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## Carbon capture powered by solar energy

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### Abstract

The urgent implementation of emissions control measures is inhibited in part by the expense of carbon capture technology. A large part of the cost of amine based approaches is in the heat regeneration of the absorbent. An alternative way to do this could be through use of abundant solar energy. In a new approach, direct chemical action on the absorbed CO<sub>2</sub> was achieved by use of a reversible photoacid. Irradiation of the CO<sub>2</sub> loaded solution resulted in CO<sub>2</sub> removal by action of light.

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### 1. CO<sub>2</sub> capture

Carbon dioxide capture and sequestration will likely be a critical component of power generation using fossil fuels to minimise atmospheric CO<sub>2</sub> emissions and mitigate climate change. CO<sub>2</sub> capture and sequestration technology may also be used to reduce atmospheric CO<sub>2</sub> concentrations by capture from air. For the former, the most readily deployable technique involves a temperature swing process applied to aqueous solutions of amines<sup>1</sup>. In the initial carbon-lean cold state, flue gas is contacted with a solution of amine such that CO<sub>2</sub> is selectively chemically absorbed by reaction with the amine. The second stage of the capture process involves taking the carbon-rich amine solution from an absorber column to a desorber column and heating the solution. Upon heating, the carbon dioxide is desorbed and may be collected for compression and storage. The best amine based temperature swing techniques are capable of excellent separation of CO<sub>2</sub> (between 70 and 99% CO<sub>2</sub> removed depending on operating requirements) and good repeatability but are criticised for their high monetary cost and energy demand. The energy required for capture of

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CO<sub>2</sub> has fallen from 4.1 GJ per tonne to 2.6 GJ per tonne in recent years (with improved absorbent formulations, this might be reduced to 2.0 GJ per tonne)<sup>2</sup>. This can be expressed in money as between 36 and 55 US dollars per tonne<sup>3</sup>. The largest operating expense is the cost of heating the solution in the second phase to desorb CO<sub>2</sub> from the amine solution. In terms of capture from a coal fired power station for example, the temperature swing process can consume 20-30%<sup>4</sup> of the power stations energy output<sup>1,5-7</sup>.

Recent work by Fernandes et al.<sup>8</sup> has emphasised that a major driver of desorption in the second phase is decreased basicity of the amine upon heating. McCann et al.<sup>9</sup> calculate that in a prototypical CO<sub>2</sub> capture process based on monoethanolamine, the enthalpy of desorption for CO<sub>2</sub> at 313 K is ~83 kJmol<sup>-1</sup>. ~50 kJmol<sup>-1</sup> is associated with deprotonation of the amine. Formation of gaseous CO<sub>2</sub> from CO<sub>2(aq)</sub> and H<sub>2</sub>CO<sub>3</sub> is ~21 kJmol<sup>-1</sup> and decomposition of the monoethanolamine-carbamate species is ~12 kJmol<sup>-1</sup>. This illustrates that the largest energy cost during desorption is due to the heat required to remove protons from the amine and lower the absorbent pH. If this lowering of pH could be achieved by another method the expense of heating could be reduced or removed.

For the removal of CO<sub>2</sub> from solution the relevant equilibria are given by equations Eq. 1 to Eq. 4. Eq. 1 shows the desorption of CO<sub>2</sub> from a carbamate species formed when CO<sub>2</sub> is reacted with an aqueous amine. Protonation of the carbamate forms carbamic acid which is unstable and reverts to CO<sub>2</sub> and free amine. Eq. 2 shows the desorption of CO<sub>2</sub> from bicarbonate which is formed when CO<sub>2</sub> reacts with water in the presence of a base or directly with hydroxide (Eq. 3). Analogous to carbamate, when bicarbonate is protonated it forms carbonic acid which is unstable and reverts to CO<sub>2</sub>. Eq. 4 is the reaction of any Brönsted bases present in the solution to absorb and release protons. In aqueous amine solutions unreacted amine acts as the base, while in carbonate solutions it is the carbonate ion CO<sub>3</sub><sup>2-</sup>.



Assuming the capacity of the base to absorb protons is exhausted, introducing protons to the solution drives the equilibria to the right and causes desorption of CO<sub>2</sub> from the solution. It would therefore be possible to achieve the desorption of CO<sub>2</sub> by adding an equivalent amount of acid.

Atmospheric levels of CO<sub>2</sub> are continuing to increase and in many future scenarios are predicted to exceed levels that may result in catastrophic climate change beyond the year 2100<sup>3</sup>. As a consequence atmospheric CO<sub>2</sub> removal technologies are under development in an attempt to provide future options to address this. CO<sub>2</sub> removal from air is significantly more challenging than from a concentrated point source due to the low CO<sub>2</sub> partial pressure which results in a greater energy demand per unit of CO<sub>2</sub> captured when using existing separation technology<sup>2</sup>. However the solution chemistry remains the same as that given above. Alternative technologies have been proposed, for example a method has been advanced by Lackner that<sup>14</sup> works by physically adsorbing CO<sub>2</sub> to an ion exchange membrane before it is stripped under low pressure and with water. This currently is expected to cost \$300 per tonne of CO<sub>2</sub> with some savings if the devices are produced in large quantities.

### Photoacids

In recent years, advances in photochemistry have given us greater control of molecular interactions with light. Molecular or material properties including, colour, electrical conductivity, size and shape, and pH may be reversibly switched by irradiating materials with photons of various wavelengths.

One mechanism of photo-generation of pH change can be seen in photochromic molecules like merocyanine-spiropyran switches, recently advanced by Shi et al<sup>10</sup>. In this example a photoexcitation leads to a molecular reorganisation such that the phenol group is incorporated into a ring structure and this gives a proton to the solution.

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