implications for OL. It may be possible to further reduce the geological storage requirement by using silicate minerals as a feedstock [52].

5. Transport and application

Transportation from the kiln to the application site would contribute considerably to the cost and energy requirements of OL. This section presents information on the oceanic transport of lime using large freight carriers. Limited land transport using data from [53] is included in the model and is discussed in the supporting information.

5.1 Transport and application in the ocean

Substantial ocean transport distances would be required to distribute lime into the surface ocean. Globally, approximately 8 billion tonnes of cargo is transported using 50,000 ships, the capacity of

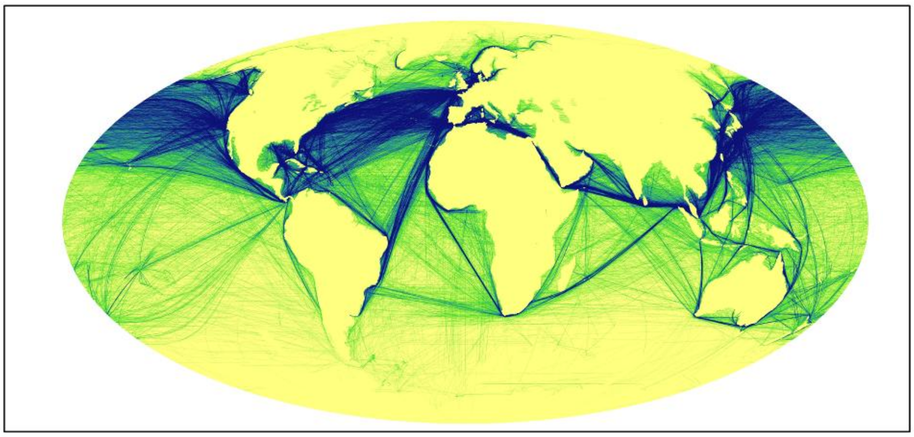

Figure 4: Global shipping traffic [55]

which could be substantially underutilised [54]. Sea freight operates across all of the Earth's major oceans (Figure 4). Augmentation of this fleet with appropriate technology and commandeering spare capacity may be a feasible method for large scale distribution of lime into the surface ocean. However, costs associated with lime distribution made in this paper assume full costs of hired ship transportation.

The energy required for dispersion from a ship is primarily related to the size of the ship and its method of propulsion. Most large carriers are oil fired, and are either steam engine, or steam turbine driven. Whilst there is some small energy demand during idle periods in dock and loading, the primary fuel usage is at sea. Typical fuel consumption for a 240,000 deadweight tonne (DWT) tanker is approximately 50 kJ tonne-km^{-1} (adapted from [56]). Lower equivalent values of 30 kJ tonne-km^{-1} for a 70,000 DWT, and 24 kJ tonne-km^{-1} for a 164,000 DWT bulk carriers have been reported [56]. The general approach taken by Psaraftis and Kontovas [58] has been used here to estimate the fuel energy costs associated with ship distribution to be approximately 100 MJ t^{-1} of material added to the ocean. The additional electrical and fuel energy consumed in loading and dockside operations is 8 MJ t^{-1} and 19 MJ t^{-1} respectively [59], which is small compared to the overall energy and carbon budget.

The total discharge time for a 300,000 DWT bulk carrier is approximately 3.5 days (assumed to be equivalent to typical loading times 1 tonne per second). Together with an additional day of steaming for open ocean discharge and return to port, and 6 days for loading, the total time is approximately 11 days. Therefore, a fleet of approximately 101 dedicated ships would be required to deliver 1 Gt a^{-1}. The application of limestone powder to upwelling regions potentially requires substantially more transport energy [14]. This is a function of the lower discharge rate (0.5 tonnes per minute), which is limited by the poor solubility of limestone. This will not be a limitation given the solubility of lime in seawater. Rapid horizontal diffusion of particulate limestone placed into the ocean was demonstrated by [60] (up to 750 m^2 s^{-1}), which is similar to the application rate of approximately 100 m by 15 knots (7.7 m s^{-1}).

6. Cost analysis

Approximately 0.9-1.3 Gt of lime would be needed for a net removal of 1 GtCO$_2$ from the atmosphere, which would be a considerable expansion of the 115 Mt [61] currently produced. Here, the capital costs were determined for a global 100 Mt yr^{-1} operation, and subsequently scaled to Gt yr^{-1}. Given that current ship freight capacity is underutilised, the cost analysis assumes the capital cost of distribution is included in the operational cost as a 'hired' service. The capital costs associated with a substantially expanded extraction and calcining industry have been investigated here based on a more representative comparison to the costs may be derived from cement plant data, where the scale of operations is an order of magnitude larger (~2.5 Gt a^{-1} [62]).

A recent study by the IEA [63] on the potential for CO$_2$ capture in the cement industry provides a basis for most of the data required to evaluate capital and running costs for this study. A detailed cost analysis spreadsheet is included with the supporting information with assumption presented in Table 2. The cost difference between lime and hydrated lime (Ca(OH$_2$)) production is minimal, in which the additional cost for hydrated lime is created by slaking lime in water. To provide a conservative cost estimate the calculations presented here are based on the production of hydrated lime. Costs are presented here in US$, and have been converted in some instances from € or AUS$ using a conversion rate of 1.4 and 0.9 respectively.

Table 2: Assumptions made in the model

Assumption	**Value**	**Details/reference**
CO_2 sequestered into the ocean (Mt)	100.00	Fixed value to define the scale of the process
Raw material cost (US$ t^{-1})	4.00	Value was assumed based on [62,64]. Here the value of crushed limestone is ~€5.3 t^{-1}. Comminution is the largest single cost in material processing (~40%; [27]) which is already accounted in the model. A range between €1.5 t^{-1} and €9 t^{-1} was assessed
CO_2 injection and monitoring (US$ t^{-1})	5.00	Assumed value and range (up to €77 t^{-1}) based on values in [65] [49]
Energy required for CO_2 compression and injection (kWh t^{-1})	111.00	
Cost process water (US$ t^{-1})	0.10	Fixed values (minimal influence on overall cost) adapted from [66]
Electricity cost (US$ GJ^{-1})	19.00	Energy costs and range, and carbon intensities converted from [67]
Natural gas cost (US$ GJ^{-1})	210.00	
Fuel cost (US$ t^{-1})	600.00	
Carbon intensity - Natural Gas ($kgCO_2$ GJ^{-1})	59.00	
Carbon intensity - Fuel ($kgCO_2$ GJ^{-1})	76.00	
Carbon intensity - Electricity ($kgCO_2$ GJ^{-1})	150.00	
Port Handling (US$ t^{-1})	2.39	Minimal influence on overall cost. Fixed value based on [68]
Ship Capacity (Mt)	0.30	Assumed Cape size vessel defined as above 150,000 dwt (although capacities in excess of 300,000 dwt have been constructed). Assumed length of vlcc/ulcc
Ship length (m)	400.00	
Ship beam (m)	60.00	
Ship draft (m)	20.00	
Feedstock purity (Oxy Fuel)	0.98	Variation discussed in paper Section 4.2
Feedstock purity (Calix)	0.95	
Absorption capacity $molCO_2$ $molCaO^{-1}$	1.70	Assumed Value - Sensitivity analysed. See Section 1.2 for discussion
Discount Rate (%)	4	Assumed value and range based on discussion in [69]. The range has been extended substantially from realistic values.
Alkalinity added that has been precipitated (%)	5	Large uncertainty – see paper Section 1.2 for discussion

6.1 *Limestone extraction and lime production*

6.1.1 *Capital*

IEA [63] indicates that the budgeted cost for a 1 Mt yr^{-1} cement plant in Northern Europe is €120 million (US$ 169 million). Similar values are given by Alsop [70], who estimates US$150 million for a 1.5 million tonne yr^{-1} cement plant expansion in the USA. IEA [63] estimates the budget cost to be ±25%. Not all the items in a cement plant are required for a lime kiln, and Table 3, which is derived from Table 5-21 of the IEA report [63], provides the breakdown and summary of individual capital equipment items, design costs, and construction, which relate to 1 Mt yr^{-1} of lime production using a pre-calciner system. This cost includes oxy-fuel firing with waste heat recovery and CO_2 capture.

Table 3: Capital costs of limestone processing and lime production (operation size of 1Mt a^{-1})[63]

Description	**Capital Cost (M US$)**
Extraction	
Primary crushing	3.4
Secondary milling/grinding	25.0
Raw meal silo	4.7
Stacker/reclaimer	2.5
Calcination	
Preheater/calciner	7.8
Fluid bed cooler	17.1
Storage silo	10.6
Electrostatic precipitator	2.1
Hydrator	18.2
Classifier/filter	3.53
Natural gas fuel system	1.13
Conveyor	1.8
Mill	5.9
Gas purification	
Air separation unit + gas recycle	11.21
compression and purification	7.5
Ancillary	
Design and engineering	71.9
Construction	69.1
External contractor services	26.8
Contingency	16.2
Fees	8.5
Owner costs	21.2
Other costs	21.2
Total	366.8
Capital costs used in this analysis[a]	**M US$ t^{-1}**
Oxy-fuel firing limestone	236.4
Calix process firing limestone[b]	290.0
Oxy-fuel firing dolomite[c]	248.8
Calix process firing dolomite[b]	231.3
Solar calciner	464.3
Kiln with amine carbon capture and storage	229.2

[a] Assuming an up-scaling factor [41]
[b] Endex cost data supplied by Calix Ltd.
[c] assuming an additional capital cost of 5% for dolomite

6.1.2 *Operating cost*

The major variable cost is fuel, and constitutes approximately half of the total running costs. Fuel prices are also the most volatile element of the calculation, and can vary by a factor of 2 depending on commercial market forces and political actions. Generally, it is the case that natural gas is the most economic option unless politically motivated incentives (carbon tax, price fixing for preferential use of indigenous fuels, import taxation policy) are used to locally distort the fuel price. The data shows that the cost of lime production is approximately US$87 $tCaO^{-1}$ for an oxy-fuel system.

6.1.3 Cost of CO_2 compression and injection

The most significant cost in post combustion CO_2 capture (of a purified CO_2 gas stream) is that associated with the compression of the gas, whilst the major uncertainly is the cost of sequestration. 1 Mt (limestone) yr^{-1} processing produces ~6000 t compressed CO_2 day^{-1}. Metz et al., [49] suggests that the electrical energy required for compression at this flow-rate would be 111 kWh tCO_2^{-1}. Here the cost of sequestration refers to the cost of injection well preparation and long term monitoring. Metz et al., [49] suggests this cost to range between US$0.2-30 tCO_2^{-1}, which has been included in the sensitivity analysis and a base case of US$5 tCO_2^{-1} has been used [65].

6.2 Distribution

The maximum distance between the process plant and port has been limited here to ~10 km to avoid costly land transport. It is possible to pump slurries for longer distances of up to 20 km, but the storage and loading facilities at the port would be more complex. Shipping has been included in this assessment as a 'hired' cost (inclusive or material and labour) of US$ 177,000 per day (~US$3.1 $t(lime)^{-1}$). The energy cost of distribution is estimated to be US$ 1.5 $t(lime)^{-1}$. Additional details of typical operational costs for port facilities are included in the supporting information.

6.3 Cost Summary

Table 4 combines the information from the previous sections to show the total capital and operational costs of OL against net CO_2 removal from the atmosphere. The capital cost required is approximately US$290 M for an operational size of a million tonnes of hydrated lime per year, and one plant is needed for every million tonnes of CO_2 that is captured from the atmosphere. A typical plant life of 40 years [60] is factored into this cost by assuming a 4% annual discount rate, which equates to approximately US$12 per tonne of hydrated lime produced.

The primary component of the operational costs are related to the energy costs (37%) and fixed costs (33%). The cost for net sequestrating one tonne of CO_2 including the discounted capital using oxy-fuel firing of limestone is US$126 tCO_2^{-1}. The cost ranges between US$72 tCO_2^{-1} and US$126 tCO_2^{-1} (Table 5) depending primarily on the magnesium content of the carbonate feed stock and if the Endex processed is used. Solar calcination is promising, but has additional capital and running costs (US$ 159 tCO_2^{-1}). Flash calination with 'conventional' amine scrubbing technology costs US$ 261 tCO_2^{-1}. Assuming a normal distribution between an appropriate range for each variable, and a mean value equivalent to the base case scenario, a Monte Carlo simulation was undertaken on the base case with 20,000 repeat analyses (see supporting information). The standard deviation of Monte Carlo simulation ranges between 7 and 41 (Table 4).

7. Discussion

The paper has covered extraction, calcination, hydration, and surface ocean dispersion of lime (or dolime) to investigate the feasibility as a potential technology for atmospheric CO_2 capture. There are a number of uncertainties that will require further investigation before implementation, particularly the biogeochemical response of the surface ocean to ocean alkalinity enhancement. Full implementation necessarily includes many social, political, logistical, and technical issues that would need to be resolved.

7.1 Cost Comparison

The energy and economic cost of OL is comparable to (but generally less than) other technologies that capture CO_2 from ambient air, which range between US$150-1000 tCO_2^{-1} (Table 5). If air capture technologies are to be used to compensate for emissions from fossil fuels a threshold of 6.7 – 17.4 GJ tCO_2^{-1} is imposed by the energy penalty from decommissioning fossil fuel. While OL shares the similar uncertainty surrounding geological storage of CO_2 with 'conventional' direct air capture technologies (although with 0.4-1.0 t of CO_2 injected for every net tonne of CO_2 removed from the atmosphere), it potentially creates additional uncertainty surrounding the environmental impact on the ocean. As OL could be located anywhere adjacent to the coast with appropriate resources, it is decoupled from the production of CO_2 and local (but sill global) energy markets. As such, direct comparison with conventional carbon capture and storage technologies is problematic. However illustrative costs have been included in Table 5.

Table 4: Cost summary of Ocean Liming in US\$ tCO_2^{-1}

	Oxy-fuel flash calciner - Limestone	**Endex CFC - Limestone**	**Oxy-fuel flash calciner - Dolomite**	**Endex CFC – Dolomite**	**Solar calciner - limestone**	**Flash calciner – amine scrubbing CCS**
	Case 1	**Case 2**	**Case 3**	**Case 4**	**Case 5**	**Case 6**
Fixed Running Costs – Calciner/extraction	41.3	35.8	35.6	26.8	101.4	67.3
Variable Running Costs – Limestone	6.8	5.7	5.9	5.2	6.1	11.4
Variable Running Costs – Energy	46.5	28.8	29.0	18.4	11.4	126.4
Variable Running Costs – Water	0.3	0.3	0.3	0.2	0.3	0.5
Variable Running Costs – Distribution Costs @ Port	6.8	5.7	5.7	5.1	6.1	11.3
Variable Running Costs – Distribution Costs Vessel Hire	3.9	3.3	3.3	2.9	3.5	6.5
Variable Running Costs – Geological Sequestration	4.9	4.7	2.5	1.8	3.4	7.1
Total operational	110.5	84.1	82.1	60.5	132.1	230.7
Discounted capital	15.1	15.4	13.2	11.0	26.6	30.8
Total Cost	**125.6**	**99.5**	**95.3**	**71.5**	**158.7**	**261.4**
Average cost from Monte Carlo Simulation	126.8	100.2	96.1	72.0	160.0	267.4
Standard deviation of cost from Monte Carlo Simulation	12.3	10.3	8.1	6.8	9.6	41.4

*including energy requirements for air separation unit and flue gas purification in cases 1 and 3

Table 5: Comparison of electrical and thermal energy requirements and financial costs of Ocean Liming and other direct air capture technologies

Technology	**GJ tCO_2^{-1}**	**US\$ tCO_2^{-1}**	**Source**
OL (Oxy-fuel flash calciner: limestone)	1.3_e 4.8_t	126	this study
OL (Endex CFC: limestone)	-0.1_e 5.5_t	100	
OL (Oxy-fuel flash calciner dolomite)	0.7_e 3.2_t	95	
OL (Endex CFC: dolomite)	-0.1_e 4.2_t	72	
OL (Solar calciner: limestone)	0.4_e 0.6_t^a	159	
OL (Calciner + amine flue gas absorption: limestone)	2.0_e 17.2	261	
Direct air capture (Cont, NaOH-$CaCO_3$)	1.8_e 6.1_t	780	[71]
Direct air capture (anionic resin)	0.8_e	220	[72]
Direct air capture (synthesis analysis)	$9.1_{primary}$	~1000	[4]
Direct air capture (Contact. NaOH-$CaCO_3$)	7.5	-	[73]
Direct air capture (Amine)	1.4_e 51.3_t	180	[74]
Direct air capture (Contact, spray)	3.7_e 0_t	150	
Direct air capture (Contact, packed)	4.4_e 0_t	-	
Electrochemical weathering (Mg-Silicate)	1.8_e 2.9_t	-	[15]
Electrochemical weathering ($CaCO_3$)	6.0_e	<100	[16]

Electrochemical CO_2 extraction from seawater	5.5_e [b]	-	[75]
Direct carbonate addition to upwelling regions	$<0.1_e$ 3.6_t	-	[14]
Energy and cost intensity of emissions	17.4_t (natural gas) 12.9_t (fuel oil) 6.7_e	>2000[d]	see supporting information
Typical values for conventional CCS[e]		30-100	[76][77][78]

[a]Additional thermal requirements from fossil fuels

[b]Per tonne of CO_2 extracted rather than net sequestration.

[d]Calculated as global GDP/total CO_2 emissions

[e]As OL is unlikely to be a replacement for conventional CCS, the comparison here is illustrative

7.2 Sensitivity analysis

Sensitivity analysis has been carried out using the model, to examine the effect of changes to the most operationally and financially significant variables on the discounted cash cost of sequestration. The analysis demonstrates that financial variation in the cost of energy is the most significant parameter. Changes in any of the major operating costs within potential norms result in price variations between US\$64 and US\$173 tCO_2^{-1} (Figure 5), the largest variation is due to the uncertainty in the cost of geological sequestration of CO_2, the cost of energy, and the proportion of the added alkalinity that may precipitate from surface waters. The sensitivity of OL to the cost of energy and geological sequestration is likely to be similar to comparable technologies (direct air capture, biomass energy carbon capture and storage). A useful exercise would be the comparison of sensitivity of these technologies within a broader framework of socio-economic forecasting. However, and important distinction for OL is the potential to deploy on a limited scale to ameliorate the effects of ocean acidification.

7.3 Environmental Impact and policy framework

The change in surface ocean chemistry is small when the effects of lime addition are distributed across the whole surface ocean, suggesting minimal environmental impact [5, 13-14]. Geochemical modelling by Harvey [14] suggests that addition of alkalinity sufficient to sequester 1 Gt C (3.7 $GtCO_2$) a^{-1}, assuming CO_2 concentrations in the atmosphere remain relatively constant, would only raise the pH of the surface ocean by 0.1 units over 400 years. A small increase in surface ocean pH may have little effect on marine organisms [79], and could be used to ameliorate the effects of ocean acidification in sensitive ecosystems [80]. However, if the rate of addition is sufficiently higher than the rate of dispersion, surface water pH would increase and ultimately retard biological productivity. Additional work is required to understand the effects of alkalinity enhancement on ocean biota and to optimise the rate of addition. The regulatory framework for adding materials to the ocean is encompassed by the London Convention/Protocol [81], which prohibits the dumping of waste into the ocean (excluding some inert materials). Rau et al., [80] suggests that this policy framework should be developed to allow for more active manipulation of ocean chemistry to solve climate change.

All extractive industries impact on the local environment particularly dust generation, noise, habitat and ecosystem disturbance, water pollution (suspended solids), and aesthetics [82]. An overview of the potential environmental risks associated with ocean liming is included in Table 6.

7.4 Required scale of operation

To stabilise climate at 2°C an emissions limit of approximately 1,000 Gt CO_2 into the atmosphere (since preindustrial) is required [83]. Currently we are approximately half way to meeting this limit and are likely to surpass it in the next 30 years unless emissions are dramatically reduced. An approach to disaggregate this challenge was proposed by Pacala and Socolow [84], in which emissions reduction schemes were difined by their ability to mitigate 1 Gt C (3.7 $GtCO_2$) a^{-1} as part of 15 ‘stabilisation wedges’. A recent revision of this [85] suggests 19 wedges are required, some of which are already exist as continued decarbonisation of the global economy, whereas others will require enormous effort to implement. The requirement for a scheme to mitigate 1 Gt C a^{-1} has been a useful benchmark for the efficacy

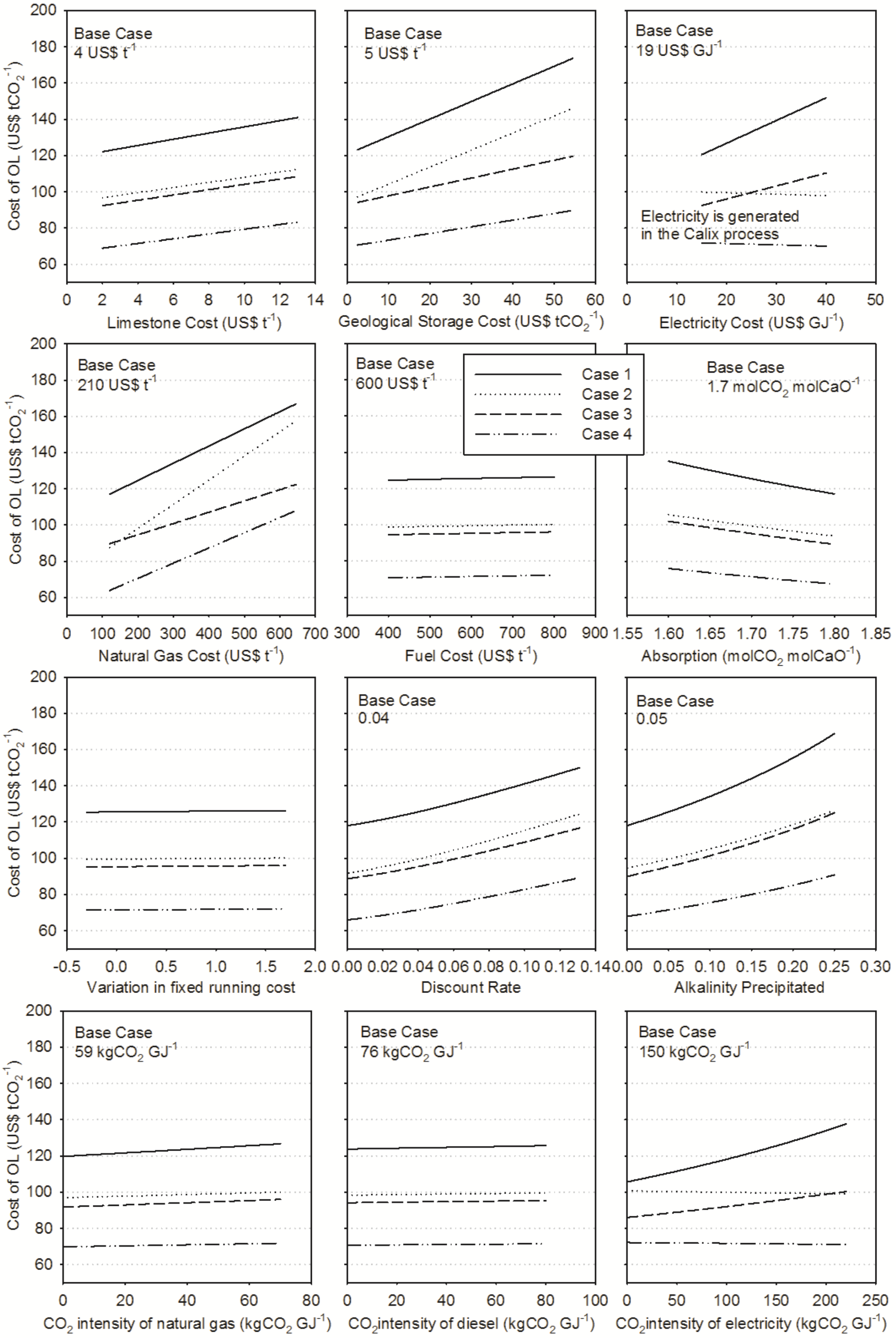

Figure 5: Sensitivity analysis of cost. Case 1 and 3 involves an oxy-fuel firing of limestone and dolomite respectively. Case 2 and 4 involves the Endex CFC for a feedstock of limestone and dolomite respectively

of some proposed technologies. Of course, the selection of 1 Gt C a^{-1} is arbitrary, and could be further demarcated into 100 schemes each mitigating 1% of emissions. However, the billion tonne scale can be used to compare natural and anthropogenic processes operating on a global scale, and has been used to discuss the potential size of an OL industry.

To remove 1 GtC (3.7 GtCO$_2$) from the atmosphere per year, approximately 6.5 Gt of limestone are needed to produce 4.5 Gt of lime.

Table 6: Environmental hazards created by ocean liming

Process	Environmental Hazard		Risk
Quarrying and comminution	Air	• Limestone dust generation and spreading • Particulate emissions from processing and transport equipment	High Moderate
	Water	• Water pollution from suspended inert solids, • Hydrocarbon release from equipment and fuel storage	Moderate Low Low
	Soil	• Disturbance of topsoil during overburden removal • Incorporation of rock residues into soils.	High Low
	Ecosystem	• Disturbance of ecosystems in and around the area of extraction.	High
Calcification	All	Calcification has the same environmental hazards as mineral extraction. However, the potential for harm is exacerbated by the presence of caustic alkaline (CaO) rock material.	
Distribution	Water	• Localised elevated surface ocean pH at the point of addition.	High

This would require approximately 4500 sites (assuming a maximum material flow per site to be limited by the capacity of the kiln, 1 Mt a^{-1}, Section 6.1.2). This is equivalent to, albeit slightly greater than, current global cement production (3.4 Gt a^{-1}) [86]. Assuming, a rock density of ~2.5 t m^{-3} and a typical extraction depth of 100 m, approximately 2220 ha (22 km^2) of land will be processed each year. This is a small operation compared with other extraction industries (e.g. <5% of current Alberta oil sands exploitation) and would be globally distributed to limit the impact of an individual site. Finally, dedicated ocean transport is small requiring 101 dedicated vessels (Section 5.1), and may be accommodated in part by spare capacity in existing freight. Additional technology development, particularly exploiting solar energy, or sourcing the oxide minerals from silicates [52] could improve OL feasibility.

8. Conclusions

This paper considers the addition of alkalinity to seawater to enhance the capacity of the ocean to act as a carbon sink and to counteract ocean acidification. The structure of the paper leads the reader through the technical issues relating to the various major steps required to achieve this objective. Analysis of energy consumption and carbon dioxide emissions from current technology used to quarry and calcine limestone (or dolomite) have shown that flash calcination is potentially the primary technology to produce lime (or dolime) for ocean addition. It is a necessary requirement of OL that the CO_2 generated during thermal decomposition of the carbonate (CO_2 from energy and chemical breakdown of carbonate minerals) is captured and sequestrated. Technologies to mitigate the carbon footprint of this processing stage have been identified and incorporated into the conceptual process design.

A technoeconomic analysis of a range of process options (oxy-fuel firing and Endex CFC, solar calcination, and calcination with amine scrubbing CCS) have been carried out to determine the viability of the proposed system. The cost to carry out this process varies between US$ 72 and 159 per tonne of captured CO_2, depending on the feedstock and process used (amine scrubbing technologies on conventional kiln are more expensive at US$261 tCO_2^{-1}). However, this evaluation was based on current state of the art technology, and future developments may reduce this cost estimate. The technology is energy intensive requiring between 0.6 and 5.6 GJ thermal and 0.1 and 1.3 GJ electrical for every net tonne of CO_2 captured, suggesting a global scale industry (4500 sites and 100 dedicated vessels) sequestering 1 $GtCO_2$ per year would consume approximately 1% of current global energy production. Given this energy requirement, the cost of OL is intrinsically linked to global energy prices, which are likely to increase in the coming century.

The addition of lime into the ocean will cause localised elevated pH around the point of addition. Small increases will have minimal environmental impact. However, sustained elevated pH will be detrimental to some organisms, and could result in carbonate precipitation which would lower the effectiveness of OL. There is a need for more experimental work in this area to investigate the ecological response to elevated alkalinity. Regulation of OL is encompassed by the London Protocol, which prohibits the dumping of materials into the ocean. It should be a pre-requisite of any technology that proposes to manipulate ocean chemistry, that the environmental consequences are fully evaluated in the context of an acidifying ocean.

Conceptually, OL swaps ambient CO_2 for high purity point source CO_2 suggesting it may be an alternative to other direct air capture technologies. Given that almost as much CO_2 is created as that drawn down from the atmosphere (most of which requires sequestration), the technical capacity of OL may be limited by the availability of appropriate underground reservoirs, and as such may compete with conventional carbon capture and storage. OL will not be appropriate for mitigating all anthropogenic CO_2 emissions, but may be a tool for mitigating some diffuse emissions or reducing atmospheric concentrations should this be required.

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