

CCUS – A POWERFUL SET OF TECHNOLOGIES AT THE SERVICE OF DECARBONIZATION

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Carbon dioxide (CO₂) emissions resulting from human activities, particularly from the combustion of fossil fuels, have led to unprecedented levels of atmospheric CO_2 concentration, contributing significantly to global warming and climate change. Due to the increasing amounts emitted by human activities, the concentration of $CO₂$ in the earth's atmosphere averages 420ppm.

This may not sound like much but consider that in pre-industrial times when anthropogenic emissions were practically absent, the concentration level was around 280ppm. There has been a 67% increase with a sharp acceleration since the 1970s.

The development of renewable energy sources in recent years has failed to compensate humanity's growing demand for energy. As a result, total $CO₂$ emissions have grown over time to approximately 37 billion tons (37Gt).

Carbon Capture and Storage technology is considered one of the most important solutions to reach carbon neutrality.

PRINCIPLES OF CARBON CAPTURE

In response to these challenges, carbon capture technology has emerged as a promising solution to mitigate $CO₂$ emissions and combat climate change.

Carbon capture technology plays a crucial role in reducing $CO₂$ emissions by capturing $CO₂$ from industrial processes and power generation facilities before it is released into the atmosphere. By preventing the release of CO₂, carbon capture technology helps mitigate climate change while enabling continued use of fossil fuels during the transition to renewable energy sources.

CCUS is an acronym that groups together all technologies, available or under development, suitable for capturing the $CO₂$ emitted by industrial facilities or directly from the air:

 $CC =$ carbon capture, it refers to the capture of the $CO₂$

- $U =$ utilization of the $CO₂$ captured
- $S =$ permanent storage of the $CO₂$ captured

The CO₂ Value Chain

The captured $CO₂$ can be transported via pipeline or transported in its liquid state by ship. Then it can be used in other industrial applications as a raw material to create other products. Finally, the captured $CO₂$ can be injected and permanently stored into deep geological formations or depleted oil and gas reservoirs which may be on land or at offshore sites.

CO₂ CAPTURE - THE CURRENT SITUATION

Today, only 45 Mt of CO_2 are captured every year in about 40 operational plants. Most of the captured CO_2 is used in EOR (enhanced oil recovery) processes to improve oil and gas extraction.

50 new capture facilities are set to be operating by 2030, increasing the total capture capacity to 383 Mt/CO₂/yr. To be on track with the NZE Scenario, the total capacity in 2030 should be at least 1.100 Mt/CO₂/yr.

Source: Global CCS Institute www.globalccsinstitute.com/resources/ccs-image-library

Enhanced Oil Recovery (EOR)

If the differential pressure between the surface and the underground well is not enough to drive the extraction, $CO₂$ is then injected to decrease the oil viscosity, enabling additional extraction.

While initial EOR developments used naturally occurring carbon dioxide deposits, technologies have been developed to inject $CO₂$ captured from industrial point sources.

TYPES OF CARBON CAPTURE TECHNOLOGIES

Carbon capture technologies can be classified into four main categories: pre-combustion capture, post-combustion capture, oxy-fuel combustion capture and direct air capture (DAC). Each type of technology utilizes different capture mechanisms and processes to capture $CO₂$ from different sources.

Pre-combustion and post combustion are mature technologies that can be useful in eliminating emissions from existing industrial plants after retrofitting operations. Here are some examples:

Oxy-fuel is a viable alternative to removing $CO₂$ from the flue gas of a conventional air-fired fossil fuel plant. The idea is to burn the fuel with almost pure oxygen to produce a flue gas composed essentially of H_2O and CO_2 . The high concentration of $CO₂$ in the flue gas will make the capture and separation easy, decreasing the overall efficiency penalty.

Some industrial processes involving the production of syngas will be described in the following chapters. It is worth remembering what syngas is and how it is produced. Syngas is a mixture of primarily hydrogen and carbon monoxide that can contain some small amount of carbon dioxide, methane and water. It is mainly produced by Steam Methane Reforming (SMR) and the gasification of coal or biomass.

The following reactions take place in SMR in the presence of a specific catalyst:

 $CH_4 + H_2O \rightarrow 3H_2 + CO$ (syngas) $CO + H₂O \rightarrow CO₂ + H₂$ (water gas shift reaction)

The first reaction is the reforming reaction and the second reaction is the water gas shift reaction which increases the amount of hydrogen produced.

Coal gasification involves the following reactions:

 $3C + O₂ + H₂O \rightarrow H₂ + 3CO$ (syngas) $CO + H₂O \rightarrow CO₂ + H₂$ (water gas shift reaction)

Syngas is used in the refinery process, for power generation and as a raw material to produce other chemical compounds.

PRE-COMBUSTION CAPTURE

Pre-combustion carbon capture allows the removal of $CO₂$ from a gas mixture before its utilization, typically from syngas. Purified syngas can subsequently be burned to produce electricity using suitable gas turbines. This process can also be used to produce Blue Hydrogen or for natural gas sweetening after extraction. The proprietary physical solvents used to capture the CO_2 are Selexol (UOP) and Rectisol (Linde/Air Liquide), which works well at a high concentration of CO_2 and can tolerate the presence of residual oxygen. $CO₂$ is then desorbed and released from the solvent by decreasing the pressure in the stripper vessel.

Industrial Process

Integrated Gasification Combined Cycle (IGCC)

Coal, petroleum coke and other feedstocks can be used to produce electricity via a gasification process.

- 1. The feedstock is gasified in the Gasifier and converted to syngas.
- 2. After cooling and desulfurization, the syngas is subjected to the shift reaction to convert the CO to $CO₂$ and obtaining a gas mixture composed primarily by H_2 and CO_2 .
- 3. The latter are removed to feed syngas with a high $H₂$ content into a gas turbine for power generation (a gas turbine that can be operated with 100% H₂ is under development, currently H₂ can only be used in mixed form).
- 4. The heat recovery steam generator (HRSG) utilizes the waste heat from the hot exhaust from the gas turbines to generate steam. This is used to produce additional power in the steam turbine phase of the combined cycle.
- 5. The captured $CO₂$ is compressed and sent to its final destination.

Production of Blue Hydrogen

In the Steam Methane Reforming process, natural gas is used to produce hydrogen having $CO₂$ as a by-product. This $CO₂$ can be captured and separated from the hydrogen.

Natural Gas processing plant

Most of the world's sources of natural gas (CH₄) also contain CO₂ and H₂S that must be removed before shipping natural gas via pipelines or liquefying it to produce LNG. This process, known as NG sweetening, is very well established in the oil and gas sector.

POST-COMBUSTION CAPTURE

The Capture and separation of $CO₂$ from the flue gas of a combustion system. First, exhausted flue gas must be purified (removal of oxygenate compounds, NOx, SOx, metal dust, etc.) and cooled, then the CO_2 is separated from the flue gas by passing the flue gas through a continuous scrubbing system. The system consists of an absorber and a stripper. Typically, amine-based solvents are used.

The release of $CO₂$ is obtained by breaking the chemical bond between $CO₂$ and the solvent by providing heat. The greater the energy required to release $CO₂$ from the solvent, the lower the overall efficiency of the process. This is why research is focusing on developing capture mechanisms that are more efficient than first-generation MEA (monoethanolamine) and more tolerant of the impurities associated with this process.

Industrial Process

Gas-fired or coal-fired power plant

A carbon capture facility is coupled with a fossil quel power plant in order to separate the $CO₂$ from the flue gas. Cleaned gas that is released into the atmosphere is composed of nitrogen and water vapor. Any $CO₂$ resulting after separation is compressed and dehydrated for transport and storage or utilization purposes.

OXY-FUEL COMBUSTION CAPTURE

In the oxy-fuel combustion process the fuel (Coal or natural gas) is burned with almost pure oxygen instead of air. When using air to burn coal, the CO₂ concentration in the flue gas is about 15%. If N₂ is removed and only O₂ is used, then the concentration increases to more than 90%.

As flue gas is composed of CO_2 and H_2O , the latter can be easily removed by dehydration to obtain high purity CO_2 . The large amount of $CO₂$ produced makes its use ideal as a working fluid in a supercritical $CO₂$ power cycle, which produces low-cost electricity and in addition compensates the cost of the air separation unit. The first utility scale power plants based on the Allam cycle are under construction in Perman Region (Texas) and will begin operation in 2027/2028 (https:// netpower.com/first-utility-scale-project).

Industrial Process

Coal-fired power plant

An air separation unit operates in front of a coal-fired power plant in order to separate O_2 from the air. Flue gasses are treated to separate SOx, NOx and other impurities. Finally, the $CO₂$ processing unit removes the water by dehydration and the $CO₂$ is compressed for storage or transportation purposes.

DIRECT AIR CAPTURE (DAC)

As we have seen the three main technologies: pre-combustion capture, post-combustion capture, and oxy-fuel combustion capture can help to reduce, or eliminate, the non-avoidable emissions when working in conjunction with an emitting industrial sites. But how can we remove the historic accumulated $CO₂$ from the air?

The answer is the Direct Air Capture (DAC) that consist in a chemical process able to remove CO_2 from the atmosphere. Capturing $CO₂$ from the air is more energy intensive – and therefore more expensive – than capturing it from a point source. This is because $CO₂$ in the atmosphere is much more dilute than, for example, in the flue gas of a power station. One way to provide the DAC system with the energy it needs could be to combine it with a clean power generation system, such as solar or wind, but the intrinsic discontinuity of these power generation technologies could be a limiting factor.

At the present time two start-ups possess the most promising technologies for DAC.

CARBON ENGINEERING

Carbon Engineering is a Canadian company that uses a capture technology on an aqueous hydroxide's solution used as liquid solvent. The most common alkali used are potassium hydroxide (KOH) and sodium hydroxide (NaOH).

Process Description

The KOH solution reacts with the CO₂ in the air contactor to form K_2CO_3 that is subsequently converted to solid CaCO₃. The calcium carbonate is heated In the calciner to around 900 $^{\circ}$ C to release the captured CO₂ and the solvent is regenerated in the closed chemical loop.

Source: CarbonEngineering.com

CLIMEWORKS

CLIMEWORKS is a Swiss company that bases its capture technology on a solid sorbent filter.

Process Description

Air is drawn into the collector with a fan. Carbon dioxide is captured on the surface of a highly selective filter. Once the filter material is full of carbon dioxide, the collector is closed. The filter material is then heated to approximately 100°C to release the carbon dioxide.

Source: Climeworks.com

Dozens of other companies are involved in researching DAC methods that can reduce the amount of energy required to support the process.

Some of the most promising capture technologies include:

- » Electro swing adsorption
- » Zeolites
- » Highly selective ion membranes
- » Metal organic framework (MOF)

THE NEGATIVE EMISSION CONCEPT

A very promising solution to provide carbon-free energy to a DAC system consists of integrating three different systems together:

- 1) BIGCC (biomass integrated gasification combined cycle)
- 2) CCS (carbon capture and storage)
- 3) DAC (direct air capture)

The combination of BIGCC + CCS is defined as BECCS (bio energy with carbon capture and storage).

The conversion of biomass into energy is considered carbon neutral because the $CO₂$ released during energy conversion is considered to have been previously absorbed by biomass during the growing process thanks to the photosynthesis. The $CO₂$ absorbed from the atmosphere during photosynthesis is simply released back. Together, the integrated systems can achieve compound negative emission.

The biomass (e.g wine lees, crop waste, livestock manure, municipal garden waste, kitchen waste) are converted into syngas by the gasification process, then the syngas is moved to the "combined cycle" power block (consisting of one or more gas turbines and steam turbines). Syngas is combusted in highly efficient gas turbines to produce electricity. The excess heat from the gas turbines and from the gasification reaction is then captured, converted into steam, and sent to a steam turbine to produce additional electricity.

The carbon capture unit sequesters the carbon dioxide resulting from the combustion of the syngas (post-combustion technology) and stores it for future transportation, use or permanent storage. Part of the electricity and heat produced by the BECCS unit is utilized to drive the DAC unit that captures CO_2 from the atmosphere and transfers it to the CO_2 storage.

This new concept of power plants can produce energy and at the same time contribute to eliminating $CO₂$ from the air and, ultimately, it offers an important contribution to waste management.

CARBON DIOXIDE: INTERMEDIATE STORAGE AND TRANSPORTATION

The captured carbon dioxide must be transported from the point of capture to the point of permanent storage or use. Intermediate storage will sometimes be necessary, especially in the case of intermittent production/shipping. The two most relevant means are pipeline transport and maritime transport using large CO₂ carriers. The experience gained from the maritime transport of LNG will be important for developing $CO₂$ transport.

Intermediate storage

After liquefaction, the $CO₂$ is intermediately stored in cylindrical tanks, spherical tanks or bullet type tanks. Operating temperatures vary according to the tank pressure design. Typical storage conditions include a pressure of 6-7 bar and a temperature of -50/-52°C.

Base materials used for the construction of this tanks are:

- » P355ML2
- » P355NL2
- » P460ML2
- » P460NL2
- » SA537 Cl.2
- » SA738 Gr.B

voestalpine Grobblech and voestalpine Bohler Welding can offer different package solutions for plates and welding consumables for this application.

The following table gives an example of filler materials typically used in the construction of storage tanks:

only for as welded condition.

If PWHT has been requested, consult the Global Welding Technology team.

The selection was made assuming a PWHT of 580 - 600°C for 3 hours.

Pipeline

For large volume pipelines, transporting $CO₂$ in dense and/or gaseous phases may be the preferred solution. The transportation of pure $CO₂$ (>99%) in dry or wet form and free of impurities is not a major problem.

On the contrary, pipeline transportation of CO_2 captured from industrial emitters (by pre-combustion, post-combustion or oxy-fuel methods) must take into account the presence of contaminants such as: N_2 , O_2 , H_2 , CH4, SOx, H₂S, NOx, CO, chlorides and H2O.

However. no matter how low the concentration of these contaminants may be, even a few hundred ppm can lead to problems of phase stability and corrosion. The possible formation of dry ice must also be taken into account which is why high demands must be placed on low temperature toughness.

International standards such as ISO 27913 and DNV-RP-F104 can support the design of new pipelines. Depending on the corrosion risk assessment, the material selection may include carbon steel pipes (e.g., API 5L X65 – X70) with internal CRA cladding or with a corrosion allowance.

Voestalpine Grobblech and voestalpine Bohler Welding offer various solutions for pipeline plates and welding consumables, either for manual or mechanised welding processes. The wide range of electrodes (basic and cellulosic), solid and flux cored wires fulfill the welding requirements in different positions.

pipeRunner® – The orbital welding system for FCAW system is designed for pipeline and process piping girth welds (from carbon steel to CRA materials).

- » pipeRunner® is designed for girth welds vertical up with flux cored wires.
- » Being one of the lightest systems on the market makes it easy to handle.
- » All of the components are first-class products designed in Germany.
- » No need for site beveling machines and internal clamps
- » Very easy to operate as the remote control has all the functions in the palm of your hand
- » For high strength pipeline steels but also perfectly suitable for piping and high-alloyed clad pipes

Liquid CO₂-cargo Vessel

Depending on the pressure and temperature conditions, the material can range from carbon steel with improved toughness properties to high-strength steel.

voestalpine Grobblech has launched two new steel grades for $LCO₂$ transportation that have been approved by all renowned classification societies.

- » F550 TMCP Toughcore for medium pressure storage design
- » F460 TMCP Toughcore for low pressure storage design.

Nickel-based welding consumables meet the high toughness requirements, low-alloy solutions are under development.

Source: HB Hunte Engineering Heavy plates for CO₂ applications (voestalpine.com)

CARBON DIOXIDE: PERMANENT STORAGE OR UTILIZATION

Once the CO₂ has been captured using one or more of the techniques described above, it can be stored permanently or used as raw material to produce other valuable products. In the IEA Net Zero Emissions by 2050 Scenario (Net Zero Scenario), about 5.9 Gt of CO₂ will be captured and stored in 2050. This will require a considerable expansion of CO₂ storage capacities.

Source: IEA

A typical option for permanent storage is to inject the captured $CO₂$ into a suitable geological reservoir where remains trapped.

- » Examples of suitable geological reservoirs are: Depleted oil and gas field
- » Saline formation

The alternative to permanent storage is to use the captured CO_2 as a raw material for the manufacture of valuable products. The creation of a CO₂ value chain will help to expand the opportunities for the use of CO₂ and will make this new market financially viable and attractive.

Some potential utilizations are:

CORROSION AND MATERIAL SELECTION FOR THE CAPTURE PROCESS

Typically, the $CO₂$ used for EOR process come from a clean source, like natural reservoirs, with well-controlled water content. For CCS, the $CO₂$ can originate from a variety of industrial sources (most are relevant for CCS hub-projects) and therefore contain a variety of impurities. Complete removal of these impurities may not be cost-effective or technically feasible. Therefore, it would be advisable to select materials that can withstand potentially unfavorable conditions at the extreme limits of the expected impurities and temperature.

Depending on the capture process and the origin on the $CO₂$, the environment may be more reducing or oxidizing. For example, the CO_2 stream coming from a pre-combustion capture plant is likely to contain more H₂S (reducing agent), while the $CO₂$ stream coming from post-combustion and oxy-combustion is expected to be more oxidizing in nature (presence of O_2 , NO₂, SO₂).

Considering that many planned projects are based on the CCS hub concept, the material selection must mitigate the corrosion risk posed by all all the potential impurities and mechanisms. Water must be present for corrosion to occur. The $CO₂$ dissolves in the water and forms carbonic acid. SOx, NOx, H₂S, and other contaminants can also react with each other to form strong acids, including nitric acid (HNO3) and sulfuric acid (H₂SO₄), and possibly elemental sulfur.

The low pH of the condensed water can also lead to the depassivation of corrosion-resistant alloys, resulting in localized corrosion and possibly stress corrosion cracking. Oxygen, H_2S and chlorides are also triggers for SCC. When selecting materials, it is important not to forget what has been learnt in the processes of the oil and gas industry and the performance of materials in flue gas desulphurisation plants and in amine treatment units.

We can analyse the following components for the $CO₂$ capture process:

» Scrubbers and dehydration

All the necessary treatments to remove the most part of impurities and water before the capture process takes place. Corrosion risk from impurities such as: N_2 , O_2 , H_2 , CH4, SOx, H_2 S, NOx, CO, chlorides in the presence of H_2O . The possible material selection includes carbon steel or low-alloy cladded materials with CRA such as 22Cr, 25Cr, and Ni-base alloy or solid wall parts made ofstainless steel

» Absorber Vessel & $CO₂$ stripper/desorber

Corrosion risk from amine/oxygen interaction, glycol and residual impurities. The possible material selection includes carbon steel or low-alloy cladded materials with CRA such as 316L, 904L, 6Mo grades and Ni-based alloys.

» Process Piping (High corrosion risk)

General corrosion risk as described above. The possible material selection includes materials like 316L, 22Cr, 25Cr and Ni-based alloys.

» Process Piping (Low corrosion risk)

Carbon steel + corrosion allowance

» Compressors

Carbon steel/low-alloy steel + CRA cladding to cover downtime condition when condensation may occur.

The AMPP Guide 21532 ed. 2023 "Guideline for Materials Selection and Corrosion Control for CO₂ Transport and Injection" proposes upper concentration limits for a number of impurities in the $CO₂$ stream. voestalpine Bohler Welding can offer a complete range of filler materials for welding and cladding stainless and Ni-based material.

https://www.voestalpine.com/welding/global-en/products/consumables/welding-consumables/

In addition, voestalpine Grobblech offers a wide range of roll-bonded clad plates with the best corrosion resistance and represents an intelligent and cost-effective alternative to solid stainless steel. This very efficient solution has been successfully used for decades in oil and gas plants as well as in FGDs . The clad plates are particularly suitable for the construction of absorbers and strippers for amine scrubbers.

CONCLUSION

The goal of decarbonization can only be achieved through a mix of current and future technological possibilities. Without an adequate implementation of CCUS, achieving this goal is difficult to imagine.

What is special about this group of technologies is that they are applicable to both existing industrial plants and future constructions.

As a provider of Welding Solutions, voestalpine Bohler Welding will once again be at the side of our customers to help them build the infrastructure necessary for this energy transition.

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