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Carbon Capture Technology - Options and Potentials for the Cement Industry

Carbon Capture Technology - Options and Potentials for the Cement Industry

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1 Executive summary

CO₂ capture and storage (CCS) may become an emerging approach for CO₂ abatement. For the cement industry it means that CO₂ arising from the combustion of fuels and from the treatment of raw materials could be captured and stored away from the atmosphere for a very long period of time. It is clear that CO₂ capture will be an item of common concern for all cement producers in the years to come. Therefore the European Cement Research Academy (ecra) took the initiative to launch this study about the state-of-the-art in CO₂ capture technologies, attempting to respond to one of today's most important environmental challenges. The study includes an evaluation of pros and cons of potential application in the cement industry. Finally, more detailed objectives are suggested for potential next steps, which could prepare a basis for future strategies. One of the main questions is, to what degree the cement industry should start research activities on carbon capture technologies. All possibilities of carbon management should be taken into consideration to maintain the competitiveness of the cement industry.

At present, CCS measures are discussed for potential CO₂ mitigation in the power sector. Transport and storage of compressed CO₂ are available techniques, however limited today to specific applications. Experiences on a larger scale are not available, neither in the power sector nor other industries like cement production - only feasibility studies have been published so far. The crucial point is that today's CCS measures would not be achievable to industries like the cement production - not only for technical but certainly for cost reasons. Also is clear that current environmental legislation, e.g. the European Emission Trading Scheme (ETS), does not provide adequate recognition for this kind of CO₂ reduction, so that would need to be amended accordingly.

In principle three basic technologies are known to capture CO₂: pre-combustion capture, oxyfuel combustion and post-combustion capture:

- Pre-combustion technologies (reforming or gasification/partial oxidation based on different fossil fuels) are applied to produce fuels (mainly hydrogen) which are more or less carbon-free. Currently there is no pre-combustion technology applied in a cement plant. In other sectors like the chemical, fertilizer and synthetic fuels industry hydrogen production and separating carbon dioxide from syngas is state-of-the-art, but in most cases designed for smaller gas volumes compared to the requirements of cement kilns. The applicability to the clinker burning process strongly depends on the technical possibility of using hydrogen as a main fuel in the kiln. Due to its explosive properties, hydrogen could not be used in existing cement kilns, but could principally be utilized after dilution with other gaseous fuels or inert gases like nitrogen or steam. Furthermore, the combustion and radiation properties of hydrogen differ significantly from those of the fuels being used today in the cement industry meaning that - even if handling problems were solved - the clinker burning process would have to be significantly modified. By pre-combustion technologies, only CO₂ from fuel combustion, but not from limestone decarbonation can be captured.
- The oxy-fuel technology relies on oxygen instead of ambient air for combustion, i.e. the nitrogen is removed in a separation plant from the air prior to being applied to the kiln.

Consequently, the concentration of carbon dioxide in flue gas is increased significantly and for CO₂-capture only a comparatively simple carbon dioxide purification is required, if any. To introduce oxy-fuel technology with flue gas recirculation into an existing cement plant is extremely challenging. To prevent air intrusion the complete plant has to be sealed or has to be operated with excess pressure. An air separation plant has to be established on the cement plant premises and the facilities of flue gas recirculation have to be included into the existing plant units. The different flue gas enthalpies and flows require a different design of all plant units. Hence implementation of oxy-fuel technology with flue gas recirculation seems to be predominantly an option for new plants.

- Post-combustion capture is an end-of-the pipe technology which can in principle be adapted to any combustion or CO₂ producing process. Different capture technologies can be considered: absorption into liquid solvents, separation of CO₂ using membranes, adsorption using specially designed solid particles and low temperature separation processes. Up to now, no trials with post-combustion capture have been carried out in the cement industry. In other industrial sectors several commercially available post combustion capture technologies exist, however, limited to comparatively small gas volumes. A special post-combustion technique is based on so called carbonate looping technology which is currently in the very early stages of research and development.

Transport and storage of CO₂ is of common concern of all industries, which consider CCS as a future abatement technology. However, the current report focuses only on capture technology and gives only a short overview about transport and storage and its costs.

Besides technical aspects the economic framework will be decisive for future applications of carbon capture in the cement industry. At the moment, the costs for CO₂ capture are estimated to amount to 20 to 50 €/t CO₂^a. This does not include additional costs for transport and storage of CO₂. Furthermore it does not include costs for potential retrofit of existing cement technology including necessary switches in fuels and raw materials. The wide range represents the very different values given in the literature for the individual technologies. Based on avoided CO₂ emissions the cost estimates range from 24 to 75 €/t CO₂. These costs are higher since more CO₂ emissions occur in plants with CO₂ capture due to their reduced overall efficiency than in a reference plant without CO₂ capture. It can be expected, that the specific capture costs depend on the plant size, so that CCS can result in lower costs at larger kilns than at small or medium-size kilns.

All capture technologies are far from being applicable to the cement industry due to technical and economic reasons. However, some capture technologies seem to be more appropriate for the potential application at cement kilns than others:

- The application of pre-combustion technology would entail the most extensive changes to the clinker burning process. Especially the change to hydrogen combustion would be very demanding and would trigger a series of research tasks to adopt the clinker burning

^a Whenever necessary, US Dollar were converted to Euro according to the following exchange rate: 1 US-\$ = 0.744 € (31 May 2007)

process to the new conditions. Consequently pre-combustion seems to be the least favorable among the discussed technologies.

- Oxy-fuel technology is a candidate for CO₂ capture at cement kilns. There are experiences from cement kilns in the USA which were operated with oxygen enrichment (to increase the production capacity). Furthermore, oxy-fuel technology will be investigated at power plants in the next years, so that some of the results obtained may be transferred to cement kilns. Oxy-fuel seems to be applicable only at new kilns, because a retrofit at existing kilns would be too costly.

- Post-combustion capture does not require fundamental changes in the clinker burning process. Therefore this technology would be available not only for new kilns, but also for retrofits at existing cement kilns. The most promising post-combustion technology is chemical absorption because there are operational experiences from several industries and high abatement efficiencies seem to be achievable. Also membrane technology seems to be a candidate for future application at cement kilns. Other post-combustion measures, e.g. physical absorption or mineral adsorption seem to be less feasible from today's point of view (because of a lack of selectivity or huge mass streams of mineral adsorbents).

If the European Cement Research Academy decides to carry out research on CCS in the next years, its Technical Advisory Board will have to decide the individual steps and

- evaluate the current report on carbon capture technologies and
- discuss a potential research agenda for the next 12-15 years including milestones and deliverables.

Without prejudice to the Board decision a research agenda is proposed in chapter 5 which could give guidance through such a project. At the beginning it is not clear to what extent the research might be successful. Consequently each step provides deliverables which allow the Board to decide how to proceed further or if the project should be terminated.

European Cement Research Academy

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Duesseldorf, 3 July 2007

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2 Introduction

Energy supply is an essential need for our modern civilization. It is obvious that the energy demand will increase significantly in the next 40 years – especially due to the economic growth in developing countries and emerging markets. Over the last two centuries emissions of carbon dioxide (CO₂) have increased to some 24 billion tons per year worldwide today (see **table 2-1**). At the same time, the atmospheric CO₂ concentration has increased from 290 to 380 ppm over the last decades.

Tab. 2-1: Energy related CO₂ emissions (million tonnes) [100]

	OECD		Transition Economies		Developing Countries		World	
	2002	2030	2002	2030	2002	2030	2002	2030
Power sector	4,793	6,191	1,270	1,639	3,354	8,941	9,417	16,771
Industry	1,723	1,949	400	618	1,954	3,000	4,076	5,567
Transport	3,384	4,856	285	531	1,245	3,353	4,914	8,739
Residential and services	1,801	1,950	378	538	1,068	1,930	3,248	4,417
Other *	745	888	111	176	605	1,142	1,924	2720
Total	12,446	15,833	2,444	3,501	8,226	18,365	23,579	38,214

* Includes international marine bunkers (for the world totals today), other transformation and non-energy use.

Today, CO₂ reduction is the main environmental target worldwide in order to stabilize or reduce the atmospheric concentration of green house gases. Technological options for reducing net CO₂ emissions to the atmosphere include [101]:

- reducing energy consumption, increasing the efficiency of energy conversion
- switching to less carbon intensive fuels
- increasing the use of renewable energy sources or nuclear energy
- sequestering CO₂ by enhancing biological absorption capacity in forests and soils
- capturing and storing CO₂ chemically or physically (CCS).

CO₂ capture and storage (CCS) may become an emerging approach for CO₂ abatement. For the cement industry it means that CO₂ arising from the combustion of fossil or renewable fuels and from process industries could be captured and stored away from the atmosphere for a very long period of time.

Anthropogenic CO₂ emissions originate from different sources: industrial installations (including power plants), traffic/transport and households (see **table 2-1**). Due to its point sources CO₂ reduction in industry and the power-sector are part of climate protection programs in many countries [101], [102]. Consequently large fossil-fired power plants, but also cement kilns, chemical plants, oil and gas production, refineries, and steel production are challenged to reduce their CO₂ emissions (see **table 2-2**).

Table 2-2: Number of large stationary point sources (emitting more than 0.1 Mt CO₂/y) and assigned CO₂ emissions [101, 80]

Process	Number of sources	Emissions [Mt CO ₂ /a]
Fossil fuels		
Power	4,942	10,539
Cement production	1,175	932
Refineries	638	798
Iron and steel industry	269	646
Petrochemical industry	470	379
Oil and gas processing	N/A	50
Other sources	90	33
Biomass		
Bioethanol and bioenergy	303	91
Total	7,887	13,466

The cement producers have significantly reduced the CO₂ emissions per tonne of cement during the last decades. However, the total global cement production is growing due to a stable economic growth in many countries worldwide. Today, the worldwide cement production is about 2.1 Gt/a (see **figure 2-1**), which results in about 5-6% of the CO₂ emissions from stationary sources [101], [103].

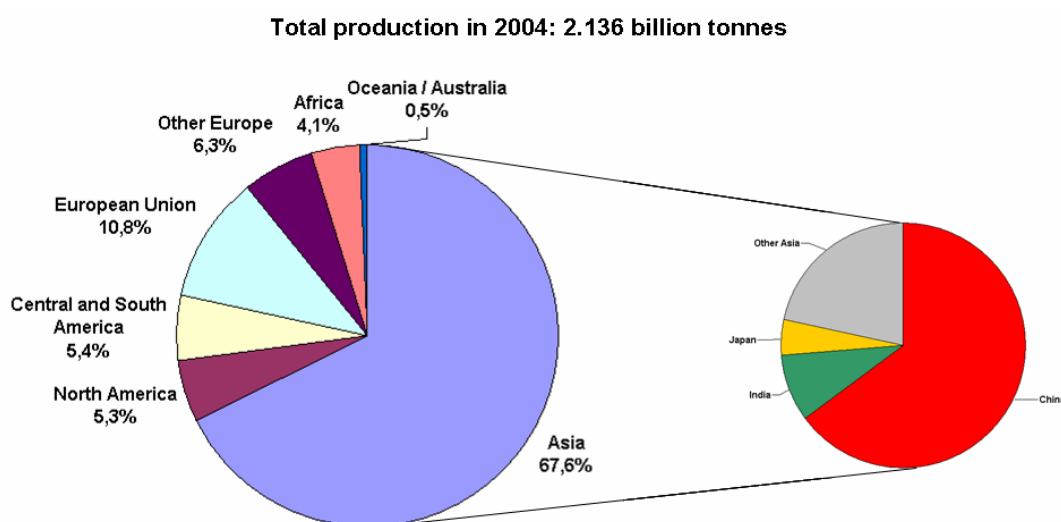


Fig. 2-1: World Cement Production in 2004 by region [103]

Up to now, the cement industry has focused on various CO₂ management approaches [105], [109-110], [141-143], e.g.

- energy efficiency measures
- production of composite/blended cements
- use of alternative fuels and raw materials.

However, further significant reduction measures will be required in the future. Consequently, advanced CO₂ management approaches are discussed in the cement industry, which are for economical and technical reasons today beyond realization e.g.

- carbon dioxide capture and storage (CCS)
- hybrid cement-energy facilities
- binders not based on Portland cement clinker (e.g. geopolymers) [81, 82],

At present, CCS measures are discussed for potential CO₂ mitigation in the power sector. Transport and storage of compressed CO₂ are available techniques, however limited today to specific applications. Experiences on a larger scale are not available, neither in the power sector or other industries like cement production [111-113] - only feasibility studies have been published so far [106, 107]. It seems that cement kilns might provide more favorable conditions for the application of carbon capture measures than other industrial installations due to the comparatively high CO₂ concentration in their off-gases (see **table 2-3**). However, such a comparison does not give a complete picture of all pros and cons and since other parameters have to be taken into account as well.

Table 2-3: Properties of candidate gas streams for application of capture technologies [101]

Source	CO ₂ concentration [Vol.-%] (dry)	Pressure of gas stream [MPa]
CO₂ from fuel combustion		
• Power station flue gas		
Natural gas fired boilers	7 – 10	0.1
Gas turbines	3 – 4	0.1
Oil fired boilers	11 – 13	0.1
Coal fired boilers	12 – 14	0.1
IGCC: after combustion	12 – 14	0.1
• Oil refinery and petrochemical plant fired heaters	8	0.1
CO₂ from chemical transformations + fuel combustion		
• Blast furnace gas		
before combustion	20	0.2 – 0.3
after combustion	27	0.1
• Cement kiln off-gas	14 - 33	0.1
CO₂ from chemical transformation before combustion		
• IGCC: synthesis gas after gasification	8 - 20	2 - 7

The crucial point is that today's CCS measures would not be achievable to industries like cement production for technical and cost reasons. Apart from this fact, an IEA study concludes, that the CO₂ reduction potential in the cement industry is about 350 Mt in 2050 [104], provided that CO₂ capture could be installed at about 350 modern cement kilns (10% of all cement kilns worldwide).

3 CO₂ capture technologies

CO₂ management in the cement industry has made good progress in recent decades taking into account various process integrated approaches such as:

- increase in energy efficiency
- use of secondary fuels
- use of biomass
- production of blended cements

In terms of end-of-the-pipe techniques CO₂ capture and subsequent storage has been described in various reviews and general reports (CCS) [114-140]. In principle three basic technologies are known to capture CO₂:

- pre-combustion capture
- oxy-fuel combustion
- post-combustion capture.

These technologies are shown in a simplified form in **figure 3-0**:

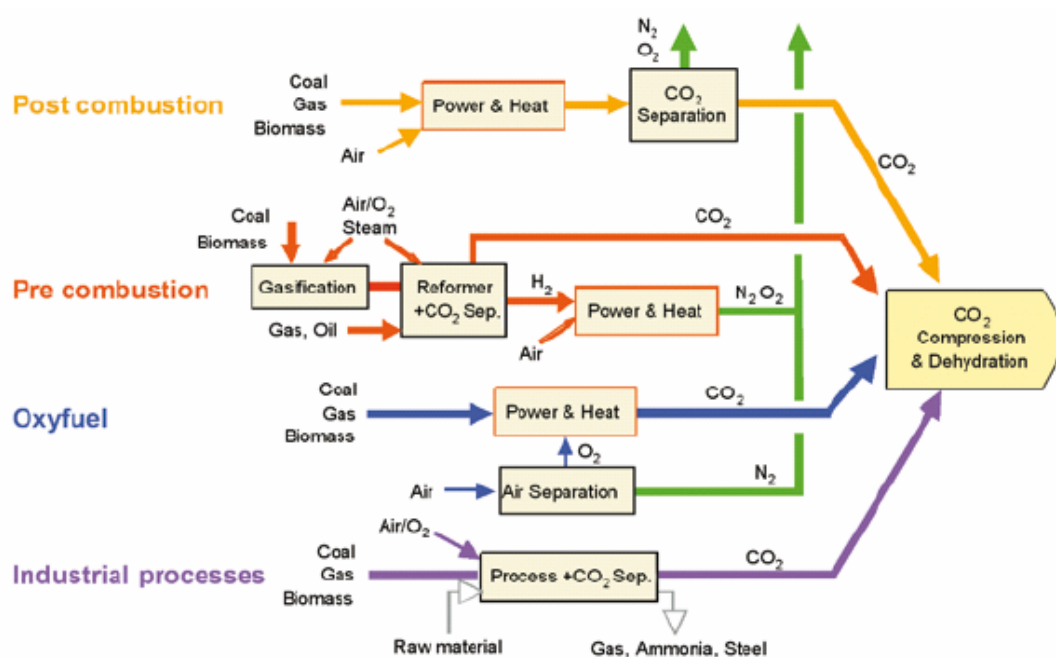


Fig. 3-0: CO₂ capture systems [101]; capture from *industrial process streams* means the application of the above mentioned techniques in the steel industry, cement industry, manufacture of ammonia, alcohols, etc.

The current chapter is structured as follows:

- A short summary of process integrated technologies is given in **chapter 3.1**.
- **Chapters 3.2-3.4** summarize capture technologies – in particular with regard to potential application to the clinker burning process.
- **Chapter 3.5** introduces hybrid and other technologies
- **Chapter 3.7** gives a preliminary summary of the different technologies.

3.1 Process integrated technologies

In cement plants carbon dioxide originates from two different sources:

- use of fossil fuels e.g. coal;
- calcination of limestone

Carbon dioxide generation is in the order of 0.65-0.92 kg CO₂ per kg cement, numbers being based on a cement plant with modern technology and equipment. On a worldwide level, the weighted average is approximately 0.83 kg CO₂ per kg of cement [83]. **Figure 3-1** shows the regional differences in process and energy CO₂ emissions.

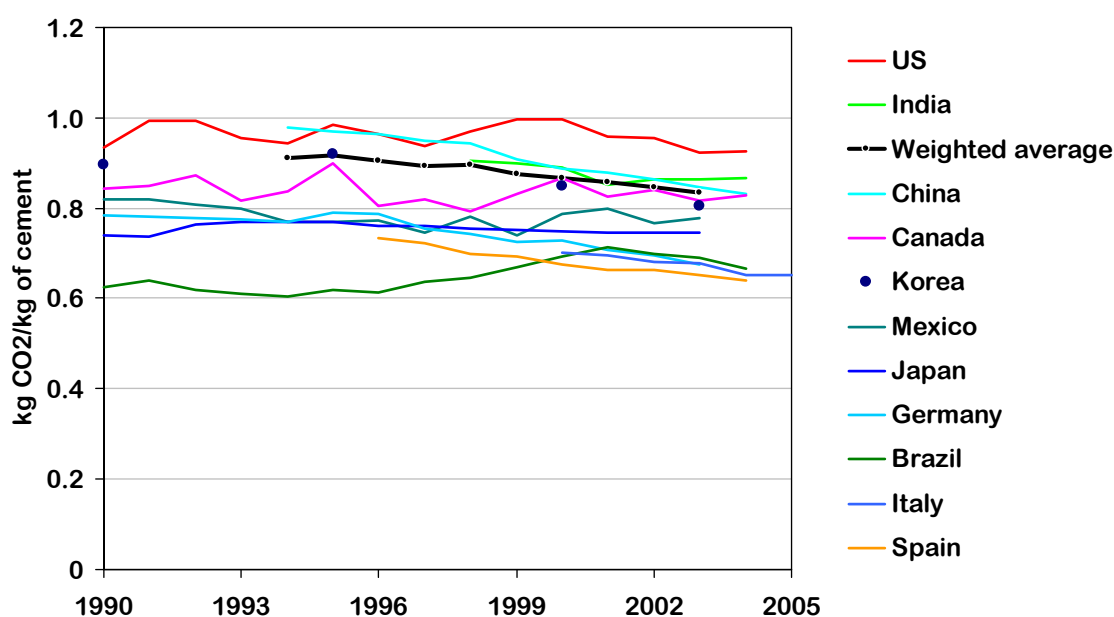


Fig. 3-1: Process and energy CO₂ emissions per tonne of cement by country, 1990-2005 [83]

A variety of measures have been successfully applied to improve the energy efficiency of the cement production process, such as improvements of the grinding systems, the pyroprocessing system or the materials handling [109]. For instance, a significant reduction in energy consumption is achievable when shifting from wet or semi-wet process to dry process plants, provided the raw material situation allows for this conversion.

Alternative fuels replace fossil fuels and subsequently reduce global CO₂ emissions, because these waste materials must not be deposited or incinerated elsewhere. Though the use of secondary fuels is widespread in the cement industry, there is still potential to significantly increase the co-incineration rate in the years to come. Some of the most important secondary fuels are waste tires, waste oil, fractions of industrial and commercial waste (pulp, paper, cardboard, plastics, etc.), solvents, etc. Another environmental benefit is that both energy and material utilization is provided through co-incineration in cement kilns.

Unlike fossil fuels, biomass is renewable and reestablishes the natural CO₂ cycle. CO₂ generated from burning biomass is considered as climate-neutral because re-growth of biomass

compensates for the emissions [85, 86]. Biomass fuels are combustible materials such as wood wastes, sewage sludge, meat and bone meal or others.

The shift towards more blended cements has already contributed to a reduction of CO₂ emissions from cement production. Consequently, blended cements will become more popular throughout the globe and its use will continue to increase in the future [110]. In Europe, blast furnace slag and pozzolanic cements account for about 12% of total cement production with Portland composite cement accounting for an additional 44%. However, the further potential of blended cements to contribute to CO₂ reduction depends on the availability of those main constituents in cement which replace clinker. Also market situations and durability aspects have to be taken into account, whenever blended cements are introduced. Today the most important constituents besides clinker in blended cements are:

- granulated blast furnace slag
- limestone
- pozzolans
- fly ash

Calcareous oil shales as examples of decarbonated materials used in the cement industry are of regional importance. Oil shale materials have been used in cement manufacture in Germany and Russia. The materials have been added to precalciners as a partial substitute for conventional energy sources. They also comprise as much as 8% of kiln feed as they contain the primary cement oxides. A German cement plant also intergrinds oil shale ash to produce blended cements [84, 87].

Also the use of other cementitious materials, so-called geopolymers or alkali-activated binders, could gain importance in the future. For example, geopolymers binders rely on an inorganic 2-component system, consisting of a solid component that contains SiO₂ and Al₂O₃ in reactive form and an alkaline activation solution. When both components come into contact, hardening results, due to the formation of an alumo-silicate network [88]. However, such binders, which are not based on Portland cement clinker are beyond today's experiences with building materials and are not covered by current codes and standards.

Cogeneration of electric power utilizing waste heat is an attractive proposition for cement plants for energy conservation. However, the applicability and the energy/CO₂ saving potential depend on the local situation at plant level, in particular the amount of excess heat available. Cogeneration is in use in the cement industry in many countries [99] not only for energy saving purposes but also to gain independence from the local power grid, if this does not provide sufficient stability.

3.2 Pre-combustion technologies

Pre-combustion technologies (reforming or gasification/partial oxidation based on different fossil fuels) are applied to produce fuels (mainly hydrogen) which are more or less carbon-free or to reduce the carbon content of hydrocarbon containing fuels. In the first case the product H_2 does not need to be absolutely pure and may contain low levels of methane, CO or CO_2 , but the lower the level of carbon-containing compounds is, the higher is the reduction in CO_2 emissions. The H_2 fuel may also contain inert diluents, such as nitrogen (e.g. when air is used for partial oxidation). Depending on the production process H_2 can be fired in a range of heaters, boilers, gas turbines or fuel cells. The carbon in the fuel is usually removed as CO_2 which can be captured and stored. Since the separating of CO_2 from H_2 is the main task in pre-combustion capture, technologies using membranes, absorption or adsorption processes have to be applied.

Currently there is no pre-combustion technology used in a cement plant. In other sectors like the chemical, fertilizer and synthetic fuels industry hydrogen production and separating carbon dioxide from syngas is state-of-the-art, but in most cases designed for smaller gas volumes compared to the requirements of cement kilns. The applicability to the clinker burning process strongly depends on the technical possibility of using hydrogen as a main fuel in the kiln. Due to its explosive properties, hydrogen could not be used in existing cement kilns, but could be utilized after dilution with other gaseous fuels or inert gases like nitrogen or steam. Furthermore, the combustion and radiation properties of hydrogen differ significantly from those of the fuels being used today in the cement industry meaning that - even if handling problems could be solved - the clinker burning process would have to be significantly modified.

Due to the comparatively low radiation heat transfer, hydrogen flames as such are not suitable for clinker burning in conventional kilns. New technologies would have to be developed to make hydrogen flames suitable for clinker burning. Either hydrogen has to be mixed with other non-carbonaceous ingredients to increase the heat transfer through radiation or new burning technologies must be developed. Recycled clinker dust boosted into the flame might be able to provide for sufficient heat transfer. Also the latest development in porous burner technology could be investigated for use in the cement industry. In such burners the fuels are burnt very efficiently and with low NO_x emission in a ceramic or metallic sponge. It is the radiation of the sponge which provides for the heat transfer. An additional advantage of a porous burner in comparison to a single rotary flame exists in achieving a defined temperature profile inside the kiln. Anyway, the costs for H_2 production are very high and would significantly increase cement production costs.

To establish pre-combustion technology in cement works the clinker burning process as well as the cement plant as such would need to be modified. At the plant location a separate hydrogen plant with carbon dioxide capture technology would have to be built. Waste heat recovery from the cement plant could provide some energy for the reforming and shift reaction in the hydrogen production process. While hydrogen production from natural gas, light hydrocarbons and coal is a well-known technology, the subsequent capture and storage of CO_2 has not yet been applied.

Handling hydrogen is not as easy as common liquid and solid fuels. Because of its explosive properties preventive measures in production, storage and burning of hydrogen must be established.

Because of the limited heat transfer through radiation from hydrogen flames, new developments in burner and combustion technology are necessary. Burning hydrogen in non-mixed open jet flames is not a state-of-the-art technology. Even if recycled clinker dust from the clinker cooler could increase the heat transfer by radiation, it is unavoidable that burners have to be redesigned due to the abrasive properties of clinker dust. In addition, impacts on product quality and emissions would need to be examined. The clinker burning process based on hydrogen flames is completely different from today's kilns which use traditional fuels. Changed temperature profiles in the rotary kiln and reduced acid components in flue gas influence the clinker burning process and the emissions of the plant.

From other industrial branches the separation costs^b for carbon dioxide and hydrogen are known [101]:

- 3.7 to 40.9 €/t CO₂ for hydrogen or ammonia production
- 27.5 to 55.1 €/t CO₂ for new natural gas combined cycle power plants
- 21.6 to 38.0 €/t CO₂ for new pulverized coal-fired power plants
- 9.7 to 27.5 €/t CO₂ for new integrated gasification combined cycle power plants.

Today hydrogen production is a commercially available technique, but it is questionable, whether H₂ will be available within the next 20 years as a standard fuel. Consequently cement companies would have to produce H₂ for pre-combustion technology on-site. However, no plant has ever been built with a size which is necessary for supplying a cement work with sufficient carbonaceous-free fuel. In principle the technique seems to be applicable to a modified existing cement plant. For carbon dioxide separation and capture, known technologies can be used. Due to the combustion properties of hydrogen, new burner and combustion technology for the clinker burning process have to be developed. It is obvious that pre-combustion technologies can only minimize CO₂ emissions from carbonaceous fuel sources. CO₂ emissions originating from the calcination of limestone will remain unaffected.

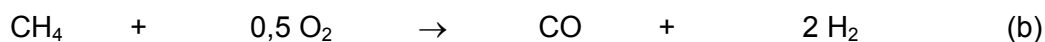
^b Whenever necessary, US Dollar were converted to Euro according to the following exchange rate:
1 US-\$ = 0.744 € (31 May 2007)

3.2.1 Steam reforming of natural gas and light hydrocarbons

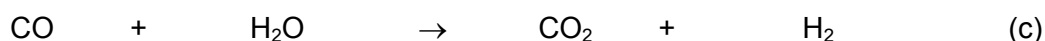
Steam reforming is the dominant technology for hydrogen production today and the largest plants produce up to 480 t/d of hydrogen. Very often the primary energy source is natural gas. Then the process is referred to as steam methane reforming (SMR), but also other light hydrocarbons, such as naphtha, can be utilized. In a first step of this process sulphur compounds are removed from the feed, since these are poisons to the nickel-based catalyst. During the next step steam is added to the gas. The catalytic reforming reaction, which is endothermic, takes place at high temperatures (800-900°C):



Heat is supplied to the reactor by burning part of the fuel (partial oxidation).



The reformed gas is cooled in a waste heat boiler which generates the steam needed for the reactions and passed into a so-called CO shift system, in which most of the CO is converted to CO₂ in an exothermic reaction:



The CO concentration in the syngas (or in hydrogen) is reduced in two steps down to 0.2-0.3%. High temperature shift reactors operating between 400°C and 550°C and using an iron-chromium catalyst leave between 2 and 3% CO in the exit gas (dry basis). Copper-based catalysts can be used at temperatures from 180-350°C and leave from 0.2-1% CO in the exhaust gas. Lower CO content favours higher CO₂ recovery. The gas is then cooled and CO₂ is removed from the CO₂/H₂ mixture.

Until about 30 years ago, the CO₂ was removed using a chemical absorption process (using amines or hot potassium carbonate) and was released into the atmosphere as a pure stream. There are many of these plants still in use. Modern plants, however, use a pressure swing adsorber (PSA) (see **chapter 3.4.3.1**), where gases other than H₂ are adsorbed in a set of switching beds containing layers of solid adsorbent (such as activated carbon, alumina and zeolites). The H₂ exiting the PSA (typically about 2.2 MPa) can have a purity of up to 99.999%. The CO₂ is - besides some traces of methane and H₂ - contained in a gas stream from the regeneration cycle. The stream is used as fuel in the reformer where it is combusted in air. For CO₂ capture the installation of a post-combustion process (see chapter 3.4) is required.

Alternatively, the PSA system can be designed not only for high recovery of pure H₂ but also to recover pure CO₂ and have a fuel gas as the third product stream. In a design study for a large modern plant (total capacity 720 t H₂/d), the overall efficiency to produce 6.0 MPa H₂ from natural gas with CO₂ enrichment, that is without CO₂ capture, is estimated to be 76% (LHV basis) with emissions of 9.1 kg CO₂/kg H₂ [89]. The process can be modified to provide a nearly pure CO₂ co-product. One possibility is to remove most of the CO₂ from the shifted,

cooled syngas in a "wet" CO₂ removal plant with an appropriate amine solvent. In this case the CO₂-deficient syngas exiting the amine scrubber is passed to a PSA unit from which relatively pure H₂ is recovered and the PSA purge gases are burned along with additional natural gas to provide the needed reformer heat. The CO₂ is recovered from the amine solvent by heating and pressurized for transport. Taking into account the power to compress the CO₂ (to 11.2 MPa) reduces the efficiency to about 73% and the emission rate to 1.4 kg CO₂/kg H₂, while the CO₂ removal rate is 8.0 kg CO₂/kg H₂.

3.2.2 Gasification/Partial oxidation of gas and light hydrocarbons

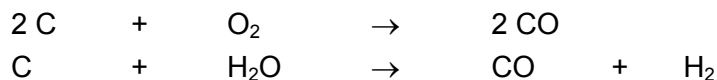
In the partial oxidation (POX) process, a fuel reacts with pure oxygen at high pressure. The process is exothermic and takes place at high temperatures (typically 1,250°C-1,400°C). All the heat required for the syngas reaction is supplied by the partial combustion of the fuel and no external heat is required. As with steam reforming, the syngas will be cooled, shifted and the CO₂ removed from the mixture as described in the previous chapter. POX is a technology in common use today, the efficiency is lower than steam reforming, but the range of fuels that can be processed is much wider.

For large-scale hydrogen production, the oxygen is supplied from a cryogenic air separation unit. The high investment and energy consumption of the air separation unit is compensated by the higher efficiency and lower cost of the gasification process and the absence of N₂ (from the air) in the syngas, which reduces the separation costs considerably.

Furthermore, a combination of the two technologies described is called auto-thermal reforming. In this case, the heat required in the reforming reactor is generated by the partial oxidation reaction using air or oxygen. Because steam is supplied to the reactor as well as excess natural gas, the endothermic reforming reaction occurs in a catalytic section of the reactor downstream of the POX burner. The addition of steam enables a high conversion of fuel to hydrogen at a lower temperature. An advantage of the process, compared to steam reforming, is the lower investment cost for the reactor and the absence of any emissions of CO₂.

3.2.3 Gasification of coal or biomass

The so-called coal gasification has been a well-known technology for many years. Ground coal or other carbonaceous materials like petroleum, biomass, waste or refinery residues, react with steam and oxygen at high pressures and temperatures (650-2,000°C) to form CO and hydrogen.



CO is further reacted with steam to produce CO₂ and more H₂ in a water gas shift reactor:



A schematic of a gasification process is shown in **figure 3-2**.

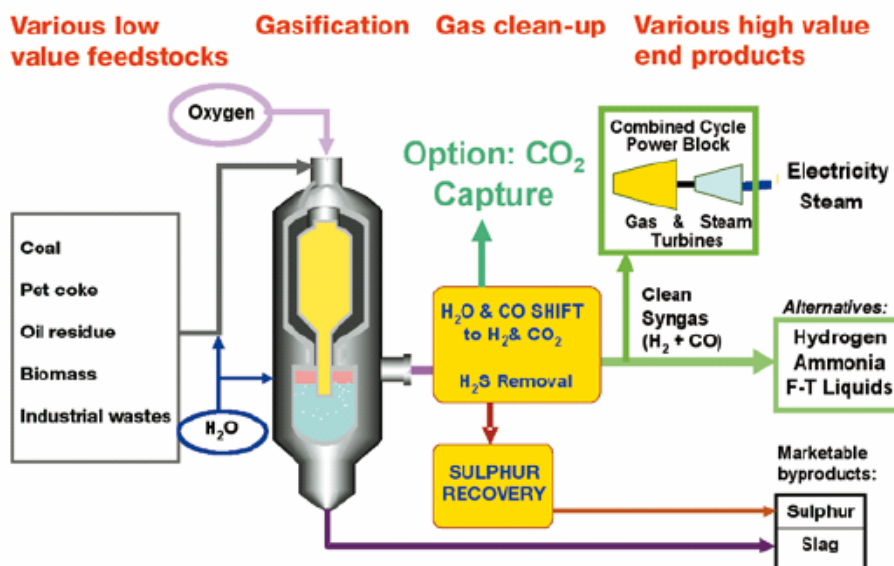


Fig. 3-2: Simplified schematic of a gasification process showing options with CO₂ capture and electricity, hydrogen or chemical production [101]

Today in more than 28 countries worldwide over 460 gasifiers in about 160 commercial projects are in operation or under construction [61]. A widespread application of hydrogen-enriched syngas from gasifiers is the utilization of the hydrogen as base chemical for synthetic fuel and fertilizer production. Within the last few years the gasification technology has more and more been applied in the electricity sector using integrated gasification combined cycles (IGCC), and producing methane and hydrogen for fuel cells. In chapter 8.3 (see annex) data from projects with gasifiers in operation, construction or design are compiled.

Different types of solid fuel gasifiers are currently available for commercial use:

- In fixed bed gasifiers the carbonaceous fuel is heaped up to a permeable bed. The gasification fluid steam or oxygen (or air) flows in counter-current or co-current configuration

through the fixed bed. The fixed bed moves down draft and will be transported out at the bottom of the gasifier.

- Oxygen (or air) or steam fluidizes the fuel in a fluidized bed gasifier. Low velocities keep the fluidized bed inside the reactor, at higher velocities heat and mass transfer increase, but the fuel bed is transported out of the reactor. In a circulating fluidized bed gasifier the fuel particles are fed back to the reactor after separation of the gas flow.
- In the entrained flow gasifier dry pulverized solid, atomized liquid fuels or fuel slurry is gasified with oxygen in co-current flow. Gasification reactions take place in a dense cloud of very fine particles.

The choice for a type of gasifier is strongly affected by the properties of fuel, ash, and slag. The mechanical strength and baking properties of the fuel must be considered as well as its dripping point or the tendency of slagging. The most widespread type is the oxygen-boosted entrained flow gasifier.

Usually the gasification and the reforming process with steam takes place in one reactor. The heat release of the partial oxidation is used for the reforming reaction. In a staged gasifier, the reforming process takes place after the gasification. Pressurized gasifiers are less common than atmospheric gasifiers. With increasing pressure the thermal efficiency of the gasifier increases, but pressurized combustion chambers need complex and costly feeding and extracting systems.

Today, syngas containing carbon monoxide and hydrogen is mainly utilized for the production of synthetic chemicals and fuels. The syngas is cooled down to be dewatered and dedusted. A desulphurization stage removes sulfur compounds. The remaining purified syngas is converted in a Fischer-Tropsch-Synthesis to carbonaceous liquids, in particular alkanes, alkenes, and alcohols. The Fischer-Tropsch-Synthesis is widespread and a state-of-the-art technology. The biggest "coal-to-liquid plants" are Sasol I – III in South Africa, operated by the South Africa Coal and Oil Ltd. The plant produces chemicals and fuels (more than 160,000 bpd) from coal [27, 52].

Integrated Gasification Combined Cycles to generate electricity have been operating since the 1970s in demonstration plants. Plants constructed in the 1990s and in the following years are now entering commercial service. Currently about 17 commercial scale fossil-fired IGCC power plants are in operation or construction. As feedstock anthracite, lignite, petroleum coke, asphalt and tar is used. The advantage of an IGCC power plant versus a coal-fired steam cycle power plant is a better overall efficiency. The electric and thermal efficiency increases by using gas combustion in a gas turbine and using flue gas heat for a steam turbine versus a direct coal-fired furnace with steam cycle. The electric efficiency of 45% of a steam cycle could be increased to more than 58% by using IGCC technology. The aim of IGCC power plants is high specific power yield per unit carbon dioxide.

Up to now no IGCC power plant which includes separation and capture of carbon dioxide has been achieved, but the newly built and currently designed plants are prepared for a later addition of such techniques.

In principle, there is no difference in the power generating process in an IGCC power plant with or without carbon dioxide separation and capture technology. After gasification of the carbonaceous fuel, the hydrogen-enriched gas is dedusted and desulphurized. The next step would be the separation of carbon dioxide and hydrogen. To keep the gas turbine flow unchanged the removed carbon dioxide should be replaced by nitrogen, otherwise a different or adapted gas turbine must be installed. Because the gasification process is oxygen-boosted, nitrogen from the air separation plant is available.

Currently two IGCC power plants with carbon dioxide separation, capture and storage technology are designed and start-up in the next decade. ZeroGen is a 100 MWe demonstration plant located near Rockhampton / Australia. The captured carbon dioxide will be pipelined 220 km and stored in deep underground saline aquifers. The project status has reached the contractor selection process. The completion and commissioning is expected for 2010 [57, 58]. Also a carbon dioxide free power plant with IGCC technology (450 MWe) is planned by RWE, Germany, and is expected for start-up in 2014 [50].

IGCC cannot be applied as such to the clinker burning process. But studies have been published on producing H₂ from coal via gasification with CO₂ capture [101, 3.5.2.7]. In principle, H₂ can be produced from solid fossil fuels in systems similar to a coal IGCC plant with CO₂ capture and could be utilized in any combustion facility.

Currently hydrocarbons or carbonaceous fuels and water steam are the most auspicious sources of hydrogen. Hydrogen production by steam reforming or gasification is state-of-the-art for decades. The technology is well proved and found in all industrial branches which use hydrogen in great quantities. On the other hand hydrogen can be produced by water electrolysis which requires extensive electric power. To obviate CO₂ penalties by electric power generation renewable energy sources like photovoltaics, wind or water power have to be devoted. Photovoltaics is a fast developing branch, but today limits of efficiency and price avert the introduction into the commercial market of power generation. Against other renewable energy sources for power generation enter the electric power market with reasonable prices for years.

A mid-size cement kiln with a daily capacity of 3000 tpd requires around 130 MW firing power. So a fuel flow of around 3.9 tph of hydrogen would be necessary to provide sufficient heat for the calcination and clinker burning process. The production costs^c of hydrogen amount to 110 - 1700 €/t by steam reforming or gasification and 300 - 4460 €/t hydrogen by using electrolysis respectively [208-211, 214, 216, 218; prices are partly based on figures from 1996]. The energy consumption amounts to about 50 MWh/t hydrogen by using electrolysis [208, 211].

^c Whenever necessary, Japanese Yens or Indian Rupees were converted to Euro according to the following exchange rates: 1,000 ¥ = 6.10 € or 1,000 Rs = 18.42 € (1 June 2007), respectively. German Marks were converted to Euro according to 1 DM = 0.5113 €.

The following **table** summarizes the most important aspects of pre-combustion technologies.

Tab. 3-1: Maturity of carbon-free burning with pre-combustion technologies

Technology used in		
	cement industry ?	no
	other sectors ?	<ul style="list-style-type: none"> • power plants • chemical industry • fertilizer industry • synthetic liquid fuels
Technology applicable to		
	existing clinker burning process ?	no
	modified clinker burning process ?	unlikely, because <ul style="list-style-type: none"> • new burner and hydrogen combustion technology required • waste heat recovery for reforming and shift reaction required
Related research projects		<ul style="list-style-type: none"> • reforming and partial oxidation are proven technologies • gasification of solid fuels
Abatement efficiency		up to 100 %, ~ 85 % overall efficiency for fuel CO ₂
Energy efficiency penalty		yes
Impact on		
	kiln operation	yes (new burner and combustion technology due to hydrogen combustion properties)
	product quality	probably yes
	other emissions	yes (reduced acids components in flue gas)
	production costs	yes, but hard to estimate. Examples from other industries indicate additional production costs of 4 – 55 €/t CO ₂ . Significant cost driver will be in any case investment costs which can at this time not be given for cement production.
Advantages		<ul style="list-style-type: none"> • hydrogen production commercially available technique
Challenges		<ul style="list-style-type: none"> • research objectives: new burner and combustion technology • cheap CO₂ separation and capture technology required • only CO₂ from fuel combustion is reduced • no reduction of process CO₂

3.3 Oxy-fuel technology

3.3.1 Oxygen Enrichment

To further increase the energy efficiency of the clinker burning process and reduction of the specific CO₂ emissions investigations with oxygen enriched combustion air have been performed by the cement industry. The major aim was an increase of production capacity, energy efficiency, or substitution with low calorific value or secondary fuels.

In comparison to combustion with ambient air, flame temperatures increase with the use of oxygen enriched combustion air. With pure oxygen the theoretic flame temperatures reach 3,500 °C [94], but in reality the flame temperatures are lower due to heat loss and dissociation of combustion products. The oxygen boosted kiln combustion leads to 'high value' energy due to minimized nitrogen content which does not have to be heated up [65]. This energy can be used for the calcination and sintering process which results in a rise of kiln capacity. For dry processes a production enhancement of 3 to 6 ton of clinker for each ton of oxygen is reported, at the same time fuel consumption reduces by 1.4 to 1.9 kJ/kg clinker for each percentage of oxygen enrichment [65, 66].

The thermal load of oxygen boosted combustion and the high flame temperatures have impacts on the kiln refractory. Some cement plant operators reported problems and damage to the kiln refractory while using oxygen enriched combustion air [67, 95]. To limit the negative impacts of high temperatures oxygen is boosted just in the part of the flame which faces the material in the sintering zone while in other areas ambient air is used. The higher absorption capability of air flames lowers the energy transfer to the kiln refractory.

In Russian experiments at laboratory and industrial scale oxygen was mixed in the primary air as well as in the secondary air. The impacts of the oxygen boosted caused a distinct shorter, tighter, brighter and hotter flame. In short-term tests with oxygen enrichment up to 35 % by volume an increase of 56 % kiln capacity was achieved. But due to higher thermal load problems with kiln refractory appeared [95]. Similar experiences were observed in the USA. The use of the principle of asymmetric oxygen boosted flames avoided impacts to the kiln refractory [67]. In a wet process kiln capacity rose by more than 35 % and specific fuel consumption dropped by nearly 20 %. But due to minimized secondary air flow heat recuperation of clinker cooler fell distinctly. Similar experience with production capacity, fuel consumption, refractory and cooler efficiency are reported by several cement plants [66, 68, 69, 70, 71, 96, 97]. Data about emissions is limited. In one case a cement plant operator reported about a rise of NO_x emissions by 50 % in wet kiln processes while CO emissions remained constant, but the oxygen boost technique is simply designed and has potential for optimization [68]. In another cement plant with dry kilns oxygen enrichment did not influence emissions of NO_x and SO₂.

Oxygen enrichment technology in the kiln has been used so far to improve production capacity. Oxygen enrichment combustion technology has not been applied to carbon dioxide emissions with the aim to capture carbon dioxide. Oxygen enrichment in combustion air may result in fuel savings and thereby avoids production of carbon dioxide. But providing oxygen enriched combustion air induces energy penalties linked first of all to the oxygen production

itself. Oxygen enriched technology as such is not a carbon dioxide capture technology. However, due to higher CO₂ concentration in the off-gas from the respective combustion capture technologies might be easier to be applied.

3.3.2 Oxy-Fuel Technology

The oxy-fuel technology relies on oxygen instead of ambient air for combustion, i.e. the nitrogen is removed in a separation plant from the air prior to being applied to the kiln. Consequently the concentration of carbon dioxide in flue gas is increased significantly. To maintain an appropriate flame temperature as in an ambient-air-based combustion, some flue gas has to be recycled. Thus, the recirculation rate adjusts the combustion temperature. **Figure 3-3** shows the oxy-fuel process with recirculating flue gas.

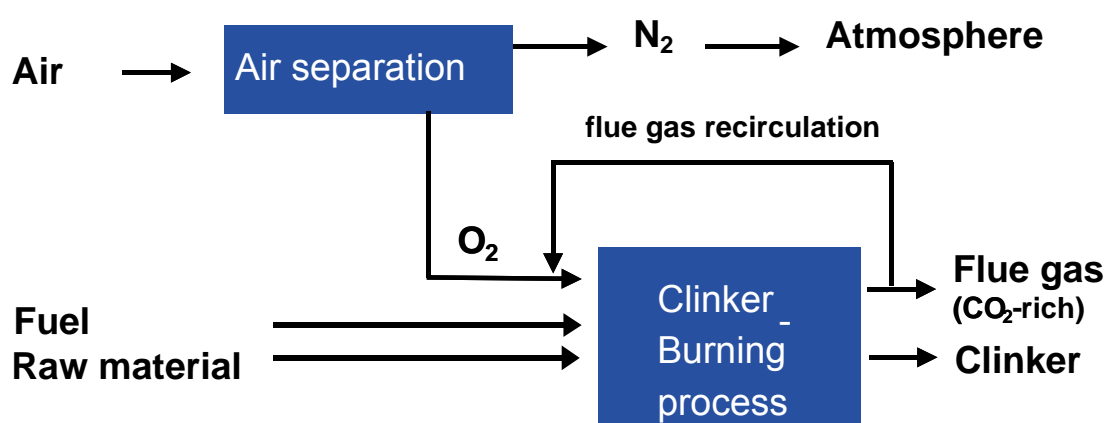


Fig. 3-3: Oxy-fuel technology with flue gas recirculation

The advantage of pure-oxygen-based combustion is that the flue gas has a carbon dioxide concentration of around or above 80%, compared to 14 - 33 Vol.-% for ambient-air-based combustion. An overview of typical CO₂ concentrations in various exhaust gases has been given in **table 2-3**. Consequently, for CO₂ capture only a comparatively simple carbon dioxide purification is required, if any. In power plants, it may be possible to omit some of the flue gas cleaning equipment which currently has to be included, such as flue gas desulphurization, which would reduce the net cost of carbon dioxide capture. Some sulphur compounds and some other impurities would remain on carbon dioxide fed to storage, which may be acceptable in some circumstances. The oxygen and carbon dioxide recycle combustion process has also a further benefit in suppressing nitrogen oxide formation, lowering abatement costs for the removal of nitrogen oxides. Oxy-fuel combustion aimed at large power generation applications has so far only been demonstrated in small scale test rigs. Larger scale applications have been seen in use in glass and steel melting furnaces [72, 73].

The Intergovernmental Panel on Climate Change evaluates oxy-fuel technology in the stage of development [74]. For technical reasons oxy-fuel technology in clinker burning process is seen as a more realistic option as compared to other techniques, because flue gas of con-

ventional cement plants already contains 15 up to 30% by volume carbon dioxide. With flue gas recirculation and oxy-fuel technology the flue gas concentration of carbon dioxide could be increased up to 80% by volume or more. The remaining part of the flue gas comprises water steam from combustion and impurities of nitrogen and sulphur oxides. Dehumidification by condensation and technology for DeNO_x and DeSO_x are well-known and widespread.

Also the energy sector has little experience with oxy-fuel technologies. The Swedish power company Vattenfall Europe plans the first pilot plant with oxy-fuel technology for power generation. The horizon of commercial implementation of oxy-fuel technology is estimated to be around the year 2020. Fundamental research [75-77] shows that flame temperatures and gas velocities decrease due to high specific heat capacity and molar mass of carbon dioxide. Also heat transfer through radiation becomes more important because emissions ratio increases with increasing carbon dioxide content.

Nitrogen oxide generation is decreased, because nitrogen oxide exclusively originates from fuel-based nitrogen. Furthermore, nitrogen oxide is dissociated by recirculating the flue gas. In terms of combustion performance the oxygen content in the combustion gas is 27 to 35% by volume. This is almost equivalent to ambient air, however, the ignition and burnout of fuels are positively influenced.

Currently there are no projects reported to implement oxy-fuel technology in the clinker burning process or other process firing systems. A main reason is certainly that some technical issues have not been solved so far. The oxy-fuel technology with flue gas recirculation has an important impact on plant operation and product quality. The high partial pressure of carbon dioxide certainly affects the calcination of calcium carbonate to calcium oxide and carbon dioxide. Also, unlike in steam boilers combustion in rotary kiln flames are non-premixed open jet flames. Consequently, research and experience from boilers are not applicable to rotary kilns. Also flue gas enthalpy and streams are completely different to current cement plant technique. Nevertheless, oxy-fuel technology with flue gas recirculation is considered as a potential and innovative measure to handle carbon dioxide in cement clinker burning process [72, 78].

Currently the Verein Deutscher Zementwerke e.V. is preparing a research project, which should provide the necessary basics to evaluate the key parameters of the oxy-fuel technology. The main objectives of this research project are:

- Plant and process requirements as well as limits for oxy-fuel technique (especially the degree of flue gas recirculation)
- Impacts on energy balance of process, clinker quality and plant operation
- Composition of flue gas subject to oxy-fuel enrichment

In laboratory experiments the influence of the high CO₂ partial pressure on calcination and the influence of different gas compositions on clinker burning process and clinker quality shall be examined. An already existing computational model of the clinker burning process should be extended to oxy-fuel technique, so results of the laboratory experiments could be transferred to a virtual plant.

For a medium-size cement plant with a kiln capacity of 3,000 tpd the oxygen demand is estimated to be around 50 to 55 tph. The calculation is based on an oxygen level of 1.2 % by volume in the kiln inlet and a fuel mix based on lignite, fluffy alternative materials (e.g. plastics, paper), animal meal and petroleum coke in the kiln firing and shredded tyres in the kiln inlet firing.

Such amounts of oxygen must be provided by an on-site oxygen supply system. The decision for a dedicated oxygen supply system must be based on an analysis of the specific needs of the cement plant in question. Oxygen can be produced on the cement plant premises by several methods. For very large usage a cryogenic air separation is the preferred choice. This technology is well-known and widespread. Alternative systems are based on pressure swing adsorption (PSA) or membrane systems. PSA plants are available in capacities up to 60 tpd, but multiple plants can be installed. Gas separation membranes rely on differences in physical and chemical interactions between gases and membrane material (see chapter 3.4.2). Currently membrane technology is a fast developing industrial branch. Selectivity, quality and throughput increases rapidly, whereas in comparison to cryogenic production of oxygen, air separation by membranes provides the cheaper solution, both in terms of capital and operating costs [98].

The costs^d for oxygen produced by cryogenic separation amounts to 40 €/t and 250 €/t oxygen by PSA [212, 213,217]. The energy consumption amounts to 0.2 to 0,35 MWh/t or 0.5 to 1 MWh/t oxygen by cryogenic separation or PSA, respectively [212, 213, 217].

To introduce oxy-fuel technology with flue gas recirculation into an existing cement plant is extremely challenging. To prevent air intrusion, the complete plant has to be sealed or has to be operated with excess pressure. A new air separation plant has to be established on the cement plant premises and the facilities of flue gas recirculation have to be included into the existing plant units. The different flue gas enthalpies and flows require a different clinker cooler efficiency. Consequently all plant units have to be redesigned to the requirements of the new technology. Hence implementation of oxy-fuel technology with flue gas recirculation seems to be predominantly an option for new plants.

^d Whenever necessary, Japanese Yens or Indian Rupees were converted to Euro according to the following exchange rates: 1,000 ¥ = 6.10 € or 1,000 Rs = 18.42 € (1 June 2007), respectively. German Marks were converted to Euro according to 1 DM = 0.5113 €.

The most important aspects of oxy-fuel technology are summarized in the following **table**:

Tab. 3-2: Maturity of oxy-fuel technology

Technology used in		
	cement industry ?	no
	other sectors ?	<ul style="list-style-type: none"> • glass industry
Technology applicable to		
	existing clinker burning process ?	no
	modified clinker burning process ?	in principal yes, but new kiln design required
Related research projects		The carbon dioxide free power plant, Schwarze Pumpe (Vattenfall Europe)
Abatement efficiency		very high
Energy efficiency penalty		high (due to oxygen production)
Impact on		
	kiln operation	yes (containment technique, flue gas recirculation)
	product quality	probably (flue gas composition)
	other emissions	unknown
	production costs	yes, but hard to estimate. Significant cost driver will be in any case investment costs which can at his time not be given for cement production.
Advantages		<ul style="list-style-type: none"> • air separation/oxygen production is state-of-the-art technology • no CO₂ capture from flue gas is necessary due to high CO₂ concentration
Challenges		<ul style="list-style-type: none"> • combustion in O₂/CO₂ atmosphere in pre-mature state • flue gas recirculation required • impacts of O₂/CO₂ atmosphere on calcination and sintering process as well as on product quality completely unknown

3.4 Post-combustion technologies

Post-combustion capture means an end-of-the pipe technology which can be adapted to any combustion or CO₂ producing process [114-140], [144-145]. In most cases, CO₂ is captured from a flue gas at low pressure and low CO₂ content. Generally, the efficiency of post-combustion abatement technologies increases with CO₂ concentration in the exhaust gas. Compared to other combustion processes, the clinker burning process produces exhaust gases with very high CO₂ concentrations (~ 30% after preheater compared to 10-15% in coal fired power plants) and therefore – in principle - provides more favorable conditions for CO₂ capture as compared to other industrial processes. CO₂ needs to be removed from a mixture of mainly nitrogen and oxygen, in addition the impact of flue gas impurities (SO_x, NO_x, particulates) needs to be taken into account.

In principle post-combustion technologies can be applied to large power plants, cement kilns, industrial boilers and furnaces or other CO₂ producing processes. Different capture technologies can be considered:

- absorption, where CO₂ is selectively absorbed into liquid solvents
- membranes, where CO₂ is separated by semi-permeable plastic (polymer) or ceramic membranes
- adsorption, where CO₂ is separated using specially designed solid particles and
- low temperature processes, where separation is achieved by chilling and/or freezing the gas stream

Up to now, no trials with post-combustion capture have been carried out in the cement industry. However, in other industrial sectors several commercially available post-combustion capture technologies exist (with comparatively small gas volumes) which in principle can be used also for CO₂ capture from cement exhaust gases from a technical point of view. In the following chapters, these technologies will be described and assessed.

3.4.1 Absorption processes

Gas separation by absorption [146-156] relies on the principle that a gas species (in this case CO₂) is transferred between the feed gas (e.g. syngas or flue gas) and a liquid phase, the absorbent or solvent. The liquid and the gas phases are brought in contact, and, based on the solubility of the components of the feed gas, gas species can be selectively absorbed into the liquid solvent, while the remaining components of the feed gas pass through the absorber and are released in the atmosphere. As a last step, after absorption, the solvent, rich in CO₂, is regenerated by the application of heat or pressure (depending on the type of solvent). The captured CO₂ is separated from the absorbent and collected, while the lean absorbent is recycled.

Carbon dioxide separation by absorption can be achieved by physical, chemical and hybrid methods, the difference being the type of bonding between the absorbent and CO₂. In physical absorption, CO₂ is absorbed in a solvent according to Henry's law. In chemical absorption, CO₂ reacts with the absorbent, creating weakly bonded compounds, e.g. carbamates in case of amine solvents. Hybrid systems combine the attributes of physical and chemical absorption. A major difference between chemical and physical absorption is that the solubility of a target gas in physical solvents increases linearly with the target gas partial pressure, while chemical solvents have a high absorption capacity at relatively low partial pressures but reach a plateau at higher partial pressures. Therefore chemical absorption is preferred for the separation of CO₂ at low partial pressures (e.g. in flue gas treatment), while physical absorption is favoured at high partial pressures, for example for syngas treatment in pre-combustion decarbonisation and in hydrogen production.

3.4.1.1 Chemical Absorption

The leading technology and the only commercially proven method of flue gas CO₂ capture in post-combustion capture is chemical absorption using amines. Amine scrubbing technology has been established for over 60 years in the chemical and oil industries, for removal of hydrogen sulphide and CO₂ from gas streams. This experience is largely on natural gas streams and/or with chemically reducing (primarily oxygen deficient) gases but there are several facilities in which amines are used to capture CO₂ from flue gas streams today. At the moment a pilot-project is being carried out in a Danish power plant [90]. As a typical end-of-pipe technology, a retrofit to existing cement kilns would be feasible. High CO₂ recovery rates of up to 98% can be achieved with a purity of > 99%.

Typically, prior to the CO₂ removal stage, the flue gas is cooled, treated to reduce the levels of particulates and other impurities present. Afterwards the actual scrubbing process is carried out as follows (see **figure 3-4**):

- An aqueous alkanolamine solution is contacted in an absorber column with natural gas or flue gas from combustion processes containing CO₂.
- The basic amine reacts with the acidic CO₂ vapors to form a dissolved salt. The purified flue gas exits the absorber.

- The CO₂ rich amine solution is regenerated in a stripper column (desorber), where the pressure is reduced and/or the temperature increased to roughly 120°C in order to release the CO₂ and to yield a concentrated gas stream.
- Lean solution is cooled and returned to the absorber so that the process is repeated in a closed loop.

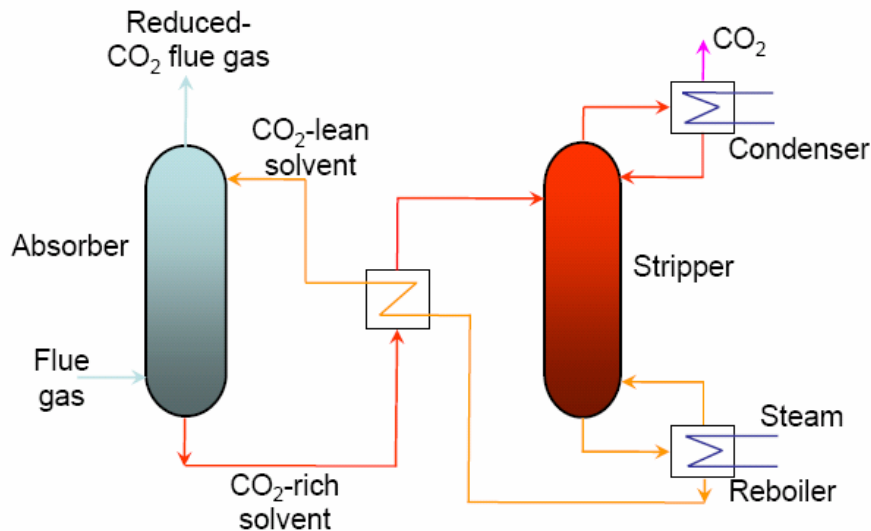
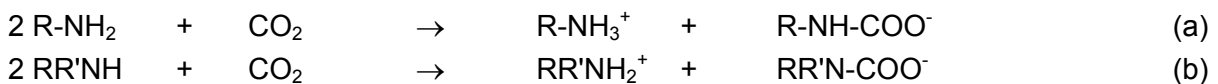
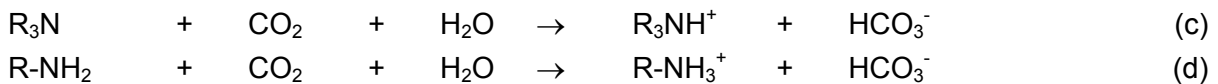


Fig. 3-4: Schematic diagram of liquid solvent scrubbing [111]

The most commonly used solvent is Monoethanolamine (MEA), HO-CH₂-CH₂-NH₂, a so-called primary amine (R-NH₂). Both primary and secondary amines (R-NH-R') react with CO₂ to form so-called carbamates:



Tertiary amines (R₃N) and so-called sterically hindered amines react with CO₂ according to the following equations:



The idea behind sterically hindered amines is based on attaching a bulky substitute to the nitrogen atom of the amine molecule. This molecular configuration plays an important role in process performance, by affecting the capacity of absorption and the desorption temperature. In the case of CO₂ removal, the capacity of the solvent can be greatly enhanced if one of the intermediate reactions, such as the carbamate formation reaction, can be slowed down by providing steric hindrance to the reacting CO₂.

Kansai Electric Power Company (Kepco) and Mitsubishi Heavy Industries (MHI) have been developing sterically hindered amines, the most well known are called KS-1 and KS-2 [157]. These amines have the advantage of a lower circulation rate due to a higher CO₂ loading dif-

ferential, a lower regeneration temperature and a lower heat of reaction. They are also non-corrosive to carbon steel at 130°C in the presence of oxygen. A first commercial plant using KS-1 is a fertilizer plant in Malaysia which has been in operation since 1999 (see **figure 3-5**).



Fig. 3-5: Post-combustion capture at a fertilizer plant in Malaysia [157]

The most important licensors for amine scrubbing technology are ABB Lummus and Fluor Daniel (ECONAMINE FG process) [101, 135, 153]. Furthermore amine absorbents were developed by chemical companies and are marketed as aMDEA (BASF) or ADIP-X (Shell) technology [146].

One of the main disadvantages of amine absorbents is that they are often degraded by oxygen and "impurities" like SO_x and NO_x . The presence of oxygen in the flue gas can increase corrosion and solvent degradation in the absorption system. Uninhibited alkanolamines such as monoethanolamine (MEA) and diethanolamine (DEA) can be oxidized to give carboxylic acids and heat-stable amine salts. A solution to this problem is to apply an inhibitor to both passivate the metal and inhibit amine degradation. Sulphur oxides (SO_x) react irreversibly with MEA based solvents to produce non-reclaimable corrosive salts. As a consequence of this it is estimated that it is less expensive to install a SO_x scrubber than accept the solvent loss at flue gas SO_x levels exceeding 10 ppm(v). Nitrogen oxides have led to corrosion problems and amine degradation in some absorption plants. The main problem is NO_2 , which reacts to form nitric acid in the amine solvent and ultimately heat stable salts. An NO_2 level of usually < 20 ppm(v) is recommended. In cement kiln flue gases, the proportion of NO_2 is < 5% from the total NO_x concentration. If the plant applies secondary NO_x reduction measures like SNCR (Selective Non-Catalytic Reduction), the limit on NO_2 should be of minor concern.

However, one of the main disadvantages is the high energy demand for solvent regeneration and the very big size of equipment. One of the main objectives in current research projects is to develop improved absorbents with lower energy demand for solvent regeneration.

A Norwegian study says that the installation of a MEA scrubber in a Norwegian cement plant (3,000 t/d cement kiln) would result in investment costs of about 100 Mio. € and operating cost of 30 Mio. €/year [106]. The specific costs would be about 45 €/t CO₂. Furthermore the study draws the conclusion that additional steam rising capacity in a fired boiler would be necessary because heat recovery from cement kiln off-gases could provide only < 15% of the energy need for the stripping column.

The specific costs^e for the application of MEA technology at power plants vary between 21.6 and 55.1 €/t CO₂ avoided [101]. The figures show, that up to now chemical absorption belongs to the most expensive capture technologies.

Research projects, which are being carried out, focus on the development of new solvents to reduce the solvent losses, energy consumption and corrosion effects in order to reduce the operating costs and the specific costs of CO₂ capture respectively (< 20 €/t CO₂). Recently, more advanced amines have been developed and are starting to be applied.

A novel concept for chemical absorption is the use of so-called "ionic liquids", which is investigated only in laboratory-scale. Ionic liquids can dissolve CO₂ and are stable at temperatures up to several hundred °C. Furthermore they require little heat for CO₂ recovery. However, they would be very expensive, as they are not produced commercially up to now [158].

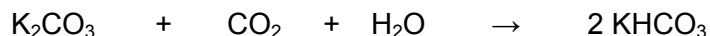
Chemical absorption can be complemented with gas absorption membranes that act as contacting devices between the gas flow and the liquid flow (see chapter 3.4.2). The gas and the amine solution are thereby not brought into direct contact and elements in the flue gas that deteriorate the amine solution, such as oxygen, are not transferred to the amine solution to the same extent. The problem of evaporation into the cleaned flue gas is reduced. The column pressure drop is also reduced, when compared with conventional packing, and the efficiency reduction can therefore be smaller. The equipment can also be made more compact, due to the increased gas-liquid contact area, which is of particular importance in off-shore applications. The membrane technology was developed by Aker Kvaerner and used in gas separation applications within the oil and gas industry [162]. Scale-up to sizes required to capture CO₂ from large power plants or cement kilns is considered to be a difficult issue.

Inorganic absorbents:

Many processes have been developed for carbon dioxide removal utilizing the alkali salts of various weak acids. Many salts have been proposed such as sodium and potassium salts of carbonate, phosphate, borate, arsenite and phenolate. The most popular salts in the industry

^e Whenever necessary, US Dollar were converted to Euro according to the following exchange rate:
1 US-\$ = 0.744 € (31 May 2007)

have been sodium carbonate and potassium carbonate. Carbon dioxide capture with K_2CO_3 is achieved according to the following chemical reaction:



Hot potassium carbonate (HPC or "Hot Pot") is effectively used in many ammonia, hydrogen and natural gas plants. Usually, the compound is mixed with activators to improve CO_2 removal and inhibit corrosion; the resulting absorbent being called "activated hot potassium carbonate" (aHPC). Licensed systems using potassium carbonate as an absorbent are [101, 136, 145, 148]:

- Benfield process (UOP, USA) (minimum feed gas pressure more than 10 atm)
- Catacarb process (Eickmeyer & Associates, USA)
- Flexsorb HP process (Exxon, USA)
- G-V process (Giammarco-Vetroke, Italy)

The Benfield and Catacarb processes are suitable for CO_2 capture when its partial pressure is at least 200-350 kPa. Finally, current research effort is focused on the use of calcium oxide, an option that relies on the same capture mechanism as the hot potassium carbonate.

Sodium and potassium carbonate aqueous solutions have a number of problems in practice. The solutions tend to react only relatively slowly with carbon dioxide and the heat requirements for regeneration of the solution is large compared to the various alkanolamine based processes. Potassium carbonate promoted by piperazine or other promoters has been considered for CO_2 separation. Vacuum stripping for solvent regeneration has been used, and vapor recompression may be required. Low cost and minimal degradation of the solvent are the primary advantages of this process.

Solution concentrations are limited by the precipitation of bicarbonate salts and solution temperatures are high. Foaming is also reported to be a concern. Corrosion problems may be severe depending on input gas composition, but various corrosion inhibitors have been employed effectively in some circumstances. Sometimes stainless steel has been used for the plant.

The following **table** summarizes the potential of chemical absorption technologies for CO_2 capture at the clinker burning process.

Tab. 3-3: Maturity of chemical absorption technology

Technology used in		
	cement industry ?	no
	other sectors ?	<ul style="list-style-type: none"> • chemical industry • oil and gas industry • power plants (pilot project)
Technology applicable to		
	existing clinker burning process ?	no
	modified clinker burning process ?	<ul style="list-style-type: none"> • waste heat recovery for sorbent regeneration required • SO₂ abatement (< 10 ppm) required • NO₂ abatement (< 20 ppm) required
Related research projects		(see chapter 3.1)
Abatement efficiency		> 98 %
Energy efficiency penalty		very high (due to energy demand of sorbent regeneration)
Impact on		
	kiln operation	limited
	product quality	no
	other emissions	no (minor reduction of other acid flue gas components)
	production costs	<ul style="list-style-type: none"> • yes; ~ 45 €/t CO₂ for MEA technology at a 3,000 t/d cement kiln [106] • examples from other sectors (MEA technology) from 21.6 to 55.1 €/t CO₂ avoided [101] • Significant cost driver will be in any case investment costs which can at this time not be given for cement production.
Advantages		<ul style="list-style-type: none"> • already commercially available • can be applied to modified plants
Challenges		<ul style="list-style-type: none"> • at present the most expensive technology • very big size of equipment • research objectives: lower energy consumption, development of improved absorbents

3.4.1.2 Physical Absorption

For physical absorption, CO₂ is absorbed in a solvent according to Henry's Law, which means that it is temperature and pressure dependent with absorption occurring at high partial pressures of CO₂ and low temperatures. The solvents are then regenerated by either heating or pressure reduction. The advantage of this method is that it requires relatively little energy; but the CO₂ must be at high partial pressure making this approach suitable for syngas/pre-combustion decarbonisation. Typical feed gas pressures could be in the range of 20-130 atm with CO₂ gas concentration from 5% to 35-60% by volume, depending on the solvent. The removal efficiency of CO₂ is around 90%.

The majority of physical absorption solvents are based on organic solvents with high boiling points and low vapour pressures. Typical solvents are cold methanol (Rectisol[®] process) and dimethylether of polyethylene glycol (Selexol[®] process) (see **table 3-4**) [115, 125, 139, 145]. Other than methanol, most of these solvents can be used at ambient temperatures without appreciable vaporization losses, but many require special water washing stages to reduce solvent losses.

The Selexol process was introduced in the 70's and according to UOP (Universal Oil Products), one of the leading equipment suppliers, there are currently more than 50 units in service. The process has been traditionally used for treating natural gas and syngas streams, for the selective removal of H₂S in IGCC plants and of CO₂ in gasification plants used for the production of high purity hydrogen, for refinery and fertilizer use, and for natural gas treatment. The process uses a mixture of dimethylethers of polyethylene glycol as a solvent, which is chemically stable, non-toxic and biodegradable. It is regenerated by application of heat, by flashing or by stripping gas. Rectisol uses an organic solvent, typically methanol at subzero temperatures. However, methanol is a volatile compound that leads to solvent losses. It is traditionally used to purify syngas from CO₂ in two stages. Initially, shifted syngas enters the Rectisol unit and the CO₂ concentration is reduced to 3% using flash-regenerated methanol. The remaining 3% is removed using hot-regenerated cold methanol (up to 3% by volume). Regeneration of the absorbent is done by reducing the pressure. Rectisol units are operational worldwide for the purification of hydrogen, ammonia and methanol syngas. Due to the low operation temperature, Rectisol is also favourable for cryogenic downstream processes. It is important to note that, since the physical solvents do not react chemically with CO₂, thus they are not subject to degeneration. In addition, they do not create corrosion problems to the infrastructure.

Hybrid absorption processes use solvents that offer a combination of chemical and physical absorption. Processes currently used with coal syngas for removal of CO₂ and sulphur compounds are the Shell Sulfinol[®] process and the Amisol[®] process developed by Lurgi (see **table 3-4**).

Table 3-4: CO₂ capture processes with physical or combined physical / chemical absorption

Process	Absorption type	Solvent	Developer / Licensor
Selexol	physical	Dimethylether of poly-ethylene glycol	Union Carbide, UOP (USA)
Rectisol	physical	Methanol	Linde AG, Lurgi (Germany)
Purisol	physical	N-Methyl-2-pyrrolidone	Lurgi (Germany)
Morphysorb	physical	4-Formyle-morpholine	Uhde (Germany) [159]
Fluor Solvent	physical	Propylene Carbonate	Fluor Enterprises
Sulfinol-D, Sulfinol-M	physical / chemical		Shell (Netherlands)
Amisol	physical / chemical	mixture of Methanol and MEA or DEA (or other amine mixtures)	Lurgi (Germany)

Especially due to the feed gas requirements, the applicability of physical absorption technologies to cement kilns is unlikely.

The following **table** summarizes the potential of physical absorption technologies for CO₂ capture at the clinker burning process.

Tab. 3-5: Maturity of physical absorption technology

Technology used in		
	cement industry ?	no
	other sectors ?	<ul style="list-style-type: none"> • sweetening of natural gas • coal gasification plants
Technology applicable to		
	existing clinker burning process ?	no
	modified clinker burning process ?	with several restrictions (see challenges)
Abatement efficiency		~ 90 %
Energy efficiency penalty		moderate
Impact on		
	kiln operation	no
	product quality	no
	other emissions	no
	production costs	yes; amount unknown. Significant cost driver will be in any case investment costs which can at this time not be given for cement production.
Advantages		<ul style="list-style-type: none"> • less energy required compared to chemical absorption • solvents are less susceptible to the impurities in the gas stream
Challenges		<ul style="list-style-type: none"> • high operating pressure required • very high CO₂ concentration in off-gases required

3.4.2 Membrane Processes

Membranes are basically barrier films that allow for the selective and specific permeation of different gases. Selectivity depends on system parameters and on gas conditions and therefore different membranes are being designed for the variety of roles in capture systems [160-165]. For example, membranes are being developed to capture CO₂ during the downstream shift conversion in gasification systems. In post-combustion systems, membranes are used to capture CO₂ from low concentration flue gases. Other membranes are being developed for oxygen separation in oxy-fuel systems. Today the main CO₂ capture application is the removal of CO₂ from natural gas. Abatement efficiencies > 80% should be available with membrane processes.

Two basic membrane types are being considered for CO₂ capture: gas separation and gas absorption membranes (see **figure 3-6**). The first group rely on the variations in physical and/or chemical interactions between different gases and the membrane material, with the intention to have one component pass through the membrane faster than another (thus driving the separation process). This technique relies on the diffusivity of gas molecules, and taking advantage of different pressures on either side of the membrane. Various versions of gas separation membranes are available today including ceramic, polymeric and ceramic / polymeric hybrids. Up to now, most of the commercially viable membranes for CO₂ capture are polymer-based (e.g. cellulose acetate, polyimides, polyamides, polysulfone, polycarbonates, polyetherimide).

The second group, gas absorption membranes, are micro-porous solid membranes which act as contacting devices between gas flow and liquid flow. While flue gases flow on one side of a membrane, an absorptive liquid is used on the other side to selectively attract certain components. In this case, it is the absorption liquid (not the membrane) that drives the selectivity.

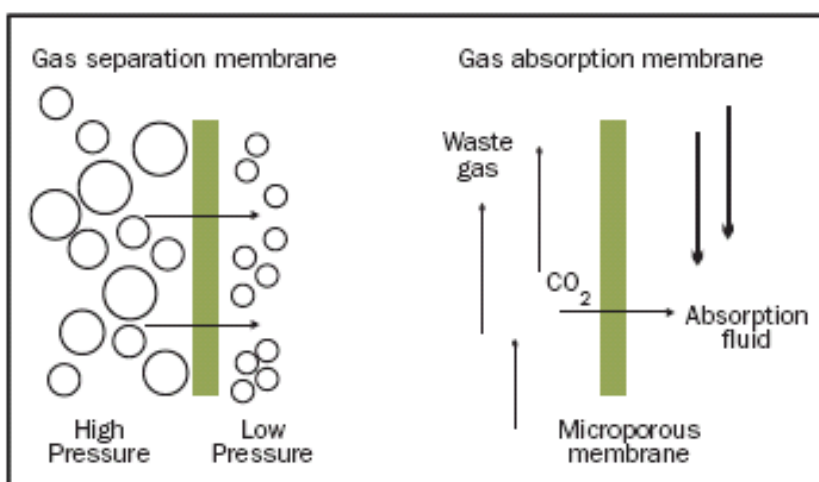


Fig. 3-6: Principles of gas separation and gas absorption utilizing membranes [134]

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

Membrane units are small in volume (see **figure 3-7**), operationally simple, can be positioned either horizontally or vertically and require little attention once commissioned. Furthermore no regeneration energy is required and no waste streams are generated. They will thus readily fill niche markets for carbon capture such as in offshore and remote locations.

However, membranes also show unfavourable characteristics:

- sensitivity to sulphur compounds and other trace elements
- sometimes low degrees of separation (multiple stages or recycling is necessary)
- polymeric membranes are mostly intolerant against high temperatures

Large-scale applications of membranes still need large R&D efforts to improve selectivity, permeability and durability at higher temperatures. Another objective of all research activities is to reduce the costs of membrane processes significantly. At the moment, the application of membranes for CO₂ capture in the cement industry seems to be unlikely. However, it is expected, that the technology itself is very promising and within five to ten years, membranes may be able to provide strong competition for solvent based systems (absorption processes).



Fig. 3-7: Membrane skid [160]

The following **table** summarizes the potential of membrane technologies for CO₂ capture at the clinker burning process.

Tab. 3-6: Maturity of membrane technology

Technology used in		
	cement industry ?	no
	other sectors ?	niche applications at remote locations
Technology applicable to		
	existing clinker burning process ?	no
	modified clinker burning process ?	not yet
Abatement efficiency		> 80 % (target value)
Energy efficiency penalty		low
Impact on		
	kiln operation	no
	product quality	no
	other emissions	no
	production costs	yes; but probably very high
Advantages		<ul style="list-style-type: none"> • upcoming, promising technology • space efficient
Challenges		<ul style="list-style-type: none"> • requires very high operating pressures (separation membranes) • separation efficiency and temperature resistance has to be improved • scale up to full size implementation required

3.4.3 Solid sorbent processes

Adsorption is a process where a molecule becomes selectively attached (adsorbed) onto a surface of another phase (see **figure 3-8**). Thus, by using special solids (so-called adsorbents), substances from gaseous (or liquid) mixtures can be selectively removed. The separation of a substance, the adsorbate, is achieved by its accumulation at the surface of the adsorbent. This process is different from absorption, described in the previous section, the latter term being used when describing the uptake of a substance into the bulk of a solid or liquid phase and not on the surface of a solid.

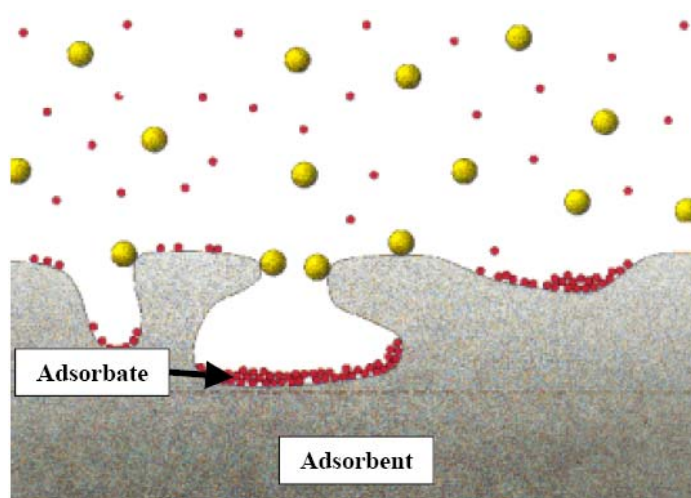


Fig. 3-8: A schematic of the adsorption process [139]

There are two principal mechanisms of adsorption of molecules on surfaces: physical adsorption (physisorption) and chemical adsorption (chemisorption). The difference lies in the nature of the bonding between the captured molecule and the surface. In physical adsorption bonding is by weak van-der-Waals-type forces, whereas in chemisorption bonding is chemical, e.g. with ionic or covalent character. A special type of solid sorption processes is the so-called mineral carbonation where the adsorbent reacts with CO_2 to form metal carbonates (see **chapter 3.4.3.2**).

Some of the solid sorbent processes require large amounts of sorbent materials to be handled. This would in most cases not be applicable in the cement industry, unless these materials could be regenerated, recycled or reused for other purposes.

3.4.3.1 Physisorption processes

From a practical point of view, chemisorption from a gas generally takes place only at temperatures above 200°C and may be slow and irreversible. For this reason, most commercial applications rely on physical adsorption. The major types of adsorbents used are activated alumina, silica gel, activated carbons, zeolites and polymeric adsorbents. In selecting the appropriate adsorber for a specific application the following criteria should be met: The adsorber should demonstrate high selectivity to the gas species to be separated (CO_2 in this

case), high capacity to minimize the amount of adsorbent needed, fast adsorption kinetics, chemical and thermal stability and high surface area to volume ratio. The central advantage of physical adsorption methods is the possibility for low energy requirement to regenerate the sorbent material and comparatively low costs [115, 125, 139, 166-169].

Adsorption processes operate on a repeated cycle with the basic steps being adsorption and regeneration. In the adsorption step, gas is fed to a bed of solids that adsorbs CO₂ and allows the other gases to pass through. When a bed becomes fully loaded with CO₂, the feed gas is switched to another clean adsorption bed and the fully loaded bed is regenerated to remove the CO₂. In pressure swing adsorption (PSA), the adsorbent is regenerated by reducing pressure. In temperature swing adsorption (TSA), the adsorbent is regenerated by raising its temperature and in electric swing adsorption (ESA) regeneration takes place by passing a low-voltage electric current through the adsorbent.

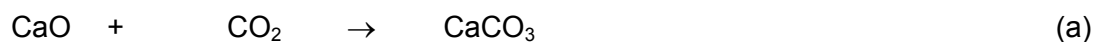
PSA and TSA are used commercially for gas separation and are used to some extent in hydrogen production and in removal of CO₂ from natural gas. ESA is not yet commercially available but it is said to offer the prospect of lower energy consumptions than the other processes.

Adsorption is not yet considered attractive for large-scale separation of CO₂ from flue gas because the capacity and CO₂ selectivity of available adsorbents is low. However, it may be successful in combination with another capture technology. Basic research work has to be carried out to achieve improved sorption characteristics (e.g. higher selectivity at lower costs). Therefore adsorption processes cannot be regarded as mature technology for potential application at cement kilns.

3.4.3.2 Mineral carbonation

Another type of solid adsorption of CO₂ is based on the chemical reaction of an oxide to form a carbonate in the presence of CO₂ (carbonation). The reverse reaction (calcination) is desired to desorb CO₂ which implies the regeneration of the sorbent. This reaction behaviour is known for alkali and alkaline earth metal oxides, e.g. calcium oxide (CaO), but it applies for some other materials too. These solids can react with CO₂ to form a carbonate (in the case of Ca and Li oxides) at high temperatures (~600°C) or a bicarbonate (in the case of Na and K carbonates) at lower temperatures (carbonation process). In a different reactor, the sorbent is then regenerated (calcination) at high temperature (~1,000°C), where pure CO₂ is produced. In principle, the CO₂ carbonation-calcination loop can be applied to separate CO₂ in both post-combustion and pre-combustion systems. The disadvantage of this option is that relatively large amounts of sorbents are required due to the degradation in sorption activity. It also generates a new waste stream [170-176].

The most important solids for absorbing CO₂ might be divided into calcium containing and lithium containing materials. The first group is characterized by the carbonation of CaO according to the following reaction:

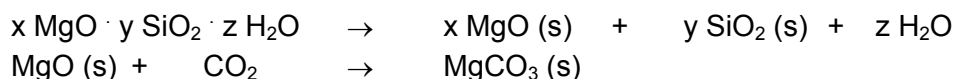


Recent investigations have identified lithium containing oxides as a considerable alternative to calcium based absorbents [167]. Lithium zirconate (LiZrO₃) and lithium orthosilicate (Li₄SiO₄, Fe-doped) were reported to be the most attractive candidates among these mixed oxides. The absorption of CO₂ corresponds to the reactions



Higher practical capacity and its superior reactivity (Li₄SiO₄ absorbs CO₂ at 500 °C about 30 times faster than Li₂ZrO₃ does) qualify lithium orthosilicate as the most promising absorbent amongst lithium containing materials. Additionally it seems to be suitable for cyclic use.

Also magnesium silicates like Serpentine (Mg₃Si₂O₅(OH)₄) and Olivine (Mg₂SiO₄) could be utilized for fixation of CO₂ in the form of solid, highly stable magnesium carbonates [170, 176]. Huge resources of good quality minerals appear to exist at or near large-scale mining activities for non-ferrous metals.



However, enormous amounts of minerals are required: 1 kg of CO₂ may require 2 kg of serpentine for disposal, so that it wouldn't be applicable in most cases. Further research and technical development is necessary to extract the reactive component MgO from the mineral in order to reduce the mass streams which have to be handled at the CO₂ source. Furthermore the reaction kinetics of the binding reaction (MgO + CO₂ → MgCO₃) has to be improved.

Like other post-combustion technologies, mineral sequestration could be applied to cement kilns in principle. However, the exhaust gas has to be heated up to 500 or 600°C both for the adsorption and the regeneration of the adsorbent. This would result in a high energy penalty.

One of the main challenges is to reduce the enormous material streams which would be necessary to adsorb the CO₂. If a cement plant is located close to a deposit of Lithium or Magnesium silicates, an application of that technology would be conceivable.

The following **table** summarizes the potential of adsorption technologies for CO₂ capture at the clinker burning process.

Tab. 3-7: Maturity of adsorption technology

Technology used in		
	cement industry ?	no
	other sectors ?	<ul style="list-style-type: none"> • hydrogen production • removal of CO₂ from natural gas
Technology applicable to		
	existing clinker burning process ?	no
	modified clinker burning process ?	not yet
Abatement efficiency		
Energy efficiency penalty		moderate to high
Impact on		
	kiln operation	no
	product quality	no
	other emissions	no
	production costs	yes; but probably very high
Advantages		<ul style="list-style-type: none"> • very high CO₂ removal is possible
Challenges		<ul style="list-style-type: none"> • requires very high operating pressures • poor selectivity • scale up to full size implementation required • reuse of sorbent material

3.4.3.3 Carbonate looping

A power plant with integrated capture of CO₂ by carbonation is a specific application of the solid sorbent processes mentioned before. The carbonation process is based on the equilibrium of calcium carbonate to calcium oxide and carbon dioxide at various temperatures and pressures. In a carbonation process calcium oxide is put in contact with the combustion gas containing carbon dioxide to produce calcium carbonate. In a subsequent calcination process the calcium carbonate is regenerated to the carbon dioxide sorbent (the calcium oxide). The carbonation could take place in-situ in the combustion chamber or in a carbonator placed in the flue gas downstream from the chamber. Currently both methods are discussed and investigated for power plants.

For the in-situ carbonation, activated calcium oxide is blown into the combustion chamber. To increase the transfer of carbon dioxide to the sorbent a fluidized bed combustion is necessary. At the usual combustion temperatures of 850°C for pulverized coal-fired fluidized bed combustion a minimum pressure of 3 bar is needed in order the carbonation process to take place. That is the equilibrium partial pressure of carbon dioxide and calcium oxide with calcium carbonate. Pressurized fluidized bed power plants operate with pressures between 10 and 20 bar. To keep the material flow and feeding systems as easy as possible the subsequent separation of calcium carbonate and flue gas as well as the calciner for capturing the carbon dioxide should operate at the same pressure as the pressurized combustion chamber. The degree of carbon dioxide separation at a pressure of 15 bar amounts up to 80%, further pressure raise increases the degree of separation slightly. The gas phase of the calciner consists nearly complete of carbon dioxide due to a combustion with pure oxygen. At

12 bar pressure the calcination temperature has a minimum at 1,110 °C which is higher than the ash softening temperature. The calcined sorbent is fed back to the combustion chamber [62].

Currently worldwide just six commercial scale pressurized fluidized bed power plants are in service. The start-ups were in the 1990s and the plants have the status of demonstration plants. The pressurized combustion technology improves the thermal efficiency of the power plant. The known plants reach electric efficiencies from 33-42% and have electric capacities from 70 to 350 MW, but also thermal power is generated. In fact the pressurized combustion technology is complex and susceptible and the availability of the plants is low [63].

The atmospheric carbonation for carbon dioxide capture is an end-of-pipe solution, which takes place in the flue gas downstream the combustion chamber or the furnace. In power plants working under atmospheric conditions the flue gas contains carbon dioxide with a partial pressure of around 0.15 bar. The carbonator should operate at average temperatures between 600 and 750°C, which are adequate for a rapid reaction to form calcium carbonate. The flue gas coming out from the carbonator contains a reduced amount of carbon dioxide. The carbon dioxide captured by the sorbent is directed to the calciner for regeneration of the sorbent. The gas stream coming out from the calciner shows increased CO₂ concentration so that it can be separated easily. For a gas stream rich in carbon dioxide the calciner has to be fired with pure oxygen. At atmospheric pressure and a carbon dioxide partial pressure of nearly 100 percent by volume, the calcination in the calciner proceeds at 900°C.

Due to the nature of adsorption reactions (surface reactions) only a part of the separated calcium carbonate particles will be calcined. Just a split stream is led to the calciner where the particles will be regenerated. For thermal power generation the main stream of the partial loaded sorbent flows through a fluidized bed heat exchanger and returns to the carbonator where non-converted calcium oxide could react with carbon dioxide [59, 62]. With every cycle of the sorbent particle the activity reduces due to a decrease of particle porosity – resulting in a limited sorbent life time. After around 30 cycles the sorbent particles have to be discharged.

Instead of particulate sorbents like burnt lime meal also a calcium hydroxide solution can be used. It has to be atomized and sprayed into the carbon dioxide containing flue gas [62]. The reaction with carbon dioxide forms calcium carbonate and water steam. A similar process is well known for desulphurization of flue gases.

Both the pressurized and atmospheric carbonation for carbon dioxide capture deal with enormous mass streams. A mid-sized cement plant with a clinker production of 3,000 tpd and specific carbon dioxide emissions of 0.9 t CO₂/t clinker produce around 112.5 t CO₂/h. Based on calculations of mass streams in a small power and heat generation plant with similar carbon dioxide emissions of 127 t CO₂/h [62] the mass streams in a mid-sized cement plant are estimated. The mass of the fluidized bed in the carbonator amounts to around 12,000 t/h. Just a split stream with 190 t/h is desorbed in the oxygen-fired calciner. Around 11,700 t/h flows through a fluidized bed heat exchanger for heat recovery back into the carbonator, where yet non-converted sorbent reacts. Due to loss of sorbent material 250 t/h cal-

cium carbonate has to be fed to the cycle, while 3 t/h have to be discharged because of the limited sorbent life time. In comparison to 200 t/h kiln feed for clinker production, the capture process for carbon dioxide has to deal with mass streams 60 times of the clinker process. In addition to the thermal power need of around 115 MW of the cement plant, around 120 MW thermal power for the oxygen-fired calciner is needed. Further heat for the carbonator is required unless the carbonator is placed in the pre-warming step of the kiln feed.

The atmospheric carbonate loop as an end-of-pipe solution could be installed in the flue gas after the preheater tower. The flue gas is already preheated up to 280-400°C, but the reaction velocity between the calcium oxide and carbon dioxide to form calcium carbonate could be too slow, so a heat-up to 650-700°C to speed up the reaction would be necessary. After separation of the sorbent particles, the sorbent has to be regenerated in an oxygen-fired calciner. The hot flue gas, low in CO₂, should be suitable for preheating and drying of the raw material. The atmospheric carbonate loop can principally be achieved in existing cement works. The loop could be placed between preheater and raw mill.

As an alternative, the carbonator could replace one of the middle cyclone stages to prevent the additional heat-up of the carbonator. The raw material flows in a bypass to the cyclone stage below the carbonator. The stream coming out of the carbonator is directed to the cyclone stage above. The separated particle flow to the oxygen-fired calciner for carbon dioxide capture. The carbon dioxide-poor flue gas heats up the raw material in the top cyclone stages of the heat exchanger. Carbon dioxide capture by carbonation integrated in the heat exchange process step would probably require completely rebuilding the preheater tower. The investment costs are higher than end-of-pipe carbonation but because of fuel saving for carbonation the operating costs are lower. Obviously the carbonate loop integrated heat exchanger is just suitable for new-building of cement works or by modernizing and replacing of existing preheating towers.

The carbonate looping technology is currently in the stage of research and development. University laboratories already built up experimental apparatus for research reasons. There is no application in the industrial sector yet. The carbonation technology for carbon dioxide capture can be applied to existing plants as an end-of-pipe technology as well as to a modified plant because of energy reasons. In the last case a new preheater tower with integrated carbonator has to be built. Just in a pressurized system an abatement efficiency of around 80% is possible, because of thermodynamics the efficiency in an atmospheric system is lower. The enormous handled masses do not allow temporary storage of gaseous carbon dioxide, so the capture system has to be part of the clinker production process. Due to the end-of-pipe configuration only a minor impact on the kiln operation can be expected. The same applies to the clinker burning process and the product quality. Depending on kiln design, other emissions could be influenced. Besides CO₂, the main exit gas leaving the calciner will be water vapour. After dehumidification the carbon dioxide is prepared for transport and storage. Depending on the downstream handling of carbon dioxide the gas stream has to be purified from sulphur and nitrogen oxides. This carbonation technology is still in a very early stage and consequently no capture costs have been reliably estimated. It is clear however, that due to the heat demand of the calciner fuel costs will at least double.

In comparison to chemical absorption processes (see **chapter 3.4.1.1**) the degree of carbon dioxide separation from the flue gas is lower. While with absorptive washing methods a nearly carbon dioxide-free flue gas can be reached, the flue gas of carbonation processes are CO₂-poor, but not free of CO₂ due to the equilibrium reaction of carbon dioxide, calcium oxide and calcium carbonate.

3.4.3.4 Metal Organic Frameworks (MOF)

A new class of materials, so-called metal-organic frameworks (MOFs) or "crystal sponges", can store extremely high amounts of carbon dioxide [177-178]. MOFs are nanoporous materials synthesized in a "building-block" approach by self-assembly of metal or metal oxide vertices interconnected by rigid organic linker molecules. The carbon dioxide capacities are 3 and 7 times larger, respectively, than those for high porosity zeolites. Functional groups (e.g. amine groups) can be added to MOF linkers in order to improve the adsorption capacity and selectivity.

Up to now, research work is carried out only at laboratory level, so that practical applications could be possible only in the long term.

3.5 Hybrid systems

3.5.1 Synergy of a cement and a power plant using carbonate looping

As mentioned in **chapter 3.4.3.3** a loop of carbonation and calcination could be used for capturing carbon dioxide from flue gas of combustion chambers. Due to the decrease of particle porosity the activity of the sorbent decreases with every cycle and results in a limited sorbent life time. Consequently a discharge of used particles is necessary. If the discharge is placed downstream of the calciner the degraded calcium oxide could be used as precalcined raw material in a cement works (see **figure 3-9**). So the lime from the quarry is at first used as a sorbent before it is processed to clinker. For the cement plant the carbon dioxide from limestone calcination is simultaneously captured with the carbon dioxide in the flue gas of a power plant.

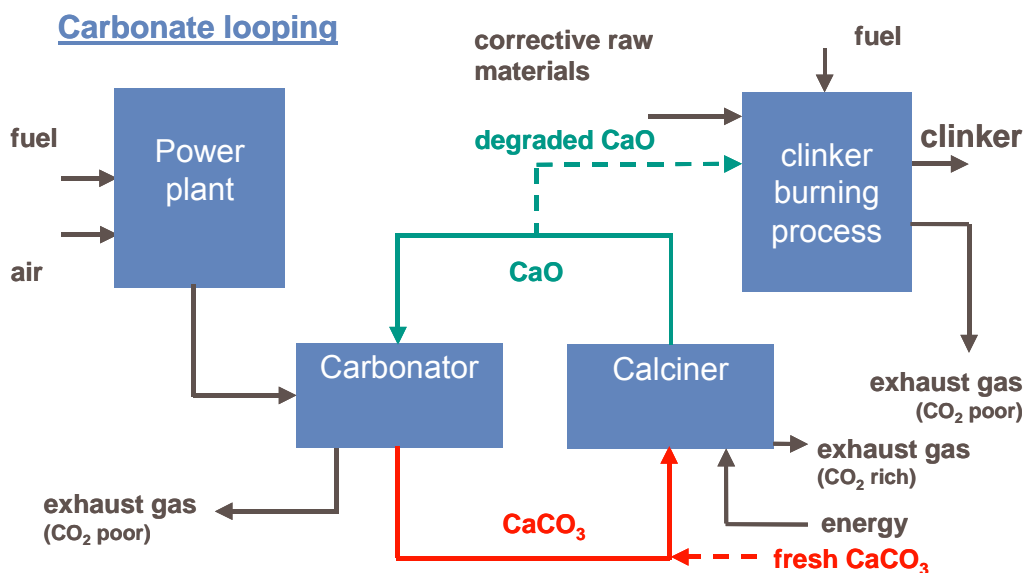


Fig. 3-9: Schematic of a hybrid carbonate looping process combining a power and a cement plant.

A modern anthracite or lignite fired power plant has a specific emission of 750 or 950 g CO₂/kWh, respectively. With an assumed life time of 30 cycles of the sorbent particles in a 800 MWe power generation block around 620 or 780 tpd of degraded calcium oxide must be discharged. So a mid-sized cement plant with a clinker production of 3,000 tpd would use the precalcined calcium oxide of approximately three power plants as raw material [60]. If the cement kiln would use precalcined raw material, the design of the clinker burning process would look different from the existing one, because the ratio between combustion gas enthalpy and reaction enthalpy of the raw material is significantly different. The flue gas from the cement plant contains only fuel based carbon dioxide and can be added to the flue gas stream of the power plant which is treated in the carbonate loop process. If the bleed stream would be taken from the carbonate downstream of the carbonator, the process could be applied to existing cement kilns. In this case no modifications at the cement plant have to be done. The flue gas of the kiln line will be treated in the CO₂ capture part of the power plant.

Carbonation technology is currently not available for carbon dioxide capture. Also, there is no operational link between a cement and power plant yet, as it would be required in order to use discharged calcium oxide from the CO₂ capture plant as raw material in an existing cement plant. In this case the clinker production process has to be redesigned due to different enthalpies of flue gas and reactions. Also impacts on the calcination process and product quality are to be expected due to altered raw material composition and quality. Advantages might consist in a reduced preheating system. On the other hand only carbon dioxide from raw material is reduced. For abatement of carbon dioxide from combustion the flue gas has to be led to the carbon dioxide capture plant (i.e. the carbonator) of the power plant. In case of taking over discharged calcium carbonate the material can be used as raw material in an existing cement plant. For CO₂ abatement the flue gas has to be treated in the CO₂ capture plant of the power plant. While the combination of a cement and a power plant might be of advantage for CO₂ capture reasons due to the big gas and mass transfers between the plants, it is clear that both installations have to operate in combination in order to minimize temporary storage of material.

3.6 Other systems

3.6.1 Chemical looping

Chemical-looping combustion (CLC) is a combustion technology with inherent separation of the greenhouse gas CO₂. The technique involves the use of a metal oxide as an oxygen carrier which transfers oxygen from combustion air to the fuel, and hence a direct contact between air and fuel is avoided. Two inter-connected fluidized beds, a fuel reactor and an air reactor, are used in the process [179-181] (see **figure 3-10**).

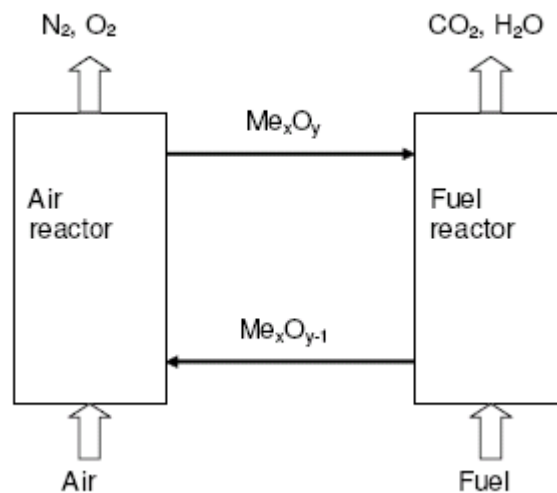
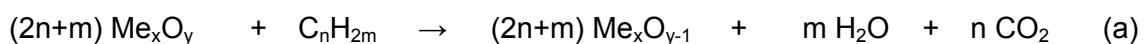


Fig. 3-10: Chemical looping combustion

The fuel is introduced in the fuel reactor, which contains a metal oxide, Me_xO_y. The fuel and the metal oxide react according to:



The exit gas stream from the fuel reactor contains CO₂ and H₂O, and a stream of CO₂ is obtained when H₂O is condensed. The reduced metal oxide, Me_xO_{y-1}, is transferred to the air reactor where it is oxidized, reaction (2):



The air which oxidizes the metal oxide produces a flue gas containing only N₂ and some unused O₂. Depending on the metal oxide and fuel used, reaction (a) is often endothermic, while reaction (b) is exothermic. The total amount of heat evolved from reaction (a) and (b) is the same as for normal combustion, where the oxygen is in direct contact with the fuel. The advantage of chemical-looping combustion compared to normal combustion is that CO₂ is not diluted with N₂ but obtained in a separate stream without any energy needed for separation. The concept of CLC was actually proposed already in the 1980's as an alternative to normal combustion. It was postulated that the use of certain oxygen carriers in such a system could result in higher efficiencies in comparison to normal combustion.

Considerable research has been conducted on CLC in the last decade with respect to oxygen carrier development, reactor design, system efficiencies and prototype testing. The technique has been demonstrated successfully with both natural gas and syngas as fuel in continuous prototype reactors based on interconnected fluidized beds within the size range 0.3 – 50 kW, using different types of oxygen carriers based on the metals Ni, Co, Fe, Cu and Mn. From these tests it can be established that almost complete conversion of the fuel can be obtained and 100% CO₂ capture is possible at a low cost. Further work is going on to adapt the technique for use with solid fuels and for hydrogen production.

A number of possible options for application of chemical-looping combustion for CO₂ capture have been identified: i) Combustion of gases such as natural gas, refinery gas and syngas from solid fuels, ii) direct combustion of solid fuels and iii) partial oxidation/reforming processes for hydrogen or combined hydrogen/power production.

CLC is a very promising technology with significant advantages:

- > 98% CO₂ capture
- no air separation unit for oxygen production
- no energy penalty for oxygen production
- one of the best candidates for 20 €/t CO₂ target
- CFB technology would be well-suited to CLC applications with already proven components to built large boilers

However, the application of CLC at the clinker burning process is unlikely due to the large volumes of gas to be handled (unless for H₂ production and subsequent utilization as fuel in cement kilns).

3.6.2 Solar Cement Plant

Solar cement plants are certainly very visionary and not based on capture technology. Nevertheless it is claimed that cement can be produced with less CO₂ from fuels. Since it is a far-reaching technology, it is mentioned here in the report.

The Solar Technology Laboratory and the Paul Scherrer Institute, Switzerland, along with its industrial partner, QualiCal, Italy, have jointly explored the potential of a technology for production of lime by using concentrated solar energy. The Solar Lime Project started in September 2000 and finished in January 2003. The specific purpose of the project was a feasibility study on the production of high purity lime in a solar calcination plant [48, 49].

In laboratory experiments with an electric furnace the Paul Scherrer Institute has found, that a residence time of about 7 minutes at 1,340 °C is sufficient for the complete calcination of 2 to 3 mm samples. With increasing CO₂ content in the gas phase, the calcination proceeds at higher temperatures. The Solar Lime Pilot Reactor with a 10 kW solar input is a horizontally positioned rotary steel drum. The sunlight reflected by heliostat mirrors is focused by a parabolic reflector to the sunlight entrance of the kiln. Inside the aperture area a maximum power of 19 kW with a peak concentration of the solar flux intensity of 4,000 kW/m² was

measured. At 1,150 °C and a throughput of 1.3 kg CaO/h a degree of calcination of 97.7% was reached [48].

The sequence of the thermal process steps for a solar cement plant would be the same as for the conventional industrial process, except that the preheated raw material is calcined in a solar calciner. Three solar concentrating systems are in principle possible for a solar calciner [43]:

- A Parabolic Dish System: The reactor is installed in the focus of the parabolic reflector. To reach the maximum power the complete system tracks the sun position throughout the day. The three-dimensional movement has negative implications on the feeding and extracting of particles and gases as well as on the reactor operation. One of the biggest parabolic dish worldwide only yields 300 kW and the use of dispatched dish systems with several reactors is not acceptable for economic reasons [48].
- A Tower System: The mirrors of a heliostat field reflect the sunlight directly to the reactor, which is placed on the top of the tower. The preheated raw material has to be transported with a pneumatic conveyer system to the solar calciner at the top of the preheating tower (see **figure 3-11**) [43, 48].
- A Tower Reflecting System: The parabolic reflector on the top of the tower sends the reflected sunlight of the heliostat field down to the reactor on the ground. Because of a loss of the solar flux intensity the heliostat area has to be larger, but a reactor operating on the ground is much easier and reduces costs (no material feeding systems) [48].

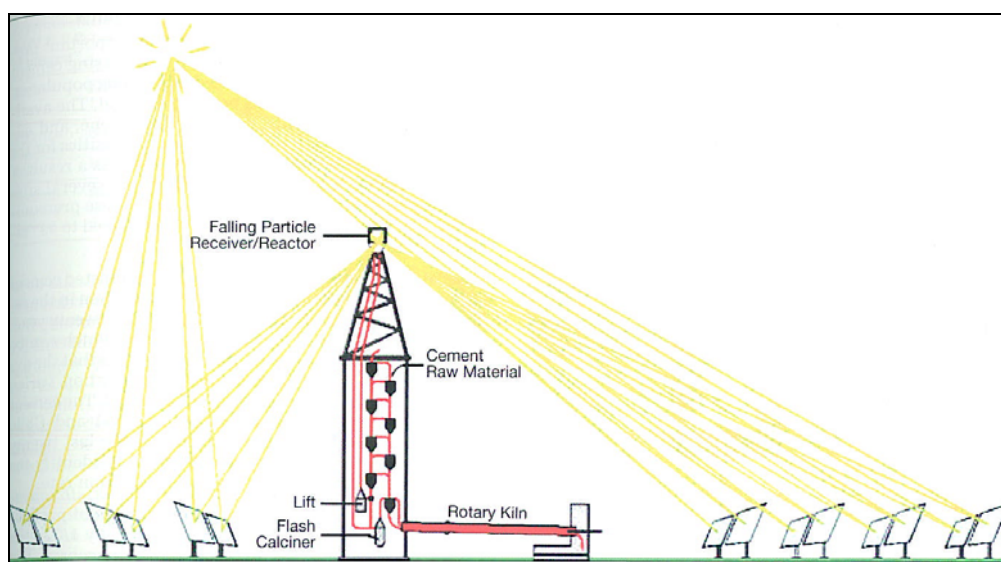


Fig 3-11: Hybrid solar cement plant [43]

An alternative reactor is the Falling Particle Receiver. The raw material is fed to the top of the reactor and falls through it by gravity. The particle curtain absorbs the concentrated solar radiation. For minimizing the convective heat loss and the loss of preheated raw material the vertical hole as sunlight entrance should be closed by a transparent or opaque window [43].

In a modern cement plant around 60% of the fuel is burnt in the calciner and 40% in the rotary kiln. Due to the constant temperature of the calcination process at relatively low temperatures around 900 °C solar power is said to be suitable for dissociation of the limestone. During the night a flash calciner with waste or biomass fuels must be used instead of the solar calciner. After dissociation the raw material is fed into a usual rotary kiln where the lime is sintered conventionally at 1,450 °C with fuel.

For a 3,000 t/d cement plant it is estimated that the application of solar energy calciner reduces the fossil fuel demand by about 20,000 t/a and by that emissions of carbon dioxide by about 51,000 t/a. Due to the high costs of cement transporting solar cement plants could find applications not only in sunny locations with a high cement demand but also in sunny rural areas with much smaller cement consumption. For this reason “mini cement plants” are covering the cement needs of remote areas in Africa, China and India as well as in the Arabic world. For these markets, small plants with a production capacity of less than 1,000 t/d could be envisaged [43]. There are no costs for CO₂ capturing, because CO₂ is avoided in the process. A cement plant could be run profitably at CO₂ tax of 50 US\$/t CO₂.

Today hybrid solar cement plants are only looked at in rather theoretical or laboratory investigations. In energy sectors small demonstration plants for electric power generation are in existence. A heliostat field focus sun beams at a water boiler on a tower. A steam cycle runs a turbine for power generation. In material sciences sunlight is used directly for material heat-up. In a solar oven of research institutes temperatures more than 4,000 °C have been reached to melt material for academic reasons. But there is no industrial application of using solar energy for process heat. The Paul Scherrer Institute currently develops solar calcination facilities, which can be applied to a modified clinker burning process.

The abatement efficiency of carbon dioxide reduction amounts to 20% for a state-of-the-art lime plant and 40% for a conventional cement plant. Unlike capture technologies in this case carbon dioxide is avoided, because of fuels saved. Fuel energy is replaced by solar power. The calcination process is completely changed to a conventional one and possibly impacts the product quality. Due to reduced fuel input the other emissions are lower. While the operation costs are considered to be lower than in conventional cement plants, investment costs are expected to be extremely high. In principle the solar calcination process can be applied to a modified existing cement plant. Several sites within the world's sun belt would provide an adequate solar irradiation. All other locations will not be suitable at all for this technology. At present the Paul Scherrer Institute concentrates on research transfer solar flux into a cement kilns calciner.

3.7 Comparative analysis of CO₂ capture technologies

CO₂ concentrations in the exhaust gases from cement kilns are between 14 and 33% by volume (see **table 2-3**) and should offer more favorable conditions to apply capture technologies than those in other industrial processes. However, there are no operational experiences with capture technologies in the cement industry – neither at technical-scale nor at pilot- or laboratory-scale. In the context of a carbon constraint world it is the question to what degree CO₂-capture technologies might become applicable for the cement industry. Technical issues still have to be solved and the economic impact is still open. In order to get a better view of the various capture techniques and their potential application to the cement industry research should only be initiated to examine those scenarios which might be - if at all - most promising. Based on this, an assessment of the applicability and maturity of potential capture technologies is given in the following **table 3-8**.

Tab. 3-8: Maturity of capture technologies and potential application at cement kilns

	Post-Combustion				Oxy-fuel	Pre-combustion
	Chemical absorption	Physical absorption	Adsorption	Membranes		
maturity of technology	commercial in selected industrial sectors	commercial in selected industrial sectors	research and pilot-scale level	research level	research and pilot-scale level	commercial in selected industrial sectors
applicable to cement kilns ?	yes	unlikely	unlikely	yes	yes	unlikely
CO ₂ captured	fuel CO ₂ + process CO ₂	fuel CO ₂ + process CO ₂	fuel CO ₂ + process CO ₂	fuel CO ₂ + process CO ₂	fuel CO ₂ + process CO ₂	fuel CO ₂
retrofit possible ?	yes	yes	yes	yes	no	unlikely
assessment for R&D	yes	unlikely	unlikely	yes in the long-term	yes	unlikely

Note:

The table is based on a technical assessment and does not take into account economic aspects. A cost analysis reveals high costs for all technologies listed, details are given in the respective chapters of this report.

Further information (advantages, challenges, impact on process and emissions, etc.) about the individual capture technologies is given at the end of the respective sub-chapters.

It is expected, that absorption technologies for CO₂ capture will be the first to fulfil the needs of the market. But it is also assumed that once membrane technology is developed, it will progressively replace absorption technology. Furthermore, the oxy-fuel process could be an interesting option for new kilns in the future.

3.8 Energy Penalty

The application of CCS requires an additional amount of energy. As a consequence of this, the total efficiency of the process decreases, resulting in a so-called energy penalty. These energy penalties significantly affect the cost of CO₂ capture and storage and result in higher

costs per unit of product [207]. A qualitative assessment of the energy penalties of the main capture technologies is given in the summarizing tables at the end of the respective sub-chapters..

Therefore the economic framework will be decisive for future applications of carbon capture in the cement industry. At the moment, the costs for CO₂ capture amount to 20 to 50 €/t of separated CO₂. The wide range represents the very different values given in the literature for the individual technologies. Even for one and the same technology the estimated costs exhibit a similar bandwidth. Based on avoided CO₂ emissions (see **figure 3-12**), the cost estimates range from 24 to 75 €/t CO₂. These costs are higher since more CO₂ emissions occur in plants with CO₂ capture due to their reduced overall efficiency than in a reference plant without CO₂ capture. The target value for capture costs in the power sector is mentioned to be in the order of 20-30 €/t CO₂ avoided. In any case, it can be expected, that the specific capture costs depend on the plant size. Even if the total costs are still unknown and subject to the development of CCS technologies capture costs in the cement industry will be lower for larger kilns than for small or medium-size kilns.

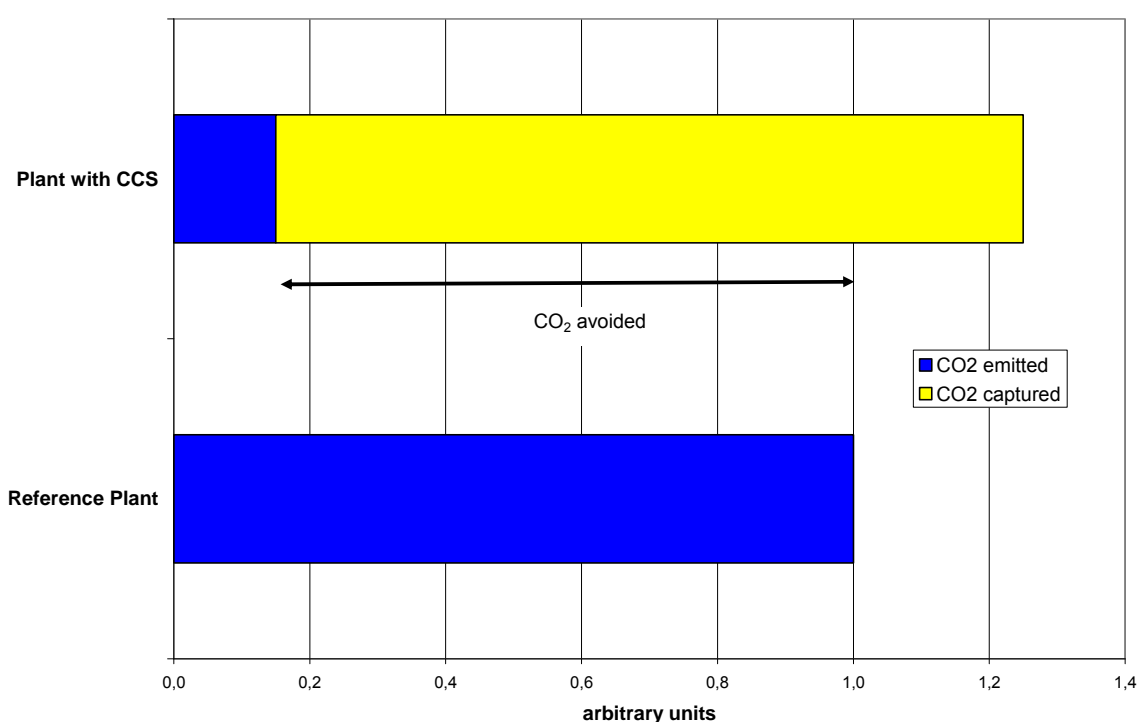


Fig. 3-12: Schematic representation of avoided CO₂ compared to the captured CO₂

Besides economic aspects (barriers) other issues have to be resolved [91]:

- compliance with legal frameworks must be given
- monitoring and verification standards have to be defined
- long-term ownership of storage facilities have to be ruled
- public acceptance and social acceptance must be guaranteed
- future climate policy should become apparent.

4 Transport and Storage of CO₂

Transport and storage is an essential issue in all discussions about CCS. Many research projects and even small-scale projects are being carried out worldwide (see **chapter 8**). The following chapter will give only a summary about the most important technical and economic aspects.

4.1 Transport

The transportation of large volumes of CO₂ collected by CO₂ capture is only economic in a supercritical or liquid state. In a gaseous form, the volumes to be transported would be too large. In principle, there are two types of CO₂ transport:

- pipelines
- tankers (ship designs will be based on current tankers used to carry LPG).

CO₂ transport by trucks or trains would be appropriate only for small-scale capture projects.

The costs of CO₂ transport depend on the distance between the CO₂ source and the utilization/storage site, the volume of CO₂ transferred and the presence of existing infrastructure. On average, transport costs vary between 0.4 € and 1.8 € per 100 km and tonne of CO₂. Compression, if needed, costs about 9-10 €/t CO₂. The following diagram (**figure 4-1**) shows the specific transport costs for onshore and offshore pipelines as well as ships.

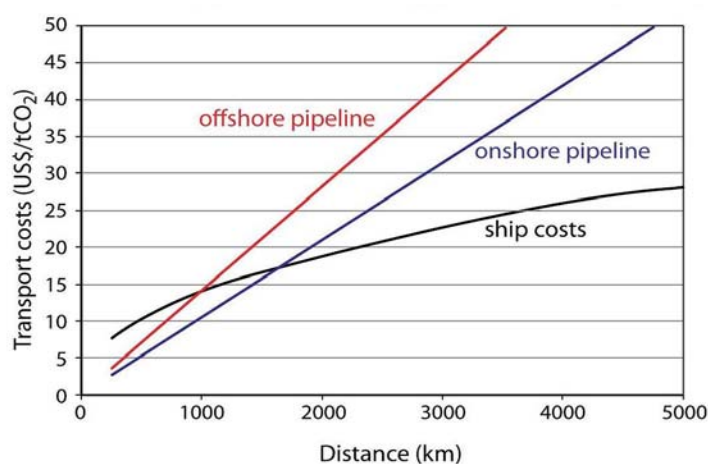


Fig. 4-1: Cost for onshore pipelines, offshore pipelines and ship transport [101]

At present no CO₂ transportation infrastructure exists in Europe. The construction of a pipeline network would entail a considerable capital investment^f (see **table 4.1**).

^f Whenever necessary, US Dollar were converted to Euro according to the following exchange rate: 1 US-\$ = 0.744 € (31 May 2007)

Tab. 4-1: Costs for constructing and operating a pipeline network [92]

Throughput	Length of pipeline (100 km / 400 km)		
	Capital Cost [Mio €]	Operating Cost [Mio €/y]	Total Cost [€/t CO ₂]
0.1 million t/y	6.7 / 24.6	0.98 / 3.8	9.7 / 37.9
5 million t/y	23 / 100	3.9 / 15	0.8 / 3.1
50 million t/y	102 / 560	15 / 82	0.3 / 1.6

4.2 Storage

The captured CO₂ needs to be stored safely and permanently, at a low cost and in a way that is environmentally compatible and in accordance with international treaties and national legislation. The main options for storing CO₂ are (see also **figure 4-2**):

- underground in suitable geological formations (geological storage)
- in the ocean (ocean storage)

In principle geological CO₂ storage reservoirs are:

- deep saline formations
- depleted natural gas reservoirs
- depleted oil reservoirs
- deep unmineable coal seams
- deep saline-filled basalt formations
- other (salt caverns, organic shales, etc.).

In Europe, CO₂ storage in geological formations (aquifers, depleted oil and gas fields) seems to be favored. Ocean storage is not considered.

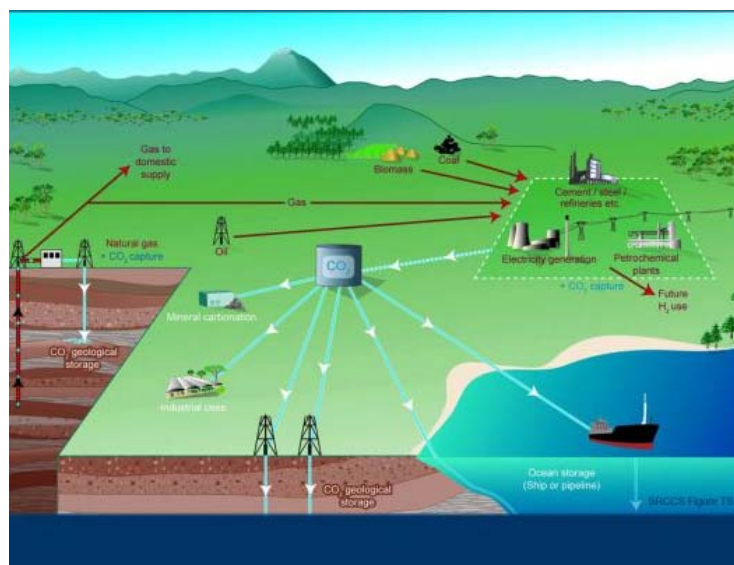


Fig. 4-2: Schematic diagram of possible CCS systems

CO₂ can be stored in geological formations in several ways – as a fluid within porous rock, by absorption into interstitial fluid or within a fixed matrix, e.g. as a mineral carbonate.

The estimated worldwide geological reservoir capacities (upper estimates) [101] are:

- 900 Gt CO₂ in disused oil and gas fields
- 200 Gt CO₂ in unmineable coal seams
- possibly 10,000 Gt CO₂ in deep saline formations

In 2002, the global CO₂ emissions from fuel combustion amounted to about 24 Gt CO₂. These figures show, that there is enough storage capacity for a foreseeable period of time. CO₂ storage in aquifers is being demonstrated on an industrial scale, e.g. in the Sleipner and In Salah projects.

The estimated European CO₂ storage capacity in some of these formations is given in **table 4-2**.

Tab. 4-2: Estimated European underground CO₂ storage capacities [117]

Storage location	Onshore [Gt CO ₂]	Offshore [Gt CO ₂]
Aquifers	57	716
Oil fields	0.2	5.9
Gas fields	12.5	14.4

Furthermore the world's oceans may be a large potential sink for anthropogenic CO₂ emissions. However, potential changes to the ecosystem functions have to be carefully considered.

The storage costs⁹ vary between 0.15 and ~ 22.3 €/t CO₂ – depending on the storage site. For onshore storage in European saline formations, a cost range from 0.74 to 4.6 €/t CO₂ is estimated [101]).

⁹ Whenever necessary, US Dollar were converted to Euro according to the following exchange rate: 1 US-\$ = 0.744 € (31 May 2007)

5 Definition of technical priorities and suggestion of detailed objectives for further steps

5.1 Principle options for further steps

It is clear that climate protection will gain more importance in the decades to come. Consequently, the European Commission has stated that most likely, in 15 years all new power plants will have installed measures for CO₂ mitigation, if CCS has proven to be applicable on an industrial scale. In this case, the likelihood is quite high, that environmental legislation will be adapted accordingly and other relevant industrial and energy-related CO₂ sources will be examined to what degree capture technologies can be installed to reduce their CO₂ emissions significantly.

For the cement industry climate protection has been a main issue for many years. The current activities focus on measures to improve the energy efficiency (e.g. changing from wet to dry process), alternative fuel combustion, reducing the clinker/cement ratio, etc.

The worldwide cement production will increase due to the population growth and the need for essential construction materials for housing and infrastructure. Obviously fossil fuels will be needed for clinker production in the foreseeable future while renewables will only play a minor role. To what degree new binders might be developed in the near future is an open question. Therefore the cement industry should at least prepare itself to be able to have the technical answers available. Against this background, it will be inevitable also for the cement industry to examine the potential application of CO₂ capture technologies. Of course the applicability depends strongly on the expected avoidance costs as compared to avoidance costs in other sectors, which will determine the price for CO₂ certificates under current and future trading schemes.

The relevance of CCS measures and potential research depends on the period of time that has to be assessed:

For short-term periods (up to 2012) CCS has no relevance for the cement industry, because the technology is not available and the costs are very high. Furthermore there are still other (conventional) methods to achieve CO₂ reductions in the cement sector.

In the medium-term (up to 2020) the necessity of CCS measures is strongly dependent on policy decisions ("Post Kyoto" climate policy) and the progress in technical developments of capture technologies.

In the long-term (up to 2050) a high relevance of CCS measures could however be possible, when other mitigation measures – e.g. in the power industry - are largely exhausted. It can be expected that the additional costs for CCS measures will be on the same level for the cement industry and other industries.

Though a lot of CCS research projects and even pilot projects are being carried out worldwide - mainly in the energy sector - a "know-how-transfer" from power plants to cement plants would be possible only on a limited scale. All known technologies would need re-

search and development, pilot and demonstration plants to get design data for full-scale plants. Principle options for research activities are:

Joint research projects:

CCS is an item which is of general concern for all cement companies, especially in Europe. It should be possible to coordinate projects and to build up a research consortium as well. The joint research projects might be co-financed by the European cement industry and by public funds (e.g. EU 7th Framework Programme).

Individual research projects:

Individual research projects could take advantage from national funding possibilities. Also in this case, an alignment of the different research projects would be advisable.

5.2 Identification of potential CO₂ capture technologies

As a result from the technical descriptions in **chapter 3**, all capture technologies are far from being applicable to the cement industry due to technical and cost reasons. However, some capture technologies seem to be more appropriate for the potential application at cement kilns than others.

The application of pre-combustion technology would entail the most extensive changes to the clinker burning process. Especially the shift to hydrogen combustion would be very demanding and would trigger a series of research tasks to adopt the clinker burning process to the new conditions. Another disadvantage is that process CO₂ from the calcination of limestone would not be captured. Consequently pre-combustion seems to be the least favorable among the discussed technologies.

Oxy-fuel technology is a candidate for CO₂ capture at cement kilns. There are experiences from cement kilns in the USA which were operated with oxygen enrichment (to increase the production capacity). Furthermore, oxy-fuel technology will be investigated at power plants in the next years, so that some of the results obtained may be transferred to cement kilns. Oxy-fuel seems to be applicable only at new kilns, because a retrofit at existing kilns would be too costly.

Post-combustion capture is an end-of-the-pipe technology which does not require fundamental changes in the clinker burning process. Therefore this technology would be available not only for new kilns, but also for retrofits at existing cement kilns. Both types of CO₂ – fuel and process CO₂ – is captured when applying post-combustion measures. The most promising post-combustion technology is chemical absorption because there are operational experiences from several industries and high abatement efficiencies seem to be achievable. Also membrane technology seems to be a candidate for future application at cement kilns. However, in this case even basic research would have to be carried out before an application at cement kilns could be discussed in more detail. Other post-combustion measures, e.g. physical absorption or mineral adsorption seem to be less feasible from today's point of view (because of a lack of selectivity or huge mass streams of mineral adsorbents).

5.3 Research objectives for CO₂ capture technologies

When new technologies shall be applied to an established industrial process, extensive research and development work has to be carried out. The application of capture technologies to cement kilns would require even basic research on a laboratory level. If these turn out to be promising investigations at pilot plants could be performed. Only based on these experiences gained could a demonstration plant possibly be built.

Objectives of potential research projects could be:

- to be able to significantly reduce the CO₂ emissions from the cement production process (clinker burning process)
- to provide essential contributions to the development of capture technologies for the cement industry – not only for new kilns, but also for existing kilns (retrofit)
- to set-up a research agenda for the next 12-15 years
- to influence technical developments of equipment from various suppliers via joint CCS projects
- to regularly assess (scientific, economic, political) CCS projects
- to participate in the exchange of knowledge within the international scientific community and integration of the cement industry in international CCS networks

The research work should be carried out in the frame of international projects including the cement industry, universities, research organizations, equipment suppliers etc. It can be expected that – due to the high priority of climate policy – sufficient public funds are available to draw up a research budget. However, also own resources would be necessary to start a research project.

It is clear that this kind of network is required to gather broad experience and knowledge in such a challenging programme. The cement industry has certainly to take a leadership role in future research projects as the input of specific process know-how will be indispensable.

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7 Annex

7.1 International CCS research projects and information networks

Worldwide numerous research projects about CCS are being carried out – especially in North America, Europe, Japan and Australia [182-189]. Furthermore there are information networks for knowledge transfer of CCS. The following list shows some selected projects and activities.

CACHET:

Subject: The overall goal of the CACHET project is to develop innovative technologies which will substantially reduce the cost of CO₂ capture whilst simultaneously producing H₂ from natural gas fuel.

Website: <http://www.cachetco2.eu/>

Budget:

Funded by: EU (7.5 Mio. €)

Coordinator: BP (UK)

No. of partner: 28

Start: 01.04.2006

Duration: 36 months

Reference: [206]

Carbon Sequestration Program

Subject: The U.S. National Energy Technology Laboratory manages a portfolio of laboratory and field R&D focused on technologies with great potential for reducing greenhouse gas emissions and controlling global climate change. Most efforts focus on capturing carbon dioxide from large stationary sources such as power plants, and sequestering it using geologic, terrestrial ecosystem, or oceanic approaches. Control of fugitive methane emissions is also addressed.

Website: http://www.netl.doe.gov/technologies/carbon_seq/index.html
http://www.netl.doe.gov/publications/carbon_seq/refshelf.html
<http://www.fossil.energy.gov/programs/sequestration/capture/>

References: [188]

CASTOR (CO₂ from Capture to Storage):

Subject: Capture and geological storage of 10% of the CO₂ emissions of Europe, which corresponds to about 30% of CO₂ emitted by European power and industrial plants. Cost reduction of post-combustion capture from 50-60 €/t CO₂ to 20-30 €/t CO₂

Website: www.co2castor.com

Budget: 15.8 Mio. €

Funded by: EU, 6th Framework Program (8.5 Mio. €)

Coordinator: IFP (France)

No. of partners: 30
Start: 01.02.2004
Duration: 4 years
References: [190, 191]

CATO:

Subject: The aim of CATO is to identify whether and how CO₂ capture and storage (CCS) can contribute to a sustainable energy system in the Netherlands, from an economical, technical, social and ecological point of view and under which conditions this option could be implemented in the energy system.

Website: <http://www.co2-cato.nl/>
Budget: 25.4 Mio. €
Funded by: Dutch Government (12.7 Mio. €)
Coordinator: Utrecht Centre for Energy Research
No. of partners: 14
Start: 2004
Duration: 2004-2008
References: [192]

CCCSTN (Canadian CO₂ Capture and Storage Technology Network):

Subject: This Canadian Network has been established due to the growing interest in the use of CO₂ capture and storage (CCS) technologies, both in Canada and abroad, as a greenhouse gas mitigation option and as a pollution abatement technology. CCCSTN provides information for the coordination of research, development and deployment efforts of national CCS initiatives as well as timely information on technology advancements.

Website: <http://www.co2network.gc.ca/>
References: [189]

Climate VISION / Vision 21:

Subject: The U.S. federal government and industry organizations in 12 energy-intensive economic sectors joined in a voluntary partnership called Climate VISION that works with industry to identify and pursue cost-effective solutions to reduce emissions using existing technologies; develop tools to calculate and report emission intensity reductions; speed the commercial adoption of advanced technologies; and develop strategies to reduce emissions intensity in other economic sectors

Website: <http://www.climatevision.gov/index.html>
<http://www.fossil.energy.gov/programs/powersystems/vision21/>

CO₂ Capture Project:

Subject:	The CO ₂ capture project is an international effort that addresses the issue of reducing emissions in a manner that will contribute in an environmentally acceptable and competitively priced continuous energy supply for the world. The project seeks to develop new technologies to reduce the cost of capturing CO ₂ from combustion sources and safely store it underground. These technologies will be applicable to a large fraction of CO ₂ sources around the world - such as power plants and other industrial processes.
Website:	http://www.co2captureproject.org/index.htm
Budget:	24 Mio. \$
Funded by:	Industry (8 companies), EU, government co-funding
Coordinator:	CCP Board
No. of partners:	11
Start:	2004
Duration:	36 months (Phase 2: 2004-2007)
References:	[193, 194]

CO2CRC (The Cooperative Research Centre for Greenhouse Gas Technologies):

Subject:	CO2CRC is the Australian Research Program for Capturing CO ₂ . The Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) is one of the world's leading collaborative research organizations focused on carbon dioxide (CO ₂) capture and geological storage (geosequestration). Major support from industry, research parties and government organizations, along with international collaborators, ensures that CO2CRC has a strong role to play in the mitigation of carbon dioxide emissions to the atmosphere
Website:	www.co2crc.com.au
No. of partners:	Consortium consisting of research, government and industrial participants
Reference:	[186, 195]

CO2 NET:

CO2NET is a Carbon Dioxide Knowledge Transfer Network, which was initially set up under the European Commission's FP5 Programme. The Network comprises in excess of 54 companies or organizations, covering 18 countries.

Website:	http://www.co2net.com/
Budget:	2.1 Mio. €
Funded by:	European Commission (1.4 Mio €)
No. of partners:	54 companies or organizations
References:	[115], [196]

CO2 Sink:

Subject: Pilot-scale project that will test and evaluate CO₂ capture and storage at an existing natural gas storage facility near Berlin, Germany, and in a deeper land-based saline aquifer. A key part of the project will be monitoring the migration characteristics of the stored CO₂.

Website: <http://www.co2sink.org/>

Budget:

Funded by: EU, German Ministry of Economics and Labour (BMWi), Industry

No. of partners: 15 consortium members

Coordinator: GeoForschungsZentrum (GFZ) Potsdam (Germany)

References: [197]

COORETEC:

Subject: A large demand for new fossil fired power plants will arise within in the next twenty years. In the frame of the COORETEC project (CO₂ Reduction Technologies), the requirements for future power plants were drawn up by 4 working groups, consisting of high level experts from research and industry. Furthermore both existing and future power plant technologies were evaluated.

Website: www.cooretec.de

Funded by: German Federal Ministry of Economics and Technology

References: [198, 199]

CSLF (Carbon Sequestration Leadership Forum):

Subject: The CSLF is a framework for international cooperation in research and development for the separation, capture, transportation and storage of CO₂.

Website: <http://www.cslforum.org/>

No. of partners: The CSLF is currently comprised of 22 members, including 21 countries and the European Commission.

References: [200]

DYNAMIS:

Subject: Preparing for large-scale H₂ production from decarbonized fossil fuels with CO₂ geological storage

Website:

Budget: 7.5 Mio. €

Funded by: EU (4 Mio. €)

Coordinator: SINTEF (Norway)

No. of partners: 30

Start: 01.03.2006

Duration: 3 years

References: [201]

ENCAP (Enhanced capture of CO₂):

Subject. The target of ENCAP is to provide pre-combustion technologies in power cycles operated by natural gas, residue oil, hard coal and lignite with the objective of achieving:

- at least 90% capture rate for CO₂
- 50% capture cost reduction

Website: <http://www.encapco2.org/>

Budget: 22.2 Mio. €

Funded by: EU (FP6) (10.7 Mio. €)

Coordinator: Vattenfall AB (Sweden)

No. of partners: 33

Start: 01.03.2004

Duration: 60 months

References: [202]

IEA Greenhouse Gas R&D Programme:

Subject. Information on technologies for reducing greenhouse gas emissions with emphasis on CO₂ Capture and Storage (CCS)

Website: <http://www.ieagreen.org.uk/>
<http://www.co2captureandstorage.info/co2db.php4>

Budget: Each member pays into a common research fund.

Coordinator: International Energy Agency (IEA), UK

No. of partners: 15

Start: 1991

References: [203]

ISCC (Innovative In Situ CO₂ Capture Technology for Solid Fuel Gasification):

Subject: Innovative in situ CO₂ capture technology for solid fuel gasification. The project aims to develop a new process for upgrading high-moisture low-rank brown coals yielding three valuable products:

- a fuel gas consisting mainly of hydrogen
- a purge gas stream containing > 95% CO₂, ready for transportation to sequestration or chemical fixation
- a precalcined feed for a cement kiln consisting of CaO, coal ash and required additional minerals

Website: <http://www.eu-projects.de/ISCC>

Budget: 2.9 Mio. €

Funded by: EU (1.9 Mio. €)

Coordinator: University of Stuttgart (Germany)

No. of partners: 14

Start: 2004

Duration: Jan. 2004 – Dec. 2006

References: [204, 205]

ITC (International Test Centre):

Subject: ITC (University of Regina, Canada) carries out R&D work in collaboration with national and international partners in order to develop appropriate CO₂ mitigation technologies. The project is examining improvements to the chemical absorption process (using a variety of solvents) as well as developing new technology and carrying out technology screening studies

Website: <http://www.co2-research.ca/>

Budget:

Funded by: Governments of Canada, Saskatchewan and Alberta, industrial partners

Coordinator: ITC / University of Regina

No. of partners: 10 (ITC, University of Regina and 8 industrial partners)

Start: 1999/2000

7.2 Recently announced industry-led CCS initiatives

References: [183, EC, DG Environment]

Companies	Project	Country	Technology options	Plant capacity [MW _e]	Estimated costs	Start of operation
Total	Lacq	France	Oxy-fuel	50		2006
Vattenfall	Schwarze Pumpe	Germany	Thermal oxy-fuel pilot coal power plant with CO ₂ capture	30	40 mio. €	2008
	Kårstø	Norway	NGCC	385		2009
ZeroGen		Australia	IGCC power plant with CCS in a saline aquifer	100		2010
Progressive Energy	Teeside	UK	IGCC power plant with off-shore injection (EOR)	800	1.5 bn. \$	2011
BP, SSE	Peterhead Miller	UK	power plant with H ₂ as fuel; CO ₂ capture, transport and use for EOR	350	600 mio. \$	2010
Powerfuel	Hatfield	UK	IGCC	900		2010
SSE	Ferrybridge	UK	SCPC, retrofit	500		2011
Statoil, Shell	Tjeldbergodden	Norway	NGCC; capture and transport of CO ₂ for offshore injection (EOR)	860	1.2-1.5 bn. \$	2011
EON	Killingholme	UK	IGCC	450		2011
Nuon	Magnum	Netherlands	IGCC multifuel	1,200	1 bn. €	2011
SaskPower		Canada	combustion of low-sulfur lignite coal, post-combustion or oxy-fuel technology for CO ₂ capture, EOR	300		2012
FutureGen		USA	coal gasification for electricity generation and H ₂ production	275		2012
PowerFuels		UK	IGCC with CCS	900		Post-2012
EON		UK	IGCC with CCS	450		Post-2012
RWE		Germany	IGCC power plant, CO ₂ capture and storage	450	< 1 bn. €	2014
Siemens		Germany	IGCC (Polygasification process + CCS + polygeneration)	1,000	1.7 bn. €	2011
Statoil	Mongstad	Norway	NGCC	820		2014
RWE	Tilbury	UK	supercritical technology combined with post-combustion CCS	1,000	800 mio. £	2016
Vattenfall	Schwarze Pumpe	Germany	based on the above mentioned pilot plant a larger commercial scale plant will be built	250		2020

7.3 List of selected pre-combustion projects

The following list contains selected pre-combustion projects, in which hydrogen is produced or the plant is already designed for a supplementation of a carbon dioxide capture facility.

PreC-02: CO₂ free gas power plant

Location: Scotland, UK

BP, ConocoPhillips, Shell

Gas turbine power plant with 350 MW in Scotland. Natural gas is converted in carbon dioxide and hydrogen. The hydrogen is used for power generation. The carbon dioxide is transported by pipeline and pressed into an oil field. Through the enhanced oil-recovery technique the natural resource should produce oil and natural gas for 10 to 15 years. No data about separation and capture technology.

PreC-09: Hydrogen from biomass

H&C Engineering GmbH, DMT Coking Plant and Fuel Technology Division

Allothermal gasification of waste material and biomass. Experience with a pilot plant in a scale of 500 kg/h coal for 8 years. Gasification process for biomass possible with air or oxygen. Syngas is a medium calorific gas with a high proportion of hydrogen.

PreC-13: Gasification of Coal

Location: Spreetal, Germany

Siemens Power Generation

Siemens introduces new activities into the power generation market with technology of coal gasification. During 3 years a coal gasification plant should be delivered to Spreetal, Germany. The gasifier plant has an thermal power of 1,000 MW. The produced syngas should be used for a 600,000 t/a methanol production. In future the gasifier plant should be completed with separation and capture technology for carbon dioxide.

PreC-14: Gasification of Coal

Location: Carson-Refinery, California/USA

BP, Edison Mission Group

Ideas of a hydrogen production plant for clean power generation.

PreC-43: Yueyang Sinopec-Shell Coal Gasification Project

Location: Yueyang, China

Shell Coal Gasification Company Ltd.; Yueyang Sinopec

Shell technology to produce syngas (2,000 t/d) as feedstock for fertilizer production.

PreC-44: Shuanghuan Yincheng Coal Gasification Project

Location: Hubei, China

Shell Coal Gasification Company Ltd.; Hubei Shuanghuan Chemical Group Co. Ltd.

Coal gasification replacing oil gasification to produce syngas (900 t/d) for fertilizer manufacturing.

PreC-45: Shenhua d-CTL Gasifier hoisting

Location: Shenhua, China

Shell Coal Gasification Company Ltd., China; Shenhua Coal Liquefaction Corporation

Shell coal gasification process (2x 2,000 t/d) used to produce hydrogen.

PreC-46: Shell Coal Gasification Licence: Liuzhou

Location: Liuzhou, China

Shell Coal Gasification Company Ltd.; Liuzhou Chemical Industry Co. Ltd.

1,100 t/d plant to supply a fertiliser plant.

PreC-47: Shell Coal Gasification Licence: Sinopec Hubei

Location: Hubei, China

Shell Coal Gasification Company Ltd.; Sinopec Hubei Chemical Fertiliser Co.

2,000 t/d plant to supply a fertiliser plant.

PreC-48: Shell Coal Gasification Licence: Sinopec Anqing

Location: China

Shell Coal Gasification Company Ltd.; Sinopec Anqing Company

2,000 t/d plant to supply a fertiliser plant.

PreC-49: Shell Coal Gasification Licence: Yunnan Tiana

Location: China

Shell Coal Gasification Company Ltd.; Yunnan Tianan Chemical Co. Ltd.

2,700 t/d plant to supply a fertiliser plant.

PreC-50: Shell Coal Gasification Licence: Yunnan Zhanhua

Location: China

Shell Coal Gasification Company Ltd.; Yunnan Zhanhua Co. Ltd.

1,100 t/d plant to supply a fertiliser plant.

PreC-55: Shell Coal Gasification Licence: Tianjin Soda

Location: China

Shell Coal Gasification Company Ltd.; Tianjin Bohai Chemical Group

2x 2,000 t/d plant to supply ammonia and methanol plants.

PreC-56: Shell Coal Gasification Licence: Guizhou

Location: GuizhouChina

Shell Coal Gasification Company Ltd.

2,000 t/d plant to supply ammonia and methanol plant.

PreC-59: GE's Gasification Technology

Location: Nanjing Jinling, Jiangsu, China

GE, Sinopec Jinling Chemical, Tianchen Chemical Engineering

Pressurized oxygen-blown coal gasification and petroleum gasification for ammonia and hydrogen production.

PreC-62: GE's Gasification Technology

Location: Weinan, ShaanXi, China

GE, Weihe Chemical Fertilizer, Ube

Pressurized oxygen-blown coal gasification for producing ammonia, methanol and DME.

PreC-63: GE's Gasification Technology

Location: Nanjing, Jiangsu, China

GE, Sinopec, Nanjing Chemical

Pressurized oxygen-blown coal and petroleum coke gasification for ammonia production.

PreC-66: Linggu-Project

Location: Jiangsu, China

Siemens, Germany; Jiangsu Linggu Chemical Industry Co. Ltd., China

Project for a 85,000 Nm³/h syngas pressurized gasifier (2x 200 MW) for an ammonia plant with a 300,000 t/a production.

PreC-78: ZeroGEN project: IGCC and CSS

Location: Rockhampton, Australia

Shell International Renewables

Integrated coal gasification with carbon capture and storage. An IGCC co-fired power plant with carbon capture and sequestration demonstration facility is planned and designed beside an existing 1,400 MW coal-fired power plant. The project has reached in 2006 the contractor selection process. Plant completion is dated for 2010. 85% of the CO₂ should be captured and pipelined to a geosequestration area 200 km next Rockhampton. There are no data about the capturing and sequestration technology. The net IGCC efficiency amount 40% without carbon capture and 34,3% with carbon capture.

7.4 List of selected post-combustion projects

PostC-01:

Location: Keda Darul Aman / Malaysia
Company: Petronas Fertilizer (Keda)
Process: KEPCO/MHI
CO₂ capture: Amine scrubber etc., sterically-hindered amines as absorbents
Start of operation: 1999
Capture capacity: 210 t CO₂/day
CO₂ use: Urea production
Additional information: Installation at a urea production plant, steam reformer flue gas

PostC-02:

Location: Rio de Janeiro / Brasil
Company: Prosint GPC
CO₂ capture: MEA-based scrubber
Process: Fluor Daniel
Start of operation: 1997
Capture capacity: 90 t CO₂/day
CO₂ use: Food-grade
Additional information: Gas-fired boiler at a methanol plant

PostC-03:

Location: Darussalam / Brunai
Company: Brunai LNG
CO₂ capture: Amine-based scrubber (MDEA + Piperazine)
Process: Sulfinol™ technology, Shell
ADIP-X, aMDEA™ technologies
Start of operation: 1972
Capture capacity:
CO₂ use:
Additional information: Liquefied natural gas plant

PostC-04:

Location: Norwegian North Sea / Norway
Company: Statoil
CO₂ capture: Chemical Absorption with MDEA (100 bar)
Process:
Start of operation: 1996
Capture capacity: 2,800 t CO₂/day
CO₂ use: Injection into a saline aquifer below the North Sea
Additional information: CO₂ reduction in natural gas from 9% to 2.5%

PostC-05:

Location: Beulah, North Dakota / USA
Company: DAKOTA Gasification Company
CO₂ capture: Physical Absorption
Process: Rectisol process (using methanol)
Start of operation: 2000
Capture capacity:
CO₂ use: Enhanced oil recovery at the Weyburn oil field (Canada)
Additional information: Lignite fired gasification plant

PostC-06:

Location: Cumberland, Maryland / USA
Company: AES Warrior Run, Inc.
CO₂ capture: Chemical absorption with MEA
Process: ABB Lummus
Start of operation: 1999
Capture capacity: 150 t CO₂/day from a slipstream (5% of the total)
CO₂ use: Food industry
Additional information: Coal fired circulating fluidized bed combustor

PostC-07:

Location: Chiba / Japan
Company: Kokusai Carbon Dioxide / Sumitomo Chemicals
CO₂ capture: Chemical absorption with Diglycolamine
Process: MHI, Fluor Daniel
Start of operation: 1994
Capture capacity: 150-165 t CO₂/day (99.9% purity)
CO₂ use: Food-grade
Additional information: Gas boilers plus oil/coal boilers

PostC-08:

Location: Esbjerg Power Station / Denmark
Company: Elsam
CO₂ capture:
Process:
Start of operation: 2006
Capture capacity: 24 t CO₂/day
CO₂ use:
Additional information: Greatest post-combustion pilot project at power plants worldwide ??

PostC-09:

Location: Panama, Oklahoma / USA
Company: AES Shady Point, Inc.
CO₂ capture: Chemical Absorption with MEA
Process: ABB Lummus
Start of operation: 1991
Capture capacity: 200 t CO₂/day (from a fluegas slipstream)
CO₂ use: Food industry
Additional information: Coal-fired power plant with two CFD boilers

PostC-10:

Location: Trona, California / USA
Company: North American Chemical Co.
CO₂ capture: MEA
Process: Kerr-McGee
Start of operation: 1978
Capture capacity: 800 t/day
CO₂ use: Carbonation of brine
Additional information: Coal boiler

PostC-11:

Location: Bridgeport, Texas / USA
Company: Mitchell Energy
CO₂ capture:
Process: Inhibited MEA
Start of operation: 1991
Capture capacity: 493
CO₂ use: EOR
Additional information: Gas heaters, engines, turbine

PostC-12:

Location: Bellingham, MA /USA
Company: Northeast Energy Associates
CO₂ capture:
Process: Fluor Daniel
Start of operation: 1991
Capture capacity: 320 t/d
CO₂ use: Food-grade
Additional information: Gas turbines

PostC-13:

Location: Sua Pan / Botswana
Company: Soda Ash Botswana
CO₂ capture: MEA
Process: Kerr-McGee
Start of operation: 1991
Capture capacity: 300 t/d
CO₂ use: Carbonation of brine
Additional information: Coal boiler

PostC-14:

Location: Poteau, OK / USA
Company: Applied Energy Systems
CO₂ capture: MEA
Process: Kerr-McGee
Start of operation: 1991
Capture capacity: 200 t/d
CO₂ use: Food-grade
Additional information: Coal boiler (fluidized bed)

PostC-15:

Location: China
Company: Luzhou Natural Gas
CO₂ capture: MEA
Process: Dow
Start of operation: 1998
Capture capacity: 160
CO₂ use: Urea production
Additional information: NH₃ plant reformer exhaust

PostC-16:

Location: India
Company: Indo Gulf Fertilizer Co.
CO₂ capture: MEA
Process: Dow
Start of operation: 1998
Capture capacity: 150 t CO₂/day
CO₂ use: Urea production
Additional information: NH₃ plant reformer exhaust

PostC-17:

Location: Australia
Company: Liquid Air Australia
CO₂ capture: MEA
Process: Dow
Start of operation: 1985
Capture capacity: 2 x 60 t CO₂/day
CO₂ use: Food-grade
Additional information: Gas-boiler