# Electrochemically-Mediated Amine Regeneration in $CO_2$ Scrubbing Processes

## primary project goal

The Massachusetts Institute of Technology (MIT) advanced a novel carbon dioxide ($CO_2$) capture technology using traditional amine-based solvents, but with the key innovation of using electrochemical regeneration of the solvent instead of conventional thermal regeneration. By utilizing cost-effective reduction/oxidation of metal ions to electrochemically enable the capture and release of $CO_2$ by traditional amine sorbents and thereby eliminating the demand for steam characteristic of conventional amine regeneration technology, the parasitic power requirement for operating the process was markedly less than that of conventional methods. This enabled substantial savings in the cost of electricity (COE) for carbon capture process scenarios, with promise to meet programmatic U.S. Department of Energy (DOE) carbon capture goals.

## technical goals

- Develop an optimized electrochemical cell configuration/design and size, allowing best efficiency and cost performance for scalable carbon capture processes for commercial-scale coal-fired plants.
- Validate system using electrochemically mediated amine regeneration in a $CO_2$ scrubbing cycle for capture of at least 90% of $CO_2$ from coal-derived flue gas while demonstrating significant progress toward achievement of the DOE target of less than 35% increase in levelized COE (less than $40/tonne $CO_2$).
- Reduce energy requirements 20–40% relative to that of baseline monoethanolamine (MEA) capture. Achieve specific regeneration energy of 0.91 gigajoules (GJ)/tonne $CO_2$.
- Demonstrate electrochemical cell stability over 15 days continuous operation, at simulated flue gas flow rate enabling capture of 0.01 kg $CO_2$ per day.

## technical content

MIT termed their technology as Electrochemically Mediated Amine Regeneration (EMAR). In conventional amine regeneration-based capture processes, a standard amine solvent such as MEA is contacted in countercurrent flow with $CO_2$-containing flue gas in an absorption column at relatively low temperature (less than 60°C). At lower temperatures, $CO_2$ readily reacts with the amine forming an amine-$CO_2$ complex, and given suitable contact time and solvent flow in the absorption column, high levels of $CO_2$ removal (greater than 90%) can be attained. The rich amine solvent (containing elevated levels of absorbed $CO_2$) exiting the absorber column is preheated in a countercurrent heat exchanger and introduced into the desorber column, where it is further heated with low-pressure steam withdrawn from the power plant's steam cycle, to reach temperatures greater than 110°C. At elevated temperatures, the $CO_2$ is released from the solvent as a relatively pure stream of $CO_2$ that can be recovered. Hot lean solvent is cooled and returned to the absorption column. This conventional thermal regeneration-based process is depicted in the top half of Figure 1.

### program area:
Point Source Carbon Capture

### ending scale:
Laboratory Scale

### application:
Post-Combustion Power Generation PSC

### key technology:
Solvents

### project focus:
Electrochemical Regeneration of Amine Solvents

### participant:
Massachusetts Institute of Technology

### project number:
FE0026489

### predecessor projects:
N/A

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### partners:
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### start date:
08.01.2017

### percent complete:
100%

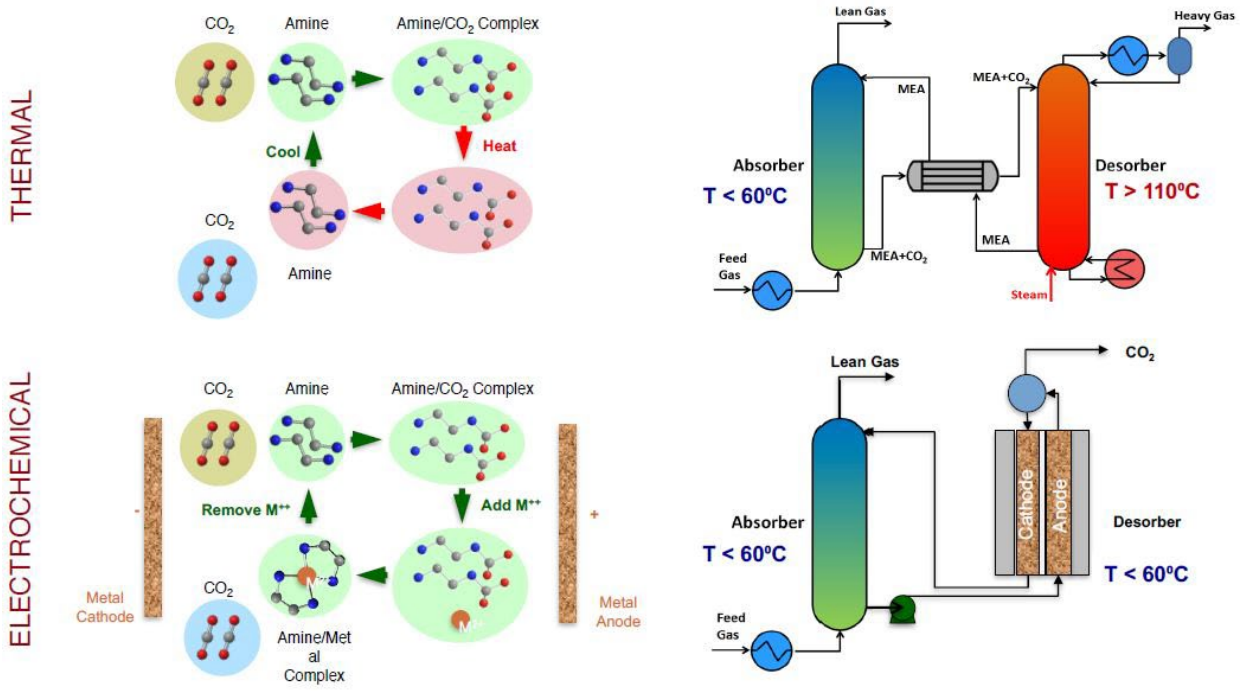



**Figure 1: Electrochemically mediated versus thermal amine regeneration.**

In EMAR (depicted in the bottom half of Figure 1), the process used the same type of absorption column and operating conditions therein. However, the rest of the process was significantly different. Instead of regenerating the rich solvent by increasing its temperature, the solvent passed sequentially through the anodic and cathodic sides of an electrochemical cell. On the anodic side, certain metal ions enter solution and react with the amine/$CO_2$ complexes in the rich solvent. If the metal ions have sufficiently strong binding with the amines, they displace the $CO_2$ and cause it to be liberated in pure gaseous form, enabling its separation. On the cathodic side, the amine metal compound remaining behind is stripped of the metal ions, resulting in lean amine solvent ready to return to the absorber. Temperature remains essentially constant throughout the process, eliminating heat exchange operations and their associated energy losses and capital costs.

Because the EMAR process requires only a limited amount of electrical power to operate the electrochemical processes in the cells, it avoids the need to use steam withdrawn from the power plant's steam cycle, minimizing parasitic energy consumption. This is depicted in Figure 2, which compares the amounts of $CO_2$ capture work (units of kilojoule [$kJ_e$]/mol $CO_2$ captured) associated with the EMAR system, and those of comparative thermal amine systems. Note the EMAR system advantage in respect of steam withdrawals.

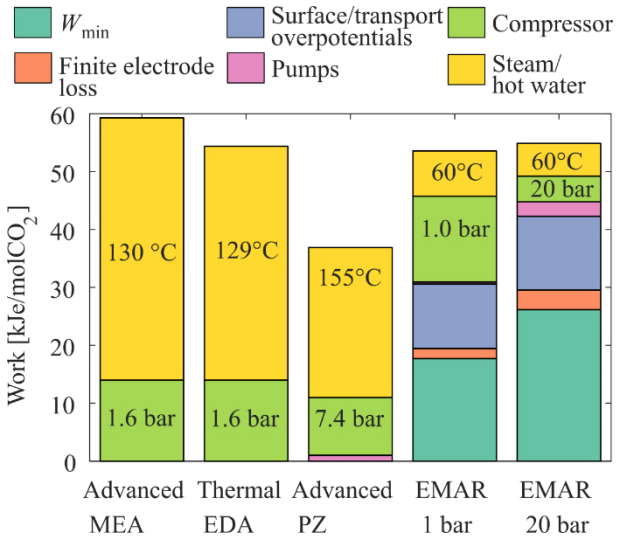



**Figure 2: Comparison of capture work of thermal amine systems and EMAR systems.**

This process concept has been proven at lab-scale, and ongoing work has been refining/optimizing the technology in terms of optimal selection of amine and metal ions, improving electrochemical kinetics, and optimizing cell design, as discussed below.

**Amine Selection**—Binding energies of metal ions with amines are specific to the amine. The binding energies must be strong enough to overcome the amine/$CO_2$ complexation, but higher binding energies demand high power consumption in the electrochemical cell to remove metal ions from the amine/metal complexes. Therefore, amine selection is important in optimizing the process. Adequate amine stability in the process is required. Candidate amines evaluated have included the following:

- MEA
- Diethanolamine (DEA)
- Diethylenetriamine (DETA)
- 2-Amino-2-methyl-1-propanol (AMP)
- Ethylenediamine (EDA)
- Pentamethyldiethylenetriamine (PMDTA)
- Aminoethylethanolamine (AEEA)
- Triethylenetetramine (TETA)
- Piperazine (PZ)

**Metal Ions**—Ion species, including $Co^{2+}$, $Fe^{3+}$, $Fe^{2+}$, $Cr^{2+}$, $Cu^{2+}$, $Zn^{2+}$, and $Ni^{2+}$, have been evaluated as possibilities for the optimal choice for metal/amine complex according to the following essential criteria:

- No precipitation in alkaline solvent.
- Redox active on metal electrode.
- Stability.

Screening of amine/metal complexes considering the candidates above has been performed. The screening methodology considered metal/amine stability in EMAR operating conditions, measurement of $CO_2$ capacity, testing of electrochemical reversibility, and validation of the $CO_2$ separation via electrolysis in batch reactors. Via the stability measurement, MIT concluded that only copper (Cu), zinc (Zn), and nickel (Ni) are plausible candidates to form metal-ligand complexes using off-the-shelf aqueous amine solvents. Nevertheless, only Cu-EDA can be modulated with electrochemical methods without incurring hydrogen evolution (i.e., water splitting). Therefore, MIT concluded that Cu-EDA is the most suitable candidate to be integrated into the envisioned EMAR process.

**Electrochemical Kinetics**—Rapid reaction rates of the complexes in the electrochemical cells are needed to accommodate the high solvent throughputs typical of large-scale post-combustion capture process scenarios. The EMAR cathode ideally operates in the absence of $CO_2$, but in practice $CO_2$ is present and tends to hinder the kinetics. Chlorides in solution have been found to improve performance significantly.

MIT investigated the thermodynamic potential of Cu-EDA and provided detailed speciation modeling of the Cu-EDA-water ($H_2O$) electrolyte. Results are informing modeling of the EMAR process, which will enable estimates of the energy consumption of an EMAR process in context of a post-combustion carbon capture cycle. The kinetics of the electrochemical reactions have been examined via deposition and dissolution experiments performed with rotating disk electrodes. The cathodic deposition of Cu is the slower process of the two Faradaic reactions and would require higher overpotential to drive out the desired reaction rate (i.e., current density). Suitable electrolyte combinations (with supporting salt) to decrease ohmic resistances and to minimize unwanted reactions have been identified. Both the Cu-EDA-$H_2O$-sodium (Na)-sulfate ($SO_4$) and Cu-EDA-$H_2O$-Na-chloride (Cl) systems were identified as stable electrolyte formulations. These electrolyte combinations have been further implemented in a bulk electrolysis setup that validates the electrochemical-thermal separation of $CO_2$. Results from systematic study and experimental validation of the $CO_2$ solubility constants have aided ongoing revision/improvement of the proposed thermodynamic cycle.

**Cell Design**—Ongoing work is optimizing cell architectures for fluid flow configuration and operational efficiency. Because $CO_2$ bubbles are formed in the cells, the design needs to efficiently accommodate removal of the gas. Prototype architectures are being developed for continuous $CO_2$ gas removal by utilizing gas/liquid separation membranes. In addition, cell stacking strategies to optimize volumetric efficiency and fluid flow will be investigated. Figure 3 gives an idea of the present configuration of cell engineering, showing metallic electrodes, channels, seals, etc. Figure 4 depicts a cell stacking concept.

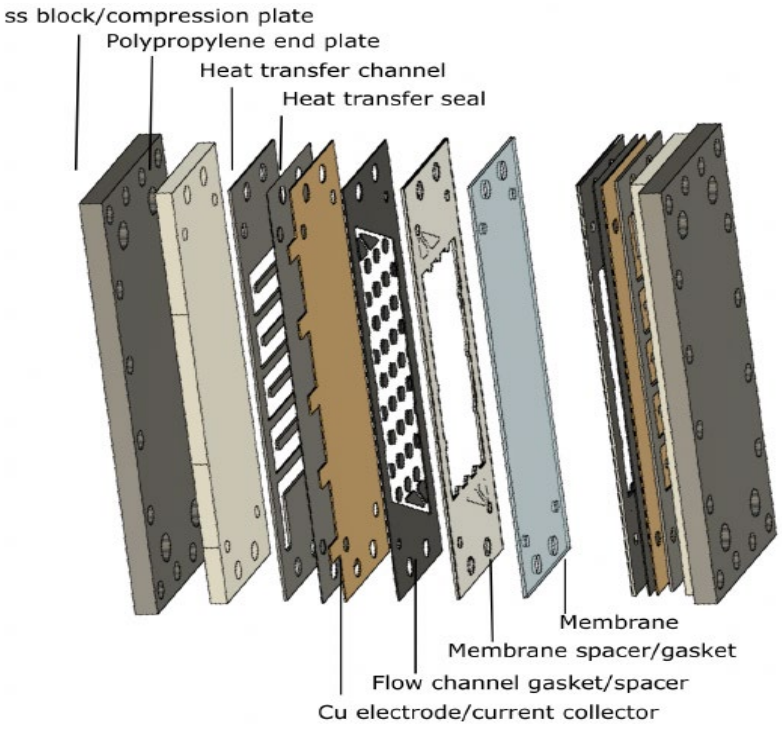



Figure 3: Electrochemical single-cell engineering.

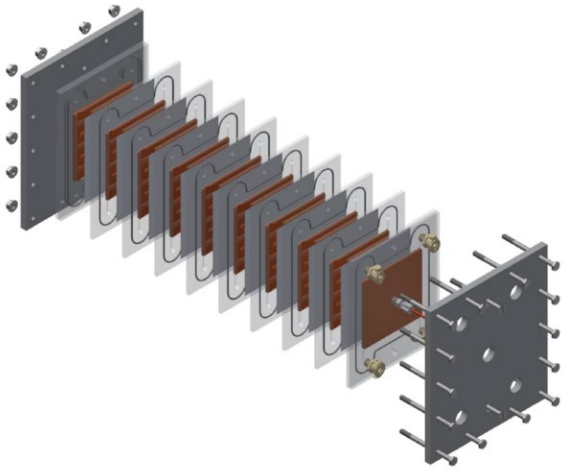


Figure 4: Cell stacking.

**Process and Costs**—MIT has created a process model accounting for all process unit operations (e.g., absorbers, heat exchangers, compressors), as well as additional energy efficiency losses (e.g., kinetic overpotentials) associated with an EMAR system in a full-scale power plant context. Figure 5 depicts the flowsheet for this model.

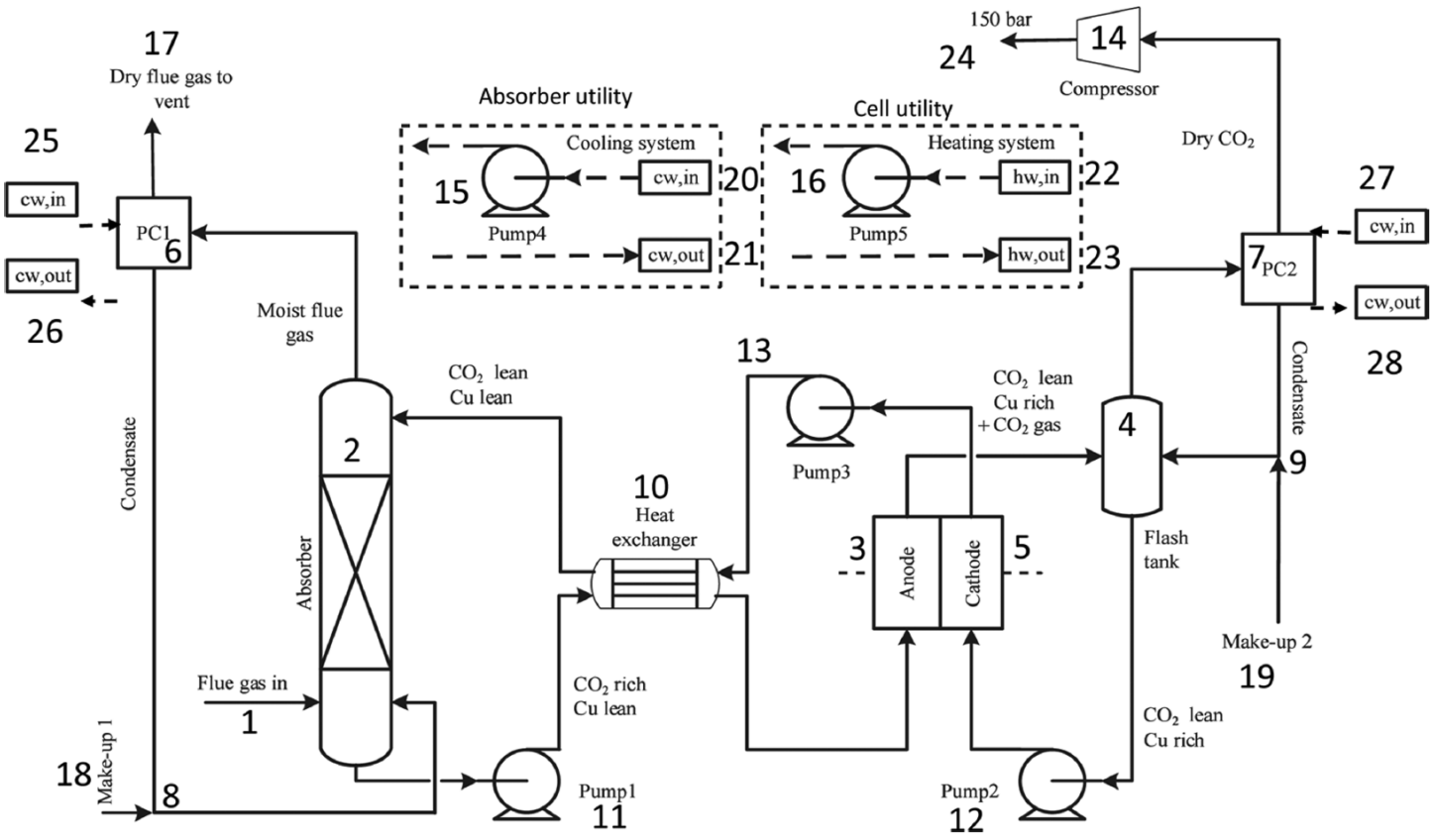
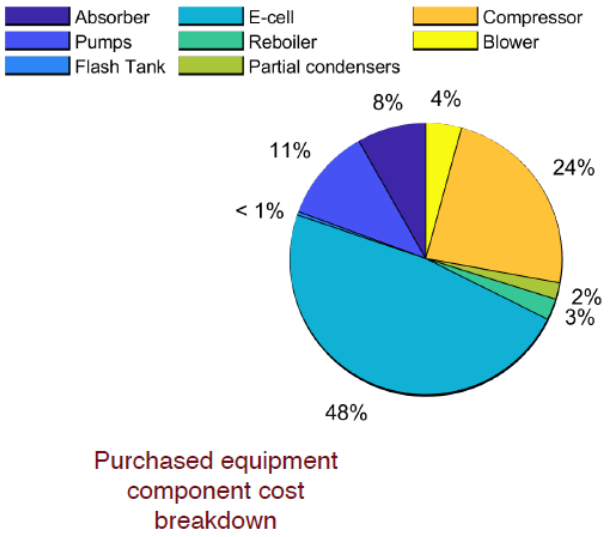



**Figure 5: Detailed flowsheet simulated for EMAR process for carbon capture. Heat exchanger (#10) included for cases where heat recovery is necessary when desorption temperature is high in the stripping section. 1: flue gas source; 2: absorber; 3: anode; 4: flash tank; 5: cathode; 6 and 7: partial condenser; 8 and 9: mixers; 10: heat exchanger;11−13: pump; 14: compressor; 15 and 16: utility pump; 17: flue gas vent; 18 and 19: makeup streams; 20, 21, and 25−28: cold water source and sink; 22 and 23: hot water source and sink; and 24: compressed $CO_2$. (Int. J. Greenhouse Gas Control 2019, 82, 48−58)**

A range of operating conditions and operation schemes were varied parametrically to identify reasonable overall energetics in the EMAR system process. Interesting findings of the process simulations include the realization that net energy demands can be significantly reduced if waste heat is available at temperatures below 90°C, and that the EMAR process is able to desorb $CO_2$ at pressures up to 20 bar with negligible additional energy penalty. Preliminary cost analysis of a full-scale EMAR process indicates a cost of around $60 per tonne of $CO_2$ avoided ($40 per tonne of $CO_2$ captured) in capture from post-combustion flue gas from a 550-megawatt (MW) coal-fired power plant. It is postulated that further reduction in cost should emerge from advanced process design, process optimization, and improved solvent formulation.

MIT has preliminary estimates of capital and operating costs of an EMAR system, as well as comparisons to baselines. Figure 6 shows the expected breakdown of equipment costs and offers COE comparisons to a no-capture case and conventional amine-based capture cases.



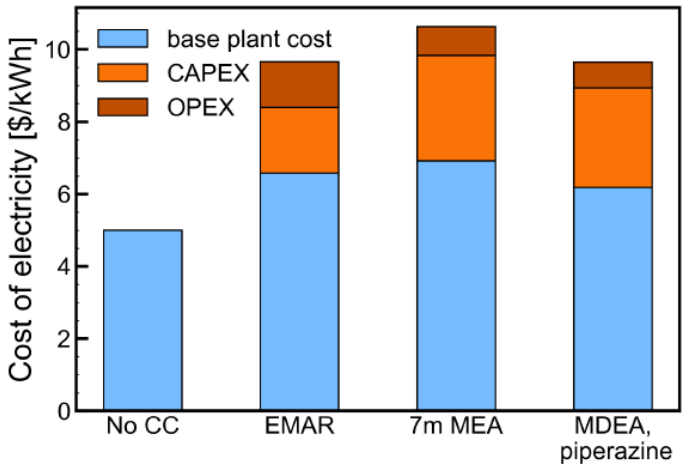




**Figure 6: Capital cost breakdown and COE estimates/comparisons.**

## technology advantages

- Amine scrubbing with electrochemically mediated amine regeneration offers a combination of fast kinetics, low parasitic energy requirements, and process flexibility.
- Carbon dioxide gas recovered from the regenerator was at elevated pressure (up to 20 bar), lessening downstream compression requirements and saving energy.
- The process optimally operated at a regeneration capacity between 0.5–0.8 mol-$CO_2$/mol-amine.
- At a membrane unit price of less than \$10/$m^2$, the $CO_2$ capture cost may be reduced to below \$50/t$CO_2$ with optimized process conditions (e.g., desorption pressure and utilization of waste heat).
- Techno-economic analysis (TEA) indicated that the electrochemically mediated capture technology could have a significant economic advantage over state-of-the-art thermal amine processes, cutting capture costs by 30–60%.

## R&D challenges

- Possible sensitivity of the process to disturbances and long-term operation viability. Since the system needed to switch the polarity of the electrodes and the corresponding process stream, this required implementation of an automation system that can accomplish both tasks for long-term operation stability.
- Validation of the basis for scale-up of the process to commercial-scale capability.
- Cell fluid flow channeling was a problem. Gas trapping in the fluid channel will reduce effective ionic conductivity, leading to reduced $CO_2$ separation. High velocities of liquid on the surface of the electrode will need to be ensured to minimize boundary layer thickness.
- Surfactants were evaluated to reduce $CO_2$ bubble size and minimize copper precipitation from electrodes.

## status

MIT's electrochemically mediated amine regeneration technology has been previously developed from concept to a proof-of-concept lab-scale device, validating the feasibility and potential of the approach. Additional lab-scale work has been completed to further optimize the performance of the technology, with a Cu-EDA amine/metal complex identified as needed. Cell architecture, cell operation and kinetics, and process optimization were investigated. This study conclusively demonstrated the advantages of the EMAR process relative to conventional amine-based thermal swing capture processes. The EMAR process does not rely on steam integration, which leads to a more easily deployed system for a range of $CO_2$ capture applications.

## available reports/technical papers/presentations

T. Alan Hatton, Electrochemically-Mediated Amine Regeneration in $CO_2$ Scrubbing Processes, Final Project Review presentation by, MIT, at NETL Pittsburgh on March 3, 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=9716&filename=Electrochemically+Mediated+Amine+Regeneration+in+CO2+Scrubbing+Processes.pdf*

T. Alan Hatton, Electrochemically-Mediated Amine Regeneration in $CO_2$ Scrubbing Processes, Budget Period 2 project review presentation by MIT, at NETL Pittsburgh on November 14, 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=9715&filename=Electrochemically+Mediated+Amine+Regeneration+in+CO2+Scrubbing+Processes.pdf*.

T. Alan Hatton, Electrochemically-Mediated Amine Regeneration in $CO_2$ Scrubbing Processes, presented by MIT, 2019 NETL CCUS Integrated Project Review Meeting, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/A-Hatton-MIT-Mediated-Amine.pdf*.

T. Alan Hatton, Electrochemically-Mediated Amine Regeneration in $CO_2$ Scrubbing Processes, presented by MIT, Kickoff meeting presentation, December 2017. *https://www.netl.doe.gov/projects/plp-download.aspx?id=9711&filename=Electrochemically-Mediated+Sorbent+Regeneration+in+CO2+Scrubbing+Processes.pdf*.

T. Alan Hatton, Electrochemically-Mediated Amine Regeneration in $CO_2$ Scrubbing Processes, presented by MIT, 2017 NETL $CO_2$ Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/4-Thursday/T-A-Hatton-MIT-Electrochemically-Mediated-Sorbent-Regeneration-.pdf*.

Rahimi, Mohammad; Zucchelli, Federico; Puccini, Monica; Alan Hatton, T. Improved $CO_2$ capture performance of electrochemically mediated amine regeneration processes with ionic surfactant additives, ACS Applied Energy Materials **2020**, 3, (11), 10823-10830.

Wang, Miao; Shaw, Ryan; Gencer, Emre; Hatton, T. Alan, Technoeconomic analysis of the electrochemically mediated amine regeneration $CO_2$ capture process, Industrial & Engineering Chemistry Research **2020**, 59, (31), 14085-14095.

Rahimi, Mohammad; Diederichsen, Kyle M.; Ozbek, Nil; Wang, Miao; Choi, Wonyoung; Hatton, T. Alan, An Electrochemically Mediated Amine Regeneration Process with a Mixed Absorbent for Post-combustion $CO_2$ Capture, Environmental Science & Technology **2020**, 54, (14), 8999-9007.

Wang, Miao; Hatton, T. Alan, Flue Gas $CO_2$ Capture via Electrochemically Mediated Amine Regeneration: Desorption Unit Design and Analysis, Industrial & Engineering Chemistry Research **2020**, 59, (21), 10120-10129.

Wang, Miao; Herzog, Howard J.; Hatton, T. Alan, $CO_2$ Capture Using Electrochemically Mediated Amine Regeneration, Industrial & Engineering Chemistry Research **2020**, 59, (15), 7087-7096.

Wang, M.; Rahimi, M.; Kumar, A.; Hariharan, S.; Choi, W.; Hatton, T. A. Flue Gas $CO_2$ Capture via Electrochemically Mediated Amine Regeneration: System Design and Performance. *Applied Energy* **2019**, 255, 113879.

Wang, M.; Hariharan, S.; Shaw, R. A.; Hatton, T. A. Energetics of Electrochemically Mediated Amine Regeneration Process for Flue Gas $CO_2$ Capture. *International Journal of Greenhouse Gas Control* **2019**, 82, 48–58.