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ANALYSIS OF ELECTROCHEMICAL CAPTURE OF CO₂ FROM OCEANWATER COUPLED WITH HYDRATES-BASED SEABED SEQUESTRATION

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ABSTRACT

Novel energy efficient and scalable carbon capture and sequestration technologies are critical to meeting the goals of the Paris Agreement. In this study, we present a first-order system-level assessment of an integrated carbon capture and carbon sequestration plant that couples electrochemical CO₂ capture from oceanwater with co-located long-term carbon sequestration as CO₂ hydrates (ice-like solids) on the seabed. Separate recent experimental results associated with electrochemical capture and hydrate formation form the basis for this energetics-focused analysis, which evaluates power consumption of all the key components associated with capture and sequestration. Hydrates can be formed from both pure water as well as seawater, and the implications of including a desalination plant to provide pure water for hydrate formation are studied. All analysis is conducted for a 1 plant which captures and sequesters 1 megaton CO₂ annually. Our results indicate the carbon capture will consume significantly more energy than carbon sequestration despite the use of a low-energy consuming electrochemical technique. From a sequestration standpoint, there are clear benefits to forming hydrates at high pressures, since the elevated formation rates reduce the number of hydrate formation reactors significantly. It is also seen that the addition of a desalination plant to provide pure water for hydrate formation (which speeds up hydrate formation) will not affect the energetics of the overall process significantly; however the CAPEX and operational aspects of including a desalination plant need to be analyzed in greater detail. Overall, this study seeds a novel CCS concept which can be deployed via decommissioned oil-gas platforms to capture CO₂ from surface oceanwater and store CO₂ right below on the seabed after appropriate sealing (artificial or natural).

Keywords: carbon capture and sequestration, CO₂ hydrate sequestration, electrochemical CO₂ capture, desalination

NOMENCLATURE

A_e Cell Electrode Area
 c_p Specific Heat of Water,

D_h Hydraulic Diameter
 g gravitational acceleration
 h total dynamic head loss
 E_{CP} Energy of Cell Pump
 E_{EC} Energy of Electrochemical Cells
 E_{intake} Energy of Intake Pump
 $E_{pretreatment}$ Energy of filtration
 $E_{VP,O_2/N_2}$ Energy of Vacuum Pump
 f Friction Factor
 F Faraday constant
 $F_{m,O_2/N_2}$ Molar Flow Rate of O₂ and N₂
 i Current Density
 k Isentropic Exponent
 $\dot{m}_{CO_2}$ Mass Flow Rate of CO₂
 M Molar Mass of CO₂
 n_{cells} Number of Electrochemical Cells
 p CO₂ Removal Efficiency after Gas Separation
 ΔP_{CF} Cartridge Filter Pressure Drop
 ΔP_{DF} Disk Filter Pressure Drop
 ΔP_{UF} Ultrafiltration Pressure Drop
 P_{comp} Compressor Power per Stage
 P_{HXPump} Heat Exchanger Pumping Power
 $P_{VP,i}$ Permeate Side Pressure
 $P_{VP,o}$ Atmospheric Pressure
 Q Heat Removal
 Q_{OW} Oceanwater Volumetric Flowrate
 $Q_{OW,C}$ Oceanwater Volumetric Flowrate per Cell
 r Ratio of Electron to Proton Transfer
 R Universal Gas Constant
 T Temperature
 Z Compressibility Factor
 δ Cell Gap
 κ_{O_2/N_2} Adiabatic Constant of O₂ and N₂
 η_{is} Isentropic Efficiency
 η_{FE} Faradaic efficiency
 η_p Pump Efficiency

η_m	Motor Efficiency
ρ	Density
$\bar{U}_w$	Ionic Conductivity

1. INTRODUCTION

While significant decarbonization-related efforts are underway globally, it is becoming increasingly clear that they will not be timely enough to mitigate the increasing negative effects of climate change. Negative emission technologies will need to be implemented at large scales to reduce excess CO₂ from the earth's atmosphere and oceans. Carbon Capture and Sequestration (CCS) is therefore necessary to meet the Paris Agreement's target of limiting global temperature rise to <1.5°C. According to the Intergovernmental Panel on Climate Change (IPCC), up to 10 gigatons of CO₂/yr will need to be captured and sequestered by 2050 [1]. However, as of 2020, existing global capacity was ~40 MT/yr [2]. This highlights the need for novel CCS approaches that can be deployed at scale globally.

Presently, the most commonly used carbon capture approach is chemical absorption with a liquid sorbent such as an amine [3,4]. This is the approach taken to separate CO₂ from the flue gas streams of most point-sources such as power plants. Plate towers, packed columns, spray columns, and bubble columns are various configurations used to maximize the mass transfer associated with liquid absorption [5-8]. Other post-combustion techniques for capture include microalgae bio fixation, membrane separation, and solid adsorption [9-11].

While the capture of CO₂ from combustion processes and point-sources is critical to CCS efforts, it cannot capture all emissions from a variety of sources. Direct Air Capture (DAC) addresses planet-scale carbon removal via large scale air contactors to capture CO₂ directly from atmospheric air [12]. In addition to the large capital cost, current DAC technologies require nearly three times more energy (as compared to capture from coal-based flue gas) because of the low concentrations of CO₂ (~0.04%) in air [12].

Surface waters, including oceans, have absorbed 30-40% of all anthropogenic CO₂ emissions since the beginning of the industrial revolution [13]. While this absorption has contributed significantly towards reducing atmospheric CO₂ concentrations, it has come at the cost of ocean acidification and harm to ocean life [14]. Volumetric concentrations of CO₂ in oceanwater are higher than in atmospheric air. Oceanwater concentrations of CO₂ on a volumetric basis are 100 mg/L compared to 0.77 mg/L in atmospheric air [15]. This strongly highlights the potential advantages of oceanwater-based CO₂ capture [16,17].

One of the biggest challenges limiting the realization of any carbon removal technology is the high energy consumption associated with regenerating the sorbent (for reuse). Consequently, on-going research has focused on alternatives to conventional carbon capture approaches. Recently, Kim et al. developed a novel approach to capture CO₂ from seawater using a membrane-free, electrochemical process [18]. This approach requires only electrical energy and not thermal energy, which

significantly reduces the total energy requirement for capture, as well as making it more viable for use with zero-carbon energy sources [18].

Capturing CO₂ is only the first step in CCS; viable long-term sequestration technologies are essential for the overall success of CCS. While multiple carbon capture technologies exist or are under development [9-11], the only well-established large-scale CO₂ sequestration technology today is geological injection. However, despite decades of R&D, there are only seven US sequestration sites currently operating with annual sequestration capacity greater than 1 megaton CO₂ [19]. Importantly, the lack of appropriate geology restricts the application of this carbon sequestration technology in many high emission regions such as China, India, Japan, etc. [20]. Other challenges associated with geological injection include the risk of leakages, decades-long monitoring and potential seismic risks.

Recent research has explored the viability of sequestration via CO₂ hydrate, as an alternative to geological injection [20]. Gas hydrates are ice-like solids of hydrogen-bonded water molecules which form a cage around a guest gas molecule. CO₂ hydrates typically require 6 water molecules to trap 1 CO₂ molecule [20, 21]. Sequestration of CO₂ on the seabed (or under marine sediments) is attractive since hydrates are thermodynamically stable at seafloor conditions wherever temperatures are less than 3°C and pressures greater than 350 psi [20]. Furthermore, hydrates exist naturally in permafrost regions, and have been known to remain stable for geological timescales [20]. Additional key advantages of hydrates-based sequestration include their high storage capacity wherein 1 megaton CO₂ can be sequestered in a 1 km² area as a 3 meter thick layer of solid hydrate [20]; this area requirement is at least 10 times smaller than the area footprint of geological injection projects. It is noted that the present group has developed several technological solutions to speed up hydrate formation significantly, which is essential for the techno-economic viability of hydrates-based sequestration [22,23,24].

This study conceptualizes and analyzes the coupling of the recently proposed electrochemical approach to remove CO₂ from surface oceanwater, with hydrates-based sequestration via the formation of CO₂ hydrates in state-of-the-art bubble column reactors (BCRs). Such technological solutions could be located and deployed on decommissioned off-shore oil-gas production platforms in the future, which will enable surface water CO₂ capture (which then allows the water to passively absorb further CO₂ from the atmosphere). Presently, a first-order system-level technical assessment of an integrated electrochemical CO₂ capture plant coupled with subsea sequestration via CO₂ hydrates is conducted. The electrochemically captured CO₂ is compressed and converted into a CO₂ hydrate slurry by bubbling CO₂ through water in a bubble column reactor. This slurry would then be gravity-transported to the sequestration site, compacted (to remove water and excess gas), sealed (artificially or by sediments) and then deposited on the seabed for permanent sequestration. In addition to process-related advantages (eg. low energy consumption) another key advantage of this approach includes co-located processes which eliminate CO₂

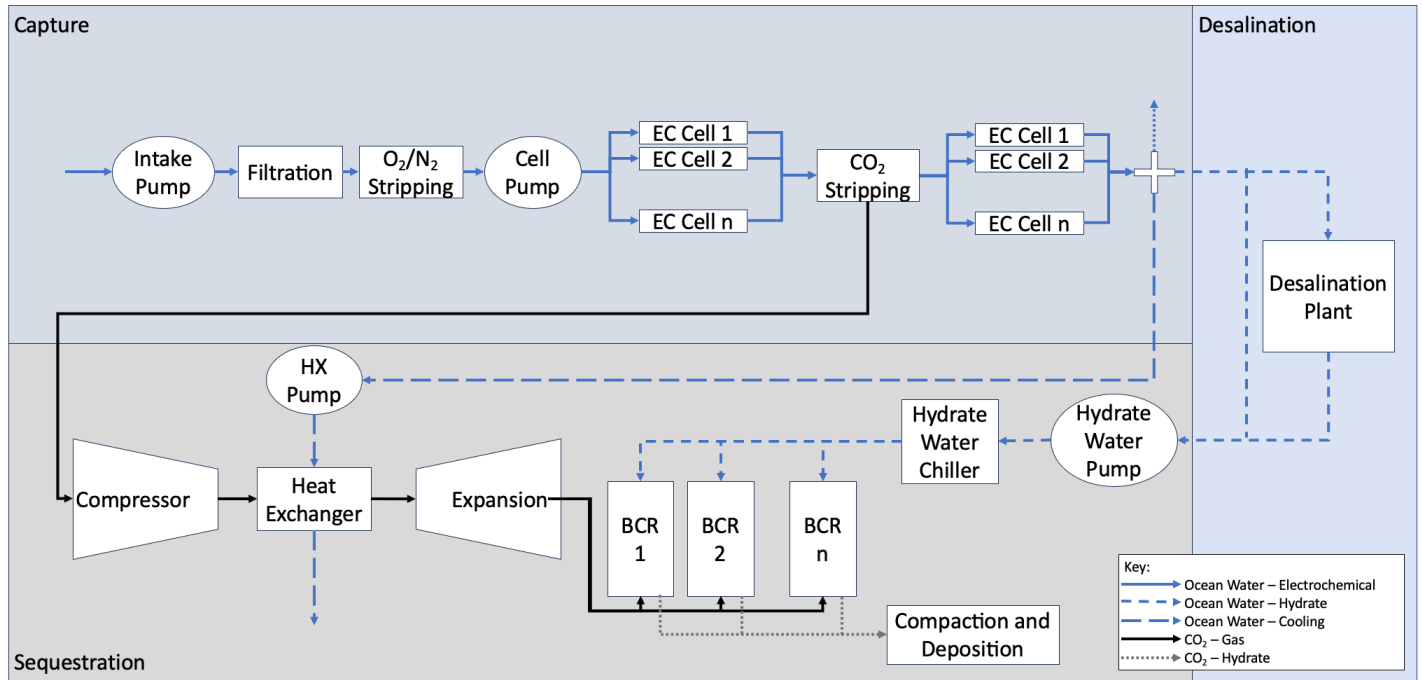


FIGURE 1: SYSTEM-LEVEL SCHEMATIC OF ELECTROCHEMICAL OCEANWATER CO₂ CAPTURE COUPLED WITH CO₂ HYDRATES-BASED SEABED SEQUESTRATION.

transportation costs which range from \$2-\$14 per ton CO₂ for distances of 180 km [25,26].

This study analyzes all key components in the capture and sequestration processes to quantify the corresponding energy requirements. This includes analysis of the use of both seawater and freshwater for hydrate formation, noting that there are technological as well as economic ramifications associated with the type of water used. This study quantifies the electricity cost savings when the capture and sequestration plants are co-located. Importantly, it is a starting point for further optimization of this system. The results of this study can be used to compare the proposed approach with existing CCS approaches and also serves as the foundation for detailed techno-economic and lifecycle analysis of this concept.

2. SYSTEM DESCRIPTION AND TECHNICAL ANALYSIS

Figure 1 shows a system-level schematic of the proposed CCS approach with all key equipment and process streams depicted. Capture involves intaking surface oceanwater, followed by filtration and stripping of dissolved gases. The oceanwater is then pumped through the electrochemical cells, where the pH is lowered to convert the dissolved inorganic carbons (DIC) from carbonates and bicarbonates back into dissolved gaseous CO₂ [18]. This dissolved gaseous CO₂ is removed from the water via vacuum stripping, before the oceanwater goes into another electrochemical cell which raises the pH to counter the ongoing acidification of the ocean. This treated oceanwater is then either returned to the ocean or used as

an inlet source for the gas-cooled heat exchanger or as the water supply for hydrate formation. This study also analyzes a scenario where the water used for hydrate formation is desalinated noting that hydrate formation rates increase with the use of freshwater as compared to seawater. The water to be used for hydrate formation is then pumped up to formation pressure and cooled via a standalone water chilling cycle. The stripped CO₂ will go through multistage compression, cooling, and expansion processes to reach the desired temperature and pressure conditions for hydrate formation in bubble column reactors. CO₂ gas and water enter the bubble column reactors where the gas is continuously recirculated for steady formation of a hydrate slurry which is sent for eventual seabed sequestration. This study analyzes only the production aspects of this hydrate slurry. It is important to note that for permanent sequestration on the seabed, the slurry will need to be compacted into plugs and sealed in a polymeric sleeve or buried under marine sediments.

2.1 Detailed Methodology for Analysis of Electrochemical Capture

The working principle for the capture of CO₂ from oceanwater is described in detail in a recent study from Kim et. al [18]. The approach uses an asymmetric chloride-mediated electrochemical process to modulate the pH of the oceanwater such that dissolved gaseous CO₂ can be stripped out using a vacuum pump, without the use of expensive bipolar membranes [18]. This study uses the optimized parameters for the current density and cell gap in the electrochemical capture provided in [18]. The optimized conditions are used for a 1MT/yr plant to

estimate the required power, number of units, for sizing components, and determining the flowrates of the streams of CO₂ and treated oceanwater. This process is assumed to operate at 1 atm and 25°C (unless otherwise noted). All the energy requirements for components are calculated on a kWh per kg CO₂ basis for comparison.

The intake pump supplies the necessary ocean water and brings it into the facility for operation. In the case of an on-platform facility, this distance is assumed to be 10 m; for onshore facilities it would be on the order of 1500 m. The energy required to pump oceanwater from the surface into the facility can be estimated as:

$$E_{intake} = Q_{OW} \frac{\rho g h}{(3.6 \times 10^6) \eta_p \eta_m \dot{m}_{CO_2}} \quad (1)$$

where Q_{OW} is the oceanwater flowrate (m³ h⁻¹), ρ is oceanwater density (1025 kg m⁻³), g is acceleration of gravity (9.8 m s⁻²), h is total dynamic head loss (m), η_p (94%) and η_m (82%) are the pump and motor efficiencies, respectively, and $\dot{m}_{CO_2}$ is the mass flow rate of CO₂ captured (kg h⁻¹) [16,17].

Oceanwater contains impurities such as algae, organic materials, sand, and other particulates, which must be removed so as not to damage downstream equipment. This requires three stages of multimedia filtering (disk filter, cartridge filter, ultrafiltration) each with a corresponding pressure drop. The pretreatment energy is assumed to be the pumping energy required to overcome the corresponding pressure drops and is given by:

$$E_{pretreatment} = Q_{OW} \frac{(\Delta P_{CF} + \Delta P_{DF} + \Delta P_{UF})}{36 \eta_p \eta_m \dot{m}_{CO_2}} \quad (2)$$

where ΔP_{CF} , ΔP_{DF} , and ΔP_{UF} are the pressure drops of each filter (0.3 bar, 0.22 bar, and 3 bar, respectively) [16, 27].

Prior to the electrochemical process, the gases occurring naturally in oceanwater (primarily O₂ and N₂) must be removed. This is done via a degasification vacuum pump. The energy requirement for this is calculated by:

$$E_{VP,O_2/N_2} = \frac{F_{m,O_2,N_2} R T \kappa_{O_2,N_2}}{(3.6 \times 10^6) (1 - \kappa_{O_2,N_2}) \eta_{VP} \eta_m \dot{m}_{CO_2}} \left[\left(\frac{P_{VP,O}}{P_{VP,i}} \right)^{(\kappa_{O_2,N_2} - \frac{1}{\kappa_{O_2,N_2}})} - 1 \right] \quad (3)$$

where F_{m,O_2,N_2} is the molar flow rate of O₂ and N₂ saturated with water vapor (mol h⁻¹), R is the gas constant (8.314 J K⁻¹ mol⁻¹), T is the temperature (K) and κ_{O_2,N_2} is the adiabatic constant of O₂ and N₂ (1.4), $P_{VP,i}$ and $P_{VP,O}$ are the permeate side pressure (0.08 atm) and atmospheric pressure, respectively. η_{VP} and η_m are the vacuum pump and motor efficiencies (60% and 82% respectively). Values of properties of O₂ and N₂ for the initial degasification were used in accordance with experimental data for oceanwater [16,28].

The filtered, degassed oceanwater is then pumped through individual electrochemical cells. Cell pumping and

electrochemical processes can be considered together since both are the focus of the study by Kim et. al. [18]. Cell pumping moves the filtered oceanwater through the parallel asymmetric electrode pairs. This model uses the optimized conditions determined by Kim et. al. for a 1MT plant which sizes the cell electrode area (A_e), current density (i), and cell gap (δ). Physical design tradeoffs determined the optimum conditions for a 1 MT plant. Low current densities require a large electrode area and therefore a large CAPEX, while high current densities increase the ohmic losses and increase the pumping cost required to match the electron flux into the oceanwater. For small cell gaps, pressure drop is very large and therefore pumping costs dominate, while large cell gaps result in increased ohmic losses.

Given these optimum electrochemical parameters, the cell pumping requirement for a single cell can be determined by matching the flux of electrons from the electrodes to the flux of CO₂ flowing through the cell with the equation:

$$Q_{OW,C} = \frac{i A_e \eta_{FE}}{F} \frac{1}{pr [CO_2]} \quad (4)$$

where F is Faraday constant, η_{FE} is Faradaic efficiency, p is the CO₂ removal efficiency after gas separation, r is the ratio of electron transfer to proton transfer (3/2), and $[CO_2]$ is the molarity of CO₂ in mols/L. With the flow rate through a single cell known, the pressure drop across that cell is calculated by:

$$\Delta P = \frac{f \rho}{2} \left(\frac{Q}{\delta w} \right)^2 \frac{w}{D_h} \quad (5)$$

Use of the above equation involves estimating the friction factor (f) (which is determined by the Reynolds number). Other terms in Equation 5 include the density (ρ) and the effective hydraulic diameter (D_h). The total pumping power is then calculated by:

$$E_{CP} = \frac{\Delta P Q_{OW,C}}{(3.6 \times 10^6) \eta_{pump} \dot{m}_{CO_2}} \cdot n_{cells} \quad (6)$$

where n_{cells} is the number of cells required to capture 1 MT CO₂ per year.

Electricity costs for the electrochemical process include both the base energy required for the reaction and the ohmic losses through the electrolyte. This study uses the experimentally measured base energy of 122 kJ/molCO₂ (750 kWh/tCO₂) reported in Kim et. al. [18]. The equation to estimate the energy requirement is:

$$E_{EC} = \left(\frac{750 \text{ kWh}}{\text{tCO}_2} + \frac{2rF}{\eta_{FE}} \cdot \frac{i\delta}{\mathcal{U}_w} \cdot \frac{1}{M_{CO_2}} \cdot \frac{1 \text{ kWh}}{3.6 \cdot 10^6 \text{ J}} \cdot \frac{10^6 \text{ gCO}_2}{\text{tCO}_2} \right) \cdot \frac{1 \text{ tCO}_2}{1000 \text{ kgCO}_2} \quad (7)$$

where $\mathcal{U}_w$ is the ionic conductivity [18]. The first term is the base energy required for the reaction to which the ohmic losses through the electrolyte is added to determine the total energy requirement.

Following the electrochemical reaction, the pH is shifted such that the DIC converts back into molecular, dissolved gaseous CO₂. At this point another vacuum pump is used to strip CO₂. Using Equation 3, the energy required for stripping CO₂ from the oceanwater is calculated with CO₂ specific properties. The adiabatic constant of CO₂ is 1.3 and the molar flow rate is determined by the first electrochemical pH swing process [16,28].

The CO₂ depleted oceanwater is re-alkalized in the final step of the electrochemical process via a reverse reaction in another electrode. The electrochemical cells are regenerated by this process for the next cycle, allowing for continuous operation. The capture process ends with the CO₂ depleted oceanwater which can either be used to form hydrates or returned to the ocean to absorb more atmospheric CO₂ [18].

2.2 Methodology for Analysis of Hydrates-based Sequestration

The proposed approach for sequestration involves the formation of CO₂ hydrates in bubble column reactors (BCRs). Use of BCRs yields very high hydrate formation rates when CO₂ is bubbled through water at high flow rates. Such bubbling enhances mass diffusion, disrupts hydrate shells, and enhances convective heat dissipation, leading to the highest reported formation rates in literature [29], as per a recent study from the present group. BCRs require a supply of cold, pressurized CO₂ gas and water. The capture process produces a low pressure, ambient temperature CO₂ gas stream and a filtered saltwater supply at an ambient pressure and temperature, both of which are inputs into the BCRs.

Technical inputs for the present analysis of sequestration are based on a recent experimental study on accelerated hydrate formation in BCRs [29] from the present group. Inlet conditions and corresponding gas consumption rates (GCR) associated with sequestration are summarized in Table 1, with all results based on a 2°C temperature of the reactor. The GCR greatly improves for higher pressure conditions as well as with the use of deionized (pure) water with up to 2.4 kg CO₂ sequestered per hour per liter of BCR volume. However, implementing such conditions will require additional power to pressurize the inlet CO₂ and water, as well as a standalone desalination plant to remove salt from the filtered ocean water.

Table 1: SUMMARY OF EXPERIMENTAL CONDITIONS AND CORRESPONDING CO₂ CONSUMPTION RATES ASSOCIATED WITH RAPID HYDRATE FORMATION IN BUBBLE COLUMN REACTORS. RESULTS ARE BASED ON A RECENT EXPERIMENTAL STUDY BY THE PRESENT GROUP [29].

Case	Pressure of BCR (psig)	Salt or pure water usage	CO ₂ Gas Consumption Rate (g/hr/lit)
1	400	Salt	13.7
2	400	Pure	310
3	500	Salt	1901
4	500	Pure	2464

CO₂ cooling and pressurizing is achieved by over-compressing the gas stream, cooling it down to ambient conditions, and then expanding the gas to the desired pressure, which subsequently cools the gas to the desired temperature. CO₂ leaving the capture system is assumed to be at ambient temperature and 0.08 atm pressure due to the process of vacuum stripping. With that inlet condition and a known desired outlet condition of temperature (2°C) and pressure (400 or 500 psig), the overall cooling and pressurization requirement can be estimated. Compression is done via a multistage centrifugal compressor. The power requirement for each stage is calculated by:

$$P_{comp} = \frac{\dot{m}ZRT}{M\eta_{is}^{\frac{k-1}{k}}} \left[\left(\frac{p_2}{p_1} \right)^{\frac{k-1}{k}} - 1 \right] \quad (8)$$

where $\dot{m}$ is the mass flow rate of CO₂, Z is the average compressibility factor between the suction and discharge conditions using the Peng-Robinson equation of state, R is the universal gas constant, T is the absolute temperature, k is the isentropic exponent, p is the absolute pressure, M is the molar mass of CO₂, and η_{is} is the isentropic efficiency [30]. Each stage uses a compression ratio of 4. The power requirement assumes no interstage cooling. The overall power requirement for the compressor is the sum of the power consumed in all the compressor stages.

Cooling to ambient conditions is achieved via heat exchange between the compression and expansion stages, which makes use of the filtered oceanwater that the capture system produces. The power requirement for this heat exchange is associated with pumping the water stream accounting for the pressure drop of the heat exchanger:

$$P_{HXPump} = \frac{\dot{m}\Delta p}{\rho\eta_{pump}} \quad (9)$$

where P_{HXPump} is the pumping power, Δp is the pressure drop across the heat exchanger, ρ is the density of water, and η_{pump} is the efficiency of the water pump. As with the other components in the system, the power requirement for the cooling and compression of the CO₂ gas stream is converted to an electricity per kgCO₂ basis [kWh/kgCO₂] for the 1MT/yr plant.

Similar to the gas supply to the BCR, the water supply for hydrate formation must also be cooled and pressurized to formation conditions. This is achieved by a water pump to increase pressure and a standalone water chiller via a refrigeration cycle. The water pump power requirement is calculated using the same pumping power equation above, but for a significantly larger increase in pressure. The water chiller assumes a coefficient of performance (COP) of 2.5 which is reasonable for the required size and cooling requirements. The required heat removal is calculated by:

$$Q = \dot{m}c_p\Delta T \quad (10)$$

where Q is the required heat removal, c_p is the specific heat of the water, and ΔT is the temperature difference between the inlet and outlet conditions.

In addition to the supply of CO_2 gas and water at hydrate forming temperatures (HFT), the BCRs must also be maintained at those temperatures for the continued formation of hydrate slurry. Since the formation of hydrates is an exothermic reaction, the heat generation must be removed from the system. The dissociation energy is 60 kJ/mol of CO_2 hydrate [31]. In this study, we use the experimental formation rates from Table 1 to determine how many discrete BCRs would be necessary to achieve the 1 MT/yr sequestration rate. Each BCR is considered to be 1 m in diameter and 10 m tall. The BCRs will require additional cooling to maintain their temperatures against ambient natural convection. However, in this study it is assumed each BCR is perfectly insulated and therefore it is only the latent heat generation that is accounted for in the cooling requirements.

For the hydrate formation cases in which pure (deionized) water is used, a standalone desalination plant will be needed to treat the oceanwater after the capture process, as shown in Figure 1. This study assumes that a traditional reverse osmosis (RO) desalination plant will be used, and data from real-world plants of similar capacities is used to estimate the required energy [32]. While desalination is generally energy intensive, the plant in this study benefits from using the already filtered and treated water from the capture system as it's supply, which reduces intake pump and filtration costs, which account for 10% of the overall energy requirement [33]. The Marsa Matrouh plant in Egypt, with a capacity of 24,000 m^3/d , has a RO energy requirement of 2.2 kWh/m^3 of water desalinated [32]; this value is used in the present study.

3. RESULTS AND DISCUSSIONS

Since the already-optimized conditions of the IOC electrochemical system were used in this study, the results from the capture processes do not vary between cases, but rather provide the inputs for the rest of the CCS system. Figure 2 shows the energy requirements of each component in the capture system on a per kgCO_2 captured basis. It is observed that the pre-treatment (filtration) and electrolysis processes account for 49% and 37% of the total energy requirement, respectively. While filtration is a power-intensive process, our approach maximizes the use of the filtration since the filtered water from the capture system can be the input to either the desalination or hydrates-based sequestration processes without the need for additional filtration. In cases where the plant is located far from the ocean water source, intake pumping can be a significant power draw. An onshore commercial plant may require a 1500m long intake pipe with a corresponding energy penalty of 2.37 kWh/kgCO_2 [16,34]. This is nearly double the total energy requirement for the entire capture system. However, for a co-located plant located on a decommissioned oil-gas platform, the transportation distance is on the order of 10m and the corresponding intake pumping costs are much lower.

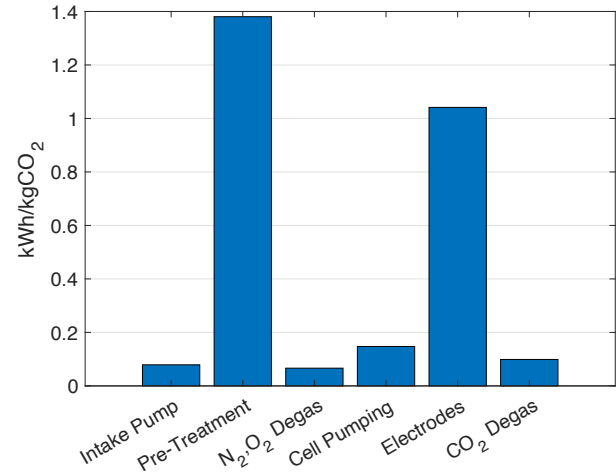


FIGURE 2: BREAKDOWN OF ENERGY REQUIREMENTS FOR EACH COMPONENT IN THE ELECTROCHEMICAL CO_2 CAPTURE PROCESS.

Overall, the capture process requires a combined 2.81 kWh/kgCO_2 to produce the CO_2 gas stream and the pH-adjusted, filtered ocean water stream. Assuming electricity comes from a zero-carbon footprint source at a price of $\$0.03/\text{kWh}$ [18], the capture cost considering only the power requirement is $\$84.4$ per tCO_2 . For the case of a 1 MT/yr plant under continuous operation, the power consumption works out to be 321.1 MW. With the optimized conditions for capture given by Kim et. al. [18], a 1MT/yr system will require 202,370 individual cells to supply a continuous stream of 31.7 kg/s CO_2 . These individual cells will need to be packaged together to form “stacks”. The physical footprint and real estate requirements with respect to an oil platform will need to be considered in future work. The captured CO_2 is supplied to the sequestration system at ambient temperature (25°C) and 0.08 atm pressure while the filtered, pH adjusted oceanwater exits at ambient temperature and pressure at a flow rate of 345 m^3/s . All of these results are summarized in Table 2.

Table 2: KEY RESULTS FOR THE OPTIMIZED CAPTURE SYSTEM FOR A 1 MT/YR CCS PLANT.

Electricity (kWh/kgCO_2)	Power consumption (MW)	Number of Electrochemical Cells needed	Oceanwater Flow Rate (m^3/s)
2.813	321.1	202,370	345

Results for the sequestration process for each of the 4 sequestration cases mentioned in Table 1 are summarized in Table 3. The first thing to note is that the energy requirements do not differ in the four cases; the energy requirement for sequestration only slightly increases ($\sim 4.5\%$ at most). However the number of bubble column reactors needed to reach 1 MT/yr

of storage decreases significantly from Case 1 to Case 4 (Case 4 has only 0.6% of the number of BCRs needed for Case 1). It is apparent that a system containing 1000+ BCRs will not be practical from a logistical and operational standpoint. This consideration also informs the primary tradeoff when considering the operating conditions to use for hydrates-based sequestration; while higher pressures increase OPEX-related costs, they reduce CAPEX-related costs.

When using desalination, co-location is more advantageous since it makes use of the filtered water as the input into the desalination plant vs. a standalone desalination plant that needs to filter the oceanwater. The co-location power savings are ultimately not very significant because of the relatively small amount of water needed for sequestration and cooling as compared to the amount of water processed for the capture system. The capture system produces 345 m³/s of water, but the supply of water to the BCRs to maintain the required formation rates is only 0.076 m³/s of water and the gas cooling heat exchanger only requires 0.64 m³/s of water. Therefore, less than 0.25% of the produced water is used for hydrate formation or potential desalination. The eliminated transportations costs and reduced intake distances are the major benefits of co-location. At an electricity cost of \$0.03/kWh, the electricity cost range for the below cases is 9.2-9.6 \$/tCO₂.

Table 3: KEY RESULTS FOR THE 4 CASES (DESCRIBED IN TABLE 1) OF HYDRATES-BASED SEQUESTRATION.

Case	Electricity (kWh/kgCO ₂)	Power (MW)	# of BCRs require for 1 Mt/yr	Co-location Power Savings (\$/tCO ₂)
1	0.307	35.0	1061	0.01
2	0.312	35.6	47	0.08
3	0.315	36.0	8	0.01
4	0.321	36.6	6	0.08

It is noted that the associated sensible heat needed for running >1000 reactors has been neglected in the analysis, leading to a similar net power requirement reported for the 4 cases. Furthermore, the model has also neglected the natural convection losses for the BCRs, leading to a lower estimate of the power requirement associated with BCRs. Due to the aforementioned reasons, the power requirement is found to not strongly correlate with the number of BCRs.

The breakdown for the energy consumed in key processes associated with sequestration is shown in Figure 3 for Case 3 (500 psig without desalination) and Case 4 (500 psig with desalination). For each case, the power requirements for the water chilling and BCR latent heat removal remain constant since the formation temperatures and total amount of hydrates formed do not change. There is a slight increase in the power consumption for the water side pump for cases 3 and 4 since the pump must raise the pressure to 500 psig instead of 400 psig. For Cases 1 and 2, the hydrate water pump requires 0.0022 kWh/kgCO₂ and for Cases 3 and 4, it requires 0.0028

kWh/kgCO₂. This is an increase of just 0.2% from the total sequestration power required. Likewise, the power associated with gas side compression and cooling increase for Cases 3 and 4. For Cases 1 and 2, gas compression and cooling requires 0.1268 kWh/kgCO₂; for Cases 3 and 4, it requires 0.1346 kWh/kgCO₂. This is a 2.5% increase from the total sequestration power required. Cases 2 and 4 each have a desalination power requirement that does not exist when saltwater is used. Since both cases require the same amount of water for hydrate formation, both Cases 2 and 4 have a desalination energy requirement of 0.0054 kWh/CO₂. This accounts for just 1.8% of the total sequestration energy requirement of Case 4. Figure 3 shows that the energy penalty for desalination is small compared to the energy requirements of other sequestration steps. The cost of desalination, from an energy requirement basis, is quite insignificant compared to the energy requirements of the rest of the sequestration processes. However, this study does not include the significant CAPEX associated with a standalone desalination plant for this process. While desalination does reduce the required number of BCRs, higher operating pressure has a much more significant impact on the production of CO₂ hydrates, without much additional pressurization costs.

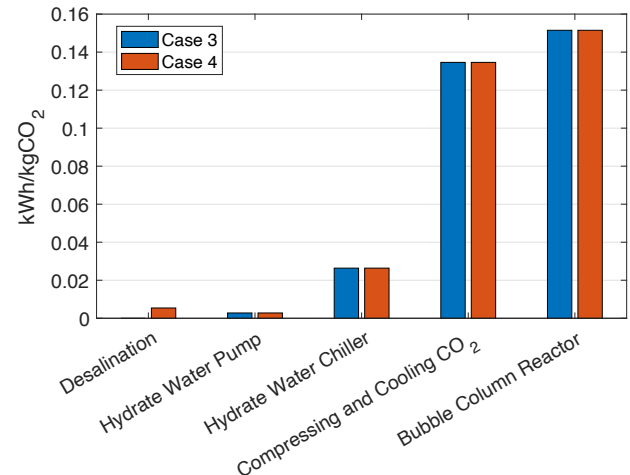


FIGURE 3: BREAKDOWN OF ENERGY CONSUMPTION FOR SEQUESTRATION COMPONENTS FOR CASE 3 (500 PSIG WITHOUT DESALINATION) AND CASE 4 (500 PSIG WITH DESALINATION).

Overall, figures 2 and 3 show the key numbers associated with the energetics of the capture and sequestration processes. Comparing them puts into perspective the relatively low energy requirements for the sequestration processes when compared to the capture processes. Much of this has to do with the large volumes of water that needs to be processed on the capture side. The energy requirements for gas compression and cooling and the BCRs are an order of magnitude smaller than the energy requirements for oceanwater pretreatment and the electrochemical process. This is consistent with existing CCS technologies where the bulk of the energy is used up in the capture process.

4. CONCLUSIONS

In summary, this study conducted a first-order analysis of various components (and the energetics) of a CO₂ capture and sequestration plant which is based on electrochemical oceanwater capture and hydrates-based seabed sequestration. The main takeaway is the improved formation rates and the reduced number of BCRs, achieved by operating at 500 psig hydrate formation conditions, which by itself does not significantly increase the power consumption. Between Case 1, (lowest power requirement) and Case 4 (largest power requirement), the power to operate the sequestration plant increased by only 1.6 MW for a 1 MT/yr sequestration plant. Cases 1 and 2 are not realistic options for hydrates-based sequestration due to the amount of BCRs needed. However, Cases 3 and 4 are promising and require just 8 and 6 BCRs, respectively, to sequester 1 MT/yr of CO₂.

From an energy requirement perspective, both the use of freshwater as well as seawater for hydrates formation appears feasible. However, the implications of a desalination plant (to produce freshwater) need to be analyzed in detail and is beyond the scope of this study. Also assessments of the physical footprint of such capture and sequestration systems are needed to determine if a standalone capture and sequestration plant can in fact be located on existing decommissioned oil-gas production platforms. Overall, this study can seed further analysis and assessments of this novel concept of synergistic carbon capture and sequestration from oceanwater.

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