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Reactive Carbon Capture using Saline Water: Evaluation of Prospective Sources, Processes, and Products

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Reactive carbon capture (RCC) processes involve the capture of carbon dioxide (CO₂) and conversion to a value-added product using a single sorbent/reaction medium. Not only can RCC processes generate valuable byproducts that can reduce the cost of carbon capture, but RCC tends to have lower energy demand than processes involving the transfer of CO₂ between the mediums used for capture and subsequent reactions. Saline water has been proposed as a potential medium for RCC due to its relative abundance and low cost. Additionally, the composition and chemistry of many saline water sources: 1) elevates the CO₂ content (as compared to atmospheric concentrations), 2) provides various cations that can form valuable products with CO₂, and 3) enhances the kinetics of chemical reactions used to convert CO₂ to stable byproducts. In addition to established industrial processes for converting CO₂ into inert or valuable byproducts, we found 20 new processes and technologies that have been developed specifically to capture and convert CO₂ using saline water. Both preexisting and emerging processes can be broadly classified as electrochemical or chemical titration processes. When assessing the potential viability of applying any of these processes for large scale carbon capture, several factors must be considered, such as the net carbon footprint of the process, the market size, location of customers and value of the end product, the energy demand and chemical costs of the process, and any other environmental impacts. The feasibility of many emerging saline-based RCC processes is difficult to determine, as many technologies were tested using synthetic saline waters and/or concentrated CO₂ sources. Notwithstanding the early stage of development of many saline-based RCC technologies, the major limitation to implementation of this approach to carbon capture is the mismatch in the scale of the markets for products of saline-based RCC and the scale of carbon capture needed to meet climate goals. However, because the products of many of the processes reviewed here are stable and non-hazardous, these technologies may also be used for carbon sequestration efforts where the products are managed as waste, in which case the carbon capture potential of these technologies can surpass the market-imposed limitations on RCC. Thus, the potential benefits of saline water-based RCC identified in this review encourage further study and development of these technologies.

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Introduction

Reducing atmospheric CO₂ is a critical component of mitigating climate change, but reducing emissions alone will not be enough to meet climate goals set by the IPCC¹. In addition, historic carbon emissions will need to be removed from the atmosphere, and at a rapid pace. While there are existing biological and geological processes that can sequester atmospheric CO₂, these processes are too slow to achieve the level of sequestration necessary. Thus, numerous processes have emerged, some of which enhance the naturally occurring carbon sequestration processes, and some of which are novel industrial processes. Among these processes are reactive carbon capture processes, which convert atmospheric CO₂ to value-added products, making the processes more economically favourable. In reactive carbon capture, the reactions that convert the CO₂ to the end product occur within the medium that captures the CO₂. One medium that has been identified for reactive carbon capture is saline water, which often has an enhanced capacity to dissolve CO₂ compared to freshwater, is widely available, and contains numerous chemical components that can react with dissolved CO₂ to form valuable products. While a recent review by Mustafa et al.² summarized technologies that can be used to capture carbon in reject brine, many of the technologies included in that review are not considered here as potential saline-based RCC processes, as they either 1) don't capture carbon directly in the saline water stream but use a product from the saline water to subsequently capture carbon (³, ⁴, ⁵) or 2) don't generate a value-added product directly from the saline water (⁶, ⁷). Here, we will review technologies that have been specifically developed to capture CO₂ using saline water, as well as a number of technologies developed for other purposes that can also be applied to RCC.

To begin, we will discuss the fundamental chemistry of carbon capture in saline water, and then review different saline water sources. Then, we will cover some of the fundamental chemistry of the conversion of dissolved CO₂ to stable chemical products before discussing the variety of technologies that apply this chemistry. Additionally, we will discuss potential products of saline-based RCC, evaluate costs associated with energy and chemical demand, and consider the overall environmental impacts of these processes.

Saline Water as a Sorbent for CO₂

Whereas the majority of conventional, non-biological carbon capture, utilization, and sequestration (CCUS) technologies involve dissolution of gaseous CO₂ into a basic solvent, such as aqueous hydroxides or amines, or absorption with an amine-based solid

sorbent⁸, there are a growing number of technologies that capture CO₂ in saline water⁹. This includes saline-based reactive carbon capture processes (RCC), which use saline water as the medium to both capture and convert CO₂ into a value-added product. As the adsorption/absorption of CO₂ by any medium is often an equilibrium process, the CO₂ capture capacity of both conventional and aqueous-based processes is in part determined by the concentration of CO₂ in the gaseous phase in contact with the solvent and/or sorbent. As the concentration of CO₂ in the gaseous feed stream targeted for capture decreases, the volume of the solvent or sorbent required to capture a given amount of CO₂ increases. The concentration of CO₂ in point source emissions such as flue gas ranges from 3-20%¹⁰, but is only around 420 ppm (0.04%) in the atmosphere¹¹, which makes carbon capture and sequestration from ambient air using conventional technologies difficult due to the large volumes of air and sorbent that would be required. Still, there is a need for processes that can capture and sequester atmospheric CO₂, as at least 40% of global CO₂ emissions are from non-point or mobile sources, and because removing legacy CO₂ emissions inherently requires treating atmospheric CO₂^{8,12}. The abundance and low cost of saline water (in comparison to conventional solvents and sorbents) make it an attractive alternative medium for both CCU in general and RCC in specific.

When gaseous CO₂ dissolves into water, it undergoes a series of rapid acid/base reactions, which leads to the formation of different carbonate species (the distribution of which depends on solution pH and the presence of cations, such as calcium, that can form sparingly soluble species). Because of this, CO₂ concentrations in seawater are at least 140 times larger compared to their atmospheric concentrations¹² (Freshwater CO₂ concentrations are much more variable, ranging from soft waters that contain very little CO₂ to hard waters that can have more than double the CO₂ concentration in seawater¹³). However, the limited availability of freshwater and its value as drinking water makes using these sources for RCC less attractive than saline waters). The elevated concentration of CO₂ in water creates an opportunity for more efficient capture and sequestration of CO₂ from non-point sources. Thus, saline water-based CCU technologies, including RCC, have the potential to play a key role in achieving carbon sequestration equivalent to the 80% reduction in CO₂ emissions called for by the IPCC⁸. RCC technologies make up an important subset of CCU technologies as they directly convert captured carbon into valuable end products and have many potential applications for saline water-based CO₂ capture.

Not only does saline water have the potential to capture large volumes of CO₂ (atmospheric or otherwise) efficiently and inexpensively, but various constituents of saline water can be used to directly convert the dissolved CO₂ into valuable chemical products. Potentially high-value materials in saline waters comprise salts of sodium (Na⁺), lithium (Li⁺), calcium (Ca²⁺), magnesium (Mg²⁺), barium (Ba²⁺), and strontium (Sr²⁺). Additionally, it has recently been demonstrated that some valuable organic products can be directly produced from carbonates and hydrogen present in saline water ¹⁴, (Sullivan et al., Zhang et al. 2023). Processes used to generate either inorganic or organic chemicals from carbonates in saline water can be classified as reactive carbon capture (RCC) processes, wherein the sorbent (saline water) serves both as the medium for carbon capture and conversion to a value-added product. This type of carbon capture process is particularly attractive because it can eliminate the need for downstream CO₂ handling, such as the burial of the concentrated gas in a geological formation, or transfer of captured carbon into another medium used for sequestration, thereby reducing energy demand, process complexity, and cost. An additional potential benefit of using saline water as the source of carbon sequestering cations is the reduction in energy/chemical demand compared to processes that use solid wastes/ores as the cation source for carbon capture ¹⁵.

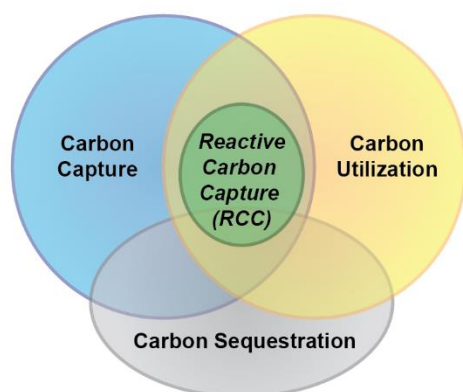


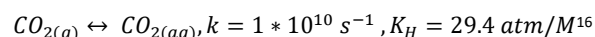
Figure 1. Reactive carbon capture processes involve the capture of gaseous CO₂ and conversion to a value added product within the same medium (for instance, saline water). RCC is inherently a combination of carbon capture and utilization (sometimes referred to as "CCU") but in some instances can also achieve sequestration when the end products are long term stable sinks for CO₂. However, many RCC processes generate products that when used re-release the CO₂.

CO₂ Capture Chemistry

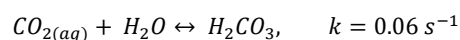
To understand how saline water can be used to efficiently convert atmospheric CO₂ into valuable products, the mechanisms for CO₂ dissolution into water and precipitation out of water must be understood. When a gaseous mixture containing CO₂ is in contact with liquid water, the gaseous CO₂ will reach equilibrium with

various carbonate species in the water ¹⁶. It should be noted that while the gas-liquid phase equilibrium of CO₂ is governed by Henry's law at temperatures and concentrations relevant to most applications reviewed here, the equilibrium between the two phases is not well described by Henry's law for temperatures above 100 °C ¹⁷, or aqueous mol fractions ($X_{\text{CO}_2, (\text{aq})}$) above 2% (~44 g/L) ¹⁸. Water-based RCC technologies operating outside of these conditions would require more careful consideration of the CO₂-water equilibrium.

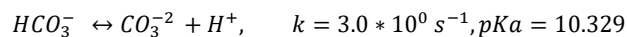
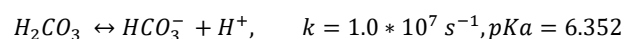
Several reactions govern the aqueous CO₂ system, beginning with the rapid dissolution of CO₂ into water:



Note: All equilibrium constants presented in this section are for standard temperature (25°C and 1 atm) unless otherwise noted. Given pure water at equilibrium with air at standard temperature and pressure and with a CO₂ concentration of 420 ppm_v, the concentration of CO_{2(aq)} in water is approximately 1.42x10⁻⁵ M. This value is lower than the atmospheric concentration of CO₂ (420 ppm_v, ≈ 1.71 x10⁻⁵ M air), but because of the carbonate system, CO_{2(aq)} rapidly transforms to the various carbonate species, which increases the total amount of CO₂ that can be dissolved. Once dissolved, CO₂ hydrates to form carbonic acid (H₂CO₃) ¹⁹.



Carbonic acid then rapidly deprotonates to form bicarbonate and carbonate[16],¹⁹.



The total sum of [CO_{2(aq)}] + [H₂CO₃] + [HCO₃⁻] + [CO₃²⁻] is known as the total dissolved inorganic carbon or "C_T". At a pH of approximately 5.85, the C_T in pure water is equal to the concentration of CO₂ in the atmosphere, while at pH >5.85, the C_T in pure water is greater than to the concentration of CO₂ in the atmosphere. For example, in pure water at neutral pH (7) in equilibrium with air, the formation of carbonic acid, bicarbonate, and carbonate increases the C_T from 1.42x10⁻⁵ M to 8.59x10⁻⁵ M. As the pH of the water increases, the equilibrium of the above equations shifts further to the right, leading to an increase in C_T.

Carbonate System in Saline Water

The dissolution of CO₂ and formation of carbonate species occurs in all waters that are in contact with the atmosphere, such as seawater, surface water, and wastewater. It should be noted that groundwater not in contact with the atmosphere, but in contact with carbonate minerals can also contain carbonate species formed by mineral dissolution ²⁰. The total dissolved inorganic carbon ("DIC", analogous to C_T) in these waters is often higher than in pure water due to the alkalinity of saline waters, so the C_T can even further surpass the concentration of CO₂ in air. The alkalinity shifts

ARTICLE

Journal Name

the carbonate system towards the formation of bicarbonate and carbonate, allowing for further dissolution of CO₂ and effectively increasing the total inorganic carbon content in real waters compared to pure water. For example, in seawater, the C_T is 2.3x10⁻³ M²¹.

The impact of salinity on the aqueous carbonate system can be understood by considering the influence of salinity on the ionic activity of the carbonate species and thus impacting the thermodynamic constants governing carbonate speciation. The equilibrium constants for the formation of HCO₃⁻ and CO₃²⁻ are functions of the ionic activity (" $\{X\}$ ") of the species, which is the product of concentration, and an activity coefficient (γ), which is a function of temperature and salinity. While the thermodynamic equilibrium constant (K^o) is a function of ionic activity, it is common to use a distribution coefficient (K^*) (which is a function of concentration) to describe equilibria.

$$\{X\} = \gamma[X]$$

$$K^* = \frac{[X_{products}]}{[X_{reactants}]} \text{ and } K^o = \frac{\{X_{products}\}}{\{X_{reactants}\}}$$

$$K^* = K^o \frac{\gamma_{reactants}}{\gamma_{products}}$$

The activity coefficients can be calculated using a variety of models, many based off the Pitzer equations for the activity coefficient²², which account for electrostatic interactions and ion pairing in complex solutions. The activity coefficient, and thus activity, of ionic species in water tends to decrease with increasing ionic strength, though this trend does not necessarily hold at high ionic strengths (> 1M)¹⁶. Using the activity coefficients determined for seawater at standard temperature (25°C) with a salinity of 35 g/L, the carbonate distribution coefficients ($pK_1^* = 5.8401$ and $pK_2^* = 8.9636$ ²²) are found to be lower than the constants for the carbonate system in freshwater ($pK_1^* = 6.352$ and $pK_2^* = 10.329$ ¹⁶). The lower pK_a^* values mean that equilibrium favors the formation bicarbonate and carbonate more in seawater as compared to pure water. While this is generally the case for saline waters, the exact value of the equilibrium constants will vary with composition, which should be considered in the design and optimization of saline RCC. As some RCC approaches involve increasing the ionic strength of a saline water either through chemical addition or concentration, more careful consideration of activity coefficients and their impact may be needed in designing these systems, as trends in ionic strength and activity can invert at high concentrations¹⁶.

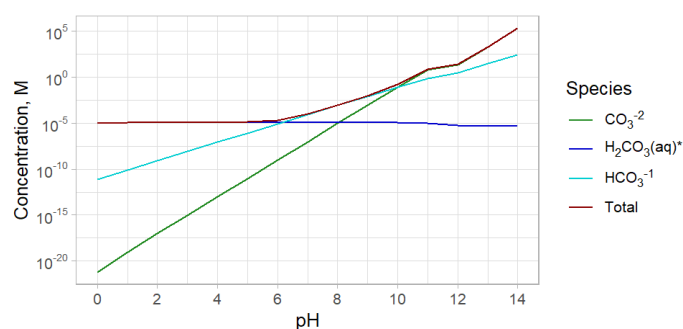
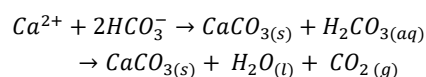


Figure 2. Concentration of carbonate species in seawater (modelled as 0.6 M NaCl) in contact with ambient atmosphere containing 400 ppm CO₂. Note that H₂CO₃* indicates the total of dissolved CO₂ and carbonic acid (H₂CO₃). At near neutral pH, the typical pH of seawater, the dominant carbonate species is HCO₃⁻. Note that the region between pH 11 and 12 has a reduced rate of increase of CO₃²⁻ concentration due to carbonate precipitation.

The elevated CO₂ content of saline waters, the relative abundance of these waters, and the ability to produce valuable end products makes RCC processes using saline water ideal for large-scale CCUS purposes. The elevated concentration of dissolved CO₂ in water (compared to air) makes it easier (by reducing kinetic limitations) to drive chemical reactions²³ that can transform dissolved CO₂ into stable minerals (e.g., CaCO₃) that can permanently sequester CO₂. While solvents and sorbents used in conventional CCUS can have even greater CO₂ capacity (further enhancing sequestration kinetics), these technologies require significant volumes of manufactured media to capture CO₂, rather than using a natural resource such as saline water. Thus, saline water-based CO₂ capture and sequestration can strike the balance between enhancing sequestration kinetics and utilizing an abundant, low-cost medium. In this review, we will cover recent efforts in this area of RCC in saline streams. Because these processes involve the handling of large volumes of water and the modification of various water quality parameters, there are many parallels between RCC and conventional water treatment processes. While these processes were not originally designed and optimized for RCC, we will discuss the extent of carbon capture currently achieved using these processes as well as how the chemistry and process design can be applied more expressly for RCC.

Though saline waters make an ideal medium for capturing and converting CO₂ for the reasons listed above, it should be noted that not all carbonate solid formation results in carbon capture. For instance, precipitation of MgCO₃ or CaCO₃ from saline waters such as seawater, which have the majority of carbonates present as HCO₃⁻, actually can cause a net release of CO₂, as the divalent cation can sequester 2 mol CO₂ as HCO₃⁻/mol cation in the aqueous phase, but only sequesters 1 mol CO₂ as a solid carbonate²⁴.



This can be addressed in one of two ways – adding alkalinity to the saline water source to retain the DIC²⁴, or by avoiding the formation of divalent carbonates and instead designing processes to generate bicarbonate solids such as NaHCO₃. Generally, further discussion below of methods employing divalent carbonate formation for RCC all include some form of alkalinity addition.

Saline Water Sources

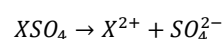
Just as the technologies used for gaseous carbon capture can differ for concentrated point sources versus atmospheric capture, the development of RCC technologies for carbon capture from saline water must take into consideration the composition of the saline water. Water with a total dissolved solids concentration exceeding 10 g/L is classified as saline²⁵; a variety of different water resources fall into this classification, including seawater, some surface and groundwater, and many waste streams and brines. (While some sources classify waters with TDS below 30 g/L as “brackish” and waters with TDS over 100 g/L as “brines”²⁵, here we will refer to saline waters as all waters with TDS over 10 g/L to encompass all potential source waters for saline RCC). The suitability of these sources for RCC applications varies according to the total salinity of the water, its alkalinity, the species of the dissolved solids capable of reacting with carbonates to form value-added products, and whether other constituents in the water can interfere with the RCC process.

Seawater. The overall abundance, relatively high salinity, and carbonate-forming cation content of seawater make it an attractive medium for RCC. The salinity of seawater ranges from about 30 to about 40 g/L globally^{26,27}. The vast majority of salinity in seawaters can be attributed to Na⁺ and Cl⁻ ions, which make up roughly 86% (wt/wt) of the total dissolved solids in seawater²⁶. Other major ionic species include SO₄²⁻, Ca²⁺, Mg²⁺, K⁺, and HCO₃⁻ (as the pH of seawater is ~8.2, HCO₃⁻ is the dominant carbonate species). While the overall salinity of seawater varies globally due to effects of precipitation and evaporation, the ratio of many of the ionic species within seawater is nearly constant²⁷. This is particularly relevant to RCC processes using seawater as a source of carbonate forming cations such as Ca and Mg. The Mg:Ca ratio in seawater is considered as semiconservative throughout the ocean, ranging between 4.9 – 5.3 mol/mol²⁸. While the formation of CaCO₃ is kinetically favorable under standard conditions compared to the formation of magnesium-containing carbonates (such as magnesite (MgCO₃) and dolomite (CaMg(CO₃)₂)²⁹, RCC processes that can overcome this barrier to produce magnesium carbonates would theoretically be able to sequester up to 5 times as much carbon as processes that solely produced calcium carbonates due the greater concentrations of magnesium in seawater (again noting that alkalinity addition would be required in either case to prevent net CO₂ release). Similarly, as sodium is approximately 45 times as concentrated as Ca and 9 times as concentrated as Mg in seawater²⁶, processes that use Na to sequester carbon (as NaHCO₃) can further increase the total carbon sequestration potential (and would not require alkalinity addition to achieve net carbon

capture). Obviously, the viability of mineral precipitation as a form of RCC is tightly linked to the solubility of the mineral. As such, the highly soluble NaHCO₃ ($K_{sp} = 2.82 \times 10^{-1}$) would require the seawater to be dramatically concentrated to induce its precipitation. It should be noted that the viability of RCC processes relies not only on the carbon sequestration potential but on the value of the products generated, as will be discussed in greater depth later in this review.

Another factor of seawater composition that impacts the design of RCC processes utilizing seawater is the ratio of carbonates relative to various carbonate-forming cationic species. Carbonates (primarily as HCO₃⁻) are significantly less abundant (more than 250 times lower²⁶) than the dominant anion in seawater, chloride, which serves as the counterion to the vast majority of the cations in seawater. As a result, there are more cations capable of forming solid carbonates than there are dissolved carbonates in seawater. This can be understood by considering the differing sources of ions in seawater. Ca, Mg, and many other metals found in seawater enter the oceans via dissolution of terrestrial minerals, which are then transported through runoff or river flow to the ocean²⁸. Meanwhile, DIC in seawater is primarily a result of CO₂ dissolution across the gas/water interface between the ocean and the atmosphere³⁰. Since these are distinct processes, the amount of carbonate species present in seawater does not directly correlate to the amount of carbonate-forming cations, as would be the case if the ionic species were formed by the direct dissolution of a carbonate minerals. For instance, the concentration of Ca and Mg ions are roughly 5 and 25 times greater, respectively, than the concentration of carbonates (as HCO₃⁻) on a mol basis²⁶. As a result, RCC processes can be designed to increase the concentration of carbonate species relative to the concentration of various cations, such as by contacting the seawater with a CO₂-rich gaseous or aqueous stream, which can increase the potential amount of carbon capture beyond the amount of DIC naturally present in seawater, if sufficient alkalinity is present to facilitate additional CO₂ dissolution into the water.

A final aspect of seawater composition that is relevant to RCC are constituents of the water that may interfere with RCC processes. These include ions that are not directly relevant for carbon capture, but which can impact the RCC process. For instance, sulfate (SO₄²⁻) is 13 times more concentrated in seawater than HCO₃⁻ on a mol basis²⁶, and forms solids with many ions present in seawater, such as CaSO₄ ($K_{sp} = 4.93 \times 10^{-5}$), SrSO₄ ($K_{sp} = 3.8 \times 10^{-7}$), and BaSO₄ ($K_{sp} = 1.1 \times 10^{-10}$). (K_{sp} values for dissociation reaction of metal sulfates “XSO₄” as shown below).



For RCC processes designed to generate CaCO₃ ($K_{sp} = 2.8 \times 10^{-9}$) from seawater³¹, the formation of CaSO₄ is unlikely to consume Ca ions as its solubility product is over 10⁴ times greater than CaCO₃ (meaning it would require much greater concentrations of Ca and/or SO₄²⁻ to precipitate than CaCO₃). While the solubility products of SrSO₄ and BaSO₄ are much lower than CaSO₄ (increasing

their tendency to precipitate), Sr and Ba are present at much lower concentrations than other major cations (Na, Mg, Ca) in seawater²⁶, reducing the likelihood of formation of these solids. However, as many emerging RCC processes involve a concentration step to improve the kinetics of product formation, the impact of increased concentrations on the saturation of other precipitating species needs to be carefully considered in process design. This is particularly relevant for membrane-based RCC processes, as concentration polarization at the membrane/water interface can lead to precipitate formation (scaling), which results in significant losses in process efficiency³¹. In other RCC processes, the major issue posed by the formation of non-carbonate precipitates is the reduced purity of the desired product.

Other seawater constituents beyond dissolved solids which can impact the viability of seawater-based RCC process include dissolved organic matter (known as “dissolved organic carbon”, “DOC”), as well as larger suspended organic and inorganic matter (known as “total suspended solids,” “TSS”). These constituents can contribute to clogging, surface fouling, and deterioration of system components, reducing efficiency and increasing operational costs. TSS are defined as aqueous constituents that are removed by a 0.45 µm filter, while DOC represents the organic fraction that passes through the filter. DOC concentrations vary throughout the ocean, typically ranging between 30-80 µM³². DOC concentrations fall at the higher end of this spectrum in coastal waters³², an important consideration in locating systems for seawater-based RCC, as organic matter can cause fouling on system surfaces, reducing process efficiency³³. Studies of organic fouling in seawater reverse-osmosis processes have shown that the formation of an organic foulant layer on membrane surfaces is exacerbated by the presence of divalent cations³⁴, which is particularly relevant to RCC processes that increase the concentrations of these ions to improve carbon-capture kinetics. Various pretreatment technologies, such as screening and filtration, are available to remove TSS and DOC from seawater³³ prior to RCC processes sensitive to the presence of these constituents. In addition, drawing seawater from beach wells, rather than relying on an open ocean intake, has been shown to dramatically reduce DOC concentrations [35]. However, the cost of pretreatment/beach well intake and any impacts on carbon capture capacity should be considered when evaluating the feasibility of using seawater for the RCC process.

Other Surface Waters. While seawater is by far the most abundant saline surface water on the planet, some other surface waters are saline with appreciable concentrations of hardness, such as inland salt lakes. The average salinity of these waters is 39.4 g/L TDS, but inland salt lakes vary in salinity much more than seawater, ranging in concentration from 10 g/L TDS (the minimum to be considered here as “saline”) to above 100 g/L TDS³⁵. The major ionic species in many inland saline lakes are largely the same as the major ionic species in seawater – cations Na⁺, Ca²⁺, Mg²⁺, along with anions Cl⁻ and SO₄²⁻³⁶. The relative proportion of these ionic species is less conservative than in seawater, as the chemical composition of the

surrounding geology largely determines the chemical composition of salt lakes³⁵. Though typically lower in concentration than the dominant anions, carbonates are also present in salt lakes due to equilibrium with the atmosphere. As with seawater, the underabundance of carbonate species relative to cationic species capable of forming carbonate precipitates makes these waters an attractive medium to capture and convert CO₂ into valuable solid products.

Though the composition of some inland salt lakes may lend themselves to the chemistry of RCC processes, the actual availability of inland saline waters may limit their viability for meaningful carbon capture efforts. Even if all inland saline waters were available for RCC purposes, they account for only 0.9% of all water on Earth, whereas seawater accounts for 96.5%³⁷. However, only a much smaller portion of this already relatively small volume of available inland saline water would be likely to be usable, as these waters often host ecosystems that are sensitive to changes in volume and/or composition of the water body³⁶. Additionally, the presence of dissolved solids, dissolved organics, and suspended solids in surface waters poses similar challenges to RCC applications as described previously for seawater.

Groundwater. Groundwater often contains higher concentrations of dissolved carbonates compared to seawater. Because these carbonates come from mineral dissolution and will not be released to the atmosphere so long as these waters are not in contact with the atmosphere, the carbon dissolved in these waters does not require further sequestration efforts. However, groundwaters with high salinity and low carbonate content (i.e., contain elevated concentrations of non-carbonate hardness) may allow for further carbon capture. Indeed, one approach to CCUS is to pump groundwater to the surface, saturate it with carbonates, and return it to the aquifer for long-term storage³⁸. Alternatively, supercritical CO₂ can be injected into deep saline aquifers where the CO₂ reacts with hardness to form stable carbonate minerals³⁹. However, while the injection of CO₂ into saline aquifers can effectively sequester CO₂, this approach does not typically generate any useful value-added product, and thus should not be considered as an RCC approach.

Some groundwater resources are rich in valuable elements⁴⁰, and there is precedent for extraction of saline groundwater to recover valuable constituents such as lithium⁴¹ in the form of lithium carbonate. A large percentage of global lithium production comes from the mining of brines in South America⁴². In North America, there is a significant effort to extract lithium from lower-quality brines, such as produced water from oil and gas extraction and geothermal brines used for power generation⁴⁰. These North American brines are very rich in calcium. For example, Smackover brines (generated from the oil and gas fields of southern Arkansas) have calcium concentrations as high as 1 M, making them attractive for RCC⁴³. Importantly, these brines are already being brought to the surface – a byproduct of other industries, potentially reducing the overall cost of the RCC. The extent to which this type of reactive

carbon capture could be applied to produce other products is likely an economic question, as the lesser value of other carbonate products may not be sufficient to justify the extraction of groundwater, which can be energy and cost-intensive.

While it is difficult to quantify the volume of saline groundwaters worldwide, approximately 16% of the total land area on earth has underlying saline water at depths of 500 m or less ⁴⁴, indicating that this is a potentially vast resource. (Note that groundwater exists at depths below 500 m, but is typically only extracted as a byproduct of oil and gas production ⁴⁵, which is covered in the subsequent section on wastewater.) As with surface waters, understanding the source of salinity in these waters informs the chemistry of these waters and thus their suitability for RCC. The majority of these waters became saline either through evaporation of surface water, dissolution of formation minerals, a combination of evaporation and dissolution, or saline water was present at the time the aquifer geology was formed ("connate water") ⁴⁴.

Due to variations in the source of groundwater salinity, there is significant variation in the TDS of different groundwaters – for example, saline aquifers are reported to have salinities ranging from <50-340 g/L TDS in Israel ⁴⁶, 10-350 g/L TDS in China ⁴⁷, and 10-300 g/L TDS in the United States ⁴⁸. While the ionic composition of groundwater is also variable, major ions found in groundwater typically include Na⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻ ⁴⁹. As with saline surface waters, the overabundance of cations that can form carbonate precipitates relative to the DIC in groundwater indicates the potential for processes that can capture additional CO₂ as solid minerals.

As NaCl is the major constituent of saline groundwaters (which typically have lower TSS and DOC contents compared to surface waters ⁵⁰), fewer process modifications and pretreatment steps may be needed to remove these constituents to enable the use of saline groundwater for RCC as compared to other potential saline water sources. However, as with other water sources, the presence of other precipitating ions may interfere with RCC purposes. Because groundwaters have varying ionic compositions, the potential for formation of competing precipitates such as CaSO₄ should be evaluated on a source-by-source basis.

One additional constituent that can inhibit the utilization of these waters for RCC is naturally occurring radioactive materials (NORM) present in some groundwater. While the prevalence and distribution of NORM in groundwater is difficult to assess, monitoring of groundwater in the US has found many regions where groundwater contains radionuclides of radium and uranium at levels above 5 and 10 pCi/L, respectively ⁵¹. Uranium is most mobile in low TDS, carbonate-rich groundwaters, whereas radium is more mobile in high TDS, chloride-dominant groundwaters ⁵¹, making radionuclides of radium more likely to occur in groundwaters targeted for RCC. Additionally, it should be noted that water treatment methods including electrodialysis and lime softening have been applied to remove up to 90% of radionuclides

from groundwaters ⁵¹, capturing the NORM as a liquid concentrate or in a solid sludge, respectively. While this is useful for water treatment purposes, it raises concerns about RCC processes, which a) use electrodialysis to concentrate carbonate-capturing cations, or b) use precipitative softening to react cations with carbonates to produce solids. In both cases, the radionuclides could become concentrated in the product, rendering it radioactive, and complicating its further use or disposal.

Wastewater. A variety of industries including agriculture, food processing, water treatment, oil/gas production, mining, and chemical production generate significant volumes of saline wastewater. The composition of the wastewater varies much more than in naturally occurring saline waters, with typical TDS reported between 2 and 100 g/L depending on the specific industry and process generating the wastewater ⁵², and even higher salinities of up to 400 g/L reported for specific industries such as oil and gas production ⁵³. It is worth noting that the high salinity wastewaters from the oil and gas industry are typically "produced waters" extracted from oil- or gas-bearing formations, making them akin to groundwater sources. However, for this review, they are considered as wastewater, as they have already been brought to the surface, may contain significant levels of contaminating process chemicals, and often require some degree of treatment prior to discharge or reinjection ⁵⁴. A more detailed discussion of waste brine composition by industry can be found in numerous previous reports (^{52,53,55}); here we will briefly discuss the concentration of ions important in RCC processes (Na⁺, Ca²⁺, and Mg²⁺) and the presence of other wastewater constituents, which may impact the suitability of the water for RCC.

Wastewater which typically contains Na⁺ and Ca²⁺ concentrations equal to or greater than the concentration of seawater (~0.4 M Na and 0.01 M Ca²⁶) include desalination brines, landfill leachates, flue gas desulfurization effluent, and wastewaters from the dairy and oil and gas industries ⁵³. Similarly, desalination brines, flue gas desulfurization effluent, and wastewater from the oil and gas industry have typical Mg²⁺ concentrations equal to or greater than in seawater ⁵³. While the Na⁺, Ca²⁺, and Mg²⁺ in less concentrated wastewater could still be used for RCC processes, it is useful to consider seawater as a gauge to determine which wastewater provides a similar or greater carbon capture potential than this low-cost, abundant saline water source. Bicarbonates found in oil and gas wastewater, desalination brines, and municipal wastewaters, and carbonates found in pharmaceutical wastes are all present at concentrations much lower than concentrations of carbonate-forming cations, presenting similar carbon capture potential as in other carbonate-depleted saline water sources reviewed here.

While some wastewaters have high salinity levels, which make them attractive for use in RCC, they can also have high levels of DOC and TSS, and may contain hazardous or toxic materials ⁵⁵, making them unsuitable for reuse in RCC processes without additional pretreatment. DOC and TSS can be removed from saline wastewater using a variety of treatment methods, with filtration

methods potentially being suitable here as they can reject larger particulates and organic compounds found in saline wastewater⁵⁵ while allowing the passage of the ions that can be used in RCC. However, some hazardous contaminants in saline wastewater, such as heavy metals⁵⁶, cannot be easily separated from other salt ions during filtrations and would require more careful process design to ensure that any products generated during RCC would not be contaminated. Precipitative processes using elevated pH to generate Ca, or Mg solids would require such process design, as many heavy metals readily precipitate at lower pH than these solids¹⁶.

Despite some wastewater requiring pretreatment to make their composition suitable for RCC processes, there are still compelling cases for using at least some wastewater in RCC. Wastewater is unique amongst saline water sources for RCC in that many of these sources must already undergo some treatment processes prior to discharge or disposal, so additional processing to capture carbon may be integrated with these processes. For instance, one of the common treatment objectives for high-salinity wastewater is TDS reduction⁵². This provides the opportunity to synergistically pair RCC processes that remove dissolved solids through the formation of solid carbonate species with desalination operations, effectively lowering the TDS and minimizing surface scaling while producing valuable carbonate solids. Some wastewater treatment processes, such as precipitative softening, already convert carbonates into solids⁵⁷, lending themselves to modification for RCC purposes. However, the extent to which RCC efforts can be integrated with existing treatment infrastructure will be determined by the ability to meet the required level of treatment (for all contaminants of concern, not just TDS) while also achieving a meaningful level of carbon capture⁵⁸.

Synthetic Saline Waters. Many of the RCC technologies discussed in this review were demonstrated using synthetic rather than real saline waters (a summary of the saline water composition used in each technology demonstration included in this review can be found in Table 3). The carbon capture potential and energy demand of many systems is inherently linked to the composition of the saline water source. Therefore, this is a critical area for research needed to evaluate the real-world implementation of saline-based RCC. NaCl solutions were the most commonly used synthetic saline water, particularly for systems producing NaHCO₃ and/or Na₂CO₃^{59 60 61 62}. Many of these systems simply used 1 M NaCl to demonstrate the process, limiting the fidelity of their results to scenarios using real saline waters. Concentrations of Na may be lower (as in seawater) or much higher (as in waste brines) than the tested concentration. For many of these systems, characterization of the CO₂ capture potential and energy demand across various concentrations is a reasonable next step in assessing the feasibility of applying these technologies at scale. Systems used to produce CaCO₃ and/or MgCO₃ often used synthetic seawater or wastewater, typically containing Na, Ca, Mg, K, and Sr cations with Cl⁻ and SO₄²⁻ anions^{48 63 64 65}. The concentrations of the ions in these solutions

were representative of the saline water source they were intended to model. As a result, the demonstrated carbon capture potential and energy demand of these technologies are likely more representative of their performance when applied at scale.

Beyond the impact of the saline water composition on carbon capture potential and energy demand, operational considerations such as equipment scaling/damage and product purity are impacted by the composition of the saline water source. Concerns related to the composition of different saline waters are discussed in the preceding sections. However, these concerns have not been addressed for many of the technologies discussed in this review. For technologies where these concerns were assessed, discussions of their impacts can be found in the following sections on each specific technology.

CO₂ Conversion Processes

Various chemical processes can be used to capture carbon and generate valuable products using saline water. Here, we will discuss the underlying chemistry by which these processes convert carbon to a stable product. Additionally, we will review actual processes and technologies used to achieve saline-based RCC. The technologies and processes are divided into processes that are currently in development, as these are being optimized for CO₂ capture, and established processes that were developed and optimized for purposes other than CO₂ capture with saline water but have the potential to be optimized for RCC.

CO₂ Conversion Chemistry

Carbon Capture in Saline Water. Water-based RCC methods require a step to convert CO₂ dissolved in water into a product to effectively capture atmospheric CO₂. This is because most saline waters (apart from groundwater) are naturally at equilibrium with atmospheric CO₂, so in order to further dissolve atmospheric CO₂, equilibrium must be shifted by either 1) removing dissolved carbonates, 2) contacting the water with gases containing elevated CO₂ concentrations, or 3) increasing the carrying capacity of water by increasing alkalinity. Dissolved carbonates can be removed by the formation of inorganic products (or, to a lesser extent, organic products such as formic acid or simple alkanes) products through reaction with other species present in the water. Note that when divalent cations are used to form carbonate solids (i.e. CaCO₃) from waters where the carbonate species is HCO₃⁻, it is essential to increase the alkalinity to prevent a net release of CO₂.

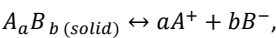
Formation of products from the DIC in saline waters temporarily decreases the concentration of dissolved carbonates, allowing the water once in contact with the air to absorb more atmospheric CO₂, driving the carbon capture process. In conditions where the bulk CO₂ partial pressure is effectively constant (i.e. the atmosphere), the total amount of CO₂ is also maintained at a constant concentration, following Henry's law. As such, when some of the dissolved CO₂ converts to HCO₃⁻ and CO₃²⁻ to maintain equilibrium,

more CO₂ will then dissolve, satisfying equilibrium with the bulk gas phase. If a saline water is maintained in a nonequilibrium state (i.e. carbonate solids are continuously precipitated and removed), such reactions can continue until available reactants in the saline water source are consumed through the product formation process. Thus, if the correct conditions (i.e. pH, temperature) are maintained, the carbon-capture potential of saline waters extends beyond their initial DIC concentration (e.g., by bubbling air or other CO₂-containing gas through the water) and is ultimately determined by the concentration of reactants other than CO₂. However, such a process would be limited by the DIC concentration, which is determined largely by the concentration of CO₂ in the gaseous phase¹⁶. Thus, contacting waters with gaseous streams containing elevated CO₂ concentrations is a straightforward way to capture additional CO₂ more efficiently in the aqueous phase. To prevent equilibrium shifting back and re-releasing CO₂, sufficient alkalinity must be present in the aqueous stream. This is particularly critical for systems removing divalent carbonate solids (CaCO₃, MgCO₃). Below we will summarize the chemical reactions that can effectively convert DIC, whether dissolved from the atmosphere or a CO₂-concentrated gas, into stable products, thus enabling RCC.

Inorganic Product Formation. Once CO₂ has been captured in a saline water stream, it can react with various cations present in the water to form stable precipitates and thus generate valuable solid materials. Various factors impact both the rate and total amount of carbonate solids formed precipitation, including the concentration of species forming the desired precipitate (carbonate species and various cations), the presence of competing anions, as well as the pH, temperature, and pressure of the medium in which precipitation occurs, each of which will be briefly discussed below.

The formation of precipitates is governed by equilibrium between the solid and dissolved ionic phases. For a solid precipitate to form, ion activity potential (IAP) of the species forming the solid must be greater than the solubility product (K_{sp}) of the solid¹⁶. (The solubility product of various carbonate solids is listed below in table 1)

For the reaction



$$IAP = \{A\}^a\{B\}^b$$

$$K_{sp} = \{A\}_{eq}^a\{B\}_{eq}^b$$

It should be noted that many solids will not begin to precipitate until the IAP greatly exceeds the K_{sp} (i.e. the solution becomes supersaturated with respect to this solid). For instance, seawater is already oversaturated with respect to both CaCO₃ and MgCO₃ by a factor of 2, but additional concentration or other processing is required to induce precipitation⁶⁶. Some processes can reduce the degree of oversaturation required for solid formation by reducing thermodynamic barriers to solid formation. However, even when oversaturated and thermodynamically favoured, some carbonates,

such as MgCO₃ are still extremely slow to form – see following discussion on the kinetics of carbonate formation. The dissociation constants for various carbonate solids (XCO₃ or XHCO₃) are included below in Table 1, for generic dissociation reactions shown below.

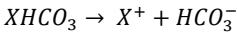
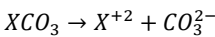


Table 1. Solubility Products of Various Carbonates		
Solid	Ksp (STP)	ref
BaCO ₃	2.58x10 ⁻⁹	67
CaCO ₃	2.8x10 ⁻⁹	67
CaCO ₃ (calcite)	3.36x10 ⁻⁹	67
CaCO ₃ (aragonite)	6x10 ⁻⁹	67
CaMg(CO ₃) ₂ (dolomite)	1x10 ⁻¹¹	67
MgCO ₃	6.82x10 ⁻⁶	67
MgCO ₃ ·H ₂ O	2.38x10 ⁻⁶	67
Na ₂ CO ₃ ·10 H ₂ O	4.9x10 ⁻²	68
NaHCO ₃	2.82x10 ⁻¹	69
LiCO ₃	2.5x10 ⁻²	67
KCO ₃	5.01x10 ⁻⁴	69
SrCO ₃	5.6x10 ⁻¹⁰	67

As carbonate is rarely the sole anion present in saline waters, it is important to also consider other solids which can form from saline waters, as they may either reduce the efficiency of an RCC process or diminish the purity of the generated products, as noted in the discussion of competing ions present in saline water sources. For instance, many cations readily form solids with hydroxides¹⁶. As hydroxide ion addition is used to increase alkalinity (and drive the carbonate system equilibrium towards elevated concentrations and CO₃²⁻ speciation), it is possible that this alkalinity is consumed through the formation of relatively insoluble species such as Mg(OH)₂²⁹. The dissociation constants for various hydroxide solids (XOH or X(OH)₂) are included below in Table 2, for generic dissociation reactions shown below.

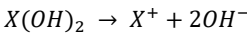
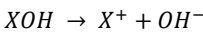


Table 2. Solubility Products of Various Hydroxides		
Solid	Ksp (STP)	ref
Ca(OH) ₂	5.5x10 ⁻⁶	67
Fe(OH) ₂	4.87x10 ⁻¹⁷	67
Mg(OH) ₂	5.61x10 ⁻¹²	67

Another major consideration for RCC processes based upon precipitation is the rate of precipitate formation.

$$K_{eq} = \frac{\{Products\}^p}{\{Reactants\}^r} = \frac{k_{forward}}{k_{backward}}$$

Should the rate of precipitation be lower than the rate of competing reactions, inhibition of production formation could occur. For instance, in many waters the rate of precipitation of $\text{Mg}(\text{OH})_2$ can be greater than the rate of precipitation of CaCO_3 ¹². The formation of $\text{Mg}(\text{OH})_2$ reduces solution pH, shifting carbonate equilibrium away from CO_3^{2-} and thus can inhibit the formation of CaCO_3 . In some waters, this can be prevented by maintaining solution pH above the pH needed for CaCO_3 formation but below the pH for $\text{Mg}(\text{OH})_2$ formation – de Lannoy et al. achieved this separation by maintaining pH between 9.3–9.6 in synthetic seawater¹². However, in other waters, such as the synthetic seawater used by Xie et al., $\text{Mg}(\text{OH})_2$ precipitated first around a pH of 10, with CaCO_3 precipitating later at a pH of 12.3¹⁵. Again, this demonstrates that a thorough understanding of solution composition as well as the reaction kinetics relevant to precipitate formation aids in designing or optimizing RCC processes.

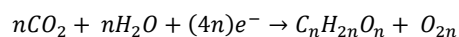
Even without the impact of competing ions, some carbonate minerals are still slow to form, such as MgCO_3 . For these kinetically hindered carbonates, increasing the temperature and/or pressure can enhance the rate of precipitation⁷⁰, but may incur an energetic cost that outweighs the carbon capture potential. Researchers have identified understanding and enhancing the kinetics of carbonate formation under ambient conditions as a critical topic for further study to aid the development of carbon capture technologies⁷⁰. It should be noted that at the time of this review, even within reviews focused on aqueous mineral carbonation, discussion of mineral carbonation kinetics primarily focused upon dissolution of Ca or Mg rich minerals, rather than on formation of mineral carbonates⁷¹. RCC using saline water largely avoids these kinetic limitations by utilizing the ions already dissolved. Additionally, in the specific case of magnesium carbonates, several hydrated phases have more favourable kinetics and thus form more readily under ambient conditions (i.e. nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) or hydromagnesite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$))⁷⁰. Whether designing processes which produce more readily precipitated forms of a carbonate (either with or without post-processing to convert to the desired carbonate product) are viable for saline-based RCC is a techno-economic question, influenced by the relative value of the various phases of the carbonate and the energy demand required to generate the desired phase.

Overall, the formation of inorganic carbonate solids from saline solutions is at first a seemingly straightforward precipitation reaction. However, when considering complex saline water sources with varying chemical compositions, the concentration and solubility of each constituent must be considered. Carbonate-forming cations with low solubility and/or high concentrations are generally good candidates for carbon sequestration via precipitation. Additionally, carbonates with favourable kinetics under ambient conditions are favourable, as they can rapidly form without incurring additional energetic cost.

Organic Product Formation. The formation of organic compounds from CO_2 is typically a biological process, falling out of the purview

of saline-based RCC processes discussed here, which convert chemical constituents in saline water into the end product. While there are biological carbon capture processes that occur in saline water, the carbon conversion reactions typically occur within the organisms such as algae or seagrass rather than in the bulk saline water, thus excluding these from the classification of saline RCC processes, which involve direct conversion of carbon in saline water. Hence, further discussion of biological carbon capture processes is left out of this review and can be found in numerous other reviews of carbon capture technologies^(10, 72, 73). However, some technologies have emerged that specifically convert DIC in saline water into organic products, which are included in this review^(14, 74, 75, 76).

To convert CO_2 into an organic product, the carbon must be reduced from a valence state of +4 to 0, requiring an energy source to provide electrons to the reaction⁷⁷.



While many carbon capture technologies rely on autotrophic organisms to facilitate this reaction (i.e. through photosynthesis), this process can also be driven electrochemically, as reviewed later in this section.

Processes Designed for Reactive Carbon Capture

As capture and conversion of CO_2 has emerged as an important objective towards mitigating climate change, focus has increased on RCC processes, including those that utilize saline water. To begin, we will discuss the technologies that have been specifically developed for carbon capture and conversion into a valuable product using saline water. As these saline-based RCC processes are an emerging carbon-capture approach, there are a limited number of technologies that currently fall into this category. However, many preexisting technologies and processes achieve some degree of CO_2 capture via saline water, though this is not the express intent of these technologies. Because of the pressing need for CO_2 capture and the massive potential benefits of saline-based RCC processes outlined in this review, it is worthwhile to discuss how these technologies that have not been specifically developed for saline-based RCC can be modified to optimize CO_2 capture and utilization – see the subsequent section, “Reactive Carbon Capture Using Pre-Existing Technologies and Processes.”

Chemical Titration Processes. Some emerging RCC processes produce carbonate solids by directly adding chemicals to saline water. Two main approaches emerge – the addition of chemicals to increase pH and shift equilibrium towards carbonate formation, and the addition of CO_2 to increase saturation and enable precipitate formation. Depending on the composition of the saline water source, either or a combination of both approaches can be used – as carbonates are typically undersaturated in saline water sources, most processes at least involve the dissolution of additional CO_2 to enable precipitation. Because the formation of carbonate precipitates via chemical addition has long been employed, current

studies of these approaches generally involve investigation of process optimizations, such as the order of chemical addition, method of CO₂ delivery, or reduction of thermodynamic barriers via addition of catalysts or “seed” substances.

Though processes that use saline water to convert CO₂ to a solid precipitate via chemical addition have existed long before interest in carbon capture, some aspects of these systems that are critical to optimizing carbon capture, such as the rate of carbonate formation and % conversion of cationic species to solids, have only recently been studied. For instance, De Vito et al.⁷⁸ monitored the rate of precipitate formation in a system designed to produce carbonate solids by bubbling CO₂ in a brine solution, finding that the concentration of the saline water impacted the carbonate formation rate and process. Their system provided pure CO₂ bubbles to a synthetic MgCl₂ brine at concentrations between 7 and 32 g/L, achieving nearly 100% conversion of the Mg to carbonate precipitates (primarily nesquehonite, MgCO₃·3H₂O) in time frames ranging from 10 minutes to 30 days, respectively. This is an interesting result because typically increasing the concentration of the precipitate-forming species increases the rate of precipitation, whereas in this study, the lowest concentration solution achieved the most rapid carbonate formation. This suggests that the reaction may have been limited by CO₂. If so, this has several implications for the development of precipitative processes for carbon capture – first, methods to improve CO₂ dissolution (such as the use of microbubbles⁷⁹) are likely to be important to achieving rapid and scalable saline-based RCC; second, RCC processes capturing CO₂ from more dilute sources than the pure CO₂ gas used by De Vito et al. will be even further rate-limited by the lower CO₂ concentrations, again pointing to the need to enhance dissolution; and third, there may be instances in which the kinetic benefits of pre-concentrating the saline water prior to carbon capture provide little benefit, as the reaction is limited by the concentration of CO₂ rather than by the concentration of cationic species.

Many emerging saline-based RCC processes that utilize chemical addition to induce precipitation, such as the one demonstrated by Bang et al.⁷⁹, feature novel approaches to adding CO₂ to the saline water to enhance carbon capture. In their system, real brine from a seawater desalination facility was repeatedly cycled through pH adjustment with sodium hydroxide (NaOH) followed by contact with CO₂ microbubbles and filtration to collect precipitates. Adding base to solutions has two impacts relevant to precipitative carbon capture, as previously discussed – first, it raises the pH, shifting the carbonate equilibrium towards formation of CO₃²⁻, thus improving the kinetics for carbonate precipitation, and second, it increases the concentration of OH⁻, which can increase the formation of hydroxide precipitates. The formation of hydroxide precipitates may seem counter to the objective of carbon capture, as it sequesters cations in hydroxide solids that may otherwise be able to form carbonate solids. However, Bang et al. found that in the instance of magnesium, the formation of hydroxide solids prior to contact with CO₂ microbubbles facilitated the formation of magnesium carbonate, achieving 86% conversion of Mg in the brine

to carbonate solids, along with 99% conversion of Ca. While this study did not consider the % conversion of CO₂ to carbonate solids or the rate of CO₂ capture, it provides a useful demonstration of the principles of precipitative CO₂ capture and highlights how the interactions of different cationic species in real saline waters can impact the overall carbon capture potential of these processes.

Additionally, it should be noted that this process and the one demonstrated by de Vito et al. achieve net carbon capture by adding CO₂ to a solution that is undersaturated with respect to carbonates. This is because these approaches use additional CO₂ to drive the formation of carbonate solids rather than simply precipitating carbonates that were already present in the saline water and releasing CO₂ in the process. (It should be noted that simply dissolving the CO₂ to form aqueous HCO₃⁻ would result in greater CO₂ capture (2 mols CO₂ per mol Ca or Mg, versus 1 mol CO₂ per mol when forming solids), but this approach does not yield saleable products and thus falls out of the purview of our discussion of RCC technologies.

While RCC processes achieving carbon capture by chemical titration like those demonstrated by De Vito et al. and Bang et al. seek to optimize the conversion of carbon to an end product (% CO₂ converted) and the rate of conversion (CO₂ converted/time), an additional optimization is likely required to make carbon capture via chemical addition viable from a carbon accounting perspective. Life cycle analyses completed by Beeftink et al. found that the amount of carbon sequestered during conventional precipitative processes like drinking water softening – 0.95 kg CO_{2eq} per person per year, equivalent to 84 kg CO_{2eq} per million gallons (MG) treated water – offset only about 20% of the carbon footprint of the energy and chemicals used for the process⁸⁰. However, their analysis showed that when considering downstream impacts of drinking water softening, such as improved household appliance efficiency and reducing scaling in pipes and appliances, precipitation processes had a net negative carbon footprint of -1.93 kg CO_{2eq} per person per year or -170 kg CO_{2eq} per MG treated water⁸⁰. Thus, if precipitation-based processes are to be applied for carbon sequestration purposes through RCC, the energy and chemical demand will need to be reduced or the process will need to be paired with applications where softening can improve downstream efficiency to maintain a carbon negative footprint. The main approach reported for reducing the carbon footprint of chemicals used in water softening is through electrochemical generation processes, covered in subsequent sections. Other novel approaches to improving the net carbon capture capacity of processes that can be applied for saline-water based RCC are covered below.

One way to reduce the energy demand of precipitative RCC processes is to reduce the thermodynamic barriers to precipitate formation. Lowering the saturation index (SI) required for precipitation to initiate means, for example, less energy needs to be spent to concentrate the saline water to the necessary SI. Burhenne et al.⁸¹ demonstrated the application of a bench-scale fluidized bed pellet reactor that precipitated CaCO₃ from a feed of K₂CO₃

generated from atmospheric CO₂. While K₂CO₃ is not an ideal representative solid of most saline waters (even after contact with concentrated CO₂) due to the elevated solubility of K₂CO₃ compared to other carbonate salts, this process provides a critical demonstration of the impact of seeding material on carbonate precipitation, which can be applied to other carbonate species (e.g., CaCO₃) precipitation from saline waters.

Another way to improve the thermodynamics of precipitate formation is by using a catalyst. Dindi et al. modified the Solvay process for producing NaHCO₃ (discussed in further detail in following subsection) to utilize desalination brine as both the sorbent for CO₂ capture and the source of Na⁺ ions for the process. In this process, an amine-based solvent is added to the brine prior to contact with CO₂ in flue gas. As the CO₂ dissolved into the brine, it forms carbamates with the amine, which can then react with sodium in the brine to form NaHCO₃. This process provides an important advantage over more conventional amine-based CO₂ capture processes, as the use of brine as the bulk sorbent solution allows for the removal of absorbed CO₂ through precipitation, shifting equilibrium to allow further absorption of CO₂. The authors evaluated multiple amine catalysts and ultimately found that the optimal CO₂ absorption, salt removal, and NaHCO₃ production were achieved using 30% 2-amino-2-methyl-propanol (AMP) mixed with the brine. While the process was successfully demonstrated for synthetic brines at concentrations typical of desalination brines (0.85 M NaCl), as well as at both lower and higher concentrations (0.6 - 1.8 M NaCl), the authors noted that similar studies found that the increased ionic strength of the brine has been reported elsewhere to limit CO₂ absorption capacity. Absorption capacity was not evaluated in this study but is an important factor for process design and viability, and further development of the process will likely require further evaluation of the impact of brine concentrations on this parameter. An additional part of the process developed by Dindi et al. that may require further refinement is the amine-catalyst recovery process – after evaluating distillation, amine-chloride precipitation, and ultra-high lime with aluminum (UHLA) recovery methods, they found that the UHLA process was the only viable process⁸². While this process was able to recover the AMP catalyst, it reduces the CO₂ sequestration potential of the process as it requires desorption of any CO₂ that remains bound to the AMP prior to recovery, and it consumes lime (CaO), a chemical whose production often has a significant carbon footprint⁸³.

Another material that has recently been studied for its ability to reduce the thermodynamic barrier to carbonate formation is carboxylated polystyrene (PS). Power et al. added carboxylated PS microspheres to batch reactors containing solutions of MgCl and NaHCO₃, and demonstrated the formation of magnesite (MgCO₃) after a 60 day reaction time without additional energy input²⁹. The study suggests that the carboxyl groups on the PS help to dehydrate the Mg ions, overcoming a critical energetic barrier to MgCO₃ formation. This represents a major advancement from conventional methods of producing MgCO₃ as it eliminates some of the energy

demand to drive this kinetically unfavourable reaction. However, the extremely long reaction time makes this process less attractive for large scale implementation, so further process development would be needed to utilize this material as a catalyst in RCC processes. Additionally, the primary benefit to producing magnesite as opposed to more readily precipitated phases of magnesium carbonate (such as nesquehonite) presented by Power et al. is the stability of MgCO₃, which is more stable than many of the other metastable phases of magnesium carbonate²⁹. For RCC purposes, which emphasize the generation of a valuable end product, the stability of the product is a lesser concern than the saleability of the product – see section “Products from Saline Water RCC” for discussion of the value of various forms of magnesium carbonate (note that within the broader context of CCS in which product value is not emphasized, the stability of the end sequestration product is a critical consideration). Whether this process to directly generate magnesite from solution provides benefits over methods to form other phases of magnesium carbonate or not, it is still critical to note that the significant increase in overall carbon capture potential from saline waters that could be realized by producing magnesium carbonates in addition to calcium and sodium carbonates merits further study of potential applications of this material for RCC purposes.

A different approach to increasing the CO₂ absorption capacity and precipitate production from brines is mixing them with materials rich in carbonate-forming species. Soong et al.⁶⁴ evaluated the CO₂ sequestration capacity of brines produced during oil production mixed with fly ash, which can contain significant levels of calcium. Two process approaches were evaluated – mixing the ash with the brine and contacting the resultant slurry with CO₂ gas, and contacting filtrate collected from the ash brine mixture with CO₂ gas. For CO₂ contact with ash-brine slurries of 10 wt.% using fly ash from various sources, they demonstrated CO₂ consumption of 0.06-0.32 mol/L, and for CO₂ contact with the slurry filtrates they demonstrated consumption of 0.38-0.55 mol/L. Importantly, as the composition of the fly ash varied by source, the composition of recovered solids also varied, particularly when the fly ash was not separated from the brine after initial contact. Using this approach, different fly ash sources yielded 30-50% CaCO₃ in the recovered solids. However, when the fly ash was separated from the brine prior to contact with CO₂, the solids recovered contained above 90% CaCO₃.⁶⁴ This study demonstrates that while the addition of carbonate-forming species to brines can increase the CO₂ sequestration capacity, careful process design such as the inclusion of an intermediate filtration step is essential to ensuring that the process can generate products (such as CaCO₃) that are sufficiently pure for beneficial use. Additionally, this process was only demonstrated as a proof-of-concept using pure CO₂ gas, and the CO₂ sequestration capacity using ambient air was not evaluated, limiting the ability to assess this process as a stand-alone CO₂ capture approach. However, as increasing the concentration of species such as Ca and Mg can shift the carbonate system equilibrium to allow for an increase in the total amount of dissolved

carbonate species, contacting brines with fly ash or other Ca or Mg rich materials is likely to increase the carbon sequestration capacity for precipitative processes when compared to raw brines. This approach demonstrates a potential method to adding alkalinity in processes designed to precipitate CaCO_3 , a step that is essential to ensuring net carbon capture.

Some processes have combined multiple methods to optimize the amount of CO_2 mineralized. For instance, Zhang et al.⁶⁵ utilized both a catalytic material (nickel nanoparticles) and an additional source of carbonate-forming cations (blast furnace slag) to achieve 100% conversion of calcium in a synthetic desalination brine into calcium carbonate. While both the catalyst and added cations were shown to enhance the carbon capture in the plug flow precipitator used in the study as compared to system operating without catalyst or cation addition, there are major drawbacks to this approach, including a relatively slow carbon capture rate, contamination of the end material with the catalyst, and toxicity concerns related to the nickel nanoparticle used as catalyst. While studies of strategies to enhance carbon capture efficiency of different technologies can be illuminating, the overall carbon capture rate is a major design parameter governing whether a RCC technology can achieve a meaningful volume of carbon capture on a reasonable time scale.

Ultimately, many of the saline-based RCC processes which have emerged in the past two decades are still at low levels of technical readiness. Most of the processes reviewed above have only been demonstrated at a bench scale, and often utilize synthetic saline waters and/or a concentrated CO_2 source. Still, trends that indicate how chemical titration processes may be implemented to achieve efficient, scalable CO_2 capture and conversion emerge in the literature, including: 1) enhancement of CO_2 dissolution into saline water (via pH adjustment (e.g., alkalinity addition) and more efficient gas contacting) and 2) enhancement of the rate of carbonate formation (using seed materials, catalysts, or process design). Still, whether these can be implemented while also decreasing the overall energy intensity of this RCC approach to make it viable as a carbon-negative process remains to be seen.

Electrochemical Processes.

Many emerging RCC technologies rely on electrochemical reactions to drive the formation of the desired chemical products from carbonates in saline water. Many of these electrochemical processes have emerged as a potential means to reduce the carbon footprint associated with the other RCC processes by reducing required chemical addition. Under the umbrella of electrochemical RCC, some technologies utilize electrodialysis systems with configurations that allow ions in feed streams (usually saline water and a carbonate-rich stream) to be separated and then combined to generate desired products. Other novel applications of electrochemistry for RCC can involve direct reaction of carbonates on electrode surfaces to generate valuable chemical products. Both ED and other electrochemical processes often take advantage of

the ability to separate H^+ and OH^- to generate the alkalinity, which is then used to shift equilibrium towards the formation of carbonate solids.

Electrodialysis for the Generation of Inorganic Products

Electrodialysis is a process in which a saline stream is fed through channels separated by ion exchange membranes in a “stack” between two electrodes, which cause the charged species within the saline stream to migrate across the membranes towards the electrode with an opposite charge. By orienting membranes that are only permeable to cationic or anionic species in a specific order within the electrode stack, the migration of ions can be stopped so that certain streams become concentrated with ions, while other streams become diluted, as is typical in desalination applications⁸⁴. Modifications of ED can capitalize on specific membrane properties and/or membrane stack configuration to separate the desired ions for carbon capture from other ions present in saline waters⁸⁵. See Figure 2 for a comparison of ED schematics covered in this review.

While in theory ED water could be applied to simply concentrate saline waters in order to increase the saturation level of carbonate-forming species and thereby decrease the barrier to precipitate formation, there are several limitations to the actual viability of such applications. Indeed, no example of this approach was found at the time of this review. Though ED is a potentially lower-carbon approach to concentrating saline waters when compared to thermally driven concentration processes⁸⁶, it is often not as energy efficient as reverse osmosis⁸⁷. Multiple other factors may also limit the practicality of using ED to simply concentrate saline waters to enhance capture carbon. First, most saline waters already contain high concentrations of non-carbonate hardness (see previous discussion of saline water compositions), so processes that can specifically increase the concentration of the inorganic carbon species rather than simply increasing the concentration of all species may be more efficient. (Also note the distinction between processes that concentrate all species and processes that increase the concentration of cationic species, as the latter can lead to increased CO_2 capture within the saline water when supplemental CO_2 is provided, as previously discussed.) Another factor that may limit applications of ED for concentrating saline waters for RCC is the existence of a limiting concentration beyond which the concentrated stream cannot be increased⁸⁶. As the concentration gradient between the concentrate and dilute streams increases, osmosis and diffusion increase in the opposite direction of the electrically driven separation, limiting further transport of ions across the membrane. Though this can in part be overcome by increasing the current density of the ED system, the associated increase in energy consumption can become prohibitive⁸⁶. Finally, ED systems are more susceptible to scaling than systems such as RO that can also be used for concentrating saline water, which can pose major limitations in processes designed to produce carbonate solids⁸⁷.

An additional barrier to the application of ED to saline-based RCC processes that produce carbonate solids is scaling within the

membrane stack, which can greatly reduce the efficiency of the process. Scaling, the accumulation of precipitated solids on membrane surfaces, can be comprised of carbonate solids and/or other solids such as gypsum (CaSO_4). While carbonate precipitation is ultimately desirable to collect the carbonate end products in RCC, if it occurs within the ED stack it can cause scale formation on membrane surfaces in the concentrated channels. Thus, RCC processes utilizing ED must be carefully designed and optimized to achieve precipitation outside of the membrane stack. Generally, this is addressed by 1) operating the system such that concentration polarization at the membrane surfaces is minimized by convective mixing within the channel⁸⁶ and 2) operating at concentrations below the required saturation index for precipitation. The latter approach means additional steps would be required after ED to induce precipitation and collect the desired carbonate solids. Here, the use of seeds or catalysts outside the stack to allow precipitation at lower saturation index has been investigated⁶³.

Instead of using ED to concentrate saline waters used in RCC, many processes utilize unique membranes and/or stack configurations to combine target ions from two separate feed streams to generate a product stream containing the ionic species of the desired product (i.e. NaHCO_3 , CaCO_3 , etc.). Some systems have an additional product stream of another valuable, non-carbonate chemical. The feed streams are typically saline water that provides the desired cations, and a stream with high Cl^- . Some of these systems also have stack configurations that allow transport of alkali (as OH^-) to the product stream. Additionally, the use of bipolar membranes to generate acid and alkalinity in separate streams within an ED stack can reduce the reagent demand in processes that consume alkali⁶³. Below, we will provide a summary of the configuration of 4 RCC processes using ED in this manner, as this is the defining feature that enables these systems to capture CO_2 .

One application of ED for saline-based RCC was demonstrated by Dara et al.⁶⁰, who designed an electrodialysis system to use saline water and carbonic acid generated by dissolved CO_2 in deionized water to produce sodium bicarbonate (NaHCO_3) and hydrochloric acid (HCl). Their system featured 4 channels between a Ti mesh cathode and a Pt/Ir-coated Ti anode separated by ion exchange membranes: a feed stream containing carbonic acid separated by an AEM from the first product stream, which was in turn separated by a CEM from a feed stream containing NaCl, which was separated by an AEM on the other side from the second product stream. The electrodes were oriented such that anions and cations would move out of the feed streams and into the product streams: HCO_3^- and Cl^- moved toward the cathode into the first and second product streams, respectively, while Na^+ and H^+ moved toward the anode into the first and second product streams, respectively. This system design effectively created two product streams – concentrated NaHCO_3 and concentrated HCl – both of which are useful for various industrial applications (see discussion in following section). Additionally, the system effectively desalinated the saline feed

stream, demonstrating additional benefits for the treatment of saline wastewater. A major drawback of this system is the low conductivity of the carbonic acid stream, which was attributed to low rate of diffusion of the carbonate species⁶⁰. This study was an early-stage proof of concept and did not evaluate the amount of carbon capture potential of the system. Additionally, only a synthetic saline stream of 1 M NaCl was investigated, whereas most real saline waters contain a variety of ionic species, which may hinder the ability of the system to produce pure chemical products and/or reduce the system efficiency due to membrane scaling. However, it may be possible to use ion-selective membranes within the ED stack to prevent ions besides Na and Cl from entering/leaving the saline stream, better ensuring the purity of the produced chemical streams⁸⁵. Also, it should be noted that as the CO_2 captured in this system is initially captured in DI water, this may not technically be considered as “saline-based RCC,” but it may be possible to use of saline water to initially capture the CO_2 and generate the carbonic acid stream.

Indeed, other applications of ED have taken this approach. Mustafa et al.⁵⁹ designed an electrodialysis system which used carbonates from a saline stream to generate NaHCO_3 and Na_2CO_3 , capitalizing on the increased CO_2 content of saline waters and eliminating the need to dissolve additional CO_2 into the source water. In this system, alternating CEMs and AEMs created four chambers between the anode and cathode compartments of the electrodialysis stack – a chamber to collect produced acid, a chamber fed with a NaCl brine, a chamber that collected NaHCO_3 and Na_2CO_3 (we will refer to this as the “product stream”), and a chamber fed with a saline, carbonate rich stream. During optimization trials of the system, increasing voltage and CO_2 concentration led to greater CO_2 uptake into the product stream, while the impact of the concentration of the brine stream had a more nuanced impact on CO_2 uptake. Uptake increased at a brine concentration of 0.75 M NaCl, after which the uptake declined, which the authors attributed to loss of system efficiency due to scaling caused by formation of precipitate within the ED stack. This highlights scaling as a critical issue for systems designed to concentrate precipitating species such as sodium carbonate – determining and maintaining an optimal concentration that is low enough to prevent precipitation within the system, while still high enough to improve the kinetics of downstream precipitative product recovery. Another unique approach to carbon capture employed in the study by Mustafa et al. was the dehydration of the $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ stream using freeze-drying rather than heating, effectively preventing CO_2 evolution. While they found that the solids produced by freeze-drying had a 15% greater NaHCO_3 content compared to the liquid product solution, the solids produced this way were still far from pure, consisting of only 55% NaHCO_3 , with much of the remainder being Na_2CO_3 ⁶⁰. Depending on the intended use case of the produced solids, this purity level may not be sufficient for RCC purposes, and further process modification may be needed to achieve a substantially pure carbonate or bicarbonate product.

ED systems for saline-based RCC have also been used to produce solids other than sodium carbonate and bicarbonate. While sodium is the most abundant cation in most saline waters, sodium carbonates are more soluble than many other carbonate solids (see previous section on inorganic product formation from aqueous carbonates). The lower solubility of other carbonate solids makes them attractive for saline-based RCC processes, and it can also exacerbate the impact of scaling within an ED stack. As such, the design of ED systems intended to produce lower solubility carbonates such as CaCO_3 may include additional features or modifications to overcome this.

Zhao et al.⁶³ recently designed an electrodialysis stack with bipolar membranes (BPMED), which when used in tandem with a crystallizer achieved sequestration of carbon as CaCO_3 without significant membrane fouling. Their system was comprised of a series of groups of bipolar membranes and AEMs between a cathode and an anode. Each group of membranes formed 3 distinct channels, beginning with a bipolar membrane nearest to the cathode, followed by a channel fed with alkali solution, and AEM, a channel fed with seawater, another AEM, a channel fed with acid solution, and another bipolar membrane. The bipolar membranes were oriented such that the positive face was in contact with the alkali channel, where OH^- generated by water hydrolysis in the BPM collects, while the negative face within contact with the acid channel, where H^+ generated by hydrolysis collected. The AEMs enclosing the seawater channel prevented Ca and Mg from depositing on the bipolar membranes, effectively preventing fouling on these surfaces. This allowed for continued generation of alkalinity in the form of OH^- , which was able to transport across the AEM into the seawater stream, where it helped maintain a sufficiently high pH to allow for CaCO_3 precipitation when the seawater stream was subsequently circulated through a crystallizer. The major benefits of this system are the reduced reagent demand for seawater softening and the ability to use a membrane-based system to soften the seawater without major efficiency losses due to fouling⁶³.

Another approach to reducing the impact of scaling on BPMs used to generate alkali in saline based RCC processes is to demineralize water that is contacted with the BPMs, as discussed by de Lannoy et al.¹². While this approach may seem counterintuitive in a system in which the ultimate objective is to produce carbonate minerals from the saline feed water, their proposed system demineralizes only a small portion (not quantified) of saline water stream that was then fed to a BPMED system to generate acid and/or base. The acid or base is then used to shift the pH of the remaining saline water stream to convert the DIC to either gaseous CO_2 or solid CaCO_3 , respectively. This system is distinct from the other ED applications reviewed here for several reasons. First, by only using a demineralized fraction of the seawater for acid/base generation, they reduce scaling within the ED stack, potentially increasing the efficiency and reducing the need for membrane cleaning or replacement¹². Second, the ability of the process to generate two

different products out of the dissolved carbonates is unique and makes the system adaptable to market demands (though the low current value of pure CO_2 gas⁷³ means this is not a likely candidate for RCC purposes). While these differences between the systems developed by de Lannoy et al. and others may be beneficial for carbon capture applications, other differences indicate potential downsides of these systems. For instance, unlike the systems developed by Dara et al. and Mustafa et al., which utilized the most abundant cation in most saline waters (Na^+) to capture DIC as solid carbonates, this proposed system utilizes Ca^{+2} ions to generate carbonate solids. Furthermore, while tests of the base addition step of their system demonstrated complete DIC removal from the seawater, it should be noted that this is an underutilization of the Ca^{+2} ions in seawater, which outnumber DIC on a 5:1 mol basis. However, methods utilized in other processes reviewed here to increase the carbonate concentration in seawater could be used to ensure that the entire carbon capture capacity of the system is realized.

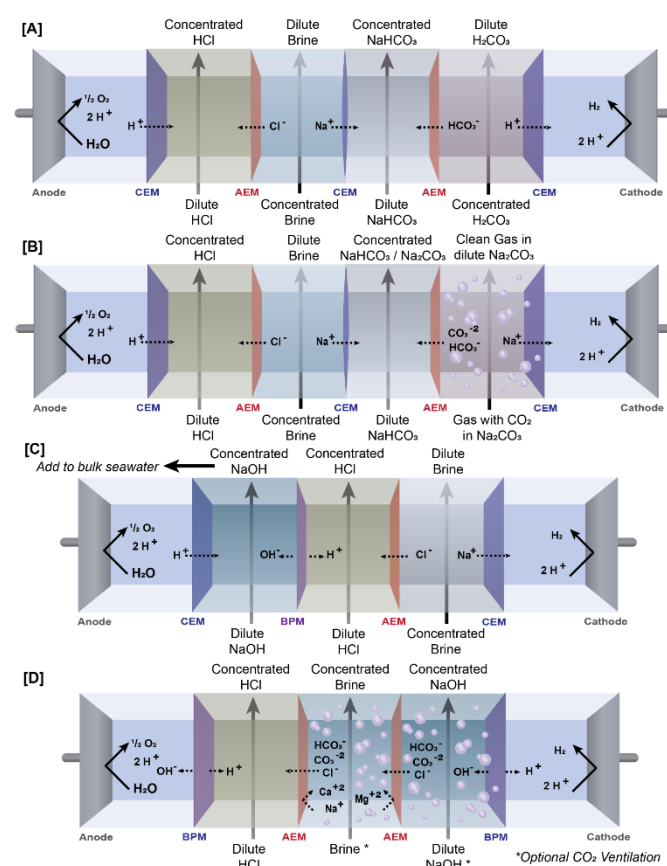


Figure 3. Comparison of ED stack schematics from A) Dara et al., B) Mustafa et al., C) de Lannoy et al., and Zhao et al.

Other Electrochemical Processes Generating Inorganic Products.

While ED systems provide numerous advantages including continuous operation, physical barriers between feed and product streams⁵⁹, lower energy demand⁶⁰, and lowered chemical

demand¹² compared to non-electrochemical processes, other electrochemical approaches have been demonstrated for saline-based RCC that offer at least some, if not all, of the same benefits. These approaches often focus on using electrolysis to generate alkali that can be used to increase pH and shift equilibrium towards carbonate formation, two of which are summarized below.

Xie et al.¹⁵ demonstrated a membrane electrolysis process that increase the pH of synthetic seawater, which was then bubbled with CO₂ gas to generate CaCO₃, along with Mg(OH)₂ (which was later converted to Mg₅(CO₃)₄(OH)₂·4H₂O (hydromagnesite)). In their system, the seawater was fed to the cathode chamber, where water was split by the cathode to produce OH⁻, thus maintaining an elevated pH to facilitate precipitation. When the pH of the cell reached 10.1, Mg(OH)₂ precipitated and was filtered out of the solution. Subsequently, CO₂ was bubbled into the cell, allowing CaCO₃ to precipitate. The Mg(OH)₂ was converted into hydromagnesite by heating a suspension of the Mg(OH)₂ with bubbled CO₂. This system converted over 99% of both the Mg⁺² and Ca⁺² into carbonate solids¹⁵. A major benefit of the system developed by Xie et al. is the production of pure, separate calcium and magnesium solids, which was achieved through careful control of the system pH and timing of the CO₂ addition. This eliminates any need for additional costly product purification processes. Additionally, the anion exchange membrane used in their system primarily serves to separate acid generated at the anode and alkali generated at the cathode, rather than to allow selective transport of ions between feed and product streams. As such, reductions in flux due to scaling on the surface of the membrane are likely less of a concern in such systems, and scaling was not discussed as an issue. However, further study is required before it can be concluded that the carbonate production by membrane electrolysis systems is less impacted by scaling, but if this is the case, this would be a major benefit of such systems, particularly when compared to ED.

While systems such as those demonstrated by Xie et al. effectively convert Ca and Mg in seawater to stable carbonates, RCC systems utilizing sodium to capture CO₂ may have a greater overall carbon capture capacity, as sodium is typically more abundant in saline waters (see previous section on saline water composition). While a major benefit of processes that generate calcium and magnesium carbonates is the durability of these solids (as this enables their use for long-term carbon sequestration), the durability of sodium carbonates is generally less discussed in relation to carbon capture processes. Instead, the focus is on producing NaHCO₃ and Na₂CO₃ for consumption, so the long-term durability of these products is less of a concern than the ability to generate them efficiently. An additional benefit to processes using sodium to convert CO₂ to solids is that the formation of NaHCO₃ avoids the need to add alkalinity to prevent the net release of carbon when forming carbonates with divalent cations. While ED systems have been demonstrated as a way to combine Na from seawater with carbonates, the low mobility of bicarbonate and carbonate ions can limit the efficiency of these systems and prevent them from

reaching the full carbon capture potential provided by the sodium ions⁶⁰. As such, other electrochemical systems with geometries that do not require the transport of bicarbonate or carbonate across membrane interfaces may be an approach to reach the full carbon capture potential more efficiently.

A prototype system developed by Park et al.⁶² used a two chamber system separated by a ceramic membrane to electrolytically convert seawater first to NaOH and then to NaHCO₃. In this system, the anode is within an inner chamber created by the ceramic membrane, which allows separation between the H⁺ generated at the anode and OH⁻ generated at the cathode. Unlike the membranes used within ED systems, the ceramic membrane allows transport of both cations and anions, so Cl⁻ ions move across the membrane towards the anode and Na⁺ moves across the membrane towards the cathode, thus producing HCl in the inner anode chamber and NaOH in the outer cathode chamber. The NaOH solution generated via electrolysis was subsequently bubbled gaseous CO₂, forming aqueous NaHCO₃. This eliminated the need to transport bicarbonate/carbonate ions across the membrane interface and was achieved at ambient temperature and pressure. It should be noted that in this study, the ultimate end product was CaCO₃, which was produced by adding CaCl₂ to the NaHCO₃ solution. By using NaHCO₃ as an intermediate product and adding supplemental Ca, their system surpassed the carbon capture capacity of forming CaCO₃ directly from seawater, while still taking advantage of the solubility reduced solubility of CaCO₃ compared to NaHCO₃ and NaCO₃. The precipitation of CaCO₃ was also achieved without increasing temperature or pressure, which can be major energetic demands in conventional CaCO₃ production processes. However, the actual amount of CO₂ captured was not quantified, so an objective comparison of the energy savings of this process cannot be made at this time. Still, the system developed by Park et al. demonstrates how the chemistry of a saline water can be manipulated using electrochemical approaches to enhance the uptake of CO₂ and facilitate more thermodynamically favourable formation of the desired carbonate products. The extent to which such a system can be considered as an RCC process depends largely on the net carbon footprint of the process, and whether it can be applied to capture carbon from non-concentrated CO₂ sources.

Electrochemical Processes Generating Organic Products. While many processes being developed for saline-based RCC can be used to simultaneously capture CO₂ and generate valuable mineral products, a few RCC technologies that generate valuable organic products have also emerged. For instance, Nakata et al.¹⁴ used seawater as the electrolyte in their system designed to electrolytically convert CO₂ into formaldehyde, a valuable chemical used in numerous industrial processes. Their system used a boron-doped diamond (BDD) cathode to reduce CO₂ (which had been dissolved into the electrolyte) into formic acid and then into formaldehyde, using electrons and protons provided by various electrolytes including methanol, NaCl solution, and seawater. While they found that the conversion of CO₂ into formaldehyde was less

efficient (36% Faradaic efficiency) in seawater than in methanol (74% Faradaic efficiency), they noted that the abundance of seawater still makes this application attractive. Additionally, the efficiency in the NaCl solution (62% Faradaic efficiency) was greater than the seawater, suggesting that impurities present in the seawater reduced the efficiency¹⁴. Determining the exact impurities causing losses in efficiency is an important step to improving the viability of this process, as numerous water treatment technologies may be available to pretreat seawater to improve formaldehyde recovery. Benefits of this system include low production of H₂ gas, which is unique to the use of the BDD electrode – while H₂ gas can be a valuable fuel source, it requires significant additional handling considerations. Though not necessarily a drawback of the system, it is important to note that as with other electrolytic technologies, the energy demand per kg CO₂ capture and converted will also be an important consideration for the viability of this technology, and the system will require renewable energy sources to maintain a negative carbon footprint. Conversion of aqueous carbonates to organic products was also demonstrated by Zhang et al., who modified a membrane electrolyzer to allow for the generation of formates (KHCO₂ and NaHCO₂) from KHCO₃ and NaHCO₃ solutions with 97% and 93% carbon conversion efficiency, respectively⁷⁶. The ability of their system to achieve this efficiency relied upon maintaining bicarbonate as the dominant carbonate species, which means that careful control of pH was required. The bicarbonate reacts with H⁺ generated by the anode and passes across a CEM to form CO₂* within the cathode compartment, where it can then be reduced on the cathode surface to produce formate. They were able to achieve this through the use of a near-neutral anolyte solution, reactor design, and control of CO₂ partial pressure in the reactor headspace⁷⁶. Importantly, the presence of Cl⁻, SO₄²⁻, and I⁻ were shown to have no impact on the conversion efficiency of this system when present at concentrations equal to or less than the concentration of bicarbonate⁷⁶. However, further testing with solutions containing concentrations of these anions that are more representative of the composition of saline waters (where non-bicarbonate anions typically dominate) (e.g., those tested in the study by Nakata et al.¹⁴) are needed to further demonstrate the applicability of this technology for saline-based RCC. Discussion of this type of system often involves using a hydroxide solution to dissolve carbonates (Sullivan et al.) but does not thoroughly investigate the use of saline waters as the carbon capture medium.

Another system similar to the one developed by Zhang et al., but which generates CO rather than formate from an aqueous bicarbonate stream, was recently demonstrated Li et al.⁸⁸. CO is primarily used as a feedstock to generate organic chemicals⁸⁹, and for that reason we chose to include discussion of this system in this section. In their electrolyzer, a bipolar membrane was oriented so that H⁺ are generated within the compartment being fed a bicarbonate solution. As in the system demonstrated by Zhang et al., this leads to the generation of CO₂*. This compartment is bound on the other side by an Ag-coated carbon support that catalyses the

conversion of CO₂ to CO (rather than allowing the CO₂ to reach the cathode where it could be converted to formate, similar to Zhang et al.'s system). While the researchers highlight the ability to generate CO as the major benefit of this system⁸⁸, it should be noted that this system was only able to achieve a maximum of 83% carbon conversion (lower than that demonstrated by Zhang et al.). An additional shortcoming of this system is that it has only been demonstrated with a KHCO₃ solution, and thus further study is needed to determine if this can be applied for RCC from real saline waters. However, the flexibility of the system developed by Zhang et al. to operate with a sodium-based solution and with other anions present indicates that there may be potential for the system developed by Li et al. to be applied for solutions more representative to real saline waters.

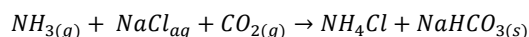
Other Processes. While the vast majority of saline-based RCC processes emerging at the time of this review use either a chemical titration or electrochemical approach to convert CO₂ capture in saline water into valuable products, at least one example could be found of a process using an approach other than this. In a system developed by Islam et al.⁷⁴, CO₂ and H₂ gas are combined in a saline solution. By exposing the solution to ultrasonic conditions (20 kHz-1Mhz), cavitation microbubbles formed. Upon the collapse of these bubbles, extreme temperature and pressure conditions were created (~500 OK, 2000 atm), which induced the *Sabatier* and *Fisher-Tropsch* reactions, converting the CO₂ and H₂ to various simple hydrocarbons. Importantly, the yield of hydrocarbons increased with increasing salinity (up to 1 M NaCl). NaCl prevented the formation of H₂O₂, an oxidizing agent formed during cavitation bubble collapse, which inhibits CO₂ reduction to hydrocarbons. Similar enhanced hydrocarbon yield was observed in synthetic seawater (salinity of 0.6 M). Though this approach has the benefit of neither consuming nor concentrating the salinity (thus allowing easier reuse or discharge), the produced hydrocarbons require additional separation for either the gas or aqueous phase for recovery, which may be energy-intensive.

Reactive Carbon Capture Using Pre-existing Technologies

While current research on saline based RCC is focused on optimizing the amount of carbon capture, many processes using similar chemistries (i.e. carbonate solid precipitation) have long been employed in a variety of industries, but optimized for metrics other than carbon capture. In some instances, the processes are designed specifically to produce a desired carbonate product (such as the Solvay process), whereas in other instances the production of valuable carbonates is a byproduct of another process (such as water softening). Understanding these preexisting processes for converting salinity into valuable carbonates provides important insight into not only the chemistry of carbonate solid production, but also into the implementation of such processes at larger scales than much of the current CCU research.

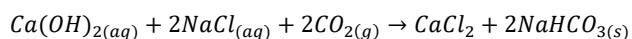
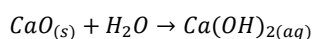
The Solvay Process and Modifications for Carbon Capture and Utilization. The Solvay process is a widely employed industrial process used to generate NaHCO₃ and/or Na₂CO₃ from NaCl and

CO₂ gas through a reaction facilitated by ammonia (NH₃)⁹⁰, or other amine-based catalyst².



At least one quarter (though likely much more) of the world's soda ash is produced using processes similar to the Solvay process, accounting for at least 14 million metric tonnes annually⁹¹ (much of the remainder is mined from natural deposits). Though originally developed as a purely production process, growing interest in carbon sequestration has led to the study of this process for carbon sequestration purposes. In 2019, Palitsakun et al. demonstrated a Solvay process utilizing synthetic brines at concentrations intended to model seawater and desalination brine, and demonstrated up to 100% capture of a pure CO₂ stream using ammonia gas as the reaction intermediate⁶¹. The Solvay process has been demonstrated using various CO₂ sources, including diesel exhaust (4.8 % CO₂) and flue gas from a natural gas power plant (10% CO₂), capturing 99 and 98% of the CO₂, respectively⁹², indicating the robustness of the process for CO₂ capture from a variety of sources. While the overall reaction chemistry of the Solvay process involves the precipitation of a carbonate solid from a saline solution, the conventional Solvay process has an associated carbon footprint of 1.61 - 2.29 tonnes CO₂ emitted/ton NaHCO₃ produced⁴, so it cannot be classified as a saline water-based RCC process. The carbon footprint of the Solvay process is largely associated with the energy intensive catalyst and solid recovery steps⁹³, which typically require heat and result in 1.48-2.04 tonnes of indirect CO₂ emissions per tonne NaHCO₃ produced⁴. However, the increased interest in carbon capture and utilization processes has motivated recent studies of modifications to the Solvay process, which can decrease the energy demand and thus make it viable as a CCU process.

A common approach to modifying the Solvay process is to replace ammonia as a catalyst, which can reduce the energy demand associated with its regeneration. For instance, El Naas et al. demonstrated a modification of the Solvay process which used lime (CaO) instead of ammonia to maintain the pH required for NaHCO₃ to precipitate.



This process produced NaHCO₃ at a 30% energy savings compared to the conventional Solvay process, half of which was due to the elimination of the ammonia recovery step⁹³. It should be noted that lime can have a high associated carbon footprint when produced using conventional methods (calcining CaCO₃), and while the authors did not assess the carbon footprint of their process versus the conventional Solvay process, it is possible that some of the reduction in carbon footprint from the lower energy demand may be offset by carbon footprint of the process chemicals.

Water Softening. While generating bicarbonate/carbonate solids is the primary objective of industrial processes like the Solvay process, there are also processes which produce carbonate solids as a byproduct. For instance, some commonly used water softening methods, such as lime softening, can convert mineral hardness (Ca and Mg) into carbonate solids, effectively capturing and converting CO₂ which was dissolved in the source water. To that extent, many technologies developed for water softening can be considered reactive carbon capture processes. These technologies may not have been evaluated or optimized for carbon capture potential but nonetheless bear consideration and can be used to inform the development of processes specifically intended for carbon capture and/or simultaneous carbon capture and water softening.

Precipitative water softening processes often use a pH shift toward basic conditions to shift the carbonate equilibrium towards CO₃²⁻ formation, improving the kinetics of CaCO₃ precipitation. The pH shift can be induced by adding chemicals, such as NaOH, or through electrochemical generation of alkalinity. While the latter approach has the benefit of reducing the chemical demands of the softening system, quenching of OH⁻ alkalinity produced at the cathode in electrochemical systems by H⁺ ions produced by the anode can significantly reduce the efficiency of electrochemical softening processes. To that end, Ba et al.⁹⁴ developed an integrated electrolysis-microfiltration-ion exchange (IEMI) system for water softening, which features a porous, tubular anode oriented such that protons generated at its surface can be drawn through the anode and out of the electrolytic cell, preventing quenching of alkalinity generated in cell. This novel system design allowed for higher pH to be reached in the electrolytic cell (effluent pH 11.9) than in conventional electrolytic cells (effluent pH 11) using ion exchange membranes to separate the OH⁻ and H⁺. The electrolytic cell with the porous anode achieved production of CaCO₃ (1.9 kWh/kg CaCO₃), which was as or more efficient than a conventional (CEM separated) electrolytic cell (1.4-11.2 kWh/kg CaCO₃) with the same current density (18 mA/cm²) applied and hardness removal efficiency achieved (~65%) in each cell. In the system developed by Ba et al., the majority of the calcium hardness was removed in a crystallizer fitted with a microfilter, with the ion exchange column receiving the filtrate from the crystallizer used to primarily remove remaining magnesium hardness. While the addition of the ion exchange column helped improve the overall hardness removal of the IEMI system to above 90%⁹⁴, it bears less relevance to reactive carbon capture objectives. However, the novel use of a porous anode to abstract protons from the electrolytic cell, enabling more energy efficient production of CaCO₃ is directly applicable to electrolytic systems designed to capture carbonate from saline waters and produce CaCO₃. While the CO₂ sequestration capacity of the system was not directly analyzed or optimized in the study by Ba et al, they did investigate the impacts of increasing the HCO₃⁻ concentration in the synthetic brine fed to the electrolytic cell, and found that the removal of calcium hardness increased with increasing HCO₃⁻ alkalinity from 100 to 400 mg/L as CaCO₃⁹⁴.

Solids Separation and Management. For any saline-based RCC process which converts carbon to solids, separation and management of the solids formed during the process will be required. Carbonate solids management methods from the water and wastewater treatment industry can be used to inform solids management for saline-based RCC processes. The scale of carbonate solids management practices in the water treatment industry far surpasses the scale of solids managed in the lab or pilot scale RCC processes covered previously, and thus many engineering design principles and practices developed in the industry can be used to enable a smoother scale up of saline water-based RCC.

Management of precipitation softening sludges includes collecting and dewatering the precipitates. During the initial collection of precipitates, the solids will act as a slurry due to high water content, whereas after dewatering they must be handled as a sludge. Solids may initially be concentrated by methods such as gravity thickening, followed by dewatering using either drying beds or mechanical dewatering such as centrifugation or filtration, sometimes followed by further volume reduction through pelletization or recalcination, before offtake of the solids⁵⁷. While methods like recalcination which re-release the CO₂ from the precipitate are not appropriate for CCUS purposes, many of the processes used in management of softening sludges can be applied to water based CCUS.

At water treatment facilities, precipitated solids are usually initially separated from water by gravity. Clarifiers settle solids formed during water softening to produce a slurry with 15-20% (wt/wt) solids content, which can be further dewatered in thickeners to reach solids contents of 25-30%⁹⁵. A major parameter for clarifier design is the solids settling velocity, as the clarifier area must be large enough to maintain an overflow rate below the settling velocity in order to retain the solids⁹⁶. The composition of solids formed during carbonate precipitation can significantly impact the settling velocity and thus the footprint required for solids management. For instance, the Ca:Mg ratio in softening sludges is correlated to their dewaterability during settling, with high ratios (indicative of less Mg, often in the form of Mg(OH)₂) indicating improved settleability. Interestingly, supplementary CO₂ can re-dissolve the Mg in settled sludge, providing as much as a 3-fold reduction in area required to settle the sludge⁹⁷, and providing an additional opportunity to sequester carbon (as bicarbonate ions). Other lightweight components within softening or coagulation sludges, such as aluminum hydroxide flocs and organics, also reduce settleability⁹⁵. The settleability of solids formed in water based CCUS processes using gravity separation methods is a key design parameter and should be carefully considered. As such, the extensive knowledge base on solids settleability and gravity settler design within the water/wastewater treatment (W/WWT) industry can be applied to aid CCUS efforts.

An additional design parameter for solids management is the desired end solids content. It is known that higher solids content must be achieved for handleability of softening sludges (>50%), though the exact solids content required for handleability varies

and often must be determined empirically⁹⁷. As such, water treatment facilities usually employ an additional dewatering step after gravity separation to produce solids which can be easily transported – saline water-based RCC processes which produce carbonate solids would likely also need to employ additional dewatering, if these solids are meant to be used by another entity or buried. Examples of such dewatering steps include filter presses⁹⁸, centrifuges⁹⁵, and thermal drying⁹⁹. The energy demand for solids dewatering should be a major consideration in the design of RCC processes. The carbon footprint of the energy required to dewater solids generated from water softening can effectively cancel out the carbon capture achieved by generating the solids⁸⁰.

Another important but easily overlooked consideration for the dewatering of precipitated carbonate solids is the management of the effluents produced during dewatering. Many water and wastewater treatment facilities dispose of the effluents by discharge or by returning them to the plant's headworks⁹⁵. However, this option may not be viable for saline water-based RCC processes which are not co-located with a W/WWT facility. Additionally, the composition of these effluents can vary depending on the carbonate precipitation method and the chemical composition of the influent water source, which may prohibit direct discharge of the effluents in cases where they contain elevated concentrations of regulated pollutants. Additionally, effluents from dewatering of lime softening sludge can have elevated pH and calcium concentration - as high as pH 12.24 and 380 mg/L Ca⁹⁵ - due to dissolution of unreacted lime from the softening sludge. For RCC purposes, ensuring maximal conversion of available calcium to carbonate solids is critical for efficient sequestration, so steps to further react calcium in dewater effluents may be employed.

Summary of Recent Studies of Potential Saline water-based RCC Technologies

Table 3 summarizes each of the RCC processes reviewed in the section of this review focused on CO₂ conversion processes and products. Qualitative features, including the technology type, saline water source, CO₂ source, products, and concurrent processes, as well as quantitative features including CO₂ capture and energy consumption are reported as they were discussed in each respective article. The technology stage, benefits, and limitations are based upon information within the reports as well as assessment by the authors of this review.

ARTICLE

Table 3. Summary of Recent Studies of Saline-based RCC Technologies

Paper	Technology	Saline Water Source	CO ₂ Source	CO ₂ Captured	Energy Demand	Products	Concurrent Processes	Technology Stage	Benefits	Limitations
Dara et al. 2017	Electrodialysis	Synthetic (1 M NaCl)	Pure CO ₂ gas, dissolved in DI water	Not reported	Not reported	HCl NaHCO ₃	Desalination	Proof of Concept	Simultaneous CO ₂ capture, water treatment, a chemical production	Current limited by low conductivity of carbonic acid stream (attributed to low rate of diffusion of carbonate species in the stream and low mobility of the species)
Dara et al. 2019	Gas-Fed Electrodialysis	Synthetic (1 M NaCl)	CO ₂ Gas (0-50% in O ₂ Gas)	Not reported	Not reported	HCl NaHCO ₄	Desalination	Proof of Concept	Utilization of Sodium (more abundant) for RCC	Low conductivity of carbonate stream potentially elevates energy demand/slow reaction
Zhao et al. 2020	BMED with Crystallizer	Synthetic Seawater	CO ₂ Gas, dissolved in alkali water	Not reported	0.89 kWh/kg CO ₂	CaCO ₃	Seawater softening	Bench Scale	Prevention of membrane fouling	Utilization of divalent cation (Ca) for carbon capture requires alkalinity addition for net CO ₂ capture
Nakata et al	Electrolysis with BDD Cathode	Seawater and NaCl Solution	CO ₂ gas dissolved in solution	Not reported	Not reported	Formaldehyde Formic Acid	None	Proof of Concept	Chemical production, reduced H ₂ generation	Lower efficiency due to impurities in seawater, lower solubility of CO ₂ in seawater vs methanol
Islam et al	Sonication	Synthetic seawater and NaCl Solution	CO ₂ gas and Flue gas	Not reported	Not reported	Methane, Ethane, Ethylene	None	Proof of Concept	Organic Chemical Production	Additional purification steps

Journal Name

ARTICLE

										needed for product recovery
Dindi et al	Amine-catalyzed Precipitation	Synthetic Desalination Brine	Synthetic Flue gas (15% CO ₂)	Not reported	Not reported	NaHCO ₃	Desalination	Proof of Concept/Bench Scale	Utilization of Sodium (more abundant) for RCC	Use of lime, which can have a large carbon footprint when produced by calcining limestone
Soong et al	Carbonate Precipitation	Oriskany Sandstone aquifer brine	Pure CO ₂ gas	0.031-0.273 mol CO ₂ /hr	Not reported	CaCO ₃	None	Proof of Concept	Use of waste products (produced water brine and fly ash)	Not all available Ca consumed NaCl impurity in solids collected from 2 step method Solids in 1 step method in slurry with fly ash, inhibiting recovery for beneficial use
Mustafa et al	Electrodialysis	Synthetic (NaCl solutions)	Synthetic (NaCO ₃ solution)	1.9 mol CO ₂ /hr	11.2 kWh/kg CO ₂	HCl NaHCO ₃ Na ₂ CO ₃	Desalination	Bench Scale	Use of waste products (alkaline and NaCl brines)	Optimal conditions for CO ₂ removal differ from optimal conditions for brine desalination
Power et al	Enhanced precipitation	Synthetic (NaHCO ₃ /MgCl Solution)	Synthetic (NaHCO ₃ /MgCl Solution)	Not reported	Not reported	MgCO ₃	None	Proof of Concept	Room temperature magnesite formation	Long reaction time (60 days), Utilization of divalent cation (Mg) for carbon capture requires alkalinity addition for net CO ₂ capture
Taniguchi et al	Electrodialysis	Synthetic	Flue Gas	9900 kmol/hr CO ₂ (proposed)	0.225 (ED), 0.525 (overall) kWh/kg CO ₂	CO ₂ gas	None	Described systems	Low energy consumption	CO ₂ absorption capacity of Potassium solution likely higher than natural saline waters; energy demand is theoretical, and system has not

ARTICLE

Journal Name

										been demonstrated
de Lannoy et al	Bipolar Membrane Electrodialysis	Seawater	DIC in seawater	20 kmol CO ₂ /hr (proposed)	2.72-3.85 kWh/kg CO ₂	CaCO ₃ or CO ₂ gas	None	Described prototype based on Bench Scale	System flexibility to generate solid or gaseous process depending on BPME product used	Utilization of divalent cation (Ca) for carbon capture requires alkalinity addition for net CO ₂ capture
Ba et al	Integrated Electrolysis Microfiltration Ion Exchange system	Synthetic Industrial Wastewater	HCO ₃ ⁻ alkalinity in water source	Not reported	Not reported	CaCO ₃	Water Softening	Bench Scale	Use of membrane-less ED system with tubular electrode reduces capital and O&M costs associated with fragile IEMs, makes ED system tolerant to higher salinity influent	Demonstrated for low salinity influent which limits CO ₂ capture potential, Utilization of divalent cation (Ca) for carbon capture requires alkalinity addition for net CO ₂ capture
el Naas et al.	Modified Solvay Process	Multi-stage flash desalination brine	Synthetic flue gas (10% CO ₂)	1.25 mol CO ₂ /hr	0.773 kWh/kg CO ₂	NaHCO ₃ , CaCl	None	Bench Scale	Eliminates use of ammonia in solvay process, reducing associated energy demand for separation and regeneration	Use of lime, which can have a large carbon footprint when produced by calcining limestone; Utilization of divalent cations (Ca,Mg) for carbon capture requires alkalinity addition for net CO ₂ capture
Xie et al	Membrane Electrolysis	Synthetic seawater	Pure CO ₂ gas	0.078 mol CO ₂ /hr	1.22 kWh/kg CO ₂	MgCO ₃ , CaCO ₃ , HCl	HCl generation	Bench Scale	Separation of magnesium and calcium solids, oxidation of H ₂ at the anode rather than Cl	Involves H ₂ gas management (produced at cathode, supplied to anode); Utilization of divalent cations (Ca,Mg) for carbon capture requires

Journal Name

ARTICLE

										alkalinity addition for net CO ₂ capture
Palitsakun et al.	Modified Solvay Process	Synthetic Brine (NaCl)	Pure CO ₂ gas	2.5 mol CO ₂ /hr	Not reported	NaHCO ₃ , Na ₂ CO ₃	None	Bench Scale	Ammonia is less expensive and toxic than other amine catalysts	Incomplete recovery of ammonia, Solid composition mixed between NaHCO ₃ and Na ₂ CO ₃
Zhang et al	Continuous plug flow reactor with Nickel nanoparticle catalyst	Synthetic desalination brine	Pure CO ₂ gas	0.036 mol CO ₂ /hr	Not reported	CaCO ₃ , MgCO ₃ (various)	None	Bench Scale	Carbonic acid formation accelerated by nickel NPs	Separation of catalyst and precipitate not discussed, Toxicity of Nickel nanoparticles; Utilization of divalent cations (Ca,Mg) for carbon capture requires alkalinity addition for net CO ₂ capture
Bang et al.	Precipitation with Microbubbles	RO Desalination Brine	Pure CO ₂ Gas	Not reported	Not reported	CaCO ₃ , MgCO ₃ (various)	None	Proof of Concept	Formation of both magnesium and calcium carbonates	Significant chemical consumption (NaOH); Utilization of divalent cations (Ca,Mg) for carbon capture requires alkalinity addition for net CO ₂ capture
Chaalal et al.	Modified Solvay Process	Ammonated Seawater	10% CO ₂ in methane; Diesel exhaust (4.8% CO ₂)	0.162 mol CO ₂ /hr	Not reported	NaHCO ₃ , Na ₂ CO ₃	Brine desalination	Bench scale	Applicable to multiple CO ₂ containing gas streams	Ammonia regeneration can be energy/cost intensive
Park et al	Membrane Electrolysis	Synthetic Brine (NaCl)	Pure CO ₂ Gas	Not reported	Not reported	CaCO ₃ , HCl	None	Proof of Concept	More rapid formation of CaCO ₃ compared to natural processes at	Requires addition of carbonate forming species; Utilization of divalent cations (Ca) for carbon

ARTICLE

Journal Name

									room temp/pressure	capture requires alkalinity addition for net CO ₂ capture
de Vito et al	Enhanced precipitation	Synthetic Industrial Wastewater (MgCl)	Pure CO ₂ Gas	0.002 - 1.64 mol CO ₂ /hr	Not reported	MgCO ₃ *3H ₂ O , MgCO ₃ *5H ₂ O	None	Pilot Scale	Formation of more readily precipitated Magnesium carbonates at room temperature, pressure	Only demonstrated with pure MgCl
Zhang et al.	Membrane Electrolysis	KHCO ₃ and NaHCO ₃ solutions	KHCO ₃ and NaHCO ₃ solutions	Not reported	Not reported	Formate Solids	None	Bench Scale	Demonstrated with K and Na, and performance sustained in presence of other anions	Careful gas and pH management required
Li et al.	Bipolar Membrane Electrolysis	KHCO ₃ solutions	KHCO ₃ solutions	Not reported	Not reported	CO	None	Bench Scale	Generation of CO feedstock for organic products	Only demonstrated with pure KHCO ₃

ARTICLE

Products of Saline Water-based RCC

Here, we evaluate the products that are formed by current saline-based processes, as well as discuss a selection of other products, which while not currently generated at scale, have been or could be feasibly produced using a saline-based RCC process. To evaluate each product, we will consider the advantages posed by replacing conventional production methods with RCC processes, current and prospective demand for the product, and the carbon footprint of use cases for each product. It is important to consider whether the end use of the solids generated during RCC will re-release the captured carbon in evaluating the life cycle impact of the RCC process. While end uses which re-release the CO₂ generally increase the carbon footprint, in instances where RCC-generated chemicals can replace chemicals generated using more carbon-intensive processes, the overall carbon footprint of the end use can still be reduced.

When assessing the value of potential products of saline water-based RCC, average market prices of the various products are considered. However, there is likely to be a trade-off between the purity of products from RCC, the energy required, and the market price of different product purities. Each RCC process should be individually evaluated to determine the product purity which is the most cost- and carbon- effective.

The economic benefit of generating valuable products rather than simply sequestering carbon is understood to be a major driver of this trend toward CCU processes. Reactive carbon capture processes fall into the classification of carbon capture and utilization (CCU) technologies – processes that convert the captured carbon into a valuable product. The volume of carbon capture by CCU technologies, currently between 10–15 MT CO₂/yr, exceeds the volume of carbon capture by technologies solely developed to sequester carbon (CCS), and is continuing to grow at a more rapid rate compared to CCS⁷³. However, not all CCU processes generate the same products – for instance, some non-saline based RCC processes use biological mechanisms to generate complex organic products – so it is essential to understand the value of the products generated by each respective process when comparing CCU approaches and evaluating their potential for large-scale implementation.

Carbonate Solids

The majority of saline water-based RCC processes generate inorganic products, often in the form of carbonate solids. Once carbonate solids have been collected and dewatered, they can be

sold as valuable chemical products. A wide range of carbonate solids can be generated, depending on which cation(s) are present in the saline water source and the method of carbonate formation employed.

Generally, solids can be produced at a larger volume with lower quality, or at a smaller volume with higher quality (i.e. more pure)⁹⁷. Both methods can be employed for saline-water based RCC. The advent of ion-selective aqueous separation processes, such as ion-selective electrodialysis or adsorption, creates the potential to extract the more valuable elements from saline streams to produce valuable, high purity products. However, higher energy demand and/or lower production volume of high purity products can reduce the carbon capture potential of such RCC processes. Potential trade-offs between the value of the generated products and the amount of CO₂ captured create a compelling case for integrated RCC processes capable of utilizing the dominant cations in saline waters (Na, Ca, Mg) to provide the majority of carbon capture, while utilizing other cations (i.e. Li) to produce valuable end products. Thus, we will include a selection of carbonate solids produced from cations which are present at low levels in saline water in our analysis below, in the instances where these carbonates have compelling value.

Many of the solids which can potentially be produced using saline-based RCC have end uses which may result in the re-release of the CO₂ captured in the solids. In these instances, carbon sequestration is not achieved, but net emissions reductions are still possible when these products are used in lieu of carbonates produced from carbon emitting processes.

Sodium Bicarbonate and Carbonate. Sodium can form both bicarbonate (NaHCO₃) and carbonate (Na₂CO₃) salts during RCC processes. Na₂CO₃ is known as “soda ash” and is used to produce numerous consumer goods, including glass, soaps/detergents, paper, as well as for other chemical production processes⁹¹. In 2018, the global consumption of soda ash was 56.9 MT with an average value of \$148.69/metric tonne⁹¹, roughly equating to a market value of \$8.46 billion. Sodium bicarbonate consumption is generally lesser than soda ash consumption, accounting for roughly 10–15% of soda ash production⁹⁵.

Currently, these carbonates are produced by mining geological deposits or are extracted from saline brines⁹⁵. Much of NaHCO₃ and Na₂CO₃ production currently utilizes the Solvay process, which combines NaCl-rich brines with an ammonia catalyst and a CO₂ source to generate NaHCO₃, which can be converted to Na₂CO₃ via heating². This process can be CO₂-intensive due to the energy

demand for heating and catalyst recovery (see previous discussion of Solvay process).

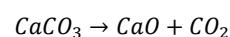
The end use of NaHCO_3 and Na_2CO_3 determines whether RCC processes that produce these minerals are net carbon negative or simply carbon neutral. Na_2CO_3 is primarily used as a feedstock within the chemical industry, and is used in chemical processes in various other industries, whereas NaHCO_3 is primarily produced as a consumer good ⁹⁶. In either case, the solid is typically dissolved and/or reacted, which means the carbon is not permanently sequestered. Still, replacing Na_2CO_3 and NaHCO_3 produced by conventional processes with large carbon footprints with Na_2CO_3 or NaHCO_3 produced by RCC can reduce the overall carbon footprint of these end uses.

Calcium Carbonate Calcium carbonate is another of the potential products of saline-water based RCC. High grade CaCO_3 is used in chemical production and various industrial processes, while lower grade CaCO_3 is widely used for construction and agricultural applications, as well as for cement and lime (CaO) production ⁹⁸. Low grade CaCO_3 is typically produced through mining, while more advanced processes are used to refine ores or other resources to produce high grade CaCO_3 . To produce high grade CaCO_3 , solids can be generated from aqueous solution (i.e. a brine resource or solubilized ore) through direct precipitation (requiring sufficient concentrations of both Ca and CO_3^{2-}), or indirect precipitation induced by 1) bubbling CO_2 gas into calcium rich solution, 2) reverse emulsion of $\text{Ca}^{2+}/\text{CO}_3^{2-}$ rich solution, or 3) contact of CO_3^{2-} from an intermediate source (such as NH_4HCO_3) with a Ca^{2+} -rich solution ⁹⁹. Most of the RCC technologies reviewed here utilize direct precipitation after a step to concentrate the saline water, or indirect precipitation using bubbled CO_2 in combination with concentrated saline water. Precipitative processes generate a metastable amorphous phase of CaCO_3 , which can be transformed into various stable forms of CaCO_3 , including calcite, aragonite, and vaterite. A review by Tan et al. thoroughly covers how different process parameters, such as pH, temperature, ageing time, and utilization of additional chemicals can impact the morphology of CaCO_3 ⁹⁹. The value of and market for CaCO_3 solids varies between the different morphologies, so controlling the precipitation process to produce the desired morphology can impact the net cost of saline-based RCC processes.

The global production of high-grade CaCO_3 was 114 MT/yr as of 2013, and the price ranges between \$30-350 /metric tonne ⁷³. It is estimated that by using carbon capture methods to generate CaCO_3 to meet this demand, 50 MT/yr of CO_2 could be captured and utilized ⁷³. However, much larger amounts of lower-grade calcium carbonate minerals, such as limestone and dolomite (CaMgCO_3 , see discussion below on complex inorganic carbonates), are produced and consumed annually. Over 54 and 901 MT/yr of dolomite and limestone, respectively, are consumed in the United States alone ¹⁰⁰, with similar rates of consumption worldwide. These minerals are much less valuable than high purity CaCO_3 , with prices just above \$10/metric tonne in 2018 ⁹⁸. However, as annual

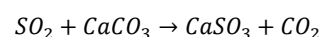
consumption of these minerals is significantly greater than of high-grade CaCO_3 , using RCC processes to meet the demand for calcium carbonate minerals may significantly increase the amount of carbon capture and utilization as compared to the carbon capture potential for high-grade CaCO_3 production alone.

In assessing the potential demand for CaCO_3 produced from RCC processes as a replacement for CaCO_3 generated from conventional mineral extraction processes, the end use case must be considered. For instance, based on reported data on limestone and dolomite consumption by use by the USGS ¹⁰⁰, it can be estimated that at least 12% of limestone and 6% of dolomite is used as coarse crushed aggregate stone, a product that cannot easily be generated from the CaCO_3 produced by saline-based RCC processes. However, other processes may be more suited to utilize CaCO_3 generated from saline-base RCC. For instance, cement manufacturing accounts for 10% of limestone consumption in the U.S. ¹⁰⁰, and there is evidence that CaCO_3 generated from precipitative carbon capture processes can be substituted for limestone in cement production ^{101,102}. This use case is particularly attractive as it provides a stable medium for long-term CO_2 storage. Other processes such as lime production, which accounts for roughly 4% of limestone consumption¹⁰⁰, re-release the CO_2 from the calcium carbonate, making them unsuitable for carbon sequestration efforts.



However, if the CaCO_3 used in these processes is replaced with RCC-generated CaCO_3 , new CO_2 emissions can be prevented, effectively “closing the loop” for carbon in the process.

Current examples of how lower-grade carbonate solids are valorised can be found in the management of softening-sludges generated in the water treatment industry. Many municipalities generate large volumes of carbonate minerals as a byproduct of lime softening, and then sell the carbonate-rich sludges to offset sludge management costs ¹⁰³. As municipalities often produce more softening sludge than there is demand for lime within their region (the cost of transporting softening sludges long distances to meet additional demand for lime production can become prohibitive), other applications such as flue gas SO_x scrubbing and wastewater pH control have previously been investigated ¹⁰⁴. While the dissolution of carbonates into acidic wastewaters does not directly lead to release of CO_2 gas, this approach may not be viewed as suitable for long-term, permanent CO_2 storage. The use of lime sludges for flue gas scrubbing does result in release of CO_2 gas ¹⁰⁴, again making this disposal approach unsuitable for long term sequestration.

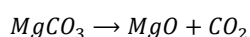


Again, in instances where RCC-generated CaCO_3 is used in in flue gas scrubbing in place of CaCO_3 generated using more carbon intensive methods, these applications may still result in net reductions in CO_2 emissions.

Magnesium Carbonate Though MgCO_3 is less readily precipitated than CaCO_3 , magnesium carbonates are still an important product of saline water-based RCC processes due to the abundance of Mg in many saline water sources. Magnesium carbonates have a variety of applications, including use as a pigment, flame retardant, and mineral filler ². There are numerous magnesium carbonates (including dypingite, hydromagnesite, lansfordite, artinite, and nesquehonite), some of which can have greater value due to their properties and applications. For instance, nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) is valued for use in building materials ², and it has recently been demonstrated to have cementitious properties ¹⁰⁵, furthering its potential value as a building material. Overall, 27 MT of crude magnesite (MgCO_3) are produced annually worldwide (excluding the United States) as of 2018, with an approximate value of \$150/metric tonne ¹⁰⁶. Magnesite is conventionally produced by mining/mineral extraction. As RCC methods develop, more in-depth analysis of the demand for more readily precipitated phases of magnesium carbonate (i.e. nesquehonite) would aid in determining whether processes that produce these phases are economically viable, and/or if post-processing to convert the magnesium carbonates into magnesite would improve the cost effectiveness of these processes.

Though the production of MgCO_3 can require more process steps than for Na_2CO_3 or CaCO_3 , its chemical value and relative abundance still make it an attractive product for RCC. Saline-based RCC processes may prove advantageous over other carbon capture technologies which generate MgCO_3 as it avoids the energy costs associated with converting magnesium to a form which readily reacts with CO_2 . Some carbon-capture processes generate MgCO_3 by crushing and then dissolving Mg-rich minerals, but these two steps are associated with a high energy demand, corresponding to a net production of 1.3 kg $\text{CO}_{2\text{eq}}$ generated for every kg of CO_2 consumed in MgCO_3 production ¹⁰⁴. Saline based processes utilize Mg already dissolved in the source water, so the energy expense of solubilizing the minerals is effectively eliminated. Many other magnesium compounds, such as MgO (magnesia) and $\text{Mg}(\text{OH})_2$, are already produced from aqueous resources to avoid the costs of mineral processing ¹⁰⁶.

Similar to CaCO_3 , the end use of MgCO_3 informs the overall carbon capture potential of RCC processes. For instance, MgCO_3 is used to produce magnesia, but this process releases the CO_2 from the mineral ¹⁰⁶.



As with lime production, the release of CO_2 prevents RCC processes with this end use from being truly carbon negative but enables carbon neutrality by preventing release of CO_2 from newly extracted MgCO_3 .

Lithium Carbonate. The concentration of lithium in most saline waters is significantly lower than the concentration of other carbonate forming species (i.e. Na, Ca, Mg) – for instance, the concentration of Li in seawater is <0.2 mg/L ¹⁰⁷, more than 10,000

times less than the concentration of Na ²⁶. However, geographic scarcity of lithium and the increasing demand for lithium carbonate for battery production ⁴⁰ makes this carbonate significantly more valuable than other carbonate products of saline-based RCC. Therefore, we include discussion of Li_2CO_3 as a potential RCC product, as producing even a small quantity of this carbonate can significantly impact the economics of RCC.

While Li_2CO_3 is predominantly used for battery applications, it is also used for glassmaking and other industrial processes ¹⁰⁸, as well as for medical applications ¹⁰⁹. In 2018, the worldwide production of Li_2CO_3 was over 95,000 metric tons/yr ⁴⁰. The price of lithium carbonate has generally increased over the past decade, and was \$37,000/metric tonne in 2023 ⁴².

As with other carbonates, it is vital to compare Li_2CO_3 production from RCC to current/conventional production method. Lithium carbonate is typically produced by adding soda ash (Na_2CO_3) to Li-rich brines, or by reacting concentrate generated from lithium-rich ores with Na_2CO_3 and CaCO_3 ¹¹⁰. A thorough TEA-LCA of the production of lithium carbonate via both conventional methods has been completed by Kelly et al., finding that brine production has a significantly lower carbon footprint than ore production of Li_2CO_3 (3 vs 20 tonnes $\text{CO}_{2\text{eq}}$ /ton Li_2CO_3 , respectively). They also found that for brine-based production, the soda ash was the most significant contributor to the carbon footprint for Li_2CO_3 production, while for ore-based production, the energy demand was the most significant contributor ¹¹⁰. These findings have multiple important implications for RCC processes. First, saline water-based RCC processes for Li_2CO_3 production would be similar to brine-based processes, and thus are likely to also have a lower carbon footprint than ore-based processes (depending on the energy consumption needed to concentrate the saline water source). Second, as previously discussed, soda ash can be generated using RCC processes, so further reductions of the overall carbon footprint of Li_2CO_3 production may be possible.

The end use of lithium carbonate also informs the carbon footprint of RCC processes generating Li_2CO_3 . The primary use of Li_2CO_3 is for batteries – more specifically, for generation of cathode materials. Li_2CO_3 is directly used to generate cathode materials such as lithium (manganese and/or nickel and/or cobalt) oxides, releasing the CO_2 stored in the solid in the process ¹¹⁰. It should be noted that the electrolyte in most lithium ion batteries consists of a non-carbonate lithium salt dissolved in an organic carbonate solvent ¹¹¹, so Li_2CO_3 is only sometimes used indirectly for the generation of the non-carbonate salt, a process that would also release the CO_2 ¹¹². Thus, as with other end uses that release the CO_2 from the carbonate product, RCC-generated Li_2CO_3 can only provide CO_2 emission reductions when used in lieu of Li_2CO_3 generated using conventional methods.

Barium Carbonate. Though barium has displayed similar CO_2 fixation potential to calcium and magnesium ¹¹³, the low concentration of barium in most saline waters (approximately 10 mg/L in seawater ¹¹⁴) makes it less likely to be a major product of

saline water-based RCC. In 2018, the value of BaCO_3 was just above \$1,000 per metric tonne¹¹⁵ – while this is more valuable on a per tonne basis than carbonates formed with more abundant ions (Na, Ca, Mg). However, compared to lithium, it is significantly less valuable and generally less abundant. For cations present at relatively low concentrations in seawater like lithium and barium, a significant cost benefit is needed to justify their targeted recovery in RCC processes, as they provide less carbon capture potential due to their low concentrations. It should be noted that another barium mineral, barite (BaSO_4), is considered a critical mineral as of 2022 due its geographic scarcity and its extensive use in drilling muds in the oil and gas industry¹¹⁶. At the time of this review, it is seen to be unlikely that BaCO_3 production can be used to address the critical nature of barite, as no reports could be found of a) use of BaCO_3 to synthesize barite, or b) use of BaCO_3 in lieu of barite in drilling muds. No accurate assessment of global BaCO_3 consumption could be found at the time of this review.

Strontium Carbonate. Strontium Carbonate (SrCO_3) is used for production of magnets, glassware/ceramics, and other strontium chemicals, as well as for various industrial processes¹¹⁷. The typical production methods for SrCO_3 are direct mining or indirect production from mined celestite (SrSO_4). As with other carbonates, use cases that release the CO_2 from strontium carbonate, such as strontium chemical production, prevent long term sequestration of the carbon. However, using SrCO_3 produced from RCC processes rather than from mined materials can prevent additional CO_2 emissions.

While no accurate assessment of global SrCO_3 consumption could be found at the time of this review, the demand can be indirectly estimated using global celestite production as a proxy, as the majority of celestite is processed to produce SrCO_3 ¹¹⁸. Global celestite production was 219,000 metric tonnes in 2018¹¹⁸, roughly equating to 104,000 tonnes of strontium. The average price of strontium carbonate was just below \$900 per metric tonne in 2018¹¹⁸.

Strontium is less abundant in many saline waters compared to cations Na, Ca, and Mg, but at almost 8 mg/L in seawater²⁶, it is more abundant than most other cations. The value of SrCO_3 is higher than carbonates produced using the more abundant cations, but like barium, the value may not be sufficiently high to justify targeted recovery, as the relatively low concentration of Sr limits the total CO_2 capture capacity of saline water-based RCC processes producing this mineral.

Complex inorganic carbonates. While the carbonates reviewed above consist of a single cationic element paired with the carbonate, numerous carbonate minerals that contain more than 1 cationic element exist. Minerals that are particularly relevant to RCC include dolomite ($\text{CaMg}(\text{CO}_3)_2$), huntite ($\text{CaMg}_3(\text{CO}_3)_4$), pirssonite ($\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$), and gaylussite ($\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$), as these minerals are comprised of the predominant cations found in most saline waters. In many instances, the primary value of these more complex carbonates is

simply as a feedstock for synthesis of single-cation element carbonates (i.e. CaCO_3 , MgCO_3 , Na_2CO_3). Some poly-cationic carbonates, such as dolomite, have value as a construction material due to their cementitious properties⁹⁸. However, as producing these complex carbonates requires maintaining specific mol ratios and reaction conditions, they are less likely to be a desired target product for saline-based RCC, as the value of these carbonates is unlikely to justify the cost of processing saline waters to produce the desired mol ratio for production.

Organic Products

Few saline water-based processes reported at the time of this review can generate organic products. However, as many organic chemicals are currently produced from fossil fuels, which typically have high associated carbon footprints, alternative methods of producing hydrocarbons are highly compelling. Current approaches can produce simple hydrocarbons including formaldehyde and formic acid, which can be used as feedstocks for the generation of more complex and valuable hydrocarbons¹¹⁹. The value (\$/ton) of the organic products reviewed here is greater than the value of many of the carbonate salts which can be produced from the most abundant cations in saline waters ($\text{NaHCO}_3/\text{Na}_2\text{CO}_3$, MgCO_3 , CaCO_3), and the global demand is on a similar scale to the demand for aforementioned inorganic products. However, the costs associated with producing these organic products using saline water may be greater than the costs of producing these organic products from fossil fuel sources, which would reduce the viability of RCC processes generating these simple organic products.

Formic Acid. Formic acid (HCOOH) is used in a wide range of industrial and agricultural processes, and is also of growing interest for use in hydrogen storage¹²⁰. Formic acid is primarily produced via hydrolysis of methyl formate¹²¹. The world's production capacity of formic acid was 950,000 tonnes per year¹²¹, and the price of formic acid was \$700-800 per metric tonne as of 2014¹²⁰. (It should be noted that the production capacity is determined by the capacity of formic acid production facilities and thus is likely an overestimate of the demand but provides a scale of reference for demand nonetheless).

Formaldehyde. Formaldehyde (CH_2O) is widely used in chemical manufacturing, industrial processes, and medicine, and is also commonly included in a wide range of consumer products as a preservative¹¹⁹. Formaldehyde is generally produced by oxidation of methanol¹¹⁹. Global production of formaldehyde was 62 million metric tonnes as of 2019, with prices ranging between \$450-1000 per metric tonne⁷³.

Methane, Ethane, and Ethylene. These hydrocarbons are primarily used as feedstock for hydrocarbon production, and in the case of methane, as fuel¹²². Global consumption of natural gas, which is primarily methane, was over 143,000 bcf in 2022¹²³. These hydrocarbons are primarily produced either directly or as a byproduct of fossil fuel extraction; methane can also be produced through biological processes¹²². When methane is used as a fuel, CO_2 and any un-combusted methane (which is an even more potent greenhouse gas) are released to the atmosphere, so as with other

RCC products, replacing conventional production with RCC only serves to reduce the carbon footprint rather than offer long term storage. As biological production of methane is already a widely used lower-carbon method¹²², there may be little incentive to use RCC processes to generate this product.

Summary of Product Values and Market Sizes

The product values, market size, and market value of each product is summarized in Figure 4. The products formed using the cations that are most abundant in most saline waters (Na, Ca, and Mg) are the least valuable, while LiCO_3 is significantly more valuable than other products. However, the market size for both CaCO_3 and Na_2CO_3 are much larger than the other products (with the exception of formaldehyde). As a result, the market value of CaCO_3 and Na_2CO_3 outweighs the value of products from less abundant cations in seawater. The high demand for these products makes saline-based RCC processes more economically attractive, so long as the solids can be produced at a low cost (due to the low value of the products). Additional techno-economic analysis of saline water-based RCC processes could be valuable. As previously noted, some of these processes can produce multiple mineral carbonate products. Additionally, there could be the potential to combine processes that are used to generate different mineral carbonate products. Saline-based RCC processes that generate multiple mineral carbonates could allow capitalization on both the large market size of products such as CaCO_3 and Na_2CO_3 , as well as the high value of products like Li_2CO_3 . However, little analysis of systems producing multiple mineral carbonates can be found at present. Such analysis could provide insights into the feasibility of saline-based RCC processes. It may also highlight the potential benefits of using real saline waters, which contain multiple carbonate-forming cationic species, as feedstocks for RCC.

It is also important to contextualize the market size of the potential products of saline-based RCC. A thorough techno-economic analysis by Shokrollahi et al. compared 34 CCU products and ranked CaCO_3 product as the most favorable product in terms of environmental impact and immediate applicability, and second most favorable in terms of economic potential (Syngas produced from CO_2 ranked first in this category.)¹²⁴. (Note – this analysis only considered Mg, Ca, and Na carbonates). This highlights the outsize potential of saline-based RCC processes capable of producing CaCO_3 within the field of carbon utilization.

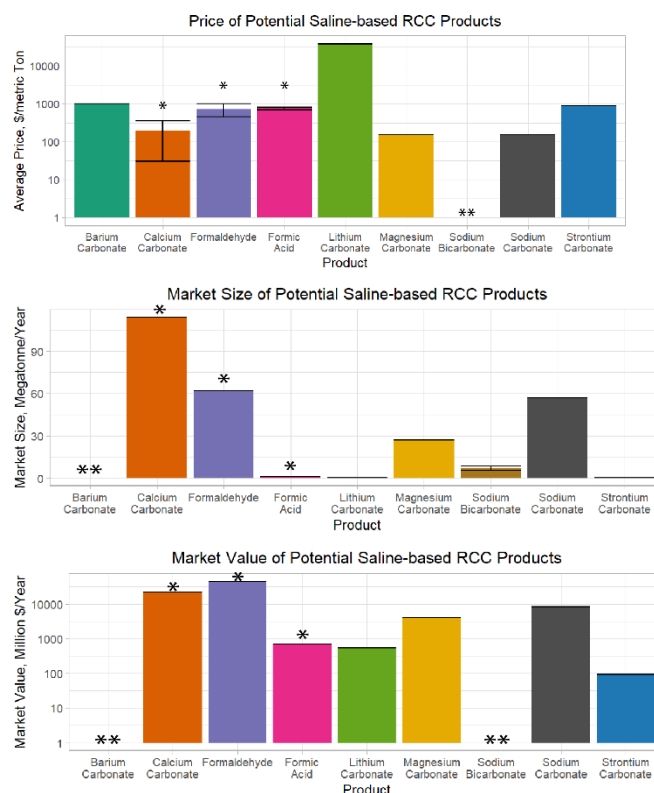


Figure 4. The price per tonne, market size (megatonnes/year), and market value (million \$/year) of potential products of saline-based RCC. Note that all values are from 2018, unless indicated with a single asterisk (CaCO_3 data from 2013, Formaldehyde from 2019, and Formic Acid from 2014). Double asterisks indicate missing data. Note that Price and Market Value are plotted on a logarithmic scale.

Costs of Saline-water based RCC

One of the primary purposes of saline water based RCC processes is to offset the cost of carbon capture with the value of the generated products. The cost of carbon capture varies widely between different technologies both in terms of capital and operation and maintenance (O&M) costs. Major differences in O&M costs emerge due to energy and chemical demands of the different processes, the saline water source used, and any associated waste handling. The overall cost of different RCC processes is also impacted by the value of the products generated – a process that has greater energy or chemical cost but produces a significantly more valuable product may have a lower overall cost per tonne of carbon captured than processes that are more energy or chemical efficient, but that generate less valuable products.

At the time of this review, few technologies reviewed here have been analyzed to determine the cost per tonne of CO_2 captured. Processes using electrolytically generated alkalinity to induce CaCO_3 precipitation, such as that proposed by de Lannoy et al., are estimated to cost \$300-600/ton net CO_2 captured [12]. This value reflects the cost per net capture of CO_2 , which was determined using technoeconomic/lifecycle analyses that considered factors

such as the energy demand and associated carbon footprint¹²⁵. However, many emerging CO₂ capture technologies that are actively being commercialized are reporting roadmaps to an eventual cost <\$100/ton net CO₂ captured, the threshold considered as commercially viable¹²⁶. This value does not include any offsets to costs from the sale of the CaCO₃ generated in the process. However, at a market price of between \$30-350/ton CaCO₃ (equivalent to \$13-150/ton CO₂), such processes may not be profitable.

A techno-economic review of CCUS technologies published in 2022 noted that systems that convert CO₂ to chemical products such as mineral carbonates are still in the development stage (technical readiness level 6)¹²⁷. In addition, the quantification of CO₂ capture costs and the potential of CCU technologies (which include saline-based RCC) is uniquely complicated amongst CCUS technologies as it requires analysis of complex market dynamics¹²⁷. The high energy intensity of many CCU processes has been implicated in limiting the implementation of these technologies, again emphasizing the need to a) quantify and b) reduce the energy demand for RCC technologies, as discussed in previous sections of this review. Additionally, at the date of this publication, no techno-economic analysis of RCC processes that produce high-value carbonates such as lithium in addition to large-market size products CaCO₃ and Na₂CO₃ could be found.

Aspects of the carbon capture process that most significantly impact the cost of carbon capture include the electrical demand and cost of electricity, chemical demand, and required equipment for the process¹². Thus, to provide a general evaluation of the cost of carbon capture with saline based RCC technologies reviewed here, we will discuss the energy costs, chemical costs, and relevant equipment costs of each. The equipment costs summarized here include only equipment which falls outside the purview of typical chemical processing equipment (pipes and fittings, tanks, mixers, pumps, etc.) and which may significantly impact overall cost of the technology due to either the amount required, the frequency of replacement, or relatively high price of the equipment itself. This includes equipment such as ion exchange membranes, where the number and frequency of membrane replacement required for a model RCC process had an outsized impact on overall process cost¹², and electrodes – the cost of electrodes is often the main capital expense for electrochemical processes, as electrodes are often made with expensive materials such as iridium and platinum. Yet, an often-overlooked aspect of many CCUS processes (at least in the scientific literature) is the cost of the balance of plant – the valves, control hardware and software, power source, etc. Often, these costs can be significant and should not be neglected.

When comparing the costs of RCC processes, it is critical to present the costs in terms of \$/ton net CO₂ captured, as this normalizes the costs to the amount of CO₂ capture, which can vary greatly between different technologies. Additionally, this value is normalized to the *net* amount of carbon captured, so processes which can convert a large amount of CO₂ and/or are low cost but have large associated

carbon emissions are fairly represented. Because it is crucial to evaluate the cost of RCC technologies in this way, we will also include discussion of the carbon footprint in this section. It should be understood that reducing the carbon footprint of any RCC process increases its cost effectiveness in \$/ton net CO₂ capture.

Summary of Energy, Chemical, and Relevant Equipment Requirements for Saline-Based RCC Processes

Though most saline-based RCC technologies are at early stages of development and thus typically have not been thoroughly economically evaluated, the costs of various technologies can be assessed by comparing energy, chemical, and capital infrastructure demands. Table 4 summarizes the energy costs, and also identifies chemical inputs and major equipment which contributes to capital costs. While the energy costs are a direct quantification, the other two categories are qualitative, as many of these technologies are at an early stage of development and thorough economic analyses of the process costs are not available at the time of this review.

Energy Demand

The energy cost of saline-water based RCC processes includes energy needed to move the saline water (pumping), the energy demand of the process itself (including the energy to pretreat the water and to drive the chemical processes), and the energy demand for any auxiliary operations (e.g., waste handling). Here, we will discuss the energy demand of RCC processes (including pretreatment), as this is a more consistent metric to compare technologies than energy cost, which can vary by location, power source, and time. However, it is important to note when using energy demand as the comparative metric that while energy costs generally scale with the energy demand, technologies requiring other energy sources (i.e. fuels used in thermally driven processes) may result in difference costs compared to technologies requiring electricity for the same energy demand. It should also be noted that the energy cost of saline-based RCC processes can vary based upon the product formed. As previously discussed, some carbonates (i.e. CaCO₃, NaHCO₃) readily precipitate under ambient conditions, whereas other carbonates (MgCO₃) require additional energy to drive precipitation²⁹.

Water Conveyance. The energy required to convey the large volumes of water required for saline-based RCC can be significant and should be considered in determining the overall carbon footprint of RCC processes. Factors impacting the energy demand of water conveyance include the distance and elevation gain between the two, as well as the flow rate, intake type, and pipe design⁶⁶. Due to the early stage of technical readiness of most saline based RCC technologies, no full-scale saline based RCC facilities exist to report the energy demands associated with water conveyance at the time of this review. However, this can be estimated using the energy required to convey water to desalination facilities,

Table 4. Summary of Major Costs/Cost Contributors Associated with various Saline RCC Technologies

Paper	Energy Costs (kWh/kg CO ₂)	Chemical Inputs	Major Equipment
Dara et al. 2017 ⁶⁰	4.8	Sulfuric Acid in electrode compartments	Pt/IR coated mesh Electrodes, PC-Cell IEMs
Dara et al. 2019	CO ₂ conversion not reported		Titanium & graphite electrodes, membranes (pc-cell, fumatech)
Zhao et al. 2020 ⁶³	0.89	NaNO ₃ in electrode chambers	Electrodes, YDS BPM, IEM
Nakata et al ¹⁴	CO ₂ conversion not reported		Electrode (BDD, Pt), Membranes (Nafion)
Islam et al ⁷⁴	Energy demand not reported	hydrogen gas	Sonicator
Dindi et al ⁸²	Energy demand not reported	amine catalyst (2-amino, 2-methyl propanol (AMP) (~30% amine regeneration demonstrated)	
Soong et al ⁶⁴	Energy demand not reported	Fly ash (waste material)	
Mustafa et al ⁵⁹	11.18181818		Ti/PT/Ir electrodes, IEMs (PC Cell)
Power et al ²⁹	Energy demand not reported		Carboxylated polystyrene catalyst
Taniguchi et al ¹²⁸	0.225		ED system (electrodes, membranes)
de Lannoy et al ¹²	2.72-3.85		ED system (electrodes, Neosepta/Selemion membranes), Membrane contactor systems for degassing
Ba et al ⁹⁴	4.318181818		Ti mesh electrodes, MF Membranes, IX Resin
Galvez Martos ¹⁰⁴	Energy demand not reported	NaOH	
El-Naas ⁹³	0.732277778	CaO	Bubble Contact Reactor
Xie et al ¹⁵	1.222904492	hydrogen gas	gas diffusion anode, nickel foam cathode, AEM
Palitsakun et al. ⁶¹	Energy demand not reported	NH ₃	

ARTICLE

Journal Name

Zhang et al. ⁶⁵	Energy demand not reported	furnace slag, NaOH	nickel nanoparticle catalyst material
Bang et al. ⁷⁹	Energy demand not reported	NaOH	
Park et al. ⁶²	CO ₂ Capture not reported	CaCl ₂	ceramic membrane
De Vito et al. ⁷⁸	Energy demand not reported	NH ₃	
Liu et al. ⁶	Energy demand not reported	Buffer (HBO ₃ , Tris)	

which is reported to range from 0.45–0.58 kWh/m³ for 50–10 MGD facilities, respectively¹²⁹. This is roughly the same as the energy demand for pretreatment, indicating the outsized but often overlooked impact water conveyance can have on the cost and footprint of water projects.

Pairing saline water-based RCC processes with other processes already handling large volumes of saline water is a potential way to reduce the costs acquiring the saline water. Eisaman et al. evaluated the impact of co-locating a seawater-based carbon capture process with power facilities using seawater for cooling, and with desalination facilities¹²⁵. This effectively reduces costs of conveying water by reusing water (i.e. reject brine or waste cooling water), which has already been collected and conveyed to a facility. They found that co-location with a power plant would reduce the costs by 33%, while co-location with a desalination plant would reduce costs by 55%. The lower cost reduction associated with power plant colocation was attributed to the need for additional treatment and pumping to increase the concentration of the seawater to a concentration comparable to a desalination brine.

Pretreatment. Depending on the RCC process being used, the saline water may require pre-treatment before further processing is possible. For example, certain saline streams may have suspended solids or organic matter that requires removal prior to downstream reactions; the energy demand of such pre-treatment steps are often missing from analysis of RCC processes but can be estimated from commonly used pre-treatment steps employed in other water treatment processes, such as seawater desalination. The wide range of technologies that may be employed as pretreatment steps to RCC, as well as the varied compositions of saline water, mean that there is a high degree of variability in the amount of energy required for pretreatment. Numerous treatment methods employed in water treatment can be applied here, including screening, coagulation/flocculation, clarification, and/or filtration for removal of particulate matter, as well as disinfection to prevent biofouling on RCC equipment. Best estimates of the energy demand include the energy demand of typical drinking water treatment processes preceding precipitative softening (0.54 kWh/m³,⁸⁰) or the energy demand of pretreatment for desalination (0.24 – 0.4 kWh/m³,¹²⁹).

Non-Electrically Driven Processes. The energy demand of saline based RCC processes is largely determined by whether the process is chemically or electrically driven. Processes that generate solids and are not electrically driven can be estimated to have a similar energy demand to typical precipitative softening processes. In their lifecycle assessment of drinking water softening, Beeftink et al.⁸⁰ determined the electricity demand to reduce the hardness of 1 m³ of water by 1 mM through carbonate formation in a pellet reactor to be 0.007 kWh/m³. Assuming 1 mol hardness reduction equates to 1 mol CO₂ capture (through formation of CaCO₃), this equates to 0.159 kWh/kg CO₂ captured. This value does not consider the energy (or emissions) associated with the production of any chemicals (e.g., CaO) used in conventional precipitative softening, though Beeftink et al. identify this as another major contributor and

include it in their determination of the overall carbon footprint of softening.

Electrically Driven Processes. The energy demand of electrically driven RCC processes can be larger than chemically driven processes due to the electrical energy needed to drive thermodynamically or kinetically unfavourable reactions. For instance, 80% of the energy demand of the RCC process developed by de Lannoy et al. is attributed to the BMED used to generate alkalinity needed to drive the precipitation reaction¹². Though the overall energy demand of electrically driven RCC processes is typically greater than chemically driven processes, the differences between various electrically driven RCC processes also results in vast differences in the overall energy demand of the process - the technologies reviewed here range from <1 to >10 kWh/kg CO₂ captured (see table 4). Further discussion of the energy demand of electrically driven RCC processes will focus on processes generating inorganic products, as the processes for organic synthesis are at a much earlier stage of development and have not been thoroughly characterized in regard to their electrical demand.

In electrically driven saline-based RCC processes that involve the electrolysis of water to generate alkalinity as OH⁻, there is a base energy demand associated with this reaction. For processes that utilize bipolar membranes, the energy consumption associated with electrolysis is around 600–700 kWh/ton NaOH¹³⁰, though in practice the energy consumption is greater due to resistance caused by the ED stack. Processes that utilize conventional electrolysis via a cathode and anode typically have even greater energy consumption, due to overpotentials associated with the generation of O₂ and H₂ gas at the electrodes¹³⁰. The base energy demand associated with direct electrolysis is around 1400 kWh/ton NaOH¹³¹, though again actual energy demand is much greater.

The energy demand of RCC processes utilizing ED is also strongly impacted by the current efficiency of the ED system. Systems that use ED to generate strong acid and/or base suffer from reduced current efficiency as the concentration of the generated acid/base increases¹². As the concentration of acid/base used in RCC can impact the carbon capture efficiency¹², it is important to assess the trade-off between increased reaction efficiency and increased energy demand with concentration. Additionally, approaches to preventing or reducing losses of current efficiency during operation are an important lever to reducing energy demand in electrochemical RCC processes. Zhao et al. found that combining their ED system with a seeded crystallizer reduced the energy cost per kg CO₂ sequestered, as circulating the concentrate stream through the seeded crystallizer prevented scaling from occurring within the membrane stack, thus preventing losses in efficiency⁶³.

It should be noted that the energy demand of electrically driven CO₂ capture processes can extend beyond the energy required to drive the process, particularly in instances where the electrically driven process serves primarily to concentrate the carbonates. For instance, Taniguchi et al. determined that the energy demand for an ED system intended to concentrate carbonates captured in a

potassium solution was 0.225 kWh/kg CO₂, but the overall energy demand nearly doubled when solution circulation and CO₂ recovery from the concentrate were considered¹²⁸. While this study considered vacuum stripping to produce CO₂ gas as the recovery method (as opposed to conversion to a valuable product), it is useful in demonstrating the magnitude of energy consumption directly associated with electrically driven CO₂ capture processes with energy associated with other components of potential RCC processes.

Chemical Demand Many saline-based RCC processes utilize additional chemicals to produce favourable reaction conditions for the formation of the desired products. Bases (and to a lesser extent, acids) are a common chemical input, used to shift the pH of the reaction to promote product formation. Other chemical inputs are often catalysts that facilitate the desired reaction (CO₂ dissolution or precipitation), as well as any chemicals used in the pretreatment of water used in the process. While acids and bases are often consumed by the process and thus require continuous addition, some catalysts can be regenerated, reducing associated costs. (Note: There are two major concerns related to chemical demand of RCC processes – cost and carbon footprint. Here we will focus on cost, and in the following section we provide further discussion of the carbon footprint of chemicals required for RCC). Because approaches to saline-based RCC often involve shifting pH with base to induce CO₂ dissolution or precipitation, many electrochemical processes have been proposed to provide in situ generation of alkalinity/acidity (see previous section). This approach can reduce the chemical costs by producing base/acid directly from the saline water stream, instead incurring the expense of the energy required for electrolysis. Additionally, in instances where the electricity used to drive the process is provided by a low-carbon source (solar, wind, etc.), the carbon footprint of the chemicals required for the RCC process can be reduced.

While electrochemistry provides a promising solution for reducing the chemical costs of bases/acids used in RCC processes, regeneration methods provide the key to reducing costs associated with catalysts used in RCC. Being able to regenerate the catalyst can not only reduce the cost per tonne CO₂ captured, increasing the efficiency of regeneration can help reduce the carbon footprint. Many factors impact regenerability, including (but not limited to) the catalyst solubility and boiling point. There can be a trade-off between the CO₂ capture potential and ease of regeneration for catalysts, as demonstrated by Dindi et al in their investigation of alkanolamines as an alternative catalyst for ammonia in the Solvay process⁸². They found that while the alkanolamine catalyst 2-amino, 2-methyl propanol (AMP) increased the conversion of NaCl to NaHCO₃, the distillation process used to effectively recover ammonia from the Solvay process only achieved 20% recovery of the AMP catalyst (due to higher boiling point of AMP), though slightly higher recovery of 30% was achieved after recovery process modification⁸². Designing RCC processes to utilize more easily

recovered or regenerated catalysts can improve the project economics and carbon capture potential.

The chemical demands of saline-water based RCC processes can extend beyond the chemicals directly used in the process to include chemicals used to pre-treat the water source. As previously discussed, many saline water sources (i.e. seawater) contain other constituents (TSS, DOC) that must be removed prior to RCC processes. While some pretreatment methods such as filtration require relatively little chemical inputs, other processes such as coagulation and flocculation can be chemically intensive. For instance, Beertink et al. estimated that coagulation prior to softening consumed 4.72 g of FeCl₃/m³⁸⁰. While the amount of required coagulant will vary according to the composition of the source water and the type of coagulant used (i.e. alum, FeCl, etc.), this estimate illustrates that there can be non-negligible chemical inputs required for pretreatment to enable RCC using real saline waters. Chemical demands of pretreatment can be reduced by using more energy intensive processes such as electrocoagulation or filtration (MF, UF, NF).

Carbon Footprint

The energy and chemical requirements for RCC are major factors of the cost of saline water based RCC, as they contribute to the carbon footprint of the process. For an RCC processes to be carbon negative (i.e. to actually provide a net capture of carbon), the total carbon footprint of the energy and chemicals required to drive the carbon capture and conversion process must be lower per kWh than the amount of carbon captured per kWh. Coal-generated power has CO₂ emissions of roughly 1 kg CO₂/kWh and natural-gas generated power has CO₂ emissions of roughly 0.4 kg CO₂/kWh¹²⁶, so a net-carbon negative RCC process would need have an energy demand lower than 1 kWh/kg CO₂ if using coal-generated power or lower than 2.5 kWh/kg CO₂ if using natural gas-generated power. Of the 7 RCC processes reviewed here that had a quantified energy demand (all of which were electrically driven processes), 3 had energy demands below 1 kWh/kg CO₂, with 1 additional technology having an energy demand between 1 and 2.5 kWh/kg CO₂. While this energy demand includes the energy required to produce the chemical constituents used to convert CO₂, the energy demands reported for the RCC technologies still likely underestimate the overall process energy demand when water conveyance and pretreatment are considered, so even these technologies may not be net carbon negative if using power from these sources. Additionally, little information is available about the energy demand of chemical titration saline based RCC processes, for which the greater portion of their respective carbon footprints is associated with production of the chemical feedstocks as compared to electrically driven processes. In these instances, the carbon footprint of chemicals used in RCC processes must also be included in accounting for the net carbon capture provided by these processes and is likely to effectively decrease the net carbon capture per kWh of RCC processes, pushing them further from reaching carbon negative status.

Most chemicals used in saline-based RCC processes have an associated carbon footprint, whether they are generated as part of the process (as is typical in electrically driven processes) or purchased as a feedstock (typical to chemical titration processes). In the electrically driven processes reviewed here, the energy demand reported for each technology includes the energy required to generate these products. However, chemical titration processes often don't report the energy demand or carbon footprint associated with the chemical feedstocks they require, so we will briefly discuss the carbon footprint of some common chemical feedstocks for saline based RCC here.

One of the most common feedstocks for these processes is NaOH, which alone can contribute more than 1 kg CO₂ generated/kg CO₂ captured in carbon capture processes utilizing NaOH evaluated by Medina-Martos et al.¹³². This study assumed that the chlor-alkali process is used to produce NaOH, and found that using 100% renewable energy to drive this process (as opposed to a typical mix of 30% renewable energy sources used today) significantly reduced the carbon footprint of the process, in some cases allowing for a net negative carbon footprint¹³².

Another feedstock to chemical titration processes is lime (CaO), which is commonly used in softening processes to produce carbonate solids but has not been as extensively applied to carbon-capture purposes. Lime is typically produced by heating limestone (CaCO₃), requiring a large amount of thermal energy. This has an associated carbon footprint of 1-1.8 kg CO₂ generated/kg CaO produced¹³³. (Note that lime softening can capture between 1-2 mols CO₂ per mol of lime added, so this would equate to 1.3 – 4.6 kg CO₂ generated/kg CO₂ captured). The higher CO₂ generation per amount of CO₂ captured provides a clear demonstration of why processes using NaOH as a source of alkalinity are the focus of development for saline based RCC.

Though the chemical and energy demands of saline water based RCC processes (particularly when considering energy for conveyance and pretreatment) may exceed the allowable demand to remain net carbon-negative when using power generated using coal or natural gas, there are still ways that these processes can effectively provide carbon capture. The limit to the energy demand for a net-carbon negative RCC process increases significantly as the carbon footprint of the power source decreases to near 0 for sources such as solar, wind, and nuclear. Additionally, as previously discussed, processes that electrochemically generate the required chemicals can reduce the carbon footprint of the process. To achieve meaningful carbon capture with saline based RCC, it is important to 1) carefully plan RCC deployment to utilize low-carbon energy, and 2) continue to improve the energy efficiency of the RCC processes. More comprehensive analysis of the carbon footprint of proposed saline-based RCC facilities that include both carbon associated with the energy demand for water conveyance and pretreatment and carbon associated with chemical inputs to the process is necessary to assess the actual carbon capture potential of these technologies.

Comparison to Sequential Carbon Capture and Utilization Approaches

One of the potential benefits of RCC processes is the reduction of energy demand and costs compared to systems that involve multiple separate processes to capture and then convert CO₂ to end products (we will refer to these as “sequential CCU processes”). In their review of CCUS technologies, Hong identifies numerous carbon capture methods – industrial separation, post combustion capture, pre-combustion capture, oxy-fuel combustion, chemical-looping combustion, and direct air capture¹²⁷. These carbon capture technologies have energy demands ranging between 0.3-1.4 kWh/kg CO₂ (1-5 GJ/tonne CO₂), and an associated cost of \$34-340/tonne CO₂¹²⁷. The energy demand of these steps is similar in scale to the energy demand of saline-based RCC processes reviewed here (0.2-12 kWh/kg CO₂). However, the critical consideration of sequential CCU is that there is also an associated energy demand to convert the product of the aforementioned carbon capture processes to a saleable product. While carbon capture is often the most energy and cost-intensive step, accounting for upwards of 50% of sequential CCU costs¹²⁷, the contribution of subsequent processing required to generate value-added products from the captured CO₂ is not insignificant.

In order to compare the energy demands and other costs of RCC processes to those of CO₂ conversion processes in sequential CCU, it is necessary to clearly delineate the costs of carbon capture and costs of carbon utilization in both steps. For saline-based RCC, it is important to note that several of the technologies reviewed here used a source of concentrated CO₂ in their proof-of-concept and bench-scale studies. It can thus be understood that these technologies could be paired with any of the aforementioned carbon capture processes to act as sequential RCC, and the energy and costs of the processes would be the sum of the capture and conversion processes (thus increasing the energy demand range to 0.5-13 kWh/kg CO₂). This is why a major point of this review is the potential to use saline water sources which can capture CO₂ from the atmosphere and then be directly converted into an end product, as this carbon source eliminates the carbon capture step required for sequential CCU. As previously noted, a critical step in the development of saline-based RCC technologies is study of the impacts of using real saline waters on the energy demand and costs of these processes. Notwithstanding the impacts of the carbon source on the energy demand of saline-based RCC processes and sequential CCU processes, a direct comparison between the energy demands and costs solely related to CO₂ conversion would illuminate the potential benefits and drawbacks of these processes. However, though many reviews of carbon conversion processes exist^{134 135 136}, there has not been comprehensive quantification of the energy demands and costs of these processes at the time of this review, making such comparisons difficult.

Environmental Impacts

While the purpose of RCC processes is to positively impact the environment by reducing atmospheric CO₂, it is important to not overlook other potential environmental impacts these processes could have when implemented at scale. Two of the primary potential impacts – water pollution and ecological damage – as well as methods to mitigate these impacts are discussed in this section.

Wastewater management

The environmental impacts of saline-water based RCC processes must also include any impacts of waste generated by the process. While saline-water RCC processes can generally be compared to water softening processes, in the case of RCC, the generated solids are the desired product, and the treated water is a byproduct (whereas softened water is the desired product and solids are treated as wastes). Thus, different waste management approaches may need to be applied to saline based RCC. However, the waste management objective to reduce the amount of waste ultimately discharged to the environment can still be applied to saline-based RCC processes.

Waste diversion to beneficial reuse is a broadly employed strategy that aligns with many RCC processes. In some instances, saline water is softened and/or desalinated during RCC, and such water can be considered as a desired product when diverted for potable or non-potable beneficial reuse. Depending on the quality of the saline water used for RCC, the resulting wastewater may need to be diverted to a water treatment or reclamation facility prior to reuse.

Additionally, it should be noted that while wastewater streams produced by RCC processes may be desalinated due to the removal of ionic species through formations of carbonates, this cannot always be assumed to be the case. For instance, many of the electrochemical approaches reviewed here effectively concentrate the saline stream, so even after removal of carbonate forming species, other ionic species may remain in the water at increased concentrations. In these instances, RCC wastewater would require additional treatment prior to beneficial use or discharge. Another consideration for the management of RCC wastewater is that the wastewater may exceed the volume of water that can be beneficially reused, and thus would need to be disposed.

Discharging of wastewater can be achieved by either discharge to the environment, deep well injection, or evaporation. Discharging to the environment often requires that the wastewater is of suitable quality. A water quality standard that may prevent discharge of waters used in RCC to the environment is salinity limits. While there have not been nationwide limits on salinity for discharge, many local water quality authorities have set limits or guidelines, generally limiting discharge concentrations to around the TDS limits for water use (500 mg/L in drinking water, 1000 mg/L for other uses¹³⁷). However, as the discharge limits for salinity are determined on a case-by-case basis, there are instances in which the discharge limit may be as high as the US EPA's recommendation of 40 g/L TDS (slightly above the salinity of seawater)¹³⁸. Another water quality marker which should be considered when releasing

wastewater from RCC processes to the environment is the dissolved CO₂ content (DIC). While generally less stringently regulated than salinity, releasing CO₂-depleted water into aquatic environments can cause temporary, localized pH shifts which could harm ecosystems. Though waters released to the environment would eventually re-equilibrate with the atmosphere, in regions such as the mixed surface layer of the ocean, this process can take up to 1 year¹².

Ecosystem Impacts

Entrainment. A major concern for saline water intake is entrainment, where microorganisms living in the source water are taken into the processing facility. This poses an issue for both the RCC process and the surrounding ecosystem. Simple methods such as filtration can prevent the microorganisms from clogging or fouling downstream system components, but this does not solve the ecological harm which can occur by continuously removing microorganisms from an ecosystem. Careful location of saline water intakes is required to avoid disturbing sensitive ecosystems, such as coastal areas where microorganisms make up the base of the food chain and also account for the larval stage of many larger organisms. Again, many lessons learned from the seawater desalination industry can be applied to minimize this potential hazard.

RCC within the Carbon Capture Landscape

While there are several promising aspects of saline-based RCC, it is essential to compare the potential of this approach to the amount of carbon capture required to mitigate climate change. In their 2013 review of the prospects of CCU technologies, Aresta et al. highlight that while chemical production consumes approximately 200 megatonnes CO₂/year, this makes up less than 1% of anthropogenic CO₂ emissions, which are on the scale of 32,000 megatonnes/year¹³⁶. The production of inorganic carbonates, the primary output of many of the RCC processes reviewed here, accounts for only about a quarter of the CO₂ consumption associated with chemical production¹³⁶, further highlighting the mismatch between the potential supply and demand. It is also important to consider the capacity of other CCU/CCS approaches. For instance, urea production makes up over half of the 200 megatonnes/year of CO₂ capture associated with chemical production¹³⁶. This is the only carbon utilization pathway identified by Aresta et al. that has a greater carbon capture potential than inorganic carbonate production pathways (such as saline-based RCC). Processes that have greater carbon capture potential typically involve storage/sequestration of CO₂, such as CO₂-enhanced oil and gas recovery, ocean storage, and injection into deep saline formations (which can include in-situ mineralization). Numerous in-depth reviews of various CCUS approaches have been published^{2 127 139}.

Even though it may seem intuitive to compare the capacity of CCU and CCS processes, the "capacity" of CCU processes is determined by market demand, while the "capacity" of CCS is determined by

physical availability. The IEA identifies processes that involve carbon storage as critical to reaching climate goals and indicates that there is more than sufficient storage capacity to achieve these goals – while 94 Gt of carbon storage is needed by 2050 to meet the 2°C target, there is between 2,000–20,000 Gt of geological carbon storage potential in the United States alone¹⁴⁰. While saline-based RCC (as well as all other CCU approaches) may not suffice to fully achieve the carbon capture needed to meet climate goals due to the mismatch between the demand for CO₂-derived products and the amount of CO₂ requiring removal, it should be emphasized that this failure is related not to any technical shortcomings of RCC but instead is a result of the framework of producing saleable products to reduce the cost of carbon capture. Therefore, while there is certainly space for RCC systems to generate carbon-neutral or negative chemical products as part of carbon capture efforts, these technologies need not be restricted to implementation in instances where the products can be sold, but may also be used to generate products that can provide long term storage/sequestration of CO₂ (e.g., ex-situ mineral carbonation). Two major barriers have been identified for these types of processes – the kinetics of carbonate formation, and potential environmental impacts associated with the mineral source¹⁴¹. The first concern is addressed by many of the technologies reviewed here, which use various approaches to enhance the rate of carbonate formation. However, the ability of saline-based RCC technologies to address the second barrier is equally, if not more, important. As discussed previously, using saline water as the source of carbonate-forming cations can avoid the need to mine and dissolve carbonate-forming minerals. Additionally, for processes that ultimately generate solid carbonates, there is an added benefit of the ease of accounting for the stored carbon (which is far more difficult in many other CCUS approaches). A 2022 techno-economic review of CCUS technologies suggested a similar approach – integrating CCU technologies (such as RCC) with CCS systems to increase the carbon capture potential of these approaches. Here, saline-based RCC technologies may provide potential benefit over other CCU approaches that generate products that are less easily stored or disposed of. Inorganic carbonates have the longest CO₂ storage times of the CCU products considered in Shokrollahi et al.'s techno-economic analysis of CCU processes and products¹²⁴.

Conclusions

Several major trends emerged in our review of the existing literature on saline water-based RCC processes. Many studies focused on methods to improve the kinetics of carbonate formation, either by concentrating the saline water stream, using catalysts, or optimizing the CO₂ transfer efficiency. These approaches allowed for carbon capture at ambient temperatures and pressures, which has the potential to greatly reduce the energy demand compared to processes requiring elevated temperatures/pressures. Additionally, nearly all of the studies reviewed involved careful control of the reaction pH to produce the desired products, which falls in line with Liu et al.'s assessment that

pH was the single most important factor in determining carbon capture potential of precipitative processes⁶.

Interestingly, many studies focused on concentrating the saline water stream, whereas only a few discussed other approaches to enhancing CO₂ dissolution, though at least one study demonstrated that the precipitation reaction was limited by CO₂. This may in part be due to the fact that many of the studies reviewed used pure CO₂ or a gas stream containing CO₂ at concentrations above those found in the atmosphere. While this can simplify bench-scale analysis, it limits the applicability of many of the methods reviewed here to carbon capture from ambient air. Further study of methods to enhance gas transfer into saline waters in RCC processes would be useful, particularly in investigating the CO₂ capture efficiency of these processes from more realistic CO₂ sources. While it is in theory feasible to provide pure CO₂ produced from another carbon capture method with many of the technologies reviewed here, this such approaches cannot be classified as RCC, and would eliminate the energy savings from avoiding CO₂ gas processing, a major benefit of RCC processes.

Another limit to the existing studies of saline based RCC processes is the use of synthetic saline water sources, which are often pure NaCl (or other chloride salt) solutions. Again, while using these solutions is helpful to quantify the carbon capture potential of the process, they fall short of estimating the carbon capture potential of the process using real saline water, in which the presence of competing constituents can impact both the carbon capture efficiency and the purity of the end product. Further work investigating how these processes can be used to produce carbonate products of sufficient purity for beneficial use would be useful in demonstrating the actual viability of these technologies for RCC.

Overall, the development of saline based RCC processes is promising based on the underlying chemistry but limited in actual demonstration and evaluation. Only one of the reviewed studies provided a cost estimate of the process, and nearly one third provided no quantified information on the carbon capture potential of their respective RCC process. Most technologies reviewed here were bench scale operations. However, as discussed, the existence of processes utilizing similar chemistries in the chemical manufacturing and water treatment industries provides invaluable examples of how these technologies can be applied at scale.

Finally, we highlight that there is a significant mismatch between the scale of the markets for products of saline-based RCC processes and the scale of carbon capture needed to meet climate goals. Fortunately, because many of the products of saline-based RCC processes are stable and non-hazardous, there is the potential to apply these technologies at larger scales, although this will require treating the products as a waste rather than a value-added product (once market demands have been met). As the primary objective of RCC is to reduce atmospheric CO₂, the demonstrated carbon capture potential should encourage further study and development

of these technologies, even in instances where the market demand for the associated products is limited.

Author contributions

Anya Dickinson-Cove: Investigation, Writing – original draft, Writing – review & editing, Data Curation, Visualization. Dr. David Jassby: Supervision, Funding Acquisition, Writing – review & editing. Dr. Erika La Plante: Writing – review & editing. Dr. Eric M. V. Hoek: Writing – review & editing. Dr. Yiming Liu: Investigation, Writing – original draft. Dr. Guarav Sant: Conceptualization.

List of possible roles: conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, software, supervision, validation, visualization, writing – original draft, writing – review & editing

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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No primary research results, software or code have been included and no new data were generated or analysed as part of this review.