

Reducing Atmospheric Carbon Dioxide Through Direct Air Capture

Dr Radu Custelcean

REDUCING ATMOSPHERIC CARBON DIOXIDE THROUGH DIRECT AIR CAPTURE

Climate change is mostly the result of elevated carbon dioxide emissions. Over the past two decades, research groups have been searching for new technologies that capture carbon dioxide from the atmosphere as an effective way of reversing climate change. **Dr Radu Custelcean** and his colleagues at the Oak Ridge National Laboratory in the US specialise in this endeavour. The team is developing novel materials and methods that filter carbon dioxide out of the air in an energy-efficient manner.

The Challenges Ahead

There is a range of strategies that attempt to address climate change, many of which are focused on reducing our carbon dioxide emissions. Another promising approach is known as the 'direct air capture' method, for removing carbon dioxide from the atmosphere. In this process, air is filtered through a solution or solid matrix, referred to as the 'sorbent', to absorb or 'capture' carbon dioxide. The filtered air is then returned to the atmosphere.

Direct air capture methods have the potential to remove over 10 billion tonnes of carbon dioxide per year. Currently, however, the technology is still considered to be underdeveloped. Dr Radu Custelcean and his team at Oak Ridge National Laboratory in the US have been researching new direct air capture methods that could provide a simple, energy-efficient and environmentally friendly technology for atmospheric carbon dioxide removal.

Once captured, carbon dioxide presents several potential options. It can be transported through pipelines before

being either injected underground, or supplied to industries that use it. As such, it's important for Dr Custelcean's team to develop sorbents that not only capture carbon dioxide efficiently, but also release it in a controlled, energy-efficient and sustainable way.

There are plenty of challenges for Dr Custelcean and his team. A sorbent that can strongly bind to carbon dioxide is advantageous for the absorption stage of the process, but much less so for the release stage. Additionally, although atmospheric carbon dioxide levels have risen substantially over the past few decades, its overall concentration is still very low, at about 0.04%, thereby requiring very large volumes of air to be handled. Furthermore, other gas molecules, including water and nitrogen, can also become absorbed as air is passed through the sorbent. Therefore, the ideal sorbent would need to be able to selectively separate low concentrations of carbon dioxide while letting other gases pass through, and then release carbon dioxide with a low energy input when needed.

Trapping and Releasing Carbon Dioxide

One class of sorbents that has been previously explored is an 'inorganic alkaline' solution of sodium hydroxide and calcium hydroxide in water. The overall procedure involves two connected cycles. During the first 'absorption' cycle, carbon dioxide reacts with the solution and produces dissolved sodium carbonate. During the second 'regeneration' cycle, calcium hydroxide then reacts with sodium carbonate to produce solid calcium carbonate while regenerating sodium hydroxide. Since calcium carbonate is solid, it can be filtered from the sorbent. It can then be heated to release carbon dioxide and regenerate calcium oxide, which when mixed with water, regenerates calcium hydroxide. The sorbents are thus recycled and the capture, regeneration, and release steps are repeated.

Inorganic alkaline solutions are known to quickly react with carbon dioxide, despite its low concentration in air. However, these solutions can be corrosive, and the temperatures (around



900°C) and energy demands needed to heat calcium carbonate to release carbon dioxide are quite high.

Alternatives to inorganic alkali sorbents are organic, amine-containing sorbents. Amines are nitrogen-containing organic compounds, which produce an alkaline solution when dissolved in water. There are, however, disadvantages to using amines. They are volatile, toxic compounds, and eventually evaporate to the atmosphere over time. There have been efforts to bind amines to solid frameworks to prevent them from evaporating, but these solid-supported amine sorbents are slow to absorb carbon dioxide and found to degrade in air over time.

Dr Custelcean's team recently discovered a class of organic sorbents known as 'bis(iminoguanidines)', abbreviated as BIGs, which partly resemble amines in structure, and dissolve in water to produce an alkaline solution. The alkaline solution of BIG can react with carbon dioxide and form an insoluble carbonate salt. The solid salt, when filtered from the sorbent, can be heated at relatively low temperatures (around 100°C) to release carbon dioxide and regenerate the BIG sorbent. Unfortunately, the carbon dioxide capacity and rate at which it is absorbed is low; therefore, modifications are needed to increase the amount of carbon dioxide captured and speed up carbon dioxide absorption.

Amino Acids as Sorbents

Dr Custelcean's team considered the two-cycle approach and decided to investigate the pairing of 'amino acids' with BIG compounds as the sorbent mixture, analogous to the sodium hydroxide and calcium hydroxide mixture. That is, amino acids are involved in the absorption cycle and BIG compounds are involved in the regeneration cycle. Amino acids are the building blocks of proteins and therefore have a much lower toxicity than inorganic alkalis. They are also far less volatile than amines.



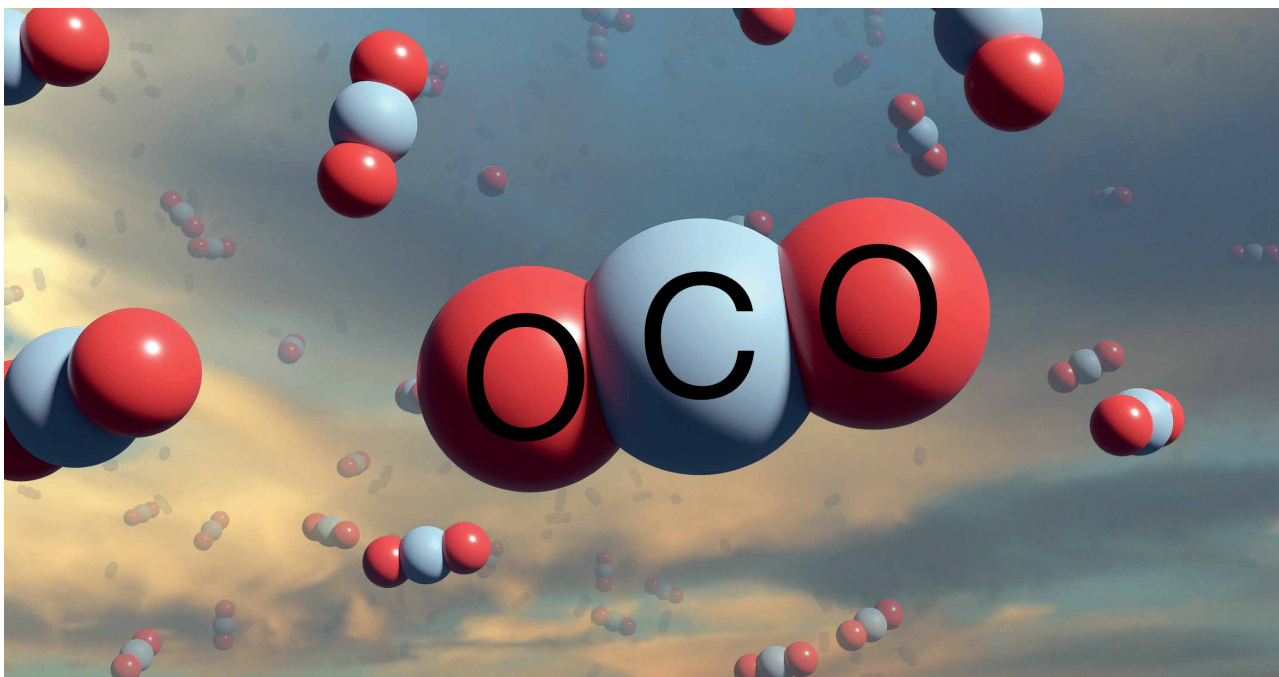
In a study published in 2018, Dr Custelcean's team found that the reaction between atmospheric carbon dioxide and aqueous amino acid solutions was very fast, on par with that between carbon dioxide and sodium hydroxide or amines. The resultant carbonate ions could then be crystallised using a BIG derivative, called PyBIG, at room temperature. Encouragingly, the team found that the PyBIG-carbonate salt, when heated to 120°C for 30 minutes, released most of the carbon dioxide and was converted back to PyBIG in near quantitative yield. This result demonstrates that sorbent regeneration could be achieved at temperatures much lower than those needed when using inorganic alkalis, with negligible loss of material.

The group then heated a sample of the PyBIG-carbonate salt in air for one week, equivalent to 336 30-minute heating cycles, to test the chemical stability of the PyBIG sorbent. They then added the regenerated PyBIG sample to an amino acid-carbonate mixture to detect whether prolonged heating or usage would affect the carbon dioxide capture efficiency. The group's results indicated only a very small difference compared to freshly prepared PyBIG, demonstrating that the sorbent would have a long life-cycle.

Heating methods that avoid the use of energy sources that emit carbon dioxide are an important consideration in direct air capture technologies. As part of their PyBIG study, Dr Custelcean's team demonstrated the use of concentrated solar power as a source of sustainable energy to heat the PyBIG-carbonate salt and release nearly all of the captured carbon dioxide.

Other Derivatives of BIG

Following the successful proof-of-concept studies with amino acids and PyBIG, Dr Custelcean's team then looked to further their investigation by exploring other derivatives of BIG that are cheaper and more effective than PyBIG. Their next target was a derivative referred to as BBIG. Structurally similar to PyBIG, BBIG has a single nitrogen atom replaced with a pair of carbon and hydrogen atoms. This minor structural modification means



that BBIG is much cheaper to prepare compared to PyBIG. However, a downside is that the BBIG-carbonate solid formed is less crystalline and more sludge-like, making filtration more difficult. This observation is important to note particularly as the methodology could eventually be scaled up from a laboratory gram-scale to an industrial tonne-scale. On the other hand, the heating conditions required to release carbon dioxide from BBIG-carbonate are very similar to those involved in the PyBIG study.

In another investigation, Dr Custelcean's team explored the carbon dioxide capture abilities of GBIG, one of the simplest and oldest BIG derivatives, first reported by German scientists at the end of the 19th century. While the team found that GBIG was quite an effective and energy-efficient sorbent for carbon dioxide capture from more concentrated streams, such as the flue gas emitted from coal-burning power plants, it was not very efficient at direct air capture. Unlike PyBIG and BBIG, GBIG formed less stable crystals with carbon dioxide. While the lower crystal stability led to a smaller regeneration energy, it also reduced the direct air capture efficiency of GBIG.

These findings contribute to the overall understanding of the structural and thermodynamic factors that determine the suitability of a sorbent for direct air capture. Based on this fundamental understanding, very recently Dr Custelcean's team demonstrated that when combined with small peptides, GBIG led to an effective direct air capture process with significantly lower energy requirements compared to state-of-the-art technologies.

Correlating Structure with Direct Air Capture Function

Following Dr Custelcean's GBIG publication, the team then focused on the development of new BIG sorbents with

improved direct air capture performance, by incorporating one or two 'methyl' groups into GBIG (they use the label 'methyl-GBIG' to refer to these new compounds). A methyl group is composed of one carbon atom and three hydrogen atoms.

In most cases, a methyl group is thought to repel water and make the given molecule less water-soluble. Surprisingly, the team found that methyl-GBIG was much more soluble in water than GBIG, leading to the expectation of a significant increase in the carbon dioxide capture efficiency. Solid precipitates generally form when dissolved molecules cluster together and start resembling a pure solid. Based on X-ray and neutron diffraction measurements, Dr Custelcean's team reasoned that the methyl groups prevented the methyl-GBIG molecules from self-assembling in solution and packing efficiently in the crystals.

On the other hand, Dr Custelcean's experimental and computational analyses of the carbonate salts of methyl-GBIG derivatives showed that, unlike GBIG, the methyl-GBIG derivatives form stable carbonate crystals that are relatively insoluble in water. Thus methyl-GBIG derivatives, like PyBIG, are suitable as direct air capture sorbents. Their thermodynamic properties, such as temperatures and energies of regeneration, are very similar to those of the PyBIG prototype.

Moving forward, Dr Custelcean's team is interested in scaling-up these direct air capture systems, optimising their performance, and testing them over multiple capture-release cycles, with the ultimate goal of developing an energy-efficient, sustainable direct air capture technology that can help address climate change. Towards this goal, Dr Custelcean seeks to team up with industrial partners and attract capital investments for moving this promising scientific discovery from the laboratory bench to the real world.



Meet the researcher

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Dr Radu Custelcean is a Senior Research Scientist at Oak Ridge National Laboratory. He received his PhD in Chemistry from Michigan State University in 2000 under the supervision of Professor James E. Jackson, followed by postdoctoral training with Professor Michael D. Ward at the University of Minnesota. Dr Custelcean started his independent career in 2003 at Oak Ridge National Laboratory, where for the past 18 years has been pursuing research in the areas of self-assembled molecules and materials for environmental and energy applications, crystal engineering, separation science and technology, anion recognition, and carbon capture. In 2008, he received the Margaret Etter early career award from the American Crystallographic Association.

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