

Mineralisation to capture and use CO₂ from steam methane reforming

Where CCS with underground CO₂ storage is not possible, mineralisation of the CO₂ to chemicals such as soda ash or sodium bicarbonate is an emerging solution

Stephen Harrison
sbh4

Carbon capture is an essential tool in the global decarbonisation tool kit

Much has been said about CCS – carbon capture and storage. The need to decarbonise is clear. Renewable power generation and green hydrogen may do much of the heavy lifting as they scale up in coming decades, but there are legacy assets that must also be decarbonised, and there are several processes that release CO₂ from within the process chemistry.

Neither renewable power nor green hydrogen will be able to avoid CO₂ release from calcium carbonate rock during the calcination of limestone to make lime or cement. Also, steam methane reformers (SMR) release CO₂ from the process chemistry. So, even if the required heat for the endothermic reaction is provided by renewable power, CO₂ emissions from the conversion of the methane to hydrogen-rich syngas would still occur (see **Figure 1**).

While the benefits of capturing CO₂ emissions before they reach the atmosphere are widely accepted, the possibility of storing CO₂ underground in depleted gas fields or saline aquifers relies heavily on having the right sub-surface geological conditions. In addition to geological constraints, public opinion and political will must also be aligned before underground CO₂ storage can be considered a sequestration method.

Carbon capture and mineralisation (CCM) is an alternative to CCS. The starting point is, in principle, the same: CO₂ emissions are captured before they are released into the air. However, instead of storing the CO₂ underground, it is reacted with chemicals to form inert mineral

salts. CCM is, in essence, an example of carbon capture and utilisation.

The chemicals that react with the CO₂ to form the minerals can also be used to capture the CO₂ from the flue gas, thereby differentiating from established carbon capture technologies that consume either high amounts of steam or electricity at the CO₂ capture location.

Airovation Technologies, based in Israel, has developed an innovative CCM process that reacts commonly available chemicals, such as sodium hydroxide, with CO₂ from flue gases to produce mineral salts, such as sodium carbonate and sodium bicarbonate, which have a wide range of commercial applications.

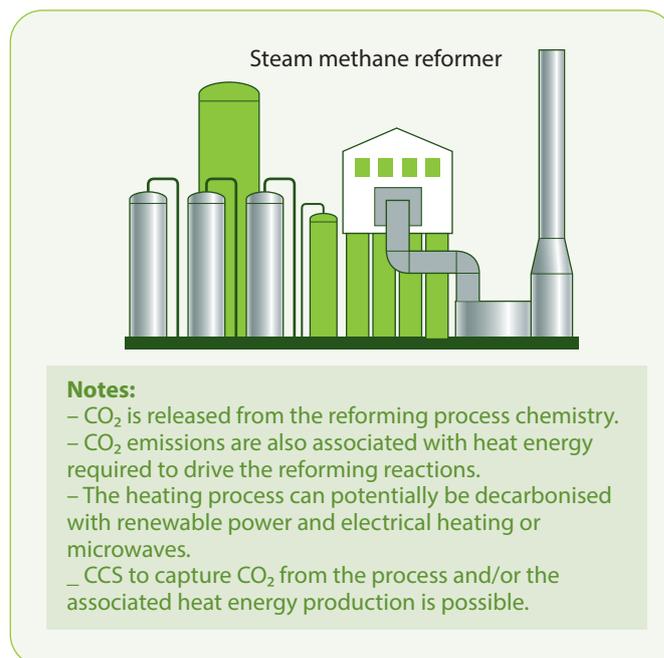


Figure 1 Steam methane reforming decarbonisation

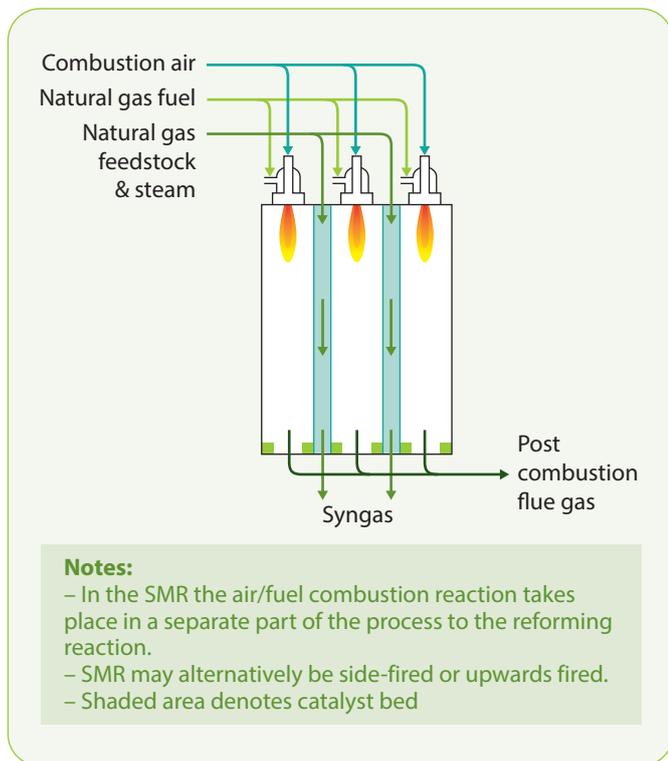


Figure 2 Steam methane reforming chemistry

CO₂ generation during steam methane reforming

Renewable power supplied to an electrolyser can produce green hydrogen, and many new-build hydrogen plants will operate this way. However, the most common hydrogen production process, used to generate about 80% of the world's hydrogen, is steam methane reforming. There is a legacy of more than 1,000 operational SMRs around the world. Retrofitting CCM, or another carbon capture technology, can decarbonise these assets and extend their life.

Steam methane reforming uses natural gas, refinery gas, or naphtha as feedstocks. When these fossil feedstocks are used to generate hydrogen without capturing the CO₂ emissions, it is called 'grey' hydrogen. If most of the CO₂ from the SMR is captured, the hydrogen is referred to as 'blue'.

CO₂ is released from the SMR in two locations: firstly, as the feedstock is transformed to hydrogen, CO₂ is produced as an unavoidable by-product. Secondly, CO₂ emissions from the combustion of fossil fuels (generally a portion of the natural gas feedstock) create the heat required to drive the reforming chemical reactions that convert the feedstock to hydrogen (see **Figure 2**).

CO₂ is unavoidably released from the process

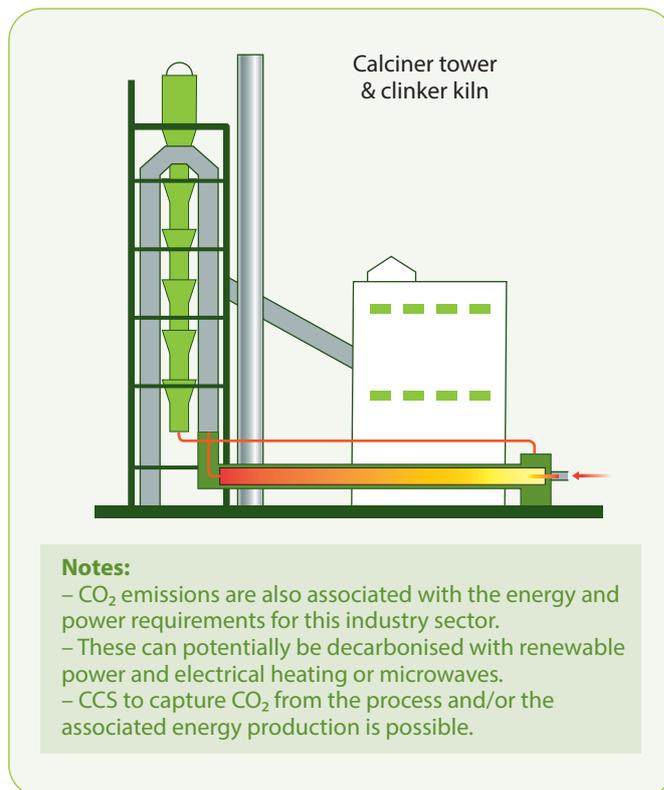


Figure 3 Difficult to decarbonise industries – cement making

during reforming, cement, glass and steel production. The flue gas streams from these processes are rich in CO₂ at about 15%. This can double to 30% if oxy-fuel combustion has been used. This compares with flue gas from a normal gas- or coal-fired combustion process, which typically contains 2-6% CO₂ (see **Figure 3**).

Whilst these processes are responsible for high CO₂ emissions globally, they are also some of the best processes to target for CO₂ capture because removing CO₂ from these flue gases is more cost effective per tonne of CO₂ sequestered than capturing CO₂ from a very dilute flue gas stream, such as the emissions from a gas-fired turbine power plant.

The Airovation Technologies CCM process is ideal for treating steam methane reforming flue gases and other flue gases with similarly elevated CO₂ concentrations. It benefits from the process intensity, and the reactions respond well to the elevated CO₂ concentrations.

Conventional SMR carbon capture technologies can stress utilities infrastructure

The most widespread technology for carbon capture uses a twin tower process, where CO₂ from the flue gas is absorbed into an amine-

based solvent in the first tower. The CO₂-lean flue gas flows to the atmosphere. The CO₂-rich amine is pumped to a second stripper tower, where steam is used in vast quantities to boil the CO₂ away from the amine solvent. The regenerated, CO₂-lean amine solvent is pumped back to the absorber tower to collect more CO₂, and the process operates continuously, with the amine being recirculated from the absorber to the stripper.

Variations of the amine-based carbon capture process use chilled ammonia, methanol or potassium bicarbonate as the solvent to absorb the CO₂. The process configuration is similar. All these processes require a huge heat energy input to boil the CO₂ out of the solvent. Unfortunately, this additional energy is not always available at the site where the CO₂ must be captured. The ramp-up in natural gas or fuel oil supplies may stress the local infrastructure beyond its capability (see **Figure 4**).

Vacuum swing adsorption (VSA) and temperature swing adsorption have also been used for refinery SMR CO₂ capture. VSA locks the CO₂ into a solid molecular sieve adsorbent. In the VSA system, a rapid pressure reduction releases the CO₂ from the adsorbent. Electrical power is required in large quantities, and the local power supply infrastructure may not be sized for the additional demand.

VSA has been demonstrated effective in removing CO₂ from SMR process gases. Air Products operates two SMRs at Port Arthur, Texas, to supply hydrogen to the neighbouring Valero refinery. Both SMRs use VSA technology to capture the CO₂ by-product. The resultant

CO₂ is compressed, dried, and transferred to a nearby location through a pipeline. The CO₂ is utilised and permanently stored underground in an enhanced oil recovery scheme. This is an example of carbon capture, utilisation, and storage (CCUS).

SMRs generally use natural gas, refinery gas or naphtha as their feedstock. The hydrocarbon feedstock is combined with steam and converted to syngas over various reforming and water gas shift catalysts. The resultant syngas has a typical composition of 76% hydrogen, 17% CO₂, and 7% unreacted methane and other gases. The syngas pressure is around 25 bar at this stage in the process (see **Figure 5**).

An SMR typically emits 9.5 kg of CO₂ per kg of hydrogen, making hydrogen produced from fossil fuels without carbon capture unsustainable. To capture much of the CO₂ from the process gas on the Air Products SMRs, the VSA units were installed between the water gas shift reactors and the hydrogen purification PSA unit. For established CO₂ capture technologies such as amine wash or VSA, this is a highly cost-effective location to capture the CO₂ due to the high pressure and high CO₂ concentration, which combine to result in a high partial pressure of CO₂. CO₂ can be produced from the VSA units with a purity of 95% and a recovery rate (from this process stream) of over 90%.

In addition to the process CO₂, there are additional post-combustion CO₂ emissions on the SMR. It is more challenging to capture CO₂ from the post-combustion flue gases using conventional amine wash or VSA

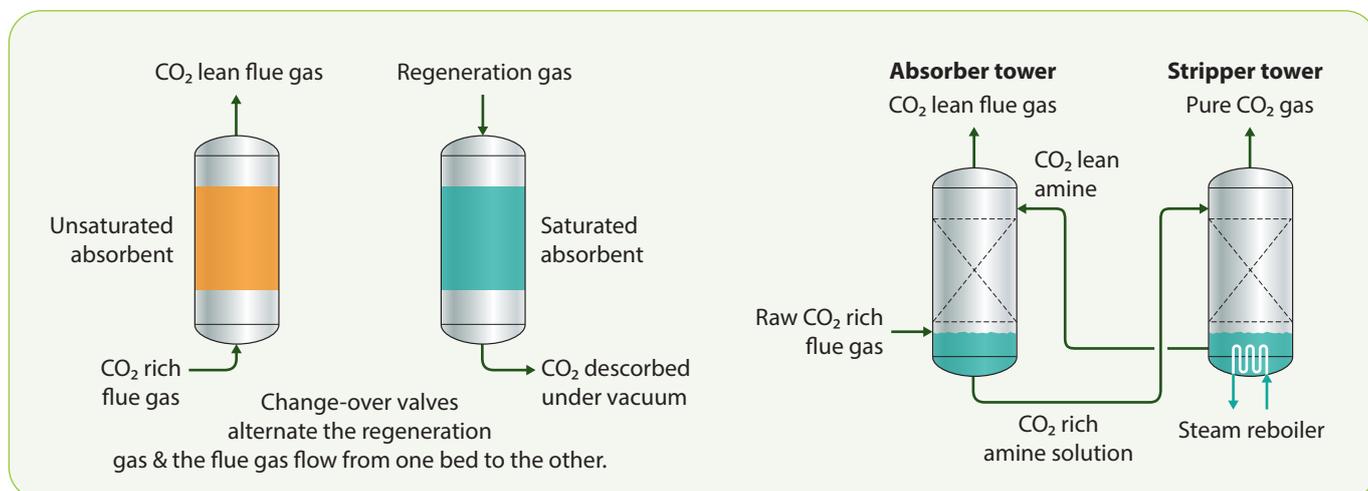


Figure 4 Established carbon capture technology – VSA and amine solvent

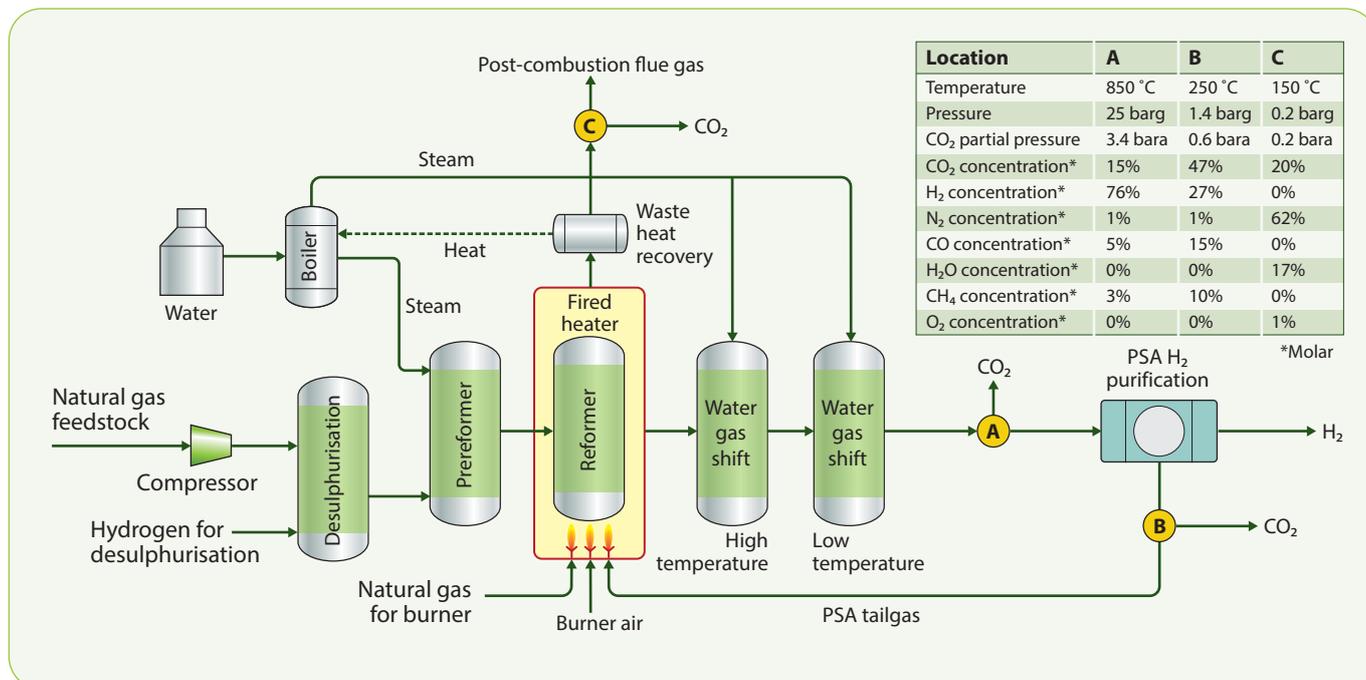


Figure 5 Potential locations for CO₂ capture from steam methane reforming

carbon capture technologies because the CO₂ concentration and the pressure are both low.

However, if a high overall CO₂ capture rate is required, the low-pressure post-combustion CO₂ emissions must be captured in addition to the high-pressure process CO₂. An advantage of the Airovation mineralisation process is that it is rather agnostic to the CO₂ stream pressure, making it viable for use with the low-pressure post-combustion flue gas to achieve the highest overall capture rate.

Carbon capture and mineralisation – putting captured CO₂ to good use

Unlike the amine-based systems that require additional heat and natural gas or the VSA system that requires extra power at the carbon capture site, the Airovation Technologies CCM process avoids the need for additional utilities infrastructure at the CO₂ capture location.

The idea of reacting the CO₂ in a liquid to form a new mineral chemical is core to CCM. The minerals produced can have a much higher value than the CO₂ gas recovered from traditional solvent absorption or alternative adsorption technologies.

CCM is at the heart of the Airovation Technologies process for CO₂ sequestration. The minerals produced can be any one of the following:

- Sodium carbonate (Na₂CO₃)

- Sodium bicarbonate (NaHCO₃)
- Potassium carbonate (K₂CO₃)
- Potassium bicarbonate (KHCO₃)

The CO₂-rich flue gas is reacted with sodium hydroxide (NaOH) or potassium hydroxide (KOH) alkali solutions to produce the sodium or potassium minerals, respectively. These alkalis are produced worldwide using chloralkali electrolysis either as the main product or as a by-product when chlorine gas or hydrogen chloride are the desired products. In any case, the feedstocks for the process are widely available and highly transportable (see **Figure 6**).

Each of the mineral salts listed above has a breadth of applications. Sodium carbonate (Na₂CO₃), or soda ash, is the 10th most widely used inorganic chemical in the world. Used extensively in flat glass and container glassmaking, it can comprise up to 30% of the glass melt feedstock by mass. This application for Na₂CO₃ allows for circularity within the glassmaking process, and the glassmaker can avoid the transportation and procurement costs of high tonnages of soda ash.

Potassium salt minerals are broadly known as potash. Potassium carbonate is used for glassmaking and producing soaps and detergents. Potassium bicarbonate is widely applied as a fertiliser, especially to neutralise acidic soils and simultaneously increase the potassium level.

Life cycle analysis confirms the environmental benefits of CCM

The environmental impact or benefit of a process can be confirmed using a technique known as life cycle analysis, or LCA. For the Airovation mineralisation process, the main input is the alkali feedstock, and the main output is the mineral. Also, CO₂ emissions are avoided due to capture and mineralisation of the flue gas.

If the mineral is subsequently used, for example when baking soda is used for baking bread and the CO₂ is released into the dough, the full life cycle environmental benefit of the capture process is somewhat neutralised. On the other hand, the avoidance of CO₂ emissions from alternative production processes to make the baking soda must be considered. In this respect, the Airovation process scores highly in the LCA.

As an example, soda ash is a major ingredient in glassmaking. When it is combined with sand and melts during the glass-forming process, CO₂ is liberated. However, using Na₂CO₃ from the mineralisation of flue gas CO₂ consumes no CO₂ and CO₂ emissions are avoided. On the other hand, the conventional Bayer synthetic Na₂CO₃ process liberates many kilograms of CO₂ per tonne of soda ash produced – avoiding these emissions boosts the environmental benefit of the Airovation CCM process when valuable commercial products are generated. Natural soda ash is produced from Trona mineral ore in the US, Turkey, and from some African Trona deposits. Whilst this route to natural Na₂CO₃ is slightly less CO₂ intensive than the Bayer process, the energy requirement to crush and refine the Trona ore is large and significant CO₂ emissions result. These emissions are avoided in the LCA for the Airovation Technologies CCM process when valuable mineral products at marketable specifications are produced.

Chemistry behind the CCM process

Airovation has innovated a proprietary chemical oxidation process based on the in-situ generation of highly concentrated superoxide radicals in an aqueous environment (Stoin, Barnea, & Sasson, 2014). The superoxide radical is extremely reactive and rapidly catalyses the

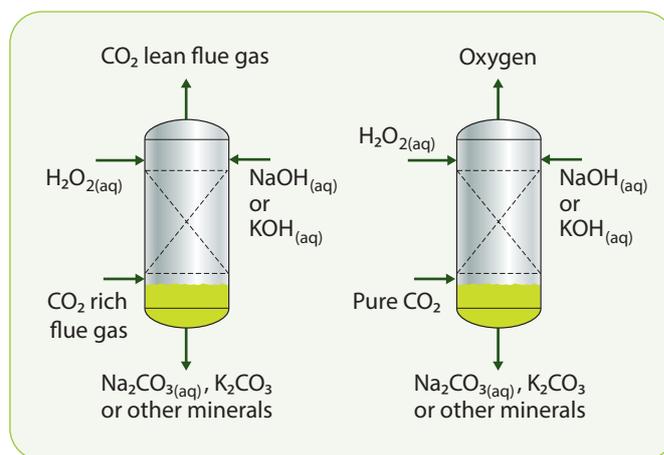


Figure 6 Airovation mineralisation processes for CO₂ capture and utilisation using alkalis and the superoxide radical

removal of CO and CO₂ from flue gas streams with capture rates exceeding 95%. The carbon capture reaction consumes either NaOH or KOH as a strongly alkaline aqueous solution used as the contact medium through which the flue gas is passed. Hydrogen peroxide (H₂O₂) is consumed to generate the superoxide radicals that catalyse the carbonation reactions.

Hydrogen peroxide is purchased as a standard high-strength solution in water and is dosed continuously to the process at a rate according to the mineralisation product requirement and the associated stoichiometry. The hydrogen peroxide is consumed rapidly in the reaction pathway, and residual concentration in the reactor is low.

CO₂ capture rates of 98% have been achieved using KOH and up to 100% using NaOH, and it compares favourably with conventional CO₂ capture technologies, which tend to operate between 90 and 95% capture rates. Uniquely, in the CCM process, both CO₂ and CO are removed from the flue gas, with capture efficiencies of more than 99% for both gases.

CCM process parameters and economics

The process flowsheet for the Airovation process involves two gas/liquid contactors. They are both extremely compact due to the rapid reaction kinetics and concentrated solutions used in the process. The feedstocks, NaOH (or KOH) and H₂O₂, flow counter-current to the flue gas through the two contactors to ensure high capture rates of CO₂ within the compact process equipment (see **Figure 7**).

The carbonate or bicarbonate mineral solution

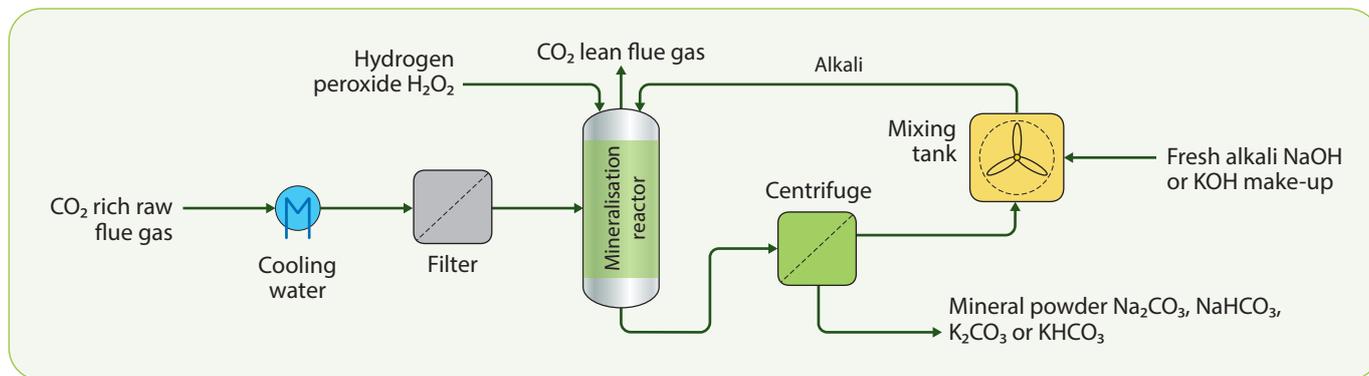


Figure 7 Airovation - alkali mineralisation of CO₂ using the superoxide radical

from the process is enriched using a centrifuge and hydrocyclone: conventional mineral solution processing equipment. If required, a dryer may be incorporated to yield a solid mineral product. Heat exchangers, filters, pumps, flue gas fans, feedstock tanks, and product storage make up the balance of plant.

The mineralisation reaction stoichiometry governs the consumption of the NaOH or KOH alkali feedstock. For sodium carbonate formation, a 2:1 ratio of NaOH to CO₂ is required, equivalent to 1.8 kg of NaOH per kg of CO₂ captured. For sodium bicarbonate, a 1:1 NaOH to CO₂ molar ratio is required, equivalent to 0.9 kg of NaOH per kg of CO₂ captured. Per kg of CO₂ sequestered by the mineralisation process, the formation of bicarbonate has a lower alkaline feedstock input requirement and, therefore, lower operating cost.

NaOH is added as a highly concentrated aqueous solution. This can either be delivered to site or made on-site from solid NaOH mineral salt crystals, which are dissolved in water prior to being introduced into the process. The use of highly concentrated or solid NaOH reduces the volume of feedstock required to be

transported by road or rail tanker to the CO₂ capture location (see Figure 8).

Process design, operating conditions, and the catalytic dosage can be adjusted to determine whether NaHCO₃ or Na₂CO₃ is produced. A crucial factor used to control the product formation pathway is the alkalinity, requiring a pH greater than 8. Airovation Technologies will be able to finely tune the process to control the selectivity of the reactions and avoid the need for any subsequent separation processes between the mixed formation of Na₂CO₃ and NaHCO₃.

Economic considerations

At present, a major driver for operators to reduce their CO₂ emissions is taxation, with Emissions Trading Schemes in place in the European Union and many other jurisdictions. Pull-through from customers is also a strong motivation to decarbonise, and many companies selling their products in European, Japanese, South Korean or US markets will face pressure to reduce the CO₂ footprint of their products. Corporate strategies and national decarbonisation targets being implemented by government-owned entities are also powerful decarbonisation drivers.

If the Airovation Technologies process is integrated into a chloralkali electrolysis site focused on chlorine gas or hypochlorite production, the co-produced sodium hydroxide may be regarded as a low-value by-product. Under these circumstances, the economics for the Airovation CCM process can become highly favourable.

The main balance of plant operating costs is related to electrical power and cooling water provision. With a flue gas of the above CO₂

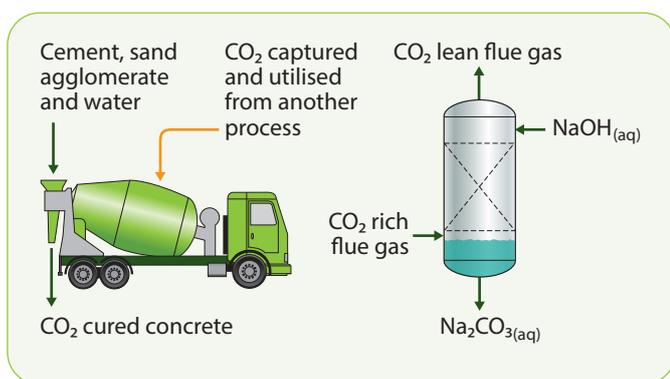


Figure 8 Mineralisation processes for CO₂ capture and utilisation from steam methane reforming

concentration and a temperature of circa 170°C, process analysis has shown that less than 100 litres of recirculated cooling water are required per tonne of CO₂ mineralised. This cooling water is required to cool the flue gas and mitigate the heat generated from the exothermic mineralisation reactions. Heat from the flue gas is also recovered within the process to maximise efficiency. It is used to dry the mineral salts to powders for ease of transportation. The power requirement is modest, in the order of 300 kWh per tonne of CO₂ mineralised.

Mineralisation can either be applied to the full flue gas stream or a slipstream. The balance of the flue gas can be processed using other complimentary CCUS technologies or left as an emission for today and be decarbonised in the future. Airovation Technologies CCM plant designs are modular and allow incremental scale-up. The approach also fits well to support demonstration projects and pilots so that operators can gain exposure to a range of decarbonisation solutions.

Carbon capture and mineralisation for concrete curing

Concrete curing takes advantage of the sequestration capability of concrete by injecting an additional 1.5 kg of CO₂ per tonne of cement during concrete preparation. This increases the strength of the concrete because additional calcium carbonate is formed as the CO₂ reacts with the cement fraction of the concrete. The result is that 5% less cement is required to make the concrete, which translates to a reduction in CO₂ emissions.

A disadvantage of this type of mineralisation application is that the CO₂ must be liquefied after capture and transported from the SMR site to the construction site. Liquefaction requires power and additional capital equipment, and the demand for CO₂ in concrete curing in any given region is highly variable, according to the nature and scale of any major construction projects taking place at any time.

VIEW REFERENCES



Stephen Harrison
sbh@sbh4.de

References

Stoin, U., Barnea, Z., & Sasson, Y. (2014). New Technology for post-combustion abatement of carbon dioxide via an in site generated superoxide anion-radical, *RCS Adv.*, 2014, 4, 36544-36552. <https://doi.org/10.1039/C4RA03844D>