Cryogenic technologies for CCTUS

Carbon dioxide capture, transportation, utilisation & storage

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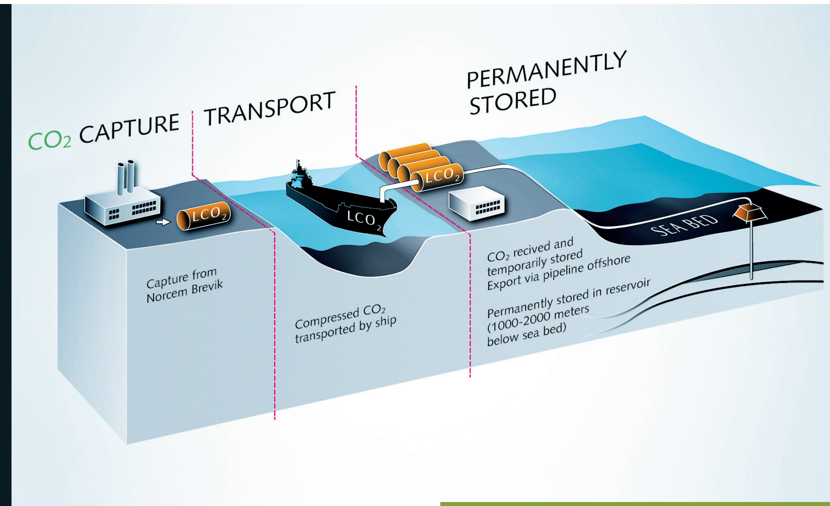

© Norcem | **Northern Lights CCTS Illustration**

CCTUS refers to carbon dioxide (CO_2) capture, transportation, utilisation, and storage. CO_2 transportation or distribution is often required between the CO_2 capture location and the place where the CO_2 will either be permanently stored, or utilised.

Moving large amounts of CO_2 cost-effectively can be achieved through liquefaction of the CO_2. The alternative is compression of the CO_2 to more than 80 bar so that it exists as dense, supercritical CO_2 and can be transmitted by pipeline.

Cryogenics makes CO_2 compact for transportation and storage. Gaseous CO_2 at atmospheric pressure and ambient temperature requires 588 times more volume than liquid CO_2.

Cryogenic CO_2 capture technologies are ideal where liquid CO_2 distribution will be required to the utilisation or sequestration location. This will be the case where the CO_2 is destined to be used in food, beverage, or other industrial gases applications.

Liquid CO2 storage bullet tanks

It is also likely that liquid CO_2 distribution for carbon capture and sequestration (CCS) projects will be required for many years, since almost no CO_2 pipeline infrastructure exists today. For example, the Northern Lights CCS project (which will permanently store CO_2 emissions from a waste to energy plant and Norcem's Brevik cement plant in Norway) will use liquid CO_2 distribution. Ships will transport liquid CO_2 from the capture locations to the underground injection location, offshore in the North Sea.

Other gas-phase CO_2 capture technologies may be more suitable if CO_2 compression and pipeline transmission is required, or if onsite gaseous CO_2 utilisation is possible. In these cases, the energy requirement can potentially be reduced due to the avoidance of the power needed to liquefy CO_2.

CO_2 capture through direct liquefaction

Direct liquefaction of mixed gases is difficult. For example, when CO_2 is present in a mixture with nitrogen, the nitrogen is incondensable at the temperature at which the CO_2 can be liquefied. This means that the CO_2 liquefier heat exchanger becomes shrouded with nitrogen gas and there is no longer any contact with the CO_2 gas to be liquefied.

The potential solution would be to vent nitrogen gas from the system, but the vent gas would also contain CO_2. Much of the CO_2 would be vented and lost, meaning this is rarely a viable solution.

On the other hand, direct liquefaction of very pure CO_2 is viable. In this context, 'very pure' would typically a purity greater than 98%. Biogenic CO_2 released from bioethanol fermentation or brewing produces CO_2 at this purity.

Direct liquefaction of CO_2 from fermentation broths requires drying of the CO_2 prior to liquefaction. This is essential to avoid formation of solid ice particles within the CO_2 liquefier. It also ensures that the CO_2 product is suitable for commercial applications in the food and beverage sector or for metallurgical welding applications.

Companies such as Pentair Haffmans and SIAD Tecno Project Industriale (TPI) have installed hundreds of small-scale direct CO_2 capture and liquefaction installations ▸

© Norcem | **Norcem cement plant Brevik**

© Chart Industries | **Chart's Sustainable Energy Solutions cryogenic carbon capture pilot plant**

worldwide, mostly at breweries. Similar technology is used to remove CO_2 during upgrading of biogas to biomethane. But, in this case separation of the methane and CO_2 is required prior to liquefaction. This is often achieved using a membrane or amine solvent CO_2 capture process.

Cryogenic carbon capture

It is only recently that technology has been developed for the direct liquefaction of CO_2 from lower concentration CO_2 streams. The US start-up Sustainable Energy Solutions, now part of Chart Industries, has developed the Cryogenic Carbon Capture (CCC) process during the past decade.

CCC does not actually use direct liquefaction of CO_2, rather it relies on direct sublimation of CO_2 gas to solid CO_2. Hence it can capture CO_2 from dilute flue gas streams. After the solid CO_2 has been formed, it is dissolved into liquid CO_2. The product is high purity liquid CO_2.

The CCC process relies only on electrical power for gas blowers and compressors for its operation. There is no heat input required. The implication is that it is aligned to operation with renewable electricity, meaning that no CO_2 emissions are created from capturing the CO_2.

A further advantage of the CCC technology is that it sufficiently robust to treat 'dirty' post-combustion flue gases that contain oxides of sulphur or nitrogen. This means that it is ideally suited to capture CO_2 from emissions generated from burning coal, waste, or heavy fuel oil. In contrast, amine-based absorption and molecular sieve adsorption processes for CO_2 capture are very sensitive to sulphur impurities, meaning that a pre-purification stage would be required.

Cryocap™ H_2: for SMR CO_2 capture

CO_2 capture from steam methane reformers (SMRs) is often regarded as a 'quick-win' in the decarbonisation of industrial processes. The CO_2 concentration, pressure, and partial pressure in the SMR process gas is high. This leads to cost-effective CO_2 capture. Furthermore, CO_2 has been captured from SMRs for decades so that the CO_2 can be used to make urea fertiliser, when reacted with ammonia that is produced from hydrogen made on the SMR. There is, therefore, a wealth of experience to leverage.

The use of cryogenics to capture and purify CO_2 from SMRs is likely to be the next milestone in the development of CO_2 capture from these units. The Cryocap™ H_2 process from Air Liquide combines cryogenic separation of CO_2 from the SMR process gas stream with membrane separation of hydrogen.

A demonstration project at an SMR in Port Jérôme, on the river Seine in France, showed that an additional 12% hydrogen yield from the SMR is achievable using the Cryocap™ H_2 process. This can have a tremendous positive impact on operational economics and can help to fund the investment in the Cryocap™ H_2 equipment.

With Cryocap™ H_2 directing more hydrogen to the product stream, there is less hydrogen available for the SMR fired heater, so additional natural gas is required to compensate for the reduced heat energy available. However, the additional hydrogen production can more than offset the ▶

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Cryogenic liquid CO_2 road tanker

cost of the additional natural gas.

If liquid CO_2 is required for food and beverage applications, additional CO_2 purification is required. In the Cryocap™ H_2 process, oxygen is added to react with hydrogen in the CO_2 stream to produce water using catalytic oxidation. The water is then removed on regenerative dryer adsorption beds. Excess oxygen is separated from the liquid CO_2 using cryogenic distillation. Mercury removal is a final polishing stage which is achieved on an activated carbon filter bed.

Captured CO_2 liquefaction and storage

CO_2 liquefaction is achieved using a heat exchanger to condense CO_2 gas. The cold side of the heat exchanger is generally fed with a refrigerant gas from a typical mechanical refrigeration circuit. Electrical power is required to operate the refrigeration equipment, so the process can be decarbonised using renewable electricity.

The CO_2 side of the liquefaction circuit is operated at a pressure of 15 to 25 bar. At elevated pressure, common refrigerant gases such as CO_2, ammonia or F-Gases can be used to achieve the temperature required to liquefy the CO_2. This differs from the cryogenic liquefaction process used on air separation units, where expansion of the air itself on a turbine is used to generate the cold energy required for liquefaction of the air.

As an alternative to mechanical refrigeration, ammonia absorption refrigeration can be used. This process avoids the mechanical compression of a refrigerant gas and derives the cold energy instead from the absorption and desorption of ammonia in water. To drive the ammonia out of the water, heat energy is required. If waste heat is available, this process can be more efficient than mechanical refrigeration.

After liquefaction, CO_2 is stored and transported in tanks which are insulated to minimise boil-off. A small amount of heat ingress to the storage tank is inevitable. This is due to the temperature difference between ambient air and the liquid CO_2, which would be around -30°C at 15 bar pressure.

Typically, liquid CO_2 storage tanks are constructed of carbon steel and insulated with polyurethane foam. Often, a refrigeration unit is used to re-liquefy boiled off CO_2. This avoids CO_2 losses and over-pressurisation of the CO_2 storage tank.

Storage of liquid CO_2 differs from cryogenic storage of liquid oxygen, argon and nitrogen which are much colder. They require an austenitic grade of stainless steel for the tank and vacuum insulation to prevent vaporisation of the cryogenic liquid. gw

Refinery at Port Jerome, France