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Separation of Carbon Dioxide from Flue Gas Using Ion Pumping

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Abstract

We are developing a new way of separating carbon dioxide from flue gas based on ionic pumping of carbonate ions dissolved in water. Instead of relying on large temperature or pressure changes to remove carbon dioxide from solvent used to absorb it from flue gas, the ion pump increases the concentration of dissolved carbonate ion in solution. This increases the overlying vapor pressure of carbon dioxide gas, which can be removed from the downstream side of the ion pump as a nearly pure gas. This novel approach to increasing the concentration of the extracted gas permits new approaches to treating flue gas. The slightly basic water used as the extraction medium is impervious to trace acid gases that destroy existing solvents, and no pre-separation is necessary. The simple, robust nature of the process lends itself to small separation plants. Although the energy cost of the ion pump is significant, we anticipate that it will compete favorably with the current 35% energy penalty of chemical stripping systems in use at power plants. There is the distinct possibility that this simple method could be significantly more efficient than existing processes.

Introduction

Existing uses of liquid absorbers such as amines to separate gases depend on both selective absorption of the desired gas, and changing the vapor pressure (properly the fugacity) of the gas over the solvent. Instead of increasing the fugacity by physical means, we can also change it by chemical manipulation. For instance, adding acid to an aqueous solution will cause carbon dioxide to leave solution, but is not practical on a large scale. An alternative is to increase the concentration of the dissolved species in solution (Figure 1), which will result in a nearly linear increase in the gas pressure over the solution (of course there are nonlinearities, but when removing a neutral gas from an ionic solution, the “salting out” effect disproportionately favors gas evolution at higher concentration). This increase in concentration can be achieved using water desalination methods such as reverse osmosis or electrodialysis.

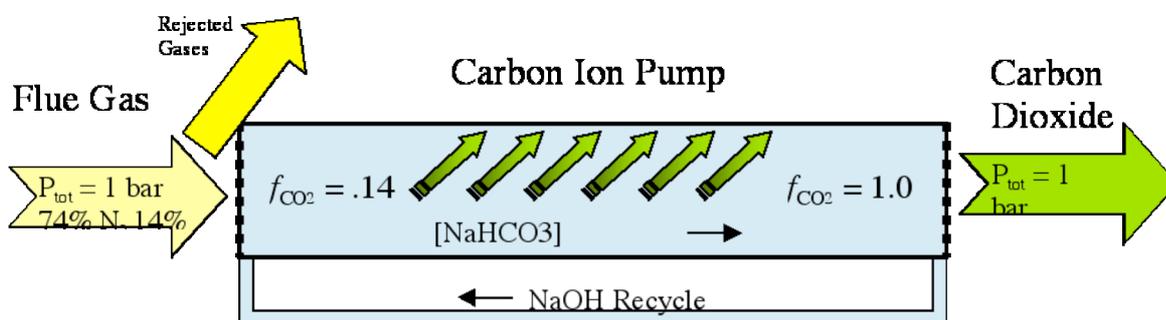


Figure 1. Schematic function of the ion pump. Flue gas dissolves in buffered water, effectively excluding most of the nitrogen and non-acid gases. The concentration of dissolved carbonate ions (and carbon dioxide fugacity) is increased by reverse osmosis or electrodialysis, until nearly pure carbon dioxide can be removed

Coal Flue Gas Proportion			Dissolved concentration
13.9 %	$\text{CO}_2 + \text{H}_2\text{O}$	$\Rightarrow \text{H}^+ + \text{HCO}_3^-$	1200 ppm
.07 %	$\text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$	$\Rightarrow \text{H}^+ + \text{HSO}_4^-$	(all of it)
.02 %	$\text{NO}_x + \sim\text{H}_2\text{O}$	$\Rightarrow \text{H}^+ + \text{HNO}_3^-$	(all of it)
73.8 %	$\text{N}_2 + \text{H}_2\text{O}$	$\Rightarrow \text{N}_2 + \text{H}_2\text{O}$	13 ppm
3 %	$\text{O}_2 + \text{H}_2\text{O}$	$\Rightarrow \text{O}_2 + \text{H}_2\text{O}$	3 ppm

Table 1 Dissolution of flue gas (yellow) into aqueous solution (blue) effectively excludes nitrogen and oxygen, which are not ionized.

Carbon dioxide makes up from 5% (modern gas-fired plants) to 19% (modern coal plants) of the flue gas from a power plant. The remainder is mainly nitrogen, unused oxygen, and oxides of nitrogen and sulfur (which are strong greenhouse gases in addition to contributing to poor air quality). The initial dissolution phase of our process strongly excludes nitrogen and oxygen (Table 1), which do not significantly dissolve in water. There is about a 300x increase in the relative ratio of carbon dioxide to nitrogen when flue gas is dissolved in water. Sulfur and nitrogen oxides are also partitioned into the water phase. The effects of aqueous concentration are well known. The ion pump process enables us to separate the dissolved gases from the aqueous solution without a large energy penalty.

Modelling

We have modeled the effects of the ion pumping process for a simple sodium bicarbonate-phosphate water system. The ion pump effectively increases the concentration of bicarbonate (red line) with a corresponding increase in carbon dioxide pressure. We assume here that the carbon dioxide is released at a pressure of one bar. The ion pump increases the HCO_3^- concentration. Starting with a CO_2 concentration representative of flue gas from a coal-fired power plant, the ion

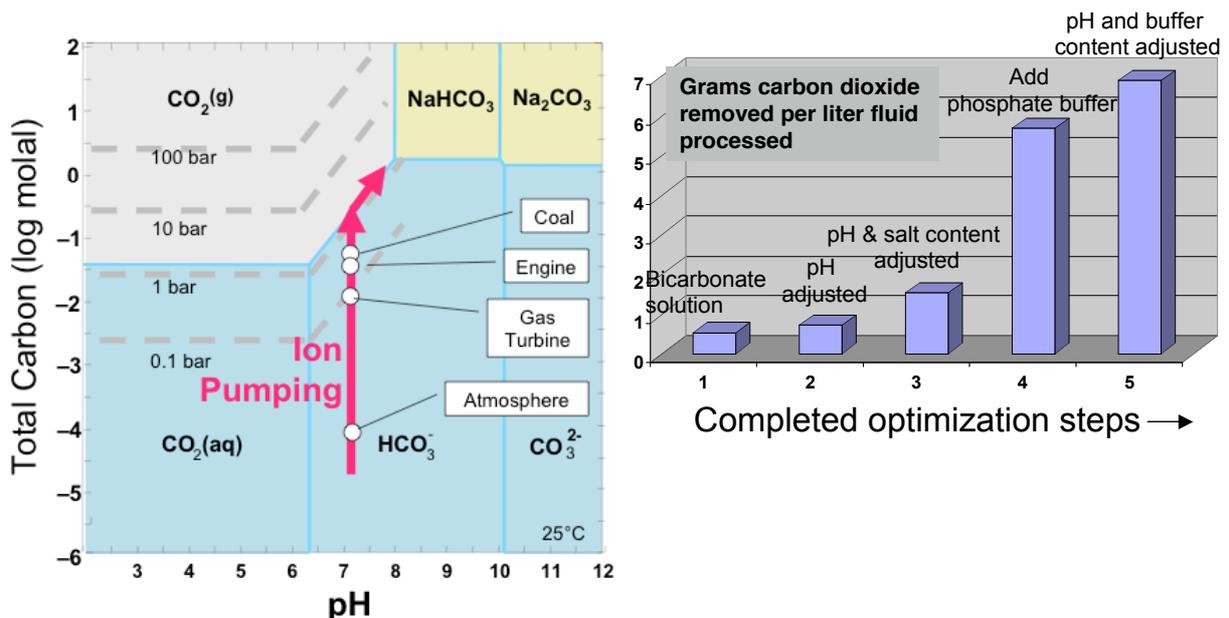


Figure 2. Geochemical modeling indicates that pH 7 gives the optimal carbon dioxide yield (maximum solubility without solid phases occurring during degassing).

pump would be required to increase the carbonate concentration by a factor of 30 in order to release about 6.5 grams of pure carbon dioxide per liter of fluid. Preliminary laboratory experiments using electro dialysis to increase the carbonate concentration confirm these modeling results. An important aspect of the modeling is the presence of an optimal region around pH 7 where the solution carries a large amount of CO₂, and there are not solid precipitates formed as the ions are concentrated (as occurs above pH 8, see figure 2).

Experimental Results

We conducted tests of the method using electro dialysis to treat a solution of potassium phosphate saturated with air and carbon dioxide, increasing the ionic strength (total salt in solution) by a factor of ten (Figure 3). The solution rapidly effervesces carbon dioxide during treatment (Figure 4). Results match our calculations well, indicating that we can confidently use geochemical modeling to design these experiments.

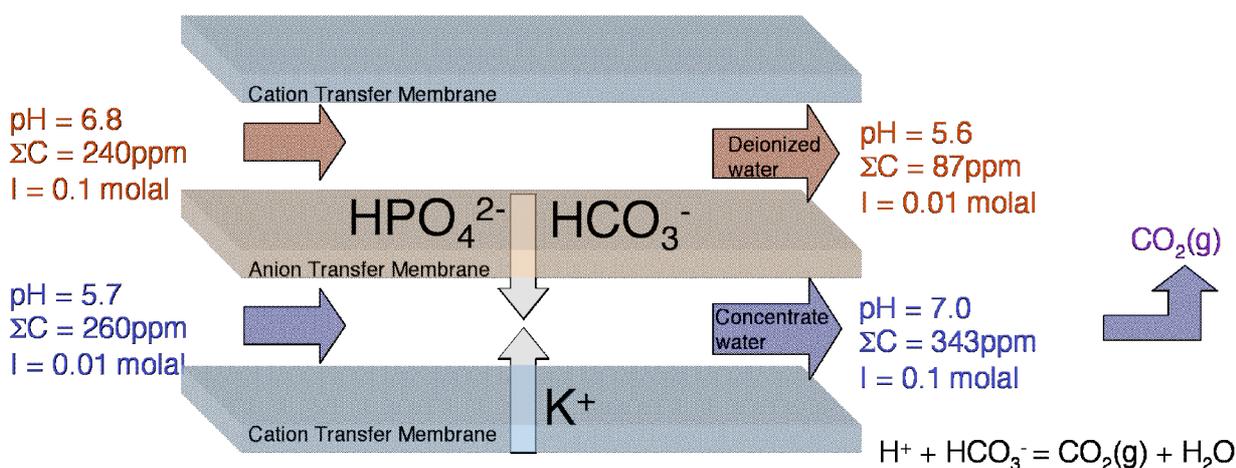


Figure 3. Schematic of the electro dialysis apparatus with chemical data from a representative experiment.

The ion pumping concept shown in Figure 1 is most directly applicable to reverse osmosis methods. We instead chose electro dialysis for initial testing simply because we had an appropriate-sized unit available (Ionics Stackpack Experimental Unit). The anion- and cation-membranes are flexible, 0.5 mm thick cloth-reinforced resin sheets that are insoluble in aqueous solutions. All spacers in the stack are polypropylene. Both ion concentration and pH change in the membrane, so we expect to see changes in carbonate ion speciation across the membranes. The gas evolution occurs on the distal side of the membrane (Figure 3), complicating our ability to model the process relative to reverse osmosis, where ion concentration and gas evolution both occur on the proximal side of the membrane. The degassing of the solution occurs rapidly, and throughout the apparatus. This makes it difficult to measure the released gas even though it is readily visible in samples (Figure 4). Instead of measuring total released carbon dioxide gas, we measured the before and after total dissolved carbon in the two water phases using an O-I Corporation Model 524D Carbon Analyzer. Reagent grade magnesium perchlorate was used as the



Figure 4. Effervescent solution resulting from ion pump concentration of carbonate and bicarbonate ions.

desiccant. A calibration curve was constructed using NIST Traceable 0.05N Na_2CO_3 . Known volumes of samples were reacted with a 25% H_3PO_4 fluid. These results are shown in Figures 3 and 5.

Two phosphate solutions were prepared for the test: a dilute saline solution (0.01M of both KH_2PO_4 and Na_2HPO_4) for the initial 10 L “concentrate” side reservoir of the electro dialysis unit, and a more concentrated solution (0.1M of both KH_2PO_4 and Na_2HPO_4) to initially fill the 10 L “diluate” reservoir. Dry ice was added to both solutions until the pH stabilized at values of 5.7 and 6.7 for the “concentrate” and “diluate” solutions, respectively.

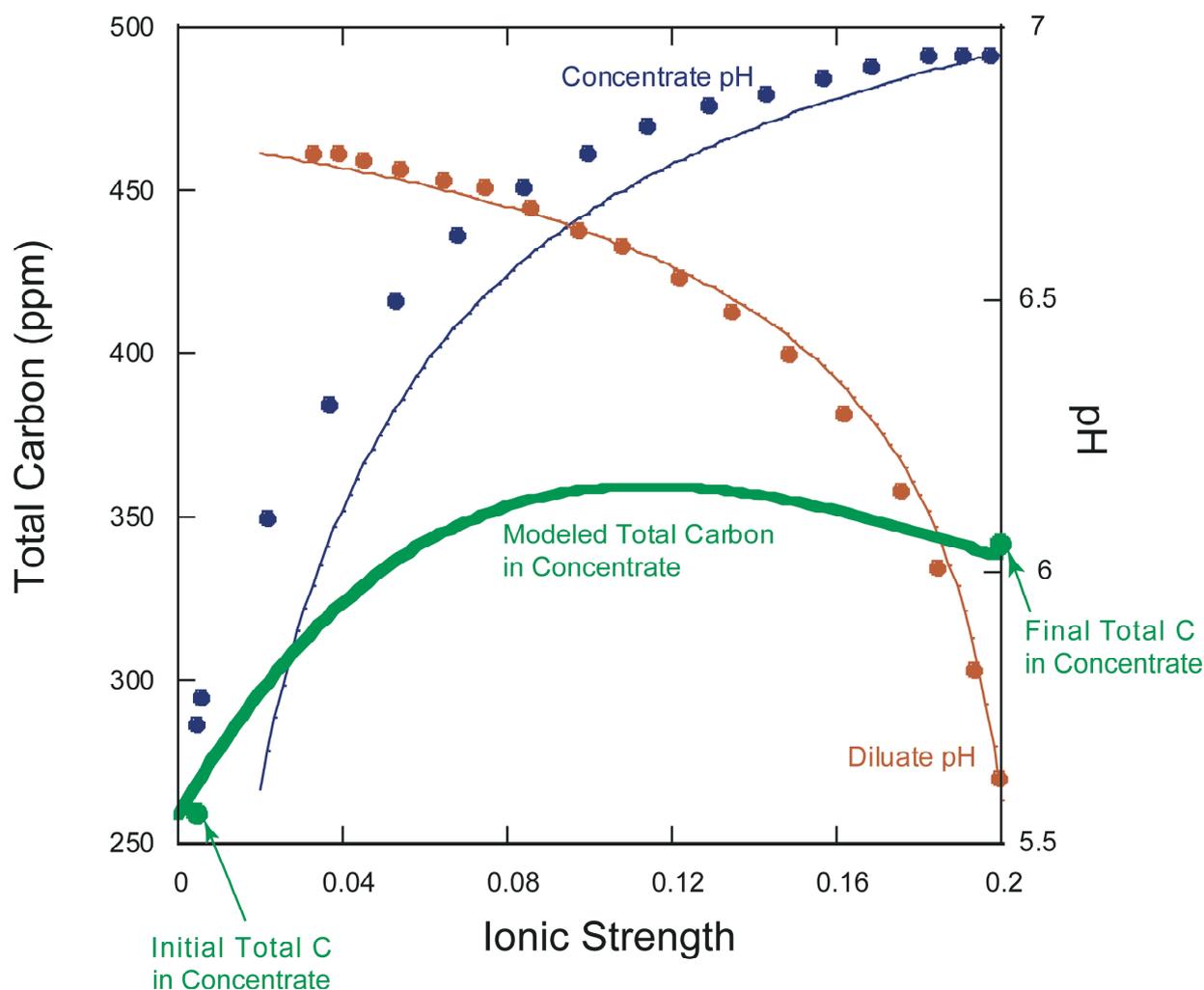


Figure 5. Experimental data (points) and model predictions for the test shown in figures 3 and 4.

In total, about 1 g/liter of carbon was removed as carbon dioxide during the desalination process. The total dissolved carbon on the concentrate side increases as bicarbonate ions are transported through the ED membrane (Figure 3). The results of the experiment and modeling are shown in Figure 5. Because we are transferring ions from one fixed volume reservoir to another, we create an artificial limit to the total amount of carbon that can be removed. In future tests, this batch process will be replaced by a continuous process in which continuous new solution is fed to the diluate side, and the concentrate side remains static as a working fluid. This will permit much larger amounts of carbon dioxide to be removed from solution. These test conditions will be chosen to approximate those expected for an actual flue gas extraction process.

Potential Applications

We envision a process where the flue gas is first dissolved in slightly alkaline water. The water passes into the ion pump, which may initially simply be a conventional water desalination system operated to maximize carbon dioxide release, rather than recovery of potable water.. Carbon dioxide is released from the ion pump concentrate stream. . Phosphate is added to buffer pH and increase CO₂ carrying capacity. The concentrate is recombined with the dilute stream and re-cycled to the water wash. Nitrate and sulfate will be concentrated with the bicarbonate and either removed separately as solids or evolved in gas form (they are more stable in solution than the carbonate). Alternatively, the dilute output of the ion pump could be used separately as a clean water source. The ultimate source of water could be brackish or even sea water, provided it undergoes softening prior to flue gas capture.

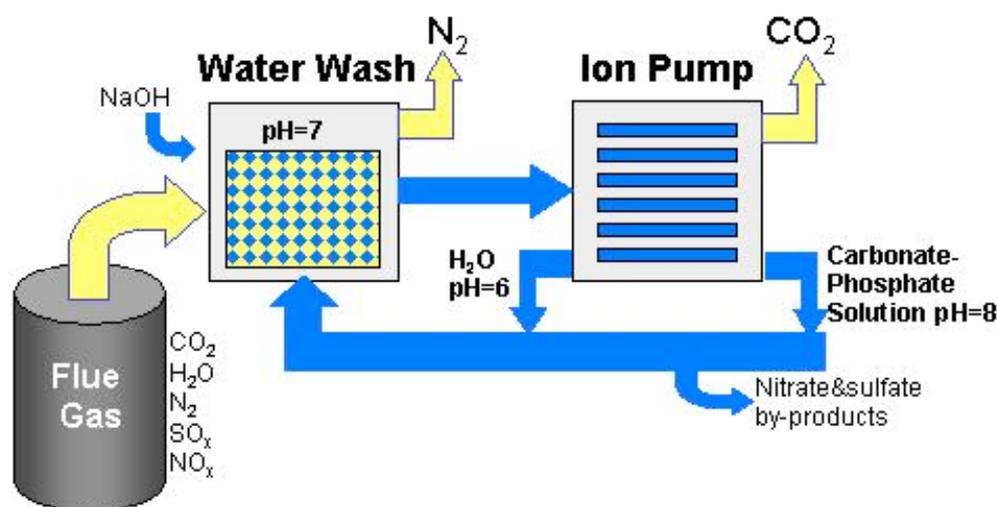


Figure 6. Conceptual industrial application of the ion pump to removing carbon dioxide from flue gas.

A significant cost benefit of this process is simplicity. It does not require sensitive reagents or large heating and cooling steps. The capital investment would therefore be smaller than for amine processes. This will have industrial benefits, but it will also facilitate testing the method on small scale. Water treatment equipment is readily available at all scales from benchtop, which we have used in our experiments, to that required for a full scale power plant, which would be equivalent to the largest commercial reverse osmosis drinking water production plants in use today. Scaling these costs to our initial modelling and experiments indicates that the process could be operated today for less than \$100/ton carbon avoided. We anticipate that optimization of the chemistry and operation of the ion pump process will produce costs that compete favorably with other CO₂ separation processes in use today.

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