### TECHNICAL REPORT

ISO/TR 27922

First edition 2021-02

# Carbon dioxide capture — Overview of carbon dioxide capture technologies in the cement industry

Captage du dioxyde de carbone — Vue d'ensemble des technologies de captage du dioxyde de carbone dans l'industrie du ciment





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Published in Switzerland

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#### Foreword

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This document was prepared by Technical Committee ISO/TC 265, *Carbon dioxide capture, transportation, and geological storage*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at <a href="https://www.iso.org/members.html">www.iso.org/members.html</a>.

#### Introduction

Concrete is the most-used manufactured substance on the planet in terms of volume. For example, it is used to build homes, schools, hospitals, workplaces, roads, railways and ports, and to create infrastructure to provide clean water, sanitation and energy. These are important for quality of life, public health, and social and economic well-being.

Raw materials for concrete are abundant and available in most parts of the world. Concrete is affordable, strong, durable and resilient to fire, floods and pests. It has the flexibility to produce complex and massive structures. There is currently no other material that is available in the quantities necessary to meet the demand for buildings and infrastructure.

Cement is used to manufacture concrete. It is described as the glue that binds the aggregates together. The demand for concrete, and therefore for cement, is expected to increase, by 12 % to 23 % by 2050 compared to 2014, as economies continue to grow, especially in Asia.

Increasing global population, urbanisation patterns and infrastructure development will increase global cement production. The use of concrete and cement is expected to become more efficient, and concrete pours at the application phase are expected to decrease. The cement sector faces the challenge of meeting an increasing demand for its product while cutting direct  $\mathrm{CO}_2$  emissions from its production [Z]. The cement industry is a large emitter of  $\mathrm{CO}_2$  worldwide. The industry is committed to reduce their carbon footprint to meet the targets of the 'Paris Agreement' on climate change.

Process emissions arising from the production of cement clinker present a fundamental challenge to decarbonization of cement. In normal cement production processes, these process emissions are in the range of  $500 \text{ kg CO}_2$ /tonne clinker to  $540 \text{ kg CO}_2$ /tonne clinker [1], corresponding to  $250 \text{ kg CO}_2$  to  $500 \text{ kg CO}_2$  per tonne of cement depending on the type of cement. Replacement of limestone as raw materials with alternative raw materials with lower carbonate content can reduce these process emissions, but availability of these alternatives is limited, and the replacement potential is also limited (depending on required cement qualities).

Combustion emissions are another contributor to  $\mathrm{CO}_2$  emissions in addition to the process emissions. Replacement of carbon-based fuels by non carbon-based energy sources and thermal energy from biomass sources (being considered as  $\mathrm{CO}_2$  neutral) will contribute to lowering the carbon intensity of the energy supply for the cement industry in the future.

One way to reduce  $\mathrm{CO}_2$  emissions is capturing  $\mathrm{CO}_2$  that is released in the production of cement (both direct emissions during the production process and emissions related to local energy production).  $\mathrm{CO}_2$  capture is an emerging approach for  $\mathrm{CO}_2$  abatement in the cement industry. It means that  $\mathrm{CO}_2$  arising from the combustion of fuels and from the treatment of raw materials could be captured and permanently stored or re-used. The integration of  $\mathrm{CO}_2$  capture equipment typically increases the specific energy intensity of cement manufacture, as additional energy is needed to operate the  $\mathrm{CO}_2$  capture plant, followed by drying, purification and compression of the captured  $\mathrm{CO}_2$  for transportation, (geological) storage and/or utilization<sup>[7]</sup>.  $\mathrm{CO}_2$  transportation, (geological) storage and utilization are beyond the scope this document.

To date, no large-scale  $\mathrm{CO}_2$  capturing technologies have been installed in the cement industry. However, different technologies are under development to support the cement industry in achieving their objectives. Various cement companies participate in one or more research, development and/or demonstration projects in the field of  $\mathrm{CO}_2$  capture. These projects provide useful information about the application of the various technologies in the cement industry.

To facilitate the assessment and comparison of the different  $\mathrm{CO}_2$  capturing technologies, this document summarizes these technologies that are currently under development. This summary supplements and updates the information provided in ISO/TR 27912:2016, Clause 10 on capture from cement production processes. This document will inform the cement industry and their stakeholders on  $\mathrm{CO}_2$  capture technology options and other relevant aspects.

 ${\rm CO_2}$  capture will be an item of interest for all cement producers in the years to  ${\rm come^{[5]}}$ . Currently, about 2 000 cement plants with relevant  ${\rm CO_2}$  emissions are operating worldwide [14] with the majority of these plants being located in Asia.  ${\rm CO_2}$  capture implementation in the cement industry at global level would need a transport and storage infrastructure to facilitate the decarbonization of cement plants not located close to a geological storage facility or  ${\rm CO_2}$  use facility. Together with the investments in  ${\rm CO_2}$  capture facilities, this will be a major cost factor for the cement industry.

## Carbon dioxide capture — Overview of carbon dioxide capture technologies in the cement industry

#### 1 Scope

This document provides an overview of technologies that are under development to capture carbon dioxide ( $CO_2$ ) that is generated during cement manufacture.

This document is intended to inform users about the different technologies, including the characteristics, the maturity and the boundaries of these technologies.

This document is applicable to organizations involved in the cement industry and other stakeholders (e.g. policy makers).

This document addresses technologies for  $\mathrm{CO}_2$  capture that have potential applications in the cement industry. This document does not address  $\mathrm{CO}_2$  transport,  $\mathrm{CO}_2$  storage or  $\mathrm{CO}_2$  utilization.

#### 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 27917, Carbon dioxide capture, transportation and geological storage — Vocabulary — Cross cutting terms

#### 3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 27917 apply.

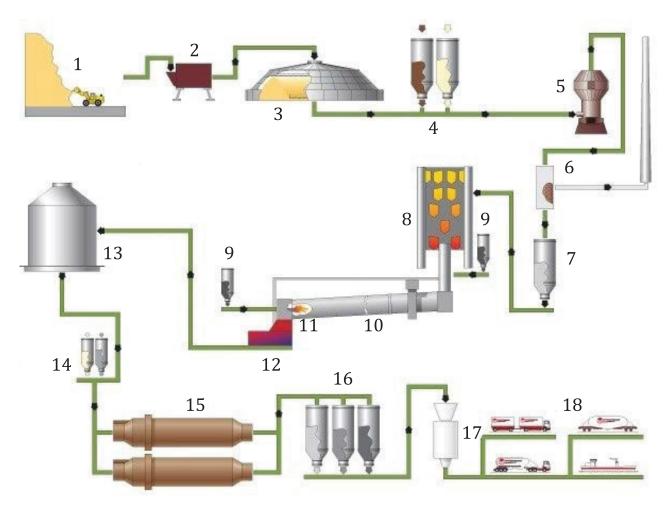
ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <a href="https://www.iso.org/obp">https://www.iso.org/obp</a>
- IEC Electropedia: available at <a href="http://www.electropedia.org/">http://www.electropedia.org/</a>

#### 4 CO<sub>2</sub> and the cement industry

#### 4.1 Cement manufacture

Cement manufacture is a three-stage process: raw materials preparation, clinker production and clinker grinding with other components to produce cement. Figure 1 illustrates the process of manufacturing cement. Different raw materials are mixed and milled into a homogeneous powder, from which clinker is produced in high-temperature kilns where direct emissions of  $\mathrm{CO}_2$  occur. Calcium oxide from the calcination of limestone is a precursor to the formation of calcium silicates that gives cement its strength<sup>[Z]</sup>.



Kev	

- 1 quarrying raw materials 10 kiln calcination-burning raw meal to clinker 2 crushing limestone 11 3 storage and pre-homogenization of raw material cooling 4 other raw materials 13 clinker storage 5 raw mill 14 secondary additives 6
- 6 filter and chimney 15 cement mills
  7 raw meal homogenization 16 cement storage
  8 preheating 17 cement dispatch
- 9 pulverized coal 18 transportation by bulk or bags

Figure 1 — Cement manufacture<sup>[17]</sup>

Clinker is ground together with gypsum to produce cement. Depending on the required technical properties of the finished cement, other components, including fly ash, ground granulated blast furnace slag and fine limestone, can also be ground together with clinker or blended to produce different cement types. Cement can be produced at the kiln site, or at separate grinding or blending plants. Blended cements or "combinations" can also be produced at the concrete plant. The cement making process is complex – it requires control of the chemical formulation and involves multiple steps that require specialised equipment<sup>[Z]</sup>.

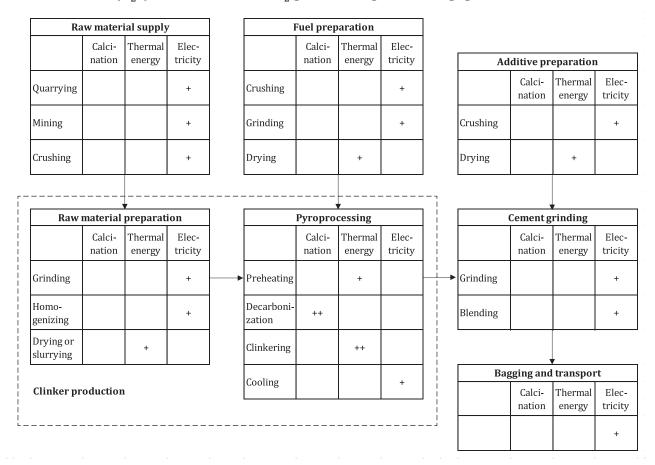
#### 4.2 CO<sub>2</sub> emissions from the cement industry

#### 4.2.1 Production process description

Figure 2 schematically shows the process steps of cement manufacture. There are two main sources of direct CO<sub>2</sub> emissions in the production process of cement:

- calcination of raw materials in the pyro-processing stage (60 % to 70 % of direct CO<sub>2</sub> emissions resulting from the chemical breakdown of limestone when it is heated to high temperature); and
- combustion of kiln fuels (30 % to 40 % of direct  $CO_2$  emissions).

Flue gas in the cement industry has a relatively high  $\mathrm{CO}_2$  content (typically 20 % to about 30 %  $\mathrm{CO}_2$ ). Other  $\mathrm{CO}_2$  sources include direct greenhouse gas (GHG) emissions from non-kiln fuels (e.g. dryers for cement constituents products, room heating, on-site transport and on-site power generation), and indirect GHG emissions from e.g. external power production and transport. Apart from methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>0), emissions of non- $\mathrm{CO}_2$  greenhouse gases are negligible<sup>[1]</sup>.



#### Key

++ major CO<sub>2</sub> emission source

+ minor CO<sub>2</sub> emission source

Figure 2 — Process steps in cement manufacture with indication of  $CO_2$  emission sources<sup>[1]</sup>

#### 4.2.2 Process emissions from calcination

In the clinker production process,  $\rm CO_2$  is released from the chemical decomposition of calcium carbonates, magnesium carbonates and other carbonates (e.g. from limestone) into lime by heating up the raw materials to above 900 °C:

```
CaCO_3 + heat \rightarrow CaO + CO_2

MgCO_3 + heat \rightarrow MgO + CO_2
```

This process is called "calcining" or "calcination". It results in direct  $CO_2$  emissions through the kiln stack<sup>[1]</sup>.

#### 4.2.3 Combustion emissions

The cement industry traditionally uses various fossil fuels to operate cement kilns, including coal, petroleum coke, fuel oil, and natural gas. Fuels derived from waste materials have become important substitutes for traditional fossil fuels. These alternative fuels include fossil fuel-derived fractions such as waste oil and plastics, as well as biomass-derived fractions such as waste wood and dewatered sludge from wastewater treatment. Furthermore, fuels which contain both fossil and biogenic carbon (mixed fuels) are increasingly used. Examples are (pre-treated) municipal and (pre-treated) industrial wastes (containing plastics, textiles, paper, etc.) or waste tyres (containing natural rubber and synthetic rubber)<sup>[1]</sup>.

#### 4.2.4 Emissions compared to other sectors

Due to the nature of the production process (combustion, calcination for limestone and the drying of raw materials), the exhaust gas of a typical cement plant is significantly different from other production processes (e.g. thermal power generation). This difference is characterized by the cement exhaust gas conditions, such as flue gas composition, temperature, and dust and moisture content. Consequently, (standard)  $\mathrm{CO}_2$  capture technologies are not necessarily applicable in the cement industry.

#### 4.3 CO<sub>2</sub> purification after capture

For  $\mathrm{CO}_2$  transport,  $\mathrm{CO}_2$  storage and/or  $\mathrm{CO}_2$  utilization, purity levels above 96 %  $\mathrm{CO}_2$  are recommended. Different approaches are available to increase the  $\mathrm{CO}_2$ -product purity level. A common approach is to add extra adsorption stages with recycling of the low-grade side stream. High-pressure flash separation can reduce investment and/or energy use. High-pressure flash separation can be attractive, as the produced  $\mathrm{CO}_2$  flow will be compressed before transport. Similarly, separation by low-temperature liquefaction of  $\mathrm{CO}_2$  can be attractive, as the product can be in a liquid state which is suitable for transport by ship or can easily be compressed with low energy penalty. Purification of the captured  $\mathrm{CO}_2$  is not specifically addressed in this document.

#### 4.4 Abatement technologies in general

For decades, several  $CO_2$  emission abatement technologies and measures have been used in the cement industry to reduce the process and combustion emissions. They generally fall into four categories<sup>[7]</sup>:

- a) Improving energy efficiency: deploying existing state-of-the-art technologies in new cement plants and retrofitting existing facilities to improve energy performance levels when economically viable.
- b) Switching to alternative fuels (fuels that are less carbon intensive than conventional fuels): promoting the use of biomass and waste materials as fuels in cement kilns to offset the consumption of fossil fuels. Utilizing wastes, including biogenic and non-biogenic waste sources, which would otherwise be sent to a landfill site, burnt in incinerators or improperly destroyed.
- c) Reducing the clinker to cement ratio: increasing the use of blended materials and the market deployment of blended cements, to decrease the amount of clinker required per tonne of cement or per cubic metre of concrete produced.
- d) Using emerging and innovative technologies that:
  - contribute to the decarbonisation of electricity generation by adopting waste heat recovery technologies to generate electricity from recovered thermal energy, which would otherwise be

lost, and support the adoption of renewable-based power generation technologies, such as solar thermal power;

- integrate carbon dioxide capture into the cement manufacturing process for long-lasting or permanent storage;
- integrate carbon dioxide capture and re-use for new products, including recarbonation of concrete and mineralisation of (recycled) aggregates.

The  $\mathrm{CO}_2$  emissions reduction impact of these levers is not always additive since they individually affect the potential for emissions reductions of other options. For instance, the use of alternative fuels generally requires greater specific thermal energy and electricity due to their higher moisture content than fossil fuels, the operation of the kiln with increased input of ambient air compared to conventional fossil fuels and the pre-treatment of alternative fuels<sup>[7]</sup>.

#### 5 Overview of CO<sub>2</sub> capture technologies

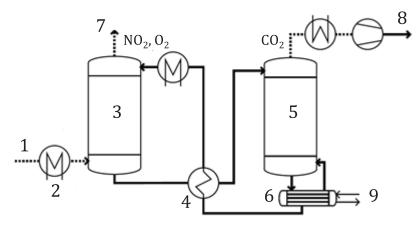
#### 5.1 Absorption with amines

The principle of post-combustion technologies is the separation of  $CO_2$  from flue gases after combustion. Flue gases are normally at atmospheric pressure and high temperatures.  $CO_2$  is removed from a mixture of primarily nitrogen, oxygen and water with flue gas impurities such as SOx, NOx and particulates.

Gas separation by absorption relies on the principle that  $\mathrm{CO}_2$  can be selectively, and reversibly, removed from the flue gas with a chemically reactive liquid in an absorption column. The  $\mathrm{CO}_2$ -rich flow is then transferred to a desorption column/stripper and heated up to release the  $\mathrm{CO}_2$ . The released  $\mathrm{CO}_2$  is dried, purified and compressed while the regenerated absorbent is cooled and returned to the absorption column. A schematic representation of the absorptive  $\mathrm{CO}_2$  capture is shown in Figure 3.

In chemical absorption post-combustion capture, aqueous amine solutions are often used to chemically bond  $\mathrm{CO}_2$  to the amines. Absorption liquids based on monoethanolamine (MEA) are first generation and still widely used for  $\mathrm{CO}_2$  separation having high selectivity, fast reaction rates and low cost. MEA has a thermal energy requirement for regeneration of absorbent of at least 3 MJ/kg $\mathrm{CO}_2$ [6]. In cement plants, the thermal energy is provided via waste heat recovery and/or an external unit. Equipment corrosion when using MEA solutions is an issue as well as oxidative degradation. Amine-based post-combustion processes require a prior clean-up (desulfurization and denitrification) as amines will react with SOx and NOx. These aspects increase the plant footprint as well as the capital and operating costs. Reported MEA requirements are between 0,5 kg MEA/tonne  $\mathrm{CO}_2$  and 3,1 kg MEA/tonne  $\mathrm{CO}_2$ [21].

Improved amine solutions, e.g. based on sterically hindered amines and amino acid salts, which require a lower regeneration temperature, are non-corrosive to carbon steel at 130 °C in the presence of oxygen and have a better resistance to degradation, and are also commercially available.



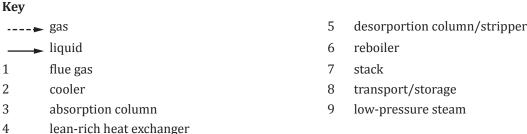


Figure 3 — Schematic representation of absorptive CO<sub>2</sub> capture [6]

The technology was evaluated in the period 2013 to 2015 for the cement application at the Norcem cement plant in Brevik (Norway). During this pilot trial, a slipstream from the kiln flue gas was treated with an amine technology prototype. The amine solution showed good stability and a capture ratio of 90 % was obtained. The energy for the capture system was provided by waste heat from the cement plant [15].

Next generation amine based  $CO_2$  capture processes with demixing solvents show improved absorption properties of  $CO_2$ , leading to significant capture cost reduction compared to the standard 30 % MEA process<sup>[8]</sup>.

#### 5.2 Absorption with chilled ammonia

Another feasible approach for the capture of  $\mathrm{CO}_2$  is the chilled ammonia process. This approach uses ammonia/ammonium carbonate as the absorbent and the capture process causes ammonium bicarbonate to precipitate as a solid. Although ammonia is a cheap solvent, with a low energy requirement for regeneration and insensitivity to flue gas impurities, the process requires refrigeration facilities to cool the flue gas to less than 10 °C. In addition, complex washing in the column heads is required as  $\mathrm{NH}_3$  is a fugitive solvent and extra measures needs to be employed to prevent escape of  $\mathrm{NH}_3$  into the atmosphere. Furthermore, ammonium bicarbonate precipitating in the solvent should be separated from the circulating solvent using a hydro cyclone<sup>[6]</sup>. Recent projects have shown that the precipitation of ammonium bicarbonate can be avoided by selecting other process conditions in the absorber. There is also a risk of explosion associated with the dry  $\mathrm{CO}_2\text{-NH}_3$  reaction (explosion limit for  $\mathrm{NH}_3$  is 15 % to 28 %)<sup>[6]</sup>.

The chilled ammonia process has been demonstrated at the  $CO_2$  Technology Centre Mongstad (Norway) <sup>[Z]</sup>. The absorber, direct contact cooler, and water wash were tested specifically for (synthetic) cement flue gas in the CEMCAP project at GE's plant in Växjö (Sweden)<sup>[19]</sup>.

#### 5.3 Sorbent-based adsorption technologies

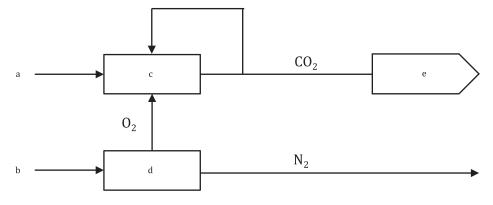
Sorbent-based processes separate and recover  $CO_2$  by a cyclic, thermal swing, adsorption-desorption process similar to the conventional solvent processes. Solid sorbents are considered promising,

because they can exhibit high  $\mathrm{CO}_2$  loadings, have low heat capacities, are typically less corrosive, and avoid toxicity/volatility issues associated with liquid solvent systems. Supported amine sorbents can be particularly attractive and have the potential to reduce the regeneration needed to carry out  $\mathrm{CO}_2$  capture from industrial exhaust gases. Generally, adsorption technologies, like pressure swing adsorption (see 5.5) or temperature swing adsorption, deliver good  $\mathrm{CO}_2$  removal (above 90 %), but lower  $\mathrm{CO}_2$ -production purity (below 90 %) in the product.

The adsorption technology has also attracted the interest of the cement industry and has been evaluated in a pilot plant installation in the Norcem plant in Brevik (Norway). Pilot-scale tests and process simulations carried out in 2016 resulted in a significant increase in capital expenditures (CAPEX) and operational expenditures (OPEX), due to a poorer sorbent performance than anticipated [19].

#### 5.4 Oxy-fuel combustion technology

The oxy-fuel technology relies on pure oxygen instead of ambient air for combustion. To enable this, the nitrogen is removed from ambient air in a separation unit and the remaining oxygen is supplied to the kiln. Consequently, the concentration of  $\mathrm{CO}_2$  in the flue gas significantly increases [6]. The gas properties are significantly different from those in a conventional kiln operation which has a corresponding impact on the clinker burning process. Additionally, the theoretical flame temperature in the sintering zone increases, the flame becomes shorter and brighter compared to combustion in ambient air. To maintain an appropriate flame temperature, part of the flue gases should be recycled. Thus, the recirculation rate adjusts the combustion temperature. Figure 4 shows the oxy-fuel process with recirculating flue gas.



- a Coal, gas or biomass.
- b Air

- d Air separation.
- e CO<sub>2</sub> compression and dehydration.

c Combustion and calcination.

Figure 4 — Oxyfuel combustion technology<sup>[7]</sup>

The flue gas resulting from the oxyfuel process has a  $\mathrm{CO}_2$  concentration of around 80 % compared to 14 % to 33 % for combustion in ambient air. Consequently, for  $\mathrm{CO}_2$  capture purification is required. The remaining flue gases comprise steam, excess oxygen and impurities of nitrogen and sulphur oxides which can be easily removed by condensation, denitration and desulfurization. For a medium-sized cement plant with a kiln capacity of 3 000 tonne clinker/day, the oxygen demand is estimated to be in the range of 25 t/h to 30 t/h. The large quantities of oxygen required for oxy-fuel combustion can only be provided by an on-site oxygen supply system. Cryogenic oxygen production is currently the most energy-efficient technology to produce of large quantities of oxygen.

Oxy-fuel combustion has been applied in power generation and in the glass and steel sector. Although the test results from the energy sector constitute a helpful starting point, the transferability to the cement industry is limited. This is due to the different operating requirements of the plant with oxyfuel in cement manufacture combining combustion, clinker calcination and clinker sintering processes. Early experiences in the cement industry with the handling of oxygen for combustion were made in the

United States and other countries. However, the focus was on an increase of production capacity and not on the reduction of the specific CO<sub>2</sub> emissions.

Up to now, two different basic scientific approaches have been followed regarding oxy-fuel technology for  $\mathrm{CO}_2$  capture at cement kilns:

- a) Full oxy-fuel technology: This technology includes the entire kiln plant and therefore requires the adaptation of the kiln and of the cooler. Since the temperature profile under oxy-fuel conditions is slightly different from conventional operations, the choice of refractory and its location in the transition zone should be adjusted accordingly, and the area of basic lining expanded. Additionally, due to the higher oxygen content, the ignition of any type of fuel is improved, which is an advantage for many types of alternative fuels. Capture rates of 90 % to 99 % can be achieved, however the capture rate is plant-specific. The biggest impact on the capture rate is the moisture content of the raw materials.
  - NOTE See Clause 6 of Reference [6] for full details regarding the design and operational aspect of the full oxy-fuel technology.
- b) Partial oxy-fuel technology: This technology applies to the flue gases from the calciner and one preheater string, while the kiln is operated in conventional mode. The advantage of this partial mode is that it requires fewer modifications, however the capture rate is limited to 55 % to 75 %.

Both approaches require a final purification step to ensure the  $\mathrm{CO}_2$  is suitable for transport, storage and/or utilization. In addition, both approaches require a sophisticated heat recovery system due to the recirculation of flue gases and the minimization of air ingress through the sealing points to maintain a high- $\mathrm{CO}_2$  concentration in the flue gas.

#### 5.5 Pressure swing adsorption separation technology

Pressure swing adsorption is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material. It operates at near-ambient temperatures. Specific adsorptive materials (e.g. zeolites, activated carbon, molecular sieves) are used as a trap, preferentially adsorbing the target gas species (e.g.  $\mathrm{CO}_2$ ) at high pressure. The process then swings to low pressure to desorb the adsorbed gas species. A schematic illustration of the pressure swing adsorption technology is given in Figure 5<sup>[21]</sup>.

The advantages of pressure swing adsorption technology are simple process flow, low energy consumption and low secondary pollution. The disadvantages are that the adsorption performance and adsorption efficiency of the adsorbent material are affected by many factors, such as gas species, temperature, and humidity, and it is necessary to choose an appropriate adsorbent material. Meanwhile, multi-stage pressure swing adsorption is required to obtain high-purity  $\text{CO}_2^{[23]}$ .

The pressure swing adsorption technology has been successfully industrialized in the cement industry in China. In 2016, the first  $\mathrm{CO}_2$  capture and utilization demonstration project, which adopted pressure swing adsorption technology, was built and put into operation successfully by BBMG Group Co. Ltd<sup>[7]</sup>.

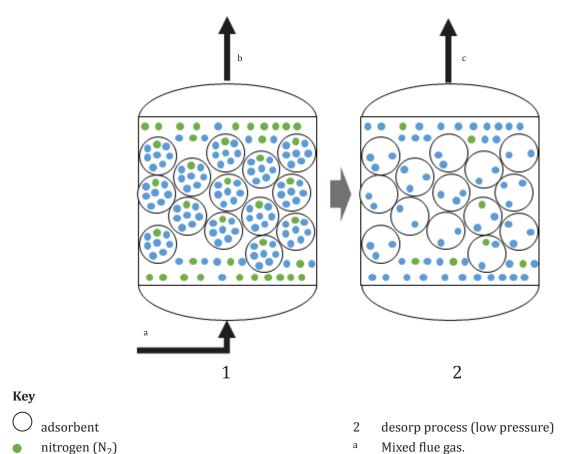


Figure 5 — Principles of pressure swing adsorption technology<sup>[21]</sup>

High concentration of N<sub>2</sub>.

High concentration of  $CO_2$ .

#### 5.6 Separation with membranes

adsorp process (high pressure)

carbon dioxide (CO<sub>2</sub>)

1

Gas separation by membranes relies on differential solubility and diffusivity of gas molecules in the membrane material. The driving force of this process is a partial pressure difference across the two sides of the membrane.

Various membrane materials have been investigated for  $\mathrm{CO}_2$  capture. The most relevant membrane types for post-combustion  $\mathrm{CO}_2$  capture are polymer membranes, microporous organic polymers, fixed-site-carrier membranes, mixed matrix membranes and carbon molecular sieve membranes<sup>[11]</sup>.

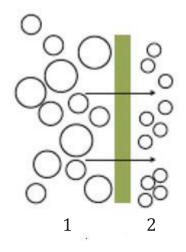
Gas separation membranes are manufactured in two different forms: flat sheets and hollow fibres. The flat sheets are typically wound into a spiral element and the hollow fibres are grouped into a bundle similar to a shell-and-tube heat exchanger.

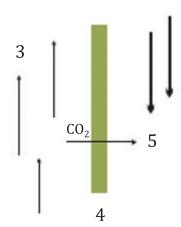
The main advantages of gas separation membranes are that no heat is required for regeneration and no waste streams are generated. On the other hand, membranes are often sensitive to impurities in the gas stream and can be fouled by trace amounts of particulates and degraded by components such as SOx and NOx, depending on the membrane type. Issues with frequent membrane replacement due to degradation can be mitigated by purification of the gas prior to the membrane unit. Some membrane materials can be deteriorated at high temperatures, which means that cooling is required before membrane separation.

Important parameters, such as  $CO_2$  capture rate and selectivity, vary among the different membrane types. Typically, membranes with high  $CO_2$  capture rates have low selectivity and the other way

around. Therefore, multiple pass stages are required to obtain an adequate separation. Alternatively, the membrane process can be combined with a liquefaction process to obtain a high  $CO_2$  purity.

In addition to gas separation membranes (gas/gas membranes), gas absorption membranes (gas/liquid membranes) are considered for  $\mathrm{CO}_2$  capture. The gas absorption membranes act as contacting devices between a gas flow and a liquid flow. The flue gas flows on one side of the membrane and an absorptive liquid is used on the other side to selectively attract certain components. Schematic illustrations of gas separation membranes and gas absorption membranes are given in Figure 6.





a) gas separation membrane

b) gas absorption membrane

#### Key

- 1 high pressure
- 2 low pressure

- 3 waste gas
- 4 microporous membrane
- 5 absorption fluid

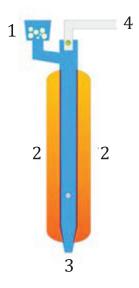
Figure 6 — Principles of gas separation and gas absorption using membranes<sup>[5]</sup>

Fixed-site-carrier membranes are the most mature membrane type for cement application and have been tested for a slip stream from the cement kiln at the Norcem cement plant in Brevik (Norway) in the period of 2013 to  $2015^{[Z]}$ .

#### 5.7 Direct separation

Indirect heating can produce a near pure  $\mathrm{CO}_2$  stream from calcination, which accounts for about two-third of the overall direct  $\mathrm{CO}_2$  emissions. In this process, raw limestone is fed through a vessel or pipe, which is heated from the outside to temperatures above 900 °C. This process was developed and is demonstrated at commercial scale for processing of magnesite. Applying this technology to a cement plant requires careful engineering as the materials are calcined at higher temperatures and at a larger scale.

At the core of the direct capture is the direct separation reactor. A steel reactor enables the separation of emission streams (combustion and process emissions). As no external gases enter the direct separation reactor, the gas coming out of it is a  $\rm CO_2$ -steam mix (process  $\rm CO_2$  stream). A schematic illustration for the direct separation reactor is given in Figure 7.



#### Key

- 1 raw material
- 2 heat

- 3 processed material
- 4 released CO<sub>2</sub> that will be captured

Figure 7 — Direct CO<sub>2</sub> separation reactor<sup>[15]</sup>

The concept for the direct capture technology and its scale up is being validated within the LEILAC project that aims to develop a suitably sized pilot plant  $(240 \text{ t/d})^{[15]}$ . Constructed in Lixhe (Belgium) the pilot plant is functioning in a realistic operating environment.

#### 5.8 Calcium looping

Calcium looping, also called carbonate looping, makes use of the chemical reaction between solid calcium oxide (CaO) and the captured gaseous  $CO_2$  resulting in solid calcium carbonate (CaCO<sub>3</sub>):

$$CaO + CO_2 \leftrightarrow CaCO_3$$

The reverse reaction is used for releasing  $CO_2$  bound in the carbonate again. As the reactions do not reach full equilibrium during the calcium looping, only the surface of CaO particles react to carbonate and back. In that respect, the CaO particles act like physical adsorbents. A schematic illustration of calcium looping is given in Figure 8.

The combustion gas containing  $\mathrm{CO}_2$  is put in contact with the CaO in a carbonator to produce  $\mathrm{CaCO}_3$ . The carbonation reaction is exothermic and occurs between 600 °C and 700 °C. The high-grade heat from this process can be used to generate additional electricity. The produced  $\mathrm{CaCO}_3$  is directed to a calciner for regeneration to CaO and  $\mathrm{CO}_2$ . This occurs in an endothermic reaction at temperatures above 900 °C. The recycled adsorbent is transferred back to the carbonator and maintained in a cycle.

With every cycle the sorbent reduces its activity due to the decrease in particle porosity resulting in a limited sorbent life time. After around 30 cycles, the sorbent particles should be discharged. The advantage for the cement industry is that the discharge can be done in the kiln, using the CaO stream as raw material for the clinker production.

For a  $\mathrm{CO}_2$ -rich gas stream, the calciner is fired with pure oxygen (oxy-fuel combustion) to avoid diluting  $\mathrm{CO}_2$  with air. Thus, the gas stream exiting the calciner has a high  $\mathrm{CO}_2$  concentration (above 90 %) and can then be supplied to storage or utilization.

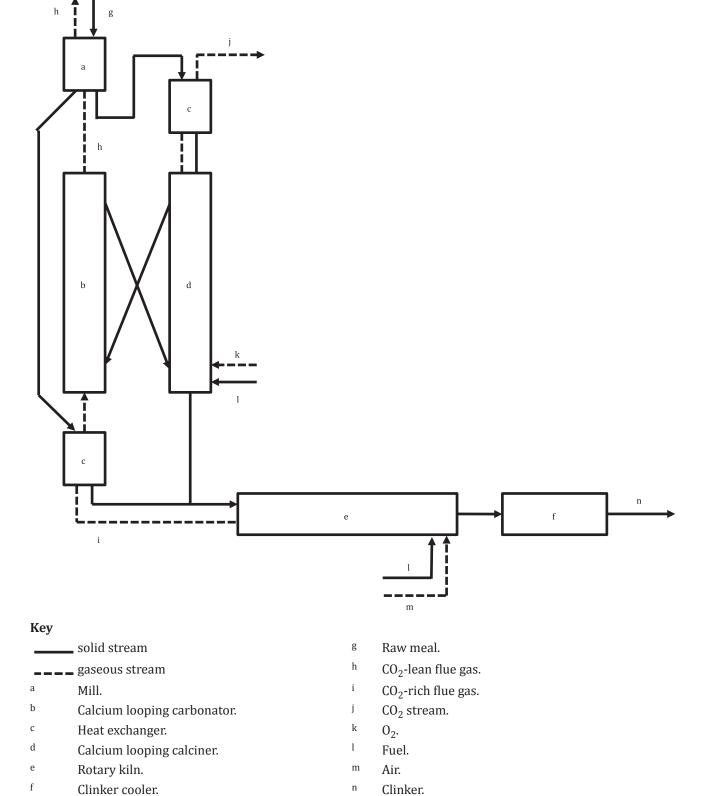


Figure 8 — Principle of cement plant with calcium looping

An advanced option for a cement plant is an integrated process where calcium looping substitutes the conventional precalciner. A certain amount of CaO is diverted to the carbonator reactor where it reacts with the  ${\rm CO_2}$  generated in the rotary kiln. The remaining CaO is fed into the rotary kiln as raw meal. The  ${\rm CaCO_3}$  which is generated in the carbonator is directed to the calciner where  ${\rm CO_2}$  is released in a

concentrated gas stream. After final purification, the  $\mathrm{CO}_2$  can be transported to the storage site or to a reuse facility.

Within the CEMCAP project the technology has been tested for cement flue gas in a 30-kW pilot plant at the Spanish National Research Council (CSIC), and a 200 kW pilot plant at the University of Stuttgart. A significant increase of fuel input (+270 %) has been calculated from the mass and energy balances with respect to the reference cement kiln without  $\rm CO_2$  capture, leading to specific primary energy for  $\rm CO_2$  captured of 3,26 MJ/kg $\rm CO_2$ <sup>[11]</sup>. The Taiwan's Industrial Technology Research Institute (ITRI) has developed a high efficiency calcium looping technology. They started a demonstration project with this technology at a Taiwan cement plant in 2013, which captures 1 tonne  $\rm CO_2/h$  out of 3,1 t  $\rm CO_2/h$  using the rotary kiln as calciner<sup>[11]</sup>.

#### 6 Overview and assessment

#### 6.1 Assessment factors of CO<sub>2</sub> capture technologies

Several factors play a role in the assessment of the application of  $CO_2$  capture technologies by a cement plant. Both generic factors and site-specific/local factors will influence the technical and economic feasibility of a  $CO_2$  capture technology.

Generic factors include, but are not limited to:

#### a) CO<sub>2</sub> abatement costs

Each technology in combination with local characteristics will have an associated  $\mathrm{CO}_2$  capture cost. Investments (CAPEX), operational costs (OPEX) and possible savings by reducing  $\mathrm{CO}_2$  emissions to air ('carbon credits') will determine the feasibility of any project. The  $\mathrm{CO}_2$  abatement costs will depend on the baselines used for calculation, which can differ in studies comparing the economics of technologies.

#### b) Additional energy use

Many, if not all  $\mathrm{CO}_2$  capture technologies in the cement industry will need an additional supply of energy over and above that required for the cement production processes (e.g. electricity, fuels). The additional energy use of the  $\mathrm{CO}_2$  capture technology (as well as the availability of energy) will be important in deciding the technology and scope. This additional energy consumption will add to the  $\mathrm{CO}_2$  abatement costs of the project.

#### c) Implementation period

Many of the  $\mathrm{CO}_2$  capture technologies in the cement industry are in a relatively early phase of development. Most of them will need ten or more years to achieve commercial availability, and some technologies might even never achieve commercial deployment. A limited number of other technologies are already available for industrial deployment, but might not form a commercially attractive investment.

Site-specific/local factors include, but are not limited to:

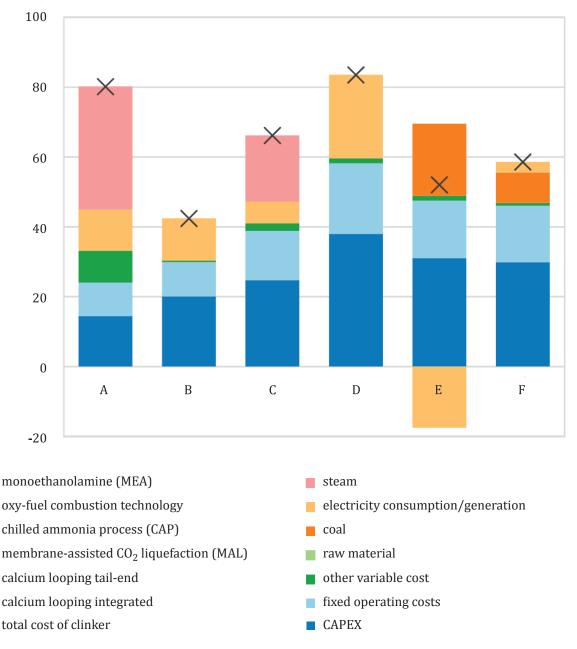
- the availability of space in the cement plant;
- the composition/lay-out of the cement plant;
- the access to supply of renewable energy (e.g. for electrification of processes);
- the possibility to connect to CO<sub>2</sub> infrastructure.

Given the wide variety of generic and site-specific/local factors, a general statement about the assessment of the available  $CO_2$  capture technologies for a specific cement plant is not possible. Other factors, such as political or societal factors, can also play a role in the decision making.

Y

#### 6.2 Case study of technological and economic evaluation of CO<sub>2</sub> capture technologies

The CEMCAP project<sup>[4]</sup> studied five of the seven technologies described in <u>Clause 5</u>. Only the direct separation technology and solid adsorption technologies were outside the scope of the CEMCAP project. In the project, techno-economic evaluation was performed on the oxy-fuel technology, the chilled ammonia process, membrane-assisted CO<sub>2</sub> liquefaction, normal calcium looping tail-end and integrated calcium looping, and amine-based absorption with MEA was used as reference.



NOTE Y-axis indicates cost of  ${\rm CO_2}$  captured expressed in  ${\rm \notin /t_{CO2}}$  based on results of CEMCAP project. Actual cost can vary depending on generic and site-specific/local factors and might be lower due to technology improvements since the pilot projects.

Figure 9 — Example of break-down of cost of  $CO_2$  captured for the base case of investigated  $CO_2$  capture technologies in the CEMCAP project<sup>[7]</sup>

Key

Α

В

C

D

E

F

The main key performance indicators (KPIs) from the techno-economic comparison are:

- specific primary energy consumption for CO<sub>2</sub> captured;
- cost of clinker:
- cost of cement;
- cost of CO<sub>2</sub> captured.

All five technologies were found to have lower specific primary energy consumption compared to the reference technology MEA $^{[2]}$ . Figure 9 provides an example of the cost break-down of  $\mathrm{CO}_2$  captured for the technologies investigated. The costs depend on the additional energy requirement and on economic parameters that vary over time and between regions. The generic and site-specific/local factors should therefore be taken into account in the overall assessment of  $\mathrm{CO}_2$  capture technologies.

#### 6.3 Ability to retrofit existing cement plants with CO<sub>2</sub> capture technologies

In its analysis of the possibility to retrofit  $\mathrm{CO}_2$  capture technologies into existing cement plants, the CEMCAP project concluded that the post-combustion technologies are generally easier to retrofit than more integrated technologies (oxy-fuel and calcium looping). Based on these evaluations, no single silver bullet solution was found among the  $\mathrm{CO}_2$  capture technologies. All cement plants are different, both in terms of the conditions relevant for the techno-economic evaluation such as primary energy consumption and  $\mathrm{CO}_2$  intensity of the electricity mix, electricity price and steam price, and practical constraints relevant to retrofitting such as space and local electric grid capacity. The technologies investigated in the CEMCAP project are fundamentally different from each other and provide a portfolio of technologies with different attributes. The selection of the optimal technology should be done for every cement plant [4].

<u>Table 1</u> shows the assessment of development status of different  ${\rm CO_2}$  capture technologies in the cement industry. The assessment is comparable, but not equal to the technical readiness level (TRL) assessment used in research funding systems.

CO <sub>2</sub> capture technology	Development status	Next step	
Post combustion with amines	Tested at semi-industrial scale	Ready for full-scale demonstration	
Post combustion with chilled ammonia	Tested in laboratory and small pilot plants	Ready for semi-industrial scale testing	
Oxy-fuel combustion technology	Tested in laboratory	Ready for pilot plant or semi-industrial scale testing	
Pressure swing adsorption	Tested in laboratory	Ready for testing at pilot plant level	
Separation with membranes	Tested in small scale in operational cement plant	Ready for pilot plant	
Direct separation	Used at (small) industrial scale in lime industry; pilot plant installed and in test phase	Ready for semi-industrial scale testing	
Calcium looping	Tested in laboratory and small pilot plants	Ready for semi-industrial scale testing	

Table 1 — Development status of CO<sub>2</sub> capture technologies for cement industry

#### 7 Final considerations

The implementation of  $CO_2$  capture technologies in the cement industry is still at an early stage. Only a few demonstration scale projects are under development, while several pilot plants have started or will soon started, operation (status: early 2020). Several options exist to capture  $CO_2$  for further use and/or (geological) storage. These will provide an opportunity for the cement industry to reduce its emissions. The relatively high proportion of process emissions (about 60 %) compared to combustion emissions

(about 30 %) are a specific challenge for the cement industry. Focus on only reducing combustion emissions, or only reducing process emissions, will not be sufficient. The complete system should be considered to make informed decisions.

In this document, an overview is given of technologies that are under development to capture  $\mathrm{CO}_2$  that is generated during the cement manufacturing processes. It informs users, governments and other stakeholders about these different technologies, including their characteristics, maturity (i.e. technology readiness level) and boundaries.  $\mathrm{CO}_2$  transport,  $\mathrm{CO}_2$  storage or  $\mathrm{CO}_2$  utilization are not addressed in this document but should be considered in the overall assessment of commercial projects.

Several technologies for  $\mathrm{CO}_2$  capture from cement production are described in this document, including a rough assessment of the development status and technology costs. As the development of these technologies has not yet lead to commercial-scale implementation, it is recognized that the overview in this document is subject to changes based on the results of ongoing projects. For this reason, and given that deployment will depend on local factors, conclusions about the application of any  $\mathrm{CO}_2$  capture technology are not provided.

General criteria for the assessment of application of CO<sub>2</sub> capture technologies include:

- a) CO<sub>2</sub> abatement costs;
- b) additional energy use;
- c) implementation period.

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