



**Politecnico  
di Torino**

**Politecnico di Torino**

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**Carbon removal technologies:**  
pre-feasibility study of a chloride-mediated electrochemical  
Direct Ocean Capture process and comparison with bipolar  
membrane electrodialysis

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## Introduzione

Il cambiamento climatico rappresenta una delle principali sfide ambientali, economiche e tecnologiche del XXI secolo. L'aumento della concentrazione di gas serra in atmosfera, in particolare dell'anidride carbonica, è strettamente legato alle attività antropiche, tra cui la combustione di combustibili fossili, la produzione industriale, il settore dei trasporti, l'agricoltura e i cambiamenti nell'uso del suolo. La riduzione delle emissioni rimane la strategia prioritaria per limitare l'aumento della temperatura media globale, ma negli ultimi anni è emersa con crescente evidenza la necessità di affiancare alle misure di decarbonizzazione anche tecnologie di rimozione dell'anidride carbonica, note come Carbon Dioxide Removal (CDR).

Le tecnologie CDR comprendono un insieme eterogeneo di soluzioni finalizzate alla rimozione della  $\text{CO}_2$  già presente nell'ambiente. Tra queste rientrano approcci terrestri, come la riforestazione e il bioenergy with carbon capture and storage, tecnologie ingegneristiche come la Direct Air Capture e soluzioni basate sugli oceani. Queste ultime stanno ricevendo crescente attenzione poiché gli oceani rappresentano uno dei principali serbatoi naturali di carbonio del pianeta e svolgono un ruolo centrale nel ciclo globale del carbonio.

Dall'inizio dell'era industriale, gli oceani hanno assorbito una frazione rilevante delle emissioni antropiche di  $\text{CO}_2$ . Questo assorbimento contribuisce a limitare l'accumulo di anidride carbonica in atmosfera, ma comporta anche conseguenze sulla chimica marina, tra cui l'acidificazione degli oceani. La  $\text{CO}_2$  assorbita dall'atmosfera si dissolve nell'acqua di mare e partecipa a una serie di equilibri chimici che determinano la distribuzione del carbonio inorganico disciolto, o Dissolved Inorganic Carbon (DIC), tra diverse specie:  $\text{CO}_2$  disciolta, bicarbonato e carbonato.

In condizioni tipiche dell'acqua marina, il carbonio inorganico disciolto non è presente principalmente sotto forma di  $\text{CO}_2$  molecolare, ma soprattutto come ioni bicarbonato e, in misura minore, come ioni carbonato. Questa caratteristica rende gli oceani un serbatoio di carbonio molto più concentrato rispetto all'atmosfera su base volumetrica, ma introduce anche una sfida tecnologica: per estrarre  $\text{CO}_2$  dall'acqua marina è necessario spostare gli equilibri del sistema carbonatico verso la formazione di  $\text{CO}_2$  molecolare, che può poi essere separata dalla fase liquida.

Le tecnologie di Direct Ocean Capture (DOC) si basano proprio su questo principio. Esse mirano a manipolare la chimica dell'acqua marina in modo da favorire la conversione di bicarbonati e carbonati in  $\text{CO}_2$  disciolta, seguita dalla separazione del gas e dal ripristino delle condizioni chimiche della corrente trattata prima dello scarico. In generale, un processo DOC può essere descritto attraverso tre passaggi fondamentali: acidificazione dell'acqua marina, estrazione della  $\text{CO}_2$  e ripristino dell'alcalinità. Le tecnologie disponibili o in fase di sviluppo differiscono per il metodo con cui viene indotto lo swing di pH, per il sistema di separazione della  $\text{CO}_2$  e per il grado di maturità tecnologica.

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Tra le tecnologie DOC elettrochimiche, una delle configurazioni più studiate è la Bipolar Membrane Electrodialysis (BPMED). Essa utilizza membrane bipolari per produrre correnti acide e basiche attraverso la dissociazione dell'acqua sotto l'effetto di un campo elettrico. La corrente acida viene utilizzata per convertire il DIC in CO<sub>2</sub> molecolare, mentre la corrente basica consente di ripristinare l'alcalinità dell'acqua trattata. La BPMED è una tecnologia relativamente più matura rispetto ad altri approcci DOC emergenti, ma presenta criticità legate al costo delle membrane, al fouling, allo scaling, alla complessità dello stack elettrodialitico e ai consumi energetici.

In questo contesto si inserisce il processo elettrochimico chloride-mediated proposto dal Massachusetts Institute of Technology. Questo processo utilizza uno swing di pH indotto elettrochimicamente attraverso reazioni reversibili che coinvolgono elettrodi a base di bismuto e argento/cloruro d'argento. Il principio fondamentale consiste nello sfruttare gli ioni cloruro naturalmente presenti nell'acqua marina per generare e consumare protoni, evitando l'utilizzo di membrane bipolari. Durante la fase di acidificazione, il pH dell'acqua marina viene ridotto e gli equilibri del carbonio inorganico vengono spostati verso la formazione di CO<sub>2</sub> molecolare. Dopo la separazione della CO<sub>2</sub>, la corrente trattata viene rialcalinizzata mediante la reazione inversa, in modo da ripristinare le condizioni chimiche prima dello scarico.

Il processo MIT ha mostrato risultati sperimentali promettenti a scala di laboratorio, con una rimozione di circa l'87% del DIC e un consumo energetico elettrochimico specifico pari a 122 kJ mol<sup>-1</sup> di CO<sub>2</sub> rimossa. Tuttavia, la dimostrazione sperimentale è stata condotta su acqua marina sintetica e su scala ridotta. Di conseguenza, rimangono aperte numerose domande riguardo alla possibile implementazione del processo a scala pilota o industriale. In particolare, è necessario valutare l'impatto delle grandi portate di acqua marina, dei sistemi di pompaggio, del pretrattamento, della separazione della CO<sub>2</sub>, del condizionamento del prodotto e dei costi associati alle principali apparecchiature.

## Obiettivi

L'obiettivo principale di questa tesi è valutare, a livello preliminare, la fattibilità tecnico-economica di una tecnologia emergente di Direct Ocean Capture basata sul processo elettrochimico chloride-mediated proposto dal Massachusetts Institute of Technology. Il lavoro nasce dall'esigenza di comprendere se i risultati ottenuti a scala di laboratorio possano costituire una base ragionevole per lo sviluppo di una configurazione di processo a scala pilota. La finalità dello studio non è quindi quella di dimostrare la piena maturità industriale della tecnologia, ma di analizzarne il comportamento quando il principio sperimentale viene tradotto in un sistema impiantistico più completo.

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Il processo considerato sfrutta uno swing elettrochimico di pH dell'acqua marina per convertire le specie carbonatiche e bicarbonatiche in  $\text{CO}_2$  molecolare, che può successivamente essere separata dalla fase liquida. Tale configurazione risulta di interesse perché evita l'impiego di membrane bipolari, tipiche di altre soluzioni elettrochimiche di Direct Ocean Capture, e utilizza reazioni reversibili che coinvolgono elettrodi a base di bismuto e argento/cloruro d'argento. Tuttavia, la tecnologia è ancora in una fase iniziale di sviluppo e i dati disponibili derivano da prove sperimentali condotte su scala ridotta. Per questo motivo, è necessario valutare quali implicazioni emergano quando il processo viene inserito in un flowsheet comprendente anche le sezioni ausiliarie necessarie al funzionamento dell'impianto.

A partire dai dati disponibili in letteratura, è stato quindi definito un caso studio di riferimento per un impianto pilota con capacità nominale pari a 1000 t $\text{CO}_2$  all'anno. Tale configurazione è stata utilizzata come base per lo sviluppo di un modello in Aspen Plus, nel quale le celle elettrochimiche sono state rappresentate con un approccio black-box, mentre le principali sezioni di processo sono state descritte tramite modelli semplificati a livello impiantistico. In questo modo è stato possibile valutare non solo la conversione e il recupero della  $\text{CO}_2$ , ma anche il ruolo delle unità ausiliarie, come il pompaggio dell'acqua marina, il pretrattamento, la separazione della  $\text{CO}_2$  e il condizionamento del prodotto gassoso.

Un aspetto centrale dello studio è la distinzione tra la prestazione della sola sezione elettrochimica e la prestazione complessiva del processo. Infatti, mentre il consumo energetico delle celle rappresenta un indicatore fondamentale della tecnologia, la prefattibilità di un impianto di Direct Ocean Capture dipende anche dalla gestione di grandi portate di acqua marina e dai consumi associati alle apparecchiature ausiliarie. La tesi si propone quindi di quantificare i bilanci di materia ed energia dell'intero sistema, individuando le sezioni che incidono maggiormente sulla prestazione complessiva.

Infine, il lavoro mira a fornire una prima valutazione economica del processo, attraverso la stima preliminare del CAPEX e dell'OPEX delle principali sezioni impiantistiche. I risultati ottenuti vengono poi confrontati con una tecnologia benchmark più matura, la Bipolar Membrane Electrodialysis, considerata nel caso stand-alone. Questo confronto consente di evidenziare i potenziali vantaggi del processo chloride-mediated, ma anche i principali limiti e le incertezze che dovranno essere affrontati prima di una possibile applicazione su scala più ampia.

## Metodologia

La metodologia adottata nella tesi è articolata in più fasi. La prima fase riguarda l'analisi della letteratura scientifica e tecnica. Sono stati studiati i principi del carbonio inorganico disciolto nell'acqua marina, le tecnologie di Direct Ocean

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Capture e, in particolare, il processo elettrochimico chloride-mediated proposto dal MIT. La letteratura è stata utilizzata per ricavare i principali dati sperimentali di riferimento, tra cui l'efficienza di rimozione del DIC, il consumo energetico specifico delle celle elettrochimiche e le condizioni operative del processo. La stessa analisi ha permesso di selezionare la BPMED come tecnologia benchmark, grazie alla maggiore disponibilità di dati di processo e studi tecnico-economici.

La seconda fase è stata la definizione del caso studio. È stata scelta una capacità nominale di 1000 tCO<sub>2</sub> all'anno, tradotta in una portata continua di CO<sub>2</sub> pari a 114.2 kg h<sup>-1</sup>, corrispondente a circa 2.60 kmol h<sup>-1</sup>. Assumendo una concentrazione di DIC pari a 2.0 mmol L<sup>-1</sup> e un'efficienza di rimozione dell'87%, la portata di acqua marina necessaria è stata stimata pari a circa  $1.49 \times 10^3$  m<sup>3</sup> h<sup>-1</sup>. Questa portata costituisce uno dei parametri più importanti del modello, poiché influenza direttamente il dimensionamento delle pompe, del pretrattamento, delle unità di separazione e dei costi complessivi.

I confini del sistema includono le principali operazioni necessarie al funzionamento del processo: presa e pompaggio dell'acqua marina, pretrattamento, rimozione preliminare dei gas disciolti, acidificazione elettrochimica, separazione della CO<sub>2</sub>, rialcalinizzazione della corrente trattata, scarico dell'acqua marina e condizionamento preliminare della CO<sub>2</sub> fino a 1 bar. Sono invece escluse dal modello quantitativo alcune voci non direttamente rappresentabili con i dati disponibili, come la progettazione dettagliata delle infrastrutture offshore, la produzione e sostituzione degli elettrodi, la manutenzione, il fine vita delle apparecchiature, la compressione finale per trasporto o stoccaggio geologico e una valutazione ambientale di ciclo di vita.

La terza fase ha riguardato lo sviluppo del modello Aspen Plus. La composizione dell'acqua marina è stata definita in modo da rappresentare condizioni marine realistiche, includendo acqua, gas disciolti, principali ioni salini e specie del carbonio inorganico. Il metodo termodinamico scelto è ELECNRTL, adatto alla descrizione di soluzioni acquose elettrolitiche ad alta forza ionica. Questo metodo consente di rappresentare il comportamento non ideale delle specie ioniche e la separazione di fase associata alla rimozione della CO<sub>2</sub> sotto vuoto.

Nel modello Aspen Plus, la sezione di pretrattamento è stata rappresentata attraverso blocchi semplificati basati su perdite di carico. Sono stati inclusi filtrazione grossolana, filtrazione fine e ultrafiltrazione, con una pompa booster dedicata a monte della sezione di ultrafiltrazione. Questa scelta è stata adottata per rendere più realistica la rappresentazione del trattamento di grandi portate di acqua marina, pur senza modellare fenomeni dettagliati come fouling, backwashing, cleaning chimico o gestione del retentato.

Prima della sezione di acidificazione è stata introdotta una rimozione preliminare dei gas disciolti, principalmente azoto e ossigeno. Questa sezione è stata rappresentata con un separatore operante a pressione ridotta, seguito da compressione e raffreddamento della corrente gassosa rimossa. Lo scopo di questa unità non è

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recuperare CO<sub>2</sub>, ma ridurre la quantità di gas non condensabili che potrebbero entrare nelle sezioni successive del processo.

La sezione di acidificazione elettrochimica è stata modellata con un blocco RStoic. Il blocco riproduce il passaggio da condizioni marine iniziali a condizioni acide, convertendo le specie carbonatiche e bicarbonatiche verso CO<sub>2</sub> molecolare. L'effetto dei protoni generati elettrochimicamente è stato rappresentato mediante una corrente equivalente contenente H<sup>+</sup> e Cl<sup>-</sup>, interpretata non come aggiunta reale di acido minerale, ma come rappresentazione di processo del rilascio di protoni associato alla reazione elettrochimica.

La separazione della CO<sub>2</sub> è stata implementata con un flash sottovuoto. Questa rappresentazione differisce dalla configurazione sperimentale MIT, nella quale viene utilizzato un membrane contactor con sweep gas di azoto, ma consente di valutare il comportamento della corrente acidificata mediante una rappresentazione di equilibrio semplificata. La pressione del flash è stata selezionata attraverso una Design Spec in modo da riprodurre l'efficienza di rimozione del DIC adottata come riferimento.

La corrente gassosa ricca di CO<sub>2</sub> uscente dal separatore contiene anche vapore d'acqua. Per questo motivo è stata introdotta una sezione di condizionamento, costituita da raffreddamento, separazione della condensa, compressione fino a 1 bar, secondo raffreddamento e ulteriore separazione della condensa. La corrente finale viene interpretata come prodotto di CO<sub>2</sub> preliminarmente condizionato a pressione atmosferica, mentre la compressione a pressioni idonee al trasporto o allo stoccaggio geologico è stata esclusa dai confini del modello.

Dopo la separazione della CO<sub>2</sub>, la corrente liquida decarbonata viene inviata alla sezione di rigenerazione. Anche questa sezione è stata modellata con un blocco RStoic, con lo scopo di riprodurre l'aumento di pH associato alla fase di rialcalinizzazione del processo chloride-mediated. Come per l'acidificazione, la rigenerazione è rappresentata a livello di processo e non attraverso una modellazione dettagliata dell'elettrochimica.

La quarta fase metodologica è stata l'analisi dei risultati Aspen Plus. Sono stati valutati il bilancio del carbonio, la portata di CO<sub>2</sub> recuperata, la distribuzione del carbonio residuo nella corrente trattata e i consumi energetici delle diverse sezioni. Il consumo elettrochimico è stato calcolato utilizzando il valore sperimentale di 122 kJ mol<sup>-1</sup> CO<sub>2</sub>, mentre i consumi ausiliari sono stati ricavati direttamente dai risultati delle pompe e dei compressori modellati in Aspen Plus. I carichi termici di raffreddamento sono stati riportati separatamente, poiché la loro conversione in consumo elettrico dipende dal tipo di tecnologia di raffreddamento adottata.

La quinta fase ha riguardato la valutazione preliminare economica. Il flow-sheet Aspen Plus è stato tradotto in sezioni impiantistiche reali: pompaggio, pretrattamento, rimozione preliminare dei gas disciolti, sezione elettrochimica e separazione/condizionamento della CO<sub>2</sub>. Per ciascuna sezione è stato stimato

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un CAPEX preliminare, utilizzando correlazioni di costo, dati di letteratura o assunzioni semplificate compatibili con il livello di dettaglio dello studio. Il CAPEX è stato poi annualizzato e convertito in contributo levelized per kg di CO<sub>2</sub> rimossa. L'OPEX è stato limitato alla componente energetica, utilizzando un prezzo dell'elettricità di riferimento.

Infine, i risultati del processo chloride-mediated sono stati confrontati con quelli di un benchmark BPMED stand-alone. Il confronto è stato condotto su diversi piani: consumo energetico, CAPEX/OPEX, complessità strutturale, maturità tecnologica e limiti del modello. La scelta di confrontare il processo con il caso stand-alone deriva dalla necessità di mantenere confini di sistema coerenti, poiché anche il modello Aspen sviluppato rappresenta una configurazione indipendente e non integrata con impianti esistenti.

## Risultati

Il primo risultato rilevante riguarda il bilancio di massa e, in particolare, il bilancio del carbonio. Il modello Aspen Plus è stato costruito per riprodurre una rimozione di DIC pari a circa l'87%, coerentemente con il valore sperimentale adottato come base di progetto. La corrente finale di CO<sub>2</sub> recuperata contiene 2.595 kmol h<sup>-1</sup> di CO<sub>2</sub>, corrispondenti a 114.20 kg h<sup>-1</sup>. Questo valore è coerente con la capacità nominale di 1000 tCO<sub>2</sub> all'anno scelta per il caso studio.

La recovery complessiva del carbonio inorganico disciolto è pari all'86.83%, in ottimo accordo con il valore di riferimento dell'87%. Questo risultato indica che la combinazione tra acidificazione, separazione sottovuoto e rigenerazione è in grado, nel modello Aspen Plus, di riprodurre il target di rimozione assunto dalla letteratura. Il carbonio non recuperato come CO<sub>2</sub> rimane principalmente nella corrente di acqua marina trattata, sotto forma di bicarbonato e carbonato. Le perdite di carbonio associate alle correnti di condensa e alla rimozione preliminare dei gas risultano limitate rispetto alla portata di CO<sub>2</sub> recuperata e al carbonio residuo nella corrente finale.

Dal punto di vista del processo, il bilancio di massa conferma la funzione della sezione di acidificazione. La riduzione del pH sposta gli equilibri del carbonio inorganico verso la formazione di CO<sub>2</sub> molecolare, rendendola disponibile per la separazione. La sezione di flash sottovuoto consente poi di trasferire la CO<sub>2</sub> dalla fase liquida alla fase gassosa. Dopo la separazione, la corrente liquida viene rialcalinizzata, riportando il sistema a condizioni più compatibili con lo scarico dell'acqua trattata.

Il secondo gruppo di risultati riguarda il consumo energetico. La potenza associata alla sola sezione elettrochimica è pari a 87.94 kW. Rapportata alla portata di CO<sub>2</sub> recuperata, essa corrisponde a 770.0 kWh tCO<sub>2</sub><sup>-1</sup>. Questo valore

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rappresenta esclusivamente l'energia richiesta per lo swing elettrochimico di pH e deriva dal consumo specifico sperimentale di  $122 \text{ kJ mol}^{-1} \text{ CO}_2$ .

Tuttavia, uno dei risultati principali della tesi è che il consumo elettrochimico non è sufficiente a descrivere la prestazione energetica dell'intero processo. Una volta inclusi i contributi ausiliari delle pompe e dei compressori, la domanda elettrica complessiva raggiunge  $419.70 \text{ kW}$ , pari a  $3675.1 \text{ kWh tCO}_2^{-1}$ . Il contributo dominante è associato al pompaggio dei liquidi, che rappresenta circa il 74.8% del consumo elettrico totale. La sezione elettrochimica rappresenta circa il 21.0%, mentre la compressione dei gas contribuisce per circa il 4.3%.

Questo risultato è particolarmente importante perché evidenzia una differenza fondamentale tra la valutazione di una cella elettrochimica a scala di laboratorio e la valutazione di un processo DOC a scala impiantistica. Anche se la tecnologia MIT mostra un consumo elettrochimico promettente, la necessità di trattare grandi portate di acqua marina rende il pompaggio e il pretrattamento elementi centrali nella prestazione complessiva. In altre parole, un basso consumo delle celle non garantisce automaticamente un basso consumo dell'intero impianto.

Anche i carichi termici risultano rilevanti. La sezione di condizionamento della  $\text{CO}_2$  richiede raffreddamenti per condensare parte del vapore d'acqua presente nella corrente gassosa. Il carico termico totale è stato riportato separatamente rispetto alla domanda elettrica, poiché può essere soddisfatto con tecnologie di raffreddamento diverse. In uno scenario illustrativo, assumendo un coefficiente di prestazione pari a 3 per un sistema frigorifero, il contributo di raffreddamento potrebbe aumentare l'OPEX energetico da 0.368 a circa  $0.422 \text{ \$ kgCO}_2^{-1}$ .

La valutazione economica preliminare ha portato a un CAPEX totale pari a  $10.57 \text{ M\$}$ . Il CAPEX annualizzato corrisponde a  $1.077 \text{ M\$ yr}^{-1}$ , equivalente a un contributo levelized di  $1.077 \text{ \$ kgCO}_2^{-1}$ . La sezione dominante è il pretrattamento, che rappresenta circa il 66.8% del CAPEX totale. Questo risultato è legato principalmente all'elevata portata di acqua marina richiesta dal processo e alla conseguente dimensione della sezione di ultrafiltrazione. La seconda voce più rilevante è la sezione di separazione e condizionamento della  $\text{CO}_2$ , che contribuisce per circa il 14.1% del CAPEX totale. Seguono la rimozione preliminare dei gas disciolti, la sezione elettrochimica e la sezione di pompaggio.

L'effetto del costo specifico dell'ultrafiltrazione è stato considerato come una delle principali incertezze economiche. Variando l'assunzione di costo della sezione UF, il CAPEX levelized complessivo varia da  $0.974$  a  $1.343 \text{ \$ kgCO}_2^{-1}$ . Questa variazione conferma che il pretrattamento è uno dei fattori più critici del processo e che una valutazione più dettagliata di membrane, configurazione dei moduli, recovery, backwashing, cleaning e sostituzione sarebbe necessaria in uno studio tecnico-economico successivo.

L'OPEX considerato nel modello è limitato alla componente energetica, poiché il modello Aspen Plus non include manutenzione, sostituzione degli elettrodi, costo

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del lavoro, materiali di consumo o strategie operative a lungo termine. Utilizzando il prezzo dell'elettricità assunto come riferimento, l'OPEX elettrico del processo chloride-mediated è pari a  $0.368 \text{ \$ kgCO}_2^{-1}$ . Come già discusso, includendo in modo illustrativo il raffreddamento tramite un COP pari a 3, il valore salirebbe a circa  $0.422 \text{ \$ kgCO}_2^{-1}$ .

Il confronto con la BPMED stand-alone mostra che il processo chloride-mediated presenta un consumo energetico totale inferiore rispetto al benchmark considerato. Il modello chloride-mediated richiede circa  $3.677 \text{ kWh kgCO}_2^{-1}$ , mentre il benchmark BPMED stand-alone è riportato a  $5.82 \text{ kWh kgCO}_2^{-1}$ . Questa differenza deriva principalmente dal minore consumo elettrochimico del processo MIT rispetto alle configurazioni BPMED riportate in letteratura.

Dal punto di vista economico, il costo parziale levelized del processo chloride-mediated è pari a circa  $1.445 \text{ \$ kgCO}_2^{-1}$  considerando CAPEX annualizzato e OPEX elettrico. Includendo il contributo illustrativo del raffreddamento, il valore aumenta a  $1.499 \text{ \$ kgCO}_2^{-1}$ . Il benchmark BPMED stand-alone presenta invece un intervallo di costo pari a  $1.87\text{--}2.05 \text{ \$ kgCO}_2^{-1}$ . Anche in questo caso, il confronto suggerisce un potenziale vantaggio del processo chloride-mediated, ma tale risultato deve essere interpretato con cautela a causa delle diverse ipotesi e del diverso livello di maturità delle due tecnologie.

## Discussione e conclusioni

I risultati ottenuti mostrano che il processo chloride-mediated rappresenta un concetto promettente per la Direct Ocean Capture, ma evidenziano anche che la sua valutazione non può essere limitata alla prestazione della sola cella elettrochimica. Il principale contributo della tesi è proprio la traduzione di un processo sperimentale di laboratorio in una configurazione di processo a scala pilota, nella quale emergono contributi energetici ed economici non trascurabili.

Dal punto di vista chimico e concettuale, il processo MIT presenta un aspetto innovativo: l'utilizzo di reazioni reversibili basate su bismuto e argento/cloruro d'argento permette di generare uno swing di pH senza ricorrere a membrane bipolari. Questo riduce la complessità della sezione elettrochimica rispetto alla BPMED e può potenzialmente limitare alcuni costi associati agli stack a membrane. Inoltre, il consumo energetico elettrochimico riportato sperimentalmente è inferiore rispetto ad altri processi elettrochimici DOC presenti in letteratura.

Tuttavia, quando il processo viene analizzato a livello di impianto, il vantaggio elettrochimico deve essere ridimensionato. La portata di acqua marina richiesta per rimuovere  $1000 \text{ tCO}_2$  all'anno è molto elevata, a causa della bassa concentrazione di DIC rispetto alle portate industriali normalmente trattate in impianti chimici. Di conseguenza, pompaggio, filtrazione, ultrafiltrazione e gestione idraulica

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assumono un peso determinante. Il fatto che il pompaggio rappresenti circa tre quarti della domanda elettrica totale del modello dimostra che gli sviluppi futuri della tecnologia dovranno concentrarsi non solo sull'ottimizzazione delle celle, ma anche sulla riduzione della portata richiesta, delle perdite di carico e dei requisiti di pretrattamento. Un'altra criticità riguarda la separazione della  $\text{CO}_2$ . Nel modello Aspen Plus, questa sezione è stata rappresentata con un flash sottovuoto calibrato per raggiungere la rimozione desiderata. Questa scelta è adeguata per una valutazione preliminare di processo, ma non sostituisce il dimensionamento reale di un membrane contactor, di una colonna di stripping o di un sistema di degasaggio sottovuoto. Inoltre, il modello non include esplicitamente il consumo energetico del sistema di vuoto reale, né le limitazioni di trasferimento di massa, il tempo di residenza, l'area di contatto gas-liquido o eventuali fenomeni di trascinamento. Questi aspetti potrebbero influenzare sensibilmente le prestazioni del processo a scala maggiore.

La valutazione economica conferma che il pretrattamento è il principale driver del CAPEX. Questo risultato è coerente con la natura del processo: la Direct Ocean Capture richiede il trattamento di grandi volumi di acqua marina e, in presenza di sezioni elettrochimiche e di separazione sensibili al fouling, il pretrattamento diventa essenziale per proteggere le unità a valle. Tuttavia, la stima sviluppata è preliminare e non include aspetti che potrebbero risultare molto importanti, come la sostituzione delle membrane di ultrafiltrazione, i cicli di lavaggio, i prodotti chimici per la pulizia, la manutenzione, la disponibilità dell'impianto e la gestione del retentato.

Il confronto con la BPMED evidenzia una possibile convenienza del processo chloride-mediated in termini di energia e costo parziale, ma non consente di concludere che esso sia già industrialmente competitivo. La BPMED è una tecnologia più matura, supportata da una letteratura più ampia, da una maggiore esperienza nell'ambito dei processi a membrana e da studi tecnico-economici più dettagliati. Il processo chloride-mediated, invece, si trova ancora a un livello di maturità più basso e presenta incertezze sperimentali significative.

Tra le principali limitazioni del processo MIT vi sono la stabilità a lungo termine degli elettrodi, la dissoluzione dell'argento, la possibile precipitazione di specie minerali durante la fase di rialcalinizzazione, il fouling degli elettrodi e la stabilità del funzionamento ciclico. Questi aspetti non sono stati inclusi nel modello quantitativo, ma potrebbero incidere in modo rilevante sui costi operativi, sulla disponibilità dell'impianto e sulla vita utile delle apparecchiature. Inoltre, i dati sperimentali di riferimento sono stati ottenuti con acqua marina sintetica, mentre il modello Aspen Plus adotta una composizione più rappresentativa dell'acqua marina reale. Questa differenza introduce un'ulteriore incertezza, poiché le prestazioni sperimentali non sono ancora state validate in condizioni marine naturali. Un'altra limitazione riguarda la rappresentazione delle celle elettrochimiche. Il modello usa

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un approccio black-box, adatto a uno studio preliminare, ma non descrive corrente, tensione, area elettroica, densità di corrente, perdite ohmiche, overpotential, trasporto ionico, distribuzione del pH o fenomeni di degradazione. Questi elementi saranno fondamentali per passare da una valutazione di processo a una progettazione più dettagliata. In particolare, il dimensionamento della sezione elettrochimica richiederà una descrizione più accurata della relazione tra portata trattata, area degli elettrodi, tempo di residenza, efficienza faradica e consumo energetico.

Nel complesso, la tesi mostra che il processo chloride-mediated può essere considerato una tecnologia DOC promettente, ma ancora fortemente condizionata da sfide di scale-up. Il modello Aspen Plus conferma la possibilità di riprodurre a livello di processo il target di rimozione del DIC assunto dalla letteratura, mentre la valutazione energetica ed economica evidenzia che le sezioni ausiliarie hanno un peso determinante. L'analisi dimostra quindi che la fattibilità del processo non dipende solo dal miglioramento delle celle elettrochimiche, ma anche dall'ottimizzazione dell'intero sistema impiantistico.

Gli sviluppi futuri dovrebbero concentrarsi su più direzioni. In primo luogo, è necessaria una validazione sperimentale con acqua marina reale, per verificare l'effetto di ioni multivalenti, materia organica, particolato, microrganismi e fenomeni di scaling. In secondo luogo, è necessario studiare la durabilità degli elettrodi e quantificare eventuali perdite di materiale, in particolare per quanto riguarda l'argento. In terzo luogo, occorre sviluppare un modello più dettagliato della sezione elettrochimica, includendo densità di corrente, perdite ohmiche, trasporto ionico e distribuzione del pH. Inoltre, la sezione di separazione della CO<sub>2</sub> dovrebbe essere progettata in modo più realistico, considerando membrane contactors, vacuum degassers o stripping columns. Da un punto di vista economico, una techno-economic analysis più completa dovrebbe includere manutenzione, sostituzione di membrane e filtri, sostituzione degli elettrodi, costi di installazione, opere civili, infrastrutture offshore, sistemi di controllo, disponibilità dell'impianto, compressione finale della CO<sub>2</sub>, trasporto, stoccaggio e monitoraggio ambientale. Sarebbe inoltre necessario valutare l'impatto dello scarico dell'acqua trattata, sia in termini di pH sia in termini di composizione ionica, per garantire la compatibilità con l'ambiente marino.

In conclusione, il processo chloride-mediated proposto dal MIT rappresenta una soluzione innovativa nel panorama delle tecnologie di Direct Ocean Capture, soprattutto per la possibilità di evitare membrane bipolari e ridurre il consumo energetico elettrochimico. Tuttavia, la sua applicazione a scala pilota o industriale richiede ulteriori studi sperimentali e modellistici. La tesi fornisce una prima valutazione di prefattibilità e mostra che, sebbene il processo presenti potenziali vantaggi rispetto alla BPMED stand-alone, la sua competitività dipenderà dalla capacità di ridurre i costi e i consumi delle sezioni di bilancio di impianto, in particolare pompaggio, pretrattamento e separazione della CO<sub>2</sub>.



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# Abstract

The increasing urgency of addressing atmospheric carbon dioxide accumulation has led to growing interest in Carbon Dioxide Removal (CDR) technologies, which are regarded as a complementary approach to conventional decarbonization strategies. Among these, Direct Ocean Capture (DOC) technologies are emerging as a promising route for CO<sub>2</sub> removal, exploiting the ability of seawater to absorb and store carbon dioxide in the form of dissolved inorganic carbon. The aim of this thesis is to assess the preliminary feasibility of an emerging DOC technology based on the chloride-mediated electrochemical process proposed by MIT. The process relies on an electrochemical pH swing of seawater to convert bicarbonate and carbonate species into molecular CO<sub>2</sub>, which is then separated from the liquid phase and recovered as a concentrated stream. The reference experimental process showed the removal of approximately 87% of dissolved inorganic carbon, with a specific electrical energy consumption of 122 kJ/mol CO<sub>2</sub>.

Based on data available in the literature, a process model was developed in Aspen Plus to simulate a pilot plant with a nominal capacity of 1000 tCO<sub>2</sub>/year. The electrochemical cells were represented using a black-box approach, while the main auxiliary sections, including seawater pre-treatment, CO<sub>2</sub> separation and final compression of the captured product, were included through simplified process-level representations. The model was employed to obtain the material and energy balances of the plant, to determine the main variables affecting process performance, and to support a preliminary economic assessment through the estimation of CAPEX and OPEX for the main process sections. The results of the MIT-based process model were then compared with those of a Direct Ocean Capture technology based on Bipolar Membrane Electrodialysis (BPMED), selected as a benchmark due to its higher technological maturity. The comparison focused on the main process indicators, including energy consumption, CO<sub>2</sub> capture efficiency, plant complexity, CAPEX and OPEX estimates, and overall process performance. This analysis made it possible to highlight the potential advantages of the chloride-mediated process, as well as the main limitations that still need to be addressed before future scale-up and implementation. Overall, the study provides a preliminary assessment of the proposed chloride-mediated Direct Ocean Capture process and offers a perspective

on the main opportunities and challenges associated with its future development, scale-up and implementation.

# Chapter 1

## Introduction

Climate change is widely recognized as one of the most pressing global challenges of the twenty-first century. The increase in global greenhouse gas concentrations, particularly carbon dioxide, is mainly driven by fossil fuel combustion, industrial production, transport, agriculture and land-use change. This accumulation enhances the greenhouse effect and contributes to the observed rise in global average temperature, with consequences such as sea-level rise, more frequent extreme weather events and impacts on ecosystems [1].

In response to these challenges, governments and international organizations have established ambitious climate targets to limit global temperature rise. The Paris Agreement aims to hold the increase in global average temperature well below 2 °C above pre-industrial levels and to pursue efforts to limit the temperature increase to 1.5 °C. Within this framework, the European Union has adopted the European Climate Law, which makes climate neutrality by 2050 legally binding and sets an intermediate target of reducing net greenhouse gas emissions by at least 55% by 2030 compared with 1990 levels [2].

Although deep decarbonization remains the priority strategy for climate mitigation, emission reductions alone may not be sufficient to achieve long-term climate targets. Residual emissions from hard-to-abate sectors and the large amount of carbon dioxide already accumulated in the atmosphere have led to increasing interest in Carbon Dioxide Removal (CDR) technologies [1, 3].

Among the different CDR pathways currently under development, ocean-based approaches have attracted growing attention because the oceans play a central role in the global carbon cycle. Since the beginning of the industrial era, the oceans have absorbed a significant fraction of anthropogenic CO<sub>2</sub> emissions and represent one of the largest active carbon sinks on Earth [4]. Moreover, seawater contains dissolved inorganic carbon at much higher concentration than CO<sub>2</sub> in air on a volumetric basis, making it an attractive medium for carbon dioxide removal [4].

Direct Ocean Capture (DOC) technologies aim to remove carbon dioxide from seawater by manipulating the carbonate chemistry of the aqueous phase. In most configurations, this requires converting bicarbonate and carbonate species into molecular  $\text{CO}_2$ , separating the released gas, and restoring suitable chemical conditions before the treated seawater is discharged.

Within this context, electrochemical DOC processes are particularly interesting because they can induce pH variations without the continuous addition of external acids or bases. Among them, the chloride-mediated electrochemical process proposed by MIT represents an emerging alternative to membrane-based approaches, as it exploits chloride ions naturally present in seawater and reversible electrode reactions to generate the pH swing required for  $\text{CO}_2$  release and alkalinity restoration [4].

The present thesis focuses on this chloride-mediated process and assesses its preliminary feasibility at process level. The analysis is developed by translating the experimental concept into a pilot-scale process model and by comparing its main performance indicators with those of a more mature Direct Ocean Capture benchmark technology.

## 1.1 State of the Art of Direct Ocean Capture Technologies

Carbon dioxide removal (CDR) technologies are being increasingly recognized as an indispensable tool for sustainable emission reduction in order to achieve long-term climate goals. Direct Ocean Capture (DOC) has already emerged as a promising solution because oceans dominate the global carbon cycle and hold vast amounts of carbon.

The development of DOC technologies is closely associated with the chemical and physical processes that exchange carbon dioxide between the atmosphere and seawater. This understanding of these processes is necessary to understand the principles, advantages, and disadvantages of existing technologies. In addition, a detailed analysis of the current development of DOC systems is required to contextualize the process we are investigating here and find the best benchmark technologies.

In this chapter, we first introduce the oceans' role in the global carbon cycle and the basic principles associated with dissolved inorganic carbon in seawater. We then discuss the operating principles of Direct Ocean Capture technologies and review the major approaches in the literature. Finally, we compare the technologies, and the benchmark is chosen.

## 1.2 Carbon in the Oceans and Its Role in the Global Carbon Cycle

The oceans represent one of the largest active carbon reservoirs on Earth and play a central role in the regulation of the global climate system. Through continuous air–sea exchange, they absorb a significant fraction of anthropogenic CO<sub>2</sub> emissions, thereby limiting the accumulation of carbon dioxide in the atmosphere. Since the beginning of the industrial era, approximately 25–30% of anthropogenic CO<sub>2</sub> emissions have been absorbed by the oceans, highlighting their importance in the global carbon cycle [5].

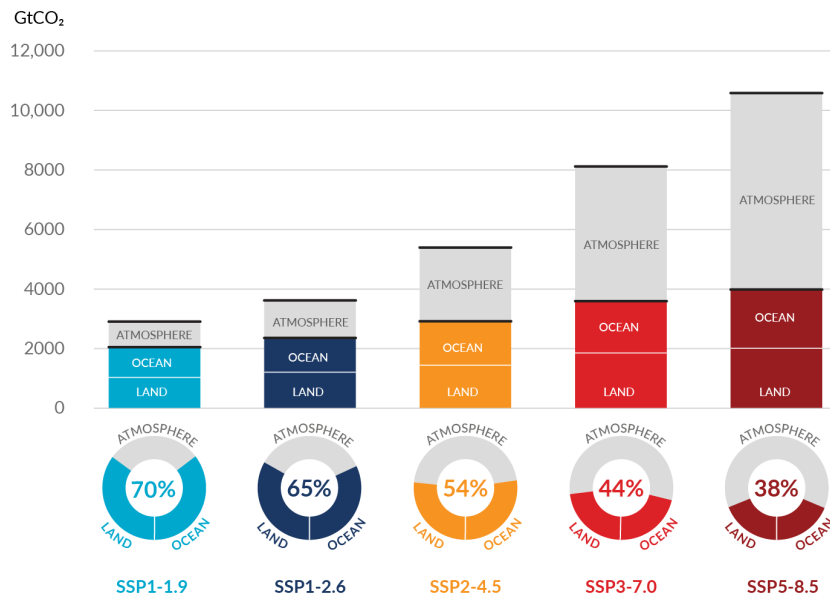


**Figure 1.1:** Distribution of cumulative anthropogenic CO<sub>2</sub> emissions. [6].

As shown in Figure 1.1, anthropogenic CO<sub>2</sub> emissions are distributed among the atmosphere, land and ocean reservoirs. The stacked bars indicate cumulative emissions under different Shared Socioeconomic Pathway scenarios, while the pie charts show the relative contribution of land and ocean uptake.

The ability of seawater to store carbon is related to a combination of physical, chemical and biological processes. Once CO<sub>2</sub> is absorbed from the atmosphere, it does not remain only as molecular CO<sub>2</sub>, but is redistributed among different dissolved inorganic carbon species. The relative abundance of these species is governed by the carbonate chemistry of seawater.

Understanding these mechanisms is essential for the analysis of Direct Ocean Capture technologies, because DOC processes rely on the controlled manipulation

of seawater chemistry to shift the distribution of dissolved carbon species and promote  $\text{CO}_2$  extraction from the aqueous phase.

### 1.2.1 Atmospheric $\text{CO}_2$ Absorption

The exchange of carbon dioxide between the atmosphere and the oceans is driven by differences in the partial pressure of  $\text{CO}_2$  in the air-sea interface. When the atmospheric partial pressure is above the equilibrium value in the ocean, then the dissolved  $\text{CO}_2$  is released back to the atmosphere and can be formed as the partial pressure of the atmosphere increases.

The dissolution of carbon dioxide in seawater can be described by Henry's law:

$$C_{\text{CO}_2} = k_H P_{\text{CO}_2} \quad (1.1)$$

where  $C_{\text{CO}_2}$  is the concentration of dissolved carbon dioxide,  $k_H$  is Henry's constant and  $P_{\text{CO}_2}$  is the partial pressure of carbon dioxide in the gas phase.

The absorption of atmospheric  $\text{CO}_2$  is supported by physical and biological processes. Ocean circulation constantly transports carbon-rich surface waters to deeper layers through the so-called solubility pump and marine organisms contribute to carbon sequestration by photosynthesis and the subsequent transfer of organic matter to the ocean deep below the water surface, a process known as the biological pump.

These two mechanisms combine to enable the oceans to be a long-term carbon sink and determine the global carbon balance.

### 1.2.2 Dissolved Inorganic Carbon (DIC)

The carbon dissolved in seawater is commonly referred to as Dissolved Inorganic Carbon (DIC). It is the total concentration of inorganic carbon in the aqueous phase and is the primary carbon storage in the oceans.

DIC is conventionally defined as:

$$\text{DIC} = [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (1.2)$$

where  $\text{CO}_2(\text{aq})$  denotes dissolved carbon dioxide,  $\text{HCO}_3^-$  is bicarbonate and  $\text{CO}_3^{2-}$  is carbonate.

The DIC concentration in seawater is between 2.0 and 2.3  $\text{mmol L}^{-1}$  depending on temperature, salinity, biological activity and geographic location [7]. The atmosphere contains around 420 ppm of  $\text{CO}_2$  and so is at a total of around 0.017  $\text{mmol L}^{-1}$  (in standard case). As a result, inorganic carbon in seawater is more than two orders of magnitude higher than that in air.

A key feature of seawater chemistry is that dissolved carbon is not uniformly distributed among the different inorganic carbon species of the dissolved inorganic carbon in the water. In typical oceanic chemistry, bicarbonate ions constitute the dominant part of DIC with about 85-90% of the total dissolved inorganic carbon in the water as a fraction of all dissolved carbon in every oceanic molecule. Carbonate ions contribute between 10-15% and dissolved carbon dioxide takes only small fractions below 1% of the total DIC content [8, 7].

This distribution has important implications for Direct Ocean Capture technologies. As only a small fraction of dissolved carbon can be readily removed from the atmosphere as molecular  $\text{CO}_2$ , the removal of carbon must be done by converting bicarbonate and carbonate ions into dissolved carbon dioxide prior to its extraction. A comprehensive understanding of the mechanisms of carbon storage in the oceans is important for the analysis of Direct Ocean Capture technologies. These processes rely on the controlled manipulation of seawater chemistry to change the distribution of dissolved carbon species and promote the extraction of carbon dioxide from the aqueous phase.

### 1.2.3 Carbonate System in Seawater

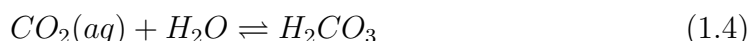
In seawater, dissolved inorganic carbon exists in different chemical forms whose relative abundance is determined by the carbonate equilibrium system.

#### Carbonate Equilibria

The carbonate system originates from the dissolution of atmospheric carbon dioxide into seawater:



After dissolution, carbon dioxide is hydrated to form carbonic acid:



Carbonic acid is a weak acid that dissociates according to two consecutive acid-base equilibria. The first dissociation generates bicarbonate ions:



while the second dissociation produces carbonate ions:



The distribution of dissolved inorganic carbon across these species is largely determined by the position of the equilibria and is greatly influenced by the

concentration of hydrogen ions. For this reason, even relatively small variations in pH can influence the relative abundance of dissolved carbon species [8, 7].

### Carbon Speciation and pH Dependence

The relative proportions of dissolved carbon dioxide, bicarbonate, and carbonate ions are mainly determined by the pH of the seawater [8, 7]. The carbonate system shows a characteristic speciation behavior, with different types of carbon dominating when pH is different. At acidic pH, the equilibrium is shifted towards dissolved carbon dioxide, and  $\text{CO}_2(\text{aq})$  is the dominant carbon species. As pH increases, bicarbonate ions gradually become the dominant form of dissolved inorganic carbon. At even higher pH values, carbonate ions become more abundant and may eventually become the dominant carbon species. This strong dependence of carbon speciation on pH is one of the key features of seawater chemistry and is the basis of most Direct Ocean Capture technologies [9]. The relationship between pH and carbon speciation is commonly represented through a carbonate distribution diagram, which shows the fraction of each carbon species as a function of pH.

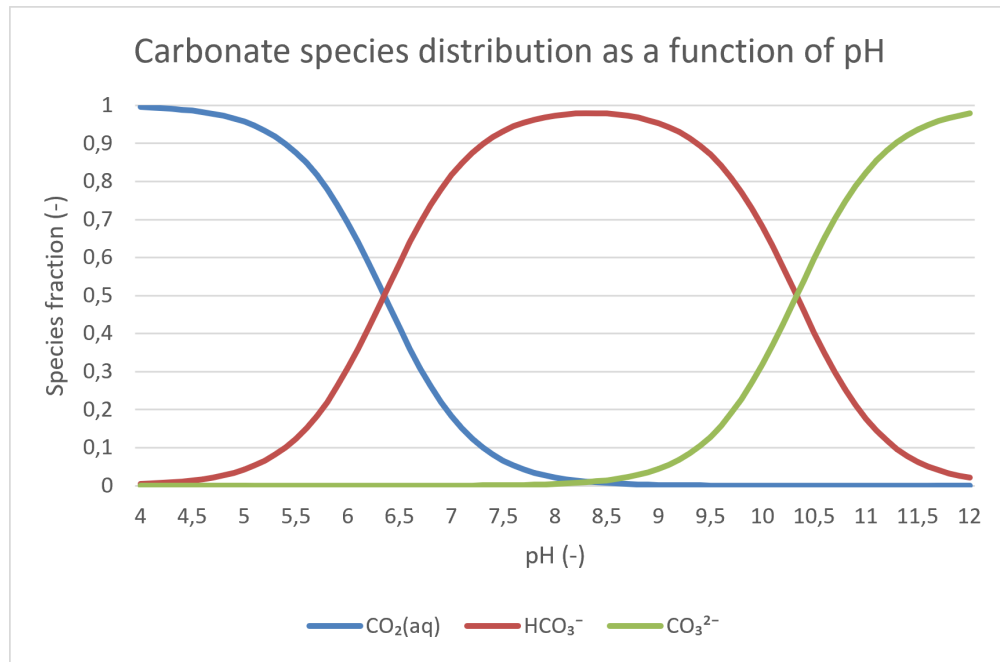


**Figure 1.2:** Distribution of dissolved inorganic carbon species as a function of pH, calculated from carbonate equilibrium relationships. Under typical seawater conditions ( $\text{pH} \approx 8.1$ ), bicarbonate is the dominant species. Decreasing pH shifts the carbonate equilibrium toward dissolved  $\text{CO}_2$ , increasing the fraction of carbon available for extraction.

The carbonate distribution diagram in Figure 1.2 was drawn by the author using the equilibrium equations of the carbonate system and the dissociation constants reported by Zeebe and Wolf-Gladrow [8]. The fractions of dissolved  $\text{CO}_2(\text{aq})$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  were calculated over the pH range 4-12 assuming thermodynamic equilibrium conditions. Such diagrams clearly show how the decrease of pH enables the conversion of bicarbonate and carbonate ions into dissolved carbon dioxide, which increases the amount of  $\text{CO}_2$  available to be extracted from seawater [4].

### Buffering Capacity of Seawater

An important consequence of the carbonate system is the buffering capacity of seawater. The presence of bicarbonate and carbonate ions allows seawater to absorb significant amounts of  $\text{CO}_2$  while limiting variations in pH. This carbonate buffer system is one of the reasons why the oceans have acted as major carbon sinks since the beginning of the industrial era [10, 11].

The most significant effect of the carbonate system is buffering capacity of seawater. The ocean will be able to take up significant amounts of  $\text{CO}_2$  without changing pH because of the presence of bicarbonate and carbonate ions. It is referred to as the carbonate buffer system, and this is one of the reasons that the oceans have been an effective carbon sink during the industrial era [10, 11].

The buffering mechanism is because of the reversible nature of the equilibria of carbonate. When more  $\text{CO}_2$  is added to water, some of the dissolved  $\text{CO}_2$  will be changed to bicarbonate and carbonate ions, decreasing the amount of dissolved  $\text{CO}_2$ . Removal of  $\text{CO}_2$  from seawater causes the equilibria to shift in the direction that replenishes the balance of the carbon species.

The buffering capacity of seawater is thus directly related to the large carbon storage potential of oceans and the potential of Direct Ocean Capture technologies. The pH of the seawater can be lowered by chemically or electrochemically altering its pH, which may allow the seawater to be manipulated in such a way that the seawater carbonate equilibria are altered to release dissolved carbon dioxide. It will form the basis of the pH-swing processes we will discuss in detail in the following and is essential for operation of the MIT technology we are interested in in this paper.

## 1.3 Principles of Direct Ocean Capture

Direct Ocean Capture (DOC) technologies are based on the manipulation of seawater chemistry in order to promote the release and subsequent removal of carbon dioxide. Direct Air Capture systems directly process atmospheric air, but DOC systems capitalize on the great reservoir of dissolved inorganic carbon that already exists in seawater. It is possible to change the chemical equilibria involved in carbon

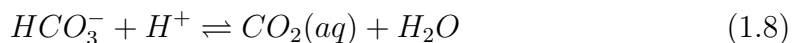
speciation, thereby enabling the transformation of bicarbonate and carbonate ions into dissolved carbon dioxide, and subsequent removal of the liquid phase.

Numerous technological solutions have been suggested but all DOC systems follow a similar operating principle of three basic steps: seawater acidification, carbon dioxide extraction and restoration of alkalinity. The technologies used for the implementation of the objectives can vary, but the chemistry is generally comparable [12, 9]. The ability to grasp these fundamental concepts is crucial to the assessment of existing DOC technologies, as well as the analysis of the operation of the MIT process investigated in this work.

### 1.3.1 Seawater Acidification

The most important step in the majority of Direct Ocean Capture processes is seawater acidification. The main goal of this phase is to lower the pH of the seawater to cause the carbonates in the seawater to shift to the side of the dissolved carbon dioxide.

Based on the following reactions, the increase of protons in seawater leads to a transformation of carbonate ions into bicarbonate ions and finally bicarbonate ions into dissolved carbon dioxide [8, 4].



When the pH decreases, dissolved  $CO_2$  increases substantially and the fraction of bicarbonate and carbonate ions decreases. This change in carbon speciation allows the release of  $CO_2$  from the seawater and is the fundamental mechanism of most DOC technologies.

Different approaches to seawater acidification have been proposed to achieve seawater acidification. Conventional methods rely on chemical acids but more advanced systems are electrochemical and can produce acid streams with pH swings from seawater or saline solutions as well.

The amount of acidification required depends on the nature of the carbon removal process and on the specific process configuration. Overall, lower pH results in greater conversion of dissolved inorganic carbon into molecular  $CO_2$ , thus increasing the amount of carbon available for extraction. However, too much acidification may lead to higher energy consumption, corrosion of materials and other challenges. Therefore, the selection of the correct operating conditions is a big part of designing and optimizing Direct Ocean Capture systems.

### 1.3.2 CO<sub>2</sub> Release and Extraction

The concentration of dissolved carbon dioxide in seawater increases significantly after acidification. In such cases the dissolved CO<sub>2</sub> concentration is far from its equilibrium value with respect to the atmosphere and the gas is released.

The extraction of carbon dioxide is generally done by gas-liquid separation, in order to achieve mass transfer between the aqueous and gaseous phases. Many technologies have been proposed for this purpose, such as vacuum degassing equipment, gas stripping equipment, and membrane contactors. The basic idea is to transfer dissolved carbon dioxide from seawater into a concentrated gas stream ready for use.

The efficiency of the extraction stage depends on several factors, including dissolved CO<sub>2</sub> concentration, operating pressure, temperature, and gas-liquid contact area.

The gas stream produced during extraction is generally composed of carbon dioxide, but some water vapour and trace gaseous species may also be present. Depending on the final application, further purification, drying, and compression steps may be needed before transportation, utilization, and geological storage of the captured carbon dioxide [9].

### 1.3.3 Alkalinity Restoration

The extraction of carbon dioxide from acidified seawater is generally followed by conditioning to restore the chemical properties of the treated effluent prior to discharge. Without such a step, the release of acidic seawater would cause unwanted environmental effects and would not be effective in its long-term treatment.

Alkalinity restoration is usually achieved by increasing the pH of the treated stream through chemical or electrochemical means. It partially or completely compensates for the alkalinity consumed during the acidification stage and promotes the re-establishment of carbonate species in the aqueous phase.

From the process perspective, alkalinity restoration has two important roles. First, it is used to maintain the discharged seawater to be compatible with the marine environment. Second, it increases the capacity of the treated water to absorb additional atmospheric carbon dioxide once it returns to the ocean. When the restored seawater is back in balance with the atmosphere, new CO<sub>2</sub> is absorbed and converted into dissolved inorganic carbon species, and the carbon removal proceeds.

A restoration of alkalinity, however, is an essential component of achieving net atmospheric carbon dioxide removal and is a key element of a number of Direct Ocean Capture technologies currently under development [12, 9].

## 1.4 Existing Direct Ocean Capture Technologies

Several technologies have been proposed to remove carbon dioxide from seawater. While all Direct Ocean Capture processes rely on the manipulation of the marine carbonate system, there are significant differences in the methods used to induce pH fluctuations, extract carbon dioxide, and restore seawater alkalinity.

The current DOC technologies can be classified into three broad categories: membrane-based electrochemical systems, ocean alkalinity enhancement approaches, and electrochemical pH-swing processes. Also, there are several emerging concepts that are being investigated at the lab level. In the following, we give an overview of the most relevant technologies in the literature and discuss their operating principles, advantages, and limitations.

### 1.4.1 Bipolar Membrane Electrodialysis (BPMED)

Bipolar Membrane Electrodialysis (BPMED) is one of the most widely studied Direct Ocean Capture technologies and currently represents one of the most mature electrochemical approaches in the literature. It was first proposed by Eisaman et al., and has since been investigated by several research groups as a promising pathway for large-scale ocean-based carbon removal [12].

The process uses bipolar membranes which convert water into hydrogen and hydroxide ions in the presence of an electric field. By carefully fitting cation exchange membranes, anion exchange membranes and bipolar membranes, the electrodialysis stack can produce acidic and alkaline streams from the seawater.

The acidic stream is used to lower the pH of the seawater and convert bicarbonate and carbonate ions into dissolved carbon dioxide.  $\text{CO}_2$  is then obtained from the dissolved water by means of a degassing unit, typically in vacuum. In parallel, the alkaline stream is used to restore the alkalinity of the treated water before discharge.

One of the major advantages of BPMED technology is that it could be applied to acidification and alkalinity restoration without external chemicals[13, 14]. Moreover, the process could be powered by renewable electricity and is suitable for low carbon energy systems [13, 14].

Despite these benefits, BPMED systems are characterized by high electrical energy requirements and huge capital cost of membrane stacks. Additional challenges include membrane fouling, scaling and long-term membrane degradation [15, 14]. Nevertheless, BPMED is still one of the most mature DOC technologies available [12, 9].

### 1.4.2 Ocean Alkalinity Enhancement

Ocean Alkalinity Enhancement (OAE) is a broader class of ocean-based carbon dioxide removal methods based on increasing the alkalinity of seawater in order to enhance its capacity to absorb atmospheric  $\text{CO}_2$ . Unlike DOC processes based on acidification and gas extraction, OAE does not generally aim to directly separate carbon dioxide from seawater. Instead it changes seawater chemistry to help dissolve the atmospheric  $\text{CO}_2$  in the ocean and is mainly stored as bicarbonate and carbonate ions [16, 17].

Several methods have been proposed to increase ocean alkalinity, including adding alkaline minerals, electrochemical generation of alkaline streams and dissolution of basic industrial residues. By increasing seawater pH and alkalinity, such processes change the carbonate equilibria to bicarbonate and carbonate production, reducing partial pressure of  $\text{CO}_2$  in surface waters and facilitating further uptake from the atmosphere [16, 17].

The main advantage of OAE is that it is scalable, as the oceans are very well-suited to store dissolved inorganic carbon. However, numerous challenges remain regarding environmental impacts, monitoring, verification, permanence and the practical logistics of large scale deployment [17]. In particular, the introduction of alkaline materials or highly alkaline streams in marine environments need to be closely evaluated to avoid negative impacts on local ecosystems.

Although OAE is an important category in ocean-based carbon dioxide removal, it is not directly comparable with the MIT process studied in this work. The latter is based on the acidification of seawater,  $\text{CO}_2$  extraction and subsequent alkalinity restoration, whereas OAE mainly enhances atmospheric  $\text{CO}_2$  uptake without leading to a separated  $\text{CO}_2$  stream. For this reason, OAE is considered to be a complete process in the present review, but not as the benchmark technology for the process comparison developed in the following chapters.

### 1.4.3 Electrochemical pH-Swing Systems

Electrochemical pH-swing systems are a rapidly emerging class of Direct Ocean Capture technologies that exploit electrochemically induced pH variations to manipulate the carbonate chemistry of seawater. Similar to BPMEDs, such technologies depend on the conversion of bicarbonate and carbonate ions into dissolved carbon dioxide through seawater acidification. However, the pH variation is typically achieved in reversible electrochemical reactions involving redox-active species [4].

Electrochemical pH swing technologies are based on generating acidic and alkaline conditions through electrochemical cells. Electrochemical reactions release or consume protons to change the local pH of the solution. The resulting acid stream enables the process of converting dissolved inorganic carbon into molecular

CO<sub>2</sub> and then a subsequent alkalization process restores the chemical properties of the treated seawater.

One of the advantages of these systems is that membrane requirements can be reduced compared to the conventional BPMED setup [14]. As membrane stacks are the most expensive part of an electrodialysis system, reducing their use can help lead to lower capital investment and simpler configurations of the processes. Furthermore, reversible electrochemical reactions are also a possibility that the process can be run with high energy efficiency.

In recent years, several electrochemical pH-swing concepts have been proposed with different redox couples and reactor configurations. Examples include proton-coupled electron transfer reactions, redox-active organic compounds and chloride-mediated electrochemical cycles [18, 19]. Although many of these technologies are still under development, they have shown promise in laboratory-scale experiments and have attracted increasing interest as alternatives to BPMED-based DOC processes.

Despite their potential benefits, electrochemical pH-swing systems are susceptible to many challenges in terms of electrode stability, material robustness, side reactions and scale-up. As a result, most of these technologies in the literature are still at low Technology Readiness Levels (TRLs) [14, 9], with little experimental validation beyond laboratory settings.

Among the different electrochemical pH-swing approaches proposed to date, the chloride-mediated process at the Massachusetts Institute of Technology has attracted a lot of attention for its innovative principle and promising experimental results [4]. We discuss this technology in detail in Chapter 2.

#### 1.4.4 Emerging Technologies

In addition to BPMED, Ocean Alkalinity Enhancement and electrochemical pH-swing systems, there are other methods for ocean-based carbon dioxide removal being developed. Most of these technologies are still in progress and are mainly aimed at improving energy efficiency [14, 9], reducing operational costs or simplifying process integration [9].

Examples include membrane contactor systems for improved gas extraction, hybrid processes of electrochemical and mineral-based chemical production, and advanced electrochemical configurations to reduce overpotentials and improve electrode stability. Other ideas are to integrate carbon removal with the production of hydrogen, alkaline chemicals or desalinated water. While these technologies are mostly used for laboratory tests, they highlight the growing interest in ocean-based carbon removal and there's a huge range of possible solutions we are starting to study. Nevertheless, as performance data is not available at present and there are

no pilot-scale demonstrations, it is difficult to see if they will be effective long-term and scale up.

For this reason we focus on technologies with sufficient technical information available to support process modelling and comparative assessment.

## 1.5 Comparison of existing DOC technologies

The wide variety of Direct Ocean Capture technologies currently under development makes it necessary to establish a systematic framework for comparison. While all DOC processes seek to maximize the removal of carbon dioxide from the sea, there are significant differences in technological maturity, energy requirements, operational complexity and scalability.

A comparative assessment of the available technologies is therefore essential to identify the most promising pathways for large-scale implementation and provide a rational basis for the selection of a benchmark process. BPMED systems, Ocean Alkalinity Enhancement approaches and electrochemical pH-swing technologies are evaluated by a set of criteria relevant to process development and industrial deployment.

### 1.5.1 Technology Readiness Level

Technology Readiness Level (TRL) is commonly used to evaluate the maturity of emerging technologies and their proximity to commercial deployment. It was originally developed by NASA and subsequently adopted in many engineering areas. The TRL system provides a common scale for the development of basic scientific principles (TRL 1) to fully commercial systems (TRL 9).

Among the DOC technologies currently available, BPMED systems are generally considered the most mature electrochemical approach. Several laboratory-scale and pilot-scale studies have been done, and basic operating principles are supported by well-established electrodialysis technologies. As a result, BPMED processes often have TRL values in the range of 4-6 [13, 20], depending on the implementation.

Ocean Alkalinity Enhancement technologies are evolving according to the alkalinity method used. The fundamental chemical principles are well understood, but large-scale deployment is limited by uncertainties in environmental impacts, monitoring and verification. As a result, most OAE approaches are still in the early stages of technological development [17].

In comparison, electrochemical pH-swing systems are still at a relatively low TRL around 4 [4]. Although there have been laboratory demonstrations of a few promising results, most of the concepts have not yet been shown to be successful

from the proof of concept stage. This is especially true for recently proposed chloride-mediated systems that have been proposed by and are still under development - with the long-term operation and large-scale application still to be seen.

### 1.5.2 Operational Challenges

In addition to energy consumption, there are several operational challenges that we need to address to maintain the long-term viability of Direct Ocean Capture technologies.

For BPMED systems, membrane fouling and scaling are major concerns [15]. The presence of dissolved salts, suspended solids and biological matter in seawater will slowly decrease membrane performance and increase maintenance costs. In addition, membrane replacement takes a significant toll on operating costs.

Electrochemical pH-swing technologies face several challenges in terms of electrode stability [4, 14], material degradation and side reactions. Repeated cycling in highly acidic and alkaline conditions may affect electrode durability and process efficiency. In some cases, the use of relatively expensive materials may also limit economic competitiveness.

Ocean Alkalinity Enhancement approaches are most impacted by material sourcing, transportation logistics and environmental monitoring. The safe and effective deployment of large quantities of alkaline materials remains one of the major barriers to implementation [17].

These aspects point to the importance of assessing DOC technologies in terms of not just theoretical performance, but also practical operational constraints.

### 1.5.3 Scale-Up Potential

The success of Direct Ocean Capture technologies ultimately depends on their ability to operate at the scale relevant to climate mitigation targets. Therefore, scale-up prospects are the most important criterion for technology evaluation. BPMED systems benefit from the industrial experience gained in membrane-based separation. While engineering issues are still present, the modularity of electrodialysis stacks supports scale-up and process replication [13, 20]. Ocean Alkalinity Enhancement approaches might have the greatest scalability because of the ocean reservoir size [17]. However, they need to be managed carefully in terms of the environmental impacts and monitoring infrastructure. Electrochemical pH-swing technologies are still in their early stages of development and scale-up is therefore more difficult to assess. Laboratory-scale results are promising [4] but more work is needed to assess long-term operation, equipment durability and overall process integration at a bigger scale. On the whole, BPMED is currently the most mature and best-characterized electrochemical DOC technology known in the literature [13, 20, 14],

so it is a good reference for comparative analyses with newly developed carbon removal systems.

**Table 1.1:** Summary of the main Direct Ocean Capture technologies currently under development.

| Technology                               | Acidification mechanism                           | Main advantages                                                   | TRL |
|------------------------------------------|---------------------------------------------------|-------------------------------------------------------------------|-----|
| Bipolar Membrane Electrodialysis (BPMED) | Water dissociation in bipolar membranes           | Most mature DOC technology; extensive experimental validation     | 4–6 |
| Ocean Alkalinity Enhancement (OAE)       | Addition of alkaline materials                    | High theoretical scalability and permanent carbon storage         | 3–5 |
| Electrochemical pH-Swing                 | Electrochemical proton generation and consumption | Potentially lower energy demand and reduced membrane requirements | 3–4 |

## 1.6 Selection of the Benchmark Technology

The comparative analyses presented in the previous sections highlight the variety of technologies that are currently being considered for ocean-based carbon dioxide removal. While all technological solutions aim to improve the removal of atmospheric carbon from the atmosphere by ocean carbon cycle, there are significant differences in terms of operating principles, technological maturity, energy requirements and scale-up ability.

Since the purpose of this thesis is to check process-level pre-feasibility of a pilot-scale Direct Ocean Capture system based on the MIT electrochemical concept, the choice of the appropriate benchmark technology will be a fundamental step in the analysis. The benchmark technology must be developed to provide reliable performance data and the process to be as robust as that of the pilot-scale DOC system developed in this work.

### 1.6.1 Selection Criteria

The benchmark technology was selected according to four main criteria: technological maturity, availability of technical information, process comparability and

relevance in the current DOC landscape.

Technological maturity is of paramount importance because the benchmark process should serve as a reference from which the performance of lower-TRL technologies can be assessed. Evidence from experiments and engineering should also be available in order to design realistic models and meaningful performance comparisons.

Another important consideration is process comparability. Since the MIT process involves acidification of the seawater, carbon dioxide extraction and alkalinity restoration, the benchmark technology should ideally have the same process sequence. This allows differences in performance to be attributed to the technology, rather than the carbon removal method.

Finally, the technology chosen should be widely recognized in the scientific literature as a relevant pathway for Direct Ocean Capture applications and should have sufficient documentation for engineering analysis and process modeling.

### 1.6.2 BPMED as Benchmark Technology

Based on the criteria presented above, BPMED (Bipolar Membrane Electrodialysis) was chosen as the benchmark technology for this research.

Among the DOC technologies currently available, BPMED is one of the most widely studied and technologically mature electrochemical methods. It has a well-established operating principle and numerous studies have reported on the performance of carbon removal, energy consumption and process configuration [12, 9]. Furthermore, the technology has also gone beyond proof-of-concept and has been considered in several techno-economic and scale-up studies.

Moreover, BPMED is especially relevant as a benchmark because the MIT chloride-mediated electrochemical process was proposed as an alternative to membrane-based electrochemical DOC systems. Both technologies operate on electrochemically modified pH to convert dissolved inorganic carbon into molecular  $\text{CO}_2$ , and gas extraction and alkalinity restoration. Thus, BPMED is a natural reference to evaluate the process-level performance of the MIT-based configuration considered in this study.

At the same time, there are important differences between the two approaches. BPMED uses membrane-based electrodialysis stacks to generate acidic and alkaline streams, while MIT is based on reversible chloride electrochemical reactions. These differences may impact the required energy, the equipment complexity, the operational challenges and scale-up potential of the two technologies, and so an in-depth comparison between the two is very useful in the eyes of MIT.

For this reason, BPMED is used throughout the remainder of this thesis as the reference technology against which the performance indicators and preliminary process-level feasibility of the MIT-based DOC configuration are evaluated.

## Chapter 2

# Process Description of the MIT Direct Ocean Capture Technology

### 2.1 Process Overview

This chapter focuses on the Direct Ocean Capture process proposed by Kim et al. [4], which is based on the electrochemical modulation of seawater pH to release and subsequently remove dissolved carbon dioxide. The process takes advantage of the natural carbonate equilibrium of seawater and consists of a sequence of acidification, CO<sub>2</sub> extraction and alkalinity restoration steps which can be continuously used to treat seawater streams.

As the pH decreases, bicarbonate and carbonate species are converted toward molecular CO<sub>2</sub> which can be separated from the liquid. After extraction of carbon dioxide, the treated seawater undergoes an alkalization step before being returned to the marine environment [9, 4].

The pH swing is achieved via reversible electrochemical reactions involving chloride ions which are naturally present in seawater. Two chloride-reactive electrodes based on bismuth and silver chloride are used in the system, which allows for the proton generation and consumption at alternating stages of the system. This can be done without the constant addition of chemical reagents [4].

The process consists of three main functional parts: an electrochemical acidification unit, a CO<sub>2</sub> degassing unit and an electrochemical alkalization unit. These parts are embedded in a cyclic system where two electrochemical cells perform acidification and regeneration functions. Below we discuss the operating principles of the electrochemical system and the design of the process.

## 2.2 Electrochemical Principles

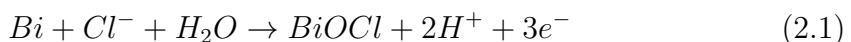
The electrochemical Direct Ocean Capture process is based on the controlled pH modulation of seawater through reversible faradaic reactions of chloride ions naturally present in seawater [4, 9]. In contrast to traditional electrochemical electrodialysis systems, where proton and hydroxide are generated by the dissociation of the water in a bipolar membrane, our current technology is based on electrochemical chloride capture and release reactions at two electrodes [4, 9].

The electrochemical system uses a bismuth electrode and a silver chloride electrode whose different reaction stoichiometries allow for protons to be generated or used in the reaction [4]. The system can alternately acidify seawater for release of carbon dioxide and re-form alkalinity while also recycling the electrode materials [4].

The resulting pH swing is the driving force for the conversion of dissolved inorganic carbon species into molecular carbon dioxide and after degassing for the restoration of seawater alkalinity [4, 9]. Electrochemical reactions at each electrode are described in the next sections.

### 2.2.1 Bi/BiOCl Electrode

The active material for the proton generation is metallic bismuth. At the acidification stage, bismuth undergoes oxidation reaction in the presence of chloride ions and water, producing bismuth oxychloride (BiOCl) and releasing protons into the surrounding electrolyte [4]:



The release of protons directly lowers the pH of seawater and shifts the carbonate equilibrium towards the formation of dissolved molecular carbon dioxide [4]. Since two protons are produced for every three electrons transferred, the reaction provides the acidification mechanism to convert bicarbonate and carbonate ions into dissolved CO<sub>2</sub> [4].

In the regeneration phase, the reverse reaction occurs. Bismuth oxychloride is electrochemically reduced back to metallic bismuth and consumes protons and restores the initial state of the electrode [4]:



By this reversible conversion between Bi and BiOCl, the electrode acts as a proton source during acidification and as a proton sink during alkalization [4].

### 2.2.2 Ag/AgCl Electrode

The silver chloride electrode serves as the counter electrode in the electrochemical system and is responsible for the reversible capture and release of chloride ions during operation. Unlike the bismuth electrode, the Ag/AgCl redox couple does not directly generate or consume protons. Its primary role is to maintain charge balance in the electrochemical cell and enabling the chloride-mediated pH swing mechanism [4].

In the acidification stage, silver chloride is electrochemically reduced to metallic silver according to the following reaction [4, 21]:



As the reaction is conducted, chloride ions are released into the electrolyte to compensate for the charge transfer from oxidation of bismuth at the other electrode. Since no protons are involved in the reaction, the Ag/AgCl electrode does not directly affect the pH of the solution [4].

During the regeneration phase, the reversal of reaction takes place. Metallic silver is oxidized in the presence of chloride ions to re-form silver chloride [4, 21]:



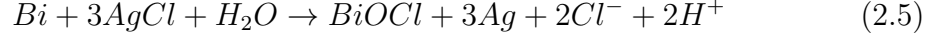
From this reversible redox process, the electrode provides a highly efficient mechanism for chloride storage and release. The Ag/AgCl couple has very fast reaction kinetics, low overpotential and high chloride storage capacity, which makes it suitable for electrochemical applications involving chloride-containing electrolytes such as seawater [4].

The different stoichiometries of the Bi/BiOCl and Ag/AgCl reactions are fundamental to the process. While the bismuth electrode generates or consumes protons, the silver chloride electrode only mediates chloride transport. The combination of these two electrochemical couples drives the overall pH swing mechanism that drives carbon dioxide extraction from seawater [4].

### 2.2.3 Chloride-Mediated pH Swing

The electrochemical pH swing of the Direct Ocean Capture process is due to the combination of Bi/BiOCl and Ag/AgCl electrode couples. The different reaction stoichiometries of these electrodes are able to adjust the proton concentration in seawater and remain charge neutral through the reversible transfer of chloride ions [4].

At acidification stage, the oxidation of metallic bismuth releases protons into the electrolyte while silver chloride is reduced to metallic silver. Combining the two half-reactions yields the overall cell reaction [4]:



The production of protons lowers the pH of seawater and shifts the carbonate equilibrium toward the formation of dissolved molecular carbon dioxide. The carbonate system is governed by a series of acid–base equilibria discussed in Chapter 1:



After degassing, electrochemical reactions are reversed to regenerate the electrode materials and restore alkalinity to the treated seawater. The overall regeneration reaction can be written as [4]:



In this stage, protons are consumed and pH increases. The remaining dissolved inorganic carbon is now converted back to bicarbonate and carbonate as the buffering capacity of treated water is restored. The electrodes are then ready for the next phase of operation.

So the chloride-mediated pH swing can be interpreted as an electrochemical method for controlling seawater carbonate chemistry without the constant addition of acids or bases. Rather than removing carbon dioxide through electrochemical reduction, the system alters the chemical environment of seawater to generate dissolved  $CO_2$ , which can then be separated into a degassing unit [4, 9].

From a process perspective, the pH swing is the link between the electrochemical and separation parts of the plant. The acidification stage creates the conditions for carbon dioxide release, and the alkalization stage brings back the electrochemical system and prepares the treated seawater for discharge. This cycle is the key to continuous carbon dioxide removal from seawater.

## 2.3 Process Configuration

The electrochemical Direct Ocean Capture process consists of three main process units: an electrochemical acidification unit, a carbon dioxide degassing unit, and an electrochemical alkalization unit. These are integrated in a cyclic setup with

two electrochemical cells operating simultaneously in acidification and regeneration mode [4].

A schematic representation of the process is shown in Figure 2.1.

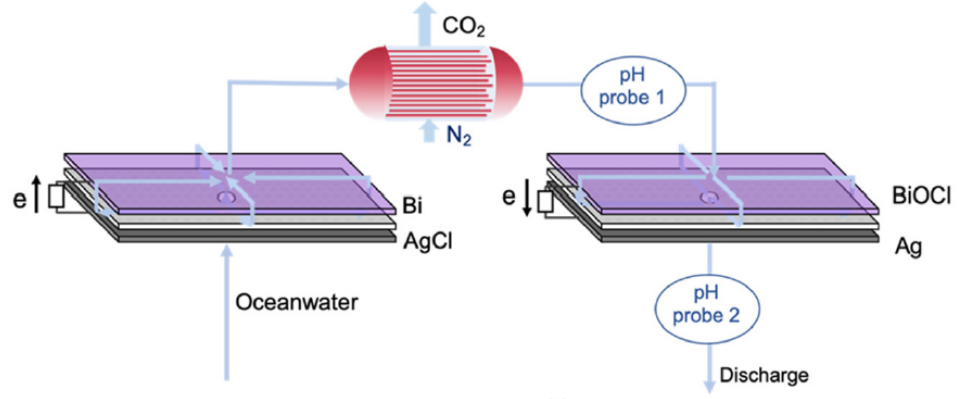


**Figure 2.1:** Schematic representation of the continuous chloride-mediated Direct Ocean Capture process [4].

Seawater first enters the acidification cell, where electrochemical reactions decrease the pH of the solution and help convert dissolved inorganic carbon into molecular carbon dioxide. The acidified stream is fed into a degassing unit for carbon dioxide extraction. Finally, decarbonized seawater enters the regeneration cell where alkalinity is restored and electrodes are regenerated before the treated stream is discharged [4].

The process is continuously run by periodically reversing the electrical polarity and the flow direction of the electrochemical cells. One cell can be acidified while the other is regenerated so that carbon dioxide removal can proceed continuously without interrupting the process.

### 2.3.1 Acidification Unit

The goal of the acidification unit is to reduce the pH of the seawater to values at which dissolved inorganic carbon is predominantly converted into dissolved molecular carbon dioxide. This is achieved by oxidizing metallic bismuth and reducing silver chloride simultaneously according to electrochemical reactions in Section 2.2.

As protons are generated at the Bi/BiOCl electrode, the pH of the seawater decreases from a value of about 8.1. Kim et al. calculated thermodynamics and showed that a pH close to 6 would be sufficient to convert most of the bicarbonate and carbonate ions into dissolved  $\text{CO}_2$ .

The acidification step is the key stage as it determines the amount of carbon dioxide available for extraction in the next separation unit. The acidification impact depends on the charge transferred to the electrochemical cell and on the buffering capacity of seawater, primarily due to dissolved inorganic carbon species.

### 2.3.2 CO<sub>2</sub> Degassing Unit

After electrochemical acidification, the seawater stream has a much higher concentration of dissolved molecular carbon dioxide. This stream is directed to a gas-liquid separation unit where carbon dioxide is extracted from the liquid phase [4].

For the experimental system developed by Kim et al., a hollow-fiber membrane contactor was used to convey the dissolved carbon dioxide into a nitrogen sweep stream that is used to simulate vacuum degassing. In an industrial setting, the same function could be accomplished with vacuum stripping systems that are operated below the equilibrium partial pressure of carbon dioxide in the acidified solution [4].

The goal of this unit is to maximize carbon dioxide recovery and minimize energy consumption and residual dissolved carbon content in treated seawater. The efficiency of the degassing stage directly affects the overall performance of the DOC process, as any residual dissolved carbon dioxide will affect the subsequent alkalization step.

### 2.3.3 Alkalization Unit

After carbon dioxide extraction, the treated seawater enters the alkalization unit. Electrochemical reactions occurring during acidification are reversed in this process, and the active electrode material is regenerated to increase the pH of the solution [4].

The reduction of bismuth oxychloride back to metallic bismuth takes protons and the silver is oxidized to recover silver chloride. As a result, the pH of the treated seawater increases considerably. Based on experiments conducted by Kim et al., the outlet pH was in the range 10-11 at operation times [4].

The alkalization stage has two functions. First, it restores the electrochemical system, and thus the process can be cyclic. Second, it restores the alkalinity of the treated seawater before discharge. The alkalized water can potentially enhance atmospheric carbon dioxide uptake via the natural carbonate equilibria [4, 9] once returned to the marine environment.

### 2.3.4 Cyclic Operation

Continuous operation can be achieved by using two identical electrochemical cells operating in alternating modes. While one cell performs acidification, the other performs regeneration. When the active material in the acidification cell approaches depletion, the polarity is reversed and the flow direction is switched. In this way, the cell previously used for regeneration becomes the acidification cell, while the other enters the regeneration phase [4].

When the active material in the acidification cell reaches depletion, the polarity of both cells is reversed and the seawater flow direction is shifted. Hence, the cell used for regeneration becomes the acidification cell, whereas the other cell is in the regeneration phase [4].

The alternating configuration allows for continuous removal of carbon dioxide without interrupting the process. The cyclic nature of the system also enables both electrode couples to be re-regenerated.

While the alternating configuration allows for repeated operation, cyclic reversibility should not be taken as an indication of indefinitely stable performance. In fact, the long-term stability of the process depends on the durability of electrode materials and the possibility of degraded processes for repeated acidification and regeneration cycles. These aspects are evaluated in the experimental results shown in the next section and also in relation to the technology limitations of the process.

## 2.4 Experimental Performance

The performance of the chloride-mediated electrochemical Direct Ocean Capture process has been investigated by Kim et al. in laboratory-scale experiments on an integrated continuous-flow system [4]. The objective of such experiments was to test the ability of the electrochemical DIC removal from seawater, and to assess the efficacy of the electrochemical pH-swing mechanism.

To this end, the system was operated in cyclic mode by alternating between acidification and regeneration stages. Synthetic seawater was continuously circulated through the electrochemical cells and the degassing unit to monitor the process in a variety of operating cycles [4].

A particular focus was on three main performance indicators: the efficiency of carbon dioxide removal, the Faradaic efficiency of the electrochemical reactions and the electrical energy required to drive the electrochemical cells.

### 2.4.1 CO<sub>2</sub> Removal Efficiency

The main goal of the process is the conversion and subsequent extraction of dissolved inorganic carbon from seawater.

The CO<sub>2</sub> generated was then removed in a membrane contactor with a nitrogen sweep. Kim et al. monitored the concentration of carbon dioxide in the gas phase and estimated how much carbon was removed in each cycle. The average dissolved inorganic carbon removal efficiency was 87%, i.e. 0.0543 mmol of CO<sub>2</sub> per cycle in the experiments under operating conditions.

The removal efficiency was slightly lower than the theoretical value predicted by equilibrium calculations. This was mainly due to incomplete degassing and transport limitations in the electrochemical cells and membrane contactor. However, the removal rate is a good indication of the pH swing concept in laboratory working and is a benchmark for the process modelling activities in this work [4].

**Table 2.1:** Main experimental performance indicators reported by Kim et al. [4].

| Parameter                         | Value                                    |
|-----------------------------------|------------------------------------------|
| DIC removal efficiency            | 87 %                                     |
| CO <sub>2</sub> removed per cycle | 0.0543 mmol                              |
| Relative Faradaic efficiency      | 90.4 %                                   |
| Specific energy consumption       | 122 kJ mol <sup>-1</sup> CO <sub>2</sub> |
| Number of cycles tested           | 10                                       |

## 2.4.2 Energy Consumption

Energy consumption is one of the most important performance indicators for carbon dioxide removal technologies, as it directly impacts both operating costs and overall environmental impact. In this proposed process, electrical energy is needed to drive the electrochemical reactions responsible for seawater acidification and alkalinity restoration [4].

Experimental measurements performed during continuous operation showed an average specific energy consumption of 122 kJ mol<sup>-1</sup> of CO<sub>2</sub> removed. It should be noted that this value refers exclusively to the electrical energy supplied to the electrochemical cells and does not include auxiliary process units such as seawater intake, pumping, degassing or CO<sub>2</sub> compression [4].

The required energy level is much higher than the thermodynamic minimum for the process. Based on equilibrium calculations, Kim et al. estimated that the minimum energy consumption to be approximately 32 kJ mol<sup>-1</sup> CO<sub>2</sub>, indicating that a large fraction of the energy is lost with electrochemical overpotentials and transport losses [4].

Even with this small gap, the experimental value is good compared with other electrochemical DOC technologies proposed previously and shows that chloride-mediated pH-swing systems can be effective in energy-efficient carbon removal.

### 2.4.3 Faradaic Efficiency

Faradaic efficiency is the fraction of electrical charge provided to the system that contributes to the desired electrochemical reactions and is thus a measure of how efficiently electrons are used for proton generation and carbon dioxide release [4]. Theoretically, based on the stoichiometry of the Bi/BiOCl reaction, two protons are produced for every three electrons transferred. Based on this, Kim et al. defined a theoretical maximum Faradaic efficiency and compared it with experimental observations [4].

During continuous operation, the system had an average relative Faradaic efficiency of 90.4%. This means that most of the electrical current supplied to the electrochemical cells was used for the desired chloride-mediated pH swing mechanism and only small losses related to side reactions or parasitic processes were reported in [4].

The high Faradaic efficiency recorded in our experiment suggests that most of the electric charge provided for the desired electrochemical reactions was contributed in laboratory-scale operation.

### 2.4.4 Comparison with Existing DOC Technologies

To assess the significance of the experimental results, it is useful to compare the performance of the chloride-mediated pH-swing process with other electrochemical Direct Ocean Capture technologies reported in the literature.

In terms of DOC technologies, bipolar membrane electrodialysis (BPMED) is the most well-studied and currently active one. Eisaman et al. (2012) developed a method for electrochemically extracting carbon dioxide from seawater through membrane acidification and alkalization. These efforts have provided solutions to CO<sub>2</sub> energy consumptions in the range of 150-250 kJ mol<sup>-1</sup> depending on the process setup and conditions.

The comparison between different types of DOC technologies is shown in Table 2.2. Although experimental conditions and system boundaries are not the same in our experiment, the chloride process has competitive energy performance and high carbon removal efficiency for the same process [4].

**Table 2.2:** Comparison of selected electrochemical DOC technologies.

| Technology                | Energy Consumption<br>(kJ mol <sup>-1</sup> CO <sub>2</sub> ) | Reference |
|---------------------------|---------------------------------------------------------------|-----------|
| BPMED DOC                 | 242                                                           | [13]      |
| BPMED with redox mediator | 155                                                           | [22]      |
| MIT chloride-mediated DOC | 122                                                           | [4]       |

## 2.5 Technological Challenges and TRL Assessment

Despite the promising results at laboratory scale, the chloride-mediated electrochemical DOC process is still at an early stage of technological development. There are several technical challenges to be overcome before large-scale deployment can be considered in the future. These issues include electrode stability, process integration, long-term operation and scaling up needs [4, 9].

One of the main issues in the experimental campaign was the stability of the silver-based electrode. The Ag/AgCl redox couple exhibited excellent electrochemical properties like fast kinetics and low overpotential, but silver was found in the treated effluent during continuous operation [4]. The concentrations were low but it is not clear if longer-term operation would have to be prevented by silver dissolution or by finding alternative chloride storage electrode material that is able to achieve similar electrochemical performance.

Another major challenge comes from mineral precipitation during alkalization. In our experiments with synthetic seawater, we found that the performance of the electrode surface was degraded due to the formation of magnesium hydroxide deposits [4]. This is due to the high local pH values generated near the electrode surface as the electrode surface undergoes regeneration. The resulting fouling layer can result in lower active surface area, increased mass transfer resistance and eventually in a lower process efficiency.

The management of seawater flow rates is also an important part of scale-up. The amount of dissolved inorganic carbon in seawater is much less concentrated compared to industrial water, which means that a large amount of water must be processed to achieve large carbon removal rates [9]. Therefore, pumping requirements, hydraulic losses and water handling infrastructure will be very important in determining the overall economics of the technology.

In addition to the electrochemical performance, integration of the degassing unit is a major engineering challenge. The efficiency of the extraction of carbon dioxide depends on the ability to achieve low partial pressure CO<sub>2</sub> in gas. To be used in industrial work, vacuum systems or a gas-liquid separation technology would be required in order to reduce energy consumption and maintain high levels of removal efficiency [4, 13].

From a materials point of view, the availability and cost of electrode components must also be considered. Although bismuth is relatively inexpensive compared to most electrochemical materials, silver could become an important economic factor at large scale. The next steps will most likely be to identify electrode chemistries that could maintain the benefits of the chloride-mediated pH-swing mechanism but at lower cost [4].

### 2.5.1 Technology Readiness Level Assessment

Based on the experimental evidence available in the literature, the chloride-mediated electrochemical Direct Ocean Capture process proposed by Kim et al. [4] can be classified between TRL 3 and TRL 4. The technology has evolved beyond a purely conceptual stage and the chloride-mediated pH-swing mechanism has been demonstrated and main process units are integrated in a continuous-flow laboratory-scale system. But the process has not yet been validated at pilot scale and its long-term operation under realistic seawater conditions is largely unexplored.

The main issues that limit the maturity of the technology are the electrochemical and operational stability of the system. As discussed in the previous sections, the remaining problems are electrode degradation, silver dissolution and mineral precipitation at alkalization, fouling of the electrode surfaces and the long-term cyclic stability. These may have a great impact on the performance of the process over several years of operation and are still important obstacles to the further development of the technology.

For this reason, the present work does not assume these limitations have been solved yet. They are regarded as essential uncertainties in the current state of development of the MIT process. The goal of the thesis is therefore not to prove the industrial viability of the technology, but to assess if the experimental performance on the laboratory scale provides a good starting point for a process-level analysis.

Within this framework, the pre-feasibility study focuses on the implications of the reported performance indicators, such as CO<sub>2</sub> removal efficiency, electrochemical energy consumption, process configuration, as compared with a more mature benchmark technology. In this sense, the analysis aims to determine if further research of the chloride-mediated process is justified despite its current electrochemical and operational limitations.

## Chapter 3

# Definition of the Reference Case Study

### 3.1 Development of the Reference Case study

The chloride-mediated electrochemical Direct Ocean Capture (DOC) process proposed in Chapter 2 has only been demonstrated in a laboratory setting under controlled experimental conditions. Although these experimental results provide valuable information regarding the performance of the process and electrochemical behaviour, they do not allow us to directly evaluate the technology at a scale that would be appropriate for practical use.

To explore the potential application of the proposed DOC concept beyond laboratory scale, a reference case study was developed and used as the basis for the process simulation and pre-feasibility assessment. The reference case is not to verify the exact performance of a commercial installation, but to assess how the technical aspects of scaling the process to a typical pilot-scale configuration are related.

To build the reference case study, we needed to combine the experimental data reported by Kim et al. with some engineering assumptions in order to define operating conditions, process boundaries, and plant capacity. The experimental parameters were always included in the reference case study when possible to keep the experimental data consistent with our process behaviour. Additional assumptions were made only when there was no information available from the experimental study or scale-up was needed to define parameters that could not be determined from laboratory measurements.

The resulting reference configuration is a continuous steady-state process suitable for implementation in Aspen Plus. Rather than reproducing the cyclic operation of the laboratory-scale system, the process is represented through a

continuous configuration that reproduces the average behaviour of the electrochemical acidification and regeneration stages. The electrochemical cells are modelled as black-box process units defined by their overall performance rather than by detailed electrochemical kinetics. This approach allows the analysis to focus on process requirements, mass and energy balances, equipment sizing and scale-up considerations, which are the primary objectives of a pre-feasibility assessment. The proposed DOC process is also compared with bipolar membrane electrodialysis (BPMED) that we have chosen as an example technology for this work. BPMED is one of the most developed electrochemical DOC systems currently available and has an overall higher level of technology maturity with more performance and techno-economic data available. The comparison is intended to provide a reference to evaluate the potential advantages, limitations, and scale-up implications of the chloride-mediated process compared to a well-established DOC technology. In the following sections, we set up the system boundaries for the study, describe the experimental parameters inherited from the MIT process, and illustrate some assumptions that are used to turn our laboratory-scale concept into a pilot-scale reference plant.

## 3.2 Definition of Plant Boundaries

The system boundaries define the part of the process included in the present pre-feasibility assessment. In this work, the analysis is limited to the main operations required to withdraw and pretreat seawater, perform the electrochemical pH swing, separate the released CO<sub>2</sub>, restore the alkalinity of the treated stream and condition the recovered CO<sub>2</sub> up to the reference outlet pressure.

The units included within the boundaries are seawater intake and pumping, coarse filtration, fine filtration, ultrafiltration, preliminary dissolved-gas removal, electrochemical acidification, CO<sub>2</sub> separation, electrochemical regeneration, treated seawater discharge and preliminary CO<sub>2</sub> conditioning to 1 bar.

The detailed design of the intake system, filtration equipment, electrochemical cells, degassing unit and discharge system is not developed in this chapter. These sections are included only at process level, in order to define the material and energy balances required for the reference case study.

Elements outside the direct process boundary are excluded from the quantitative assessment. These include electrode and equipment manufacturing, civil works, offshore infrastructure design, detailed control systems, long-term degradation, maintenance strategy, end-of-life treatment and life-cycle environmental impacts.

### 3.2.1 Units Included in the Model

The process units included within the system boundaries are shown conceptually in Figure 3.1.

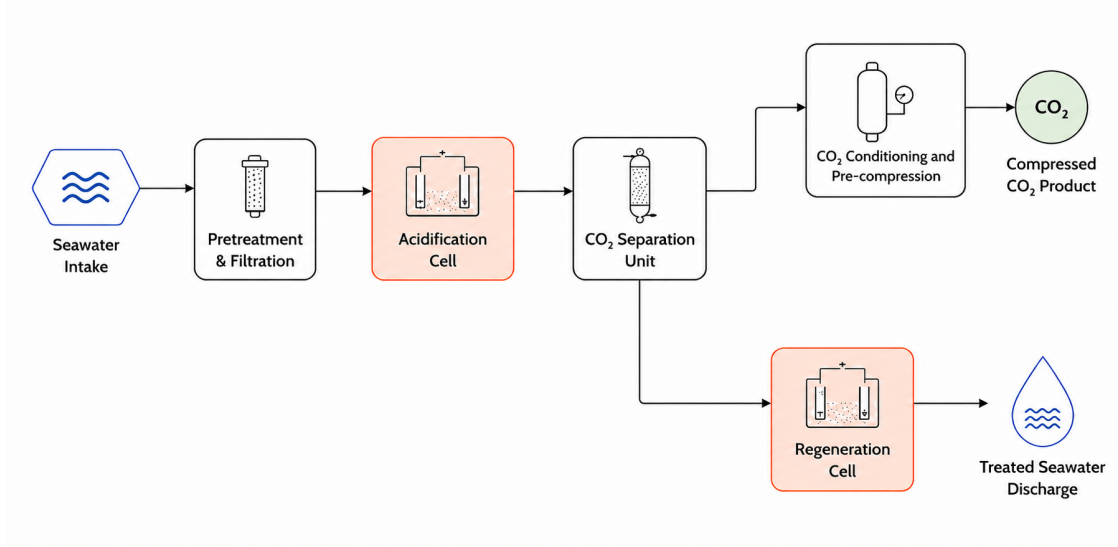


**Figure 3.1:** System boundaries and reference process configuration adopted for the present pre-feasibility study. The figure was generated using OpenAI ChatGPT based on the conceptual description provided by the author.

- seawater intake and pumping;
- coarse filtration, fine filtration and ultrafiltration;
- preliminary dissolved-gas removal for nitrogen and oxygen;
- electrochemical acidification;
- CO<sub>2</sub> separation from the acidified stream;
- electrochemical re-alkalization and electrode regeneration;
- discharge of the treated seawater;
- CO<sub>2</sub> conditioning and preliminary compression to 1 bar.

The seawater intake system provides the feed stream required by the process. Its detailed hydraulic design is not developed in this chapter, while the associated pumping requirement is considered in the energy assessment.

Pretreatment is represented by a sequence of filtration units placed upstream of the electrochemical section. Coarse filtration, fine filtration and ultrafiltration are included to represent the removal of suspended solids and biological material naturally present in seawater. These units are required to protect the downstream electrochemical and separation sections from fouling and excessive particulate loading.

The electrochemical section is represented at process level. The model does not resolve electrode-scale kinetics, internal transport phenomena or dynamic cycling behaviour. Instead, the acidification and regeneration steps are described through their overall effect on the treated seawater stream, using the experimental performance parameters available from the MIT study as reference inputs.

After acidification, the seawater stream is sent to the CO<sub>2</sub> separation section. In the experimental configuration proposed by Kim et al. [4], CO<sub>2</sub> was recovered using a hollow-fibre membrane contactor operated with a nitrogen sweep gas. In the present work, this step is represented by an equivalent gas–liquid separation section able to reproduce the target carbon removal at steady state. This choice allows the separation step to be included at process level without introducing a detailed design of the degassing equipment.

The recovered CO<sub>2</sub> stream is cooled, when required, and compressed only up to 1 bar before leaving the system boundaries. Further compression for pipeline transport, geological storage or industrial utilization is not included in the main process model, because it depends on the selected downstream pathway.

Finally, the treated seawater is sent to discharge after the re-alkalization stage. Before discharge, the outlet stream is assumed to require premixing with the receiving seawater in order to reduce local concentration and pH gradients. The detailed design of the discharge and premixing system is outside the scope of the present pre-feasibility study.

### 3.2.2 Units Excluded in the Model

The following elements are excluded from the present study:

- electrode manufacturing and replacement;
- construction and installation of process equipment;
- civil works and infrastructure requirements;
- environmental life-cycle impacts;
- detailed control systems and plant utilities;
- long-term degradation and maintenance costs.

First, the internal electrochemical behaviour of the cells is not modelled explicitly. Electrode design, electrochemical kinetics, ion transport phenomena, and cell-level optimization are not addressed in this study.

The production of electrodes, pumps, and other process equipment is not considered. Likewise, plant construction activities, civil works, and site-specific infrastructure requirements are excluded from the system boundaries.

The final destination of the captured CO<sub>2</sub> is not explicitly modeled in the quantitative analysis. The system boundary extends up to the generation of a compressed CO<sub>2</sub> stream, which can be subsequently directed in various directions. However, these downstream applications do not directly affect the material balance of the capture process. As such, we discuss potential CO<sub>2</sub> management pathways and utilization opportunities later.

Environmental assessments, including life cycle analysis and impacts on marine ecosystems, are also beyond the scope of this work. They require dedicated investigations that fall outside the objectives of a pre-feasibility study. Hence, the exclusions are consistent with the preliminary nature of the analysis and with the limited information about the large-scale implementation of the technology. Their contribution may become relevant in future techno-economic and life-cycle assessments once the process reaches a higher level of technological maturity.

## 3.3 Translation of the MIT Process into a Pilot-Scale System

The electrochemical DOC process described by Kim et al. was experimentally performed in laboratory conditions with synthetic seawater and a continuous cyclic mode. Although we know that the experiment provides the performance parameters for the feasibility of the concept, certain assumptions are necessary to define a process configuration that would be suitable for pilot-scale simulation.

We have adopted experimental parameters that are reported in the literature as far as possible in order to remain consistent with the original work. Additional assumptions have been made only when required to define operating conditions, plant capacity or process units that were not considered in our study in the laboratory.

For clarity, we thus divide the parameters used in this work into two categories: (i) experimental parameters taken from the MIT study and (ii) engineering assumptions made for scale-up and process modelling.

### 3.3.1 Experimental Parameters Adopted from the MIT Study

The reference process model was developed based on the key performance indicators reported by Kim et al. for the chloride-mediated electrochemical DOC process. The values in the original study were used as reference parameters in the development of the pilot-scale model and were adopted if possible.

Our system was equipped with synthetic seawater of about 2 mmol L<sup>-1</sup> of dissolved inorganic carbon (DIC). During continuous cyclic operation, the system achieved an average DIC removal efficiency of about 87%, where dissolved carbonate and bicarbonate species were converted to molecular carbon dioxide by electrochemical acidification and degassing. The acidified stream had pH around 5.2, and the recovered seawater at pH 10-11 after alkalisation. The average electrochemical energy consumption of the system was 122 kJ mol<sup>-1</sup> of removed CO<sub>2</sub>.

The process configuration proposed by Kim et al. was also used as the basis of the present study. The process consists of acidification of dissolved inorganic carbon to molecular CO<sub>2</sub> and a gas separation step and regeneration of the treated seawater before discharge.

Table 3.1 summarises the experimental parameters adopted from the original study and used as reference values throughout the subsequent modelling activities.

**Table 3.1:** Experimental parameters adopted from the MIT study and used as reference values for the process model.

| Parameter                          | Value                                    |
|------------------------------------|------------------------------------------|
| Initial DIC concentration          | 2 mmol L <sup>-1</sup>                   |
| CO <sub>2</sub> removal efficiency | 87 %                                     |
| Acidification pH                   | 5.2                                      |
| Regeneration pH                    | 10-11                                    |
| Electrochemical energy consumption | 122 kJ mol <sup>-1</sup> CO <sub>2</sub> |
| Process configuration              | Acidification–Degassing–Regeneration     |

### 3.3.2 Scale-Up Assumptions

The experimental work of Kim et al. [4] provides the reference performance indicators for the chloride-mediated DOC process, but it does not define a complete pilot-scale plant. For this reason, a limited set of engineering assumptions was introduced to translate the laboratory concept into a process configuration suitable for simulation and preliminary assessment.

The first assumption concerns the plant capacity. Since the original process was demonstrated at laboratory scale, a reference capture capacity was defined in this

work to provide a design basis for the Aspen Plus model and for the subsequent pre-feasibility analysis.

The second assumption concerns the operating representation of the process. Although the experimental system is based on cyclic switching between electrochemical cells, the reference plant is described through an equivalent continuous configuration. This allows the average behaviour of the acidification, CO<sub>2</sub> separation and regeneration steps to be evaluated at process level.

The electrochemical performance is introduced through global parameters rather than through a detailed cell model. In particular, the DIC removal efficiency and the electrochemical energy consumption reported by Kim et al. [4] are used as reference values for the base case.

A realistic seawater feed composition is adopted for the process model, while the experimental synthetic seawater composition is retained only as the source of the reference performance data. The detailed definition of the inlet composition is reported in Section 3.5.1.

Finally, the recovered CO<sub>2</sub> stream is conditioned within the system boundaries only up to atmospheric pressure. Long-term electrode degradation, silver dissolution, fouling phenomena and performance decay are not included in the quantitative model, but they are considered as relevant scale-up limitations in the discussion of the technology.

## 3.4 Reference Plant Capacity

The laboratory-scale system developed by Kim et al. was designed to demonstrate the technical feasibility of the chloride-mediated electrochemical DOC concept and so does not provide a suitable basis to evaluate the process requirements at larger scales. To do that, we defined a reference plant capacity in order to provide the design basis for the process simulation and a pre-feasibility analysis.

The selected capacity determines the amount of carbon dioxide to be removed, the seawater throughput required, and the size of the major process units. The following sections describe the criteria used for the capacity selection and the corresponding design flow rates used throughout the study.

### 3.4.1 Capacity Selection

The selection of a suitable plant capacity is one of the most crucial parts of developing the reference case study. Given that the chloride-mediated DOC process is still in a very early stage of technological development and has only been demonstrated at laboratory scale, the adoption of a large commercial-scale capacity would not be consistent with the maturity level of the technology.

For this reason, a pilot-scale configuration was chosen as the basis of the present work. Our reference plant is meant to remove 1000 tCO<sub>2</sub> per year, which is enough to understand process requirements, plant size, and initial economic performance but still be representative of a first-stage deployment of the technology.

The selected capacity is also consistent with the scales commonly considered in the literature for emerging electrochemical carbon dioxide removal technologies and provides a suitable basis for comparison with more mature Direct Ocean Capture approaches, particularly bipolar membrane electrodialysis (BPMED), which is adopted as the benchmark technology throughout this study.

### 3.4.2 Design CO<sub>2</sub> Flow Rate

The selected reference capacity of 1000 tCO<sub>2</sub> yr<sup>-1</sup> represents the annual amount of carbon dioxide removed by the reference plant. Since the process is modelled as a continuous steady-state system in Aspen Plus, this annual target is converted into an equivalent continuous CO<sub>2</sub> flow rate by assuming operation over the entire year.

This assumption is consistent with the objective of developing a steady-state process model and avoids introducing additional uncertainties related to plant availability, scheduled maintenance and downtime, which are not explicitly assessed in the present work. Therefore, the annual operating time is taken as:

$$t_{\text{op}} = 8760 \text{ h yr}^{-1} \quad (3.1)$$

The corresponding design mass flow rate of captured carbon dioxide is:

$$\dot{m}_{\text{CO}_2} = \frac{1000 \times 10^3}{8760} = 114.2 \text{ kg h}^{-1} \quad (3.2)$$

Using a molecular weight of 44 kg kmol<sup>-1</sup>, the corresponding molar flow rate is:

$$\dot{n}_{\text{CO}_2} = \frac{114.2}{44} = 2.60 \text{ kmol h}^{-1} \quad (3.3)$$

These values constitute the reference CO<sub>2</sub> flow rate adopted for the Aspen Plus model. The corresponding seawater flow rate required to achieve this carbon removal target is calculated in the following section.

### 3.4.3 Design Seawater Flow Rate

The flow rate of the seawater needed in this process was estimated using the experimental results of Kim et al. [4] as a preliminary design reference. In the continuous flow experiments, the chloride-mediated Direct Ocean Capture system has achieved a dissolved inorganic carbon (DIC) removal efficiency of about 87% for synthetic seawater from an initial DIC concentration of about 2.0 mmol L<sup>-1</sup>.

In this work, we modelled the process in Aspen Plus with a seawater composition representative of the real marine conditions to the reference data given by Millero [7]. However, there are no experimental data on the performance of the chloride-mediated DOC process in real seawater. Hence, the results of Kim et al. [4] are the best experimental reference for this technology.

For this reason, the DIC removal efficiency reported in the experimental study is used only as a first sizing criterion to establish the base case of the process model. The value of 87% is not assumed to be the actual performance of a system operating with real seawater and cannot be considered an intrinsic property of the Aspen Plus model developed in this study. It only serves to provide an experimental starting point to determine the required feed rate for the system and determine the reference configuration for later work.

Considering that  $1 \text{ mmol L}^{-1}$  is numerically equivalent to  $1 \text{ mol m}^{-3}$ , the amount of DIC removed per unit volume of treated seawater can be estimated as:

$$C_{\text{DIC,rem}} = 2.0 \times 0.87 = 1.74 \text{ mol m}^{-3} \quad (3.4)$$

Assuming a design  $\text{CO}_2$  removal rate of  $2.60 \text{ kmol h}^{-1}$ , the required seawater flow rate can be calculated as:

$$\dot{V}_{\text{SW}} = \frac{\dot{n}_{\text{CO}_2}}{C_{\text{DIC,rem}}} \quad (3.5)$$

where  $\dot{n}_{\text{CO}_2}$  is the molar  $\text{CO}_2$  removal rate and  $C_{\text{DIC,rem}}$  is the amount of dissolved inorganic carbon removed per unit volume of seawater.

Substituting the corresponding values:

$$\dot{V}_{\text{SW}} = \frac{2.60 \times 10^3}{1.74} = 1.49 \times 10^3 \text{ m}^3 \text{ h}^{-1} \quad (3.6)$$

The resulting seawater flow rate is the design basis for the pre-feasibility study and is the reference throughput for the initial sizing of the main process units in the system.

### 3.4.4 Summary of Design Basis

The main assumptions adopted for the definition of the reference case are summarized in Table 3.2. These parameters constitute the design basis used throughout the process modelling activities and the subsequent techno-economic assessment.

**Table 3.2:** Reference design basis adopted for the pilot-scale DOC process.

| Parameter                               | Value                                             | Origin               |
|-----------------------------------------|---------------------------------------------------|----------------------|
| Annual CO <sub>2</sub> removal capacity | 1000 tCO <sub>2</sub> yr <sup>-1</sup>            | This work            |
| Operating mode                          | Continuous steady-state                           | Assumption           |
| Operating hours                         | 8760 h yr <sup>-1</sup>                           | Assumption           |
| Design CO <sub>2</sub> mass flow rate   | 114.2 kg h <sup>-1</sup>                          | Calculated           |
| Design CO <sub>2</sub> molar flow rate  | 2.60 kmol h <sup>-1</sup>                         | Calculated           |
| Reference DIC concentration             | 2.0 mmol L <sup>-1</sup>                          | Reference assumption |
| CO <sub>2</sub> removal efficiency      | 87%                                               | MIT study            |
| DIC removed per unit volume             | 1.74 mol m <sup>-3</sup>                          | Calculated           |
| Design seawater flow rate               | $1.49 \times 10^3$ m <sup>3</sup> h <sup>-1</sup> | Calculated           |

The values reported above are the reference configuration used for the Aspen Plus model development. As discussed in the previous sections, the DIC removal efficiency is used only as a sizing parameter from the experiment of Kim et al.. Its influence on process performance and economic indicators is therefore recognized as one of the main sources of uncertainty of the present pre-feasibility assessment.

## 3.5 Modelling Assumptions

The modelling assumptions in this section describe the feed composition, electrochemical performance and operating conditions during the study. These assumptions are derived primarily from experimental results in the literature and inform the Aspen Plus simulations outlined in Chapter 4.

### 3.5.1 Seawater Composition

The seawater stream used in the present study was defined to represent natural marine conditions rather than the synthetic solution adopted in the experimental work of Kim et al. [4]. The main dissolved ions were introduced in the Aspen Plus model as individual electrolyte species, while dissolved inorganic carbon was represented through CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>.

The concentration of the main ions in the seawater was obtained from the standard seawater content (Millero 2007). The salinity of the seawater was assumed to be 35 g kg<sup>-1</sup> for open ocean conditions, and the mass contribution of each dissolved ion was calculated by its concentration in the seawater as follows:

$$w_i = \frac{m_i}{m_{sw}} \quad (3.7)$$

Where  $w_i$  is the mass fraction of species  $i$ ,  $m_i$  is the mass of the dissolved ion and  $m_{sw}$  is the total mass of seawater. For example, if chloride concentration is 19.35 g kg<sup>-1</sup> and sodium concentration is 10.77 g kg<sup>-1</sup>, then the mass fractions are:

$$w_{Cl^-} = \frac{19.35}{1000} = 0.01935 \quad (3.8)$$

$$w_{Na^+} = \frac{10.77}{1000} = 0.01077 \quad (3.9)$$

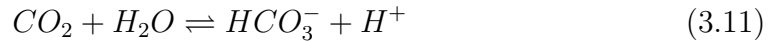
We also performed similar calculations to the other major ions (Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup> and K<sup>+</sup>), resulting in a total dissolved salt content close to the target salinity of 35 g kg<sup>-1</sup>.

The inorganic carbon species were defined by assuming a total dissolved inorganic carbon concentration of 2 mmol L<sup>-1</sup> for the feed seawater. This value was adopted as reference DIC concentration for the inlet stream, consistently with the experimental basis reported by Kim et al. [4]. The carbonate speciation was then calculated assuming an initial seawater pH of 8.1, a salinity of 35 g kg<sup>-1</sup> and a temperature of 25 °C, in order to represent typical marine conditions.

The total dissolved inorganic carbon is expressed as:

$$DIC = [CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}] \quad (3.10)$$

At the assumed pH, temperature and salinity, the carbonate system is governed by the equilibria:



Under these conditions, the inorganic carbon content was distributed as 88.17% bicarbonate, 11.56% carbonate and 0.27% dissolved molecular carbon dioxide. The assumed DIC concentration was then used to calculate the absolute concentration of each carbon species. Applying these fractions to the assumed DIC concentration yields:

$$[HCO_3^-] = 0.8817 \times 2 = 1.7634 \text{ mmol L}^{-1} \quad (3.13)$$

$$[CO_3^{2-}] = 0.1156 \times 2 = 0.2312 \text{ mmol L}^{-1} \quad (3.14)$$

$$[CO_2(aq)] = 0.0027 \times 2 = 0.0054 \text{ mmol L}^{-1} \quad (3.15)$$

The resulting concentrations were converted into mass fractions and were implemented in Aspen Plus. The entire feed composition for simulation is shown in Table 3.3.

**Table 3.3:** Seawater feed composition adopted in the Aspen Plus model.

| Group             | Component                     | Mass fraction            |
|-------------------|-------------------------------|--------------------------|
| Solvent           | H <sub>2</sub> O              | 0.965065                 |
| Dissolved gases   | CO <sub>2</sub>               | $2.32135 \times 10^{-7}$ |
|                   | N <sub>2</sub>                | $1.05 \times 10^{-5}$    |
|                   | O <sub>2</sub>                | $5.80 \times 10^{-6}$    |
| Major ions        | Na <sup>+</sup>               | 0.0107                   |
|                   | Cl <sup>-</sup>               | 0.0193                   |
|                   | Mg <sup>2+</sup>              | 0.0013                   |
|                   | K <sup>+</sup>                | 0.0004                   |
|                   | Ca <sup>2+</sup>              | 0.0004                   |
|                   | SO <sub>4</sub> <sup>2-</sup> | 0.0027                   |
| Carbonate species | HCO <sub>3</sub> <sup>-</sup> | $1.05091 \times 10^{-4}$ |
|                   | CO <sub>3</sub> <sup>2-</sup> | $1.35539 \times 10^{-5}$ |
| <b>Total</b>      |                               | <b>1.000000</b>          |

### 3.5.2 Electrochemical Performance Parameters

The electrochemical section is described through process-level performance parameters derived from the experimental study of Kim et al. [4]. This approach is consistent with the scope of the present work, which aims to evaluate the overall process performance rather than to develop a detailed electrochemical cell model.

Two parameters are used to define the reference case: the DIC removal efficiency and the specific electrochemical energy consumption. The DIC removal efficiency sets the amount of inorganic carbon removed from the treated seawater, while the specific energy consumption is used to estimate the electricity demand associated with the electrochemical pH swing.

These values are adopted as baseline assumptions for the Aspen Plus model and for the preliminary techno-economic assessment.

### 3.5.3 Operating Conditions

The reference operating conditions adopted in the present study are summarized in order to provide a consistent basis for process modelling and equipment sizing.

Unless otherwise specified, all process units are assumed to operate under continuous steady-state conditions. Since the Aspen Plus model represents an equivalent continuous process, the annual operating time is taken as  $8760 \text{ h yr}^{-1}$ . Plant availability, scheduled maintenance and downtime are not explicitly included in the steady-state simulation.

For the seawater intake and pretreatment sections, ambient temperature and pressure are employed. Pressure variations are only considered for specific unit operations such as pumping, gas-liquid separation and carbon dioxide compression.

The acidification and regeneration stages are designed to reproduce the pH swing required for carbon dioxide release and seawater re-alkalisation. The detailed implementation of these assumptions in the Aspen Plus model is presented in Chapter 4.

These operating conditions define the reference framework for the development of the Aspen Plus model and the preliminary techno-economic analysis.

**Table 3.4:** Summary of the main assumptions adopted for the reference case.

| Parameter                           | Value                                                 |
|-------------------------------------|-------------------------------------------------------|
| CO <sub>2</sub> capture capacity    | 1000 tCO <sub>2</sub> yr <sup>-1</sup>                |
| Operating mode                      | Continuous steady-state                               |
| Operating hours                     | 8760 h yr <sup>-1</sup>                               |
| Design CO <sub>2</sub> removal rate | 114.2 kg h <sup>-1</sup> (2.60 kmol h <sup>-1</sup> ) |
| Seawater composition                | Natural seawater (Millero, 2007)                      |
| Design seawater flow rate           | $1.49 \times 10^3 \text{ m}^3 \text{ h}^{-1}$         |
| Seawater temperature                | 25 °C                                                 |
| Feed pressure                       | 1 bar                                                 |
| Reference DIC removal efficiency    | 87%                                                   |
| Acidification target                | pH 5.2                                                |
| Regeneration target                 | pH 10                                                 |

## 3.6 Reference Scenario

This section defines the reference scenario adopted for the process simulation and the preliminary techno-economic assessment. The aim is not to represent a specific installation site, but to establish a consistent baseline for evaluating the technical

and economic performance of the chloride-mediated electrochemical Direct Ocean Capture process at pilot scale.

The reference scenario combines the experimental results reported by Kim et al. with the design assumptions introduced in the previous sections. In particular, the process is assessed under a generic offshore implementation, in which seawater is withdrawn from below the sea surface, pretreated, processed in the electrochemical section and finally discharged after carbon dioxide removal and alkalinity restoration.

All simulation results presented in the following chapters are based on this baseline configuration unless otherwise specified. The selected assumptions should therefore be interpreted as reference values for a preliminary assessment rather than as the outcome of a detailed site-specific design.

### 3.6.1 Plant Location Assumptions

The reference plant is assumed to be located in a generic European offshore or coastal area with direct access to seawater and electricity infrastructure. No specific country or installation site is selected, since the purpose of this work is to assess the process under representative European conditions rather than to evaluate the feasibility of a particular location.

For the reference configuration, the seawater feed stream was defined at 1 bar, which was adopted as the reference intake pressure in the Aspen Plus model. This choice was made to represent the intake stream at ambient pressure and to avoid introducing site-specific hydraulic assumptions related to intake depth, offshore platform elevation and detailed seawater lifting requirements.

Therefore, hydrostatic pressure variations associated with seawater withdrawal depth are not explicitly considered in the base-case simulation. The detailed design of the intake system and the corresponding hydraulic head would depend on the specific installation site and are outside the scope of the present pre-feasibility model. The process equipment was assumed to be installed on an offshore platform located approximately 15 m above the mean sea level. Therefore, the static contribution to the intake pump head was evaluated with respect to the elevation of the platform above the free sea surface, rather than to the intake depth itself. Additional hydraulic contributions were then considered to account for distributed and localized losses in the intake line and for the pressure drops associated with the first pretreatment units.

The European context is used as a reference for the choice of economic parameters, utility costs and general process assumptions. However, site-specific aspects such as local seawater composition, climate conditions, wave exposure, permitting requirements, marine infrastructure and regional electricity markets are not explicitly considered.

This approach provides a general and consistent basis for the preliminary assessment of the process. Therefore, the results should be interpreted as representative of a generic European implementation and not as predictions for a specific geographical location.

### **3.6.2 Reference Process Configuration**

The reference configuration adopted in this work is based on the process architecture proposed by Kim et al., in which seawater acidification, carbon dioxide separation and seawater regeneration are performed sequentially. The aim is not to reproduce the detailed experimental setup, but to represent the main process functions at a scale suitable for process simulation and preliminary feasibility assessment.

The process is therefore described as a sequence of unit operations reproducing the key transformations occurring in the system: preliminary seawater pretreatment, conversion of dissolved inorganic carbon into molecular carbon dioxide, separation of the released gas, restoration of seawater alkalinity and compression of the recovered CO<sub>2</sub> stream.

The process configuration and the corresponding Aspen Plus implementation are described in detail in Chapter 4.

## Chapter 4

# Process Modelling in Aspen Plus

### 4.1 Aspen Plus Simulation Setup

The reference Direct Ocean Capture process defined in Chapter 3 was implemented in Aspen Plus in order to translate the case-study assumptions into a process simulation model. Since the system boundaries, design basis and main modelling assumptions have already been introduced, this chapter focuses on how they were implemented through Aspen Plus components, property methods, material streams and unit-operation blocks.

The following sections describe the thermodynamic method adopted for the electrolyte system, the implementation of the main process units and the operating specifications assigned to each section of the flowsheet. The resulting model provides the basis for the mass and energy balances discussed in the following chapter.

### 4.2 Thermodynamic Method

The Aspen Plus simulation was developed using the ELECNRTL property method, which stands for Electrolyte Non-Random Two-Liquid. ELECNRTL is a thermodynamic model used for aqueous electrolyte systems and accounts for the non-ideal behaviour of liquid mixtures containing dissolved salts and ionic species. It was therefore selected because the process involves seawater streams with high ionic strength and carbonate species in both neutral and ionic forms.

The model components include water, dissolved gases, the main seawater ions and the species required to represent the dissolved inorganic carbon system. The inlet composition corresponds to the reference seawater feed defined in Chapter 3,

where the salinity, temperature, pH and DIC concentration were specified before conversion into Aspen Plus mass fractions.

The selected thermodynamic framework was used to represent the composition of the aqueous streams and the phase behaviour associated with  $\text{CO}_2$  separation under reduced-pressure conditions. Conversely, the electrochemical acidification and regeneration steps were not described from first principles. They were implemented as stoichiometric process blocks reproducing the overall effect of the pH swing on the carbonate system.

### 4.3 Process Flowsheet Implementation

The final Aspen Plus flowsheet is shown in Figure 4.1. The process can be divided into the following main sections: seawater intake and pretreatment, preliminary dissolved-gas removal, electrochemical acidification, carbon dioxide vacuum separation, carbon dioxide conditioning and compression, electrochemical regeneration, and treated seawater discharge.

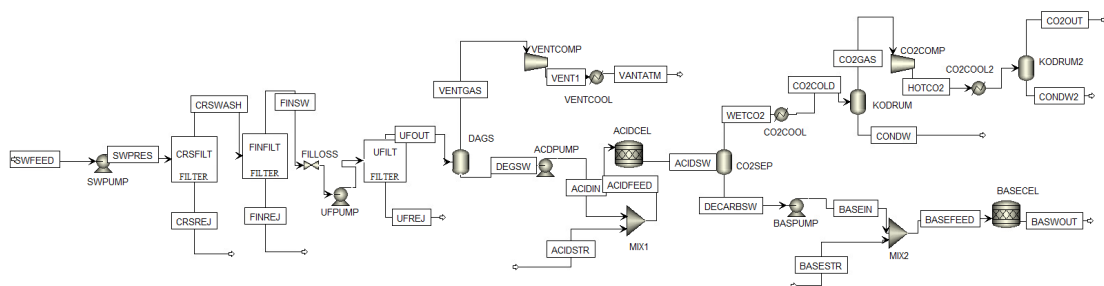


**Figure 4.1:** Aspen Plus flowsheet developed for the chloride-mediated Direct Ocean Capture process.

The seawater feed stream, labelled SWFEED, is introduced at ambient conditions and sent to the intake and pretreatment section. This section includes the main seawater intake pump, coarse filtration, fine filtration and ultrafiltration. The ultrafiltration stage was included in the base-case configuration in order to provide a more realistic representation of the pretreatment requirements associated with large seawater flow rates. In the Aspen Plus model, the filtration units were represented through simplified pressure-drop-based blocks. Therefore, membrane fouling, backwashing, cleaning cycles and detailed retentate management were not explicitly modelled.

After pretreatment, the stream enters a preliminary dissolved-gas removal section, represented by the block DAGS1. This unit partially removes dissolved nitrogen and oxygen before the electrochemical acidification stage. The removed gas stream,

labelled VENTGAS, is compressed in VENTCOMP, cooled in VENTCOOL and finally released as VANTATM. The liquid stream leaving DAGS1, labelled DEGSW, is pumped by ACDPUMP before entering the acidification section.

The acidification section is represented by the RStoic block ACIDCEL. Before entering this block, the repumped seawater stream ACIDIN is mixed with the equivalent acidification stream ACIDSTR, producing the inlet stream ACIDFEED. The ACIDCEL block reproduces the overall effect of the electrochemical pH decrease, shifting the dissolved inorganic carbon equilibrium toward molecular  $\text{CO}_2$ . The acidified stream leaving this block is labelled ACIDSW.

The acidified seawater stream is then sent to the  $\text{CO}_2$  separation section, represented by the vacuum flash block CO2SEP. This block operates at 0.03785 bar, a pressure selected through a Design Spec in order to reproduce the reference DIC removal efficiency adopted for the model. The gas stream leaving CO2SEP is a humid  $\text{CO}_2$ -rich stream, labelled WETCO2, while the liquid outlet, labelled DECARBSW, is sent to the regeneration section.

The WETCO2 stream is sent to the  $\text{CO}_2$  conditioning section. First, it is cooled in CO2COOL and the cooled stream, labelled CO2COLD, is sent to the knock-out drum KODRUM. In this unit, part of the water vapour is condensed and removed as the liquid stream CONDW. The gas stream leaving KODRUM is then compressed in CO2COMP, producing the hot compressed stream HOTCO2.

In the updated base-case flowsheet, an additional cooling and condensate-removal step was included downstream of the  $\text{CO}_2$  compressor. The HOTCO2 stream is cooled in CO2COOL2 to 10 °C at approximately 1 bar. The cooled compressed stream is then sent to the second knock-out drum, KODRUM2, modelled as an adiabatic flash operating at 1 bar. The condensed liquid is removed as CONDW2, while the final gas product leaves the process as CO2OUT.

The liquid stream leaving the  $\text{CO}_2$  vacuum separator, DECARBSW, is pumped by BASPUMP and sent to the regeneration section. The repumped stream BASEIN is mixed with the equivalent alkalization stream BASESTR, producing the inlet stream BASEFEED. The regeneration block, labelled BASECEL, restores alkaline conditions in the treated seawater before discharge. The final treated seawater stream leaving the process is labelled BASWOUT.

Further compression for transport, geological storage or utilization was not included within the main process boundaries, since it depends on the final destination of the recovered  $\text{CO}_2$  and is not intrinsic to the Direct Ocean Capture step itself.

### 4.3.1 Seawater Intake and Pretreatment

The first section of the Aspen Plus flowsheet represents seawater intake and pretreatment. The seawater feed stream was defined according to the reference composition introduced in Chapter 3 and specified at 25 °C. The intake system

was simplified as a sequence of hydraulic and pretreatment blocks, including the main seawater intake pump, coarse and fine filtration, a lamination valve and an ultrafiltration stage.

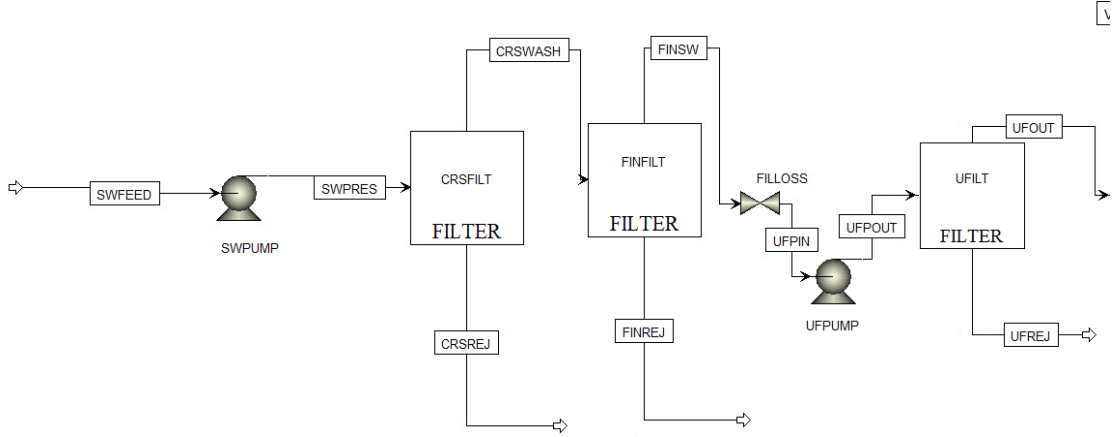


**Figure 4.2:** Seawater intake, pumping and pretreatment section of the Aspen Plus flowsheet.

The main intake pump represents the pressure increase required to transfer seawater from the intake point to the process equipment and to compensate for the main hydraulic losses occurring in the initial intake line. The pressure assigned to this pump was selected according to the preliminary hydraulic assumptions discussed in the following subsection.

After pressurization, the stream is sent to two filtration blocks, representing coarse and fine filtration. These units account for the preliminary removal of debris, suspended solids and smaller particulate matter before membrane pretreatment. In Aspen Plus, they were modelled only as pressure-drop blocks; therefore, solid accumulation, clogging, filter cleaning and backwashing were not explicitly simulated.

A lamination valve was included downstream of the filtration section to represent the remaining hydraulic losses not directly associated with the two filter blocks. These include the contributions related to the platform elevation, the intake line, localized losses and the intake screen. The valve was therefore introduced as a modelling element to reproduce the overall pressure profile of the intake section, rather than as a specific process-control device.

The pretreatment train also includes an ultrafiltration unit, introduced to account for the additional conditioning required by the large seawater flow rate. A dedicated booster pump was placed upstream of this block in order to represent the hydraulic requirement of the membrane stage separately from the main intake pump. The ultrafiltration unit was modelled as a simplified pressure-drop block,

without explicitly considering membrane fouling, permeability decline, backwashing, cleaning cycles or detailed retentate management.

This simplified implementation allows the main hydraulic and pretreatment contributions to be included in the Aspen Plus model while remaining consistent with the preliminary nature of the process assessment. The pretreated seawater leaving the ultrafiltration section is then sent to the preliminary dissolved-gas removal unit.

### 4.3.2 Hydraulic Assumptions and Pump Pressure Selection

The pressure increases assigned to the liquid pumps in the Aspen Plus flowsheet were selected from a preliminary hydraulic estimate. The aim of this calculation was not to provide a detailed hydraulic design of the seawater intake system, but to define consistent pressure levels for the pump and pressure-drop blocks used in the process simulation. In particular, the calculation was used to justify the pressure rise assigned to the main seawater intake pump and to the booster pump placed upstream of the ultrafiltration unit.

The seawater mass flow rate used in the reference Aspen Plus model was equal to  $1530 \text{ t h}^{-1}$ . Assuming a seawater density of  $1027.3 \text{ kg m}^{-3}$ , this corresponds to a volumetric flow rate of approximately  $1489 \text{ m}^3 \text{ h}^{-1}$ , or  $0.414 \text{ m}^3 \text{ s}^{-1}$ .

The seawater intake was assumed to be located 10 m below mean sea level, while the process equipment was placed on an offshore platform 15 m above sea level. Since the hydrostatic pressure at the intake compensates the elevation up to the sea surface, only the platform elevation was included as static head. Thus, the static contribution to the pump head was set equal to 15 m.

The main seawater intake pump was used to provide the pressure required to overcome the hydraulic demand of the intake and initial pretreatment line. The total head considered for this pump included the static elevation to the platform, distributed losses in the intake pipe, localized losses, the pressure loss across the intake screen, and the pressure losses across the coarse and fine filtration units:

$$H_{\text{pump}} = \Delta z + h_f + h_l + h_{\text{screen}} + h_{\text{filters}} \quad (4.1)$$

The seawater mass flow rate used in the Aspen Plus reference case was equal to  $1530 \text{ t h}^{-1}$ . Assuming a seawater density of  $1027.3 \text{ kg m}^{-3}$ , this corresponds to a volumetric flow rate of:

$$\dot{V}_{SW} = \frac{\dot{m}_{SW}}{\rho_{SW}} = \frac{1530 \times 10^3}{1027.3} = 1489 \text{ m}^3 \text{ h}^{-1} \quad (4.2)$$

or:

$$\dot{V}_{SW} = 0.414 \text{ m}^3 \text{ s}^{-1} \quad (4.3)$$

The distributed losses were estimated through the Darcy–Weisbach equation:

$$h_f = f_D \frac{L}{D} \frac{v^2}{2g} \quad (4.4)$$

where  $f_D$  is the Darcy friction factor,  $L$  is the pipe length,  $D$  is the pipe diameter and  $v$  is the design velocity. For the reference case, a pipe length of 50 m, a design velocity of  $1.2 \text{ m s}^{-1}$  and a Darcy friction factor of 0.02 were assumed. Based on the updated volumetric flow rate, the corresponding pipe diameter was estimated as:

$$D = \sqrt{\frac{4\dot{V}_{SW}}{\pi v}} = \sqrt{\frac{4 \cdot 0.414}{\pi \cdot 1.2}} = 0.66 \text{ m} \quad (4.5)$$

The resulting distributed head loss is:

$$h_f = 0.02 \frac{50}{0.66} \frac{1.2^2}{2 \cdot 9.81} = 0.11 \text{ m} \quad (4.6)$$

Localized losses were estimated using an equivalent loss coefficient:

$$h_l = K_{\text{tot}} \frac{v^2}{2g} \quad (4.7)$$

A preliminary value of  $K_{\text{tot}} = 5$  was adopted to account for bends, fittings, valves and entrance or exit effects, giving a localized head loss of approximately:

$$h_l = 5 \frac{1.2^2}{2 \cdot 9.81} = 0.37 \text{ m} \quad (4.8)$$

The intake screen was included as an additional hydraulic contribution. Screening is commonly used as the first step in water extraction systems to remove large and medium-sized pollutants before downstream treatment units. Huber reports preliminary screening for pollutants larger than about 10 mm and fine screening for contaminants in the range of 1–10 mm [23]. For the present model, the intake screen pressure loss was assumed equal to 0.05 bar, corresponding to approximately 0.50 m of head.

The coarse and fine filtration stages were represented explicitly in Aspen Plus by two pressure-drop blocks. A total pressure loss of 0.50 bar was assigned to these two filters. This value was selected as a conservative preliminary allowance. In desalination pretreatment applications, automatic screen filters are commonly used in the range of 100–500  $\mu\text{m}$  for UF membrane protection, while fine automatic screen filters can operate with differential pressures in the range of approximately 0.02–0.2 bar [24]. Therefore, assigning 0.50 bar to the combined coarse and fine filtration section was considered a conservative assumption for a preliminary process model.

The resulting contributions for the main seawater intake pump are summarized in Table 4.1.

**Table 4.1:** Estimated head contributions for the main seawater intake pump.

| Contribution                 | Head           | Pressure equivalent |
|------------------------------|----------------|---------------------|
| Static elevation to platform | 15.00 m        | 1.51 bar            |
| Distributed pipe losses      | 0.11 m         | 0.01 bar            |
| Localized losses             | 0.37 m         | 0.04 bar            |
| Intake screen                | 0.50 m         | 0.05 bar            |
| Coarse and fine filtration   | 4.96 m         | 0.50 bar            |
| <b>Total</b>                 | <b>20.94 m</b> | <b>2.11 bar</b>     |

The total pump head was therefore approximately 20.94 m. The corresponding pressure increase was calculated as:

$$\Delta P_{\text{pump}} = \rho_{\text{SW}} g H_{\text{pump}} \quad (4.9)$$

which gives:

$$\Delta P_{\text{pump}} = 1027.3 \cdot 9.81 \cdot 20.94 = 2.11 \text{ bar} \quad (4.10)$$

This pressure increase was assigned to the main seawater intake pump in the Aspen Plus flowsheet.

The implementation in Aspen Plus was distributed among different blocks. The main intake pump provides the total pressure rise required by seawater lifting, intake-line losses and initial pretreatment. Downstream of the pump, the coarse and fine filtration blocks explicitly represent the pressure drops associated with the first filtration stages. The remaining hydraulic contributions, namely the static elevation to the platform, the distributed pipe losses, the localized losses and the intake screen pressure loss, were represented by a lamination valve. This valve was therefore introduced only as a modelling element to impose the pressure drop associated with hydraulic contributions not otherwise represented by dedicated Aspen Plus blocks.

The pressure drop assigned to the lamination valve was obtained by excluding the pressure losses already represented by the coarse and fine filtration blocks. Therefore, the valve accounts for approximately 1.6 bar, corresponding to the static elevation, distributed losses, localized losses and intake screen. The two filtration

blocks account separately for the remaining 0.50 bar. As a result, the total pressure increase imposed by the main intake pump remains approximately 2.1 bar.

A second pump was introduced upstream of the ultrafiltration unit. This pump was kept separate from the main intake pump because ultrafiltration represents an additional membrane pretreatment stage with its own hydraulic requirement. In the Aspen Plus flowsheet, the UF booster pump provides the pressure required to feed the ultrafiltration block, while the UF block itself represents the pressure drop across the membrane unit.

For the base-case simulation, the ultrafiltration pressure drop was assumed equal to 0.8 bar. This value is consistent with pressurized seawater ultrafiltration data reported for the Maspalomas-I desalination plant, where a transmembrane pressure between 0.55 and 0.80 bar and a UF recovery above 97% were reported [25]. A pressure increase of approximately 1.0 bar was therefore assigned to the UF booster pump, providing a small allowance above the assumed UF pressure drop.

The final pressure assignment adopted in the Aspen Plus flowsheet is summarized in Table 4.2.

**Table 4.2:** Pressure assignment adopted for the main intake and ultrafiltration pretreatment blocks.

| Aspen Plus block          | Role in the pressure profile                                                                           | Assigned value   |
|---------------------------|--------------------------------------------------------------------------------------------------------|------------------|
| Main seawater intake pump | Provides the pressure required by intake lifting, line losses and initial pretreatment                 | +2.1 bar         |
| Coarse filter block       | Represents part of the pressure loss associated with coarse and fine filtration                        | part of 0.50 bar |
| Fine filter block         | Represents part of the pressure loss associated with coarse and fine filtration                        | part of 0.50 bar |
| Lamination valve          | Represents static elevation, distributed pipe losses, localized losses and intake screen pressure loss | about -1.6 bar   |
| UF booster pump           | Provides the pressure allowance required by the ultrafiltration pretreatment stage                     | +1.0 bar         |
| UF block                  | Represents the pressure drop across the ultrafiltration unit                                           | about -0.8 bar   |

This implementation allows the intake and pretreatment section to be represented in Aspen Plus with a consistent pressure profile, while keeping the hydraulic description compatible with the preliminary nature of the process model. The adopted values should therefore be interpreted as modelling assumptions for the

evaluation of auxiliary energy demand, rather than as the result of a detailed hydraulic design.

### 4.3.3 Preliminary Dissolved-Gas Removal

After the intake and pretreatment section, the filtered seawater stream is sent to a preliminary dissolved-gas removal unit. This block was introduced to represent the partial removal of naturally dissolved atmospheric gases, mainly nitrogen and oxygen, before the electrochemical acidification stage. In the updated Aspen Plus flowsheet, this operation is represented by the separator block DAGS1.

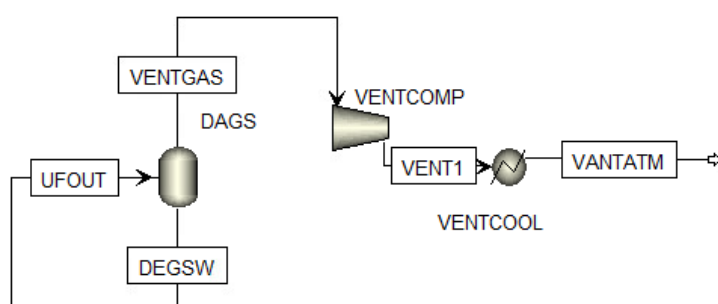


**Figure 4.3:** Removal and venting of dissolved gases from the pretreated seawater stream.

The purpose of this unit is not to recover  $\text{CO}_2$ , but to reduce the amount of non-condensable gases entering the downstream  $\text{CO}_2$  separation section. At this point of the process, seawater has not yet undergone electrochemical acidification; therefore, dissolved inorganic carbon is still mainly present as bicarbonate and carbonate species.  $\text{CO}_2$  recovery is consequently intended to occur downstream, after the acidification step, where the pH decrease shifts the carbonate equilibrium towards molecular  $\text{CO}_2$ .

DAGS1 was modelled as an adiabatic low-pressure separation block operating at 0.3 bar. This value was selected as a moderate vacuum level able to promote  $\text{N}_2$  and  $\text{O}_2$  removal while limiting the co-removal of  $\text{CO}_2$  before the acidification stage. The gas stream leaving DAGS1 is labelled VENTGAS and is mainly composed of the removed non-condensable gases. This stream is sent to VENTCOMP, which restores its pressure to approximately atmospheric pressure. The compressed vent stream, labelled VENT1, is then cooled in VENTCOOL before being discharged as VANTATM.

Since DAGS1 operates below atmospheric pressure, the liquid stream leaving the separator must be re-pressurized before entering the acidification section. For this reason, the liquid outlet stream, labelled DEGSW, is sent to ACDPUMP, which

raises the pressure before the stream is mixed with the equivalent acidification stream.

Overall, the preliminary dissolved-gas removal section was implemented as a simplified process-level representation of seawater deaeration. Its role in the Aspen Plus model is to account for the presence of dissolved  $N_2$  and  $O_2$  in real seawater, while keeping the flowsheet compatible with the preliminary scope of the process assessment.

#### 4.3.4 Electrochemical Acidification Block

After the preliminary dissolved-gas removal step, the liquid stream is pumped back to 1 bar, which was selected as the operating pressure of the electrochemical cells in the Aspen Plus model. The repumped stream is then mixed with an equivalent acidification stream and sent to the ACID block.

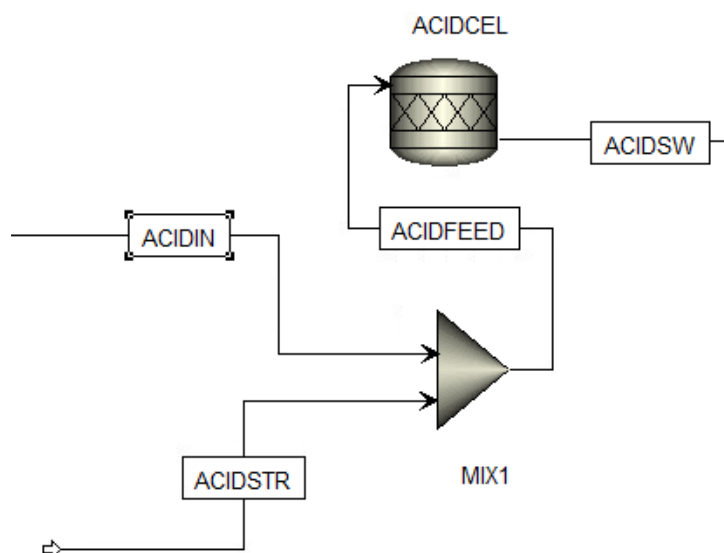


**Figure 4.4:** Acidification section of the Aspen Plus flowsheet.

The ACID block represents the first electrochemical step of the chloride-mediated pH-swing process. Its purpose is to reproduce the decrease in pH required to shift the carbonate equilibrium towards molecular  $CO_2$ , which can then be removed in the downstream separation section. In Aspen Plus, this unit was modelled using an RStoic reactor operated at 25 °C and 1 bar, with vapour-liquid phases enabled.

The acidification block includes the following stoichiometric reactions:





The first reaction was assigned a fractional conversion of 1 for carbonate ions, while the second reaction was assigned a fractional conversion of 0.9 for bicarbonate ions. The reactions were specified to occur in series, so that carbonate ions are first converted into bicarbonate and the resulting bicarbonate pool is then partially converted into molecular  $\text{CO}_2$ . This representation was introduced to reproduce, at process level, the expected shift of the carbonate system towards acidic conditions before  $\text{CO}_2$  separation.

The acidifying effect of the electrochemical cell was represented by introducing an equivalent acidification stream upstream of the ACID block. This stream contains  $\text{H}^+$  and  $\text{Cl}^-$  and should not be interpreted as the addition of an external mineral acid. It was introduced only as a modelling equivalent of the proton release occurring in the electrochemical acidification step.

The amount of  $\text{H}^+$  required in the equivalent acidification stream was first estimated from the composition of the ACIDIN stream, which represents the liquid stream entering the acidification block after preliminary dissolved-gas removal. To keep the notation compact, the inlet molar flow rates of carbonate and bicarbonate were defined as:

$$\dot{n}_{C,\text{in}} = \dot{n}_{\text{CO}_3^{2-},\text{in}} \quad (4.13)$$

$$\dot{n}_{B,\text{in}} = \dot{n}_{\text{HCO}_3^-, \text{in}} \quad (4.14)$$

where  $C$  refers to carbonate ions and  $B$  refers to bicarbonate ions. The corresponding molar flow rates were calculated from the mass flow rates reported by Aspen Plus as:

$$\dot{n}_{B,\text{in}} = \frac{\dot{m}_{\text{HCO}_3^-, \text{in}}}{M_{\text{HCO}_3^-}} \quad (4.15)$$

$$\dot{n}_{C,\text{in}} = \frac{\dot{m}_{\text{CO}_3^{2-}, \text{in}}}{M_{\text{CO}_3^{2-}}} \quad (4.16)$$

For the ACIDIN stream, the bicarbonate and carbonate mass flow rates were equal to  $199.232 \text{ kg h}^{-1}$  and  $3.63531 \text{ kg h}^{-1}$ , respectively. Using molecular weights of  $61.02 \text{ kg kmol}^{-1}$  for  $\text{HCO}_3^-$  and  $60.01 \text{ kg kmol}^{-1}$  for  $\text{CO}_3^{2-}$ , the corresponding molar flow rates are:

$$\dot{n}_{B,\text{in}} = \frac{199.232}{61.02} = 3.265 \text{ kmol h}^{-1} \quad (4.17)$$

$$\dot{n}_{C,\text{in}} = \frac{3.63531}{60.01} = 0.0606 \text{ kmol h}^{-1} \quad (4.18)$$

Since carbonate ions are first converted into bicarbonate, the total bicarbonate amount available for the second reaction was calculated as:

$$\dot{n}_{B,\text{tot}} = \dot{n}_{B,\text{in}} + X_C \dot{n}_{C,\text{in}} \quad (4.19)$$

where  $X_C$  is the fractional conversion of carbonate ions. By assuming  $X_C = 1$ , the total bicarbonate flow rate available for the second reaction is:

$$\dot{n}_{B,\text{tot}} = 3.265 + 1 \cdot 0.0606 = 3.326 \text{ kmol h}^{-1} \quad (4.20)$$

The stoichiometric proton demand was then estimated as the amount required for the conversion of carbonate into bicarbonate and for the partial conversion of bicarbonate into molecular  $\text{CO}_2$ :

$$\dot{n}_{\text{H}^+,\text{st}} = X_C \dot{n}_{C,\text{in}} + X_B \dot{n}_{B,\text{tot}} \quad (4.21)$$

where  $X_B$  is the fractional conversion of bicarbonate ions. In the reference calculation,  $X_B$  was set equal to 0.9. Therefore:

$$\dot{n}_{\text{H}^+,\text{st}} = 1 \cdot 0.0606 + 0.9 \cdot 3.326 = 3.054 \text{ kmol h}^{-1} \quad (4.22)$$

A small additional amount of  $\text{H}^+$  was added to represent the residual proton concentration associated with the target acidified pH. The target pH of the acidified stream was fixed at 5.2, consistently with the acidification level reported for the experimental MIT process. The corresponding residual proton molar flow rate was estimated as:

$$\dot{n}_{\text{H}^+,\text{target}} = 10^{-pH} \dot{V}_{\text{liq}} \quad (4.23)$$

Using the liquid volumetric flow rate of the treated seawater stream, this term is approximately:

$$\dot{n}_{\text{H}^+,\text{target}} \simeq 0.0094 \text{ kmol h}^{-1} \quad (4.24)$$

The theoretical molar flow rate of  $\text{H}^+$  required in the equivalent acidification stream is therefore:

$$\dot{n}_{\text{H}^+,\text{theor}} = \dot{n}_{\text{H}^+,\text{st}} + \dot{n}_{\text{H}^+,\text{target}} \quad (4.25)$$

$$\dot{n}_{\text{H}^+,\text{theor}} = 3.054 + 0.0094 = 3.063 \text{ kmol h}^{-1} \quad (4.26)$$

The equivalent acidification stream was defined by introducing  $\text{H}^+$  and  $\text{Cl}^-$  in equimolar amount, in order to reproduce the proton release associated with the chloride-mediated electrochemical acidification step while maintaining charge balance:

$$\dot{n}_{\text{Cl}^-} = \dot{n}_{\text{H}^+} \quad (4.27)$$

If the purely stoichiometric value of  $3.063 \text{ kmol h}^{-1}$  is used, the corresponding mass flow rates are:

$$\dot{m}_{\text{H}^+} = \dot{n}_{\text{H}^+, \text{theor}} M_{\text{H}^+} = 3.063 \cdot 1.008 = 3.09 \text{ kg h}^{-1} \quad (4.28)$$

$$\dot{m}_{\text{Cl}^-} = \dot{n}_{\text{Cl}^-} M_{\text{Cl}^-} = 3.063 \cdot 35.45 = 108.60 \text{ kg h}^{-1} \quad (4.29)$$

For a total acidification-stream mass flow rate of  $1530 \text{ kg h}^{-1}$ , the remaining flow rate is assigned to water:

$$\dot{m}_{\text{H}_2\text{O}} = \dot{m}_{\text{acid}} - \dot{m}_{\text{H}^+} - \dot{m}_{\text{Cl}^-} \quad (4.30)$$

$$\dot{m}_{\text{H}_2\text{O}} = 1530 - 3.09 - 108.60 = 1418.31 \text{ kg h}^{-1} \quad (4.31)$$

The corresponding theoretical mass fractions are:

$$w_i = \frac{\dot{m}_i}{\dot{m}_{\text{acid}}} \quad (4.32)$$

**Table 4.3:** Theoretical composition of the equivalent acidification stream before the Aspen Plus adjustment.

| Component            | Mass flow rate<br>$\text{kg h}^{-1}$ | Mass fraction<br>- |
|----------------------|--------------------------------------|--------------------|
| $\text{H}_2\text{O}$ | 1418.31                              | 0.9270             |
| $\text{H}^+$         | 3.09                                 | 0.00202            |
| $\text{Cl}^-$        | 108.60                               | 0.07098            |
| <b>Total</b>         | <b>1530.00</b>                       | <b>1.00000</b>     |

However, the direct implementation of the theoretical  $\text{H}^+$  amount in Aspen Plus led to warnings in the ACID block. In particular, Aspen Plus reduced the fractional conversion of the second reaction when the  $\text{H}^+$  flow rate reached zero

in the outlet stream. This behaviour was associated with the interaction between the RStoic reaction specification and the electrolyte speciation calculated by the ELECNRTL property method. In an electrolyte framework,  $\text{H}^+$  participates in the aqueous ionic speciation and charge-balance calculations and is therefore not treated simply as an inert independent reagent.

For this reason, the equivalent acidification stream was adjusted by introducing a moderate excess of equimolar  $\text{H}^+$  and  $\text{Cl}^-$  with respect to the purely stoichiometric requirement. This adjustment was adopted as a numerical modelling choice to allow the RStoic block to reproduce the target acidification behaviour without forcing a null  $\text{H}^+$  flow rate in the outlet stream.

For the final Aspen Plus implementation, the acidification stream was specified with a total mass flow rate of  $1530 \text{ kg h}^{-1}$  and with the mass fractions reported in Table 4.4. These values correspond to approximately  $3.60 \text{ kmol h}^{-1}$  of  $\text{H}^+$  and the same molar flow rate of  $\text{Cl}^-$ .

**Table 4.4:** Composition of the equivalent acidification stream introduced upstream of the ACID block.

| Component            | Mass fraction   |
|----------------------|-----------------|
| $\text{H}_2\text{O}$ | 0.914233        |
| $\text{H}^+$         | 0.002371        |
| $\text{Cl}^-$        | 0.083396        |
| <b>Total</b>         | <b>1.000000</b> |

The outlet stream from the ACID block is therefore an acidified seawater stream in which dissolved inorganic carbon has been shifted towards molecular  $\text{CO}_2$ . This stream is then sent to the downstream  $\text{CO}_2$  separation section, where the released carbon dioxide is removed from the liquid phase.

#### 4.3.5 $\text{CO}_2$ Separation Section

The acidified seawater stream leaving the ACID block is sent to the  $\text{CO}_2$  separation section. In this part of the flowsheet, the objective is to remove the molecular  $\text{CO}_2$  generated during the acidification step from the liquid phase. This step represents the degassing stage of the process, where reduced-pressure conditions are used to promote the release of  $\text{CO}_2$  from the acidified liquid stream.

In the Aspen Plus model,  $\text{CO}_2$  removal was represented by a single gas–liquid flash separator operating under vacuum. This configuration was adopted as the base-case representation of the  $\text{CO}_2$  recovery section, since it provides a simple process

layout for evaluating the behaviour of the acidified seawater stream under reduced-pressure conditions. The use of a single flash unit allows the main separation performance to be assessed without introducing additional staging assumptions at this level of the analysis.

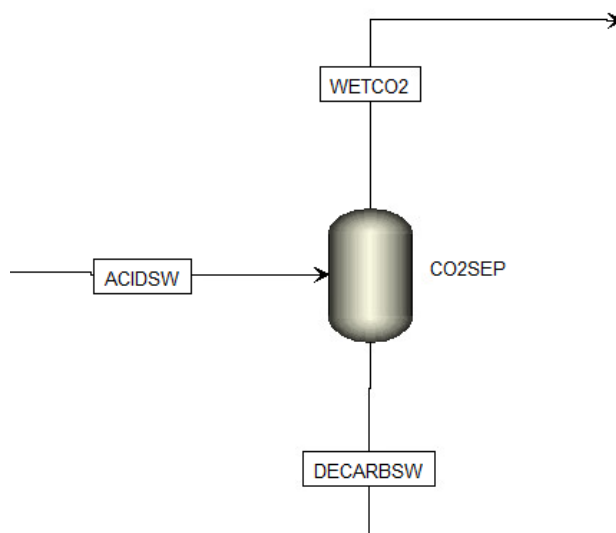


**Figure 4.5:** CO<sub>2</sub> separation section after seawater acidification.

The flash separator was modelled as an adiabatic equilibrium block. Its operating pressure was determined through a Design Spec, in which the pressure was adjusted in order to reproduce the target DIC removal efficiency of 87%, taken as reference for the simulation. The resulting pressure was equal to approximately 0.03785 bar. At this pressure, the acidified stream releases a CO<sub>2</sub>-rich gas phase, while the remaining liquid stream is depleted in dissolved inorganic carbon and is directed to the downstream regeneration section. The pressure obtained from the Design Spec is lower than the effective CO<sub>2</sub> fugacity of 0.07 bar reported for acidified seawater in the MIT study. This difference is consistent with the simplified equilibrium-flash representation adopted here, in which the pressure is used as an adjustable process variable to reproduce the target removal efficiency in the absence of detailed membrane-contactor mass transfer modelling.

The gas stream leaving the flash separator contains both recovered CO<sub>2</sub> and water vapour. For this reason, it is sent to the CO<sub>2</sub> conditioning section, where cooling and condensate separation are performed before compression to the selected product pressure. This arrangement allows the Aspen Plus model to evaluate the amount of CO<sub>2</sub> recovered in the gas phase, the amount of water removed

during conditioning, and the possible CO<sub>2</sub> loss associated with the condensed liquid stream.

As for the preliminary dissolved-gas removal unit, the CO<sub>2</sub> flash separator was implemented as a simplified equilibrium separation block. Detailed mass-transfer limitations, residence time, gas–liquid contact area, vacuum-system performance and possible entrainment effects were not explicitly considered in the Aspen Plus simulation. Therefore, the flash unit should be interpreted as a process-level approximation of the CO<sub>2</sub> recovery step. The detailed sizing of the separation and conditioning equipment is not included in this modelling section and is addressed later in the pre-feasibility and cost evaluation.

#### 4.3.6 CO<sub>2</sub> Conditioning and Preliminary Compression

The gas stream recovered from the CO<sub>2</sub> separation section contains mainly carbon dioxide, together with water vapour and minor residual gaseous species. Before leaving the system boundaries, this stream is conditioned and compressed to the reference outlet pressure of 1 bar. The objective of this section is therefore not to represent a complete compression train for transport or geological storage, but only to obtain a preliminary conditioned CO<sub>2</sub> stream at atmospheric pressure.

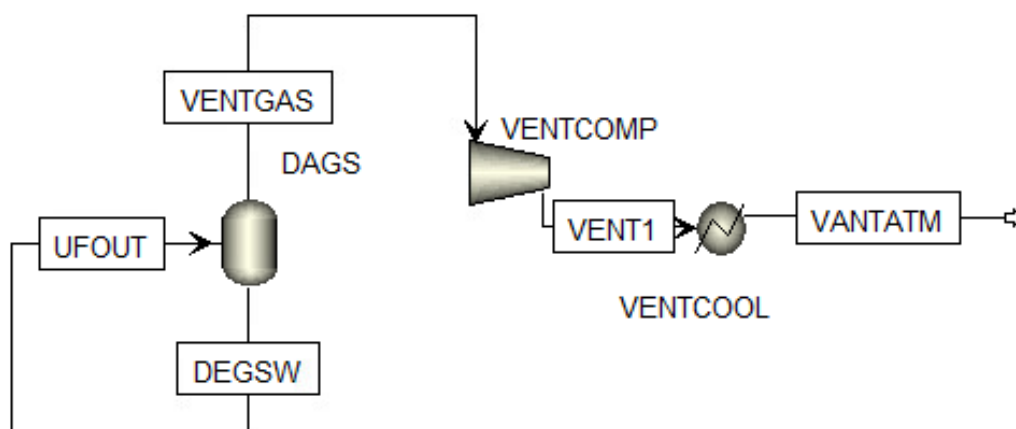


**Figure 4.6:** CO<sub>2</sub> conditioning section including cooling, phase separation and compression.

The conditioning section was implemented in Aspen Plus through a sequence of cooling, phase separation and compression blocks. First, the CO<sub>2</sub>-rich stream leaving the vacuum separation section is cooled to 10 °C in a heat exchanger. The pressure of this cooling step is kept equal to the pressure of the CO<sub>2</sub> stream leaving the vacuum separator. This step promotes the condensation of part of the water

vapour contained in the gas stream. The cooled stream is then sent to an adiabatic flash block operated at the same pressure. This flash block is used to separate the condensed aqueous phase from the CO<sub>2</sub>-rich gas phase before compression. In this way, part of the water removed during cooling is discharged as a liquid stream, while the gas stream is sent to the compressor. The resulting gas stream is compressed from the vacuum-separation pressure to 1 bar using an isentropic compressor. The compressor therefore represents only the preliminary pressure increase required to bring the recovered CO<sub>2</sub> stream to atmospheric pressure. Further compression for transport, utilization or storage is not included within the system boundaries of the present model. After compression, the CO<sub>2</sub> stream is cooled again to 10 °C in a second heat exchanger. Since compression increases the gas temperature and can leave additional water vapour in the stream, this second cooling step is introduced to further condition the CO<sub>2</sub> product before the final phase separation. Finally, the cooled compressed stream is sent to a second adiabatic flash block operated at 1 bar. This final flash removes any additional condensed liquid phase and produces the conditioned CO<sub>2</sub> product stream leaving the model boundaries at atmospheric pressure. The sequence of Aspen Plus blocks used for the CO<sub>2</sub> conditioning and preliminary compression section is summarized in Table 4.5.

**Table 4.5:** Aspen Plus implementation of the CO<sub>2</sub> conditioning and preliminary compression section.

| Block                 | Role                                                                                     | Operating specification                      |
|-----------------------|------------------------------------------------------------------------------------------|----------------------------------------------|
| First heat exchanger  | Cooling of the CO <sub>2</sub> -rich stream recovered from the vacuum separation section | 10 °C; same pressure as separator outlet     |
| First flash           | Separation of condensed water before compression                                         | Adiabatic; same pressure as separator outlet |
| Compressor            | Preliminary compression of the CO <sub>2</sub> -rich gas stream                          | Isentropic compression to 1 bar              |
| Second heat exchanger | Cooling of the compressed gas stream                                                     | 10 °C; 1 bar                                 |
| Final flash           | Final removal of condensed liquid from the conditioned CO <sub>2</sub> stream            | Adiabatic; 1 bar                             |

The final gas stream is therefore interpreted as a preliminarily conditioned CO<sub>2</sub>

product at 1 bar. Its further treatment, drying, purification or compression to transport and storage pressure is outside the scope of the present pre-feasibility model.

### 4.3.7 Electrochemical Regeneration Block

After CO<sub>2</sub> separation, the decarbonated seawater stream is sent to the regeneration section. Before entering the regeneration block, the liquid stream is pumped back to 1 bar, which was selected as the operating pressure of the electrochemical cells in the Aspen Plus model. The repumped stream is then mixed with an equivalent alkalization stream and sent to the BASIC block.

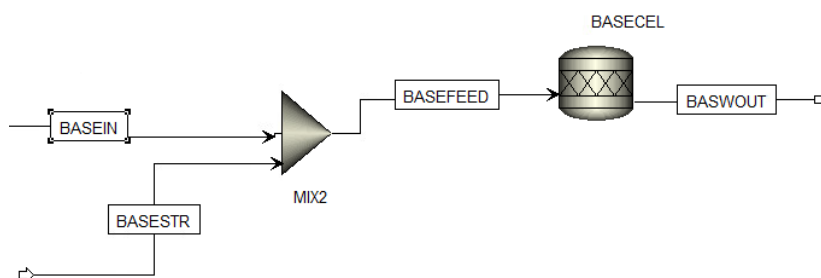
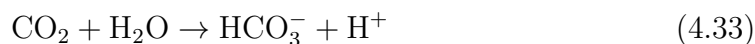


**Figure 4.7:** Alkalization section used to regenerate the treated seawater before discharge.

The BASIC block represents the second electrochemical step of the chloride-mediated pH-swing process. Its purpose is to reproduce the increase in pH required to restore alkaline conditions in the treated seawater before discharge. In Aspen Plus, this unit was modelled using an RStoic reactor operated at 25 °C and 1 bar, with vapour-liquid phases enabled.

The regeneration block includes the following stoichiometric reactions:



The first reaction was assigned a fractional conversion of 1 for molecular CO<sub>2</sub>, while the second reaction was assigned a fractional conversion of 0.9 for bicarbonate ions. The reactions were specified to occur in series, so that residual dissolved CO<sub>2</sub> is first converted into bicarbonate and the resulting bicarbonate pool is then partially converted into carbonate. This representation was introduced to reproduce, at process level, the expected shift of the carbonate system towards alkaline conditions after CO<sub>2</sub> removal.

The alkalinizing effect of the electrochemical regeneration cell was represented by introducing an equivalent alkalization stream upstream of the BASIC block. This stream contains  $\text{OH}^-$  and  $\text{Na}^+$  and should not be interpreted as the addition of an external alkaline reagent. It was introduced only as a modelling equivalent of the alkalinity restoration occurring in the electrochemical regeneration step.

The amount of  $\text{OH}^-$  required in the equivalent alkalization stream was estimated from the composition of the BASEIN stream, which represents the liquid stream entering the regeneration block after  $\text{CO}_2$  separation. To keep the notation compact, the inlet molar flow rates of molecular  $\text{CO}_2$  and bicarbonate were defined as:

$$\dot{n}_{A,\text{in}} = \dot{n}_{\text{CO}_2,\text{in}} \quad (4.35)$$

$$\dot{n}_{B,\text{in}} = \dot{n}_{\text{HCO}_3^-, \text{in}} \quad (4.36)$$

where  $A$  refers to molecular  $\text{CO}_2$  and  $B$  refers to bicarbonate ions. The corresponding molar flow rates were calculated from the mass flow rates reported by Aspen Plus:

$$\dot{n}_{A,\text{in}} = \frac{\dot{m}_{\text{CO}_2,\text{in}}}{M_{\text{CO}_2}} \quad (4.37)$$

$$\dot{n}_{B,\text{in}} = \frac{\dot{m}_{\text{HCO}_3^-, \text{in}}}{M_{\text{HCO}_3^-}} \quad (4.38)$$

For the BASEIN stream, the molecular  $\text{CO}_2$  and bicarbonate mass flow rates were equal to  $17.1469 \text{ kg h}^{-1}$  and  $0.151531 \text{ kg h}^{-1}$ , respectively. Using molecular weights of  $44.01 \text{ kg kmol}^{-1}$  for  $\text{CO}_2$  and  $61.02 \text{ kg kmol}^{-1}$  for  $\text{HCO}_3^-$ , the corresponding molar flow rates are:

$$\dot{n}_{A,\text{in}} = \frac{17.1469}{44.01} = 0.3896 \text{ kmol h}^{-1} \quad (4.39)$$

$$\dot{n}_{B,\text{in}} = \frac{0.151531}{61.02} = 0.00248 \text{ kmol h}^{-1} \quad (4.40)$$

Since residual dissolved  $\text{CO}_2$  is first converted into bicarbonate, the total bicarbonate amount available for the second reaction was calculated as:

$$\dot{n}_{B,\text{tot}} = \dot{n}_{B,\text{in}} + X_A \dot{n}_{A,\text{in}} \quad (4.41)$$

where  $X_A$  is the fractional conversion of molecular  $\text{CO}_2$ . By assuming  $X_A = 1$ , the total bicarbonate flow rate available for the second reaction is:

$$\dot{n}_{B,\text{tot}} = 0.00248 + 1 \cdot 0.3896 = 0.3921 \text{ kmol h}^{-1} \quad (4.42)$$

The proton amount generated by the regeneration reactions was then estimated as:

$$\dot{n}_{\text{H}^+,\text{gen}} = X_A \dot{n}_{A,\text{in}} + X_B \dot{n}_{B,\text{tot}} \quad (4.43)$$

where  $X_B$  is the fractional conversion of bicarbonate ions. In the reference calculation,  $X_B$  was set equal to 0.9. Therefore:

$$\dot{n}_{\text{H}^+,\text{gen}} = 1 \cdot 0.3896 + 0.9 \cdot 0.3921 = 0.7425 \text{ kmol h}^{-1} \quad (4.44)$$

The equivalent alkalization stream was then calculated in order to neutralize the protons generated by the regeneration reactions and to reach the selected alkaline condition of the regenerated stream. In the present model, the target pH for the regenerated seawater was fixed at 11, consistently with the alkaline range reported for the experimental process.

The residual hydroxide amount required to reach pH 11 was estimated as:

$$\dot{n}_{\text{OH}^-, \text{target}} = 10^{-(14-\text{pH})} \dot{V}_{\text{liq}} \quad (4.45)$$

Using the liquid volumetric flow rate of the treated stream and a target pH equal to 11, this term is approximately:

$$\dot{n}_{\text{OH}^-, \text{target}} \simeq 1.490 \text{ kmol h}^{-1} \quad (4.46)$$

The theoretical molar flow rate of  $\text{OH}^-$  required in the equivalent alkalization stream is therefore:

$$\dot{n}_{\text{OH}^-} = \dot{n}_{\text{H}^+,\text{gen}} + \dot{n}_{\text{OH}^-, \text{target}} \quad (4.47)$$

$$\dot{n}_{\text{OH}^-} = 0.7425 + 1.490 = 2.233 \text{ kmol h}^{-1} \quad (4.48)$$

The equivalent alkalization stream was defined by introducing  $\text{Na}^+$  and  $\text{OH}^-$  in equimolar amount, in order to reproduce the alkaline effect of the regeneration step while maintaining charge balance:

$$\dot{n}_{\text{Na}^+} = \dot{n}_{\text{OH}^-} \quad (4.49)$$

The final composition of the equivalent alkalization stream implemented in the Aspen Plus flowsheet was taken from the BASESTR stream results. The stream contains  $\text{Na}^+$  and  $\text{OH}^-$  in equimolar amount in order to preserve charge balance, while the remaining mass flow rate is assigned to water. As for the acidification

stream, this current should not be interpreted as the addition of an external alkaline reagent, but as a process-level representation of the alkalinity restoration produced by the electrochemical regeneration step.

The mass fractions used to define the equivalent alkalization stream were calculated as:

$$w_i = \frac{\dot{m}_i}{\dot{m}_{\text{basic}}} \quad (4.50)$$

where  $w_i$  is the mass fraction of component  $i$ ,  $\dot{m}_i$  is the corresponding mass flow rate and  $\dot{m}_{\text{basic}}$  is the total mass flow rate of the equivalent alkalization stream.

**Table 4.6:** Composition of the equivalent alkalization stream introduced upstream of the BASIC block.

| Component        | Mass flow rate<br>kg h <sup>-1</sup> | Mass fraction<br>— |
|------------------|--------------------------------------|--------------------|
| H <sub>2</sub> O | 1399.19                              | 0.92336            |
| Na <sup>+</sup>  | 66.75                                | 0.04405            |
| OH <sup>-</sup>  | 49.38                                | 0.03259            |
| Total            | 1515.32                              | 1.00000            |

The values reported in Table 4.6 correspond to the final BASESTR stream used in the converged Aspen Plus flowsheet. The BASIC block then represents the regeneration step by converting the residual dissolved CO<sub>2</sub> and bicarbonate toward carbonate species under alkaline conditions.

## 4.4 Summary of Aspen Plus Modelling Assumptions

The main modelling assumptions adopted in the Aspen Plus flowsheet are summarized in Table 4.7. These assumptions define the level of detail of the process model and clarify which process aspects were represented explicitly and which were treated through simplified process-level approximations.

**Table 4.7:** Main modelling assumptions adopted in the Aspen Plus flowsheet.

| Model element                            | Assumption                                                                      |
|------------------------------------------|---------------------------------------------------------------------------------|
| Thermodynamic method                     | ELECNRTL                                                                        |
| Operating mode                           | Steady-state continuous equivalent                                              |
| Seawater feed                            | SWFEED, 25 °C, 1 bar and 1530 t h <sup>-1</sup>                                 |
| Reference seawater composition           | Salinity 35 g kg <sup>-1</sup> , pH 8.1 and DIC close to 2 mmol L <sup>-1</sup> |
| Electrochemical cells                    | Black-box RStoic blocks                                                         |
| Acidification block                      | ACIDCEL, with equivalent H <sup>+</sup> /Cl <sup>-</sup> acidification stream   |
| Acidification target                     | pH 5.2                                                                          |
| Regeneration block                       | BASECEL, with equivalent Na <sup>+</sup> /OH <sup>-</sup> alkalization stream   |
| Regeneration target                      | pH 11                                                                           |
| Preliminary dissolved-gas removal        | DAGS1, adiabatic low-pressure separator                                         |
| Preliminary degassing pressure           | 0.3 bar                                                                         |
| Reference DIC removal efficiency         | 87%                                                                             |
| CO <sub>2</sub> separation block         | CO2SEP, adiabatic vacuum flash                                                  |
| CO <sub>2</sub> flash pressure           | 0.03785 bar, obtained by Design Spec                                            |
| Pre-compression CO <sub>2</sub> cooling  | CO2COOL, outlet temperature 10 °C                                               |
| First condensate separator               | KODRUM, adiabatic flash at CO2SEP pressure                                      |
| CO <sub>2</sub> compression              | CO2COMP, isentropic compression to 1 bar                                        |
| Post-compression CO <sub>2</sub> cooling | CO2COOL2, 1 bar and 10 °C                                                       |
| Second condensate separator              | KODRUM2, adiabatic flash at 1 bar                                               |
| Final CO <sub>2</sub> product stream     | CO2OUT, conditioned CO <sub>2</sub> product at 1 bar                            |
| Final storage compression                | Not included                                                                    |
| Vacuum-system detailed design            | Not included                                                                    |
| Detailed membrane contactor design       | Not included                                                                    |
| Mass-transfer limitations                | Not included                                                                    |
| Detailed marine discharge and mixing     | Not included                                                                    |

The CO<sub>2</sub> recovery section was represented through an equilibrium vacuum flash calibrated to reproduce the reference DIC removal efficiency. Therefore, the model does not describe the detailed geometry, residence time or mass-transfer behaviour of a membrane contactor, vacuum degasser or stripping unit. The CO2SEP pressure was obtained through a Design Spec in order to match the target CO<sub>2</sub> removal from the acidified seawater stream.

The recovered CO<sub>2</sub> stream was then treated through a simplified conditioning and preliminary compression section. The stream was first cooled to 10 °C at the same pressure as the CO<sub>2</sub>SEP outlet and sent to an adiabatic flash separator to remove condensed water before compression. The gas stream was then compressed isentropically to 1 bar, cooled again to 10 °C and finally sent to a second adiabatic flash at 1 bar. This sequence allows water condensation and associated CO<sub>2</sub> losses to be evaluated at process level, without representing a detailed design of heat exchangers, knock-out drums, vacuum pumps or gas-drying systems.

The electrochemical acidification and regeneration stages were implemented as process-level stoichiometric blocks. The corresponding H<sup>+</sup>/Cl<sup>-</sup> and Na<sup>+</sup>/OH<sup>-</sup> streams should therefore be interpreted as equivalent modelling inputs used to reproduce the pH-swing effect of the electrochemical cells, rather than as external chemical additions.

## Chapter 5

# Aspen Plus Simulation Results

This chapter presents the results obtained from the Aspen Plus model developed for the reference chloride-mediated Direct Ocean Capture process. The analysis focuses on the process-level behaviour of the simulated configuration, with particular attention to material flows, carbon dioxide recovery, auxiliary energy requirements and overall performance of the reference case. The results are discussed following the sequence of the flowsheet. First, the main material flows are analysed in order to evaluate the seawater throughput required by the reference plant and the distribution of carbon across the process. The carbon balance is then used to assess the consistency between the Aspen Plus simulation and the design removal target defined in Chapter 3. Particular attention is given to the amount of CO<sub>2</sub> recovered in the final product stream and to the residual dissolved inorganic carbon remaining in the treated seawater. After the material balance, the energy requirements of the reference configuration are evaluated. The analysis distinguishes between the electrochemical energy contribution, derived from the experimental data reported for the MIT process, and the auxiliary energy demands introduced by the process model. These include seawater pumping, preliminary dissolved-gas removal, CO<sub>2</sub> separation, cooling and gas compression. Finally, the main performance indicators of the simulated configuration are summarized in order to identify the most relevant process contributions and the sections that have the greatest impact on the overall energy demand. These results provide the quantitative basis for the preliminary feasibility assessment and for the benchmark comparison discussed in the following chapter.

## 5.1 Mass Balance

The mass balance of the reference Aspen Plus flowsheet was analysed to verify the consistency of the simulated process with the nominal CO<sub>2</sub> recovery target defined for the pilot-scale case study. The analysis focuses on the main carbon flows entering and leaving the system, the redistribution of dissolved inorganic carbon during the acidification and regeneration steps, and the amount of CO<sub>2</sub> recovered in the final product stream.

Since the process treats a very large seawater flow rate with a relatively low concentration of dissolved inorganic carbon, the mass balance is particularly useful to identify where carbon is transferred across the different process sections. In particular, the analysis follows the carbon contained in the inlet seawater, the conversion of bicarbonate and carbonate into molecular CO<sub>2</sub> in the acidification block, the recovery of CO<sub>2</sub> in the gas separation and conditioning section, and the residual dissolved inorganic carbon leaving the system with the treated seawater.

In this work, dissolved inorganic carbon is calculated as the sum of the main carbon-containing species represented in the Aspen Plus model:

$$\dot{n}_{\text{DIC}} = \dot{n}_{\text{CO}_2} + \dot{n}_{\text{HCO}_3^-} + \dot{n}_{\text{CO}_3^{2-}} \quad (5.1)$$

where  $\dot{n}_{\text{DIC}}$  is the molar flow rate of dissolved inorganic carbon,  $\dot{n}_{\text{CO}_2}$  is the molar flow rate of molecular dissolved carbon dioxide,  $\dot{n}_{\text{HCO}_3^-}$  is the molar flow rate of bicarbonate, and  $\dot{n}_{\text{CO}_3^{2-}}$  is the molar flow rate of carbonate.

Before discussing the individual process streams, the overall carbon balance was evaluated to verify the consistency of the simulated CO<sub>2</sub> recovery with the design target. The main quantities used for this assessment are summarized in Table 5.1.

**Table 5.1:** Carbon balance results obtained from the Aspen Plus flowsheet.

| Stream  | Mass flow<br>kg h <sup>-1</sup> | CO <sub>2</sub><br>kmol h <sup>-1</sup> | HCO <sub>3</sub> <sup>-</sup><br>kmol h <sup>-1</sup> | CO <sub>3</sub> <sup>2-</sup><br>kmol h <sup>-1</sup> | DIC<br>kmol h <sup>-1</sup> | pH<br>– |
|---------|---------------------------------|-----------------------------------------|-------------------------------------------------------|-------------------------------------------------------|-----------------------------|---------|
| SWFEED  | 1.530 × 10 <sup>6</sup>         | 0.009                                   | 2.666                                                 | 0.313                                                 | 2.988                       | 8.71    |
| DEGSW   | 1.530 × 10 <sup>6</sup>         | 0.009                                   | 2.666                                                 | 0.313                                                 | 2.988                       | 8.71    |
| ACIDSW  | 1.532 × 10 <sup>6</sup>         | 2.970                                   | 0.018                                                 | 4.34 × 10 <sup>-8</sup>                               | 2.988                       | 4.02    |
| WETCO2  | 361.85                          | 2.596                                   | 0                                                     | 0                                                     | 2.596                       | –       |
| CO2GAS  | 134.98                          | 2.596                                   | 0                                                     | 0                                                     | 2.596                       | –       |
| CO2OUT  | 122.86                          | 2.595                                   | 0                                                     | 0                                                     | 2.595                       | –       |
| CONDW   | 226.87                          | 4.42 × 10 <sup>-4</sup>                 | 5.40 × 10 <sup>-6</sup>                               | 5.86 × 10 <sup>-12</sup>                              | 4.48 × 10 <sup>-4</sup>     | 4.62    |
| CONDW2  | 12.12                           | 5.84 × 10 <sup>-4</sup>                 | 1.55 × 10 <sup>-6</sup>                               | 3.94 × 10 <sup>-13</sup>                              | 5.85 × 10 <sup>-4</sup>     | 3.89    |
| VANTATM | 18.16                           | 3.10 × 10 <sup>-4</sup>                 | 2.03 × 10 <sup>-9</sup>                               | 3.93 × 10 <sup>-14</sup>                              | 3.10 × 10 <sup>-4</sup>     | 5.57    |
| BASWOUT | 1.533 × 10 <sup>6</sup>         | 3.05 × 10 <sup>-6</sup>                 | 0.0509                                                | 0.341                                                 | 0.392                       | 10.28   |

To better visualize the redistribution of dissolved inorganic carbon along the process, the molar flow rates reported in Table 5.1 were normalized with respect to

the total DIC of each stream. The resulting distribution of  $\text{CO}_2(\text{aq})$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  is shown in Figure 5.1.

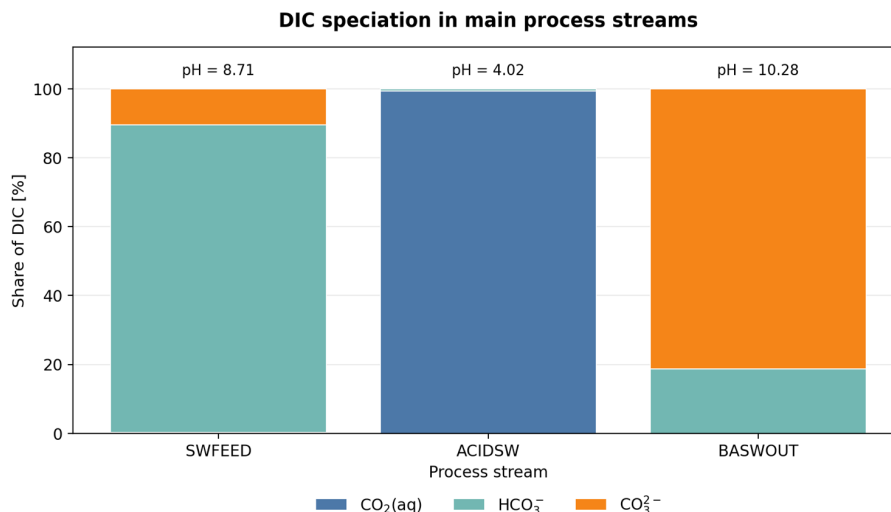


**Figure 5.1:** Distribution of dissolved inorganic carbon species in the main Aspen Plus process streams.

### 5.1.1 Carbon Balance of the Inlet Seawater Stream

The reference seawater feed stream, labelled SWFEED, has a total mass flow rate of  $1.530 \times 10^6 \text{ kg h}^{-1}$ . This corresponds to a volumetric flow rate of approximately  $1.495 \times 10^3 \text{ m}^3 \text{ h}^{-1}$ , according to the seawater density adopted in the process model. The high seawater throughput is a direct consequence of the low concentration of dissolved inorganic carbon in seawater and represents one of the main process-level implications of Direct Ocean Capture systems.

The total dissolved inorganic carbon entering the process with the seawater feed is equal to  $2.988 \text{ kmol h}^{-1}$ . In the Aspen Plus inlet stream, carbon is mainly present as bicarbonate. The  $\text{HCO}_3^-$  molar flow rate is equal to  $2.666 \text{ kmol h}^{-1}$ , while the  $\text{CO}_3^{2-}$  molar flow rate is equal to  $0.313 \text{ kmol h}^{-1}$ . Molecular  $\text{CO}_2$  represents only a small fraction of the inlet carbon, with a molar flow rate of  $0.009 \text{ kmol h}^{-1}$ .

The distribution of dissolved inorganic carbon in the inlet stream is therefore consistent with the expected carbonate speciation of seawater under alkaline conditions. Most carbon is stored as ionic carbonate species rather than as molecular  $\text{CO}_2$ . This confirms the need for an acidification step before  $\text{CO}_2$  separation, since only molecular  $\text{CO}_2$  can be efficiently transferred from the liquid phase to the gas phase in the downstream separation section.

The preliminary dissolved-gas removal unit has only a minor effect on the carbon balance. The stream leaving this section, labelled DEGSW, has the same total DIC flow rate as the inlet seawater stream, equal to  $2.988 \text{ kmol h}^{-1}$ . The molar flows of  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  also remain essentially unchanged. Therefore, the preliminary degassing section mainly affects dissolved nitrogen and oxygen, while the inorganic carbon content of the liquid stream is preserved before acidification.

### 5.1.2 Carbon Redistribution after Acidification

After preliminary dissolved-gas removal, the seawater stream is sent to the electrochemical acidification block. In the Aspen Plus model, this block reproduces the process-level effect of the chloride-mediated pH decrease by converting carbonate and bicarbonate species into molecular  $\text{CO}_2$ .

The total dissolved inorganic carbon in the acidified stream ACIDSW remains equal to  $2.988 \text{ kmol h}^{-1}$ , which is the same value obtained for SWFEED and DEGSW. This result shows that the acidification block does not remove carbon from the liquid stream. Instead, it changes the distribution of carbon among the dissolved inorganic species.

The effect of acidification is clearly visible from the change in the carbon speciation. In the inlet seawater stream, molecular  $\text{CO}_2$  accounts for only  $0.009 \text{ kmol h}^{-1}$ . After acidification, the molecular  $\text{CO}_2$  flow rate increases to  $2.970 \text{ kmol h}^{-1}$ . At the same time, bicarbonate decreases from  $2.666 \text{ kmol h}^{-1}$  to  $0.018 \text{ kmol h}^{-1}$ , while carbonate decreases from  $0.313 \text{ kmol h}^{-1}$  to  $4.34 \times 10^{-8} \text{ kmol h}^{-1}$ .

The fraction of DIC present as molecular  $\text{CO}_2$  in ACIDSW can be calculated as:

$$x_{\text{CO}_2, \text{ACIDSW}} = \frac{\dot{n}_{\text{CO}_2, \text{ACIDSW}}}{\dot{n}_{\text{DIC}, \text{ACIDSW}}} \quad (5.2)$$

Substituting the Aspen Plus values:

$$x_{\text{CO}_2, \text{ACIDSW}} = \frac{2.970}{2.988} = 0.994 \quad (5.3)$$

Therefore, approximately 99.4% of the dissolved inorganic carbon in the acidified stream is present as molecular  $\text{CO}_2$ . This confirms that the acidification step successfully shifts the carbonate system towards the species required for gas-liquid separation.

The pH of the ACIDSW stream is equal to 4.02 in the Aspen Plus results. This value is lower than the reference acidification pH adopted from the experimental MIT process. In the present model, pH is not imposed independently at the outlet of the acidification block, but is obtained from the stream composition and the electrolyte speciation calculated by Aspen Plus. For this reason, the value should

be interpreted as the result of the simplified stoichiometric representation adopted for the electrochemical acidification step.

The pH-driven redistribution observed in the Aspen Plus results can be interpreted through the carbonate equilibrium system. Figure 5.2 reports the theoretical carbonate speciation as a function of pH, with the main simulated process streams superimposed as operating points. This representation highlights the role of the acidification step in shifting the carbonate system toward molecular  $\text{CO}_2$ , and the role of the regeneration step in restoring alkaline conditions.

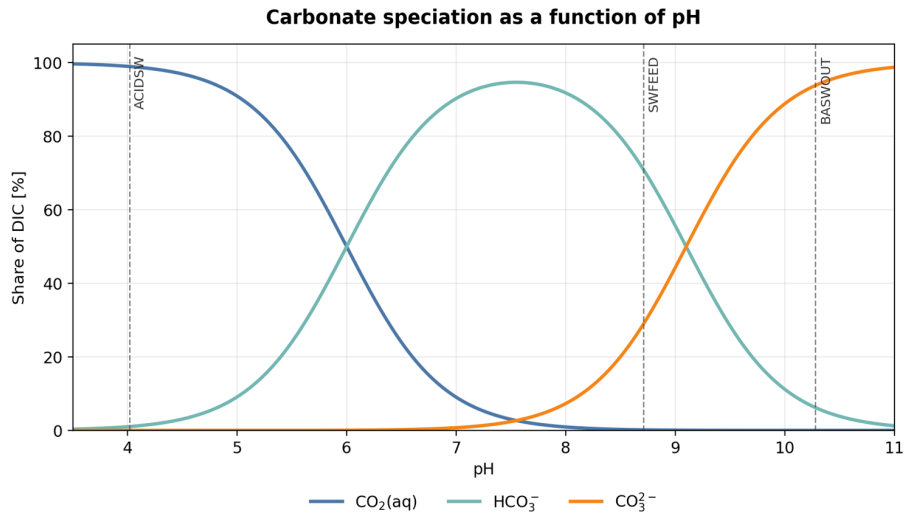


**Figure 5.2:** Carbonate speciation as a function of pH. The continuous curves are calculated from carbonate equilibrium relationships and are used as an interpretative reference.

### 5.1.3 Overall Carbon Recovery

The objective of the  $\text{CO}_2$  recovery section is to transfer the molecular  $\text{CO}_2$  generated during acidification from the liquid phase to a gas stream. The final product stream, labelled  $\text{CO}_2\text{OUT}$ , contains  $2.595 \text{ kmol h}^{-1}$  of  $\text{CO}_2$ , corresponding to  $114.20 \text{ kg h}^{-1}$ . This value is consistent with the design  $\text{CO}_2$  flow rate defined for the reference plant capacity.

The overall DIC recovery efficiency is calculated by comparing the  $\text{CO}_2$  molar flow rate in the final product stream with the DIC molar flow rate entering the process with the seawater feed:

$$\eta_{\text{DIC}} = \frac{\dot{n}_{\text{CO}_2, \text{OUT}}}{\dot{n}_{\text{DIC}, \text{SWFEED}}} \quad (5.4)$$

Substituting the corresponding values:

$$\eta_{\text{DIC}} = \frac{2.595}{2.988} = 0.8683 \quad (5.5)$$

The resulting DIC recovery efficiency is therefore:

$$\eta_{\text{DIC}} = 86.83\% \quad (5.6)$$

This value is very close to the reference removal efficiency of 87% adopted for the base-case design. The small difference is due to the detailed distribution of carbon among the different outlet streams in the Aspen Plus flowsheet, including the final CO<sub>2</sub> product, the treated seawater outlet, the condensate streams and the vent gas stream.

The residual dissolved inorganic carbon leaving with the treated seawater stream BASWOUT is equal to 0.392 kmol h<sup>-1</sup>. The corresponding residual DIC fraction is:

$$f_{\text{DIC,res}} = \frac{\dot{n}_{\text{DIC,BASWOUT}}}{\dot{n}_{\text{DIC,SWFEED}}} \quad (5.7)$$

$$f_{\text{DIC,res}} = \frac{0.392}{2.988} = 0.1312 \quad (5.8)$$

Thus, 13.12% of the inlet DIC remains in the treated seawater stream. This value is consistent with the calculated DIC recovery efficiency, since the majority of the carbon not recovered as CO<sub>2</sub> product is retained in the regenerated liquid stream.

A minor amount of carbon is also associated with the auxiliary outlet streams. The first condensate stream, CONDW, contains  $4.48 \times 10^{-4}$  kmol h<sup>-1</sup> of dissolved inorganic carbon, while the second condensate stream, CONDW2, contains  $5.85 \times 10^{-4}$  kmol h<sup>-1</sup>. The total DIC leaving with these two condensate streams is therefore:

$$\dot{n}_{\text{DIC,cond}} = 4.48 \times 10^{-4} + 5.85 \times 10^{-4} = 1.03 \times 10^{-3} \text{ kmol h}^{-1} \quad (5.9)$$

This corresponds to approximately 0.035% of the inlet DIC. The vent gas stream VANTATM contains  $3.10 \times 10^{-4}$  kmol h<sup>-1</sup> of carbon, corresponding to approximately 0.010% of the inlet DIC. These contributions are negligible compared with the CO<sub>2</sub> recovered in the final product stream and with the residual DIC retained in BASWOUT.

Overall, the carbon balance shows that the Aspen Plus model reproduces the target recovery of the reference case. Most of the inlet dissolved inorganic carbon is recovered as CO<sub>2</sub> product, while the remaining carbon is mainly discharged with the treated seawater as carbonate and bicarbonate species.

### 5.1.4 CO<sub>2</sub> Recovery and Gas Conditioning

The CO<sub>2</sub> recovery and conditioning section was analysed to evaluate both the amount of CO<sub>2</sub> recovered and the composition of the gas product leaving the system boundaries. In the Aspen Plus flowsheet, the acidified seawater stream is sent to the vacuum separation unit, where a wet CO<sub>2</sub>-rich vapour stream is generated. This stream is then treated through two conditioning steps: a first cooling and knock-out stage before compression, and a second cooling and knock-out stage after compression.

The stream leaving the CO<sub>2</sub> separation unit, labelled WETCO<sub>2</sub>, has a total mass flow rate of 361.85 kg h<sup>-1</sup>. It contains 114.25 kg h<sup>-1</sup> of CO<sub>2</sub> and 239.59 kg h<sup>-1</sup> of water. Therefore, the wet gas recovered from the vacuum separator contains a large amount of water vapour. The corresponding CO<sub>2</sub> mass fraction is 31.57%, while water represents 66.21% of the stream. Smaller amounts of nitrogen and oxygen are also present due to the dissolved gases originally contained in the seawater feed.

The WETCO<sub>2</sub> stream is first cooled and sent to the first knock-out drum. This step condenses most of the water initially present in the gas stream and removes it as the liquid stream COND<sub>W</sub>. The gas stream leaving the first knock-out drum, labelled CO<sub>2</sub>GAS, has a total mass flow rate of 134.98 kg h<sup>-1</sup>. The water content decreases from 239.59 kg h<sup>-1</sup> in WETCO<sub>2</sub> to 12.75 kg h<sup>-1</sup> in CO<sub>2</sub>GAS, while the CO<sub>2</sub> flow rate remains almost unchanged, decreasing only from 114.25 kg h<sup>-1</sup> to 114.23 kg h<sup>-1</sup>.

After this first condensate removal step, the gas stream is compressed to approximately atmospheric pressure. The compressed gas is then cooled again and sent to a second knock-out drum, where additional condensed water is removed as COND<sub>W</sub>2. The final product stream CO<sub>2</sub>OUT has a total mass flow rate of 122.86 kg h<sup>-1</sup> and contains 114.20 kg h<sup>-1</sup> of CO<sub>2</sub>. The residual water content is reduced to 0.653 kg h<sup>-1</sup>.

The composition of the main recovered gas streams is summarized in Table 5.2.

**Table 5.2:** Composition of the recovered CO<sub>2</sub> streams obtained from the Aspen Plus flowsheet.

| Component        | WETCO2<br>kg h <sup>-1</sup> | CO2GAS<br>kg h <sup>-1</sup> | CO2OUT<br>kg h <sup>-1</sup> | CO2OUT mass fraction<br>— |
|------------------|------------------------------|------------------------------|------------------------------|---------------------------|
| H <sub>2</sub> O | 239.59                       | 12.75                        | 0.653                        | 0.0053                    |
| CO <sub>2</sub>  | 114.25                       | 114.23                       | 114.20                       | 0.9295                    |
| N <sub>2</sub>   | 4.31                         | 4.31                         | 4.31                         | 0.0351                    |
| O <sub>2</sub>   | 3.70                         | 3.70                         | 3.70                         | 0.0301                    |
| Total            | 361.85                       | 134.98                       | 122.86                       | 1.0000                    |

The water removal efficiency of the gas-conditioning section is calculated as:

$$\eta_{\text{H}_2\text{O,rem}} = \frac{\dot{m}_{\text{H}_2\text{O,WETCO2}} - \dot{m}_{\text{H}_2\text{O,CO2OUT}}}{\dot{m}_{\text{H}_2\text{O,WETCO2}}} \quad (5.10)$$

Substituting the Aspen Plus values:

$$\eta_{\text{H}_2\text{O,rem}} = \frac{239.59 - 0.653}{239.59} = 0.9973 \quad (5.11)$$

Therefore, the two conditioning stages remove approximately 99.73% of the water initially present in the wet CO<sub>2</sub> stream. At the same time, the CO<sub>2</sub> loss during gas conditioning is very small. The CO<sub>2</sub> mass flow rate decreases from 114.25 kg h<sup>-1</sup> in WETCO2 to 114.20 kg h<sup>-1</sup> in CO2OUT. The corresponding loss is approximately 0.05 kg h<sup>-1</sup>, which is negligible compared with the recovered CO<sub>2</sub> flow rate.

The final CO2OUT stream is therefore substantially enriched in CO<sub>2</sub> after the conditioning section. Its CO<sub>2</sub> mass fraction is 92.95%. However, the product stream is not pure CO<sub>2</sub>, since it still contains residual nitrogen and oxygen, equal to 4.31 kg h<sup>-1</sup> and 3.70 kg h<sup>-1</sup>, respectively. These components originate from the dissolved gases initially present in seawater and not completely removed in the preliminary dissolved-gas removal section.

The final product stream leaves the system at approximately atmospheric pressure and at 10 °C. Further purification, drying or compression to transport and storage pressure is not included within the Aspen Plus system boundaries and would need to be assessed separately according to the selected downstream CO<sub>2</sub> management route.

### 5.1.5 Treated Seawater Outlet

The treated seawater stream leaving the regeneration section represents the main liquid outlet of the process. In the Aspen Plus flowsheet, this stream is labelled BASWOUT and corresponds to the seawater after CO<sub>2</sub> removal and electrochemical alkalization.

The total mass flow rate of BASWOUT is equal to  $1.533 \times 10^6$  kg h<sup>-1</sup>, which is close to the inlet seawater flow rate. This result is expected because only a small fraction of the total inlet mass is removed as recovered CO<sub>2</sub>, condensed water and vented gas. Therefore, the Direct Ocean Capture process mainly modifies the chemical speciation of the dissolved carbon compounds, while the total liquid flow rate remains almost unchanged.

The BASWOUT stream contains 0.392 kmol h<sup>-1</sup> of residual dissolved inorganic carbon. Most of this residual carbon is present as carbonate, with a molar flow rate of 0.341 kmol h<sup>-1</sup>. Bicarbonate accounts for 0.0509 kmol h<sup>-1</sup>, while molecular CO<sub>2</sub> is almost completely depleted and is equal to only  $3.05 \times 10^{-6}$  kmol h<sup>-1</sup>.

The predominance of carbonate in the outlet stream is consistent with the alkaline conditions obtained after the regeneration block. The pH of BASWOUT is equal to 10.28 in the Aspen Plus results. This value reflects the re-alkalization step of the chloride-mediated process, where the treated stream is brought back to alkaline conditions after CO<sub>2</sub> separation.

The main properties of the treated seawater outlet stream are summarized in Table 5.3.

**Table 5.3:** Main properties of the treated seawater outlet stream BASWOUT.

| Parameter                              | Value                 | Unit                           |
|----------------------------------------|-----------------------|--------------------------------|
| Total mass flow rate                   | $1.533 \times 10^6$   | kg h <sup>-1</sup>             |
| Volumetric flow rate                   | $1.497 \times 10^3$   | m <sup>3</sup> h <sup>-1</sup> |
| Temperature                            | 298.15                | K                              |
| Pressure                               | 0.987                 | atm                            |
| pH                                     | 10.28                 | —                              |
| Residual CO <sub>2</sub>               | $3.05 \times 10^{-6}$ | kmol h <sup>-1</sup>           |
| Residual HCO <sub>3</sub> <sup>-</sup> | 0.0509                | kmol h <sup>-1</sup>           |
| Residual CO <sub>3</sub> <sup>2-</sup> | 0.341                 | kmol h <sup>-1</sup>           |
| Residual DIC                           | 0.392                 | kmol h <sup>-1</sup>           |
| Residual DIC fraction                  | 13.12                 | %                              |

It is important to note that the pH and composition of BASWOUT are process-level simulation results. The Aspen Plus model does not include dilution with the

receiving seawater, hydrodynamic dispersion, local pH gradients or environmental discharge constraints. Therefore, the treated seawater outlet should not be interpreted as a final environmental discharge specification.

It is important to note that the pH and composition of BASWOUT are process-level simulation results. The Aspen Plus model does not include dilution with the receiving seawater, hydrodynamic dispersion, local pH gradients or environmental discharge constraints. Therefore, the treated seawater outlet should not be interpreted as a final environmental discharge specification. A dedicated discharge and mixing assessment would be required to evaluate the compatibility of the outlet stream with marine discharge requirements.

Overall, the mass balance shows that the reference Aspen Plus flowsheet recovers  $114.20 \text{ kg h}^{-1}$  of  $\text{CO}_2$  in the final product stream, corresponding to 86.83% of the dissolved inorganic carbon entering with the seawater feed. The remaining carbon is mainly retained in the treated seawater as carbonate and bicarbonate species. Carbon losses associated with the condensate and vent streams are small compared with both the recovered  $\text{CO}_2$  flow rate and the residual carbon in BASWOUT.

## 5.2 Energy Requirements of the Reference Configuration

The energy requirements of the reference configuration were evaluated by combining the electrochemical energy consumption adopted from the MIT experimental study with the auxiliary energy contributions obtained from the Aspen Plus flowsheet. The electrochemical contribution represents the energy required to drive the chloride-mediated pH swing, while the auxiliary contributions include the power required by liquid pumps and gas compressors.

In addition to these electrical requirements, the Aspen Plus model also includes thermal duties associated with the cooling of the gas streams. These duties were reported separately from the electrical energy demand, since they represent thermal utility loads rather than direct electrical consumption. The conversion of cooling duties into equivalent electricity would require additional assumptions on the cooling technology adopted, such as the coefficient of performance of a chiller.

The flash separation units included in the flowsheet were considered adiabatic. Therefore, no external heat duty was assigned to the flash separators. Their energetic effect is reflected in the temperature, enthalpy and phase distribution of the outlet streams. The energy required to recover the low-pressure gas streams is instead accounted for through the corresponding compression units.

### 5.2.1 Electrochemical Energy Requirement

The electrochemical energy requirement was calculated using the specific energy consumption reported for the chloride-mediated MIT process. The adopted value is equal to 122 kJ mol<sup>-1</sup> CO<sub>2</sub> removed. This value refers only to the electrochemical cells and does not include auxiliary units such as seawater pumping, gas separation, cooling or compression.

In the Aspen Plus reference simulation, the final CO<sub>2</sub> product stream contains 2.595 kmol h<sup>-1</sup> of CO<sub>2</sub>, corresponding to 114.20 kg h<sup>-1</sup>. The electrochemical power associated with this CO<sub>2</sub> recovery rate is calculated as:

$$\dot{W}_{\text{el}} = e_{\text{el}} \dot{n}_{\text{CO}_2, \text{OUT}} \quad (5.12)$$

where  $e_{\text{el}}$  is the specific electrochemical energy consumption and  $\dot{n}_{\text{CO}_2, \text{OUT}}$  is the molar flow rate of CO<sub>2</sub> recovered in the final product stream. Substituting the corresponding values:

$$\dot{W}_{\text{el}} = 122000 \frac{\text{kJ}}{\text{kmol}} 2.595 \frac{\text{kmol}}{\text{h}} = 3.17 \times 10^5 \frac{\text{kJ}}{\text{h}} \quad (5.13)$$

which corresponds to:

$$\dot{W}_{\text{el}} = 87.94 \text{ kW} \quad (5.14)$$

The corresponding specific electrochemical energy consumption, expressed per tonne of CO<sub>2</sub> recovered, is:

$$E_{\text{el, spec}} = \frac{87.94 \text{ kW}}{0.11420 \text{ tCO}_2 \text{ h}^{-1}} = 770.0 \text{ kWh tCO}_2^{-1} \quad (5.15)$$

This value represents the energy requirement associated with the pH-swing mechanism only. For this reason, it must be distinguished from the overall process energy demand obtained after including the auxiliary units of the Aspen Plus flowsheet.

### 5.2.2 Electrical Auxiliary Requirements

The auxiliary electrical requirements were obtained from the Aspen Plus equipment results for pumps and compressors. The liquid pumping section includes four main pumps: the seawater intake pump, the ultrafiltration booster pump, the pump upstream of the acidification section and the pump upstream of the regeneration section.

The seawater intake pump, SWPUMP, is the largest single pumping contribution, with an electrical consumption of 138.383 kW. This value is mainly related to the large seawater flow rate treated by the process and to the pressure increase required

at the inlet of the plant. The ultrafiltration booster pump, UFPUMP, requires 65.898 kW. The acidification and regeneration section pumps, ACDPUMP and BASPUMP, require 46.129 kW and 63.444 kW, respectively.

The total liquid pumping power is therefore:

$$\dot{W}_{\text{pumps}} = 138.383 + 65.898 + 46.129 + 63.444 = 313.854 \text{ kW} \quad (5.16)$$

Gas compression contributes less than liquid pumping. In the updated flowsheet, the CO<sub>2</sub> compressor, CO2COMP, compresses the partially dried CO<sub>2</sub>-rich gas stream leaving the first knock-out drum to approximately atmospheric pressure. Based on the updated stream enthalpy balance and assuming the same mechanical efficiency adopted for the compressor block, the corresponding electrical requirement is approximately 16.92 kW. The vent gas compressor, VENTCOMP, requires approximately 0.993 kW. The total gas compression requirement is therefore:

$$\dot{W}_{\text{comp}} = 16.92 + 0.993 = 17.91 \text{ kW} \quad (5.17)$$

The total auxiliary electrical power required by pumps and compressors is:

$$\dot{W}_{\text{aux}} = 313.854 + 17.91 = 331.76 \text{ kW} \quad (5.18)$$

The auxiliary electrical contributions obtained from the Aspen Plus equipment results are summarized in Table 5.4.

**Table 5.4:** Auxiliary electrical energy requirements obtained from the Aspen Plus equipment results.

| Unit                   | Type                         | Power<br>kW | Specific energy<br>kWh tCO <sub>2</sub> <sup>-1</sup> |
|------------------------|------------------------------|-------------|-------------------------------------------------------|
| SWPUMP                 | Seawater intake pump         | 138.383     | 1211.7                                                |
| UFPUMP                 | Ultrafiltration booster pump | 65.898      | 577.0                                                 |
| ACDPUMP                | Acidification-section pump   | 46.129      | 403.9                                                 |
| BASPUMP                | Regeneration-section pump    | 63.444      | 555.5                                                 |
| Total pumping          | Liquid pumping               | 313.854     | 2748.2                                                |
| CO2COMP                | CO <sub>2</sub> compressor   | 16.92       | 148.1                                                 |
| VENTCOMP               | Vent gas compressor          | 0.993       | 8.7                                                   |
| Total compression      | Gas compression              | 17.91       | 156.8                                                 |
| Total auxiliary demand | Pumps and compressors        | 331.76      | 2905.1                                                |

The results show that liquid pumping is the dominant auxiliary electrical contribution in the reference flowsheet. This is mainly due to the large seawater flow rate required by the Direct Ocean Capture process. Although the pressure increases assigned to the individual pumps are moderate, the high liquid throughput leads to a significant total pumping demand.

Among the pumps, SWPUMP provides the largest contribution because it processes the entire seawater feed and supplies the pressure increase required at the inlet of the pretreatment section. UFPUMP also represents a relevant contribution, since it accounts for the additional pressure increase required by the ultrafiltration stage. The ACDPUMP and BASPUMP contributions are associated with pressure changes in the acidification and regeneration sections.

By contrast, the gas compression requirement is smaller than the pumping requirement because the gas flow rate is much lower than the seawater flow rate. In the present model, the CO<sub>2</sub> stream is compressed only to approximately atmospheric pressure. Therefore, the compression power reported here does not include any additional compression that would be required for pipeline transport, geological storage or high-pressure utilization.

### 5.2.3 Thermal Utility Requirements

The Aspen Plus flowsheet also includes thermal duties associated with the cooling of gas streams. In the updated configuration, the CO<sub>2</sub> line includes two cooling steps: CO2COOL, located before the CO<sub>2</sub> compressor, and CO2COOL2, located after compression. The VENTCOOL block is also included to cool the vent gas stream before atmospheric discharge. These duties are negative in Aspen Plus, indicating that heat is removed from the corresponding process streams.

The first CO<sub>2</sub> cooling step, CO2COOL, cools the wet CO<sub>2</sub>-rich stream leaving the vacuum separation section before the first knock-out drum. This step promotes partial condensation of the water vapour carried by the recovered CO<sub>2</sub> stream before compression. The heat duty reported by Aspen Plus is equal to  $-38347.7 \text{ cal s}^{-1}$ , corresponding to a cooling requirement of  $160.45 \text{ kW}_{\text{th}}$ .

The second CO<sub>2</sub> cooling step, CO2COOL2, was introduced downstream of the CO<sub>2</sub> compressor. This block cools the compressed CO<sub>2</sub> stream to 10 °C at approximately atmospheric pressure before the second knock-out drum. The heat duty reported by Aspen Plus is equal to  $-5654.58 \text{ cal s}^{-1}$ , corresponding to a cooling requirement of  $23.66 \text{ kW}_{\text{th}}$ . This second cooling step does not modify the CO<sub>2</sub> removal efficiency, but it improves the quality of the final gas stream by promoting additional water condensation after compression.

The VENTCOOL block, used to cool the vent gas stream before discharge, has a smaller heat duty equal to  $-335.3 \text{ cal s}^{-1}$ , corresponding to  $1.40 \text{ kW}_{\text{th}}$ .

The total cooling duty of the updated reference configuration is therefore:

$$\dot{Q}_{\text{cooling}} = 160.45 + 23.66 + 1.40 = 185.51 \text{ kW}_{\text{th}} \quad (5.19)$$

The corresponding specific cooling duty, expressed per tonne of CO<sub>2</sub> recovered, is:

$$Q_{\text{cooling,spec}} = \frac{185.51 \text{ kW}_{\text{th}}}{0.11420 \text{ tCO}_2 \text{ h}^{-1}} = 1624.4 \text{ kWh}_{\text{th}} \text{ tCO}_2^{-1} \quad (5.20)$$

The cooling duties obtained from Aspen Plus are summarized in Table 5.5.

**Table 5.5:** Cooling duties obtained from the Aspen Plus heat-exchanger results.

| Unit               | Function                                                  | Aspen duty<br>cal s <sup>-1</sup> | Cooling duty<br>kW <sub>th</sub> |
|--------------------|-----------------------------------------------------------|-----------------------------------|----------------------------------|
| CO2COOL            | Pre-compression cooling of the wet CO <sub>2</sub> stream | -38347.7                          | 160.45                           |
| CO2COOL2           | Post-compression cooling of the CO <sub>2</sub> stream    | -5654.58                          | 23.66                            |
| VENTCOOL           | Cooling of the vent gas stream                            | -335.3                            | 1.40                             |
| Total cooling duty | Thermal utility requirement                               | -                                 | 185.51                           |

The cooling duty is mainly associated with the high amount of water vapour carried by the wet CO<sub>2</sub> stream leaving the vacuum separator. The first cooling and knock-out stage reduces the amount of water entering the CO<sub>2</sub> compressor, whereas the second cooling and knock-out stage further decreases the residual water content of the final CO<sub>2</sub> product stream. However, these contributions are not added directly to the electrical energy demand, since they represent thermal utility requirements. If a mechanical cooling system were considered, an additional conversion into equivalent electrical consumption would be required.

#### 5.2.4 Overall Energy Assessment

The overall electrical energy requirement of the reference configuration was calculated by summing the electrochemical contribution, the liquid pumping power and the gas compression power. Cooling duties were excluded from this electrical total and were reported separately as thermal utility requirements.

The total electrical power requirement is:

$$\dot{W}_{\text{tot}} = \dot{W}_{\text{el}} + \dot{W}_{\text{pumps}} + \dot{W}_{\text{comp}} \quad (5.21)$$

Substituting the corresponding values:

$$\dot{W}_{\text{tot}} = 87.94 + 313.854 + 17.91 = 419.70 \text{ kW} \quad (5.22)$$

The corresponding overall specific electrical energy consumption is:

$$E_{\text{tot,spec}} = \frac{419.70 \text{ kW}}{0.11420 \text{ tCO}_2 \text{ h}^{-1}} = 3675.1 \text{ kWh tCO}_2^{-1} \quad (5.23)$$

The distribution of the electrical energy demand is reported in Table 5.6.

**Table 5.6:** Overall electrical energy requirement of the reference configuration.

| Contribution                 | Power<br>kW | Specific energy<br>kWh tCO <sub>2</sub> <sup>-1</sup> | Share<br>% |
|------------------------------|-------------|-------------------------------------------------------|------------|
| Electrochemical cells        | 87.94       | 770.0                                                 | 21.0       |
| Liquid pumping               | 313.85      | 2748.2                                                | 74.8       |
| Gas compression              | 17.91       | 156.8                                                 | 4.3        |
| Total electrical requirement | 419.70      | 3675.1                                                | 100.0      |

The results show that the electrical energy demand of the reference configuration is dominated by liquid pumping. The electrochemical contribution accounts for 21.0% of the total electrical requirement, while pumping alone accounts for 74.8%. Gas compression represents only 4.3% of the total electrical demand in the present configuration.

This distribution highlights an important difference between laboratory-scale performance indicators and process-level energy requirements. The experimental energy consumption of the MIT process refers only to the electrochemical pH-swing mechanism. When the process is translated into a complete Aspen Plus flowsheet, the large seawater throughput becomes a dominant factor and significantly affects the overall energy demand.

Therefore, the energy performance of the chloride-mediated Direct Ocean Capture process cannot be assessed only from the electrochemical energy consumption. The auxiliary requirements associated with seawater intake, pretreatment and liquid circulation must also be considered. This result indicates that hydraulic optimization, reduction of pressure drops and improved integration of the pretreatment and separation sections are key aspects for future scale-up of the process.

In addition to the electrical requirement, the updated reference configuration requires a total cooling duty of 185.51 kW<sub>th</sub>, corresponding to approximately 1624.4 kWh<sub>th</sub> tCO<sub>2</sub><sup>-1</sup>. This thermal duty is mainly associated with the conditioning of the recovered CO<sub>2</sub> stream and is reported separately from the electrical energy consumption.

### 5.2.5 Annual Energy Requirements

The annual energy requirements were calculated from the power values obtained for the reference configuration by assuming continuous operation over 8760 h yr<sup>-1</sup>. This conversion allows the process energy demand to be expressed on an annual basis and compared with the selected plant capacity of 1000 tCO<sub>2</sub> yr<sup>-1</sup>.

The annual electrical energy demand associated with the electrochemical cells is:

$$E_{\text{el,yr}} = 87.94 \text{ kW } 8760 \text{ h yr}^{-1} = 0.770 \text{ GWh yr}^{-1} \quad (5.24)$$

The annual electrical energy demand associated with liquid pumping is:

$$E_{\text{pumps,yr}} = 313.85 \text{ kW } 8760 \text{ h yr}^{-1} = 2.749 \text{ GWh yr}^{-1} \quad (5.25)$$

The annual electrical energy demand associated with gas compression is:

$$E_{\text{comp,yr}} = 17.91 \text{ kW } 8760 \text{ h yr}^{-1} = 0.157 \text{ GWh yr}^{-1} \quad (5.26)$$

The total annual electrical energy requirement is therefore:

$$E_{\text{tot,yr}} = 419.70 \text{ kW } 8760 \text{ h yr}^{-1} = 3.677 \text{ GWh yr}^{-1} \quad (5.27)$$

The same conversion was applied to the cooling duties. The annual cooling duty is reported separately because it represents a thermal utility requirement and not a direct electrical consumption.

**Table 5.7:** Annual energy requirements of the reference configuration.

| Contribution                             | Power<br>kW | Annual energy<br>GWh yr <sup>-1</sup> | Energy type<br>– |
|------------------------------------------|-------------|---------------------------------------|------------------|
| Electrochemical cells                    | 87.94       | 0.770                                 | Electrical       |
| Liquid pumping                           | 313.85      | 2.749                                 | Electrical       |
| Gas compression                          | 17.91       | 0.157                                 | Electrical       |
| Total electrical requirement             | 419.70      | 3.677                                 | Electrical       |
| CO <sub>2</sub> pre-compression cooling  | 160.45      | 1.406                                 | Thermal          |
| CO <sub>2</sub> post-compression cooling | 23.66       | 0.207                                 | Thermal          |
| Vent gas cooling                         | 1.40        | 0.012                                 | Thermal          |
| Total cooling duty                       | 185.51      | 1.625                                 | Thermal          |

Overall, the reference configuration requires 3.677 GWh yr<sup>-1</sup> of electrical energy. The cooling requirement corresponds to an additional thermal duty of 1.625 GWh<sub>th</sub>

$\text{yr}^{-1}$ . These two contributions are not summed into a single total because they represent different forms of energy. In particular, the cooling duty would have to be converted into equivalent electrical consumption only if a specific cooling technology and coefficient of performance were assumed.

## Chapter 6

# Pre-Feasibility Assessment

The Aspen Plus model developed in the previous chapters provides the mass and energy balances of the reference chloride-mediated Direct Ocean Capture process. However, the simulation does not directly provide the mechanical design or the capital cost of the real equipment required to implement the process.

For this reason, this chapter extends the process simulation towards a preliminary pre-feasibility assessment. The objective is not to develop a detailed techno-economic analysis or a vendor-based cost estimate, but to identify the main capital and operating cost drivers of the reference configuration at the selected pilot scale.

The analysis first defines the economic methodology adopted for CAPEX and OPEX estimation. The Aspen Plus blocks are then associated with real equipment items or simplified equipment packages, and preliminary sizing criteria are introduced. The resulting costs are expressed as annualized and levelized contributions per unit mass of CO<sub>2</sub> removed. Finally, the results are used to identify the main cost drivers, uncertainty sources and scale-up limitations of the process.

### 6.1 Economic Assessment Methodology

The economic assessment was developed to convert the process-level results obtained from Aspen Plus into preliminary cost indicators. The analysis was performed at pre-feasibility level, and the resulting values should therefore be interpreted as order-of-magnitude estimates rather than definitive plant costs.

Three types of input data were used: Aspen Plus results, literature-based cost data, and engineering assumptions introduced when the process simulation did not provide sufficient information for equipment sizing. The Aspen Plus results were used for flow rates, pressures, equipment powers and cooling duties. Literature data were adopted for equipment items that could not be represented through

standard cost correlations, such as the electrochemical section and the ultrafiltration pretreatment system.

The assessment distinguishes between equipment included in the preliminary CAPEX estimate and elements excluded from the base-case scope. Pumps, filtration units, separators, knock-out drums and compressors were considered. By contrast, detailed civil works, offshore intake structures, detailed installation design, control systems, maintenance, replacement costs and end-of-life management were not explicitly included.

### 6.1.1 CAPEX Estimation

The capital cost estimation was based on the preliminary translation of the Aspen Plus flowsheet into real process equipment. Different cost-estimation approaches were adopted depending on the type of equipment and on the information available from the simulation.

For conventional equipment such as pumps, compressors and vessels, the CAPEX was estimated using equipment-cost correlations commonly adopted in preliminary process design. In particular, the module-costing approach described by Turton et al. was adopted as the main reference method for equipment-level cost estimation [26]. This method relates the purchased equipment cost to a characteristic size parameter, such as pump power, compressor power or vessel volume. The resulting purchased cost was then corrected using bare-module factors to account for installation-related contributions and material selection.

The cost correlations used in this work are based on a reference cost year. Therefore, the resulting costs were updated to the selected reference year using the Chemical Engineering Plant Cost Index (CEPCI). The CEPCI is commonly used in the chemical process industries to adjust plant construction costs from one period to another [27]. The cost update was performed according to:

$$C_{\text{new}} = C_{\text{base}} \frac{CEPCI_{\text{new}}}{CEPCI_{\text{base}}} \quad (6.1)$$

where  $C_{\text{base}}$  is the cost calculated in the base year of the correlation, and  $C_{\text{new}}$  is the cost updated to the reference year. For membrane pretreatment, a different approach was adopted. Since the ultrafiltration unit was represented in Aspen Plus as a simplified pressure-drop block, its CAPEX was estimated using literature-based normalized costs expressed per unit of treated-water capacity. The detailed calculation is reported in the pretreatment section. Similarly, the electrochemical acidification and regeneration blocks were not sized from first-principles stack geometry. Their contribution was therefore introduced as a literature-based leveled cost contribution, avoiding an inappropriate interpretation of the RStoic blocks as detailed electrochemical stack models.

### 6.1.2 Annualized and Levelized CAPEX

In order to compare equipment sections with different capital costs on a common basis, the estimated CAPEX values were annualized using a capital recovery factor. The capital recovery factor was calculated as:

$$CRF = \frac{i(1+i)^n}{(1+i)^n - 1} \quad (6.2)$$

where  $i$  is the discount rate and  $n$  is the economic lifetime of the project. In the reference case, an economic lifetime of 20 years and a discount rate of 8% were assumed. These values were adopted as project-level economic assumptions and do not imply that all individual equipment items have the same technical lifetime.

The annualized CAPEX of each equipment item was calculated as:

$$CAPEX_{ann,j} = CAPEX_j CRF \quad (6.3)$$

where  $CAPEX_j$  is the estimated capital cost of equipment item  $j$ . The corresponding levelized CAPEX contribution was then obtained by dividing the annualized CAPEX by the annual CO<sub>2</sub> removal capacity:

$$CAPEX_{lev,j} = \frac{CAPEX_{ann,j}}{\dot{m}_{CO_2,yr}} \quad (6.4)$$

where  $\dot{m}_{CO_2,yr}$  is the annual amount of CO<sub>2</sub> removed by the plant. For the reference case, this value is equal to 1000 tCO<sub>2</sub> yr<sup>-1</sup>, or  $1.0 \times 10^6$  kgCO<sub>2</sub> yr<sup>-1</sup>.

The levelized CAPEX values reported in this chapter represent only the annualized capital contribution of each equipment section. They should not be interpreted as the total cost of CO<sub>2</sub> removal, because electricity costs, maintenance, replacement costs and other operating expenses are treated separately or discussed as uncertainty items.

## 6.2 Translation of the Aspen Plus Flowsheet into Real Equipment

The Aspen Plus flowsheet was translated into a set of real equipment items or simplified equipment packages before performing the preliminary CAPEX estimate. The translation was carried out by preserving the process function assigned to each simulation block, without introducing a different process configuration.

This step is required because several Aspen Plus blocks were introduced as process-level approximations. Filtration units were represented as pressure-drop blocks, electrochemical cells as black-box RStoic reactors, and CO<sub>2</sub> recovery as

a vacuum flash separator. Therefore, each block was associated with a realistic equipment interpretation suitable for preliminary cost estimation.

Tables 6.1 and 6.2 summarize the real-equipment interpretation adopted for the seawater, electrochemical and CO<sub>2</sub> conditioning sections, together with the sizing or cost basis used for the preliminary CAPEX estimation.

**Table 6.1:** Translation of Aspen Plus blocks into real equipment items for the seawater and electrochemical sections.

| Aspen block | Real-equipment interpretation                           | Sizing or cost basis                               |
|-------------|---------------------------------------------------------|----------------------------------------------------|
| SWPUMP      | Seawater intake pump                                    | Aspen pump power and seawater flow rate            |
| CRSFILT     | Automatic self-cleaning coarse screen filter            | Seawater flow rate                                 |
| FINFILT     | Automatic self-cleaning fine screen filter              | Seawater flow rate                                 |
| UFPUMP      | Ultrafiltration booster pump                            | Aspen pump power                                   |
| UFILT       | Ultrafiltration membrane skid                           | Treated-water capacity                             |
| DAGS1       | Vacuum flash drum for preliminary dissolved-gas removal | Liquid holdup and gas-side check                   |
| VENTCOMP    | Vacuum pump or vent-gas compressor package              | Aspen power and minimum package size               |
| VENTCOOL    | Small vent-gas cooler                                   | Aspen cooling duty                                 |
| ACIDCEL     | Electrochemical acidification stack                     | Literature-based electrochemical cost contribution |
| BASPUMP     | Regeneration-section transfer pump                      | Aspen pump power                                   |
| BASECEL     | Electrochemical regeneration stack                      | Literature-based electrochemical cost contribution |

**Table 6.2:** Translation of Aspen Plus blocks into real equipment items for the CO<sub>2</sub> separation and conditioning section.

| Aspen block | Real-equipment interpretation                    | Sizing or cost basis                                 |
|-------------|--------------------------------------------------|------------------------------------------------------|
| CO2SEP      | Vacuum flash drum for CO <sub>2</sub> separation | Liquid holdup and WETCO <sub>2</sub> gas-side sizing |
| CO2COOL     | Pre-compression gas cooler/condenser             | Aspen cooling duty                                   |
| KODRUM      | Knock-out drum before compression                | Gas-side sizing                                      |
| CO2COMP     | Low-pressure CO <sub>2</sub> compressor          | Aspen compressor power                               |
| CO2COOL2    | Post-compression CO <sub>2</sub> aftercooler     | Aspen cooling duty                                   |
| KODRUM2     | Second knock-out drum                            | Gas-side sizing and minimum practical volume         |

The following section presents the preliminary sizing and CAPEX estimation for the main equipment groups.

## 6.3 Preliminary Equipment Sizing and CAPEX Estimation

This section presents the preliminary sizing and CAPEX estimation of the main equipment sections identified in the Aspen Plus flowsheet. The analysis is organized by process area, starting from the seawater intake and pretreatment section and then moving to the vacuum degassing, electrochemical and CO<sub>2</sub> separation sections.

### 6.3.1 Seawater Pumping Section

The seawater pumping section includes the liquid pumps required to move the seawater stream through the main process units and to restore the pressure after vacuum separation stages. In the Aspen Plus flowsheet, four pumps were included: the main seawater intake pump, the ultrafiltration booster pump, the pump upstream of the acidification section and the pump upstream of the regeneration section.

The power requirements of these pumps were obtained directly from the Aspen Plus equipment results. These values reflect the pressure profile adopted in the simulation and the hydraulic assumptions introduced in Chapter 4. Therefore, the pump sizing performed in this section is based on the process-level duty calculated by Aspen Plus, rather than on a detailed mechanical design of each pump.

For the preliminary CAPEX estimation, the pumps were treated as equivalent centrifugal pump units. This assumption was adopted in order to use standard equipment-cost correlations for preliminary process design [26]. In practice, the final selection of the seawater intake pump could require a more specific configuration, such as a vertical or mixed-flow pump, depending on the detailed intake layout, installation depth, material requirements and site-specific hydraulic conditions. These aspects are outside the scope of the present pre-feasibility study.

The purchased cost of each pump was estimated using a standard cost correlation based on the pump power:

$$\log_{10} C_p^0 = K_1 + K_2 \log_{10} \dot{W}_{\text{pump}} + K_3 (\log_{10} \dot{W}_{\text{pump}})^2 \quad (6.5)$$

where  $C_p^0$  is the purchased equipment cost in the reference year of the correlation,  $\dot{W}_{\text{pump}}$  is the pump power and  $K_1$ ,  $K_2$  and  $K_3$  are the correlation coefficients. The purchased cost was then corrected using the corresponding bare-module factor and updated to the selected reference year through the Chemical Engineering Plant Cost Index, as described in the economic methodology section.

The resulting pump CAPEX values are reported in Table 6.3. The values refer to the equipment-level estimate of the pumps included in the Aspen Plus model. They do not include the detailed civil works, offshore intake structures, pipe routing, foundations or installation layout that would be required in a complete engineering design of a seawater intake system.

**Table 6.3:** Preliminary CAPEX estimation for the pumping section.

| Pump         | Function                     | Power<br>kW    | CAPEX<br>\$   | Levelized CAPEX<br>\$ kgCO <sub>2</sub> <sup>-1</sup> |
|--------------|------------------------------|----------------|---------------|-------------------------------------------------------|
| SWPUMP       | Seawater intake pump         | 138.383        | 161675        | 0.0165                                                |
| UFPUMP       | Ultrafiltration booster pump | 65.898         | 98885         | 0.0101                                                |
| ACDPUMP      | Acidification-section pump   | 46.129         | 80141         | 0.0082                                                |
| BASPUMP      | Regeneration-section pump    | 63.444         | 96621         | 0.0098                                                |
| <b>Total</b> | <b>Pumping section</b>       | <b>313.854</b> | <b>437322</b> | <b>0.0445</b>                                         |

The total CAPEX estimated for the pumping section is therefore equal to 437322 \$. Applying the capital recovery factor adopted in this work, the corresponding annualized CAPEX is:

$$CAPEX_{\text{ann,pumps}} = 437322 \cdot 0.10185 = 44541 \text{ \$ yr}^{-1} \quad (6.6)$$

Considering the reference annual CO<sub>2</sub> removal capacity of  $1.0 \times 10^6 \text{ kgCO}_2 \text{ yr}^{-1}$ , the levelized CAPEX contribution of the pumping section is:

$$CAPEX_{\text{lev,pumps}} = \frac{44541}{1.0 \times 10^6} = 0.0445 \text{ \$ kgCO}_2^{-1} \quad (6.7)$$

This contribution refers only to the pumps represented in the Aspen Plus flowsheet. The complete design of the seawater intake system, including civil works, intake structures, foundations and pipe routing, is outside the scope of the base-case CAPEX estimate.

### 6.3.2 Pretreatment Section

The pretreatment section includes the coarse filtration, fine filtration and ultrafiltration units placed upstream of the electrochemical process. In the Aspen Plus flowsheet, these units were represented through simplified process blocks: the coarse and fine filters were modelled as pressure-drop elements, while the ultrafiltration unit was included to account for the additional membrane pretreatment required by the large seawater flow rate. Therefore, the CAPEX estimation of this section required the translation of the Aspen Plus blocks into real pretreatment equipment.

The coarse and fine filtration stages were interpreted as automatic self-cleaning screen filters. Such units are commonly adopted in seawater intake and desalination pretreatment systems to remove suspended solids, debris and particulate matter before downstream membrane units [28, 24]. In the present assessment, one coarse filter and one fine filter were considered in the base-case configuration. Their cost was estimated on the basis of the seawater flow rate treated by the process.

The ultrafiltration stage was treated separately from the coarse and fine filters. Since the UFILT block was represented in Aspen Plus only as a pressure-drop unit, the simulation did not provide a detailed membrane area, module arrangement, backwashing system or cleaning strategy. For this reason, the CAPEX of the ultrafiltration skid was estimated using normalized literature costs expressed per unit of treated-water capacity. This approach was considered more appropriate for a modular membrane system than the use of a generic equipment-cost correlation.

The volumetric flow rate treated by the ultrafiltration section was obtained from the Aspen Plus results:

$$\dot{V}_{\text{UF}} = 1494.48 \text{ m}^3 \text{ h}^{-1} \quad (6.8)$$

which corresponds to a daily treatment capacity of:

$$\dot{V}_{\text{UF,d}} = 1494.48 \cdot 24 = 35867.46 \text{ m}^3 \text{ d}^{-1} \quad (6.9)$$

Literature data for low-pressure polymeric membrane systems report normalized CAPEX values in the range of 156–257 \$ (m<sup>3</sup> d<sup>-1</sup>)<sup>-1</sup> [29]. This interval was adopted to define a low and a high ultrafiltration CAPEX estimate. A reference value of 184 \$ (m<sup>3</sup> d<sup>-1</sup>)<sup>-1</sup> was also considered, consistently with seawater ultrafiltration pretreatment data reported for a large desalination plant [25].

The ultrafiltration CAPEX was calculated as:

$$\text{CAPEX}_{\text{UF}} = \dot{V}_{\text{UF,d}} c_{\text{UF}} \quad (6.10)$$

where  $\dot{V}_{\text{UF,d}}$  is the daily treated-water capacity and  $c_{\text{UF}}$  is the normalized ultrafiltration cost. The resulting values are reported in Table 6.4.

**Table 6.4:** Preliminary CAPEX estimation for the ultrafiltration section.

| Scenario           | UF capacity<br>m <sup>3</sup> d <sup>-1</sup> | Specific CAPEX<br>\$ (m <sup>3</sup> d <sup>-1</sup> ) <sup>-1</sup> | CAPEX<br>\$ | Levelized CAPEX<br>\$ kgCO <sub>2</sub> <sup>-1</sup> |
|--------------------|-----------------------------------------------|----------------------------------------------------------------------|-------------|-------------------------------------------------------|
| Low estimate       | 35867.46                                      | 156                                                                  | 5595324     | 0.570                                                 |
| Reference estimate | 35867.46                                      | 184                                                                  | 6599613     | 0.672                                                 |
| High estimate      | 35867.46                                      | 257                                                                  | 9217938     | 0.939                                                 |

The coarse and fine filtration stages were estimated separately from the ultrafiltration skid. The preliminary CAPEX estimated for each filtration unit was equal to 228951 \$, leading to a total coarse and fine filtration CAPEX of 457902 \$. The corresponding annualized and levelized contributions are reported in Table 6.5.

**Table 6.5:** Preliminary CAPEX estimation for the pretreatment section.

| Equipment item                      | CAPEX<br>\$ | Annualized CAPEX<br>\$ yr <sup>-1</sup> | Levelized CAPEX<br>\$ kgCO <sub>2</sub> <sup>-1</sup> |
|-------------------------------------|-------------|-----------------------------------------|-------------------------------------------------------|
| Coarse filter                       | 228951      | 23319                                   | 0.0233                                                |
| Fine filter                         | 228951      | 23319                                   | 0.0233                                                |
| Total coarse and fine filtration    | 457902      | 46638                                   | 0.0466                                                |
| Ultrafiltration, low estimate       | 5595324     | 569884                                  | 0.570                                                 |
| Ultrafiltration, reference estimate | 6599613     | 672171                                  | 0.672                                                 |
| Ultrafiltration, high estimate      | 9217938     | 938847                                  | 0.939                                                 |

The results show that the ultrafiltration skid is the dominant cost item in the pretreatment section. This is mainly due to the large seawater throughput required by the Direct Ocean Capture process. Although the reference plant removes only 1000 tCO<sub>2</sub> yr<sup>-1</sup>, the low concentration of dissolved inorganic carbon in seawater requires the treatment of approximately 35867 m<sup>3</sup> d<sup>-1</sup> of seawater. As a consequence, the pretreatment section becomes one of the main capital cost drivers of the reference configuration.

Using the reference ultrafiltration estimate, the total pretreatment CAPEX is:

$$CAPEX_{\text{pretreatment}} = 457902 + 6599613 = 7057515 \text{ \$} \quad (6.11)$$

The corresponding annualized CAPEX is:

$$CAPEX_{\text{ann,pretreatment}} = 7057515 \cdot 0.10185 = 718809 \text{ \$ yr}^{-1} \quad (6.12)$$

and the resulting levelized CAPEX contribution is:

$$CAPEX_{\text{lev,pretreatment}} = \frac{718809}{1.0 \times 10^6} = 0.719 \text{ \$ kgCO}_2^{-1} \quad (6.13)$$

This value includes only the filtration and ultrafiltration equipment considered within the Aspen Plus system boundaries. It does not include the detailed design of the seawater intake structure, civil works, membrane replacement, backwashing water management, cleaning chemicals or long-term fouling effects. These aspects would require a more detailed pretreatment design and are therefore considered uncertainty items in the present pre-feasibility assessment.

### 6.3.3 Preliminary Dissolved-Gas Removal Section

The preliminary dissolved-gas removal section is represented in the Aspen Plus flowsheet by the block DAGS1, followed by the vent-gas compressor VENTCOMP and the cooling block VENTCOOL. The purpose of this section is not to recover CO<sub>2</sub>, but to partially remove dissolved non-condensable gases, mainly N<sub>2</sub> and O<sub>2</sub>, before the acidification and CO<sub>2</sub> recovery stages.

For the preliminary equipment interpretation, DAGS1 was treated as an equivalent vertical vacuum flash drum, or gas–liquid separator, operating at the pressure defined in the Aspen Plus model. This interpretation is consistent with the process-level representation adopted in the simulation. The detailed internal design of the separator, including internals, demisting devices and entrainment control, was not explicitly considered.

The preliminary sizing of DAGS1 was based on two criteria: liquid holdup and gas disengagement. The liquid holdup criterion was used to estimate the vessel volume required to accommodate the liquid phase for a specified residence time, whereas the gas-side criterion was used to verify the cross-sectional area required for the separated gas flow. This approach is consistent with standard preliminary gas–liquid separator sizing concepts, where the gas velocity must be sufficiently low to allow liquid droplets to disengage from the gas phase [30].

The liquid volumetric flow rate through DAGS1 was obtained from the Aspen Plus results and is approximately:

$$\dot{V}_{\text{liq,DAGS1}} = 1494.6 \text{ m}^3 \text{ h}^{-1} = 24.91 \text{ m}^3 \text{ min}^{-1} \quad (6.14)$$

Assuming a liquid residence time of 2 min, the required liquid holdup volume is:

$$V_{\text{liq,DAGS1}} = \dot{V}_{\text{liq,DAGS1}} \tau = 24.91 \cdot 2 = 49.82 \text{ m}^3 \quad (6.15)$$

A liquid holdup fraction of 60% was then assumed to convert the liquid holdup volume into the corresponding vessel volume:

$$V_{\text{vessel,DAGS1}} = \frac{V_{\text{liq,DAGS1}}}{0.60} = \frac{49.82}{0.60} = 83.0 \text{ m}^3 \quad (6.16)$$

The gas-side sizing criterion was also checked using the gas volumetric flow rate leaving DAGS1. The vent gas flow rate obtained from Aspen Plus is approximately:

$$\dot{V}_{\text{gas,DAGS1}} = 53.7 \text{ m}^3 \text{ h}^{-1} = 0.0149 \text{ m}^3 \text{ s}^{-1} \quad (6.17)$$

Assuming an allowable superficial gas velocity of 0.30 m s<sup>-1</sup>, the required gas-disengagement area is:

$$A_{\text{gas,DAGS1}} = \frac{\dot{V}_{\text{gas,DAGS1}}}{u_{\text{gas}}} = \frac{0.0149}{0.30} = 0.0497 \text{ m}^2 \quad (6.18)$$

The corresponding gas-side vessel diameter is:

$$D_{\text{gas,DAGS1}} = \sqrt{\frac{4A_{\text{gas,DAGS1}}}{\pi}} = 0.252 \text{ m} \quad (6.19)$$

This value is much smaller than the diameter implied by the liquid holdup requirement. Therefore, the preliminary size of DAGS1 is controlled by the liquid holdup criterion rather than by gas disengagement. The adopted equivalent vessel volume for DAGS1 was consequently set equal to 83.0 m<sup>3</sup>.

**Table 6.6:** Preliminary sizing criteria adopted for DAGS1.

| Sizing criterion  | Basis                                                                  | Result                | Controlling |
|-------------------|------------------------------------------------------------------------|-----------------------|-------------|
| Liquid holdup     | 2 min residence time and 60% liquid holdup fraction                    | 83.0 m <sup>3</sup>   | Yes         |
| Gas disengagement | Vent gas flow rate and 0.30 m s <sup>-1</sup> superficial gas velocity | 0.0497 m <sup>2</sup> | No          |

The CAPEX of DAGS1 was estimated by applying the vessel cost correlation described in the economic methodology section, using the adopted equivalent volume of 83.0 m<sup>3</sup> as the characteristic size parameter [26]. The vent-gas compressor was estimated separately. Since the Aspen Plus power requirement of VENTCOMP is below the typical range of standard compressor cost correlations, a minimum practical package size was adopted for the preliminary CAPEX estimate. This assumption avoids extrapolating the cost correlation to very small powers outside its intended range.

The VENTCOOL block was not assigned a separate CAPEX contribution in the base-case estimate. Its thermal duty is small compared with the cooling duties of the CO<sub>2</sub> conditioning section, and its detailed design was not developed at this level of analysis. Therefore, it is reported as a process requirement, but it is not included as an independent equipment cost item in the base-case CAPEX.

The resulting CAPEX values for the preliminary dissolved-gas removal section are reported in Table 6.7.

**Table 6.7:** Preliminary CAPEX estimation for the dissolved-gas removal section.

| Equipment item | CAPEX<br>\$    | Annualized CAPEX<br>\$ yr <sup>-1</sup> | Levelized CAPEX<br>\$ kgCO <sub>2</sub> <sup>-1</sup> |
|----------------|----------------|-----------------------------------------|-------------------------------------------------------|
| DAGS1          | 974193         | 99223                                   | 0.0992                                                |
| VENTCOMP       | 62261          | 6341                                    | 0.0063                                                |
| VENTCOOL       | –              | –                                       | –                                                     |
| <b>Total</b>   | <b>1036454</b> | <b>105564</b>                           | <b>0.1056</b>                                         |

The adopted cost bases for the equipment items reported in Table 6.7 are summarized as follows. DAGS1 was costed as an equivalent vertical vacuum flash drum with an adopted volume of 83.0 m<sup>3</sup>. VENTCOMP was costed as a vent-gas compressor package using a minimum practical package size. VENTCOOL was considered as a process requirement, but its CAPEX was not included separately in the base-case estimate.

The total CAPEX estimated for the preliminary dissolved-gas removal section is therefore:

$$CAPEX_{\text{DAGS}} = 974193 + 62261 = 1036454 \$ \quad (6.20)$$

The corresponding annualized CAPEX is:

$$CAPEX_{\text{ann,DAGS}} = 1036454 \cdot 0.10185 = 105564 \$ \text{ yr}^{-1} \quad (6.21)$$

and the resulting levelized CAPEX contribution is:

$$CAPEX_{\text{lev,DAGS}} = \frac{105564}{1.0 \times 10^6} = 0.1056 \$ \text{ kgCO}_2^{-1} \quad (6.22)$$

This estimate represents the equipment-level cost required to reproduce the DAGS1 function in the Aspen Plus flowsheet. Detailed vacuum-system design, separator internals, demisters, corrosion allowance and installation details were not included.

### 6.3.4 Electrochemical Section

The electrochemical section was included in the CAPEX assessment as a single economic contribution associated with the combined acidification and regeneration stages. Since ACIDCEL and BASECEL were implemented in Aspen Plus as simplified process blocks, no independent stack-level sizing was performed in this work. Therefore, the electrochemical CAPEX was not estimated through

conventional equipment-cost correlations, but introduced as a specific leveled contribution taken from literature data for the chloride-mediated process [4].

The adopted leveled CAPEX contribution for the combined electrochemical section is:

$$CAPEX_{\text{lev,EC}} = 56 \text{ \$ tCO}_2^{-1} = 0.056 \text{ \$ kgCO}_2^{-1} \quad (6.23)$$

Using the reference annual CO<sub>2</sub> removal capacity of  $1.0 \times 10^6 \text{ kgCO}_2 \text{ yr}^{-1}$ , the corresponding annualized CAPEX is:

$$CAPEX_{\text{ann,EC}} = 0.056 \cdot 1.0 \times 10^6 = 56000 \text{ \$ yr}^{-1} \quad (6.24)$$

The equivalent initial CAPEX was then calculated using the capital recovery factor adopted in this work:

$$CAPEX_{\text{EC}} = \frac{CAPEX_{\text{ann,EC}}}{CRF} = \frac{56000}{0.10185} = 549828 \text{ \$} \quad (6.25)$$

**Table 6.8:** Preliminary CAPEX contribution of the electrochemical section.

| Aspen Plus blocks   | Equivalent<br>CAPEX<br>\$ | Annualized<br>CAPEX<br>\$ yr <sup>-1</sup> | Levelized<br>CAPEX<br>\$ kgCO <sub>2</sub> <sup>-1</sup> |
|---------------------|---------------------------|--------------------------------------------|----------------------------------------------------------|
| ACIDCEL and BASECEL | 549828                    | 56000                                      | 0.056                                                    |

The values reported in Table 6.8 should therefore be interpreted as a preliminary economic contribution assigned to the electrochemical function of the process. They do not include a separate cost breakdown between acidification and regeneration, nor replacement costs for electrodes or membranes, which are considered outside the scope of the present CAPEX estimate.

### 6.3.5 CO<sub>2</sub> Separation and Conditioning Section

The CO<sub>2</sub> separation and conditioning section includes the vacuum separator CO2SEP, the pre-compression cooler CO2COOL, the first knock-out drum KO-DRUM, the CO<sub>2</sub> compressor CO2COMP, the post-compression cooler CO2COOL2 and the second knock-out drum KODRUM2. In the Aspen Plus flowsheet, this section recovers the CO<sub>2</sub> released during acidification, removes most of the water vapour from the recovered gas stream and raises the product pressure to approximately atmospheric pressure.

For the preliminary equipment interpretation, CO2SEP was treated as an equivalent vertical vacuum flash drum or gas-liquid separator. This choice is

consistent with the Aspen Plus implementation of the block as an equilibrium flash operating under reduced pressure. The real equipment was therefore sized using simplified gas–liquid separator criteria, rather than as a packed column or a membrane contactor. As for DAGS1, both liquid holdup and gas disengagement were considered. Gas–liquid separator sizing is commonly based on the need to limit gas velocity in order to allow entrained liquid droplets to separate from the gas phase [30].

The liquid stream leaving CO2SEP is DECARBSW, while the vapour stream is WETCO2. The liquid volumetric flow rate obtained from Aspen Plus is:

$$\dot{V}_{\text{liq,CO2SEP}} = 1495.7 \text{ m}^3 \text{ h}^{-1} = 24.93 \text{ m}^3 \text{ min}^{-1} \quad (6.26)$$

Assuming a liquid residence time of 2 min, the required liquid holdup volume is:

$$V_{\text{liq,CO2SEP}} = \dot{V}_{\text{liq,CO2SEP}} \tau = 24.93 \times 2 = 49.86 \text{ m}^3 \quad (6.27)$$

A liquid holdup fraction of 60% was then adopted to estimate the corresponding vessel volume:

$$V_{\text{vessel,liq,CO2SEP}} = \frac{V_{\text{liq,CO2SEP}}}{0.60} = \frac{49.86}{0.60} = 83.1 \text{ m}^3 \quad (6.28)$$

The gas-side criterion was also evaluated because the vapour stream leaving CO2SEP has a high volumetric flow rate due to the low operating pressure. The WETCO2 volumetric flow rate obtained from Aspen Plus is:

$$\dot{V}_{\text{gas,CO2SEP}} = 10579 \text{ m}^3 \text{ h}^{-1} = 2.939 \text{ m}^3 \text{ s}^{-1} \quad (6.29)$$

Assuming an allowable superficial gas velocity of  $0.30 \text{ m s}^{-1}$ , the required gas-disengagement area is:

$$A_{\text{gas,CO2SEP}} = \frac{\dot{V}_{\text{gas,CO2SEP}}}{u_{\text{gas}}} = \frac{2.939}{0.30} = 9.80 \text{ m}^2 \quad (6.30)$$

The corresponding vessel diameter is:

$$D_{\text{CO2SEP}} = \sqrt{\frac{4A_{\text{gas,CO2SEP}}}{\pi}} = 3.53 \text{ m} \quad (6.31)$$

Assuming a height-to-diameter ratio equal to 3, the equivalent vessel height is:

$$H_{\text{CO2SEP}} = 3D_{\text{CO2SEP}} = 10.6 \text{ m} \quad (6.32)$$

The corresponding gas-side vessel volume is:

$$V_{\text{vessel,gas,CO2SEP}} = A_{\text{gas,CO2SEP}} H_{\text{CO2SEP}} = 9.80 \cdot 10.6 = 103.8 \text{ m}^3 \quad (6.33)$$

The gas-side criterion therefore gives a larger volume than the liquid holdup criterion. For this reason, the adopted equivalent volume of CO2SEP was set equal to 104 m<sup>3</sup>.

**Table 6.9:** Preliminary sizing criteria adopted for CO2SEP.

| Sizing criterion  | Basis                                                                | Result               | Controlling |
|-------------------|----------------------------------------------------------------------|----------------------|-------------|
| Liquid holdup     | 2 min residence time and 60% liquid holdup fraction                  | 83.1 m <sup>3</sup>  | No          |
| Gas disengagement | WETCO2 flow rate and 0.30 m s <sup>-1</sup> superficial gas velocity | 103.8 m <sup>3</sup> | Yes         |

The knock-out drums were sized as equivalent vertical gas–liquid separators. Since the condensed liquid flow rates are small compared with the corresponding gas flow rates, their preliminary sizing was controlled by the gas-disengagement criterion. For KODRUM, the gas stream leaving the first condensation step has a volumetric flow rate of:

$$\dot{V}_{\text{gas,KODRUM}} = 2156.46 \text{ m}^3 \text{ h}^{-1} = 0.5990 \text{ m}^3 \text{ s}^{-1} \quad (6.34)$$

Using the same allowable superficial gas velocity of 0.30 m s<sup>-1</sup>, the required cross-sectional area is:

$$A_{\text{KODRUM}} = \frac{0.5990}{0.30} = 1.997 \text{ m}^2 \quad (6.35)$$

The corresponding diameter is:

$$D_{\text{KODRUM}} = \sqrt{\frac{4A_{\text{KODRUM}}}{\pi}} = 1.59 \text{ m} \quad (6.36)$$

Using a height-to-diameter ratio equal to 3, the vessel height is:

$$H_{\text{KODRUM}} = 3D_{\text{KODRUM}} = 4.78 \text{ m} \quad (6.37)$$

The resulting equivalent vessel volume is:

$$V_{\text{KODRUM}} = A_{\text{KODRUM}} H_{\text{KODRUM}} = 1.997 \cdot 4.78 = 9.55 \text{ m}^3 \quad (6.38)$$

For KODRUM2, the final gas volumetric flow rate is much smaller:

$$\dot{V}_{\text{gas,KODRUM2}} = 67.93 \text{ m}^3 \text{ h}^{-1} = 0.01887 \text{ m}^3 \text{ s}^{-1} \quad (6.39)$$

The corresponding gas-disengagement area is:

$$A_{\text{KODRUM2}} = \frac{0.01887}{0.30} = 0.0629 \text{ m}^2 \quad (6.40)$$

This gives the following vessel diameter:

$$D_{\text{KODRUM2}} = \sqrt{\frac{4A_{\text{KODRUM2}}}{\pi}} = 0.283 \text{ m} \quad (6.41)$$

Assuming again  $H/D = 3$ , the corresponding calculated volume is:

$$V_{\text{KODRUM2}} = A_{\text{KODRUM2}} 3D_{\text{KODRUM2}} = 0.0534 \text{ m}^3 \quad (6.42)$$

This calculated volume is very small for industrial equipment cost estimation. Therefore, a minimum practical vessel volume of  $1.0 \text{ m}^3$  was adopted for KODRUM2.

**Table 6.10:** Preliminary sizing of the knock-out drums in the  $\text{CO}_2$  conditioning section.

| Equipment | Gas flow rate<br>$\text{m}^3 \text{ s}^{-1}$ | Area<br>$\text{m}^2$ | Calculated volume<br>$\text{m}^3$ | Adopted volume<br>$\text{m}^3$ |
|-----------|----------------------------------------------|----------------------|-----------------------------------|--------------------------------|
| KODRUM    | 0.5990                                       | 1.997                | 9.55                              | 9.55                           |
| KODRUM2   | 0.01887                                      | 0.0629               | 0.0534                            | 1.00                           |

The CAPEX of CO2SEP, KODRUM and KODRUM2 was estimated using the vessel cost correlation described in the economic methodology section [26]. The CO2COMP cost was estimated using a compressor cost correlation based on the compressor power. In the Aspen Plus results, the  $\text{CO}_2$  compressor requires 16.92 kW. Since this value is close to the lower range of standard compressor cost correlations, a minimum practical package size of 18 kW was adopted for the preliminary CAPEX estimate.

The cooling blocks CO2COOL and CO2COOL2 were not assigned independent CAPEX contributions in the base-case estimate. Their duties were already reported as thermal utility requirements in Chapter 5. A detailed cost estimate for these coolers would require additional assumptions on heat-exchanger type, temperature approach, heat-transfer coefficient and cooling utility configuration. Therefore, they are reported as process requirements, but they are not included as separate equipment cost items in the base-case CAPEX.

The resulting CAPEX values for the  $\text{CO}_2$  separation and conditioning section are reported in Table 6.11.

**Table 6.11:** Preliminary CAPEX estimation for the CO<sub>2</sub> separation and conditioning section.

| Equipment item | CAPEX<br>\$    | Annualized CAPEX<br>\$ yr <sup>-1</sup> | Levelized CAPEX<br>\$ kgCO <sub>2</sub> <sup>-1</sup> |
|----------------|----------------|-----------------------------------------|-------------------------------------------------------|
| CO2SEP         | 1185735        | 120767                                  | 0.1208                                                |
| KODRUM         | 188413         | 19190                                   | 0.0192                                                |
| KODRUM2        | 54001          | 5500                                    | 0.0055                                                |
| CO2COMP        | 62261          | 6341                                    | 0.0063                                                |
| CO2COOL        | —              | —                                       | —                                                     |
| CO2COOL2       | —              | —                                       | —                                                     |
| <b>Total</b>   | <b>1490410</b> | <b>151798</b>                           | <b>0.1518</b>                                         |

The total CAPEX estimated for the CO<sub>2</sub> separation and conditioning section is therefore:

$$CAPEX_{CO_2, \text{section}} = 1185735 + 188413 + 54001 + 62261 = 1490410 \$ \quad (6.43)$$

The corresponding annualized CAPEX is:

$$CAPEX_{\text{ann}, CO_2, \text{section}} = 1490410 \cdot 0.10185 = 151798 \$ \text{ yr}^{-1} \quad (6.44)$$

and the resulting levelized CAPEX contribution is:

$$CAPEX_{\text{lev}, CO_2, \text{section}} = \frac{151798}{1.0 \times 10^6} = 0.1518 \$ \text{ kgCO}_2^{-1} \quad (6.45)$$

The results indicate that CO2SEP is the dominant cost item in the CO<sub>2</sub> separation and conditioning section. This is mainly due to the large volumetric flow rate of the wet CO<sub>2</sub> stream under deep vacuum conditions, which makes the gas-disengagement criterion controlling for the vessel size. By contrast, the knock-out drums and the CO<sub>2</sub> compressor provide smaller contributions to the levelized CAPEX.

The estimate should be interpreted as a preliminary equipment cost for the simplified Aspen Plus configuration. It does not include a detailed vacuum-system design, demisters, heat-exchanger costs, gas-drying systems, corrosion allowance or final compression for transport and storage.

### 6.3.6 Overall CAPEX Results

The preliminary CAPEX results obtained for the individual equipment sections were combined to estimate the total capital cost of the reference configuration.

The base-case estimate includes the pumping section, the pretreatment section, the preliminary dissolved-gas removal section, the electrochemical acidification and regeneration section, and the CO<sub>2</sub> separation and conditioning section. The costs were estimated using the equipment-costing methodology described in Section 6.1, based on Aspen Plus outputs, equipment-cost correlations and literature-based cost data [26, 27, 29, 4].

For the pretreatment section, the reference ultrafiltration estimate was adopted in the base case. This value corresponds to a specific UF CAPEX of 184 \$ (m<sup>3</sup> d<sup>-1</sup>)<sup>-1</sup>, which lies within the range reported for low-pressure membrane systems and is consistent with seawater ultrafiltration pretreatment data available for desalination applications [29, 25]. The low and high UF cost estimates are then considered separately as a sensitivity range.

The total base-case CAPEX was calculated as:

$$\begin{aligned} CAPEX_{\text{tot}} = & CAPEX_{\text{pumps}} + CAPEX_{\text{pretreatment}} + CAPEX_{\text{DAGS}} \\ & + CAPEX_{\text{EC}} + CAPEX_{\text{CO}_2, \text{section}} \end{aligned} \quad (6.46)$$

Substituting the corresponding values gives:

$$CAPEX_{\text{tot}} = 437322 + 7057515 + 1036454 + 549828 + 1490410 = 10571529 \text{ \$} \quad (6.47)$$

The corresponding annualized CAPEX was calculated using the capital recovery factor adopted in this work:

$$CAPEX_{\text{ann,tot}} = CAPEX_{\text{tot}} CRF \quad (6.48)$$

$$CAPEX_{\text{ann,tot}} = 10571529 \cdot 0.10185 = 1076712 \text{ \$ yr}^{-1} \quad (6.49)$$

Considering the reference annual CO<sub>2</sub> removal capacity of  $1.0 \times 10^6 \text{ kgCO}_2 \text{ yr}^{-1}$ , the total leveled CAPEX is:

$$CAPEX_{\text{lev,tot}} = \frac{1076712}{1.0 \times 10^6} = 1.077 \text{ \$ kgCO}_2^{-1} \quad (6.50)$$

The resulting CAPEX contributions for the base-case configuration are summarized in Table 6.12.

**Table 6.12:** Overall preliminary CAPEX estimate for the base-case configuration.

| Process section                             | CAPEX<br>\$     | Annualized CAPEX<br>\$ yr <sup>-1</sup> | Levelized CAPEX<br>\$ kgCO <sub>2</sub> <sup>-1</sup> | Share<br>%   |
|---------------------------------------------|-----------------|-----------------------------------------|-------------------------------------------------------|--------------|
| Pumping section                             | 437322          | 44541                                   | 0.0445                                                | 4.1          |
| Pretreatment section                        | 7057515         | 718809                                  | 0.719                                                 | 66.8         |
| Preliminary dissolved-gas removal           | 1036454         | 105564                                  | 0.1056                                                | 9.8          |
| Electrochemical section                     | 549828          | 56000                                   | 0.0560                                                | 5.2          |
| CO <sub>2</sub> separation and conditioning | 1490410         | 151798                                  | 0.1518                                                | 14.1         |
| <b>Total</b>                                | <b>10571529</b> | <b>1076712</b>                          | <b>1.077</b>                                          | <b>100.0</b> |

The results show that the pretreatment section is the dominant contributor to the preliminary levelized CAPEX of the reference configuration. This is mainly due to the large seawater flow rate required by the process and to the resulting size of the ultrafiltration system. The CO<sub>2</sub> separation and conditioning section represents the second largest contribution, mainly because of the large wet CO<sub>2</sub> volumetric flow rate produced under deep vacuum conditions. The preliminary dissolved-gas removal section also provides a relevant contribution, whereas the pumping and electrochemical sections contribute less to the total levelized CAPEX in the base case.

The total levelized CAPEX obtained for the base case is equal to 1.077 \$ kgCO<sub>2</sub><sup>-1</sup>. This value should be interpreted as a preliminary equipment-level estimate. It does not include detailed civil works, offshore intake structures, detailed installation design, control systems, contingency, owner costs, membrane replacement, electrode replacement, maintenance, or final CO<sub>2</sub> compression for transport and geological storage. These exclusions are important when comparing the result with more complete techno-economic assessments reported in the literature, such as the BPMED benchmark [22].

Since the ultrafiltration section is the main capital cost driver, the effect of the UF cost assumption was also evaluated. The low, reference and high UF estimates lead to the total CAPEX values reported in Table 6.13.

**Table 6.13:** Effect of the ultrafiltration CAPEX assumption on the total preliminary CAPEX.

| Scenario              | UF specific CAPEX<br>\$ m <sup>-3</sup> d | Total CAPEX<br>\$ | Annualized CAPEX<br>\$ yr <sup>-1</sup> | Levelized CAPEX<br>\$ kgCO <sub>2</sub> <sup>-1</sup> |
|-----------------------|-------------------------------------------|-------------------|-----------------------------------------|-------------------------------------------------------|
| Low UF estimate       | 156                                       | 9567240           | 974425                                  | 0.974                                                 |
| Reference UF estimate | 184                                       | 10571529          | 1076712                                 | 1.077                                                 |
| High UF estimate      | 257                                       | 13189854          | 1343388                                 | 1.343                                                 |

The sensitivity range shows that the total levelized CAPEX varies from 0.974 \$ kgCO<sub>2</sub><sup>-1</sup> to 1.343 \$ kgCO<sub>2</sub><sup>-1</sup> depending on the assumed ultrafiltration cost. This confirms that pretreatment design is one of the key economic uncertainties of the process. A more detailed evaluation of membrane area, module configuration, recovery, backwashing, cleaning strategy and membrane replacement would therefore be necessary in a future techno-economic assessment.

### 6.3.7 OPEX Estimation

After the preliminary CAPEX estimation, the operating cost of the reference configuration was evaluated. Since the Aspen Plus model provides process-level energy requirements but does not include maintenance, replacement schedules or labour requirements, the OPEX estimate was limited to the electricity-related contribution.

The electricity-related OPEX includes the electrochemical energy requirement, the liquid pumping demand and the gas compression demand. The electrochemical contribution was calculated from the experimental specific energy consumption reported for the chloride-mediated process, while the auxiliary power requirements were obtained from the Aspen Plus equipment results [4].

In the reference case, only the electricity-related OPEX directly associated with the electrochemical section, liquid pumping and gas compression was included. A reference electricity price of 0.10 \$/kWh was assumed. Cooling duties were reported separately and were not converted into equivalent electricity in the base case, in order to avoid introducing an additional assumption on the cooling system configuration and coefficient of performance.

The annual electricity cost was calculated as:

$$OPEX_{el} = E_{el,yr} c_{el} \quad (6.51)$$

where  $E_{el,yr}$  is the annual electrical energy demand and  $c_{el}$  is the assumed electricity price.

The energy contributions considered in the OPEX estimate are summarized in Table 6.14. The total electrical requirement includes the electrochemical cells,

the liquid pumping section and the gas compression section. Cooling duties are reported separately as thermal utility requirements and are not included in the base-case electricity-related OPEX.

**Table 6.14:** Energy requirements considered for the preliminary OPEX estimate.

| Contribution                             | Power<br>kW | Annual energy<br>GWh yr <sup>-1</sup> | Energy type |
|------------------------------------------|-------------|---------------------------------------|-------------|
| Electrochemical cells                    | 87.94       | 0.770                                 | Electrical  |
| Liquid pumping                           | 313.85      | 2.749                                 | Electrical  |
| Gas compression                          | 17.91       | 0.157                                 | Electrical  |
| Total electrical requirement             | 419.70      | 3.677                                 | Electrical  |
| CO <sub>2</sub> pre-compression cooling  | 160.45      | 1.406                                 | Thermal     |
| CO <sub>2</sub> post-compression cooling | 23.66       | 0.207                                 | Thermal     |
| Vent gas cooling                         | 1.40        | 0.012                                 | Thermal     |
| Total cooling duty                       | 185.51      | 1.625                                 | Thermal     |

The total annual electrical energy demand is therefore:

$$E_{\text{el,yr}} = 3.677 \text{ GWh yr}^{-1} = 3.677 \times 10^6 \text{ kWh yr}^{-1} \quad (6.52)$$

Using the reference electricity price assumed in this work:

$$c_{\text{el}} = 0.10 \text{ \$ kWh}^{-1} \quad (6.53)$$

the annual electricity-related operating cost is:

$$OPEX_{\text{el}} = 3.677 \times 10^6 \times 0.10 = 367700 \text{ \$ yr}^{-1} \quad (6.54)$$

Considering the reference annual CO<sub>2</sub> removal capacity of 1000 tCO<sub>2</sub> yr<sup>-1</sup>, the corresponding specific electricity-related OPEX is:

$$OPEX_{\text{el,spec}} = \frac{367700}{1000} = 367.7 \text{ \$ tCO}_2^{-1} \quad (6.55)$$

or, equivalently:

$$OPEX_{\text{el,spec}} = 0.368 \text{ \$ kgCO}_2^{-1} \quad (6.56)$$

The results show that the electricity-related OPEX is dominated by the auxiliary energy demand rather than by the electrochemical cells alone. In particular, liquid pumping represents the largest contribution to the annual electrical consumption.

This result is directly related to the large seawater throughput required by the reference DOC process.

The cooling duties reported in Table 6.14 were not included in the base-case electricity-related OPEX. They were kept as separate thermal utility requirements because their conversion into electricity would depend on the selected cooling technology and on the assumed coefficient of performance.

Therefore, the calculated OPEX should be interpreted as the electricity-related operating cost associated with the electrochemical section, pumping and gas compression. It does not include maintenance, labour, consumable replacement, membrane cleaning, electrode degradation, final CO<sub>2</sub> compression for transport or storage, or CO<sub>2</sub> storage costs.

## 6.4 Comparison with the Stand-Alone BPMED Benchmark

The results obtained for the chloride-mediated Direct Ocean Capture configuration were compared with a stand-alone Bipolar Membrane Electrodialysis (BPMED) benchmark. The comparison was carried out at the same nominal removal capacity adopted in this work, equal to 1000 tCO<sub>2</sub> yr<sup>-1</sup>. This normalization allows the two technologies to be compared at the same annual carbon removal target, while highlighting the differences in process architecture, seawater throughput, energy requirements and preliminary cost drivers.

The BPMED benchmark was selected because it represents one of the most mature electrochemical Direct Ocean Capture approaches reported in the literature. In particular, the stand-alone configuration reported by Digdaya et al. was adopted as the main reference for the techno-economic comparison. In that configuration, the Direct Ocean Capture system is not integrated with an existing desalination plant and must therefore include its own seawater intake, pretreatment, pumping, CO<sub>2</sub> stripping and auxiliary systems.

It is important to note that the comparison is not intended to represent a complete commercial design of either technology. The chloride-mediated process developed in this work is based on a preliminary Aspen Plus model, whereas the BPMED data are taken from literature-based techno-economic estimates. Therefore, the comparison should be interpreted as a process-level benchmark rather than as a definitive cost comparison between two fully engineered industrial plants.

### 6.4.1 Definition of the Benchmark and System Boundaries

The two configurations compared in this section have similar overall process functions, since both are based on seawater acidification, CO<sub>2</sub> extraction and alkalinity

restoration. However, the mechanism used to generate the pH swing is different. In the BPMED process, seawater acidification and alkalization are obtained through bipolar membranes, which dissociate water into  $H^+$  and  $OH^-$  ions. The acidified stream is then sent to a gas–liquid separation unit, typically based on membrane contactors or vacuum stripping, in order to recover  $CO_2$ .

The alkaline stream is used to restore the chemical properties of the treated seawater before discharge. In the chloride-mediated configuration studied in this work, the pH swing is instead generated through reversible electrochemical reactions involving bismuth and silver/silver-chloride electrodes. The Aspen Plus model does not describe the detailed electrochemical cell geometry, electrode kinetics or cyclic operation.

The acidification and regeneration units are represented as black-box stoichiometric blocks reproducing the overall effect of the pH swing on seawater carbonate speciation. The system boundaries adopted for the comparison are summarized in Table 6.15 and Table 6.16.

**Table 6.15:** System boundaries adopted for the comparison between the chloride-mediated model and the stand-alone BPMED benchmark.

| Process area                                       | Chloride-mediated model                                               | Stand-alone BPMED benchmark                            |
|----------------------------------------------------|-----------------------------------------------------------------------|--------------------------------------------------------|
| Seawater intake and pretreatment                   | Included: intake pumping, filtration and ultrafiltration              | Included in the stand-alone balance-of-system estimate |
| pH-swing section                                   | Acidification and regeneration represented by black-box RStoic blocks | BPMED stack with bipolar and ion-exchange membranes    |
| $CO_2$ release                                     | Vacuum flash calibrated to reproduce the target DIC removal           | Gas stripping or membrane contactor under vacuum       |
| $CO_2$ conditioning                                | Cooling, condensate removal and preliminary compression to 1 bar      | Included in the stand-alone auxiliary energy estimate  |
| Final $CO_2$ compression for storage               | Not included                                                          | Not included                                           |
| Long-term degradation and environmental assessment | Not quantified                                                        | Not explicitly resolved in the benchmark comparison    |

**Table 6.16:** Comparison of CO<sub>2</sub> removal capacity, DIC removal efficiency and seawater throughput.

| Parameter                        | Cl-mediated model                                 | BPMED benchmark                                   |
|----------------------------------|---------------------------------------------------|---------------------------------------------------|
| CO <sub>2</sub> removal capacity | 1000 t yr <sup>-1</sup>                           | 1000 t yr <sup>-1</sup>                           |
| CO <sub>2</sub> removal rate     | 114.2 kg h <sup>-1</sup>                          | 114.2 kg h <sup>-1</sup>                          |
| Reference DIC concentration      | 2.0 mmol L <sup>-1</sup>                          | 2.0 mmol L <sup>-1</sup>                          |
| DIC removal efficiency           | 86.83%                                            | 71%                                               |
| Estimated seawater flow rate     | $1.49 \times 10^3$ m <sup>3</sup> h <sup>-1</sup> | $1.83 \times 10^3$ m <sup>3</sup> h <sup>-1</sup> |
| Relative seawater throughput     | Reference                                         | 1.23 times higher                                 |

### 6.4.2 Energy Performance

The energy comparison was carried out by distinguishing between the electrochemical contribution and the auxiliary energy demand. This distinction is essential because the energy consumption reported for electrochemical cells alone does not represent the energy demand of a complete stand-alone Direct Ocean Capture plant.

For the chloride-mediated process, the electrochemical energy consumption was calculated from the experimental value of 122 kJ mol<sup>-1</sup> CO<sub>2</sub> reported for the MIT process. This corresponds to 770 kWh tCO<sub>2</sub><sup>-1</sup>, or 0.770 kWh kgCO<sub>2</sub><sup>-1</sup>. However, once the process is represented as a complete Aspen Plus flowsheet, the auxiliary units become the dominant energy consumers. In particular, liquid pumping requires 2.749 GWh yr<sup>-1</sup>, corresponding to approximately 74.8% of the total electrical demand.

The total electrical requirement of the chloride-mediated configuration is 3.677 GWh yr<sup>-1</sup>, equivalent to 3.677 kWh kgCO<sub>2</sub><sup>-1</sup>. In addition, the model requires a cooling duty of 1.625 GWh<sub>th</sub> yr<sup>-1</sup>. This contribution was not included in the base-case electricity-related OPEX because no specific cooling technology was selected. If mechanical refrigeration were assumed, the cooling duty would have to be converted into equivalent electricity through an assumed coefficient of performance.

For the BPMED benchmark, Digdaya et al. reported an experimental electrochemical consumption of 155.4 kJ mol<sup>-1</sup> CO<sub>2</sub>, equivalent to 0.98 kWh kgCO<sub>2</sub><sup>-1</sup>, and estimated an industrial-scale BPMED energy requirement of 1.22 kWh kgCO<sub>2</sub><sup>-1</sup>. For a land-based stand-alone system, the same study estimated an additional balance-of-system energy demand of 4.6 kWh kgCO<sub>2</sub><sup>-1</sup>, associated with oceanwater intake, pretreatment, pumping, gas stripping and cooling. The total stand-alone energy requirement is therefore:

$$E_{\text{tot,BPMED}} = 1.22 + 4.60 = 5.82 \text{ kWh kgCO}_2^{-1} \quad (6.57)$$

The energy comparison is reported in Table 6.17.

**Table 6.17:** Energy comparison between the chloride-mediated model and the stand-alone BPMED benchmark.

| Energy contribution                           | Chloride-mediated model                                 | BPMED stand-alone                        |
|-----------------------------------------------|---------------------------------------------------------|------------------------------------------|
| Electrochemical energy                        | 0.770 kWh kgCO <sub>2</sub> <sup>-1</sup>               | 1.22 kWh kgCO <sub>2</sub> <sup>-1</sup> |
| Liquid pumping and gas compression            | 2.905 kWh kgCO <sub>2</sub> <sup>-1</sup>               | Included in auxiliaries                  |
| Other stand-alone auxiliary energy            | Not fully included                                      | 4.60 kWh kgCO <sub>2</sub> <sup>-1</sup> |
| Total electrical or main energy demand        | 3.677 kWh kgCO <sub>2</sub> <sup>-1</sup>               | 5.82 kWh kgCO <sub>2</sub> <sup>-1</sup> |
| Cooling duty                                  | 1.625 kWh <sub>th</sub> kgCO <sub>2</sub> <sup>-1</sup> | Included in auxiliaries                  |
| Final CO <sub>2</sub> compression for storage | Not included                                            | Not included                             |

The comparison shows that the chloride-mediated configuration has a lower electrochemical energy requirement than the stand-alone BPMED benchmark. The cell-level contribution is equal to 0.770 kWh kgCO<sub>2</sub><sup>-1</sup> for the chloride-mediated process and 1.22 kWh kgCO<sub>2</sub><sup>-1</sup> for the BPMED benchmark. This difference reflects the lower electrochemical energy consumption reported for the MIT chloride-mediated process.

However, the overall process-level advantage is less pronounced when auxiliary requirements are considered. In the chloride-mediated configuration, the total electrical demand increases to 3.677 kWh kgCO<sub>2</sub><sup>-1</sup>, mainly because of liquid pumping and gas compression. In the BPMED stand-alone benchmark, the total reported energy demand is 5.82 kWh kgCO<sub>2</sub><sup>-1</sup>, including both the electrochemical contribution and the balance-of-system energy demand associated with seawater intake, pretreatment, pumping, gas stripping and cooling.

For this reason, the energy comparison should be interpreted with caution. The chloride-mediated value is derived from the Aspen Plus model developed in this work and includes the auxiliary units explicitly represented in the flowsheet. Nevertheless, the detailed energy requirement of a real vacuum-generation system for the CO<sub>2</sub> separation section is not explicitly included. Conversely, the BPMED

value is taken from a literature stand-alone assessment and includes a broader auxiliary energy contribution. Therefore, the results suggest a potential energy advantage of the chloride-mediated process, but they do not constitute a fully equivalent engineering comparison between two completely designed plants.

The main conclusion of the comparison is that the electrochemical section alone is not sufficient to determine the feasibility of a Direct Ocean Capture process. Both configurations are strongly affected by the need to treat large seawater flow rates, and future improvements should focus not only on reducing the cell energy consumption, but also on hydraulic optimization, pressure-drop reduction, pretreatment integration and the design of the CO<sub>2</sub> recovery section.

### 6.4.3 Effect of Cooling Duty on the Operating Cost

In the base-case OPEX calculation of the chloride-mediated model, only the electricity-related cost associated with the electrochemical section, liquid pumping and gas compression was included. Cooling duties were reported separately because their conversion into electricity depends on the cooling technology selected.

Nevertheless, the cooling requirement is not negligible. The total cooling duty of the reference configuration is 1.625 GWh<sub>th</sub> yr<sup>-1</sup>. If this cooling demand were supplied by a mechanical refrigeration system, an equivalent electrical consumption could be estimated by assuming a coefficient of performance:

$$E_{\text{cool,el}} = \frac{Q_{\text{cool}}}{COP} \quad (6.58)$$

Assuming, as an illustrative case, a coefficient of performance equal to 3, the equivalent electrical consumption becomes:

$$E_{\text{cool,el}} = \frac{1.625}{3} = 0.542 \text{ GWh yr}^{-1} \quad (6.59)$$

Using the reference electricity price of 0.10 \$ kWh<sup>-1</sup>, the corresponding cooling-related OPEX is:

$$OPEX_{\text{cool}} = 0.542 \times 10^6 \cdot 0.10 = 54200 \text{ \$ yr}^{-1} \quad (6.60)$$

Since the reference plant removes 1000 tCO<sub>2</sub> yr<sup>-1</sup>, this corresponds to:

$$OPEX_{\text{cool,spec}} = \frac{54200}{1000} = 54.2 \text{ \$ tCO}_2^{-1} = 0.054 \text{ \$ kgCO}_2^{-1} \quad (6.61)$$

Under this illustrative assumption, the total energy-related OPEX of the chloride-mediated configuration would increase from 0.368 \$ kgCO<sub>2</sub><sup>-1</sup> to approximately 0.422 \$ kgCO<sub>2</sub><sup>-1</sup>. This result confirms that the cooling duty should be considered in future detailed techno-economic assessments, even though it was not included in the base-case electricity-related OPEX.

#### 6.4.4 CAPEX and OPEX Comparison

The preliminary CAPEX estimated for the chloride-mediated configuration is 10.57 M\$, corresponding to an annualized CAPEX of  $1.077 \text{ M\$ yr}^{-1}$  and a levelized CAPEX contribution of  $1.077 \text{ \$ kgCO}_2^{-1}$ . The largest contribution is associated with the pretreatment section, which accounts for 66.8% of the total CAPEX. This result is a direct consequence of the large seawater throughput required by the process.

The electricity-related OPEX of the chloride-mediated model is  $0.368 \text{ \$ kgCO}_2^{-1}$  when only electrochemical energy, liquid pumping and gas compression are included. If the cooling duty is converted into equivalent electricity assuming a COP equal to 3, the energy-related OPEX increases to approximately  $0.422 \text{ \$ kgCO}_2^{-1}$ .

For the BPMED benchmark, Digdaya et al. reported a levelized cost in the range  $1.87\text{--}2.05 \text{ \$ kgCO}_2^{-1}$  for a stand-alone system. This range includes the major cost penalty associated with operating a stand-alone ocean capture system, where seawater intake, pretreatment and outfall infrastructure are not shared with another facility.

The cost comparison is summarized in Table 6.18.

**Table 6.18:** Preliminary cost comparison between the chloride-mediated model and the stand-alone BPMED benchmark.

| Cost indicator                                                   | Chloride-mediated<br>model     | BPMED<br>stand-alone                       |
|------------------------------------------------------------------|--------------------------------|--------------------------------------------|
| Total CAPEX                                                      | 10.57 M\$                      | Not directly reported                      |
| Levelized CAPEX                                                  | $1.077 \text{ \$ kgCO}_2^{-1}$ | Included in levelized cost                 |
| Electricity-related OPEX                                         | $0.368 \text{ \$ kgCO}_2^{-1}$ | Included in levelized cost                 |
| Cooling-related OPEX                                             | $0.054 \text{ \$ kgCO}_2^{-1}$ | Included in auxiliaries                    |
| Partial levelized cost with electrical OPEX                      | $1.445 \text{ \$ kgCO}_2^{-1}$ | $1.87\text{--}2.05 \text{ \$ kgCO}_2^{-1}$ |
| Partial levelized cost with electrical OPEX and cooling scenario | $1.499 \text{ \$ kgCO}_2^{-1}$ | $1.87\text{--}2.05 \text{ \$ kgCO}_2^{-1}$ |

The preliminary cost comparison indicates that the chloride-mediated configuration has a lower partial levelized cost than the stand-alone BPMED benchmark under the assumptions adopted in this work. The partial levelized cost of the

chloride-mediated model is 1.445 \$ kgCO<sub>2</sub><sup>-1</sup> when only the electricity-related OPEX is included, and increases to 1.499 \$ kgCO<sub>2</sub><sup>-1</sup> when the illustrative cooling scenario is considered. The corresponding literature range for the BPMED stand-alone benchmark is 1.87–2.05 \$ kgCO<sub>2</sub><sup>-1</sup>.

However, this result should not be interpreted as proof that the chloride-mediated technology is already economically superior to BPMED. The estimate developed in this work is preliminary and does not include several contributions that may become significant at larger scale, including long-term electrode replacement, silver loss mitigation, maintenance, cleaning systems, membrane or filter replacement, detailed offshore infrastructure, final CO<sub>2</sub> compression for storage, CO<sub>2</sub> transport and sequestration costs. In addition, the real cost of the vacuum system required for CO<sub>2</sub> separation is not explicitly resolved in the Aspen Plus model.

Therefore, the comparison suggests a potential economic advantage of the chloride-mediated concept within the adopted system boundaries, but it does not demonstrate industrial competitiveness. A fully harmonized techno-economic assessment would be required to compare the two technologies on an equivalent design basis.

### 6.4.5 Structural Complexity and Technology Maturity

The structural difference between the two technologies is one of the most important aspects of the comparison. BPMED relies on membrane stacks containing bipolar membranes, ion-exchange membranes and multiple liquid compartments. This configuration benefits from the broader industrial experience available for electrodialysis systems, but it is also affected by membrane cost, membrane fouling, scaling, replacement and long-term degradation.

The chloride-mediated process avoids bipolar membranes and uses reversible electrode reactions to modulate the seawater pH. This can reduce the complexity of the electrochemical stack and avoids the direct dependence on bipolar membrane performance. However, the process introduces different technological uncertainties. The most relevant are electrode stability, silver dissolution, precipitation and fouling under alkaline conditions, and long-term performance during repeated acidification and regeneration cycles.

From a maturity perspective, BPMED remains the more developed benchmark technology. Its operating principle has been demonstrated in several studies and is based on membrane technologies with existing industrial experience. By contrast, the chloride-mediated process is still at an early stage of development and has been demonstrated mainly at laboratory scale. The present Aspen Plus model should therefore be interpreted as a pre-feasibility assessment of a promising concept, rather than as a validated pilot-plant design.

### 6.4.6 Qualitative Assessment and Model Limitations

The comparison between the chloride-mediated configuration and the stand-alone BPMED benchmark shows that the two technologies differ not only in their electrochemical mechanism, but also in the type of components that determine their process performance and scale-up risks. The main qualitative aspects of the comparison are summarized in Table 6.19.

**Table 6.19:** Qualitative comparison between the chloride-mediated configuration and the stand-alone BPMED benchmark.

| Aspect               | Chloride-mediated model                                                       | BPMED stand-alone                                                     |
|----------------------|-------------------------------------------------------------------------------|-----------------------------------------------------------------------|
| pH-swing mechanism   | Reversible Bi/BiOCl and Ag/AgCl electrode reactions                           | Water dissociation in bipolar membranes                               |
| Membrane requirement | Bipolar membranes avoided                                                     | Bipolar and ion-exchange membranes required                           |
| Main cost drivers    | Pretreatment, pumping and CO <sub>2</sub> recovery section                    | Membrane stack, auxiliaries and stand-alone water handling            |
| Main technical risks | Electrode stability, silver dissolution and precipitation during alkalization | Membrane fouling, scaling and long-term membrane replacement          |
| Technology maturity  | Laboratory-scale proof of concept                                             | More mature electrochemical DOC benchmark                             |
| Scale-up uncertainty | High, due to limited validation with real seawater                            | Lower, but still affected by membrane and auxiliary-system costs      |
| Model limitation     | Aspen Plus process-level model; vacuum system not fully resolved              | Literature-based benchmark; detailed plant design not fully available |

The results indicate that the chloride-mediated process has a potential advantage in terms of electrochemical energy requirement and simplified membrane architecture. In particular, the absence of bipolar membranes reduces the dependence on membrane-stack components, which are one of the relevant cost and degradation drivers in BPMED systems. However, this advantage must be interpreted at the process level. The Aspen Plus results show that, in a stand-alone Direct Ocean Capture plant, the total energy and cost performance is strongly influenced by the balance of system, especially seawater pumping, pretreatment and CO<sub>2</sub> recovery.

For this reason, the lower electrochemical energy consumption of the chloride-mediated process cannot be directly translated into an equivalent overall plant advantage. In the reference configuration developed in this work, liquid pumping represents the dominant electrical contribution, while pretreatment is the dominant

CAPEX contribution. This means that future improvements in the electrochemical cell alone would not be sufficient to substantially reduce the overall cost of the process unless they are accompanied by reductions in seawater throughput, hydraulic losses, pretreatment requirements and CO<sub>2</sub> separation energy.

The comparison also highlights the different maturity levels of the two technologies. BPMED is more developed and is supported by broader experimental and techno-economic literature. Its main limitations are related to membrane cost, fouling, scaling and replacement. The chloride-mediated process, instead, is less mature and still affected by important unresolved uncertainties, including electrode lifetime, silver dissolution, precipitation of mineral species under alkaline conditions, fouling during regeneration and long-term cyclic stability.

Several limitations of the present model must therefore be considered when interpreting the comparison. The electrochemical cells were represented as black-box stoichiometric units, without modelling electrode area, current density, overpotentials, ohmic losses, mass-transfer limitations or degradation. The cyclic operation of the original experimental system was replaced by a continuous steady-state equivalent. In addition, the CO<sub>2</sub> recovery section was represented by an equilibrium vacuum flash, rather than by a detailed membrane contactor, vacuum degasser or stripping unit. The energy required by the real vacuum system was not explicitly modelled, and the cooling duty was reported separately from the base-case electricity-related OPEX.

Finally, the economic comparison should be interpreted as preliminary. The leveled cost estimated for the chloride-mediated configuration includes the annualized CAPEX and the electricity-related OPEX of the modelled units, but it does not include long-term electrode replacement, maintenance, silver loss mitigation, detailed offshore infrastructure, final CO<sub>2</sub> compression for transport or storage, or CO<sub>2</sub> sequestration costs. Therefore, the comparison suggests that the chloride-mediated process is a promising alternative to BPMED, but it does not demonstrate its industrial competitiveness. Further experimental validation and more detailed process modelling are required before definitive conclusions on scale-up feasibility can be drawn.

# Conclusions

The present thesis assessed the preliminary feasibility of an emerging Direct Ocean Capture process based on the chloride-mediated electrochemical pH swing proposed by Kim et al. The objective was not to demonstrate the industrial viability of the technology, but to translate the available laboratory-scale results into a process-level model and to evaluate the main implications of a pilot-scale implementation.

The study was developed starting from the definition of a reference case with a nominal capacity of  $1000 \text{ tCO}_2 \text{ yr}^{-1}$ . The process was represented as an equivalent continuous steady-state configuration and implemented in Aspen Plus. The ELECNRTL property method was adopted to describe the aqueous electrolyte system, while the electrochemical acidification and regeneration stages were modelled as process-level stoichiometric blocks. The  $\text{CO}_2$  separation section was represented through a vacuum flash calibrated to reproduce the reference DIC removal efficiency reported in the experimental study.

The Aspen Plus model reproduced the target carbon removal performance with good consistency. The final  $\text{CO}_2$  product stream contained  $2.595 \text{ kmol h}^{-1}$  of  $\text{CO}_2$ , corresponding to  $114.20 \text{ kg h}^{-1}$ . The overall dissolved inorganic carbon recovery was equal to 86.83%, in close agreement with the reference value of 87%. This result confirms that the adopted modelling approach is consistent with the design basis of the reference case.

The energy analysis showed that the electrochemical energy consumption alone does not represent the full process energy demand. The electrochemical section required 87.94 kW, corresponding to  $770.0 \text{ kWh tCO}_2^{-1}$ . However, once the auxiliary electrical requirements associated with seawater pumping, vacuum operation, dissolved-gas removal and  $\text{CO}_2$  compression were included, the total electrical demand increased to 419.70 kW, equal to  $3675.1 \text{ kWh tCO}_2^{-1}$ . This highlights one of the main findings of the work: at process scale, the management of large seawater flow rates becomes a dominant factor in the overall performance of Direct Ocean Capture systems.

A preliminary economic assessment was then carried out by translating the Aspen Plus flowsheet into real process equipment. The total preliminary CAPEX of the chloride-mediated configuration was estimated at 10.57 M\$, with an annualized

CAPEX of 1.077 M\$ yr<sup>-1</sup>. The pretreatment section was identified as the main capital cost driver, accounting for approximately 66.8% of the total CAPEX. This result is directly related to the large seawater throughput required by the process and confirms the importance of water handling and pretreatment in future scale-up studies.

The reference configuration was also compared with a stand-alone BP MED benchmark. The chloride-mediated process showed a lower total electrical consumption than the selected BP MED case, mainly due to the lower electrochemical energy requirement reported for the MIT process. The partial levelized cost of the chloride-mediated model was estimated between 1.445 and 1.499 \$ kgCO<sub>2</sub><sup>-1</sup>, depending on whether the illustrative cooling contribution was included, compared with a range of 1.87-2.05 \$ kgCO<sub>2</sub><sup>-1</sup> for the stand-alone BP MED benchmark. Nevertheless, this comparison should be interpreted as preliminary, since the two technologies differ significantly in maturity, available data and unresolved scale-up aspects.

Overall, the results suggest that the chloride-mediated electrochemical DOC process is a promising concept for further investigation, but its feasibility remains strongly dependent on issues that are not yet resolved experimentally. The main uncertainties concern long-term electrode stability, silver dissolution, mineral precipitation during alkalization, operation with real seawater, vacuum-system design, CO<sub>2</sub> separation efficiency and maintenance requirements.

Future work should therefore focus on experimental validation with natural seawater, detailed modelling of the electrochemical cells, assessment of electrode lifetime and replacement, and improved design of the CO<sub>2</sub> separation and vacuum sections. A more complete techno-economic assessment should also include maintenance costs, consumables, final CO<sub>2</sub> compression, transport and storage, as well as environmental impacts related to seawater intake and discharge. These steps are necessary to determine whether the chloride-mediated process can evolve from a promising laboratory-scale concept into a technically and economically viable Direct Ocean Capture technology.

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