

Storing carbon dioxide deep underground may be one way to reduce emissions to the atmosphere. **Chris Rochelle** (BGS) and **Ameena Camps** (University of Leicester) discuss the attractions of locking up the carbon dioxide as a gas hydrate mineral.

Cool ways to cage carbon dioxide

The capture of carbon dioxide (CO₂) from large point sources such as power stations, followed by underground storage, is one potential method for reducing anthropogenic emissions of this greenhouse gas to the atmosphere. Current approaches for deep storage typically involve injecting CO₂ down boreholes into warm, porous rocks deeper than about 800 metres. However, there is another approach involving storage under cooler temperatures — such as beneath permafrost regions or in sediments below the floor of deep oceans. This ‘cool storage’ approach has received relatively little attention, even though it may offer certain advantages for the long-term containment of CO₂, and this has been the focus of a collaborative study between the BGS and Leicester University.

A key aspect of the underground storage of CO₂ is that it must remain safely trapped for many thousands of years. Different trapping mechanisms operate at different times, and the following are important in order of increasing timescale:

- trapped as a free CO₂ phase below an impermeable caprock
- trapped as dissolved CO₂ in groundwater
- trapped in secondary solid mineral precipitates.

Trapping as solid precipitates is very attractive as it effectively immobilises the CO₂ for ‘geological’ timescales. Under sufficiently cool conditions gas hydrate minerals become stable. These unusual ice-like solids are made up of cages of water molecules — each one able to trap a molecule of gas. CO₂ hydrate can precipitate very rapidly, needing only CO₂ and water to form. It is also very effective at trapping CO₂, locking up 160 times its own volume of the gas. As a consequence,

storing CO₂ in rocks where hydrate can form could be very beneficial, providing safe and secure long-term storage.

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Storing CO₂ as a hydrate would need cool rocks at sufficiently high pressures with enough pore space. These can be found beneath regions of permafrost, or beneath the beds of deep oceans. Liquid CO₂ would be injected slightly below where it was to be stored, where the temperatures are just too warm for CO₂ hydrate to form (the temperature increasing the deeper you go into the Earth). As the slightly buoyant CO₂ slowly rises, it would move into cooler rocks where CO₂ hydrate would begin to precipitate. Over time, a ‘cap’ of

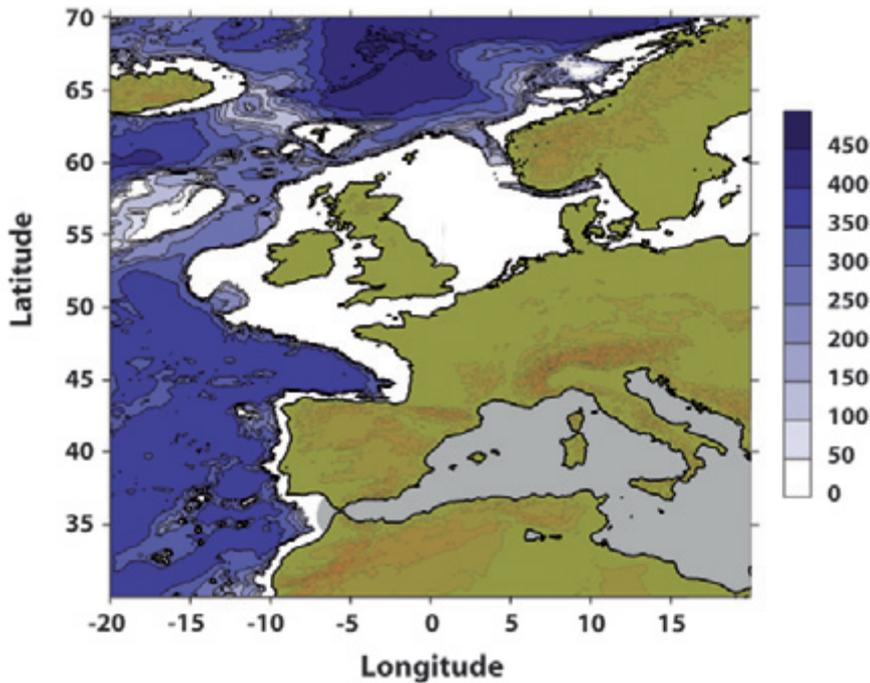
CO₂ hydrate would form above a pool of liquid CO₂, and this cap would add extra sealing to any natural caprock. If any CO₂ were ever to break through the hydrate cap, then it would meet cold water in the rocks above and form more CO₂ hydrate — effectively sealing any leak.

Forming CO₂ hydrate is only part of the story, however. There are other benefits to storing CO₂ under cool, but high-pressure conditions.

Under these conditions the stable phase of CO₂ will be *liquid*, whereas in conventional approaches the CO₂ is actually a lower density *supercritical fluid*. This density difference is important as possibly 30–40% more CO₂ could be stored in an equivalent volume of rock.



Cylindrical sample of laboratory-grown CO₂ hydrate being removed from a steel pressure vessel.



Map of predicted thickness in metres of the CO₂ hydrate stability zone within sea-bed sediments for offshore western Europe. Note that the Mediterranean Sea is not covered by this study. (A Camps, unpublished PhD thesis.)

Another benefit of the denser liquid CO₂ is its lower buoyancy, and hence reduced potential for upward migration.

Significant amounts of dissolved CO₂ will also be trapped in deep groundwaters. Indeed, cooler storage conditions favour this as CO₂ solubility increases with decreasing temperature (up to the point where CO₂ hydrate precipitates). This is important as significantly more CO₂ could be stored in groundwater in contact with liquid CO₂, compared to that in contact with supercritical CO₂.

The precipitation of large amounts of CO₂ hydrate will change the properties of the sediments, for example by reducing their permeability. It is important, therefore, to have a detailed understanding of the small-scale processes associated with this precipitation. We have investigated this through laboratory experiments that form CO₂ hydrate in sediments under realistic low temperature/high pressure conditions. By preserving samples under cryogenic temperatures (at about -180°C) detailed scanning electron microscope studies can be carried out, letting us see where, and how, the hydrate has grown within pore spaces.

To scope the potential for trapping CO₂ as a hydrate, a computer model has been developed to generate maps showing areas of theoretical CO₂ hydrate stability. The map of the sea bed off western Europe does not identify particular geological structures but shows that up to nearly 0.5 km of the upper sediments lie within the CO₂ hydrate stability zone — the region in which a ‘cap’ of CO₂ hydrate could form.

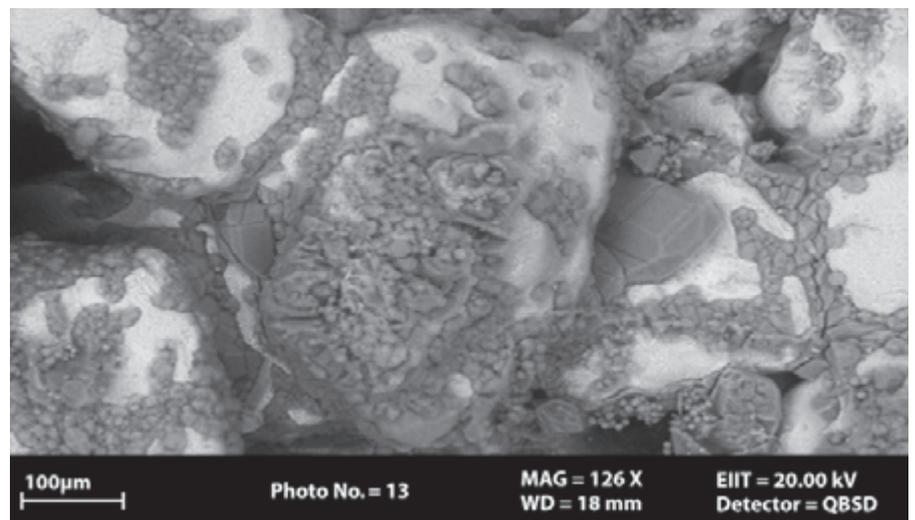
Although CO₂ hydrate is not stable below the relatively shallow waters close to the UK, there is much more potential close to other countries (such as Spain, Portugal and Norway) where deep and cold waters exist relatively close to shore.

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The underground storage of CO₂ could be a practicable way to reduce anthropogenic emissions of this greenhouse gas to the atmosphere without dramatically changing our energy-producing technologies. Trapping the CO₂ as a hydrate phase associated with liquid CO₂ is an attractive, alternative method of underground storage, and gives governments and industry a further option if their country has suitable cool deep waters or permafrost conditions.

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Scanning electron microscope image of sand grains (light grey) cemented together by films of CO₂ hydrate (dark grey). Note crystals of CO₂ hydrate growing in the pore spaces between the sand grains. (A Camps, unpublished PhD thesis.)