A Rigorous Integrated Approach to Model Electrochemical Regeneration of Alkaline CO2 Capture Solvents

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Abstract

This work develops a rigorous model for electrochemical regeneration in Aspen Custom Modeler (ACM), designed to seamlessly integrate into ASPEN Plus, allowing to model complete carbon dioxide (CO2) capture – electrochemical regeneration cycles on a single modelling platform. The modelling of CO2 electrochemical cells has gained significant attention in CO2 capture and utilization processes. This emphasizes the importance of modelling in driving the progress of CO2 electrochemical cells which combines absorption by alkaline solvents and electrochemical solvent regeneration. In such process, potassium hydroxide (KOH, or other metal hydroxides) is used as a solvent for CO2 capture. This process involves a series of chemical reactions that result in the formation of potassium carbonate (K2CO3) and potassium bicarbonate (KHCO3). After CO2 is captured through absorption, the K2CO3­/KHCO3 solution is directed towards the regeneration cell where an electrochemically driven pH swing takes place facilitating the desorption of CO2. The cell’s primary objective is to lower the pH of the solution by generating protons at the anode, thereby moving its chemical equilibrium towards carbonic acid. Given the limited solubility of CO2 in water, it desorbs once it reaches saturation. The residual solution can be reclaimed in the cathode compartment and recycled. Electrochemistry models are currently unavailable in popular simulation software like ASPEN Plus, thus making the development of integrated process models, in this case for CO2 capture, more challenging. Here, we introduced a rigorous model to be applied in ACM/ASPEN Plus software to simulate the CO2 regeneration process. The model’s validity was assessed against experimental measurements. Following this validation, the model was subsequently employed to design pilot plant campaigns for the Horizon 2020 project [ConsenCUS](http://www.consencus.eu).

**Keywords**: CO2 capture, electrochemical cell, ConsenCUS, absorption, ASPEN.

* 1. Introduction

Human actions are a key driver of global warming and its resulting impacts, thus necessitating urgent action to address the current climate crisis. The significant increase in the global average surface temperature by more than 1°C from 1880 to 2012 unequivocally indicates the effect of anthropogenic climate change. This rise in temperature has substantial negative consequences, underscoring the need to decrease carbon emissions and seek innovative solutions. The vital importance of sustainable solutions to counteract the increase in CO2 emissions has stimulated research into groundbreaking technologies for effective CO2 capture, utilization, and storage. Of these, absorption in alkaline solutions coupled with electrochemical regeneration processes may prove relevant, as the leverage electricity-based regeneration while mitigating harmful emissions from, e.g., amine-based processes. Recently, the modelling of electrochemical cells is getting considerable noticed in CO2 capture and utilization processes (Abdin et al., 2015, Ali and Kwabi, 2022, Seo and Hutton, 2023). Sabatino et al. (2020) introduced a simplified equilibrium model in MATLAB for a bipolar membrane electrodialysis regenerator for a direct air capture process. Shu et al. (2020) investigated the energetic requirements of CO2 capture using a spent alkaline solution. This study introduces a fully developed model for electrochemical regeneration specified in Aspen Custom Modeler (ACM), integrated into an ASPEN Plus flowsheet. The primary objective was to create a unified platform that models complete CO2 capture and electrochemical regeneration cycles, with an emphasis on integrating electrochemical unit operations into larger process models.

* 1. Model development

The CO2 capture process is based on alkaline absorption and electrochemical regeneration as shown in Figure 1. Potassium hydroxide (1M KOH) is used as solvent due to its ability to react with CO2, forming a potassium carbonate/bicarbonate solution (K2CO3/KHCO3) through a selective chemical reaction. Aspen Plus commercial software was utilized to design the absorption column with the primary aim of constructing a model that describes the operation of pilot plants. For the system design, we used the Electrolyte-NRTL thermodynamic property method from the Aspen Plus, which was re-regressed inhouse. The equilibrium reactions’ chemistry and kinetics were then modified according to Rastegar & Ghaemi’s work (2022).



Figure 1- Schematic of the CO2 capture process based on alkaline absorption and electrochemical regeneration. The configuration includes a recycle over the absorber to allow achieving higher solvent loading.

The absorber was simulated in ASPEN Plus with an effective packing height of 12 m and a diameter of 0.6 m, while the packing void fraction and the surface area were set equal to 0.9 and 200 m2/m3 respectively, in line with the design of the pilot plant absorber. Cement plant flue gas with a CO2 concentration of 18% was used in the simulation.

The regeneration unit includes two stacks of 126 bipolar membrane electrodialysis cells, where the solution from the absorber experiences a pH swift to facilitate the desorption of dissolved CO2. The aim is to decrease the pH of the solution by introducing protons to the solution, resulting in a change in the equilibrium state. Due to the low solubility of CO2 in water, the CO2 will degasify from the solution once it reaches its saturation point. Most of the CO2 will therefore be desorbed in a flash drum and can be sent for further processing. The remaining solution can be recovered in the cells’ cathode compartments and be recycled to the absorber. As this is a novel technology no suitable models for this process exist in ASPEN Plus. Therefore, we implemented a bespoke mathematical model in Aspen Custom Modeller to represent the regeneration unit.

The rich solvent from the absorber consists of water, dissolved carbon ions, potassium ions, plus protons and hydroxides. The series of homogeneous equilibrium reactions between the carbon ions and the water dissociation reaction results in a buffer system process as follows:

|  |  |
| --- | --- |
|  | (1) |
|  | (2) |
|  | (3) |

where and denote the equilibrium constants of reaction equations see above; is the equilibrium constant for the water dissociation reaction. , and . These Equations show that the carbon ion distribution depends on the pH. The equilibrium reactions determine the system composition in the acidifying compartment of the BPMED cells as well as in the cathode compartment. Since the potassium cations will transfer through the membrane there will be a concentration gradient along the acidifying compartment with the outlet concentration being lower than the inlet concentration. This change in the longitudinal direction has not been modelled in detail yet. The potassium inlet concentration is equal to the absorber potassium concentration. Its outlet concentration depends on the applied current density.

In principle, both and cations migrate through the membrane for the sake of charge neutrality and electrical circle completion. It has been reported by several studies that transportation is more hindered, and thus the transfer rate of is much smaller compared with the anodic generation and cathodic consumption rate (Zhang et al., 2019). This means that the cations with higher concentrations (here, K+) transfer transfer more predominantly (Cao et al., 2009) and strongly impede transportation across the membrane (Chae et al., 2008).

The Nernst-Planck equations for the flux (mol s-1 m-2) describes the movement of ions across the membrane:

|  |  |
| --- | --- |
|  | (4) |
|  | (5) |

where is flux of protons (mol m-2 s-1); a denotes ratio between diffusivities of protons and metal ions; D is diffusivity coefficient of metal ion inside the membrane; is total cation concentration inside membrane (also called fixed charge density); is electric potential; x is position inside the membrane; fK+ is concentration fractions of K+; and fH+ is concentration fraction of H+.

Furthermore, the total current density must satisfy the ionic current density through the membrane:

|  |  |
| --- | --- |
|  | (6) |

where F is Faraday constant equals to 96485 C mol-1.

The flux of CO2 produced (i.e., the amount of CO2 produced per unit of membrane area), or the production rate can then be derived from the following equation:

|  |  |
| --- | --- |
|  | (6) |

where *Q* is the rich solvent flow rate and *Aa* stands for the membrane area.

A set of Key Performance Indicators (KPIs) specific to the CO2 capture process have been presented within this framework. These KPIs play a pivotal role in evaluating the operational effectiveness, efficiency, and overall performance of the ConsenCUS CO2 capture approach. The efficiency of CO2 capture by the absorber was determined using the following equation:

|  |  |
| --- | --- |
|  | (8) |

where and represent the mole fractions of CO2 in the gas stream at the absorber's inlet and outlet, respectively.

In electrochemical regeneration part, the calculations were performed to determine the specific energy consumption (expressed in GJ per ton of CO2) and CO2 production rate.

|  |  |
| --- | --- |
|  | (9) |

where is the stack voltage , is the current density (A/m2), is the active membrane area (m2), and is the measured CO2 gas flow rate produced in the regeneration cell. It's worth mentioning that we employed two stacks consisting of 126 pairs of cells for each in the regeneration unit for the base case scenario (one stack (A) is shown in Figure 1). Additionally, the process incorporates a recycle stream that circulates from the rich solvent back to the lean solvent within the absorber unit (as shown in Figure

* 1. Results and discussion

The validity for electrochemical regeneration model was assessed against experimental measurements as shown in Figure 2. As can be seen from Figure 2, the model predictions for CO2 production at various current densities, flow rates and rich carbon loadings are compatible with experimental data. The prediction of energy consumption is more scattered (while the trend seems to be predicted well), explained by cell inefficiencies not included in the mathematical model (especially at low current densities).

|  |  |
| --- | --- |
| A diagram of a graph  Description automatically generated | A diagram of a graph  Description automatically generated with medium confidence |

Figure 2- Predicted desorbed CO2 (mol/m2s) and SEEC (kJ/mol) for electrochemical regeneration of CO2 loaded aqueous KOH versus experimental measurements.

To evaluate the performance of the whole CO2 capture unit, we opted to explore various parameter ranges and further refined our analysis using the insights gained from Figure 3. By narrowing down our focus within these selected ranges, we can investigate the regeneration unit impact on the overall efficiency of the CO2 capture process. We selected a specific range for the pilot plant solvent flow rate, ranging from 1000 to 1200 kg/hr, and for the flue gas flow rate spanning from 60 to 80 m3/hr (without recycle ratio, RR=0). The results are shown in Figure 3.

|  |  |
| --- | --- |
|  |  |
| (a) | (b) |
|  |
| (c) |

Figure 3- The relation between specific energy consumption as a function of current density and capture efficiency where lean solvent flow rate is 1000 to 1200 kg/hr and gas flow rate is 60 to 80 m3/hr (no recycle ratio).

The results show that to achieve both high capture efficiency and effective CO2 desorption, the regeneration unit should maintain a current density of 400-500 A/m2 (with one stack) for the investigated of LG ratios. When reducing the rich solvent flow rate (around 700 kg/hr), a strategic approach was employed. Specifically, we maintained a constant lean solvent flow rate of 700 kg/hr while systematically varying the recycle ratio (RR) from 0 to 0.6. The figures show there is a strong correlation between capture efficiency and the absorber's operational parameters, particularly the gas and lean solvent flow rates. However, for achieving CO2 desorption in the regeneration unit, additional factors come into play. To enable efficient CO2 desorption during the regeneration process, conditions must be met including a higher current density, a lower rich solvent flow rate, an increased lean solvent flow rate, and high rich solvent loading.

* 1. Conclusions

The conclusion drawn is that there is a strong correlation between capture efficiency and the operational parameters of the absorber, particularly the gas and lean solvent flow rates. However, achieving CO2 desorption during the regeneration process requires additional considerations. Efficient CO2 desorption and capture efficiency are dependent on specific conditions, including:

• Higher current densities leading to more CO2 desorbed and lower energy consumption.

• If the rich solvent flowrate is limited (e.g., when only one stack is used), increased absorber recycling is needed to ensure sufficient solvent flow to the absorber top.

• Ensuring high rich solvent loading is key.

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