In focus...

Circular economies and oxygen-enriched combustion

Industrial gases technologies enabling carbon capture in heavy industry

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The energy transition to net-zero emissions has been in full swing in the past year with major dynamics such as President Biden recommitting the US to the Paris Agreement goals. Also, big oil companies are under pressure. Shell was recently forced to implement stricter 2030 goals by a court in the Netherlands, and the board of ExxonMobil saw three of its members change due to the influence of activist investors.

Executives in the industrial gases sector may be familiar with the power of activist investors; in particular, the 2013 involvement of Bill Ackman and Pershing Square Capital Management in Air Products might come to mind. Decarbonisation is being pushed to the top of the agenda.

Beyond the oil and gas sector, other 'hard-to-abate sectors' like cement making, glass production, and hydrogen production for methanol or urea by means of SMR might face similar pressure. Fortunately, there are technologies readily available to support decarbonisation in these industries.

Demonstration projects using PSA and VSA gas separation systems for carbon capture have been implemented by leading industrial gases suppliers in Europe and the US. Subject to appropriate economic conditions and the composition of the waste gas stream to be treated, these technologies are now ready to be deployed at scale. Oxygen-enriched combustion is also proven to increase the carbon dioxide (CO_2) concentration in the flue gas to improve the economics of subsequent carbon capture.

Oxygen enrichment in mineral processing burners

The CO_2 emissions of 'hard-to-abate' sectors are intrinsically connected to the underlying chemistry and cannot be easily mitigated by using electrification with renewable power.

Mineral processing, such as the production of float glass, refractory brick production, and cement making have CO_2 emissions that are independent of their energy consumption and therefore cannot be eliminated using electrification. For example, during cement production limestone is decomposed into quicklime and CO_2 at 900°C.

Float glass factory in St Helens, UK.

In addition to CO_2 emissions from the chemistry within these processes, there are also emissions associated with the burner in the cement-making kiln. Natural gas, coal, wastes, or petcoke are combusted in the burner to generate the heat energy and high temperature that are required to drive the chemical reactions.

The float glass process, invented in 1952, is the most cost-effective way to make flat glass. There are 260 float glass plants operating globally, producing 800,000 tonnes of flat glass each week, in thicknesses ranging from 0.4 mm to 25 mm.

Soda-lime-silica glass is the most important type of glass. It is used for various applications, including flat glass. In the first step of production, three ground raw materials, silica (71-75%), sodium carbonate (12-16%), and limestone (10-15%) are heated to 1,500°C. Because of the high-temperature requirement, a natural gas burner is often used. During this process, the calcium and sodium atoms are integrated into the crystalline structure of the silica while releasing CO_2. Considering both the combustion emissions and the CO_2 released from the process chemistry, glassmaking results in 0.8 kg CO_2 emissions per kg glass produced. Accounting for the mixing of CO_2 released from the mineral processing and combustion, the typical CO_2 concentration in the flue gas in mineral processing is up to 15%. Although this is 375 times greater than the partial pressure of CO_2 in the atmosphere, it is still challenging to capture CO_2 from flue gas with this concentration of CO_2.

To increase the CO_2 concentration in the flue gas, it is possible to use oxygen-enriched combustion. This technology can be retrofitted to many existing mineral processing plants, including cement, lime, and glass. An additional benefit of this approach is that it can increase production capacity by 5-10% due to process intensification. This can offset some of the costs of the oxygen supply and equipment modifications.

An increased CO_2 concentration in the flue gases can make carbon capture more cost-effective. Furthermore, the mitigation of pollutant emissions such as NOx, SOx, and particulates can be simplified using combustion with oxygen-enriched air because the flue gas treatment equipment can be downsized.

VSA and PSA for decarbonisation of SMR hydrogen production

More than 95% of the current hydrogen production is derived from fossil fuels and steam methane reforming (SMR) is the dominant technology in use worldwide.

In the SMR, methane and steam are converted into hydrogen and CO_2 with a typical content of 76% hydrogen, 17% CO_2, and 7% unreacted methane and other gases. To purify the hydrogen, a pressure swing adsorption (PSA) unit is utilised, which takes advantage of the elevated pressure of the gases produced by the SMR. The tail gas from the PSA is fed back into the fired burners in the SMR, and its calorific value is used to enhance energy efficiency.

Under current practices, the CO_2 is either released into the atmosphere or, in the case of hydrogen production for ammonia for fertilizers, the CO_2 is captured to be reacted with ammonia to produce urea.

The CO_2 concentrations in the SMR product gas and flue gas from a cement kiln are similar, but the pressure is very different: SMR product gases are at about 25 bar and the flue gas from mineral processing is generally close to atmospheric pressure. The balancing constituents in the flue gas are also different, with hydrogen being the major non-CO_2 constituent from the SMR process gas emissions versus nitrogen from mineral processing. These differences mean that the optimal carbon capture technology changes from one industry to the other.

There are in principle two different flow sheet options to capture the CO_2 content from the process gases leaving the SMR. In the first flow sheet variant, the carbon dioxide is separated directly after the SMR, hence the hydrogen PSA only needs to separate additional impurities. In a second process flow sheet option, the hydrogen PSA remains unchanged, and the CO_2 is sequestered from the PSA tail gas. This process flow sheet may be favourable due to the high CO_2 concentration in the PSA tail gas of more than 80%. Both process flow sheet options have been implemented in demonstration plants by major industrial gases operators.

Air Products operates two SMR trains at its premises in Port Arthur, Texas. To capture the CO_2 content of the SMR outlet gases, Air Products opted for the first process flow sheet option and installed an additional vacuum swing adsorption (VSA) unit between the SMR and the hydrogen PSA unit. More than 90% of the carbon dioxide is removed in the VSA system. This equates to more than one million tonnes of CO_2 capture per year resulting in a major contribution to the decarbonisation of hydrogen production and industrial gases operations.

Air Liquide has developed a CO_2 sequestration process for the CO_2-rich tail gas from SMR hydrogen PSA units, which is based on the second process flow sheet. The PSA tail gas is dried by means of an additional PSA system. The gas stream is compressed to a pressure at which CO_2 can be separated by liquefaction at around -50°C, close to the triple point. An additional control loop avoids freezing of CO_2 under all operating conditions to avoid system blockages.

Within the cryogenic unit, partial condensation and distillation techniques are applied to separate the CO_2 from impurities present in the stream. The non-condensable gases are fed to a cryogenic membrane system, where additional hydrogen and CO_2 are recovered. This 'Cryogenic Capture' stage is unique to the Air Liquide process and gives its name to the technology, which is known as Cryocap™. It leads to an increased hydrogen productivity of 10-20%, as well as a CO_2 recovery rate of more than 98%. All other residual gases are sent back to the burners in the reformer furnace, where their calorific value is utilised.

The first of its kind Cryocap™ demonstration installation in Port-Jérôme at a large-scale hydrogen SMR has a CO_2 capture capacity of 100,000 tonnes per year. Since 2013 Air Liquide has been planning to install a Cryocap™ unit at its Rozenburg SMR in the Netherlands, which would have a capture capacity of 500,000 tonnes of CO_2 per year. If the final investment decision is taken in 2021, the project could start capturing and storing CO_2 by 2024, making a huge contribution to the decarbonisation of industrial gases production. gw

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