Delivering the value in CO_2 capture

By Stephen B. Harrison

Carbon dioxide (CO_2) capture is the first unit operation in a holistic value chain that extends from capture, through to transportation and utilisation or storage (CCTU/S). Optimising the CO_2 capture element without due consideration of the total cost of operating the full value chain will almost certainly result in pushing costs further down the chain – and increasing the overall capex or opex of the end-to-end system.

Start with the end in mind

To optimise the initial CO_2 capture technology, it makes sense to consider the requirement at the very end of the CCTUS value chain. What is the required purity of the CO_2? What is the required temperature and pressure condition?

If the goal is to compress supercritical CO_2 into a geological storage site, and the transmission is by pipeline, the capture technology can be selected to produce CO_2 gas which can be compressed into the pipeline.

On the other hand, if the end-game is utilisation of the CO_2 in an e-methanol or Fischer Tropsch e-fuels production process, and the transportation is using liquid CO_2 by rail, there is a requirement to produce liquid CO_2 at the capture location, or CO_2 transfer terminal where liquid CO_2 is loaded onto the train.

Capture rates count

Consider the case that a liquid solvent-based CO_2 capture system, such as a twin-tower amine process, is used upstream of a CO_2 liquefier to condition the CO_2 for transportation by rail and ship to an offshore storage facility.

The given boundary conditions are an overall CO_2 capture rate of >90% from the emissions source to geological storage and that the liquid CO_2 must comply with the Northern Lights CO_2 purity specifications.

If the amine-based CO_2 capture system were optimised in isolation, it would capture 90% of the flue gas CO_2. This minimises the size of the absorption tower to reduce capex, and minimises the reboiler energy to reduce opex.

The amine system would typically yield CO_2 of around 99% purity with

Lime making kiln

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CCUS technologies – absorption-based

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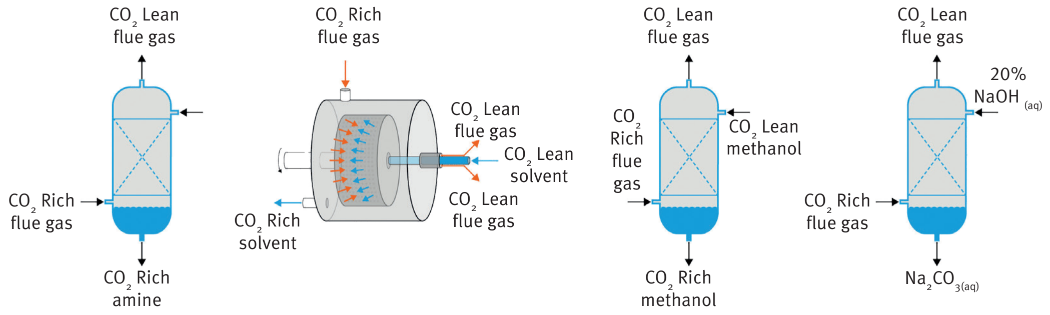

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	Amine-wash with tower contactor	Amine-wash rotating disk contactor	Methanol wash	Mineralisation
Separation principle	Absorption	Absorption	Absorption	Absorption
Specific energy demand	3 GJ/tCO_2	Predominantly electrical power, with heat	1.4 GJ/tCO_2	8.3 GJ_e/tCO_2
Typical temperature	40 - 60°C	40 - 60°C	-40°C	‹35°C
Typical pressure	Ambient	Ambient	25 - 70 bar_g	Ambient
Typical CO_2 removal	90%	90% (target)	Up to 100%	90%
Typical CO_2 purity	›99%	95% (target)	›98.5%	CO_2 mineralisation to Na_2CO
Typical plant size (Tonnes per year CO_2 removal)	40,000 - 400,000	1,000 - 500,000	› 100,000,000	1,000 - 75,000
Technology maturity level	Commercial from many suppliers	Laboratory, eg ROTA-CAP from GTI &CCSL	Commercial , eg Linde Rectisol	Demonstration, eg SkyMine

© NRG | Twin-tower amine-based CO2 capture at Petra-Nova

nitrogen as the main balance gas. This would then be fed to the CO_2 liquefier. In the liquefier, the incondensable nitrogen must be vented from the system. As it is released, it carries with it an amount of CO_2 according to the vapour / liquid equilibrium of these two gases. Typically, the vent is between 50% and 60% CO_2, with only the balance being the nitrogen which must be purged.

The implication is that the overall capture rate is less than 90% due to the additional CO_2 losses. The end-to-end system no longer meets the given constraints defined in the boundary conditions. The solution is to increase the CO_2 capture rate in the amine absorption towers, boosting the energy requirement and increasing the equipment size.

Switching CO_2 capture techs

Another common mistake when attempting to optimise the end-to-end process is to substitute one technology for another without due consideration of the downstream implications.

In the case above, it may be decided that the amine system should be replaced with a pressure or vacuum swing adsorption process using a solid zeolite sorbent to capture the CO_2. This technique is generally able to produce CO_2 of a purity of 95% cost-effectively, with nitrogen being the balance. Whilst the CO_2 capture rate might be high, at 98%, the CO_2 purity may be low.

The motivation for substituting the amine-based system for the VPSA unit may be sound, for example to reduce the capex or opex of the CO_2 capture aspect of the process. However, the knock-on effect is that a negative consequence is felt in the CO_2 liquefier.

The electrical energy input required to liquefy CO_2 of 99% purity from the amine system is lower than that required to liquefy CO_2 of 95% purity from the VPSA. This is because the compressors must do un-productive work harder to handle the inert nitrogen gas, and the system pressure is increased due to the presence of a higher amount of incondensable ▶

nitrogen. In turn, this increases the compression energy requirement.

The net result could be that the savings achieved by implementing the VPSA system are negated by the increased capex and opex in the liquefier.

Cryogenic CO_2 capture

If CO_2 is required as a gas, for example for transmission in a pipeline, the additional energy input required to liquefy the gas would have no value to the process. On the other hand, if liquid CO_2 is the requirement, the energy input must be applied at some point.

Where liquid CO_2 is the target, it would be relevant to consider integrating the CO_2 capture process with CO_2 liquefaction. This is the essence of cryogenic CO_2 capture.

The physical property of CO_2 that makes cryogenic CO_2 capture technically feasible is that it liquefies at a much higher temperature than the other major components in a typical flue gas, namely nitrogen and oxygen.

The basic process involved in cryogenic CO_2 capture is to cool the entire flue gas stream to the point where the CO_2 forms a liquid, but the other components remain as gases. When considering the operability and energy efficiency of this process, several critical aspects come to the fore.

© APCI | **Air Products VPSA Carbon Capture unit**

© NRG | Twin-tower amine-based CO2 capture at Petra-Nova

Carbon capture technologies – adsorption-based & others

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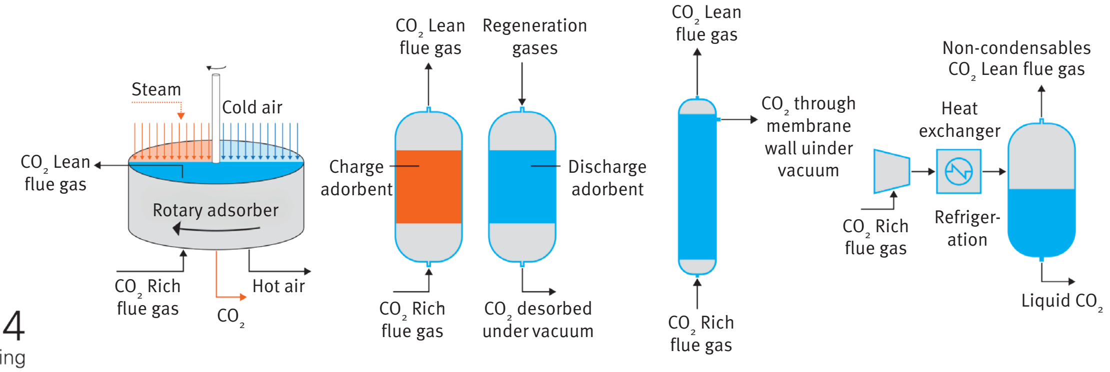

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	TSA – temperature swing adsorption and desorption	VSA – vacuum swing adsorption and desorption	Selective membrane separation	Cryogenic CO_2 liquefaction
Separation principle	Adsorption	Adsorption	Membrane	Physical (phase separation)
Specific energy demand	1.5 GJ/t_{CO_2} (mostly waste heat)	1.7 GJ/t_{CO_2} (mostly power)	1.20 GJ/t_{CO_2} (mostly power)	n.a. (mostly power)
Typical temperature	40 - 60°C	< 40°C	30 - 50°C	-50°C
Typical pressure	Ambient	Cycling between moderate pressure and vacuum	Moderate pressure flue gas, CO_2 under vacuum	20 - 50 bar_g
Typical CO_2 removal	90% (target)	< 90%	> 80%	> 99% (with CO_2 feed >50%)
Typical CO_2 purity	95% (target)	< 95%	95%	> 99% (with CO_2 feed >50%)
Typically combined with	Standalone	Cryogenic Liquefaction	Amine wash, Cryogenic Liquefaction	VSA, Membrane (eg Cryocap)
Typical plant size (Tonnes per year CO_2 removal)	200 - 2,000,000	1,000 - 500,000	10,000 - 1,000,000	> 100,000
Technology maturity level	Pilot / Commercial, eg Husky Energy SK, Lafarge Holcim Cement, BC	Demonstration / Commercial, eg Air Products Port Arthur SMRs, USA	Demonstration / Commercial	Demonstration / Commercial, eg Air Liquide Cryocap at Port- Jérôme SMR, France

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© Chart Inc | **SES Chart Cryogenic Carbon Capture**

1. Moisture in the flue gas must be removed using a drying process prior to cooling the flue gas below 0°C. This is essential to prevent ice forming, which would block the process equipment.
2. The nitrogen and oxygen in the flue gas are cooled along with the CO_2. This serves no benefit in the overall process, so the cold energy must be recovered from the nitrogen and oxygen. This can be achieved using a cryogenic heat exchanger to cool the incoming flue gas against the cold oxygen and air leaving the process.
3. CO_2 forms a solid directly from the gas under certain temperature and pressure conditions. If solid CO_2 accumulates, it will block the equipment in a similar way that frozen water would. The transition of CO_2 from gas to liquid must be carefully managed through process engineering and a deep understanding of CO_2's phase diagram.

Rising to the challenge

Several pioneers have addressed the issues associated with cryogenic CO_2 capture. The first to enter the limelight was Sustainable Energy Solutions (SES), founded in 2008 by Dr Larry Baxter and based in Orem, Utah. In 2020, Chart Industries acquired SES as part of their drive to focus its technology portfolio and business towards the energy transition.

Chart's Cryogenic Carbon Capture (or CCC) process exploits the gas to solid deposition phase change that is unique to CO_2. The entire flue gas stream is cooled to around –120°C causing deposition of gaseous CO_2 as solid particle. Once the small CO_2 particles are formed, they are converted into liquid CO_2 through subtle temperature and pressure changes.

As the flue gas is cooled, condensable pollutants such as oxides of sulphur (SO_2) and nitrogen (NOx) are converted into liquids before the CO_2 deposits as a solid. These liquids can be separated to purify the emissions from the process. Additionally, any traces of these and other pollutants that break through into the liquid CO_2 will solidify and can be removed using filtration.

The simultaneous removal of category pollutants is a feature of the CCC that maximises its economic benefits when being integrated into greenfield site projects, because it reduces the costs of upstream SO_2 and NOx removal, which are regulatory requirements. Furthermore, when retrofitting the CCC process to existing plants that do not have adequate pollutant gas removal the investment can fulfil two core objectives simultaneously.

CCC has been piloted at one tonne per day of CO_2 capture using a containerised, mobile plant at cement factories and power plants. A 30 tonne-per-day demonstration plant at Central Plains Cement Company in Sugar Creek, Missouri has also been commissioned.

Revcoo's CarbonCloud

Founded in 2021 by Hugo Lucas and based in Lyon, France, Revcoo's CarbonCloud is exactly that. Cryogenic liquid nitrogen is sprayed into the pre-cooled flue gas. As the CO_2 in the flue gas is cooled by the nitrogen, it solidifies. This CO_2 snow cloud is then separated from the gases based on density differences in a cyclone. The solid CO_2 is then warmed up to yield liquid CO_2.

To create the liquid nitrogen, mechanical energy is required in the compression stages of the liquefier. This is generally provided from electrically powered motors to drive the compressor. To maximize the energy efficiency of the process and minimize the amount of electricity required for the nitrogen liquefier, cold energy from the flue gas is recovered to pre-cool the warm incoming flue gas before it enters the CarbonCloud chamber.

Additionally, cold energy is released from the solid CO_2 as it converts to liquid. This is an additional means by which the flue gas entering the CarbonCloud is pre-cooled.

A Caron Cloud pilot plant capable of removing two tonnes per day of CO_2 was installed at the Eiffage lime kiln in France in 2024. Lime making releases unavoidable geogenic CO_2 as the calcite (limestone) rock is converted to lime. Similar to cement, the geogenic CO_2 emissions from lime making can only be decarbonized with the use of CO_2 capture.