

Special Collection

Towards the Electrochemical Retention of CO₂: Is it Worth it?

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This work focuses on the use of NaOH produced cathodically by reduction of water to retain gaseous CO₂ in a combined electrolyzer-absorber device. The process deals with two relevant environmental concerns: desalination and carbon sequestering, using only electricity and heat, which can be provided using green sources. Results demonstrate that technology is feasible, and the composition of the final product depends on the operation conditions applied. Removal rates of 130 mmol CO₂/h were obtained at 7.5 A with coulombic efficiency in the removal of CO₂ of 47.63%. Efficiency in the

production of chlorine, hydrogen and NaOH decreases at large current densities because of the promotion in the oxidation of water and the promoted transport of protons from the anodic to the cathodic compartment of the cell. Low current densities should be used to promote the formation of NaHCO₃ and avoid scaling problems (formation of deposits of Na₂CO₃) in the spray column. The use of heated air to evaporate the product of the absorption column produces evaporated water with higher quality (in terms of lower conductivity) from the product of the absorption column.

1. Introduction


Although global warming is a very complex process, in a simplistic way it can be understood through the relation between the accumulation of CO₂ in the atmosphere and the average temperature of its lower layers, because of the greenhouse effect associated to this chemical, which in turn can be easily explained because of the absorption and emission of infrared radiation by this molecule.^[1] As with many other elements in nature, carbon species are related among them by a natural cycle, which can be represented as a circle where the amount of carbon represents the diameter of the circle and it is related to average temperature of Earth.^[2] Because of the massive extraction during the last centuries of fossil fuels and raw matters (carbon first, then petrol and more recently natural gas), the concentration of CO₂ has increased very importantly and the circle has become a spiral with an increasing diameter, which reflects on an increase in the temperature of the lower levels of atmosphere, for which the only reasonable solution is to do what Nature did many time ago: 1) stop the carbon extraction to allow temperature to be kept in the present


values^[3] or 2) burying again carbon^[4] to reverse the increasing of temperature by reverting the trend of the increasing-diameter spiral down to a decreasing spiral

There are many ways in which Electrochemistry can contribute to minimize the carbon fingerprint of processes. Electrochemistry is concerned with the change of the oxidation state of species^[5] and many researchers are looking for the possibility of avoiding the need of carbon extraction by decreasing the oxidation state of carbon in CO₂ from its very stable oxidation state of +4 down to other values in which carbon can be used again as a fuel or in synthesis as a new reformatted bricks.^[6] However, all these processes have associated large amounts of electrons per molecule of CO₂ removed and, in going up in the technology readiness level (TRL) scale, it is not easy that they will be really scalable with the current technology.^[7] Anyway, they are claiming and deserving further studies, because of their potential relevance, not forgetting that, in fact, Nature is doing this change in the oxidation state with algae and plants throughout the photosynthetic process.^[8] The complexity of this process advises again the possibility of doing this in an efficient way with Electrochemistry in a more simplistic way. Electrochemistry can also be used for the concentration of CO₂ and, hence it is also worth to highlight the benefits that can be obtained from these processes.^[9]

However, there is still an important gap for electrochemists in the sequestration of CO₂:^[10] its transformation into a solid that can be later used as raw matter, or buried again,^[11] trying to avoid the accumulation of CO₂ in the atmosphere, that is what it is really aimed with many other non-electrochemical technologies for CO₂ mineralization studied during the recent years.^[12] There are many different processes reported in the literature^[13,14] but perhaps the simplest consists of the formation of a NaOH aqueous absorbent from the cathodic reduction of water. This process is the target of many patents^[15] but not many reports on its efficiency are found in the literature.^[16] As it

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is known, alkaline hydroxides can be easily produced on the cathode of electrochemical cells when electrolyzing water solutions and this species combines easily with CO₂ to form bicarbonates and carbonates as shown in Equation (1) and (2).^[17]



Thus, from the theoretical point of view, electrochemical technology can be easily applied for the reduction of CO₂ concentration by combining the production of NaOH with the absorption of CO₂ into a solution containing this NaOH.^[18] This formation of NaOH is the primary cathodic process in most electrochemical processes occurring in aqueous solutions because it is a product of the reduction of water to hydrogen^[19] as stated in Equation (3):



From the theoretical point of view, and for a process with 100% current efficiency, the expected amount of CO₂ which can be sequestered with 1.0 Ah of electric charge ranges between 18.65 mol if the final product is carbonate and 37.31 mol if it is bicarbonate, because this electric charge corresponds to 37.31 mol NaOH for a 100% current efficiency according to Equation (3).

It is important to consider that this process also produces hydrogen which is a green fuel with an extremely important value from the sustainability point of view that can be used again to regenerate electricity or burned to provide heat. It can also be used in synthesis, where it has hundreds of applications. The anodic reaction can also be used for a profitable application, being one extremely efficient the production of chlorine from the oxidation of chloride ions. However, a less interesting, but unfortunately more important reaction is the oxidation of water to form oxygen. In this context, rejection streams from electrodialysis or reverse osmosis treatments can become a suitable electrolyte to produce the NaOH to be used as absorbent and to obtain a highly added value product from the concentrated salts.^[16] As with the removal of CO₂, the removal of chlorides is also a topic of the major significance if another important environmental problem aims to be faced: the salinization of water reservoirs.

With this background, this work aims to join all the necessary technologies to demonstrate at the bench scale if electrochemical technology can be used to fix CO₂ contributing to minimize the carbon fingerprint of many current industrial processes. This is a step of the larger project EDEN[®] process (Electrochemically-based decarbonizing energy), which aims to sequester CO₂ while regulating green energy with reversible chloralkaline electrochemical cells.^[20] To do this, the absorption of a CO₂ streams into a spray absorption column is studied first, considering its great suitability for the process,^[21] with solutions of NaOH of different concentrations. Then, electrochemically produced NaOH is used for the same purpose and results are

compared to check if the technology is worth. A divided electrochemical cell is fed with water with a salinity like that of the rejection stream of electrodialysis processes and the efficiency in the production of chlorine and hydrogen in this cell is also evaluated looking for an increase in sustainability (EDEN[®] process).

2. Results and Discussion

2.1. Absorption of CO₂ with NaOH solutions

Figure 1 shows the relationship between the CO₂ retained in the absorbent and the NaOH consumed when treating in a spray absorption column a gaseous stream of CO₂ (gas flowrates in the range 5.4–26.9 Lh⁻¹) with aqueous solutions of NaOH (concentrations ranging from 0.25 to 1.00 M) using different nozzles to generate the spray (flowrate of 1.05 Lh⁻¹ with a nozzle of 0.1 mm and 2.69 Lh⁻¹ with a nozzle of 0.3 mm).

For each set of conditions (nozzle, temperature, and concentration of NaOH) the ratio between the liquid and the gas flowrates were changed in the different tests. Large points are the average of the four ratios tested in each set of tests (corresponding to different ratios gas/liquid). As expected, the amount of CO₂ retained seems to be directly related to the amount of NaOH consumed. The tests made with the wider nozzle attained a more efficient use of the NaOH, which can be related to the higher liquid flowrate associated. Likewise, and as expected, higher concentrations of NaOH in the fresh absorbent leads also to higher consumption of this species and, in turn, to larger concentrations of carbon sequestered. Temperature does not seem to have a relevant influence on results.

Average values of each series (with respect to the ratio gas/liquid flowrate) lay over the same line which indicates that, in average conditions, each mol of CO₂ needs around 1.218 mol of NaOH, a value that it is in between the theoretically required for the conversion of CO₂ to NaHCO₃ (1 mol NaOH/mol CO₂) or carbonate (2 mol NaOH/mol CO₂), and that indicates that CO₂ is

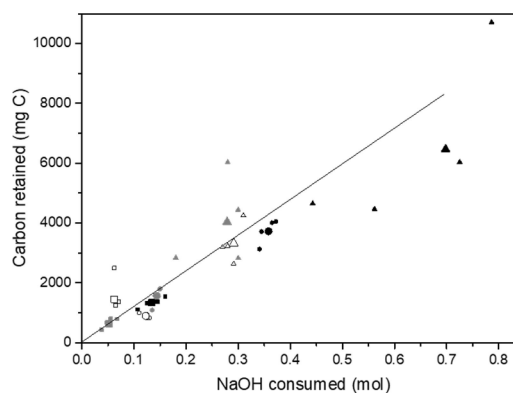


Figure 1. Relationship between the carbon retained in the solution and the NaOH consumed at different NaCl concentration (squares: 0.25 M, circles: 0.50 M, triangles: 1.00 M) and different nozzle size and temperature (black: 0.3 mm nozzle and 20 °C, grey: 0.1 mm nozzle and 20 °C, white: 0.1 mm nozzle and 60 °C).

transformed into a mixture of both species during the absorption process. Nevertheless, the great dispersion informs about the influence of the other operation conditions on the final speciation of the inorganic carbon.

In Figure 2, the percentage of CO₂ removed in each set of tests is shown. As it can be observed removals up to 100% are reached under the operation conditions evaluated in this work and this percentage increases with the concentration of NaOH in the absorbent. As pointed out in the discussion of previous Figure, the use of the wider nozzle is more efficient, and temperature does not seem to have a relevant influence on results.

On the other hand, there are important differences regarding the composition final product formed, as it is shown in Figure 3, where it can be seen that the percentage of HCO₃⁻ in this product increases when using absorbents with low concentrations of NaOH. The effect of the concentration on the NaOH is higher in the case of the larger drops (associated to the wider nozzle) and it becomes less important while operating at high temperatures. This means that the narrower nozzle leads to less efficient conditions, promoting the formation of carbonates, which is this stage can produce scaling problems in the absorption column.

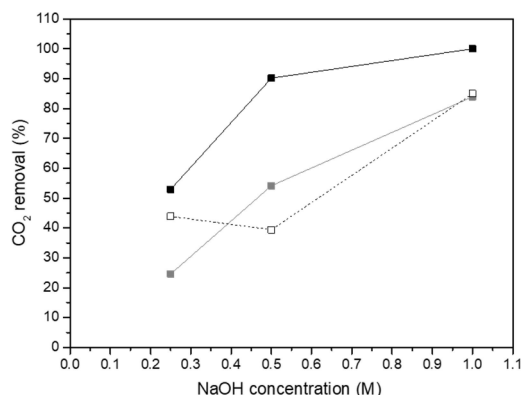


Figure 2. Percentage of CO₂ removal from the gas stream (black: 0.3 mm nozzle and 20 °C, grey: 0.1 mm nozzle and 20 °C, white: 0.1 mm nozzle and 60 °C).

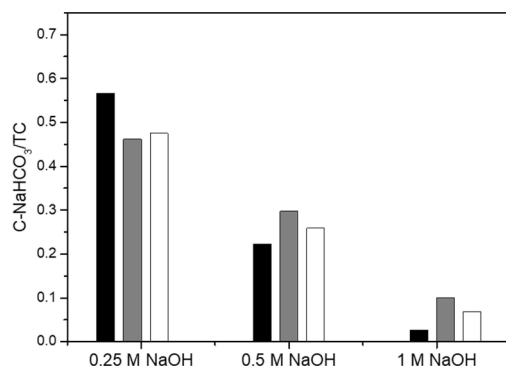


Figure 3. Ratio of bicarbonate reached in each experiment (black: 0.3 mm nozzle and 20 °C, grey: 0.1 mm nozzle and 20 °C, white: 0.1 mm nozzle and 60 °C).

Hence, the operation with the lower concentration range of NaOH at mild temperatures and with the wider nozzle promotes the formation of HCO₃⁻ and, hence, the better use of NaOH and, because of that, these conditions were selected to be tested in the later section of this work, in which the absorbents solutions are going to be produced in an electrolyzer by the reduction of a NaCl aqueous solution.

2.2. Electrochemical production of NaOH

In the industrial chloralkaline process (with membrane technology), a highly concentrated brine is used to manufacture chlorine, NaOH and hydrogen. High conductivity of the brine allows to work in conditions where mass transport does not limit the process and ionic conductivity is high. However, in our project, we are looking for a much simpler process to sequester CO₂ and, here, we are proposing to use brackish solutions which can be obtained easily as the rejection stream of electrodialysis processes, or which can be easily integrated into an electrolysis/electrodialysis cell, because the interest of our research is not to spend a commercial brine but to use electrochemistry in the most environmentally friendly way using waste streams of other processes within the circular economy principles, trying to lead to processes that simultaneously sequester CO₂ and desalinate water.^[16]

Production of these products was faced in continuous mode, feeding fresh solution continuously to the electrochemical cell. According to Figure 4, production of chlorine, hydrogen and NaOH using electrochemical cells equipped with polymer exchange membranes is as expected. As pointed out before, not a saline but a brackish solution was fed to the system (solution electrolyzed was 2.0 M in NaCl) and results obtained are, obviously, not as high as typically occurring in the chloralkaline industry. The amounts of hydrogen and chlorine increased linearly with time and efficiencies in terms of chlorine production decreases with the current intensity applied, because of the production of oxygen from the oxidation of water. This reaction competes on the anode surface with the

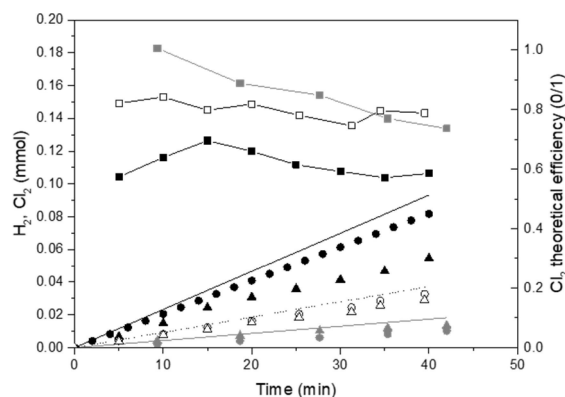


Figure 4. Speciation (circle: H₂, triangles: Cl₂) obtained in the electrolysis of a 2.0 M NaCl solution at different current (grey: 1.4 A, white: 3 A, black: 7.5 A) and efficiency in the production of chlorine (squares). Continuous line: 100% current efficiency line.

chloride oxidation^[20b,c] being more favored at higher current densities.

In our setup, the NaOH solution was split from the hydrogen and fed into the spray column. As seen in Figure 5, the concentrations of NaOH targeted (fixed by selecting the flowrate of electrolyte passed through the cell) were in the lower range (and even below) of those used in the chemical absorption tests, because this low concentration should favor the production of NaHCO₃ according to the results previously shown, avoiding potential scale problems. Also, important to highlight that these concentrations reached steady state in a very short time. Thus, after ten minutes of operation of the electrolyzer the concentrations are maintained in this value. Regarding to the efficiency in the production of this solution (shown in Part b), there is a linear relationship between the production rate of NaOH and the intensity applied and this line is, obviously, near the 100%-efficiency curve, because other competing cathodic reactions, such as oxygen reduction to hydrogen peroxide, are not promoted in this system considering the cathodes used. However, the values do not reach the expected and, in fact, the decreases in the efficiency at higher current intensities may be explained in terms of the promoted transport of protons through the membrane between both electrolyte compartments, because of the higher transfer of protons from the anode to the cathode compartment of the cell at the conditions associated to a higher gradient which, in addition contributes to a partial neutralization of the hydroxide ions formed.

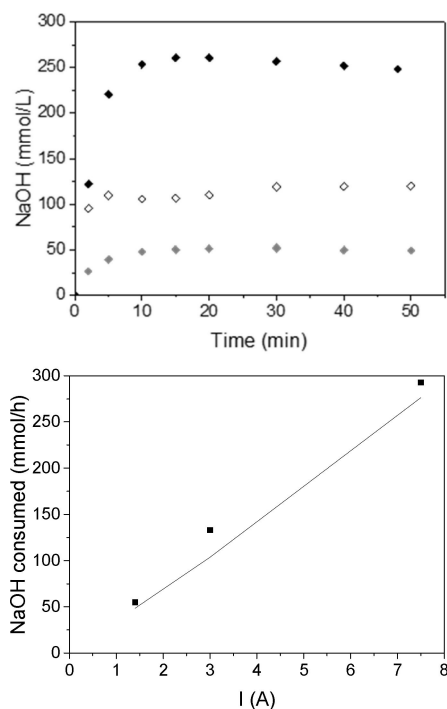


Figure 5. Production rate of hydroxyl ions at different current intensities. Continuous line: 100% current efficiency line.

2.3. Use of electrogenerated NaOH solutions as absorbents

The electrogenerated solutions containing NaOH were fed to the spray column. Operation conditions were fixed to 20 °C and the ratio between the liquid and the gas flowrates was kept at 5.4, using the 0.3 mm nozzle, which seemed to be the most advantageous conditions according to the test described previously. In addition, room temperature (20 °C) was maintained during the tests. As shown in Figure 6, in using the stream produced electrochemically in the treatment of CO₂ streams, CO₂ can be efficiently sequestered and for the conditions used in this set of tests, the removal of CO₂ from the gas stream reached 48% when using 7.5 A, which is a value close to that reached in the chemical absorption tests (53%) when using a solution of NaOH of the same concentration as absorbent. In addition, for low current densities the primary product in the absorbent is NaHCO₃, while for 7.5 A the product formed is a mixture of carbonates and bicarbonates, pointing out again that lower concentrations of NaOH in the absorbent promotes the use on only one hydroxyl ion to fix the CO₂.

In addition, the rate of CO₂ removal increases linearly with the current intensity reaching 132.5 mmol CO₂/h when using the highest current intensity tested (7.5 A). The slope of this straight line is 17.6 mmol CO₂/Ah and this means a coulombic efficiency in the removal of CO₂ of 47.2%. This value is below the expected 18.65 mol /Ah if the final product were Na₂CO₃ and 37.31/Ah mol, if it were NaHCO₃ and indicates that despite being a simple process there is still a big gap to be filled in order to reach a more efficient use of the NaOH. Thus, regarding the use of the NaOH contained in the absorbent, values range between 1.4 and 1.9, values that are slightly higher than those

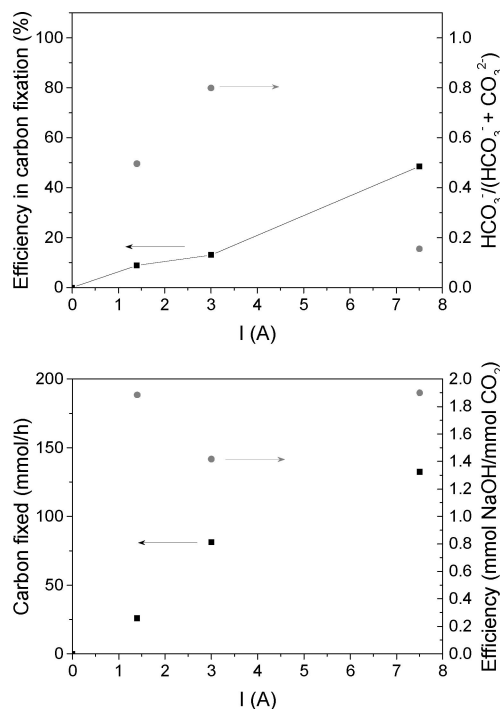


Figure 6. Percentage of CO₂ removed with the electrogenerated solutions of NaOH.

measured in the chemical tests. No NaOH was detected at the outlet of the spray column which indicates that it reacts completely with CO_2 .

2.4. Concentration of the absorbent

The effluent of the absorption column (rich in NaCl and $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$) was fed to an evaporation column which was heated in a heat exchanger with thermal oil at 145°C to concentrate the CO_2 sequester and the salts contained in the spent absorbent solution (to simulate thermal solar evaporation). On purpose, the energy applied was below the required for total evaporation of the 0.8 L/h of absorbent (576.5 W, calculated by adding the heat required to increase temperature from 20 to the boiling point and the evaporation heat), because here we aimed to evaluate the concentrations of the evaporate as the final goal of our project is to develop a technology for the simultaneous desalination and carbon sequestration which in addition produce water of high quality in the last stage. In this drying column, the flowing in counterflow mode of air was also tested. Thus, air at room temperature (c.a. 20°C) and hot air (heated at 100°C and 150°C before being fed into the column) were added at the bottom of the column. Figure 7 shows the percentages of water evaporated (part a) and the concentrations of salt and sequestered carbon (part b). As well, the conductivity and pH of the evaporate are also shown (part c). As expected, the flowing of air has a positive effect on the

evaporation rate although the temperature of air does not improve it. As seem, the heating of the air flow has very little influence on the composition of the concentrated solution and regarding the evaporate, it has a positive effect because the higher temperature of the air fed produces a product with less conductivity, that it lower amount of condensate is dragged in the system. The acidification without air or with cool air can be due to the absorption of species contained in the air flowed throughout the column, considering the very low conductivity, because the effluent of the absorption column is extremely alkaline. In a later stage the surplus liquid was fully evaporated to evaluate the quality of the solid formed. As seen in part d, the solid obtained is a pure mixture of $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ and NaCl with a high purity which can be buried in salt mines or use as raw matter in different processes.

3. Conclusion

The main conclusion of this work is that the electrochemical technology can be used to produce an efficient absorbent for capturing CO_2 in spray absorption columns. Product produced consists of a mixture of NaCl , Na_2CO_3 and NaHCO_3 . Low current intensities lead to products rich in NaHCO_3 helping to avoid scale operation problems in the absorption column. Likewise, efficiency in the production of chlorine, hydrogen and NaOH decreases at large current densities because of the promotion in the oxidation of water and the promoted transport of

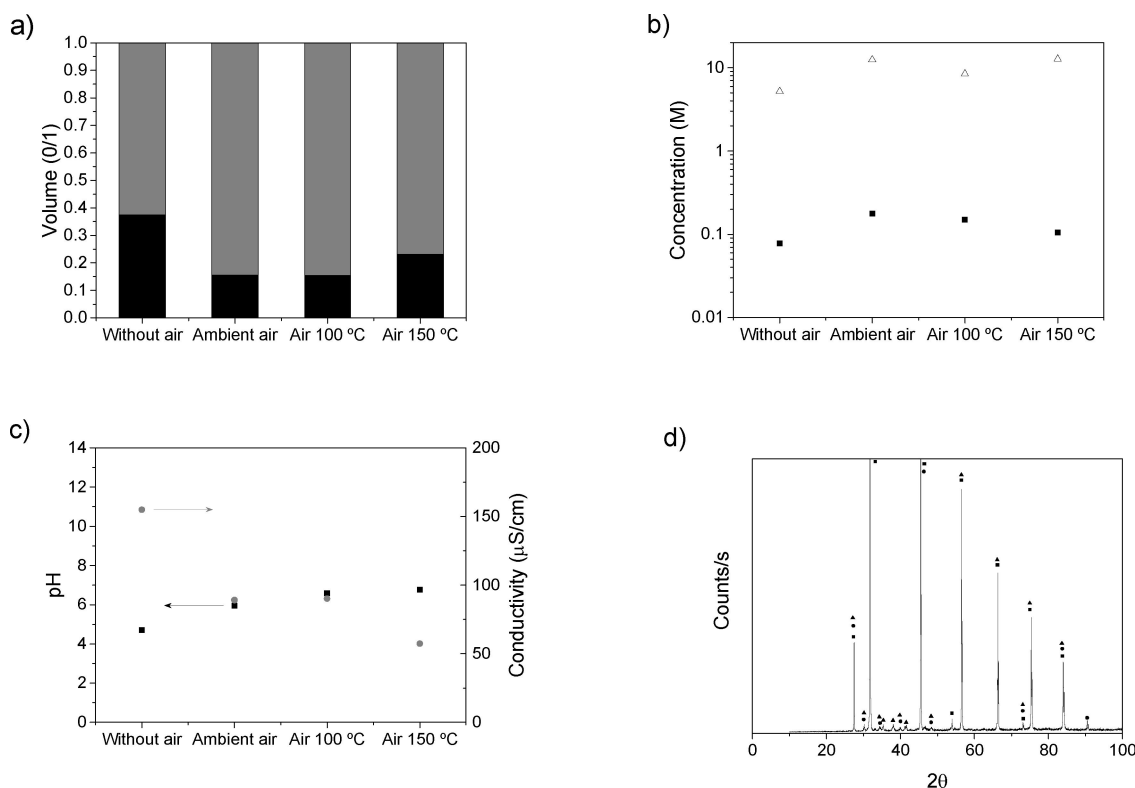
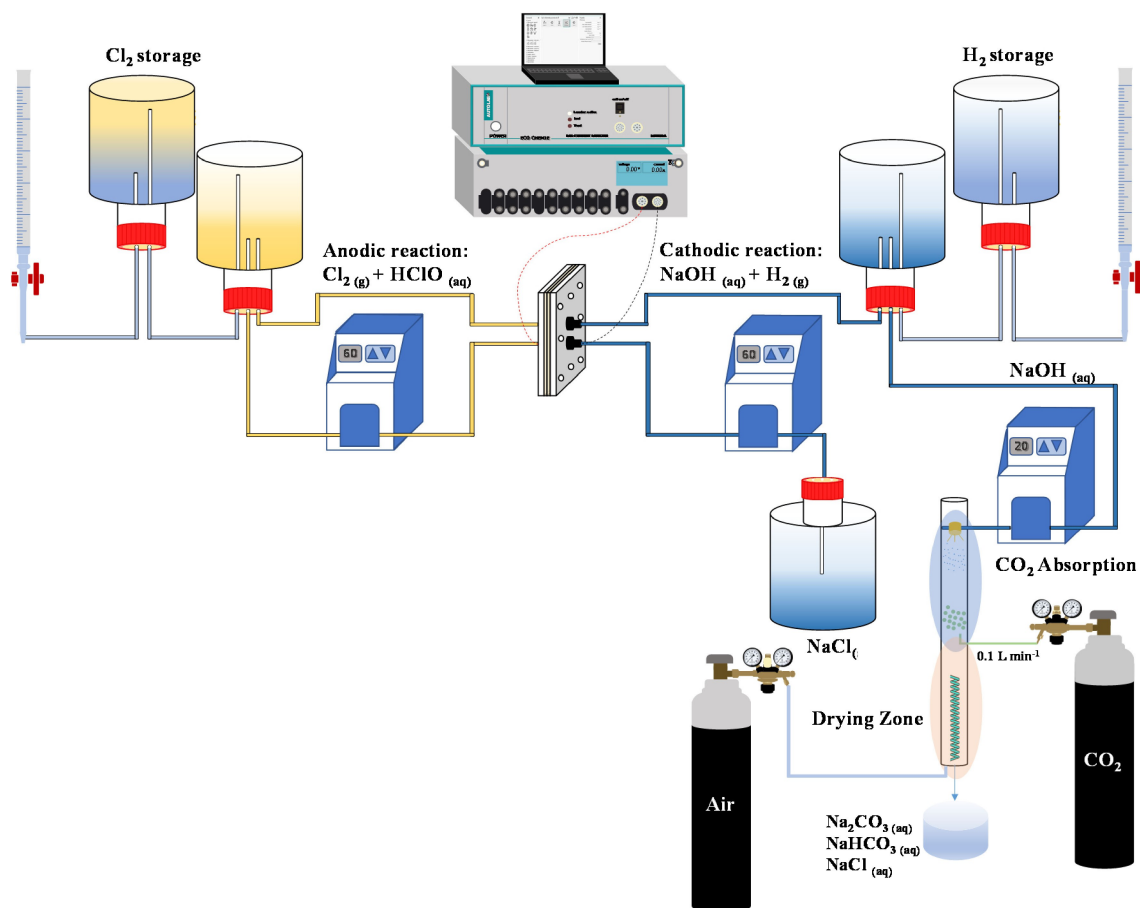


Figure 7. Evaporation of the absorbent electrolyte. Part a) Black: volume $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$, grey: volume water recovery. Part b) Concentrations of NaCl and $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ in the concentrate. Part c) pH and conductivity in the evaporated water Part d) XRD analysis of the dried solid formed (NaHCO_3 : circle; Na_2CO_3 : triangle; NaCl : square).



Scheme 1. Experimental set-up.

protons from the anodic to the cathode compartment of the cell. Removal rates of 17.77 mmol CO₂/Ah are reached and this means a coulombic efficiency in the removal of CO₂ of 47.63%. Regarding the use of the NaOH contained in the absorbent, values range between 1.4 and 1.9 mol NaOH/mol CO₂, values that are slightly higher than those observed in the chemical tests (1.218 mol NaOH/mol CO₂). Large concentrations of NaOH should not be used to avoid the formation of deposits of carbonate in the spray column and use of heated air to evaporate the product of the absorption column produces a product with less conductivity.

Experimental Section

Experimental setups

CO₂ capture with NaOH was carried out into a spray absorber tower (diameter: 0.1 m, height: 1 m). The NaOH solution was introduced in the top of the tower by a spray nozzle (0.1–0.3 mm). CO₂ entered in the absorber from the bottom of the column, interacting with the aqueous sprayed NaOH solution. Once that the CO₂ was trapped as Na₂CO₃ and NaHCO₃, the solution was introduced in a second stage of the tower. In this stage, the solution was introduced into a coil heat exchanger in countercurrent to an air flow (15 L/min). Silicon oil was used as hot fluid (145 °C) and

introduced in the inner side of the coil. The solution was concentrated, producing water steam that was recollected and condensed in the top part of the exchanger. As an alternative, NaOH was electrochemically generated by an electrolytic cell. This in-house PEM cell is formed by two electroodic chambers, which each one had a volume of 75 cm³. Both chambers were separated by a commercial Proton Exchange Membrane (Nafion-117). The electrodes were placed inside, being one of them in charge of the electrochemistry of chlorine and it consisted of a mixture of RuO₂/Pt coated titanium-plate (Ti/Ru_{0.3}Ti_{0.6}O₂Pt_{0.1}), whose best composition was studied in a previous work (molar Ru/Pt ratio of 3). The other electrode, in charge of the electrochemistry of water/hydrogen, was made of Pt/C Vulcan. Both electrodes had a geometrical area of 35.1 cm². Additional details of the cell, membrane and electrodes can be found elsewhere.^[20a] During cell operation, both compartments were fed with a solution of 2.0 M NaCl. In the anode, the electrolyte was recirculated by means of a peristaltic pump while in the cathodic compartment, the solution was fed continuously. The gas produced in the anodic compartment was measured by means of a gas collection system, which was connected to the feed tank. Instead, in the other compartment, the gaseous stream was separated from the liquid stream, which will be measured in the same way as the other gaseous stream. This solution was introduced to the spray absorber tower, as previously described.

Chemical absorption tests

Experiments were performed for 20 min and with aqueous solutions of NaOH at different concentrations (0.25 M, 0.5 M, and 1 M NaOH). For each set of tests, the gaseous stream with CO₂ was introduced to the spray absorption column at different gas flowrates: 5.4; 9.2; 14.4 and 26.9 L h⁻¹) and with two different nozzle sizes: 0.1 and 0.3 mm. All the experiments were carried out at room temperature, except with the narrower nozzle, which also operated at 60 °C. *Electrochemical absorption tests.* The electrochemical cell was connected to a supply power, and it operated at different current intensities, corresponding to 1.4, 3.0 and 7.5 A. All the experiments were carried out at atmospheric pressure and room temperature for 50 min. Scheme 1 shows the experimental set-up of the electrochemical absorption.

Chemical analysis

The NaOH generated in the electrochemical cell was measured by titration, adding sulfuric acid (0.02 N H₂SO₄) until neutralized. Hypochlorite measurement was carried out by means of an Agilent 300 Cary series UV-Vis spectrophotometer at a wavelength of 293 nm. The pH was measured with a GLP22 Crison pH meter and the conductivity was measured with a GLP 31 Crison conductimeter. Further details can be found elsewhere.^[20b] To determine the concentration of Na₂CO₃ and NaHCO₃ formed was used a standard method: Method 2320 B. This method calculates the quantity of NaHCO₃, Na₂CO₃ and NaOH containing in aqueous samples. The analysis consists of a titration with 0.02 N H₂SO₄ up to a first point that corresponds when the sample has a pH of 8.3 and an endpoint when it coincides with a pH of 4.5.

Physical characterization of solid formed

The elemental chemical composition of the solid formed after the operation of spray absorption was determined by means of a Philips PW-1700 diffractometer, applying K α corresponding to the transition from Cu radiation for each sample. Measurements of the 2 θ angle were located between 20° and 80° with a sweep speed of 0.02° min⁻¹.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: CO₂ · absorption · electrolysis · chloralkaline process

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